Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen

New Jersey's Science & Technology University

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

ELEMENTARY, PRESSURE DEPENDENT MODEL FOR COMBUSTION OF C_1, C_2 AND NITROGEN CONTAINING HYDROCARBONS: OPERATION OF A PILOT SCALE INCINERATOR AND MODEL COMPARISON

by
Chad Sheng

A 140000 BTU/hr pilot scale incinerator has been constructed, tested and run; and an on-line sampling train capable of taking *in situ* data has been established. The continuous on-line analytical instruments include a CO analyzer, an NO/NOx analyzer and an O_2 analyzer. In addition, two gas chromatographs with flame ionization detector are used to determine CH_4, $C_2H_2 + C_2H_4$ and total hydrocarbon concentrations. Typical operating conditions are at an average O_2 concentration of 6 – 8 %. The NO concentration ranged from 100 – 200 ppm. Approximately 1 ppm of CH_4 is also present at steady state operations.

The kinetic model for the combustion process in the pilot scale incinerator consists of elementary reaction kinetics for oxidation of the model fuel species: CH_4, CH_3OH, C_2H_2, C_2H_4, C_2H_6 and CH_3NH_2. Thermodynamic properties for these species are determine by *ab initio* methods and density functional theory. High-pressure limit rate constants are determine by either canonical transition state theory or variational transition states theory. In some cases, estimation techniques based on Evans-Polyani relationships are used. Pressure and temperature dependent mechanism is constructed utilizing QRRK for *k(E)* with either master equation or modified strong collision analysis for fall-off. The mechanism is constructed over the pressure range of 0.001 – 100 atm and over a temperature range of 300 – 2500 K.

A reactor configuration of an isothermal perfectly stirred reactor (PSR) followed by a plugged flow reactor with heat transfer loss (PFR1), followed by a second plugged flow reactor with a different heat transfer loss (PFR2) is used to model the pilot scale incinerator. Concentration profiles are determined from the detailed kinetic model based on the reactor configuration. Results show that O_2, is consumed and CO_2 and NO are formed mainly in the PSR. The concentration of these three components do not change throughout PFR1 and PFR2. Comparison of the NO and NOx experimental data with the model shows the data are in the same range, varying from 100 – 200 ppm, with less than 50 ppm difference. The average NO:NOx ratio for experimental data is 0.97, and the average NO:NOx ratio from the model results is 0.98.

ELEMENTARY, PRESSURE DEPENDENT MODEL FOR COMBUSTION OF C_1, C_2 AND NITROGEN CONTAINING HYDROCARBONS: OPERATION OF A PILOT SCALE INCINERATOR AND MODEL COMPARISON

by
Chad Sheng

A Dissertation
Submitted to the Faculty of New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

Department of Chemical Engineering

January 2002

Copyright © 2002 by Chad Sheng

ALL RIGHTS RESERVED

APPROVAL PAGE

ELEMENTARY, PRESSURE DEPENDENT MODEL FOR COMBUSTION OF C_1, C_2 AND NITROGEN CONTAINING HYDROCARBONS: OPERATION OF A PILOT SCALE INCINERATOR AND MODEL COMPARISON

Chad Sheng

Dr. Joseph W. Bozzelli, Advisor — Date
Distinguished Professor and Chairperson of Chemistry and Environmental Science, NJIT

Dr. Basil Baltzis — Date
Professor and Chairperson of Chemical Engineering, NJIT

Dr. Robert B. Barat — Date
Associate Professor of Chemical Engineering, NJIT

Dr. Lev Krasnoperov — Date
Professor of Chemistry, NJIT

Dr. Jeffrey Grenda — Date
Principal Investigator
Exxon-Mobil Corporate Research & Engineering

BIOGRAPHICAL SKETCH

Author: Chad Sheng

Degree: Doctor of Philosophy

Date: January 2002

Undergraduate and Graduate Education:

- Doctor of Philosophy in Chemical Engineering,
  New Jersey Institute of Technology, Newark, NJ, 2002
- Master of Science in Environmental Science,
  New Jersey Institute of Technology, Newark, NJ, 1995
- Bachelor of Science in Chemical Engineering,
  University of Wisconsin - Madison, Madison, WI, 1989

Major: Chemical Engineering

Presentations:

Sheng, C.; Bozzelli, J.W.; Dean, A.M., "Thermochemical Parameters, Reaction Paths and a Detailed Kinetic Model for the C_2H_5 + O_2 Reaction System"; *AIChE Annual Meeting*; Reno, NV; November 4-9, 2001.

Sheng, C.; Bozzelli, J.W.; Dean, A.M., "Thermochemical Parameters, Reaction Paths and a Detailed Kinetic Model for the C_2H_5 + O_2 Reaction System"; *Second Joint Meeting of the U.S. Sections of the Combustion Institute: Western States, Central States, Eastern States*; Oakland, CA; March 25 - 28, 2001.

Bozzelli, J.W.; Sheng, C.; Sun, H.; Dean, A.M., "Comparison of Chemical Activation Association Reactions: Chloromethyl and Methyl Radicals with OH"; *16th International Symposium on Gas Kinetics*; Cambridge, England, UK; July 23 - 27, 2000.

Sheng, C.; Bozzelli, J.W., "An Evaluation of Acetylene + O_2 Oxidation System: HCCH + $O_2(^3\Sigma)$, HCCH + $O_2(^1\Delta)$ and Vinylidene + $O_2(^3\Sigma)$ via Isomerization of HCCH"; *Chemical and Physical Processes of Combustion*; The Fall Technical Meeting of the Eastern States Section of the Combustion Institute; Raleigh, NC; October 1999; pp 33-36.

Thipse, S.; Sheng, C., "Evaluation and Comparison of Heat of Combustion Value and Fuel Test Data for a Synthetic Refuse-Derived Fuel"; *Chemical and Physical Processes of Combustion*; The Fall Technical Meeting of the Eastern States Section of the Combustion Institute; Raleigh, NC; October 1999; pp 285-288.

Sheng, C.; Thipse, S.; Sun, H.; Bozzelli, J.W.; Booty, M.R.; Magee, R. S.; Hoecke, D., "A Pilot-Scale Incinerator For Evaluating the Combustion of Co-Fired Plastics"; *IT3 International Conference on Incineration and Thermal Treatment Technologies*; Orlando, FL; May 1999.

Ing, W.C.; Sheng, C.; Bozzelli, J.W. "Pyrolysis and Oxidation of Methanol/Methane Mixtures: Experimental and Detailed Pressure Dependent Reaction Model"; *First Joint Meeting of the U.S. Sections of the Combustion Institute: Western States, Central States, Eastern States*; Washington DC; March 1999; pp 17- 20.

Bozzelli, J.W.; Dean, A.M.; Lay, T.; Sheng,C., "Pressure and Temperature Analysis of the C_2H_5 and H_2CCH_2OOH + O_2 Reactions"; *Fourth International Conference on Chemical Kinetics*; Gaithersburg, MD, July 1997.

Publications:

Thipse, S.S.; Sheng, C.; Booty, M.R.; Magee, R.S.; Bozzelli, J W., "Chemical Makeup and Physical Characterization of A Synthetic /Fuel and Methods of Heat Content Evaluation for Studies on MSW Incineration"; *Fuel*, Volume 81, Issue 2, 2002, pp 211-217

Sheng, C.; Bozzelli, J.W; Ritter, E.; Dean, A.M., "A Computational Code To Determine Elementary Kinetic Parameters Based On Canonical Transition State Theory: ThermKin"; In process of submitting for publication

Sheng, C.; Bozzelli, J.W; Dean, A.M.; Chang, A.Y., "Detailed Kinetic Model and Thermochemistry on C_2H_5 + O_2: Reaction Kinetics of the Chemical Activation and Stabilized CCOO* Adduct"; Submitted to *J. Phys. Chem. A* December 2001

Sheng, C.; Bozzelli, J.W, "Thermodynamic Properties (Entropy and Heat Capacity) from *ab initio*, Density Functional Theory or Other Calculations"; Submitted to *J. Chem. Edu.* September 2001

Sheng, C.; Bozzelli, J.W, "The Hydroperoxy-Ethyl Radical Reaction with O_2: Chain Branching Reactions In Hydrocarbon Oxidation"; Submitted to *J. Phys. Chem. A* September 2001

Thipse, S; Sheng, C.; Booty, M.; Magee, R.; Dreizin, E., "Synthetic Fuel for Imitation of Municipal Solid Waste in Experimental Studies of Waste Incineration"; *Chemosphere*, Volume 44, Issue 5, 2001, pp 1071-1077

Sheng, C.; Bozzelli, J.W, "*ab initio* Molecular Orbital and Density Functional Analysis of Acetylene + O_2 Reactions with ChemKin Evaluation"; *International Journal of Chemical Kinetics*, Volume 32, Issue 10, August 18, 2000, pp 623-641.

This thesis is dedicated to
my parents Mr. and Mrs. Fu-chiu Sheng

ACKNOWLEDGMENT

I would like to thank my dissertation committee members, Dr. Basil Baltzis, Dr. Robert Barat, Dr. Lev Krasnoperov and Dr. Jeffrey Grenda for their critical review and comments that contributed to this final dissertation.

The author is exceptionally appreciative to my dissertation advisor, Prof. Joseph W. Bozzelli, for guidance, support and the many cups of coffee over the round (square) table discussions. Recognition to the members of Bozzelli Research Group who has provided friendship, assistance and encouraging conversations during my studies include Dr. Larry Lay, Dr. Dustin Ho, Dr. Jeff Ing, Dr. Chiung-Ju Chen, Dr. Takahiro Yamada, Li Zhu, Jongwoo Lee, Hongyan Sun and Samuel Chern.

I would also like to thank Dr. Howard Kimmel, Siobhan Gibbons, Dr. Susan Schenk and Ivette Rosario of Pre-College for providing me with the opportunity to be able to participate in learning how to teach and reach out to the younger students. Also I would like to thank Dr. R. Kane and Ms. Clarisa Gonzalez-Lenahan for helping me organize this dissertation.

I would also like to thank David/Julie Lau, Wil/Lim Sang, Ho Cheung Lai and Dean/Kris Chin for their friendship.

I would also like to thank my family (Mike/Sandy, Joe/Irene, Jack/Rhonica and my twin “bro” Chris) for their support throughout my academic studies.

And to my wife, Chu-Feng (Jennifer), whom I want to thank for being patient, always providing encouragement and being there for me.

Praise the Lord Jesus Christ, who has allowed His Grace to be shown favorably on me by providing me with my “Daily Bread.”

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

Table **Page**

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

NOMENCLATURE

For Chapter 3

C_p	Molar heat capacity at constant pressure
C_v	Molar heat capacity at constant volume
R	Universal gas constant
P	Pressure
T	Temperature
V	volume
S	Molar entropy
H	Molar enthalpy
U	Molar internal energy
A	Helmholtz free energy
G	Gibbs free energy
M_w	Molecular weight
k	Boltzman's constant
h	Planck's constant
N_A	Avogadro's number
I, I_x, I_y, I_z	Moments of inertia about the principle axis
υ_i	ith vibrational frequency
σ	Symmetry
$\sigma_{opt.iso}$	Optical isomer
ω_0	Spin degeneracy

NOMENCLATURE
(Continued)

For Chapter 4

$\neq$	Superscript denotes transition state
k_B	Boltzmann‘sconstant
h_p	Planck’s constant
k_{forw}	forward rate constant
R	Universal gas constant
T	Temperature
K_C	Equilibrium constant in concentration units
K_P	Equilibrium constant in pressure units
$\Delta\nu$	Difference in stoichiometric coefficient between product or transition state and reactant
S_C	Molar entropy, in concentration units
S_P	Molar entropy, in pressure units
H	Molar enthalpy
U	Molar internal energy
A	Pre-exponential A-factor in classical Arrhenius expression
A_T	Pre-exponential A-factor in modified Arrhenius expression
G	Gibbs free energy
n	Temperature factor in the modified Arrhenius expression
m	Number of data point
P^0	Reference pressure at 1 atm

CHAPTER 1

INTRODUCTION

1.1 Background and Previous Studies

Over the years incineration has emerged as a viable technology for managing solid wastes.[1] Some of the advantages of incineration are volume reduction, disposal of hazardous materials and energy recovery. Combustion processes, either as a means of waste disposal or as a source of energy, also face several challenges from regulatory emissions standards specified in the 1990 Clean Air Act (CAA).[2] Some of the pollutants regulated by the CAA include CO, NOx, particulates, volatile organic compounds or VOCs and sulfur dioxide.

Wallis and Watson[3] note in their critical review that incineration has remained a controversial technology largely due to public misunderstanding. The misunderstanding arises from lack of knowledge about the incineration process, concerns over toxicity of the emissions to the environment. This leads to negative publicity without really trying to understand the actual impact of the very low emission levels or the benefits of near complete waste destruction and its conversion to non-toxic CO_2 and H_2O. They reported that only 1.3 million metric tons out of a total of 249.3 million metric tons of hazardous waste is incinerated in the U.S. They also report that hazardous waste is approximately 60% of the total waste generated. Despite this criticism the energy crisis has forced society to look for alternative sources of energy and combustion of wastes seems to be a reasonable alternative.[4]

Oxyhydrocarbon and hydrocarbon polymers such as cellulose and common plastics like polystyrene and polyethylene together constitute a significant portion of municipal solid waste (MSW). Cellulose, as the main component of paper and wood, contributes about 35% by mass, and plastics contribute about 10% to 15% by mass of typical MSW.[2] Although these materials are useful as fuels in incineration processes and refuse-to-energy conversion, because they have a relatively high heat content; there are concerns over their impact on emissions, products of incomplete combustion (PIC), and fate in municipal waste combustors (MWC).

Proper control of effluents from municipal incinerators is essential in efficient operation and proper conversion of the waste, while abiding within the legal limits permissible for the effluents. Physical characteristics of these emitted species are gaseous and solid as particulate. Liquid phase products will be in the scrubber, if one is present, and in effluent as aerosols that often form by condensation upon entering the tropospheric environment. Pollutant emissions include both inorganic and organic species. Inorganic gaseous emissions include CO, NO, NO_2 (or NOx), HCl, Cl_2, SOx, Hg and organic mercury compounds. Organic emissions can include hydrocarbons, oxygenates, chlorinates and other halogenated hydrocarbons, including polychlorinated dibenzyl dioxins and furans (PCDD/F) and aromatic species, including polyaromatic hydrocarbons (PAH). Primary targets in this study will be major pollutants, which include: CO, NOx and trace hydrocarbon species (C1 and C2 species).

A number of methods exist and these are continuously being improved; plus new techniques are being developed to minimize CO, NO and NO_2 (or NO_x) concentrations. Examples include optimizing nozzle design, use of air staged low-NOx burners, flue gas recirculation, selective catalytic reduction … etc. Flue gas recirculation takes about 20-30% of the flue gas and re-introduces this stream with the combustion air. This method can reduce the NOx level by 20% in coal-fired units and is currently in a number of industrial plants.[5] The Public Service Company of Colorado (PSCo) has tested their Arapahoe Unit 4 utility coal-fired boiler by adding low-NOx burners and a urea-based selective non-catalytic reduction (SCNR) unit to reduce NOx concentrations.[6] The low-NOx burner employs air-fuel staging techniques. The Arapahoe Unit 4, showed a reduction of about 69% in NOx with addition of a low-NOx burner installed. For the combination of low-NOx burner and SCNR, an additional 45% reduction in NOx was observed. The estimate cost for this project was in excess of $27 million; but the results – reduction in NOx were significant also.

A better understanding to combustion processes consists of experimental studies and/or computational modeling of the system. A number of studies on thermal and oxidative decomposition of polymers have reported data on products or overall rates of volatilization and reaction under non-steady state operating conditions. Many of these studies are based on experiments that use, for example: a batch reactor, or a semi-batch reactor with continuous gas flow and batch polymer inlet, a drop tube furnace, or temperature-programmed gravimetric analysis. The batch reactors report valuable product formation data, but do not determine simultaneous time of formation and fuel equivalence in the vapor phase, and are often operated at high initial fuel equivalence ratios. A drop tube furnace monitors mass loss and ignition characteristics of a particle, in addition to intermediate product formation, but time of vapor phase species reaction can vary from flow through the reactor to formation on exit. Global kinetics of polymer volatilization is determined by thermal gravimetric analysis, which monitors mass loss and products as the initial mass is exposed to a temperature ramp.[7-10] Thermal gravimetric studies are valuable in determining temperature regimes of organic species and polymer reaction, transformation and volatilization, in addition to intermediate product identification.

The study of effluent species and development of optimal design for MWCs and coal-fired power plants can be done more cost effectively by performing the study on benchtop and pilot scale experiments and on computational modeling and simulations. Several researchers have utilized computational fluid dynamic (CFD) analysis to aid in the design of air nozzles [11-13]. Han[7] used a hot-flow (theoretical) model to simulate a MWC. His experimental apparatus was a reduced-scale combustor using a gas burner to emulate gas phase reactions in a MWC. The experimental data obtained were compared with a CFD code incorporating the appropriate chemical reactions to evaluate the mixing processes within the combustor. Han was able to obtain good comparison between the experimental data and predictions of the hot-flow model. Piao, *et al.*[8] used a 30cm x 30cm bubbling type fluidized-bed combustor with "commercial size" refuse derived fuel (RDF) containing poly(vinyl chloride) (PVC) to study the effect of adjusting feed rate and secondary air flow on CO formation. They found that adjustment of air ratio and the use of secondary air injection were effective in reducing CO and improving complete combustion. HCl is formed from the pyrolytic reaction of PVC; Piao, *et al.* note that the HCl concentration in the flue gas was controlled by the calcium retained in the RDF and the level of HCl is directly proportional to the combustion temperature. Wu, *et al.*[9] studied the pyrolytic reaction of high density polyetheylene (HDPE), which is a major component of municipal solid waste, in the presence of HCl gas using thermal gravimetric analysis (TGA) and a kinetic model to determine energy resource and rate of degradation of HDPE[9]. The results show that HCl inhibits the pyrolytic reaction of HDPE. Brouwer, *et al.*[10] studied the combined effects of turbulent mixing and chemical kinetic inhibition on products of incomplete combustion (PICs) using a toroidal jet stirred reactor followed by a plug flow reactor to simulate turbulent mixing within a MWC. Their conclusion is that the model they have used is able to predict the trend and magnitude of methyl chloride burnout and CO/CO_2 ratio.

Phillips, *et al.*[14] applied the Regula Falsi method to solve the equations predicting atmospheric emissions from combustion sources. They developed and applied their model using two different approaches; a kinetic approach and an equilibrium approach. The results calculated from the kinetic approach were significantly lower than those form the equilibrium approach. They concluded that a potential for reduction in emissions is possible with improved operating conditions and optimization in design.

Tuttle[15] and Kuo, *et al.*[16], separately, performed experiments to study solid fuel combustion on grates using wood cubes as the fuel source. Results from Tuttle's study indicate that the relative distribution between overfire air (OFA, which is delivered to the hot reacting gases above the grate and fuel bed) and underfire air (UFA, which is delivered below the grate and fuel bed) is one of the most important variables determining combustion-generated particulate emissions, *i.e.* fly ash. Kuo, *et al.* used a fixed-grate laboratory-scale apparatus to study the influence of OFA and UFA air on the burning rate of wood fuel. Their results indicate that an increase in UFA causes a directly proportional increase in solid fuel burning rate which is accompanied by an increase in CO emissions, whereas an increase in OFA tends to decrease CO emissions. One of Kuo, *et al.*'s results suggest that relative CO levels are lower with OFA and higher with UFA.[16] Their model for the burning rate was based on a classical Arrhenius-type correlation, and could not adequately explain their data over the full temperature range of their experiments. Kuo, *et al.* stated that "...fundamental understanding of the mechanisms of solid fuel bed combustion is still insufficient for establishing general guidelines of broad applicability on combustion air distribution design and control."

These reactors do not, however, emulate a full-scale MWC, and the data they generate is used by the combustion community only as background material. Data are needed from research-scale and pilot-scale reactors that emulate full-scale combustors, in order to determine operating conditions required for complete conversion of materials, such as common polymers or other feeds, that are likely to produce trace level, possibly undesirable, organic species or metallic species in the effluent. Features important to accurate emulation of MWCs include steady state operation, that is, continuous uniform feed of solid waste fuel and gas flow, with continuous grate mechanism and ash movement. Some 'key' combustion parameters, such as fuel equivalence ratio, solid and gas residence times, and operating temperatures and temperature profiles, cannot be 'scaled' and must reproduce those of full-scale MWCs for accurate emulation. Similarly, the MSW stream consists of a variety of materials,[2] which behave as co-fed fuels in municipal waste combustors, and this requires direct simulation.

Besides CFD modeling of combustion process to help explain mixing and transport effects within incineration processes, detail kinetic analysis of these complex systems are also very actively pursued. The importance of modeling complex reaction systems requires accurate thermodynamic properties and detailed reaction mechanisms to describe the formation and destruction of key species in systems. Thermodynamic properties and kinetic studies for C_1 and C_2 hydrocarbon and oxy-hydrocarbons systems, such as CH_3OH, CH_4, C_2H_6, C_2H_4 and C_2H_2, are still on-going with many possible hypothesis proposed by several research groups to help explain experimental data.[17-34] The thermodynamic properties and kinetics on the study of nitrogen chemistry both experimentally and at high-level computational chemistry calculations are sparse,[35-45] yet formation of NOx is under stringent environmental regulations.[2]

1.2 Objectives of the Current Study

A pilot scale incinerator and sampling train have been designed and installed in order to evaluate its operation as an accurate emulation of a MWC and if it will provide *in situ* data acquisition.[46] A solid fuel composition is identified for the feed, to be representative of average municipal solid waste, including plastics. Commercial materials are selected as feed components with the desired carbon, hydrogen, oxygen and nitrogen elements. The materials are shredded, mixed and then fabricated into cylindrical pellets. The pellets are fed continuously into the primary combustion chamber during operation of the pilot incinerator. These feed pellets are 2.5 cm diameter and 5 cm in length.

The primary combustion chamber is of 0.11 m^3 volume with a water cooled grate, pushrods to feed the fuel source, and adjustable OFA and UFA flow. Volatization, intra-pellet combustion, and burnout zones are readily observed on the grate. The solid pellet retention time on the grate is approximately 30 min, but can be adjusted by timing relays. A secondary combustion chamber provides approximately 2 seconds residence time for reacting gases. Steady state experimental data, which include CO, O_2, NO, NOx, low hydrocarbon species (C_1-C_4), total hydrocarbon and temperature, are collected from the incinerator at different OFA and UFA flow rates.

Specific chemical species are selected to emulate or serve as surrogate chemicals in the feed include methanol (CH_3OH), ethylene (C_2H_4), ethane (C_2H_6) and mono-methylamine (CH_3NH_2), in addition to water and air as the fuel. Proportions of these target chemical species are identified to properly emulate the actual feed to the incinerator.[47] A detailed mechanism is developed based on these fuel species to model the chemistry and kinetic processes in the incinerator.

Thermochemical properties, reaction paths, kinetic parameters, combined with pressure and kinetic analysis for complex systems are determined for several key chemical reaction systems. These include: CH_3OH and $CH_2OH + O_2$, $C_2H_5 + O_2$, $C_2H_2 + O_2$, CH_3NH_2 and the radicals from loss of a H atom by the parent $CH_2NH_2 + O_2$ and $CH_3NH + O_2$. Several additional chemical activation reaction systems are further evaluated, where it is determined that the reaction system $HOOCH_2C{\bullet}H_2 + O_2$ leads to three New Chain Branching Reactions in low to moderate temperature hydrocarbon combustion / oxidation systems.

Construction of a detailed C_1-C_2 kinetic model to analyze the overall gas phase oxidation and comparison with experimental data are presented. Development of accurate detailed model for combustion is necessary to study and look for trends to the reduction of toxic pollutant emissions.[48] Extension of the developed C_1-C_2 oxy-hydrocarbon oxidation model to include complex nitrogen chemistry to model NO and NOx formation in a pilot scale incinerator is also performed. Comparison of the current mechanism is performed with data obtained from the pilot scale incinerator.

CHAPTER 2

DESCRIPTION OF EXPERIMENTAL SETUP AND APPROACH TO MODELING PILOT SCALE INCINERATOR

2.1 Experimental Apparatus

2.1.1 Pilot Scale Incinerator

The apparatus consists of a pilot-scale 40 kW (140,000 BTU/hr) combustion system which has been designed and constructed for evaluating the combustion of co-feed fuel compositions in municipal waste combustors. It is of a sufficient scale to obtain experimental data in a manner that is representative of full-scale municipal waste combustor (MWC) but at the cost and time frame of pilot plant equipment.

The incinerator consists of a primary combustion chamber (PCC), a secondary combustion chamber (SCC), a near adiabatic zone, two heat exchangers in series, a bag house and a blower fan. (Refer to Figures 2.1 and 2.2). Super-Trol's 1 and 2 circulate heat transfer fluids through specified incinerator components, *i.e.* SCC, heat exchanger 1 and heat exchanger 2. The heat transfer fluid (HTF) in SCC and heat exchanger 1 is polyalkaline glycol (*i.e.* "UCON" heat transfer fluid 500 from Union Carbide) and the HTF in heat exchanger 2 is water. The "UCON" HTF serves as a heating fluid in SCC to retard the heat dissipation that would otherwise occur if no HTF were present. The SCC is an annulus, where the heat transfer oil flows on the shell side co-current with the gas stream.

The PCC is based on a moving grate design. The grate dimensions are 0.26 m wide by 0.56 m long and the refractory lined combustion chamber is of approximately 0.11 m^3 (5525 in^3) volume. Hydraulic rams with adjustable period and dwell push solid

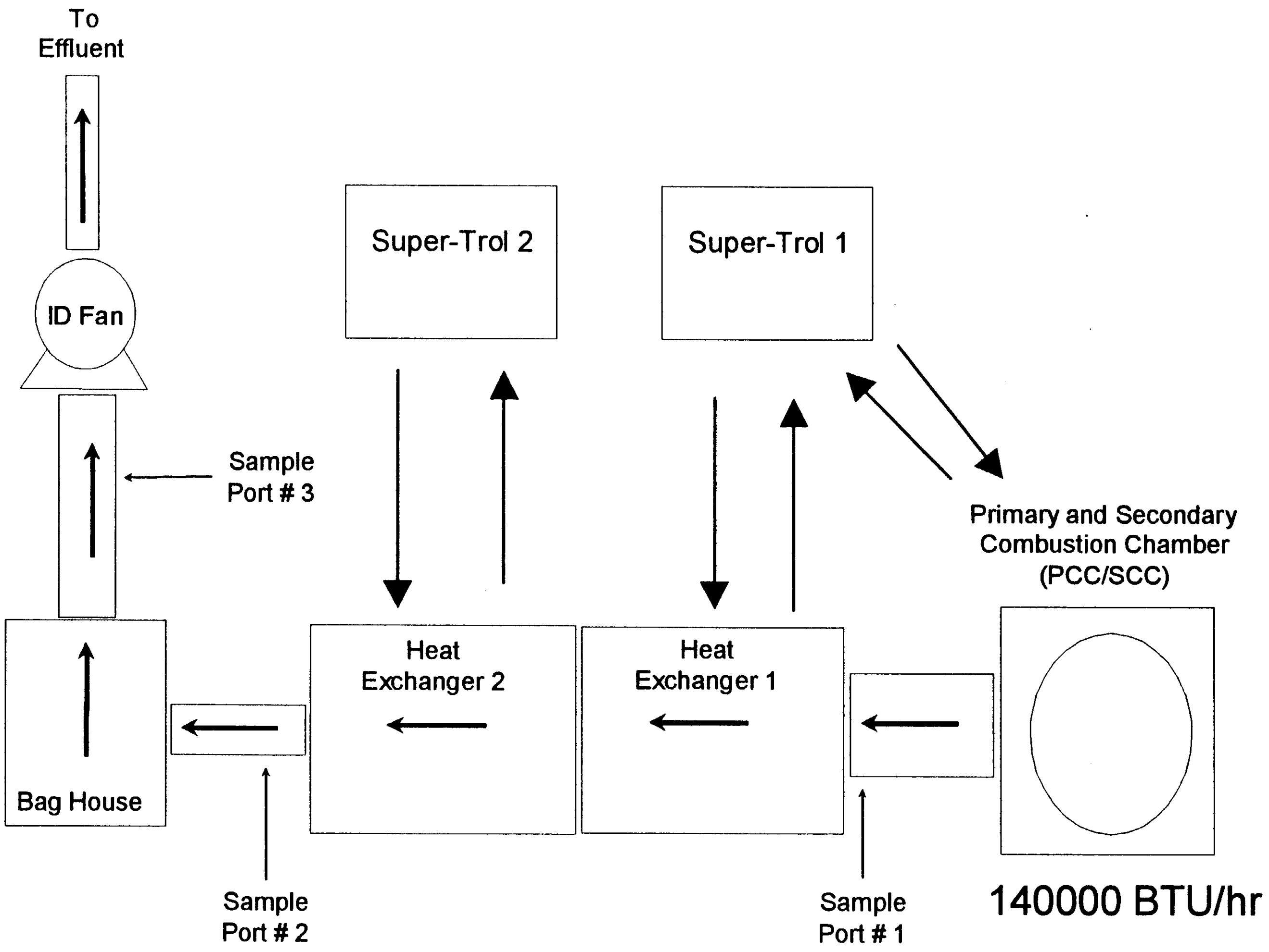


Figure 2.1 Flow diagram of the pilot scale incinerator

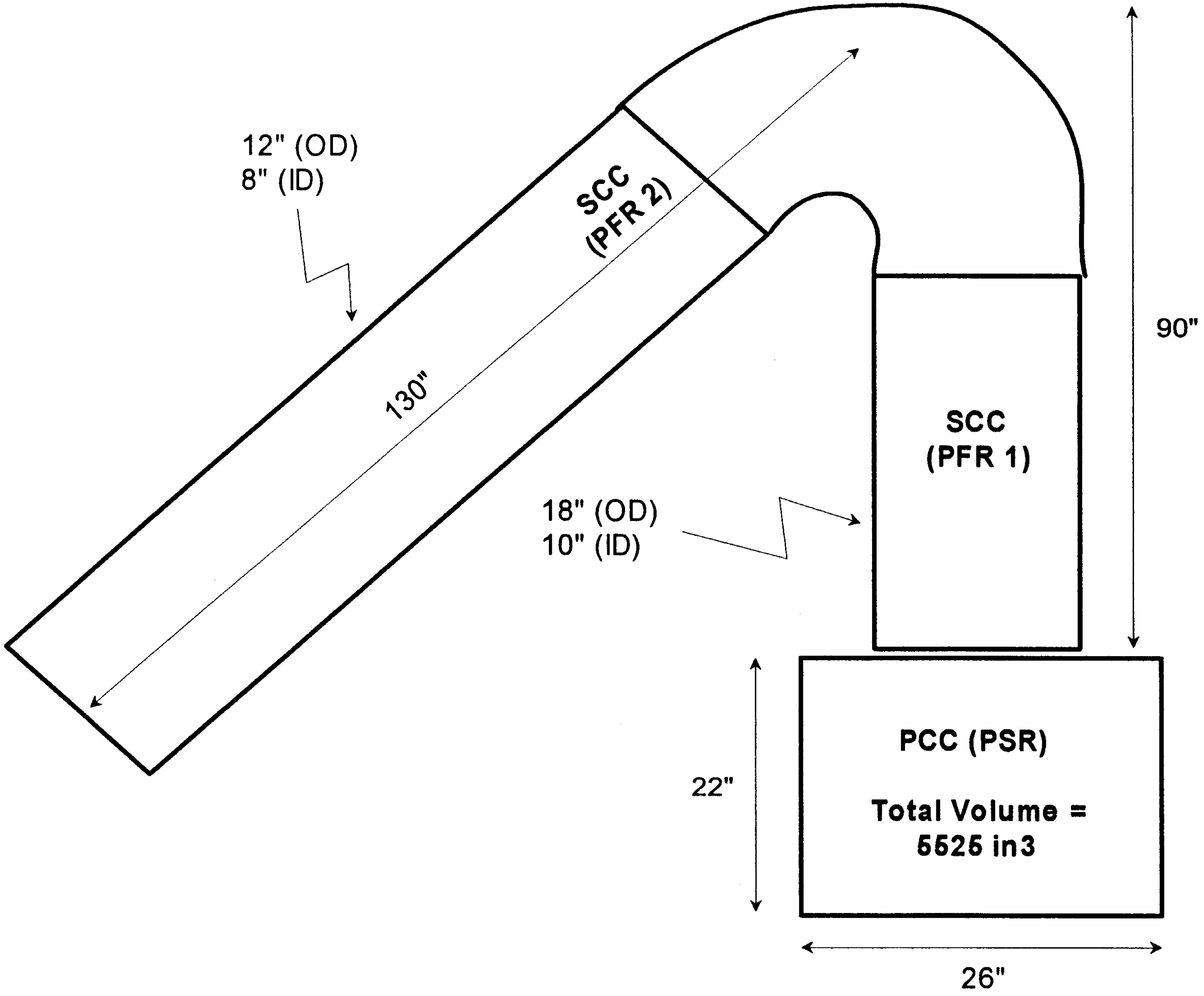


Figure 2.2 General dimensions of primary and secondary comubstion chamber

fuel from a feed hopper onto the front of the grate at a rate on the order of 8-13 kg/hr. Fuel is then directed along the grate by a system of controlled cycle reciprocating pushrods. Fuel residence time on the grate is adjustable in a range from 20 min to 40 min.

The under-fire air (UFA) is introduced into the PCC by ports that are distributed uniformly across the surface on the grate. The UFA is supplied by a Dayton shaded pole blower Model 4C006B and forced through concentric openings in the fingers on the grate. The grate is cooled by the in-house water line, flowing at ca. 80 gallons/hr. Volumetric flow rate is controlled by a butterfly valve that is mounted at the inlet of the blower. A magnahelic, with a range of 0 – 1 inch H_2O, is used to measure the pressure drop in the UFA duct, which is correlated to the volumetric UFA flow rate.

The over-fire air (OFA) is introduced by ports located on the PCC walls about 30 cm above the grate. The OFA is provided by an in-house compressed air source. A Dwyer 2 – 20 SCFM flow meter is used to monitor the volumetric OFA flow rate. OFA is introduced into the combustion zone through two different locations, where each location consists of five jets, ¼" stainless steel tubing: behind and over the feed chute and from the firewall opposite the feed chute. The jets are parallel to each other, with opposite banks providing opposed flow. The direction of OFA flow is at a slight downward angle (ca 30° below horizontal), creating a "swirl" effect within the combustion zone, to help facilitate mixing. The OFA is not directed onto the grate/pellets. Gas temperatures in the PCC are about 780°C to 850°C.

Gases effluent from the PCC pass into the SCC, in which the total residence time is about 2 seconds. The gas temperature is reduced by means of two heat exchangers, which are designed to provide a temperature profile similar to commercial MWCs. Polyalkyline glycol HTF at temperature near 260°C is utilized in the first heat exchanger and the outer shell of the SCC. The second heat exchanger utilizes water to cool the effluent gases to about 100°C prior to the baghouse. External heating of the heat transfer fluids facilitates bringing the heat exchangers to operating temperature quickly. The heat exchangers are of sufficient capacity to maintain effluent gas temperatures during steady state operation within ±3°C (port 1), ±2°C (port 2), and ±1°C (port 3).

On exit from the second heat exchanger, flue gases can be passed over a measured injection of lime to neutralize acid components. Particulate (or fly ash) is then removed from the effluent gases in a pulse-jet baghouse with P-84 fabric media filters. The exit gas flow rate is measured by an S-type pitot tube and thermocouple located downstream of the baghouse and upstream of an ID fan. One driving force for the gas stream movement is by a blower fan, creating a slightly negative pressure, relative to atmospheric, inside the incinerator. Draft and gas residence times are adjusted manually by means of a butterfly valve just upstream of the baghouse and after the heat exchangers. A butterfly valve, located at the exit of the second heat exchanger, controls the draft through the incinerator. A 0-0.5 inch H_2O magnahelic is used to monitor the relative pressure within the PCC.

2.1.2 Analytical Setup

In order to derive qualitative and quantitative performance analysis from the pilot-scale combustion system, a continuous emissions monitoring system (CEMS) is set up and operated. Three sampling ports are located along the unit: sampling port 1, at the downstream end of the annular flue in the secondary combustion chamber extension; sampling port 2, immediately downstream of the second heat exchanger; sampling port 3, between the baghouse and ID fan. Refer to Figure 2.1 for specific port location. Three sampling probes are located throughout the incinerator process: at the exit of the oxidation stage (sampling port 1), at the exit of the heat recovery stage (sampling port 2) and at the exit of the baghouse, just prior to stack emission (sampling port 3). The temperature in the sample lines are maintained above 100 C to prevent condensation of water vapor within the sampling line by heating tape and a temperature controller.

The analytical instruments currently used for data collection are a CO monitor, O_2 monitor, and a NO_x analyzer which detects NO and total NO_x. All three instruments are set up to operate continuously. The CO analyzer uses infrared to detect the presence of CO and is capable of reading between 0 and 1000 ppm via two ranges, 0-200 ppm and 0-1000 ppm. The O_2 analyzer uses the paramagnetic property of O_2 to measure the concentration of oxygen. The NO_x analyzer uses chemiluminesence to detect the presence of NO_x, and has a built-in ozonator using an in-house compress air source to produce the needed ozone reactant. The in-house compress air source is passed through a dryer system to remove water from the compressed air. Temperatures at each sampling port and at points on the primary and secondary combustion chambers are measured continuously by thermocouples, which are installed with the thermocouple tip at the center of the gas stream duct.

All data from the CEMS equipment and thermocouples are recorded simultaneously and logged by a Fluke FL2026A data acquisition unit (20 channel). The data acquisition unit is connected to a personal computer (PC) running National

Instruments' Labview software for the storage, graphics, and real time presentation of data. A second, backup monitor is installed and set up to monitor CO and O_2 levels.

Two gas chromatographs (GCs) are used to sample hydrocarbon (HC) species. A Gow-Mac Series 580 GC is used to detect total hydrocarbons, and is referred to as the total HC analyzer. The Gow-Mac uses a flame ionization detector (FID), with 1/8" stainless steel tubing, a gas sampling valve with 1 mL sampling loop and no column or stationary phase. A continuous sample flows through the gas sampling valve and is injected into the GC at 10 minute intervals. The second GC is a Varian 3700, with FID and 6' x 1/8" packed column with Super-Q as its stationary phase. This GC is used to detect the presence of low molecular weight hydrocarbons, such as C1 to C4 hydrocarbons and oxyhydrocarbons. Samples are injected into the GC column through a 6-port gas sampling valve and 1 mL loop. The resulting data from both GCs are recorded into a PC via a VG ChromServer, and the software used for GC peak integration and peak area conversion to concentration is PC Minichrome.

The CEMS and GC instruments are interconnected, through a continuous operation sample collection manifold system, to the three sampling ports on the pilot-scale combustion unit. A manifold connects the sampling ports through a dual booster pump assembly, to a 4-way crossover valve and flow meters, and then through the instruments to exhaust. The sample collection and distribution input lines are heated to between 110°C to 130°C to limit sample loss and condensation, and are maintained at pressure of 4 kPa to 7 kPa (0.5 to 1.0 psi) above atmospheric. A water trap, immersed in ice bath, is use to remove the moisture from the sample, prior to entrance into the analytical instruments. Routine verification of line pressure is required, and is controlled via a regulator near the outlet of the second booster pump. It is important that this line pressure is maintained at the desired set point for data accuracy.

The gas sampling manifold includes a versatile sample distribution system with water vapor removal and ports for a calibration gas inlet. It also incorporates flow control monitors for sample, calibration, and dry-purified air reference gases. Refer to Figures 2.3 and 2.4 for diagram of sampling manifold and sample flow path.

All analytical instruments are warmed up before data is collected. Warm-up time is at least 2 hours but is typically done overnight. Instruments are calibrated before and after each experimental run. Sample gas flow and meter readings are checked manually every30 min to assure correct operation of equipment. All GCs use 2 point data calibration with a zero and a standard (span) gas. Simultaneous calibration can be performed on all three analyzers for the zero gas.

2.1.3 Synthetic Solid Fuel

The mass percent composition of the synthetic solid fuel used in the pilot scale incinerator is shown in Table 2.1. The choice of fuel composition is based on an average of data provided for the U.S. municipal waste stream by the USEPA[2], and is representative of municipal solid waste after some recycling. The target plastic is low density polyethylene and the 1% inert material is silica and alumina in equal mass. Raw materials are individually weighed out to the desired compositions and then shredded and mixed in a hammer mill shredder. A mesh screen with 1.2 cm opening is in place at the bottom of the shredder. The solid fuel mixture are cylindrical pellets of 2.5 cm diameter

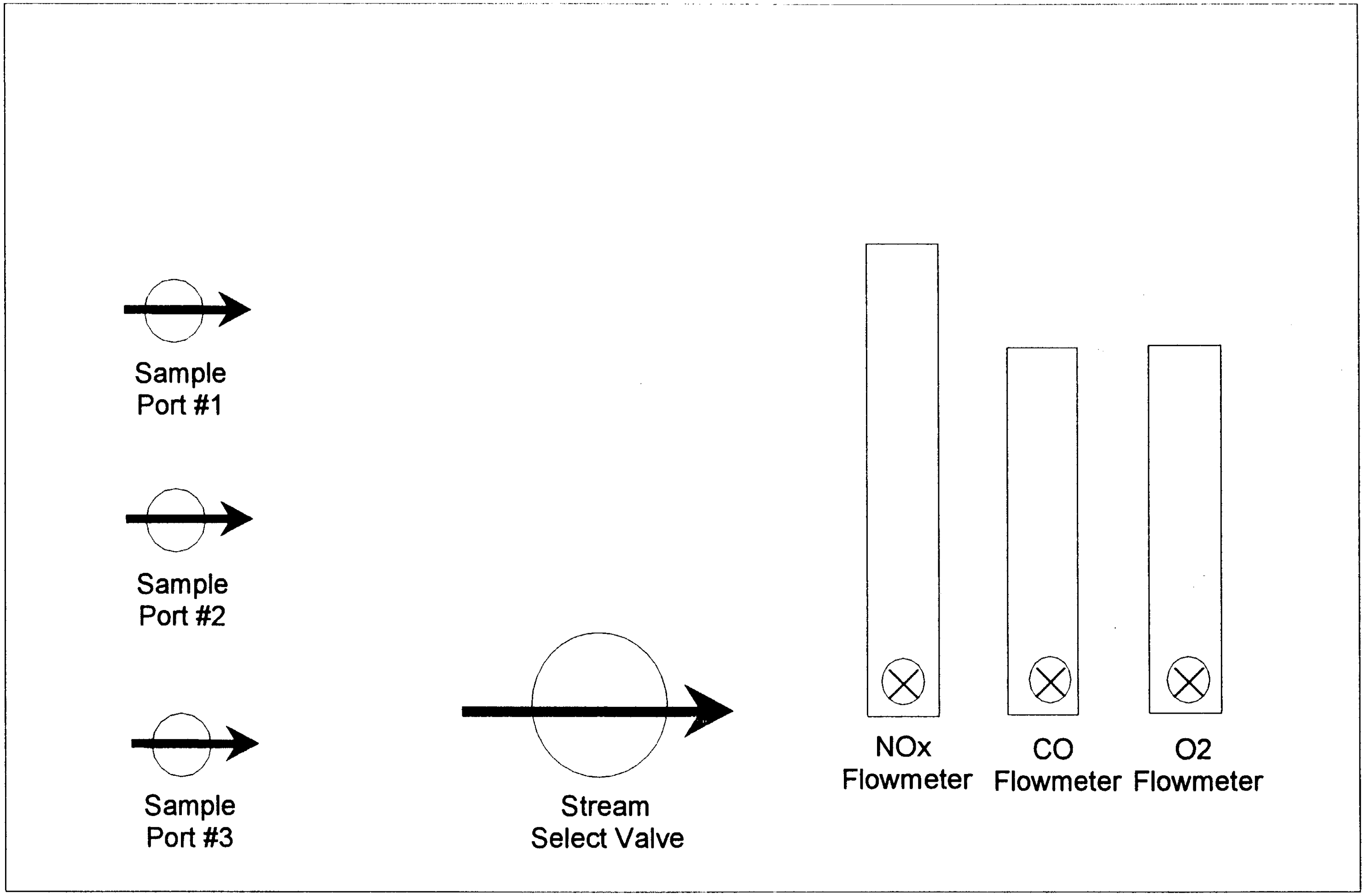


Figure 2.3 Front view of the sampling manifold

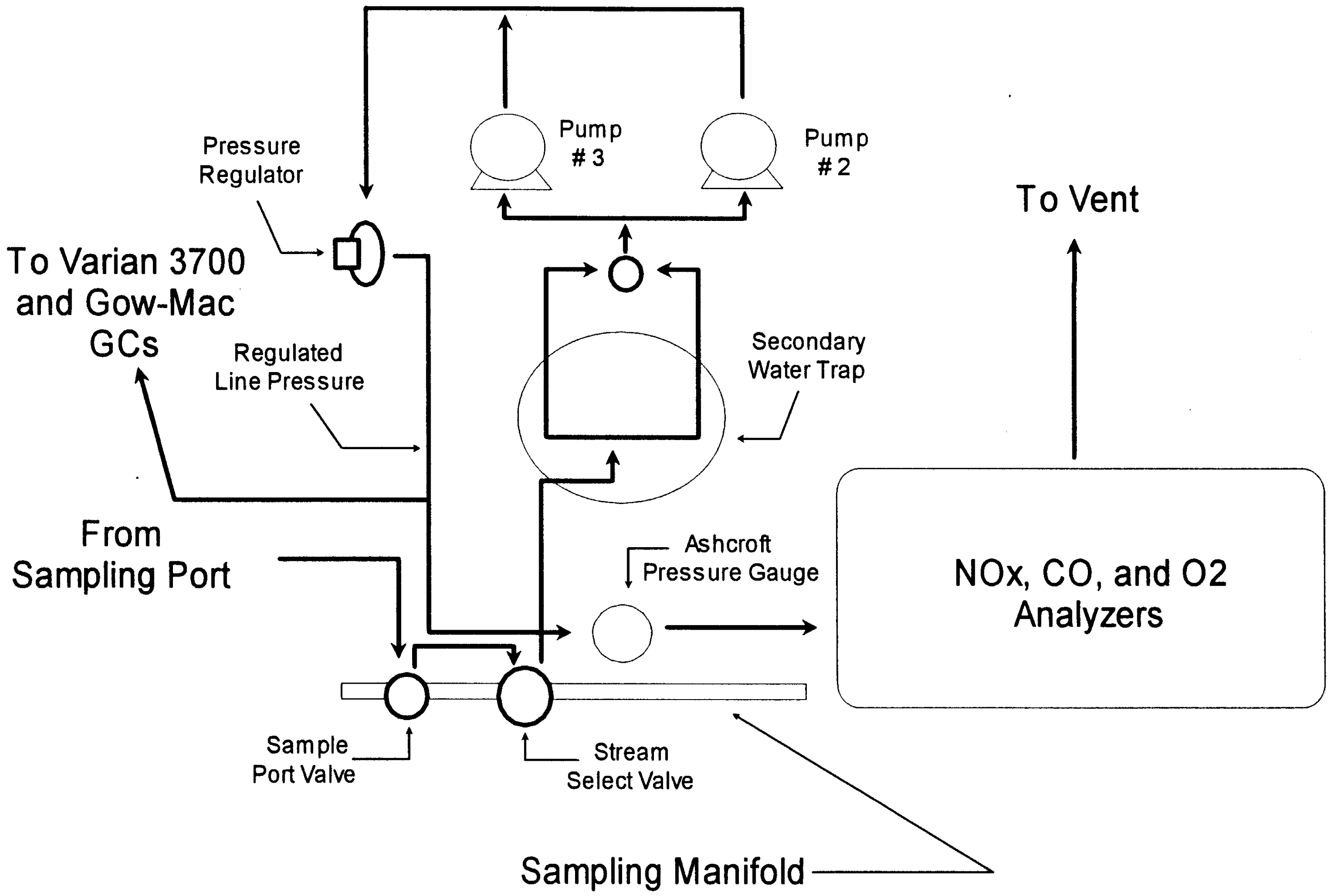


Figure 2.4 Layout of sample flow path from sampling ports to instruments

and average 5 cm length. Average values for pellet samples are solid density of 710 kg/m^3, bulk density of 542 kg/m^3.

Table 2.1 Typical Composition of Synthetic Waste Fuel by Mass

Component	Mass%
Paper (newsprint)	35
Water	20
Wood (mulch)	17
Plastic	14
Metal	8
Waste food	5
Inert particulate	1

The exact chemical formula for the fuel composition is difficult to be determined. An attempt to estimate the fuel chemical composition is made by assuming the paper and the wood component of the fuel compose of cellulose, $C_6H_{10}O_5$, and the low-density polyethylene plastic combines carbon and hydrogen in the same proportion as ethylene, C_2H_4, and the waste food is approximated to compose of monomethylamine, CH_3NH_2. Based on the mass percent of each of the components listed in Table 2.1, an approximate chemical composition of the dry fuel is determine have an empirical chemical formula of $C_{3.1}H_6O_{1.6}$ with negligible nitrogen. An ASTM test E778-87 determine that the mass percent of nitrogen in the synthetic solid fuel to be 0.42%. The "higher heating value" of the pellet, in accordance to ASTM E711-87 procedure is 4570 cal/g.

2.2 Introduction to the Modeling Approach

2.2.1 Reactor Model for Incinerator

The incinerator is to be modeled as 3 reactor zones: a perfectly stirred reactor (PSR), a heated plug flow reactor (PFR) and an adiabatic PFR. The PCC, with opposing OFA jets above the grate, creates a swirl effect within the PCC and rapid mixing. The model reactor for this effect characterizes a PSR. The exit of the PCC has a flow constraint (the effective cross-sectional flow is reduced by a baffle) to create a turbulent effect prior to entrance into the glycol-heated SCC, which would characterize a PFR.

The PSR will be model as an isothermal reactor, since the temperature data will be at steady state, where the temperature will not change. The first PFR has heated transfer oil flowing co-current through the annular region, to minimize the heat transfer loss of the gas through the walls. The second PFR is insulated, with some heat loss through this reactor zone. Heat transfer coefficients need to be estimated for both PFRs.

INFERNO, a reactor code developed by Bass[49], does offer a PSR-PFR1-PFR2 configuration, taking heat transfer effects into consideration.[50] INFERNO uses the ChemKin II interpreter, with a modified integrator to calculate the concentration and temperature profiles in a PSR-PFR1-PFR2 reactor configuration.

Complete mass and elemental balance cannot be performed on this system, due to the complexity of the solid fuel matrix, combined with the inherent nature of the system. The exact chemical composition of the fuel matrix is not known. The incinerator itself has fugitive air entrainment into the system, *e.g.* during fuel feed, the feed chute is open, which allows air flow into the system. The cause of the fugitive air entrainment occurs from the induced draft fan, which creates a slightly negative pressure inside the incinerator. The incinerator is designed to burn with excess oxygen, which is typical operating condition for municipal incinerators. McQuigg reports that total air flow, *i.e.* OFA + UFA, should be maintained within reasonable operating fuel equivalence ratios, ca. 80 - 100% excess air, for biomass incineration, which correlates to a fuel equivalence ratio of 0.5 – 0.55.[51]

One assumption that will be used is that oxidation reactions occur only in the gas phase, *i.e.* no heterogeneous oxidation reactions occur within/on the solid fuel. A mass flux with various ratios of equivalent C_1 and C_2 hydrocarbon species into the PSR, originating from the fuel bed, will be determined. C_1 and C_2 hydrocarbon species that will be used as representative equivalent fuel are CH_3OH, C_2H_4 and C_2H_6. CH_3NH_2 is to be used for nitrogen in the fuel.

The UFA is measured by a magnahelic, a differential pressure gauge, and the volumetric flow rate are derived based on the differential pressure drop. The velocity and volumetric flow rate of the UFA is estimated using the Bernoulli equation[52] and conservation of mass, with the assumptions that the system (under fire air) is: at steady state, an isothermal ideal gas with turbulent flow and negligible friction loss. The source of the under fire air is from ambient, which at room temperature and pressure, can be assumed to behave ideally.

2.3 Proposed Detailed Kinetic Model

Elementary reaction kinetics for oxidation of the model fuel species: CH_4, CH_3OH, C_2H_2, C_2H_4, C_2H_6 and CH_3NH_2 are evaluated and developed during this study. Thermodynamic properties of species are obtained from literature or from computational methods, depending on literature availability. Computational methods for thermodynamic properties will include empirical (such as THERM[53]), semi-empirical methods (MOPAC[54]) and *ab initio* methods (Gaussian[55]). Kinetic parameters for the elementary reactions will be obtained either from literature, from NIST database, homologous reaction derivations or transition state theory.

Initial model chemicals representing the fuel includes ratios of CH_3OH, C_2H_4, C_2H_6 and CH_3NH_2. To adequately explain oxidation of methane and methyl species, a detailed mechanism must include C_2 species; because CH_3 does not react rapidly with O_2 to further, stable oxidation products so methyl radical levels build up and combine to form C_2H_6, C_2H_5 and C_2H_6. CH_3 radicals are formed from abstraction reactions on CH_4 and unimolecular dissociation of CH_3OH. Further reactions of ethane, ethylene and acetylene occur with radicals in the radical pool, *i.e.* OH, H, O and minor reactions with HO_2. Ethane is formed from the association of two methyl radicals, *i.e.* $CH_3 + CH_3 \rightarrow C_2H_6$. Ethylene can be formed from ethane, via abstraction of H forming ethyl radical; and ethyl can beta scission to C_2H_4 + H. Addition of O_2 to C_2H_5, via molecular elimination also produces $C_2H_4 + HO_2$. Vinyl radical, C_2H_3, is formed by H and OH radical abstractions from C_2H_4 and formation of acetylene results from beta scission of vinyl radical.

2.3.1 CH_4 and CH_3OH

The pressure and temperature dependent methane and methanol reaction mechanism will be updated from the previous work in Bozzelli's group (at New Jersey Institute of Technology) - specifically by Wen-chiun Ing and Takahiro Yamada's doctoral dissertations.[56,57] Thermodynamic properties and kinetic parameters from their CH_4/CH_3OH and dimethyl ether systems are derived from literature, empirical and semi-empirical methods, and from *ab initio* calculations.

ab initio calculations for species in the CH_3OH unimolecular dissociation pathway have been calculated with B3LYP/6-31G(d) density functional theory (DFT) method[58], as well as with the complete basis set – atomic pair natural orbital method or CBS-APNO[59] composite method.

2.3.2 HCCH + O_2

Acetylene oxidation has been developed with consideration for four different reaction paths for this system: HCCH + $O_2(^3\Sigma)$, HCCH + $O_2(^1\Delta)$, HCCH → H_2CC: (vinylidene) follow by addition with $O_2(^3\Sigma)$ and HCCH + $^3O_2$ ⇔ ^{3}Adduct ⇔ ^{1}Adduct, as well as HCCH ⇔ H_2CC: and H_2CC: + O_2. *ab initio* calculations using MP2/6-31G(d), QCISD(T)//MP2/6-31G(d) and CBS-q//MP2/6-31G(d), as well as DFT calculations at B3LYP/6-31G(d,p) and BHandH/6-31G(d) level were performed to determine the thermodynamic properties of all reactants, adducts and products in this mechanism. Vibrational frequency calculations are determined from the DFT method of BHandH/6-31G(d). Entropy and heat capacity values are determined based on application from principles of statistical mechanics.

2.3.3 C_2H_4 Oxidation

Both Ing[56] and Yamada[57] provide this mechanism in their Ph. D. dissertation and their mechanism will be utilized in the current model. Reactions include abstraction of H from

C_2H_4 by the radical pool (H, O, OH, CH_3 and NH_2) and formation of C_2H_3, vinyl radical, as well as H, O and OH addition reactions with C_2H_4. The $C_2H_3 + O_2$ mechanism will be obtained from Chang, *et al.*'s[60] publication and updated into the proposed kinetic model.

2.3.4 $C_2H_5 + O_2$

Thermodynamic properties of this system, which initially forms the ethyl peroxy radical $CH_3CH_2OO\bullet$, have been completed at the B3LYP/6-31G(d,p) level and also at the high level composite CBS-Q//B3LYP/6-31G(d,p) *ab initio* calculations. Reaction pathway and kinetic analysis for $C_2H_5 + O_2$ are determine from either canonical transition state theory or variational transition state theory. The formation of $\bullet CH_2CH_2OOH$ by isomerization of ethylperoxy radical and by HO_2 addition to ethylene form this important intermediate.

2.3.5 $\bullet CH_2CH_2OOH + O_2$

Thermochemical and kinetic parameters of the second oxygen addition to the hydroperoxy-ethyl radical resulting from the ethyl oxidation system results in chain branching reaction processes that have not previously been investigated. Studies on this system are performed at the B3LYP/6-31G(d,p) and CBS-Q//B3LYP/6-31G(d,p) for all the reactants, adducts and transition states. High-pressure limit rate constants are determined from canonical transition state theory. At least 3 new chain branching reactions are proposed in this reaction system.

2.3.6 CH_3NH_2

The kinetic mechanism for the nitrogen-hydrogen-oxygen subsystem is obtained from Dean and Bozzelli's recent publication.[36] Analysis of the coupling of carbon to the nitrogen-oxygen-hydrogen system is done in this work, using CH_3NH_2 as the starting reagent. Detailed analysis on oxidation of CH_3NH_2 by radical pool (abstraction reactions are performed and oxidation of the important $CH_3N{\bullet}H$ and $C{\bullet}H_2NH_2$ radicals via reaction with O_2 are performed. These include new thermochemical analysis (*ab initio* and density functional theory) on CH_3NHOOH, $CH_3NHOO{\bullet}$, ${\bullet}OOCH_2NH_2$ and $HOOCH_2NH_2$ species. The accurate estimate of H_f(298K) on these species results in changes in reaction paths from previous analysis.[61] Thermodynamic properties of this system has been performed at the B3LYP/6-31G(d,p) and also at the G2(MP2) level of theory computation. Enthalpy of formation for two adducts are determined from isodesmic working reactions at the G2(MP2) level of theory.

2.4 Thermodynamic Properties and Kinetic Rate Parameters

The programs used for *ab initio* and DFT calculations are Gaussian94 and 98 to determine quantum chemical properties; through application of the principles of statistical mechanics, macroscopic thermodynamic properties can be determined. Two supplementary programs have been written to aid in converting the Gaussian results on structure and vibration frequencies to values for entropy and heat capacity at constant pressure (C_p).

GINC: A FORTRAN code to retrieve the final results from a Gaussian output file, *e.g.* optimized geometry, vibrational frequencies, zero point correction, thermal correction to enthalpy, ...etc.

SMCPS: A FORTRAN code to calculate entropy and C_p, based on principles of statistical mechanics. Thermal correction for enthalpy of formation is also incorporated into the program. Adjustments in vibrational contribution for entropy, C_p and ΔH based on Scott and Radom's analysis are implemented within the code.[62]

Kinetic rate parameters for elementary reactions can be determined by several methods, canonical transition state theory (CTST) with *ab initio* calculations of the reactants and transistion states or literature evaluation. Two FORTRAN codes have been written to aid in determining Arrhenius rate parameters.

ThermKin: This program will calculate the Arrhenius rate parameters based on rate constants from CTST. ThermKin can calculate the rate expression for both the classical Arrhenius expression, *i.e.* $k = A \exp(-E_a/RT)$, and the modified Arrhenius expression, *i.e.* $k = A T^n \exp(-E_a/RT)$.

Kfit: This program can provide Arrhenius rate parameters, both in form of classical or modified Arrhenius expression, from literature/experimental data. An important option this program provides, is user specified E_a. Method of determination is from principle of least squares.

ChemMaster: A FORTRAN code based on the quantum Rice-Ramsperger-Kassel (QRRK) analysis for *k(E)* and master equation analysis for fall off will be employed to determine kinetic parameters in complex reaction systems, such as

C_2H_5 + O_2.[60,63] The original source code for the QRRK analysis was originally developed by A.M. Dean (1985) and later by A.M. Dean, E. Ritter and J.W. Bozzelli (1990). A.Y. Chang, J.W. Bozzelli and A.M. Dean made further improvements to calculate systems with multiple wells. W.-C. Ing expanded the versatility of the QRRK with modified strong collision to express the rate coefficients in terms of Chebyshev polynomials to account for pressure dependence (1996). Recently, Sheng, *et al.*[64] updated the QRRK with master equation to also express rate coefficients in Chebyshev polynomial form to account for pressure dependence.

The current version of the QRRK computer code utilizes a reduced set of vibration frequencies which accurately reproduce the molecule (adduct), heat capacity data. Molecular density of state functions are constructed through direct convolution of single frequency density functions on a 10 cm^{-1} grid. The functions corresponding to each reduced frequency are explicitly convolved into a relative density of states ($\rho(E)$), which is normalized by the partition function (Q). The inclusion of one external rotation is incorporated into the calculations by convolving the vibration density function with the proper rotational density function. A detailed description of this and comparisons of ratios of these $\rho(E)/Q$ with direct count $\rho(E)/Q$ are shown to be in good agreement.[65] Nonlinear Arrhenius effects resulting from changes in the thermodynamic properties of the respective TS's relative to the adduct with temperature are incorporated using a two parameter Arrhenius pre-exponential A-factor (A, n) in AT^n. Fall-off is incorporated using master equation.

The individual kinetic systems described above will be compared with available literature data to test for consistency and agreement in subsequent chapters. The mechanisms will then be combined to represent a set of reactions characteristic of the incinerator combustion process. The overall mechanism consists of over 900 elementary reactions and almost 200 species. Experimental results obtained from the incinerator will be compared with the combined model.

The major components in the solid fuel pellet are cellulose (paper + wood) and plastic (poly-ethylene). The chemical formula for cellulose is $(C_6H_{10}O_5)_n$ and for poly-ethylene is $(C_2H_4)_n$. An initial concentration of ethylene would be reasonable to represent the plastic component in the solid fuel matrix. An initial choice of CH_3OH / C_2H_4 / C_2H_6 will be used to emulate the C / H / O ratio in the fuel pellet. CH_3NH_2 will be added to represent fuel nitrogen.

2.5 Combination of Physical Model and Detailed Chemistry to Represent Incinerator Operation

The combined physical model of the incinerator (combination of well mixed and plug flow reactors) with the detailed chemistry and kinetic mechanism will be tested against data collected in the incinerator. Specific test data will include calculations of hydrocarbon products effluent from the incinerator, CO, and NO_x levels.

CHAPTER 3

THERMODYNAMIC PROPERTIES (ENTROPY AND HEAT CAPACITY) FROM *AB INITIO*, DENSITY FUNCTIONAL THEORY OR OTHER CALCULATIONS

3.1 Introduction

Use of computational chemistry to determine molecular species' properties is a rapidly growing research area; it is finding a wide range of applications with the advent and rapidly increasing improvements in computer processors and systems.[66-73] The importance of computational chemistry quickly becomes apparent when data on species, such as transition state structures and enthalpies of active radicals can be computed to validate or help interpret experimental results. Thermochemical data are fundamental to Chemistry and Chemical Engineering; they are needed in analysis for enthalpies of reaction, reaction paths, equilibrium determinations, stability, kinetic parameters, ... etc.

The capabilities of a modern PC and the currently available *ab initio* and density functional computation programs[74,75] provide easy access to results of these calculations to both graduate and undergraduate students, as well as practicing engineers and scientists. There are several *ab initio* and density functional computational packages available, among which include: GAMESS, Molpro, Spartan, CADPAC, Jaguar, NWChem, Q-CHEM, HyperChem and Gaussian.[55,76-83]

The output files generated from *ab initio* calculations are usually quite extensive; they include a number of molecular parameters, *e.g.* optimized geometry, ionization potential, frequencies, dipole moment, relative energies, electron population in orbits, ...etc. Direct application of these determined properties on molecular species is not always apparent to applied users, such as engineers, kinetic modelers, students in courses, and other scientists that use thermochemical or kinetic data. Statistical mechanics determines the macroscopic thermodynamic properties directly from the quantum mechanical calculated properties. A number of equilibrium and kinetic programs are available that require thermochemical data are CHEMKIN, STANJAN, CHEMSAGE© and NASA's CEA.[84-87]

SMCPS (Statistical Mechanics for Heat Capacity and Entropy $\underline{C}_{\underline{p}}$ and $\underline{S}$), is written to determine $H-H_0$, Cp, S and zero point vibrational energy (ZPVE) of molecular species from computation chemistry results. The method of calculation is based on principles of statistical mechanics and has no empirical factors or corrections, other than physical constants.

3.2 Theory and Basis of SMCPS

In a physical system, there are many molecules, which have some probability of occupying any one of the allowable discrete energy levels; this implies that there is a distribution of molecules among the different allowable energy levels. The method of determining this probability distribution is known as statistical mechanics. Once the probability distribution is obtained, the associated energies can be calculated and derivation of thermodynamic properties achieved. The principle of statistical mechanics or chemical statistics is application of statistics to determine thermodynamic properties, e.g. enthalpy, entropy, heat capacities, free energies ... etc. The equilibrium distribution of the system is defined as the most probable distribution of the system at a given condition.

The basic foundation in statistical mechanics is the partition function; once the partition function is determined, all thermodynamic properties can be determined. The partition function describes the energy of the system over all the individual quantum levels. The canonical ensemble of the partition function is expressed as follows,

$$Q = \sum_i g_i e^{E_i/RT}$$

where Q is the partition function, g_i is the degeneracy, E_i is the energy of the i^{th} quantum level. Thermodynamic properties, as related to partition function, are as follows,

Helmholtz free energy: $A = -RT \ln Q$
Gibbs free energy: $G = A + PV$
Internal Energy: $U = RT\left(\frac{\partial \ln Q}{\partial \ln T}\right)_V = -R\left(\frac{\partial \ln Q}{\partial (1/T)}\right)_V$
Enthalpy: $H \equiv U + PV$
Entropy: $S = \frac{U-A}{T} = R\ln Q + R\left(\frac{\partial \ln Q}{\partial \ln T}\right)_V$
Molar heat capacity at constant volume:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = R\left(\frac{\partial \ln Q}{\partial \ln T}\right)_V + R\left(\frac{\partial^2 \ln Q}{\partial (\ln T)^2}\right)_V = \frac{R}{T^2}\left(\frac{\partial^2 \ln Q}{\partial (1/T)^2}\right)_V$$

The total energy of the system is the sum of all its parts that contribute to the energy, *i.e.* translational, vibrational, external rotational, internal rotational and electronic energies; $E_{tot} = E_t + E_v + E_{ext\ rot} + E_{int.\ rot} + E_e$. Substitution of the different constituents for energy, E_{tot}, and through some derivation, the partition function expression can be shown to be $Q_{tot} = Q_t\ Q_v\ Q_{ext.rot}\ Q_{int.rot}\ Q_e$. This will allow individual considerations of thermodynamic properties to be determined, as well as the total contributions from these components.

Once the partition functions are known, the thermodynamic properties from different contributions can be determined and the thermodynamic values of interest can be obtained. The goal is then to solve the individual contributions of the partition function, and then sum the individual contributions of the partition function to obtain the total thermodynamic value desired.

The translational partition function can be determined by solving the Schrödinger Equation for a system like "particle in a box." External rotation partition functions are difficult to derive, and as a result simplifications are made, *e.g.* rigid rotator or linear rotator. Vibrational partition functions are determined from assumptions that the vibrations behave as harmonic oscillators. Electronic contributions, in general, are negligible compared to the other modes at room temperature. However, one can readily include the electronic contribution, providing energies in the low-lying electronic states are known.[88] Electronic contribution may be significant in radical species with strong spin-orbit coupling or having several low-lying electronic states. Ideal gas behavior is assumed in these cases.

Final terms for thermodynamic properties, after derivation from partition functions, for entropy are

$$S_{trans} = R\left[\frac{3}{2}\ln M_w + \frac{5}{2}\ln T - \ln P + \frac{5}{2} + \frac{3}{2}\ln\left(\frac{2\pi k}{h^2}\right) - \frac{5}{2}\ln N_A + \ln R\right]$$

$$S_{rot}^{linear} = R\left[1 + \ln\left(\frac{8\pi^2 kT}{h^2\sigma} I\right)\right]$$

$$S_{rot}^{non-linear} = \frac{3}{2}R + \frac{1}{2}R\ln\left[\frac{\pi}{\sigma^2}\left(\frac{8\pi^2 kT}{h^2}\right)^3 I_x I_y I_z\right]$$

$$S_{vib} = R\sum_i\left[\frac{x_i e^{-x_i}}{1-e^{-x_i}} - \ln(1-e^{-x_i})\right] \text{ where, } x_i = \frac{h\upsilon_i}{kT}$$

$$S_e = R\ln\omega_0$$

$$S_{tot} = S_{trans} + S_{rot} + S_{vib} + S_e$$

The electronic contribution for entropy, *i.e.* $S_e = R \ln \omega_0$, will apply to radical species or species where spin-orbit coupling exists, where ω_0 is the spin degeneracy of the electronic ground state.[89] For polyatomic molecules, $\omega_0 = 2S + 1$, where S is the total spin.[88] This implies that ω_0 is equal to the multiplicity of the molecule.

The molar heat capacity at constant volume and at constant pressure with assumption of ideal gas behavior, are expressed as follow:

$$C_{V,trans} = \frac{3}{2}R \text{ and with assumption of ideal gas behavior, } C_{P,trans} = \frac{5}{2}R$$

$$C_{V,rot}^{non-linear} = C_{P,rot}^{linear} = \frac{2}{2}R \text{ and } C_{V,rot}^{non-linear} = C_{P,rot}^{non-linear} = \frac{3}{2}R$$

$$C_{V,vib} = C_{P,vib} = R\sum_i \left[\frac{x_i^2 e^{-x_i}}{(1-e^{-x_i})^2}\right] \text{ where, } x_i = \frac{h\upsilon_i}{kT}$$

$$C_{v,tot} = C_{V,trans} + C_{V,rot} + C_{V,vib} \text{ or } C_{P,tot} = C_{P,trans} + C_{P,rot} + C_{P,vib}$$

The relationships for internal energy and enthalpy are from thermodynamic definitions, with assumption of ideal gas behavior.

$$U_{trans}(T) - U_{trans}(0°K) = \frac{3}{2}RT \text{ and with assumption of ideal gas,}$$

$$H_{trans}(T) - H_{trans}(0°K) = \frac{5}{2}RT$$

$$U_{rot}^{linear}(T) - U_{rot}^{linear}(0°K) = H_{rot}^{linear}(T) - H_{rot}^{linear}(0°K) = RT \text{ and}$$

$$U_{rot}^{non-linear}(T) - U_{rot}^{non-linear}(0°K) = H_{rot}^{non-linear}(T) - H_{rot}^{non-linear}(0°K) = \frac{3}{2}RT$$

$$U_{vib}(T) - U_{vib}(0°K) = H_{vib}(T) - H_{vib}(0°K) = RT\sum_i x_i\left(\frac{e^{-x_i}}{1-e^{-x_i}}\right) \text{ where, } x_i = \frac{h\upsilon_i}{kT}$$

$$U_{tot}(T) - U_{tot}(0°K) = \Delta U_{trans} + \Delta U_{rot} + \Delta U_{vib} \text{ or}$$

$$H_{tot}(T) - H_{tot}(0°K) = \Delta H_{trans} + \Delta H_{rot} + \Delta H_{vib}$$

An important energy component in these computation chemistry calculations is the zero point energy (ZPE). ZPE is the energy of the specie at absolute zero. Quantum chemical calculations determine the minimum in the potential curve; but a molecular species at 0K also has its vibration levels populated in their lowest level. The treatment of ZPE is not from statistical mechanics, but from quantum mechanics. ZPE can be determined by the following simple expression,

$$ZPE = \frac{1}{2}\sum_{i} h\upsilon_i$$

There are two considerations that are not applied to the above statistical treatment of thermodynamic properties that may be a major factor in some molecular species. The first is contribution to S and $C_p(T)$ from internal rotors, which for some species can be significant. Molecular species that do not have internal rotors are represented by the above statistical analysis representation. However, for molecular species that have hindered internal rotors, the contributions to S and $C_p(T)$ need to be separately calculated and incorporated into the thermodynamic properties. One method to estimate the hinder rotor contributions is by using the vibration frequency for the torsion in this program. At the present time, an accurate treatment of hindered internal rotators is not included in this program; for hindered rotor barriers of 4 kcal/mol or less a more accurate treatment is recommended. More accurate methods are available and include those of Pitzer and Gwinn[90,91], McClurg , *et al.*[92,93], Knyazev[94] or Rotator[68]; the data from these rotor analysis are simply added to the data from SMCPS with contributions from torsion frequencies removed.

Optical isomers are molecules that cannot be superimposed onto each other, but are a "mirror image" of each other and these also require an added consideration. Hydroperoxy species have one pair of optical isomers. The thermodynamic property that is affected by optical isomers, is entropy. The correction for a molecule with two optical isomers is:

$$S_{opt.iso} = R \ln \sigma_{opt.iso}$$

and this correction entropy value is added to the above total entropy, S_{tot}, *i.e.*

$$S_{corrected} = S_{tot} + S_{opt.iso}$$

Thermodynamic properties, as derived from partition function, are coded into a Fortran program called SMCPS. The program has an additional assumption that is not part of the above derivations; the program assumes the system of interest is at one atmospheric pressure, where most of literature thermodynamic data are found.

3.3 About SMCPS

SMCPS is written in FORTRAN and has been compiled for Microsoft® MS-DOS™ (16 bit operating system) and the Windows® platform (32 bit operating system). The statistical mechanics treatment to determine thermodynamic properties for Cp, S and ΔH(T-0°K), as described above, has been fully implemented. The more detailed calculation of hinder rotor contributions to entropy and heat capacity are not included in SMCPS; only the torsion frequency method.

The program requires an input file, in ASCII format, that includes the molecular parameters needed by the statistical mechanics equations. The program will read from the input file and search for

- keywords (*e.g.* temperature, frequency, moment of inertia ...etc.)
- number of individual inputs (such as number of different temperatures of interest and number of frequencies)
- actual values of the variables.

The maximum number of different temperatures allowed is 40 and the maximum number of frequencies allowed is 500, which is sufficient for 166 atoms, *i.e.* for most applications. (This maximum can be readily expanded).

3.3.1 Input File

All the keywords in the input file have to start in the first column and be in capital letters, *i.e.* TEMP, FREQ, ...etc. For temperature and frequencies, the number of different temperatures or frequencies has to be entered on the line directly below the keywords. The actual values of variables has to be entered on the line directly below the keywords, except for temperature and frequencies, which will be entered on the line directly below the number of temperatures of interest and frequencies. Comments can be entered, either before or after each block of keywords and its associated values, not in between data values. The order of keywords and its associated values are not important.

The keywords used in the input file are for temperature, vibrational frequencies, moment of inertia about the principle axis, symmetry, number of rotors, molecular weight, if the molecule is linear or non-linear and optical isomers. Additional inputs for the program include comments that can be used to describe the molecule and a reference for the user in future identification of the specific calculation. An example of an input file is shown in Table 3.1.

Specific comment lines can be written to the output file to reference and identify the calculated results. The keyword is COMMENT (in capital letters). The two lines following COMMENT will be written to the output file, to help identify the specific molecular specie of interest.

Table 3.1 Example input file for SMCPS

```
NAME (name of molecule)
CH2O

COMMENTS:
B3LYP/631Gdp

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
0    number of internal rotors

MOLECULAR WT
    30.01056

OPTICAL ISOMER
1

MULTIPLICITY
1      multiplicity of molecular specie of interest

HF298
-26.67

STOICHIOMETRY (in form of "atom x" "number of atom x")
C  1 H 2  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
285.19856    38.62429    34.01734

SYMMETRY
2

NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
6
1199.9240              1274.2300              1554.5724
1846.0490              2897.4628              2954.1511
```

The units of input variables are as follows: temperature units are in degrees Kelvin, frequencies are in inverse centimeters and several commonly used units for principle moments of inertia are also available. Most commonly used units of principle moments of inertia are in units of 10^{-40} g-cm^2, GHz, amu-bohr^2, and amu-Å^2. The user is required to input the choice of units. On the following line after the keyword MOMENT, user will be required to input one of the following integers, depending on the units of the moments of inertia. The actual values of the three moments are entered on the line after the choice of units for the moment of inertia data.

1	10^{-40} g-cm^2
2	GHz
3	amu-bohr^2
4	amu-Å^2

Consideration of optical isomers and spin-degeneracy effects to entropy can be significant in some cases. All radical species exhibit spin-degeneracy. Stable molecules can also exhibit spin-degeneracy, as in the case of triplet state. The multiplicity of the specie for non-singlet state will contribute to its total entropy. SMCPS will incorporate both optical isomer and spin multiplicity into the calculation. The keywords are OPTICAL ISOMER and MULTIPLICITY, followed by the appropriate values in the respective proceeding line.

Scaling factors for calculated vibrational frequencies are also implemented. The computed values will often deviate from reported experimental values. Scott and Radom[62] are one of several studies that have estimated scaling factors for vibrational contribution toward thermodynamic properties from different basis sets. Corrections or scaling of these data are left to the discretion of the user. Scaling factors are provided in SMCPS with the following options; a default scaling factor of 1.0 (*i.e.* no scaling of frequencies), all the different basis set and methods reported by Scott and Radom, and a user-defined scaling factor. For AM1 and PM3, Scott and Radom reported only the frequency scaling factor. SMCPS will use the same scaling factors uniformly to calculate ZPE, Hvib and Svib, if the default, AM1 or PM3 are selected. All other scaling factors listed in Table 3.2 are used respective to the options selected.

A provision in the input file for reading a separately determined ΔH_f^{298} is also provided. Although SMCPS does not calculate the enthalpy of formation, the input file does accommodate for this thermodynamic property from the user's input. SMCPS will reproduce the ΔH_f^{298} in the output list file. The keyword for ΔH_f^{298} in the input file is "HF298." This is not a required keyword and SMCPS can run successfully if the user does not input a value for "HF298."

Table 3.2 List of Scaling Factors Used in SMCPS

Method	ZPE	H_{vib}	S_{vib}
[1] Default[a]	1.0	1.0	1.0
[2] AM1[b]	0.9532	0.9532	0.9532
[3] PM3[b]	0.9761	0.9761	0.9761
[4] HF/3-21G	0.9207	0.9444	0.9666
[5] HF/6-31G(d)	0.9135	0.8905	0.8978
[6] HF/6-31+G(d)	0.9153	0.8945	0.9027
[7] HF/6-31G(d,p)	0.9181	0.8912	0.8990
[8] HF/6-311G(d,p)	0.9248	0.8951	0.9021
[9] HF/6-311G(df,p)	0.9247	0.8908	0.8981
[10] MP2-fu/6-31G(d)	0.9661	1.0084	1.0228
[11] MP2-fc/6-31G(d)	0.9670	1.0211	1.0444
[12] MP2-fc/6-31G(d,p)	0.9608	1.0084	1.0232
[13] MP2-fc/6-311G(d,p),	0.9748	1.0061	1.0175
[14] QCISD-fc/6-31G(d)	0.9776	1.0080	1.0187
[15] B-LYP/6-31G(d)	1.0126	1.0633	1.0670
[16] B-LYP/6-311G(df,p)	1.0167	1.0593	1.0641
[17] B-P86/6-31G(d)	1.0108	1.0478	1.0527
[18] B3-LYP/6-31G(d)	0.9806	0.9989	1.0015
[19] B3-P86/6-31G(d)	0.9759	0.9864	0.9902
[20] B3-PW91/6-31G(d)	0.9774	0.9885	0.9920
[21] users manual input[c]			

---

[a] This will provide unscaled ZPE, H_{vib}, and S_{vib} results.

[b] Scott and Radom's scaling factor for frequency is used to scale ZPE, H_{vib}, and S_{vib}.

[c] User defined scaling factor is up to user's discretion.

3.3.2 Output File

The program produces three output files. One of the output files lists the heat capacity, entropy and thermal correction for enthalpy at the temperatures specified in the input file. The ZPE will also be calculated and written into this output file. (See example in Table 3.3). A second output file will write the specie into a specific formatted output file, consisting of the specie name, enthalpy of formation at 298K, entropy at 298K, Cp values at 300, 400, 500, 600, 800, 1000 and 1500K, comments, stoichiometric information and number of rotors. This second output file format is in the same format used in THERM[95], which can be readily transformed to the more popular NASA polynomial format. The third output file is a summary of the input variables used to calculate the thermodynamic data, it provides a check on the input data. An example of the output file generated by SMCPS for the thermodynamic properties at the user-defined temperatures is shown in Tables 3.3.

Table 3.3 Output File from SMCPS for Cp, S and H(T)-H(0K) at the Temperature of Interest and ZPE

```
CH2O
 rb3lyp/6-31gdp


    T(K)            Cp               So           [H(T)-H(0K)]
                (cal/mol/K)      (cal/mol/K)       (kcal/mol)
     1.00          7.949            6.866            0.008
     5.00          7.949           19.660            0.040
    10.00          7.949           25.169            0.079
    50.00          7.949           37.963            0.397
   100.00          7.949           43.472            0.795
   200.00          7.997           48.988            1.591
   298.00          8.399           52.235            2.390
   398.00          9.236           54.771            3.269
   498.00         10.257           56.947            4.244
   598.00         11.286           58.913            5.321
   698.00         12.248           60.730            6.498
   798.00         13.116           62.425            7.767
   898.00         13.886           64.017            9.118
   998.00         14.562           65.517           10.542
  1098.00         15.150           66.935           12.028
  1198.00         15.662           68.276           13.569
  1298.00         16.105           69.549           15.158
  1398.00         16.490           70.758           16.788
  1498.00         16.825           71.908           18.454
  1598.00         17.116           73.004           20.152
  1698.00         17.371           74.050           21.876
  1798.00         17.594           75.050           23.625
  1898.00         17.791           76.007           25.394
  1998.00         17.965           76.924           27.182
  2098.00         18.118           77.805           28.987

 Zero Point Vibration Energy (kcal/mol) =   16.443
```

3.4 Examples

Thermodynamic properties calculated using SMCPS from density functional calculations and comparisons with literature are performed for a number of molecules. The selection of species had two criteria; first is to find the species that do not have any internal rotors, since SMCPS does not take into consideration the internal rotor contribution. The second criterion is based on the availability of Cp and S value available in literature for the specie. The comparison between SMCPS calculation values and literature values is shown in Table 3.4.

Comparison of a variety of molecules are listed in Table 3.4 to illustrate that SMCPS is not limited to any particular type of molecular species. Some examples shown in Table 3.4 include simple hydrocarbons, oxy-hydrocarbon, halo-hydrocarbon, aromatics, and cyclic oxy-hydrocarbon species. Also included in Table 3.4 are four radical species. Input values to SMCPS for the species in Table 3.4 were calculated by density functional theory, B3LYP/6-31g(d,p)[58], with the exception of the 4 cyclic oxy-hydrocarbons (oxirane, 1,2 dioxetane, oxetane and 1,2 dioxolane), which were calculated at HF/6-31g(d) [96-98] level of theory. Scaling factors are used, based on Scott and Radom's suggestions.[62]

The results from SMCPS compare very well with both the NIST[99] and TRC[100] reported values for both the entropy and Cp. The average Cp difference is the difference between the SMCPS calculated value to the reported literature value. The largest average Cp difference is less than 0.6 cal/mol-K. Comparison of S(298K) shows that the largest difference occurs for the hexachloro-benzene specie, with less than 1 cal/mol-K difference between SMCPS calculated value and the TRC value.

Table 3.4 Comparison of Entropy and Cp Data Calculated by SMCPS with Literature Data

Species	S°(298K)	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)	Avg Cp difference	Remarks
CH_2ClO●	64.68	12.18	14.27	15.99	17.38	19.42	20.86	23.00		$\sigma = 2$
NIST	64.4	11.76		15.69		19.21	20.71	22.98	*0.22*	s =2
$CHCl_2O$●	72.17	15.58	17.71	19.27	20.40	21.93	22.90	24.23		$\sigma = 1$
NIST	71.6	15.03		18.75		21.62	22.64	24.13	*0.35*	s =2
CCl_3O●	79.03	19.80	21.65	22.80	23.56	24.44	24.90	25.40		$\sigma = 3$
NIST	78.4	19.23		22.40		24.33	24.78	25.38	*0.24*	s =2
HCO●	53.63	8.23	8.64	9.13	9.63	10.55	11.3	12.45		s =2
NIST	53.69	8.28	8.73	9.26	9.79	10.74	11.49	12.59	*-0.14*	
HCCH	47.66	10.07	11.57	12.65	13.46	14.72	15.74	17.58		$\sigma = 2$
NIST	48.02	10.56	12.04	13.09	13.89	15.18	16.24	18.18	*-0.48*	$s = 1$
C_2Cl_4	81.44	22.71	25.09	26.71	27.84	29.26	30.05	30.96		$\sigma = 4$
NIST	82.07	22.89	25.20	26.77	27.90	29.31	30.08	30.98	*-0.07*	$s = 1$
C_2H_4	52.32	10.13	12.43	14.63	16.56	19.67	22.06	25.97		$\sigma = 4$
NIST	52.42	10.30	12.68	14.93	16.89	20.03	22.44	26.28	*-0.30*	$s = 1$
C_2HCl_3	77.56	19.13	21.69	23.55	24.94	26.81	28.02	29.68		$s = 1$
TRC	77.73	19.24	21.8	23.68	25.07	26.95	28.16	29.83	*-0.13*	
C_6H_6	64.06	19.29	26.41	32.51	37.46	44.74	49.80	57.32		$\sigma = 12$
TRC	64.36	19.76	26.81	33.30	38.64	45.42	50.25	58.08	*-0.68*	$s = 1$

Table 3.4 Comparison of Entropy and Cp Data Calculated by SMCPS with Literature Data **(Continued)**

Species	S°(298K)	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)	Avg Cp difference	Remarks
CCl_4	74.07	20.13	22.06	23.20	23.91	24.70	25.09	25.49		$\sigma = 12$
NIST	74.01	19.82	22.14	23.25	23.88	24.57	24.94	25.41	*0.08*	$s = 1$
CH_2CHCl	62.99	12.74	15.36	17.56	19.35	22.07	24.06	27.20		$\sigma = 2$
TRC	63.11	12.89	15.49	17.73	19.60	22.33	24.28	27.5	*-0.21*	$s = 1$
CH_2CCl_2	68.76	16.02	18.72	20.76	22.32	24.56	26.12	28.47		$\sigma = 2$
TRC	68.85	16.06	18.76	20.83	22.42	24.7	26.29	28.68	*-0.11*	$s = 1$
CH_2O	52.23	8.41	9.26	10.28	11.31	13.13	14.57	16.83		$\sigma = 2$
NIST	52.33	8.47	9.38	10.45	11.52	13.37	14.81	17.01	*-0.17*	$s = 1$
CH_3Cl	55.98	9.72	11.40	13.03	14.47	16.81	18.60	21.52		$\sigma = 3$
NIST	56.01	9.76	11.52	13.17	14.64	17.04	18.84	21.77	*-0.17*	$s = 1$
CH_4	44.47	8.45	9.50	10.84	12.20	14.70	16.79	20.38		$\sigma = 12$
NIST	44.52	8.55	9.711	11.14	12.61	15.32	17.63	21.72	*-0.55*	$s = 1$
C_6Cl_6	103.40	41.89	47.91	52.34	55.61	59.82	62.23	65.00		$\sigma = 12$
TRC	104.38	42	48.09	52.53	55.77	59.94	62.35	65.08	*-0.14*	$s = 1$
C_6H_5Cl	75.40	23.81	30.53	36.15	40.66	47.23	51.75	58.42		$\sigma = 2$
TRC	75.07	23.63	30.48	36.37	41.19	47.87	52.33	59.09	*-0.34*	$s = 1$
$COCl_2$	67.76	13.86	15.31	16.27	16.97	17.89	18.46	19.16		$\sigma = 2$
NIST	67.83	13.82	15.28	16.27	16.98	17.98	18.52	19.16	*-0.01*	$s = 1$

Table 3.4 Comparison of Entropy and Cp Data Calculated by SMCPS with Literature Data **(Continued)**

Species	S°(298K)	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)	Avg Cp difference	Remarks
oxetane[a]	65.2	15.32	20.57	25.41	29.51	35.81	40.31	46.97		$\sigma = 2$
NIST		14.8	20.07	24.91	28.99	35.24	39.70	46.35	*0.55*	$s = 1$
oxirane[b]	57.85	11.36	14.78	17.94	20.59	24.65	27.56	31.93		$\sigma = 2$
NIST	58.08	11.5	14.93	17.99	20.61	24.64	27.46	31.87	*-0.03*	$s = 1$
1,2dioxolane[c]	68.39	18.13	24.13	29.53	34.03	40.83	45.61	52.6		$s = 1$
NIST		18.51	24.79	30.26	34.73	41.37	46.01	52.79	*-0.52*	
1,2dioxetane[d]	65.62	13.99	18.05	21.77	24.89	29.57	32.85	37.61		$s = 1$
NIST		13.63	17.8	21.57	24.71	29.43	32.73	37.53	*0.19*	

All units are in cal/mol-K.

NIST data are from the NIST Reference Database version number 69 dated February 2000. The database can be access through the NIST website at http://webbook.nist.gov/chemistry/.

TRC data are from the Thermodynamic Properties of the Substances in Ideal Gas State database, version 1.0M dated November 1994 developed by the Thermodynamic Research Center located in College Station, TX

Under Remarks, "*s*" is the spin degeneracy, "σ" is the symmetry

a: oxetane = C_3H_6O = cyclic CCCO
b: oxirane = C_2H_4O = cyclic CCO
c: 1,2 dioxolane = $C_3H_6O_2$ = cyclic CCCOO
d: 1,2 dioxetane = $C_2H_4O_2$ = cyclic CCOO

3.5 Summary

A program is written that calculates entropy at 298K and Cp over temperature range of 300 – 1500 K from computation chemistry results are compared with literature data. The difference in the entropy calculated by SMCPS and the two databases is less than 1 cal/mol-K for the species used in the comparison. Comparison of the average difference in Cp, over the 300-1500K temperature range, between SMCPS calculated values and the two databases is also less than 1 cal/mol-K.

SMCPS has,

- a flexibility of input file
- portability - it can be easily loaded onto any computer.
- allowable comments in the input and output file for easy identification of molecular species for future reference (up to 80 characters)
- a dedicated program to perform statistical mechanic calculations
- an output file provides thermodynamic property results in an orderly tabular format.
- the output file format can also be easily converted to the NASA polynomial data format, which is used in other computational packages, using THERM[95].

Scaling factors are optional for vibrational frequencies.

This program is useful for users of computational chemistry, such as Gaussian94,[55] where the desired thermodynamic values are not fully provided. Required input parameters to SMCPS can be extracted from Gaussian94 calculations to determine the desired thermodynamic properties. The thermodynamic properties can then be directly applied to kinetic models, or other systems requiring thermodynamic properties.

CHAPTER 4

A COMPUTATIONAL CODE TO DETERMINE ELEMENTARY REACTION RATE COEFFICIENTS BASED ON CANONICAL TRANSITION STATE THEORY: THERMKIN

4.1 Introduction

One of the more powerful tools in understanding understanding or optimizing complex chemical reaction systems is computer modeling with elementary kinetic mechanisms. The objective of an elementary reaction model for complex chemical system is the understanding it presents and its ability to accurately predict or optimize observable products. Kinetic models are widely used in many disciplines, including combustion and pyrolysis, many aspects of atmospheric chemistry and plasma etching/deposition studies.[17,28,31,40,101-103] Kee, *et al.* has developed a transportable FORTRAN code called CHEMKIN, which enables users to calculate concentration profiles of complex reaction systems using elementary mechanisms, with reverse reaction coefficients automatically calculated from thermodynamics.[87] There are also other kinetic codes available which require rate constant input.[84-87,104,105] In all cases, the user needs to provide a chemical mechanism specific for their system. The construction of accurate reaction mechanisms is a valuable resource for researchers and industry modelers requiring a quantitative means to describe their systems.

Many researchers have contributed to the development into what is termed absolute rate theory or canonical transition state theory (CTST); but it was Henry Eyring who provided the clear description of an "activated complex" which is crucial to the development of every rate process.[106,107] M. Polanyi and M.G. Evans suggested the term "transition state" to this intermediate specie.[106] The CTST is a statistical method to determine the rate at which a reactant will form a transition state (TS) along the reaction coordinate. Determination of reaction rates requires thermodynamic properties of both reactant and the TS. Reliable experimental methods to determine TS's are not available. Theoretical chemistry codes, for *ab initio* or density functional theory methods, which are based on molecular quantum-mechanical equations[74] provide a method to determine microscopic (structure parameters, energies and vibration frequencies) molecular properties of stable or radical reactants and transition state intermediates. There are several *ab initio* computational packages available, such as, GAMESS, Molpro, Spartan, CADPAC, Jaguar, NWChem, Q-CHEM, HyperChem and Gaussian.[55,76-83] . Thermodynamic properties can be determined from quantum molecular properties through the application of the principles of statistical mechanics.[108]

The use of computational chemistry to determine molecular species' properties is a rapidly growing research area; it is finding increased application with the rapidly increasing technological improvements in computer processors and systems.[66-73] The importance of computational chemistry quickly becomes apparent when experimental data on species, such as transition state structures and active radicals are difficult to obtain. The thermochemical and kinetic data are needed in analysis of reaction paths and equilibrium determinations, … etc. Although a literature article may provide enthalpies and structure data, rate coefficients necessary in kinetic models are not always provided with the computation data.

ThermKin (Thermodynamic Estimation of Radical and Molecular Kinetics) is written to determine the elementary reaction rate coefficients and express the rate coefficients in several Arrhenius forms. It utilizes canonical transition state theory to determine the rate parameters. Thermodynamic properties of reactants and transition states are required and can be obtained from either literature sources or computational calculations. ThermKin does require the thermodynamic property to be in the NASA polynomial format, which a number of equilibrium and kinetic programs, such as CHEMKIN, SENKIN, STANJAN, CHEMSAGE© and NASA's CEA, also require.[84-87,104] A number of programs are available to generate these polynomials from H_f, S and Cp(T) data.[95] Since most computational chemistry codes provide fequencies and moments of inertia, it is necessary to use statistical mechanical approaches to compute the standard thermodynamic properties, *e.g.* SMCPS.[108]

4.2 Theory and Basis of Thermkin

4.2.1 Determination of Forward Rate Constants

ThermKin evolved from a previously developed computer code, *i.e.* THERMRXN,[95] which calculates equilibrium thermodynamic properties for any given reaction. The current program maintains the full capabilities of THERMRXN, and in addition can calculate the forward rate constants and provide an Arrhenius rate expression that can be used to model reaction systems. ThermKin determines the forward rate constants, k(T), based on the canonical transition state theory (CTST). The modified Arrhenius parameters are determined from regression analysis with application of the principle of least squares.

CTST describes the forward rate constant from reactant to the transition state (TS) as a function of the equilibrium between reactant and TS. This relationship is expressed as the following,

$$k_{forw} = \left(\frac{k_B T}{h_P}\right) K^{\neq} \tag{4.1}$$

implying an equilibrium state between the reactant and TS. It is important to note the the equilibrium constant $K^{\dagger}$ is missing the degree of freedom coresponding to the reaction coordinate. The equilibrium constant for a gas phase reaction is typically expressed in pressure units, *i.e.* K_p. The relationship between equilibrium constant can be expressed in terms of Gibbs free energy,

$$K = \exp\left(-\frac{\Delta G_{rxn}}{RT}\right) = \frac{K_P}{\left(P^0\right)^{\Delta \nu}} \tag{4.2a}$$

Equation (4.2a) can be rewritten with the assumption that a "quasi-equilibrium" exists between the reactant and TS, *viz.*

$$K^{\neq} = \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \frac{K_P^{\neq}}{\left(P^0\right)^{\Delta \nu^{\neq}}} \tag{4.2b}$$

Substitution of Equation (4.1) with Equation (4.2b) provides an expression for the forward rate constant in terms of the thermodynamic property of Gibbs free energy. Recalling the thermodynamic definition of Gibbs free energy, in terms of enthalpy and entropy and writing the term in relation of a TS, Gibbs free energy can be expressed as follows,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{4.3}$$

Equation (4.2b) can be rewritten with the appropriate substitution for Gibbs free energy term expressed in Equation (4.3). Equation (4.1), with substitution from Equations (4.2b) and (4.3), results in the forward rate constant expression as,

$$k_{forw} = \left(\frac{k_B T}{h_P}\right) \exp\left(\frac{\Delta S_P^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \left(P^0\right)^{-\Delta \nu^{\neq}} \tag{4.4}$$

The subscript "p" on the entropy term in Equation (4.4) needs to be consistent since in the current derivation thus far, the equilibrium constant in Equation (4.2a) and (4.2b) is in pressure units. Typically, entropy is expressed in terms of concentration, rather than in pressure units. Another reason for expressing the entropy in concentration units is to be consistent with rate constants, which are typically expressed in concentration units as well. The consistency of the units for the forward rate constant will be discussed in more detail later in this paper. The conversion between $\Delta S_C^{\neq}$ and $\Delta S_P^{\neq}$ can be shown by utilizing the relationship between K_c and K_p; which for the ideal gas system can be shown in the following expression,

$$K = \frac{K_P}{\left(P^0\right)^{\Delta\nu}} = K_C\left(\frac{RT}{P^0}\right)^{\Delta\nu} \tag{4.5}$$

It should be noted that the exponential term is dimensionless and it is the stoichiometric difference between product (or TS) and reactant. The "P^0" term is the reference pressure, which will be assumed to be 1 atm. The reference pressure in Equation (4.5) will allow the equilibrium constants to be dimensionless. It should be further noted that the TS always have a stoichiometric coefficient of one. Expansion of the expression in Equation (4.5) for both the Kp and Kc in terms of enthalpy and entropy, the result is expressed in the following form,

$$\exp\left(\frac{\Delta S_P^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) = \exp\left(\frac{\Delta S_C^{\neq}}{R}\right)(RT)^{\Delta\nu^{\neq}}\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{4.6}$$

Cancellations of like terms and the relationship between $\Delta S_C^{\neq}$ and $\Delta S_P^{\neq}$ results in the following relationship,

$$\left(\frac{\Delta S_P^{\neq}}{R}\right)=\left(\frac{\Delta S_C^{\neq}}{R}\right)+\Delta\nu^{\neq}\ln(RT) \tag{4.8}$$

For a unimolecular reaction, Δν is zero and $\Delta S_C^{\neq} = \Delta S_P^{\neq}$ and for a bimolecular reaction $\Delta\nu^{\neq} = -1$ and

$$\left(\frac{\Delta S_P^{\neq}}{R}\right)=\left(\frac{\Delta S_C^{\neq}}{R}\right)-\ln(RT) \tag{4.9}$$

Substitution of the $\frac{\Delta S_P^{\neq}}{R}$ term in Equation (4.8) into Equation (4.4), the forward rate constant can be rewritten in terms of ΔS_c as follows,

$$k_{forw}=\left(\frac{k_B T}{h_P}\right)\exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta\nu^{\neq}}\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{4.10}$$

The forward rate constant can then be determined, provided the thermodynamic properties of the TS and reactants are known. Equation (4.10) is sufficient to calculate the forward rate constant, but further rearrangement of Equation (4.10) can be performed through an algebraic manipulation. The forward rate constant is expressed as follows:

$$k_{forw}=\left(\frac{ek_B T}{h_P}\right)\exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta\nu^{\neq}}\left[\exp\left(-\frac{\Delta H^{\neq}+RT}{RT}\right)\right] \tag{4.11}$$

The reason for this rearrangement to (4.11) is to correlate the kinetic parameters, which will be explained below. The forward rate constant can also be expressed in terms of internal energy, *viz.*

$$k_{forw}=\left(\frac{ek_B T}{h_P}\right)\exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta\nu^{\neq}}\exp\left(-\frac{[\Delta U^{\neq}+\Delta(P\bar{V})]+RT}{RT}\right) \tag{4.12}$$

One should take caution to note that the term $\bar{V}$ is the molar volume. Employment of the ideal gas law Equation (4.12) becomes,

$$k_{forw} = \left(\frac{ek_B T}{h_P}\right) \exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta\nu^{\neq}} \exp\left(-\frac{[\Delta U^{\neq} + (\Delta \nu^{\neq})RT] + RT}{RT}\right) \tag{4.13}$$

and after simplification of the exponential term, the forward rate constant, expressed in terms of internal energy take the final form of,

$$k_{forw} = \left(\frac{ek_B T}{h_P}\right) \exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta\nu^{\neq}} \exp\left(-\frac{[\Delta U^{\neq} + (\Delta \nu^{\neq} + 1)RT]}{RT}\right) \tag{4.14}$$

4.2.2 Determination of Arrhenius Rate Coefficients

The aim of kinetic modeling is to obtain an expression that can represent the rate constant over a temperature range. The most commonly used equation to represent rate constants is the Arrhenius rate equation, *viz.*

$$k = A \exp\left(-\frac{E_A}{RT}\right) \tag{4.15}$$

A modification of Equation (4.15) to incorporate a temperature dependent pre-exponential A-factor is termed the modified Arrhenius rate equation, expressed in the following equation,

$$k = A_T T^n \exp\left(-\frac{E_A'}{RT}\right) \tag{4.16}$$

It should be noted that the "A_T" term in Equation (4.16) is not equal to the pre-exponential "A" term in Equation (4.15).

The forward rate constants, as a function of temperature, can be calculated from any one of the Equations (4.10) - (4.14), provided thermodynamic properties of the TS and reactants are known. Logarithmic transformation of Equation (4.16) results in the following non-linear equation,

$$\ln(k) = \ln(A_T) + n\ln(T) - E_A^{'}\left(-\frac{1}{RT}\right) \tag{4.17}$$

The principle of least squares is applied to the logarithmic transformed Equation (4.17). Derivation from the application of the minimizing function to the 3-parameters in the logarithmic transformed Equation (4.17) is represented by the following matrix,

$$\begin{bmatrix} m & \sum_{i=1}^{m}\ln(T_i) & -\sum_{i=1}^{m}\frac{1}{RT_i} \\ \sum_{i=1}^{m}\ln(T_i) & \sum_{i=1}^{m}(\ln(T_i))^2 & -\sum_{i=1}^{m}\frac{1}{RT_i}\ln(T_i) \\ \sum_{i=1}^{m}\frac{1}{RT_i} & \sum_{i=1}^{m}\frac{1}{RT_i}\ln(T_i) & -\sum_{i=1}^{m}\left(\frac{1}{RT_i}\right)^2 \end{bmatrix} \begin{bmatrix} \ln(A_T) \\ n \\ E_A^{'} \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{m}\ln(k_i) \\ \sum_{i=1}^{m}\ln(T_i)\ln(k_i) \\ \sum_{i=1}^{m}\frac{1}{RT_i}\ln(k_i) \end{bmatrix} \tag{4.18}$$

Gaussian elimination is applied to the above matrix to minimize computation requirements. The 3-parameters, *i.e.* $\ln(A_T)$, n and E'_A, can be determined from the triangulated matrix.

The classical Arrhenius rate expression can be performed similarly, by logarithmic transformation of Equation (4.15) to the following linear expression,

$$\ln(k) = \ln(A) - E_A\frac{1}{RT} \tag{4.19}$$

The linear least-square equation can be directly applied to Equation (4.18), and with the appropriate substitutions, results in the following solution for determining the parameters in the classical Arrhenius equation, *viz.*

$$-E_A = \frac{\sum_{i=1}^{m}\left[\ln k_i\left(\frac{1}{RT_i}\right)\right] - \frac{\sum_{i=1}^{m}\ln k_i \sum_{i=1}^{m}\left(\frac{1}{RT_i}\right)}{m}}{\sum_{i=1}^{m}\left(\frac{1}{RT_i}\right)^2 - \frac{\left[\sum_{i=1}^{m}\left(\frac{1}{RT_i}\right)\right]^2}{m}} \tag{4.20}$$

$$\ln(A) = \frac{\sum_{i=1}^{m}\ln k_i}{m} + E_A\frac{\sum_{i=1}^{m}\left(\frac{1}{RT_i}\right)}{m} \tag{4.21}$$

It should be noted that the E_A term represented in the above Equations (4.17) to (4.20) could have been represented as $-\frac{E_A}{R}$, since R is the universal gas constant and can be factored out from the above "$\frac{1}{RT}$" term. For clarity, the current derivation represents the E_A term directly.

4.2.3 Relationships Between Thermodynamic Properties and Kinetic Parameters

Comparison of Equations (4.11) with Equation (4.16) show that the activation barrier is a function of the enthalpy of reaction between the reactant and TS. The pre-exponential A-factor is a function of entropy of reaction between the reactant and TS. The pre-exponential A-factor can be identified as the following,

$$A = \left(\frac{ek_BT}{h_P}\right)\exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta v^{*}} \tag{4.22}$$

and the activation barrier as

$$E_A = \Delta H^{\neq} + RT \tag{4.23}$$

Equation (4.22) and (4.23) are used rather loosely, since "A" and "E_A" are constants, and the right hand side expression are functions of temperature.

The minimum threshold energy required for the reactants to overcome the activation barrier is $\Delta H^{\neq}$, since this is the ΔH_{rxn} between the TS and reactant. Equations (4.22) and (4.23) are commonly used because both the A and E_A are within reasonable experimental values. The experimental activation energy, through the relationship of ln*k* vs T and after derivation, can be shown to be the same as E_A in Equation (4.23).[106] Similarly, expression of the activation energy in terms of the internal energy of the reacting system, the E_A term would equal to the term within the brackets shown in Equation (4.14). The $\left(\frac{ek_BT}{h_P}\right)$ term in Equation (4.22) produces a quantity of 5.64×10^{10} T with units of K^{-1} sec^{-1}. If the temperature is 500 K, $\left(\frac{ek_BT}{h_P}\right)$ would be 2.82×10^{13} s^{-1}, for $\Delta S^{\neq} = 0$. The $\exp\left(\frac{\Delta S_C^{\neq}}{R}\right)\left(\frac{RT}{P^0}\right)^{\Delta v^{\neq}}$ term, would change on either a "tighter" or "looser" TS, which would produce an entropy difference greater or less than zero, respectively. This would either increase or decrease the respective A-factor term. The units of the pre-exponential A-factor is dependent upon both the $\left(\frac{ek_BT}{h_P}\right)$ and $\left(\frac{RT}{P^0}\right)^{\Delta v^{\neq}}$. The $\left(\frac{ek_BT}{h_P}\right)$ term will have units of inverse time. Depending on type of reaction, either unimolecular or bimolecular reaction, $\Delta v^{\neq} = 0$ or -1. For unimolecular reactions, $\Delta v = 0$ and the A-factor will have units of inverse time. For bimolecular reactions, $\Delta v^{\neq} = -1$, and $\left(\frac{RT}{P^0}\right)^{\Delta^{\neq} v}$ will have units of inverse concentration and the pre-exponential A-factor will have units of inverse time-inverse concentration.

4.3 About ThermKin

THERMKIN is a FORTRAN console application and has been compiled for Microsoft® MS-DOS™ (16 bit operating system) and the Windows® platform (32 bit operating system). Macrocanonical transition state theory to determine forward rate constants for a reaction, as described above, has been fully implemented. Thermodynamic properties of reactants and transition state are required for ThermKin to run successfully.

The only other file the program requires, besides the binary executable, is a thermochemical data file consisting of the thermodynamic properties of the species of interest; this is input in the popularly used NASA polynomial format, which is also the CHEMKIN thermodynamic data format. References for description of the NASA polynomial format file can be found in several references.[84,95,109-111] THERM is one computer program that can convert thermodynamic data into the NASA polynomial format.[95] An example of a NASA polynomial format is shown in the Table 4.1.

4.4 Using THERMKIN

There are several steps required for the program to execute successfully. The first step THERMKIN requires is the user to input the thermochemical data file name. Once the thermochemical data file is read into the program, THERMKIN will request that the user specify whether the reaction is a unimolecular or bimolecular reaction. The next option will be the form of the fit desired, *i.e.* either a two-parameter fit or a three-parameter fit. The following screen will request the user to input the reaction to be calculated, i.e. the reactant and the transition state, in the form [reactant1] + [reactant2] = [transition state] for a bimolecular reaction and for a unimolecular reaction [reactant] = [transition state]. The results of the calculation will be shown on screen. The user will have an option to save the results to a file, to be reviewed later. The file is saved in ASCII format, such that any text editor may be used to view the file with no difficulties.

Table 4.1 An Example of Thermochemical Properties of Species in NASA Polynomial Format

```
THERMO
   300.000  1500.000  5000.000
O2                J 9/650   2    0    0    0G   300.000  5000.000 1375.000    01
 3.52299790E+00 1.06762110E-03-4.24843320E-07 7.28399482E-11-4.54846876E-15    2
-1.20661302E+03 4.07242932E+00 3.10345411E+00 1.43699061E-03-1.28484674E-07    3
-3.18221668E-10 9.83941334E-14-9.87446941E+02 6.56298379E+00                   4
OH                J12/700   1H   1    0    0G   300.000  5000.000 1360.000    01
 2.35304047E+00 1.68449387E-03-4.94601650E-07 6.42179721E-11-3.11943040E-15    2
 4.25783886E+03 8.71344084E+00 3.78786811E+00-9.50189982E-04 1.08262042E-06    3
-2.28848614E-10-1.23828555E-14 3.67981777E+03 7.39024772E-01                   4
HO2               J 9/81H   10   2    0    0G   300.000  5000.000 1446.000    11
 4.63734659E+00 1.68299444E-03-6.04341398E-07 9.69277697E-11-5.75245167E-15    2
 1.61343187E+02 3.87432185E-02 3.43389194E+00 2.44149913E-03 1.28874201E-06    3
-1.99754200E-09 5.61717009E-13 7.72395408E+02 7.21042937E+00                   4
TYCCXQ    CBS-Q//B3LYP  C   2H   50   2    0G   300.000  5000.000 1682.000    01
 9.76464559E+00 1.31988627E-02-4.66657674E-06 7.44823207E-10-4.41610336E-14    2
 7.29825719E+03-2.64219961E+01-3.29602049E-02 3.49869182E-02-2.16747546E-05    3
 6.21435607E-09-6.38731252E-13 1.05920096E+04 2.62776518E+01                   4
CCOO      CBS-Q/B3&isodeC   2H   50   2    0G   300.000  5000.000 1394.000    21
 8.81369237E+00 1.26389123E-02-4.30461996E-06 6.66356420E-10-3.85804792E-14    2
-7.80453890E+03-1.92675418E+01 7.43589918E-01 2.91251006E-02-1.62277623E-05    3
 4.12761784E-09-3.34699013E-13-4.76283100E+03 2.49166271E+01                   4
C2H5      CBS-Q//B3LYP  C   2H   5    0    0G   300.000  5000.000 1389.000    11
 5.46159620E+00 1.06187847E-02-3.56318553E-06 5.45874605E-10-3.13696363E-14    2
 1.15710003E+04-5.14843226E+00 1.52471168E+00 1.73349429E-02-6.94412953E-06    3
 7.50723785E-10 1.25023688E-13 1.32282904E+04 1.69443978E+01                   4
C2H4       6/17/96      C   2H   4    0    0G   300.000  5000.000 1395.000    01
 5.22176372E+00 8.96137303E-03-3.04868886E-06 4.71465524E-10-2.72739592E-14    2
 3.59383137E+03-7.47789234E+00 2.33879688E-01 1.96334647E-02-1.16833214E-05    3
 3.64246453E-09-4.77442715E-13 5.45482795E+03 1.97084228E+01                   4
END
```

4.4.1 Output File

The program does not produce any output files by default, but does provide an option to the user to save any of the calculations performed to an output file. An example of a three parameter fit output file from THERMKIN is shown in Table 4.2. All results calculated by THERMKIN have the same format, regardless of unimolecular or bimolecular reactions system. The output file generated by THERMKIN is divided into three sections, for ease of interpretation. The first section of the output file identifies the reaction. The second section is the thermochemistry of the reaction as a function of temperature. The last section describes the kinetics. A brief description of results (shown in Table 4.2) is presented for explanations.

Each output file starts with identification of the specific reaction that is calculated; Table 4.2 shows the reaction of interest is "CCOO ➔ TYCCXQ." In this specific example, "CCOO" is the ethyl-peroxy radical and "TYCCXQ" is the molecular elimination transition state to form ethylene plus HO_2. Thermodynamic properties of the respective species of interest are shown in the section below the reaction identification.

Reaction thermodynamic properties at both 298 K and the average thermodynamic properties over the temperature range of 298 – 1500 K are listed below the reaction identification. Temperature dependent thermodynamic properties are also provided in tabular form. The equilibrium constant is calculated directly from the Gibbs free energy of reaction.

Table 4.2 Sample Output File from THERMKIN

```
     THERMODYNAMIC ANALYSIS for REACTION
Rx          CCOO       = TYCCXQ
Hf {Kcal/mol}    -6.720     23.760
S {cal/mol K}    73.820     70.760

dHr {kcal/mol}    (298K) =       30.48     dHr avg (298., 1500. K) =       31.97
dU (dE) {kcal/mol} (")   =       30.48     dUr avg (298., 1500. K) =       31.97
dSr {cal/mol K}   ( " )  =       -3.06     dSr avg (298., 1500. K) =       -1.22
dGr  {kcal/mol}   ( " )  =       31.39     dGr avg (298., 1500. K) =       33.07
          Kc      ( " )  =    9.703E-24    Kc avg (298., 1500. K ) =   9.153E-09
Fit Af/Ar      : A = 1.080E-03 n =   .90 alpha =-3.595E-04 avg error    4.44 %
Fit Af/Ar w/ddU: A = 7.292E-06 n =  1.79 alpha =-1.421E-05 avg error    6.50 %

    T (K)  dH(Kcal/mol)  dU(Kcal/mol) dS(cal/mol K)      Kc       dG(Kcal/mol)
    300.00    3.048E+01    3.048E+01   -3.053E+00    1.333E-23    3.140E+01
    400.00    3.062E+01    3.062E+01   -2.663E+00    4.866E-18    3.168E+01
    500.00    3.080E+01    3.080E+01   -2.251E+00    1.102E-14    3.193E+01
    600.00    3.103E+01    3.103E+01   -1.847E+00    1.968E-12    3.213E+01
    800.00    3.154E+01    3.154E+01   -1.110E+00    1.381E-09    3.243E+01
   1000.00    3.210E+01    3.210E+01   -4.874E-01    7.546E-08    3.259E+01
   1200.00    3.266E+01    3.266E+01    2.369E-02    1.139E-06    3.263E+01
   1500.00    3.345E+01    3.345E+01    6.164E-01    1.819E-05    3.253E+01
   2000.00    3.465E+01    3.465E+01    1.305E+00    3.152E-04    3.204E+01

 The model fitted is for uni-molecular reaction.

 The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
    Aprime = 8.8006E+05         n =   2.24329       Ea =    2.9613E+04

 Temp(K)          AF(T)             T_K^n             k_calc(T)           k_fit
 300.00          1.345E+12         3.605E+05         8.330E-11         8.450E-11
 400.00          2.182E+12         6.873E+05         4.055E-05         3.988E-05
 500.00          3.356E+12         1.134E+06         1.148E-01         1.133E-01
 600.00          4.935E+12         1.707E+06         2.460E+01         2.452E+01
 800.00          9.536E+12         3.254E+06         2.302E+04         2.326E+04
1000.00          1.630E+13         5.369E+06         1.572E+06         1.592E+06
1200.00          2.530E+13         8.082E+06         2.849E+07         2.873E+07
1500.00          4.262E+13         1.333E+07         5.687E+08         5.682E+08
2000.00          8.035E+13         2.542E+07         1.314E+10         1.299E+10
```

The fitted kinetic parameters, in the modified Arrhenius expression, in Equation (4.16), is determined. The unit for the activation energy is in $\frac{cal}{mol}$, and the pre-exponential A-factor is in $\frac{1}{\sec}$ for unimolecular reactions and $\frac{cm^3}{mol \cdot \sec}$ for bimolecular reactions. Temperature dependent kinetic results are also tabulated, shown in five columns: Temp(K), AF(T), T_K^n, k_calc(T) and k_fit. "Temp(K)" is the temperature of interest. "AF(T)" is the calculated pre-exponential A-factor from the thermodynamic properties, refer to Equation (4.22). "T_K^n" is the product of the temperature raised to the power of the "n" that is determined from the fit. In the specific example shown in Table 4.2, "n" = 2.24329, *viz.* $T\_K{}^{\wedge}n = T^{2.24329}$

The results shown in the column for "k_calc(T)" is the forward rate coefficient calculated based on the thermodynamic properties, refer to Equation (4.10) or (4.11). The last column, "k_fit", is the fitted rate coefficient based on the fitted kinetic parameters, refer to Equation (4.16). In the specific example shown in Table 4.2, "k_fit" is determine from the following equation, $k\_fit = 8.8x10^{5}T^{2.24}\exp\left(-\frac{29600\frac{cal}{mol}}{RT}\right)$, which are the "A", "n" and "Ea" from the fitted model.

4.4.2 Examples

Rate constant coefficients are calculated using THERMKIN and compared to literature values for several different types of reactions. The selections of these specific reactions are chosen based on two criteria; first is to find rate constants with transition states for different types of reactions. The second criterion is based on the availability of data in literature for use in a comparison. The different types of reactions presented are abstraction and isomerization. THERMKIN can easily extend to any reaction where thermochemical parameters can describe the transition state.

Comparison of four rate coefficients over a temperature range from 250 – 2500K are presented and shown in Figures 4.1 – 4.4. The first example illustrates the comparison of rate constants calculated by THERMKIN, compared to calculation of rate constants from using Gibbs free energy of reaction. This alternate way to compute the rate coefficients calculates $K_{eq}^{\neq}$ at each temperature (from ΔH and ΔS) and then uses expression in Equation (4.1). The specific reaction shown is the unimolecular reaction of the isomerization of vinyl-peroxy radical to 2 hydroperoxy-vinyl radical. (Refer to Figure 4.1). As expected, the results are identical.

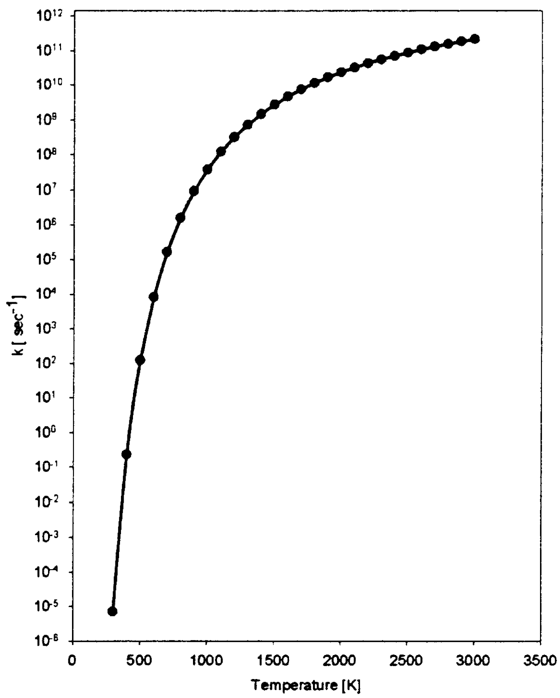


Figure 4.1 Comparison of ThermKin with calculations by DGrxn for isomerization of vinyl peroxy radical to 2-hydroperoxy-vinyl radical

The isomerization reaction of acetylene to vinylidene is presented in Figure 4.2. Laskin and Wang[72] presents their results as a bimolecular rate constant, with the buffer gas as an energy transfer reactant. Conversion of the bimolecular rate constant to a unimolecular rate constant, at a system pressure of 1 atm with ideal gas behavior is assumed. Thermochemical properties of the acetylene-vinylidene transition state is obtained from Sheng and Bozzelli.[112] Comparison of the results is shown in Figure 4.2. The difference between Laskin and Wang's rate constant and ThermKin is due to the different method of obtaining rate coefficients. Laskin and Wang used a microcanonical RRKM algorithm to determine a bimolecular rate constant expression. Although Laskin and Wang's rate constant may be more accurate, it is also more rigorous, involving quantum chemical parameters as inputs. The current simplified treatment to convert the bimolecular rate constant to a unimolecular rate constant may also attribute to the differences in the calculated rate constants.

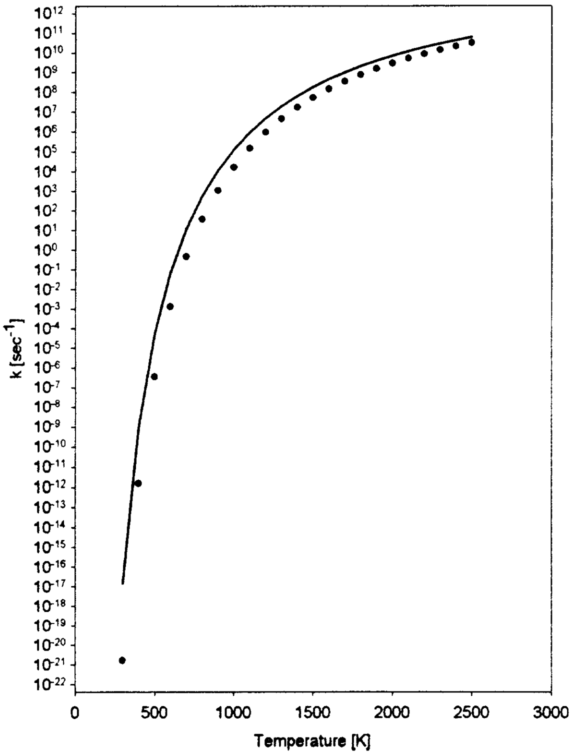


Figure 4.2 Comparison of thermkin fit to RRKM analysis of the isomerization reaction of acetylene to vinylidene

Figure 4.3 illustrates an example of a halo-oxy-hydrocarbon reaction system. Entropy and Cp values of the halo-oxy-hydrocarbon species are taken directly from Yamada, *et al.*[113] Yamada, *et al.* provided the enthalpy of formation values at absolute zero. Graphical interpretation of the potential energy diagram is utilized to obtain the enthalpy of formation at 298K. Yamada, *et al.* also provides rate constants, which they have used theory to support experimental results and show consistency. The specific reaction in Figure 4.3 is the isomerization of 1,1 dichloro 1-ol ethyl radical to 1,2 dichloro 1-ol ethyl radical. The difference between the two curves at high temperatures is about 10%. This difference is due to the graphical interpretation to determine the $\Delta H_f(298K)$; a 0.5 kcal/mol difference results in a 10% difference in rate constant.

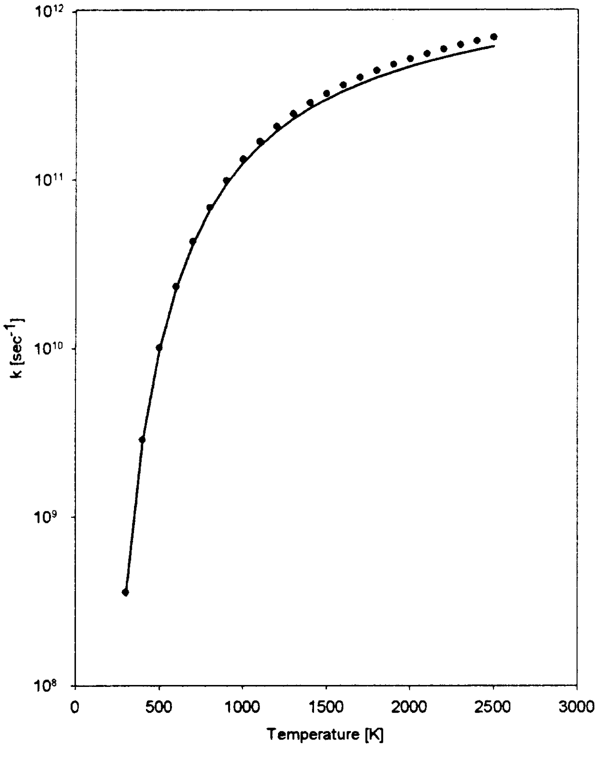


Figure 4.3 Comparison of ThermKin fit with Yamada, *et al.*'s calculated isomerization reaction of 1,1 dichloro 1-ol ethyl radical to 1,2 dichloro 1-ol ethyl radical

The fourth example is a bimolecular abstraction reaction of the methyl radical plus hydroperoxy radical to form the products methane plus the singlet oxygen molecule. (Refer to Figure 4.4). Zhu and Lin reports the calculated rate constant along with the quantum chemical properties of reactants, products and transition states.[114] Macroscopic thermodynamic properties were not explicitly provided by Zhu and Lin. The calculated thermodynamic properties are based on the vibrational frequencies and moments of inertia provided by Zhu and Lin. A simplified treatment of the hindered rotor contributions for the transition state used the torsional vibrational frequencies. Comparison of the rate constants shows reasonable agreement, especially with the consideration of a simplified treatment for hinder rotors. Zhu and Lin used microcanonical variational RRKM theory[115-119] to determine the rate constants and deviations are assumed due to difference in calculation methods. This example illustrates that there are different methods to treat hindered rotors and these differences can significantly affect the value of the rate coefficient.

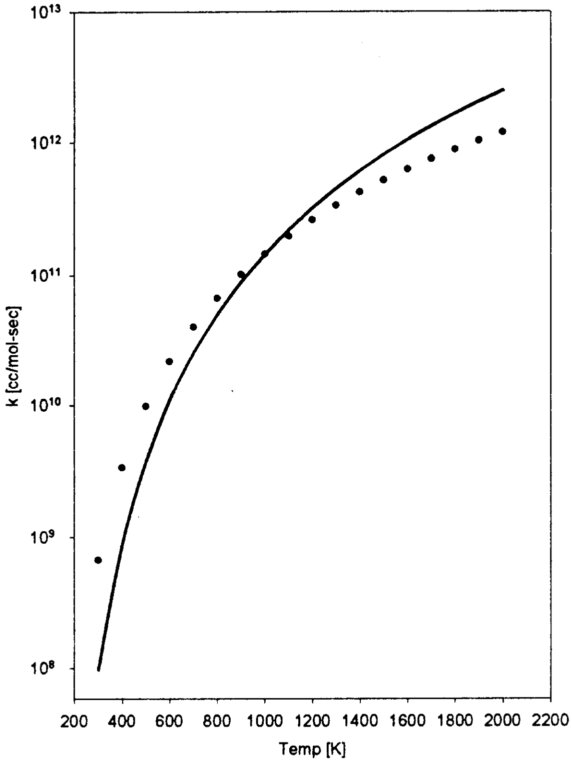


Figure 4.4 Comparison of ThermKin fit to RRKM analysis for abstraction of $CH_3 + HO_2 \rightarrow CH_4 + O$

4.5 Summary

A program is written that calculates rate constants from canonical transition state theory. Comparison of calculated rate constants are performed with literature sources. Near identical results are produced from use of Gibbs free energy method and from comparison of available literature sources.

ThermKin has,

1) portability - it can be easily loaded onto any computer running Microsoft® operating system.
2) a dedicated program to determine rate coefficients for different Arrhenius expressions.
3) an output file provides thermodynamic property results in an orderly tabular format.

4) an output file that provides both calculated rate constants directly from thermodynamic properties and from the fitted rate coefficients for quick comparison analysis.
5) provide rate constant calculations over a default temperature range of 300-2000K or user define temperature range.

This program is useful as an academic tool for both instructors and students and researchers. Researchers, either industrial or academic, who require kinetic rate parameters in reactor design, combustion models, atmospheric models, ... etc. all can benefit from use this program.

CHAPTER 5

AB INITIO MOLECULAR ORBITAL AND DENSITY FUNCTIONAL ANALYSIS OF ACETYLENE + O_2 REACTIONS WITH CHEMKIN EVALUATION

5.1 Introduction

Acetylene is an important intermediate in hydrocarbon combustion systems. In methane and other C_1 hydrocarbon oxidation, methyl or methylene radicals can be formed which can combine, or $^1CH_2$ (singlet methylene) can undergo insertion reactions to form C_2 hydrocarbons: ethane, ethyl radical and ethylene. Significant fractions of these C_2 hydrocarbons react via abstraction, then beta scission pathways under high temperature combustion conditions (1200 K and above); the reactions proceed sequentially from alkanes to ethylenes to acetylene. The C-H bond in acetylene is strong, ca 135 kcal/mol, thus it is slow to undergo abstraction with active species in the radical pool, such as OH, H and O species, where the abstractions are 15 to 31 kcal/mol endothermic. Acetylene does undergo addition reactions with these radical species; but the adducts are often considered to undergo rapid reverse reaction. Acetylene is a logical stable intermediate or product in methane, C_2 and higher carbon number oxidation processes; in fact, environmental studies often target it as a product of incomplete combustion (PIC).

Most detailed models on combustion of hydrocarbon species include reactions for both formation and oxidation of acetylene. Several researchers, in efforts to model the combustion of hydrocarbon, have indicated that they cannot account for induction times and flame speeds, in their models, without a direct $HC{\equiv}CH + O_2$ reaction.[26,32,120-122] These studies offer varied rate constants and a number of suggested product sets: HCO + HCO, $HC{\bullet}{=}C{=}O + H$, $H_2C{=}C{=}O + O$, or 2CO + 2H. Recent evaluations[32] suggest that any radical in the product set which results in propagation reactions will allow detailed models to match experimental data.

Combustion experiments performed by Procaccini, *et al.* have shown formation of acetylene as the major PIC in an ethylene/oxygen turbulent plug flow reactor. They have stated that prediction of PIC formation requires a detailed kinetic mechanism, and their model needs to incorporate additional reaction sets to describe the chemical system.[27] Marinov, *et al.* implied the need for better knowledge on the kinetics for the formation and oxidation of acetylene to explain hydrocarbon oxidation.[123] Miller, *et al.* have reported that induction time is very sensitive to this HCCH + O_2 reaction; and that it is impossible to predict simultaneously both induction time and flame speeds in their system without including a direct HCCH + O_2 reaction step.[121]

Miller, *et al.* postulated three possible reaction products, any of which can be used in their model to fit the observed experimental data satisfactorily.[121] The three possible product sets are:

$C_2H_2 + O_2 \Leftrightarrow HCCO + OH \qquad \Delta H_f{}^{(0)}{}_0 = -5$ kcal/mol

$C_2H_2 + O_2 \Leftrightarrow CH_2CO + O \qquad \Delta H_f{}^{(0)}{}_0 = -6$ kcal/mol

$C_2H_2 + O_2 \Leftrightarrow HCO + HCO \qquad \Delta H_f{}^{(0)}{}_0 = -36$ kcal/mol

Miller, *et al.* chose the first product set, ketenyl plus hydroxyl radicals, for inclusion in their mechanism. This is the same product set that Marinov, *et al.* chose; however, the pre-exponential A-factor of Miller, *et al.* is 5 times higher than that chosen by Marinov, *et al.* at the same E_a, 30.1 kcal/mol.

The HCCH + $^3O_2$ reaction appears to be an important part in modeling of hydrocarbon combustion systems, it is, therefore, surprising not to find thermochemical or kinetic evaluations on this system, with exception of empirical fitting to achieve agreement with experiment in models. Benson suggests a reaction process where triplet oxygen converts to the singlet state; then singlet oxygen adds to acetylene forming a singlet biradical.[17] This singlet biradical undergoes ring closure, forming a cyclic 4-member dioxetane radical. 1, 2 ethane-dial is then formed, via cleaving the weak O-O peroxide bond and forming two carbonyl bonds. Two formyl radicals are produced via dissociation of chemically activated glyoxal. Benson estimated the thermochemical kinetic parameters for this system, based on group additivity[88] (GA), bond additivity and empirical thermochemical analysis. Benson assumes $^3O_2 + M \Leftrightarrow {}^1O_2 + M$ to be in equilibrium, and the controlling barrier for overall process to be 30.6 kcal/mol above HCCH + $O_2(^3\Sigma)$. This barrier results from 23 kcal/mol for the triplet to singlet conversion of O_2 and 7.6 kcal/mol for the addition of $O_2(^1\Delta)$ to HCCH. The singlet biradical adduct can dissociate back to reactants (E_a = 6.6 kcal/mol) or isomerize with a barrier of 6 kcal/mol to form dioxetane, which rapidly dissociates to two formyl radicals.

Laskin and Wang[72,124] have recently proposed an alternative pathway to explain a direct acetylene plus O_2 process. They invoke acetylene isomerization to singlet vinylidene (CH_2C:), and infer that reaction kinetics of $^1CH_2C$: + $^3O_2$ will be similar to that of $^1CH_2 + {}^3O_2$. Laskin and Wang determine thermodynamic properties of vinylidene using the G2 composite method based on the optimized B3LYP/6-31G(d) geometry. The activation barrier for isomerization of acetylene to vinylidene is reported as 43 kcal/mol. The vinylidene can insert into $^3O_2$ forming a triplet CH_2=C(O•)O• adduct, which can dissociate to $^3CH_2 + CO_2$. Other spin conserved and non-conserved reactions are also suggested. The vinylidene + $^3O_2$ reaction to products is highly exothermic and is assumed to proceed rapidly; the HCCH + M $\rightarrow$ CH_2C: + M reaction is indicated as rate controlling.

The initial work of Laskin and Wang treats this reaction only in the low pressure limit for pressure dependence in formation of the active vinylidene species ($^1CH_2C:$).

This paper studies the feasibility of HCCH + $O_2(^3\Sigma)$ reaction to form an adduct which can react on the triplet surface or convert through collision to a singlet, then further react; plus further evaluation the paths of Benson and Laskin-Wang. Thermodynamic properties for the HCCH + $O_2(^3\Sigma)$ reaction system are from literature and computational methods. Kinetic parameters are determined using macrocanonical transition state theory (TST) applied over a temperature range. The current reactions are incorporated into small detailed mechanism schemes and then evaluated for acetylene conversion versus temperature and pressure. Estimation and inclusion of the pressure dependence on reaction systems of Benson and Laskin-Wang, for these comparisons are performed.

5.2 Calculation Methods

5.2.1 *ab initio*, Density Functional Theory and Semi-empirical Calculations

Molecular properties for reactants, adducts, transition states (TS) and products are estimated by *ab initio*, density functional theory (DFT) and semi-empirical methods. Literature values for acetylene and $O_2(^3\Sigma)$ are used as reference energies to convert *ab initio* and DFT calculated energies to enthalpies, $\Delta H^\circ_f(0\ K)$ and $\Delta H^\circ_f(298\ K)$. The *ab initio* calculations are performed using Gaussian94.[55] The *ab initio* methods include: Møllier-Plesset second-order perturbation theory (MP2/6-31G(d)), QCISD(T)/6-31G//MP2/6-31G(d) and CBS-q//MP2/6-31G(d)[125-128]. DFT calculations include B3LYP/6-31G(d,p) and BHandH/6-31G(d).[58,129] Single point calculations at QCISD(T) and the complete basis set, composite method — CBS-q are utilized based on the optimized MP2/6-31G(d) geometry. GA with application of hydrogen bond increment calculations are determined using the THERM program.[95,130] MOPAC PM3 is used for the semi-empirical calculations.[131-133] Additional computations are performed for the three transition states and adducts using the QCISD(T) and B3LYP levels of theory with larger basis sets. The larger basis sets include a triple split valence basis set, a larger polarized basis set and addition of diffuse function for both the heavy atoms and hydrogen atoms. The three additional basis sets utilized are 6-311++G(2d,p), 6-311++G(2df,p) and 6-311++G(3df,2p). The QCISD(T) level calculations are single point calculations at the MP2/6-31G(d) optimized geometries. The B3LYP calculations with larger basis sets are single point calculations on the B3LYP/6-31G(d,p) optimized geometries.

The DFT and MP2 calculations are spin-unrestricted Hartree-Fock. Molecular geometry for BHandH/6-31G(d), B3LYP/6-31G(d,p) and MP2/6-31G(d) are fully optimized using the Berny algorithm and redundant internal coordinates.[134] Semi-empirical calculations for doublet and triplet species and the TS's are determined using unrestricted Hartree-Fock theory.

Confirmation of TS structures for all *ab initio*, DFT and semi-empirical calculations are verified by checking for a single imaginary frequency and evaluation of the optimized geometry. Contributions of internal rotation to thermodynamic properties are incorporated based on the Pitzer-Gwinn formalism.[90] Optimized geometries determined by PM3 are utilized as the initial geometric structure in the *ab initio* and DFT calculations.

5.2.2 Thermodynamic Properties

Entropy, heat capacities at constant pressure and thermal correction for enthalpy (S, $C_p(T)$ and H(T)-H(0 K) or ΔH(T), respectively) are determined by applying the principles of statistical mechanics derived from the canonical ensemble of the partition functions based on values determined from *ab initio* and DFT calculations. Internal rotational contribution is determined from rotational barrier height and moments of inertia about the rotor of interest. Pitzer-Gwinn's general treatment of hindered internal rotational contribution to entropy and C_p is employed and thermodynamic properties are adjusted accordingly.[90]

Vibrational frequencies are calculated at the BHandH/6-31G(d) level of theory. Entropy and C_p are determined based on calculations at BHandH/6-31G(d) level of theory and the results are applied to B3LYP/6-31G(d,p), MP2/6-31G(d), QCISD(T)/6-31G//MP2/6-31G(d) and CBS-q//MP2/6-31G(d) level of theory calculations. Durant evaluated frequency values for DFT calculations and states that BHandH, B3PW91 and B3P86 accurately predict vibrational frequencies.[135]

One accurate and desired method for estimating enthalpy of formation is the use of isodesmic reactions. Fundamental requirements for an isodesmic reaction are conservation of electron pair and chemical bond type.[136] Employment of isodesmic reactions for HCCH + $^3O_2$ system cannot be done, since literature data on needed triplet biradical intermediate species are not available. ΔH_f^{298} for adducts and TS's are referenced to ΔH_f^{298}(HCCH + $^3O_2$). The experimentally reported value of 54.35 kcal/mol for ΔH_f^{298}(HCCH + $^3O_2$) is utilized.[128]

Enthalpies of formation at 298 K for intermediate species are estimated from total energies calculated by *ab initio* and DFT calculations, relative to reactants (HCCH + $^3O_2$).

Considerations for the zero point vibrational energy (ZPVE) and thermal correction from 0 to 298 K are performed accordingly. Difference between the adjusted total energy of intermediate specie and the sum of the adjusted total energy for reactants are determined and converted into kcal/mol units. The enthalpy of formation at 298 K for the intermediate species are obtained by adding $\Delta H_f^{298}(HCCH + {}^3O_2)$ to the difference.

Thermodynamic properties estimated by *ab initio* and DFT calculations are presented in Table 5.1. Entropy and $C_p(T)$ do not change, since the vibrational frequencies are calculated at the same level of theory, *i.e.* BHandH/6-31G(d). Non-adjusted semi-empirical calculation results are also presented in Table 5.1.

5.2.3 High-pressure Limit Arrhenius Rate Parameters and Rate Constants (k_∞)

Forward rate constants are determined by application of macrocanonical TST for temperatures from 300 to 2500 K. Forward rate constants from 300 – 2500 K are calculated and fitted by a nonlinear least squares method to the form of a modified Arrhenius rate expression, *i.e.* $k_{\infty,forw} = A_\infty T^n e^{-\frac{E_a}{RT}}$, to obtain the three parameters A_∞, n and E_a.

High-pressure limit kinetic parameters in the form of modified Arrhenius rate parameters are presented in Table 5.2 for both forward and reverse reactions. Both DFT calculations are presented along with CBS-q//MP2/6-31G(d) and PM3 kinetic results. The parameters "A_∞" and "n" for both DFT and CBS-q//MP2/6-31G(d) are identical, only the E_a are different. (Refer to Table 5.1). MP2/6-31G(d) and QCISD(T)/6-31G//MP2/6-

Table 5.1 Thermodynamic Properties for Species in HCCH + $^3O_2$ Mechanism. Entropy and Heat Capacity Data are Calculated at BHandH/6-31G(d) Level

SPECIES	$Hf°_{298}$	$S°_{298}$	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)
HCCH	54.35	47.66 {48}	10.07 {10.53}	11.57 {11.97}	12.65 {12.97}	13.46 {13.73}	14.72 {14.93}	15.74 {15.92}	17.58 {18}
O_2	0	46.73 {49.01}	6.98 {7.02}	7.08 {7.23}	7.25 {7.44}	7.45 {7.65}	7.82 {8.04}	8.11 {8.35}	8.5 {8.73}
^{3}[HC•=CHOO•]	79.21[a] 96.07[d] 80.77[b] 89.92[e] 104.54[c] {74.65}	69.61 {71.44}	15.39 {16.37}	17.89 {18.89}	19.85 {20.75}	21.37 {22.16}	23.55 {24.18}	25.06 {25.60}	27.3 {27.77}
TS1	89.64[a] 98.48[d] 83.59[b] 91.48[e] 117.00[c] {81.61}	70.93 {72.52}	16.21 {16.62}	18.25 {18.59}	19.71 {19.96}	20.82 {21.01}	22.44 {22.62}	23.63 {23.83}	25.61 {25.82}
TS2	92.72[a] 120.46[d] 95.65[b] 115.18[e] 128.07[c] {95.65}	67.49 {72.18}	14.25 {17.47}	16.53 {19.81}	18.37 {21.5}	19.81 {22.78}	21.88 {24.62}	23.32 {25.93}	25.53 {27.93}
TS1A	120.85[a] {122.04}	65.43 {66.55}	15.12 {16.21}	17.70 {18.57}	19.72 {20.37}	21.29 {21.78}	23.52 {23.86}	25.01 {25.27}	27.11 {27.27}
^{3}[H-y(COO)-C:-H]	90.72[a] 109.48[d] 93.54[b] 94.66[e] 95.67[c] {67.85}	67.75 {69.90}	14.98 {15.88}	17.51 {18.43}	19.56 {20.38}	21.16 {21.89}	23.46 {24.06}	25.05 {25.56}	27.42 {27.79}
TS3	99.04[a] 131.17[d] 105.16[b] 125.31[e] 133.05[c] {73.42}	67.84 {69.84}	14.33 {15.18}	16.48 {17.34}	18.27 {19.04}	19.71 {20.39}	21.82 {22.38}	23.31 {23.79}	25.57 {25.91}
^{3}[•O-CH=CHO]	-2.63[a] 26.03[d] -2.27[b] 7.22[e] 26.30[c] {7.07}	70.16 {72.35}	14.52 {15.26}	16.69 {17.33}	18.64 {19.14}	20.29 {20.67}	22.79 {23.06}	24.57 {24.80}	27.22 {27.40}
O=C•CHO	-20.12[a] -0.8[d] -18.97[b] -20.5[e] -16.23[c] {-17.1}	69.67 {62.99}	13.61 {13.36}	14.98 {15.72}	16.23 {17.56}	17.34 {19.08}	19.09 {21.53}	20.39 {22.66}	22.32
HC•=O	8.35[a] 17.88[d] 9.17[b] 8.12[e] 10.23[c] {10.9}	52.15 {53.42}	8.19 {7.64}	8.56 {7.95}	9.01 {8.5}	9.48 {9.1}	10.38 {10.21}	11.12 {11.08}	12.31

Units: $Hf°_{298}$ in kcal/mol; $S°_{298}$ and Cp(T) in cal/mol-K. Enthalpy value notations: a = BHandH/6-31G(d), b = B3LYP/6-31G(d,p), c = MP2/6-31G(d), d = QCISD(T)/6-31G//MP2/6-31G(d), e = CBS-q//MP2/6-31G(d) and PM3 data are reported within braces; {..}.

Table 5.2 Kinetic Parameters for the Elementary Reactions in HCCH + $^3O_2$ System Determined from Transition State Theory Expressed in the Modified Arrhenius Rate Expression of $k = A\,T^n \exp(-E_a/RT)$

Reaction	A	n	Ea (kcal/mol)
CBS-q//MP2/6-31G(d)			
HCCH + $^3O_2$ → ^{3}[HC•=CHOO•]	2.68E7	1.88	37.17
^{3}[HC•=CHOO•] → HCCH + $^3O_2$	1.43E12	0.52	2.05
^{3}[HC•=CHOO•] → ^{3}[H-y(COO)-C:-H]	5.50E11	0.36	25.68
^{3}[H-y(COO)-C:-H] → ^{3}[HC•=CHOO•]	8.90E11	0.44	20.93
^{3}[H-y(COO)-C:-H] → ^{3}[•O-CH=CHO]	1.50E12	0.39	31.09
^{3}[•O-CH=CHO] → ^{3}[H-y(COO)-C:-H]	5.42E10	0.71	118.36
^{3}[•O-CH=CHO] → O=C•CHO + H	1.0E13	0	26.37
^{3}[•O-CH=CHO] → HC•=O + HC•=O	2.5E13	0	14.71
PM3			
HCCH + $^3O_2$ → ^{3}[HC•=CHOO•]	6.08E7	1.68	28.59
^{3}[HC•=CHOO•] → HCCH + $^3O_2$	5.14E12	0.3	7.55
^{3}[HC•=CHOO•] → ^{3}[H-y(COO)-C:-H]	6.85E9	1.24	20.92
^{3}[HC•=CHOO•] → O=O=C•H + OH	6.44E9	0.81	47.52
^{3}[H-y(COO)-C:-H] → ^{3}[HC•=CHOO•]	9.69E9	1.31	27.72
^{3}[H-y(COO)-C:-H] → O=C•CHO + H	5.59E12	0.18	6.15
^{3}[H-y(COO)-C:-H] → HC•=O + HC•=O	5.59E12	0.18	6.15
B3LYP/6-31G(d,p)			
HCCH + $^3O_2$ → ^{3}[HC•=CHOO•]	2.68E7	1.88	29.28
^{3}[HC•=CHOO•] → HCCH + $^3O_2$	1.43E12	0.52	3.31
^{3}[HC•=CHOO•] → ^{3}[H-y(COO)-C:-H]	5.50E11	0.36	15.30
^{3}[H-y(COO)-C:-H] → ^{3}[HC•=CHOO•]	8.90E11	0.44	2.52
^{3}[H-y(COO)-C:-H] → ^{3}[•O-CH=CHO]	1.50E12	0.39	12.06
^{3}[•O-CH=CHO] → ^{3}[H-y(COO)-C:-H]	5.42E10	0.71	107.71
^{3}[•O-CH=CHO] → O=C•CHO + H	1.0E13	0	26.37
^{3}[•O-CH=CHO] → HC•=O + HC•=O	2.5E13	0	26.62
BHandH/6-31G(d)			
HCCH + $^3O_2$ → ^{3}[HC•=CHOO•]	2.68E7	1.88	35.33
^{3}[HC•=CHOO•] → HCCH + $^3O_2$	1.43E12	0.52	10.92
^{3}[HC•=CHOO•] → ^{3}[H-y(COO)-C:-H]	5.50E11	0.36	13.93
^{3}[HC•=CHOO•] → O=O=C•H + OH	4.00E9	0.93	41.67
^{3}[H-y(COO)-C:-H] → ^{3}[HC•=CHOO•]	8.90E11	0.44	2.41
^{3}[H-y(COO)-C:-H] → ^{3}[•O-CH=CHO]	1.50E12	0.39	8.76
^{3}[•O-CH=CHO] → ^{3}[H-y(COO)-C:-H]	5.42E10	0.71	101.95
^{3}[•O-CH=CHO] → O=C•CHO + H	1.0E13	0	26.37
^{3}[•O-CH=CHO] → HC•=O + HC•=O	2.5E13	0	25.05

31G(d) kinetic parameters are not presented due to E_a calculated are approximately 10 to 20 kcal/mol higher than the CBS-q//MP2/6-31G(d) determined values.

QCISD(T) calculations with larger basis sets, up to 6-311++G(3df,2p), were also performed for transition states and adducts to try and improve accuracy and convergence. Comparison of energies calculated for QCISD(T)/6-311++G(3df,2p)//MP2/6-31G(d), CBS-q//MP2/6-31G(d) and B3LYP/6-311++G(3df,2p) for the three transition states are listed in Table 5.3. The differences in energies calculated at the B3LYP level of theory with larger basis set decreased, indicating convergence. The calculated energy difference between the larger basis set calculation QCISD(T)/6-311++G(3df,2p)//MP2/6-31G(d) and CBS-q//MP2/6-31G(d) at the highest barrier, *i.e.* TS3, is less than 3.5 kcal/mol suggesting reasonable accuracy for the CBS-q level calculation.

Table 5.3 H_f(298 K) and Spin Contamination (before Annihilation) and Data for the Three Transition States Determined at (a) B3LYP and (b) QCISD(T) with Large Basis Sets.

(a) B3LYP[a]

Species	B3LYP					
	6-31G(d,p)		6-311++G(2d,p)		6-311++G(3df,2p)	
	$\langle S^2\rangle$	H_f(298 K)	$\langle S^2\rangle$	H_f(298 K)	$\langle S^2\rangle$	H_f(298 K)
^{3}TS1	2.04	83.4	2.04	86.7	2.03	86.9
^{1}TS1	0	102.3	0	104.5	0	104.8
TS2	2.04	95.5	2.04	108.0	2.04	107.9
TS3	2.30	105.0	2.29	112.4	2.03	112.8

(b) QCISD(T)[a]

Species	QCISD(T)							
	6-31G		6-311++G(2d,p)		6-311++G(2df,p)		6-311++G(3df,2p)	
	$\langle S^2\rangle$	H_f(298 K)	$\langle S^2\rangle$	H_f(298 K)	$\langle S^2\rangle$	H_f(298 K)	$\langle S^2\rangle$	H_f(298 K)
^{3}TS1	2.34	98.48	2.31	91.9	2.30	91.9	2.30	83.6
^{1}TS1	0	127.5	0	117.5	0	116.4		
TS2	2.32	120.5	2.27	124.6				
TS3	2.93	131.2	2.93	129.3			2.94	121.9

a: Units of Hf(298K) in kcal/mol.

5.2.4 Quantum Rice-Ramsperger-Kassel (QRRK) Analysis

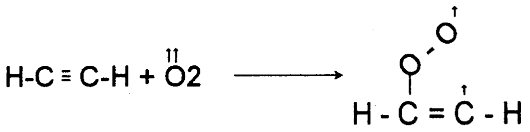
Chang, *et al.*[60,63] described a modified QRRK (Quantum Rice-Ramsperger-Kassel) analysis that is used in this paper. It is shown to yield reasonable results and provides a framework by which the effects of temperature and pressure can be evaluated in complex reaction systems. The current version of the QRRK computer code utilizes a reduced set of vibration frequencies which accurately reproduce the molecule (adduct), heat capacity data. Molecular density of state functions are constructed through direct convolution of single frequency density functions on a 10 cm^{-1} grid. The functions corresponding to each reduced frequency are explicitly convolved into a relative density of states ($\rho(E)$), which is normalized by the partition function (Q). The inclusion of one external rotation, corresponding to the symmetric top, is incorporated into the calculations by convolving the vibration density function with the proper rotational density function. A detailed description of this and comparisons of the $\rho(E)/Q$ ratios with the direct count $\rho(E)/Q$ ratios are shown to be in good agreement.[65] Nonlinear Arrhenius effects resulting from changes in the thermodynamic properties of the respective TS, relative to the adduct, with temperature are incorporated using a two parameter Arrhenius pre-exponential A-factor (A, n) in the form of AT^n. Fall-off is incorporated using modified strong collision approach (beta collision) of Gilbert, *et al.*[137]

5.3 Results and Discussion

5.3.1 Reaction Paths

Reaction path potential energy diagrams are illustrated in Figure 5.1 for BHandH/6-31G(d), B3LYP/6-31G(d,p) and PM3 calculations and in Figure 5.2 for CBS-q//MP2/6-

31G(d), QCISD(T)/6-31G//MP2/6-31G(d) and PM3 calculations. The initiation reaction for HCCH + $^3O_2$ is the addition of the oxygen to acetylene, breaking one carbon-carbon π-bond, forming a triplet peroxy-ethylene biradical adduct.



$$\text{H-C}\equiv\text{C-H} + \overset{\uparrow\uparrow}{\text{O2}} \longrightarrow \text{H-C}(\text{O-}\overset{\uparrow}{\text{O}})\text{=}\overset{\uparrow}{\text{C}}\text{-H}$$

The lowest barrier to this adduct is determined at the B3LYP/6-31G(d,p) level, with an energy barrier of 29.2 kcal/mol. The CBS-q//MP2/6-31G(d) barrier is 37.1 kcal/mol, 8 kcal/mol higher than B3LYP/6-31G(d,p).

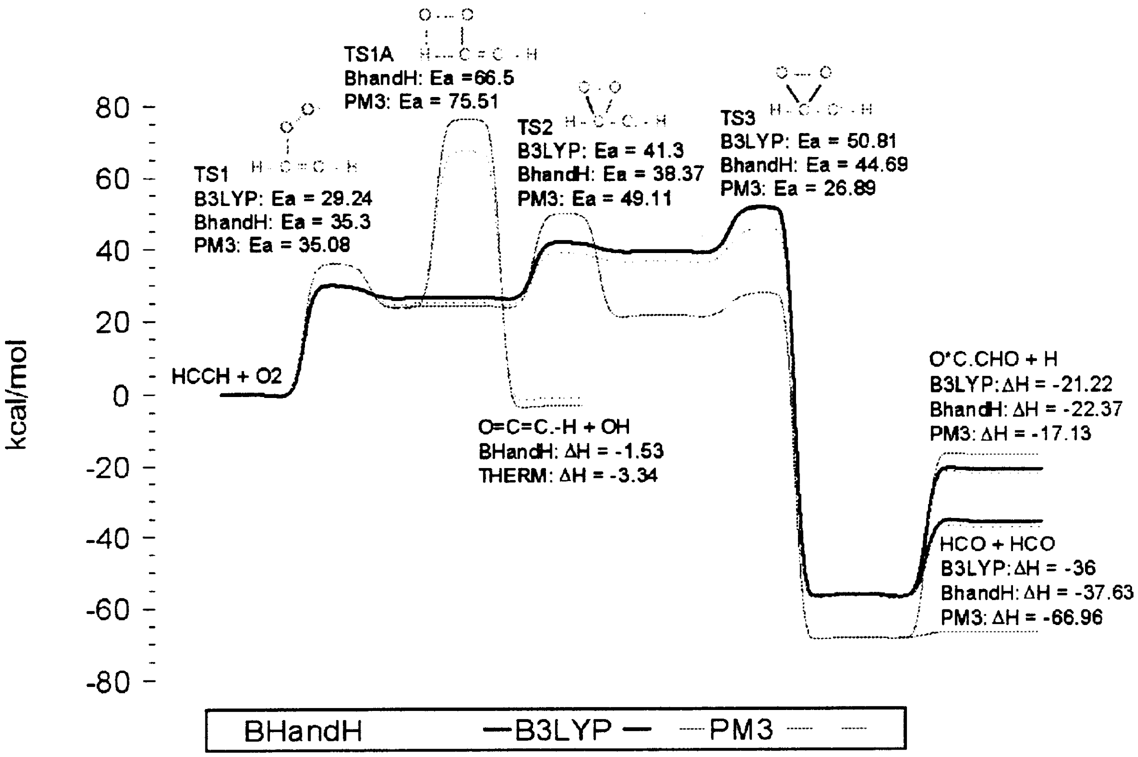


Figure 5.1 Potential energy diagram for HCCH + $^3O_2$ system, as calculated by BHandH/6-31G(d), B3LYP/6-31G(d,p) and PM3. E_a are activation barriers required to reach transition states and ΔH_{rxn} are relative to the reactants.

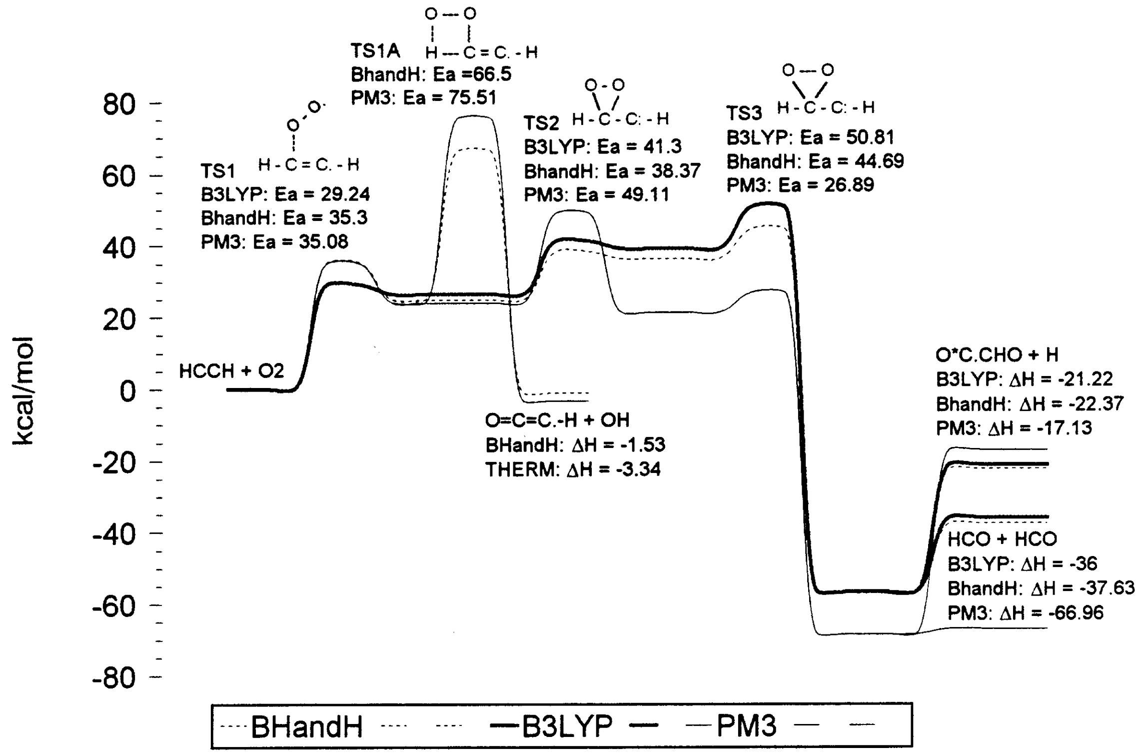


Figure 5.2 Potential energy diagram for HCCH + $^3O_2$ system, as calculated by CBS-q//MP2/6-31G(d), QCISD(T)/6-31G//MP2/6-31G(d) and PM3. E_a are activation barriers required to reach transition states and ΔH_{rxn} are relative to the reactants.

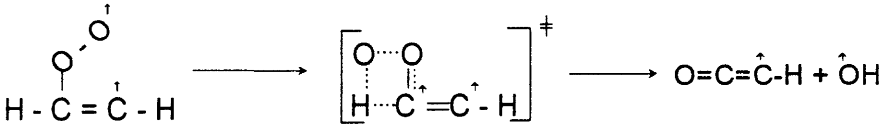
There are five possible isomerization/dissociation reactions this triplet peroxy-ethylene biradical adduct can undergo:

i. reverse reaction back to reactants
ii. peroxy radical abstraction of hydrogen from carbon, hydrogen transfer reaction through a 4-member ring TS (TS1A)
iii. oxygen radical (peroxy) addition to ipso-carbon forming a 3-member TS (TS2)
iv. peroxy radical abstraction of hydrogen from carbon with radical site, forming a 5-member ring TS (this would result in a triplet biradical at the carbon site)
v. addition of oxygen radical to carbon with the unpaired electron, forming a 4-member ring TS (this would form a 1, 2 triplet biradical dioxetane).

Results on the latter two reactions are not presented since attempts to find the transition states for these reactions were not successful and reaction enthalpies are estimated to be high. Evaluation of the product in (iv) is unstable with an endothermicity of over 45 kcal/mol. Note that both Carpenter and Mebel, *et al.* [70,138,139] show barriers for 4-

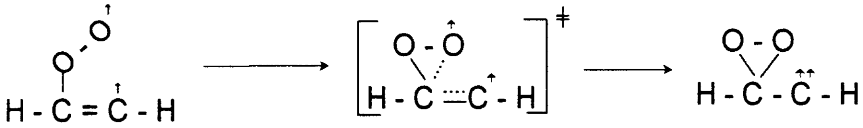
member peroxide ring formation (v from above) across a double bond are significantly higher than the barrier for ipso addition to form dioxirane. Carpenter indicates this is due to the significant strain energy in twisting the double bond. Reaction v is estimated to have a barrier in excess of 35 kcal/mol from calculations on analogous doublet reactions (4-member ring) in ethylene and propene. Both reactions iv and v are considered unimportant.

TS1A results from the peroxy radical site abstracting the hydrogen on the valence satisfied carbon; beta scission of this hydroperoxy radical forms ketenyl plus hydroxyl radicals.



This TS was only found at BHandH/6-31G(d) and PM3 levels of calculation. Both methods determine the activation barrier to products in excess of 40 kcal/mol. This reaction path is more than 20 kcal/mol higher than the next highest barrier in the respective reaction system.

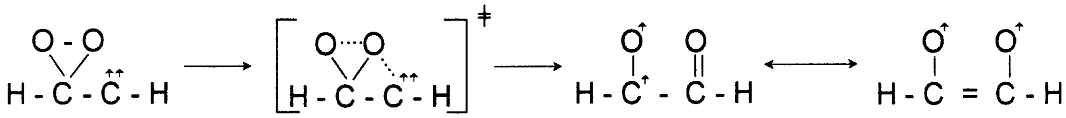
The triplet peroxy-ethylene biradical can react through a more favorable path, via a 3-member dioxirane ring transition state (TS2). TS2 is formed by the addition of the peroxy radical to the ipso-carbon.



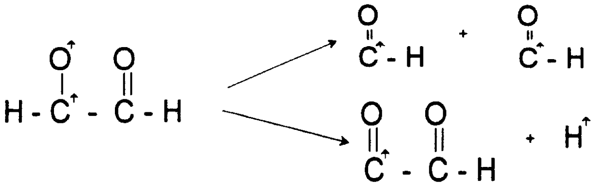
The adduct formed has two parallel-spin electrons on the carbon adjacent to the dioxirane ring. Density functional calculations result in the lowest barrier; B3LYP/6-31G(d,p) and

BHandH/6-31G(d) yield values of 14.8 and 13.5 kcal/mol, respectively. PM3 determines this barrier to be 20.1 and CBS-q//MP2/6-31G(d) methods show barriers of 25.3 kcal/mol.

The carbon radical site with two unpaired electrons then attacks one oxygen of the dioxirane ring in TS3 with formation of a new carbon-oxygen bond and cleavage of the weak and highly strained O-O peroxide bond. This results in an oxygen transfer and forms a triplet aldehyde (glyoxal) biradical, which has several resonant structures. The reaction is about 100 kcal/mol exothermic due to formation of the strong C-O bond, combined with release of ring strain and cleavage of a weak peroxide bond.



ab initio and DFT methods predict TS3 as the transition state at the highest energy, in the most favorable overall reaction path: thus the rate controlling step in this triplet reaction system. PM3, however, shows this as the lowest barrier in its system. PM3 determines this activation energy to be 5.6 kcal/mol, BHandH/6-31G(d) and B3LYP/6-31G(d,p) calculate this barrier to be 8.3 and 11.6 kcal/mol, while CBS-q//MP2/6-31G(d) give an activation barrier in excess of 20 kcal/mol. The glyoxal biradical is formed in chemically activated state, with ca 100 kcal/mol excess energy; more than sufficient to further react to two formyl radicals or hydrogen atom plus glyoxal radical, before stabilization.



The transition state structures and energetics for dissociation of this glyoxal biradical to form two formyl radicals and the hydrogen elimination reaction are not determined by *ab initio* or DFT methods. Instead, estimation techniques using kinetics from generic reactions and energetics determined for these systems are utilized for the rate constant parameters. The simple dissociation reaction is based on the dissociation of CH3CO → CH3 + CO reported by Bencsura, *et al.*, $k = 2.5x10^{13} e^{-\frac{16.38 \frac{kcal}{mol}}{RT}}$ which is $E_a = \Delta H_{rxn} + 5.7$ kcal/mol.[140] The activation barrier for the formation of two HCO radicals is estimated as $\Delta H_{rxn} + 5.7$ kcal/mol. Barriers required for formyl radicals' formation by density functional methods are about 18 kcal/mol, CBS-q//MP2/6-31G(d) results show an E_a of about 9 kcal/mol and PM3 about 40 kcal/mol.

The hydrogen elimination reaction leading to the formation of glyoxal radical plus hydrogen atom is estimated as $k = 1x10^{13} e^{-\frac{26.37 \frac{kcal}{mol}}{RT}}$ and employed for CBS-q//MP2/6-31G(d), B3LYP/6-31G(d,p) and BHandH/6-31G(d). The pre-exponential A-factor is estimated from A-factor for one half H atom plus ethylene[141] with application of microscopic reversibility. The activation barrier is estimated from Taylor, *et al.*[142] for OH + acetaldehyde as $E_a = \Delta H_{rxn} + 2$ kcal/mol. Enthalpy of reaction as determined by CBS-q//MP2/6-31G(d) is chosen, 24.37 kcal/mol, and employed as the activation energy barrier.

Spin contamination values calculated for the semi-empirical, *ab initio* and DFT methods are generally in the range of 2.03 to 2.3 for molecules, which should have a theoretical $\langle S^2 \rangle$ value of 2.0 for triplet species. DFT methods result in the least spin contamination for all species in the triplet system. PM3 results also show spin contamination, with some transition states having spin contamination exceeding 10% of the theoretical spin value of 2.0. The specie that consistently has the highest spin contamination in all the methods employed is TS3. MP2/6-31G(d), QCISD(T)/6-31G//MP2/6-31G(d) and CBS-q//MP2/6-31G(d) show large spin contamination, with spin contamination exceeding a value of 2.9 for TS3. B3LYP/6-31G(d,p) calculated a spin contamination value of 2.3; BHandH/6-31G(d) calculated a value of 2.65 and PM3 2.67 for TS3.

Spin contamination is a significant factor in these calculations on triplet adducts and transition states with calculations based on spin-unrestricted Hartree-Fock theory.[143] Significant deviation from theoretical spin suggests unreliability in the calculated values, since the calculation may be using incorrect wave functions.[144] Correction of the spin calculations would lower the energy of TS3; but would increase the rate constants only slightly as TS2 has a similar barrier height to TS3. Spin values of 2.3 or lower result in reasonable accuracy, only 15% over theoretical; but higher spin contamination is a concern.

QCISD(T) calculations are performed with 6-311++G(2d,p), 6-311++G(2df,p) and 6-311++G(3df,2p) basis sets and B3LYP with 6-311++G(2d,p) and 6-311++G(3df,2p) basis sets to try and improve, (reduce) $\langle S^2 \rangle$ spin contamination and obtain more uniform barrier energies. – The energy results and $\langle S^2 \rangle$ values are listed in Table 5.3. The B3LYP level of theory calculations show a decrease in the spin contamination, $\langle S^2 \rangle$, with larger basis set. TS3 with the large basis set of 6-311++G(3df,2p) produced an $\langle S^2 \rangle$ value of 2.03, which is very close to the theoretical $\langle S^2 \rangle$ value of 2, whereas B3LYP/6-

31G(d,p) resulted in an ‹S^2› value of 2.3. The ‹S^2› values calculated at the QCISD(T) level theory only showed slight improvements with increased basis sets.

5.3.2 Kinetic Results and Discussion

QRRK provides a formalism, which allows estimation for the overall rate constant in complex reaction systems, where reverse reaction, stabilization to adducts, isomerization and dissociation to new product channels are included. Table 5.2 lists the QRRK input kinetic parameters for *ab initio*, density functional theory and PM3 computational estimates, respectively. QRRK analyses are performed over temperatures 300 to 2500 K at pressures of 0.001 to 3 atm. Figures 5.3a and 5.3b illustrate forward rate constants, *i.e.* HCCH + $^3O_2$ ➔ products, at temperatures, between 1000 and 2500 K, over the pressure range of 10^{-3} atm to 3 atm, for data from CBS-q//MP2/6-31G(d) and B3LYP/6-31G(d,p). At temperatures below 1000 K, *ab initio* and DFT calculations do not indicate any significant reaction, *i.e.* $k_{\infty,forw} \leq 10^3$ cm^3-mol^{-1}-sec^{-1}. The forward rate constants as calculated by data from B3LYP/6-31G(d,p) do not show significant pressure dependence (Figure 5.3a).

Rate constants to specific products versus 1000/T, as determined by QRRK under isobaric condition of 1 atm, are shown in Figures 5.4a and 5.4b for B3LYP/6-31G(d,p) and CBS-q//MP2/6-31G(d), respectively. All calculations show a rate constant to stabilized Adduct 1(triplet peroxy-ethylene biradical) as significant for all temperatures.

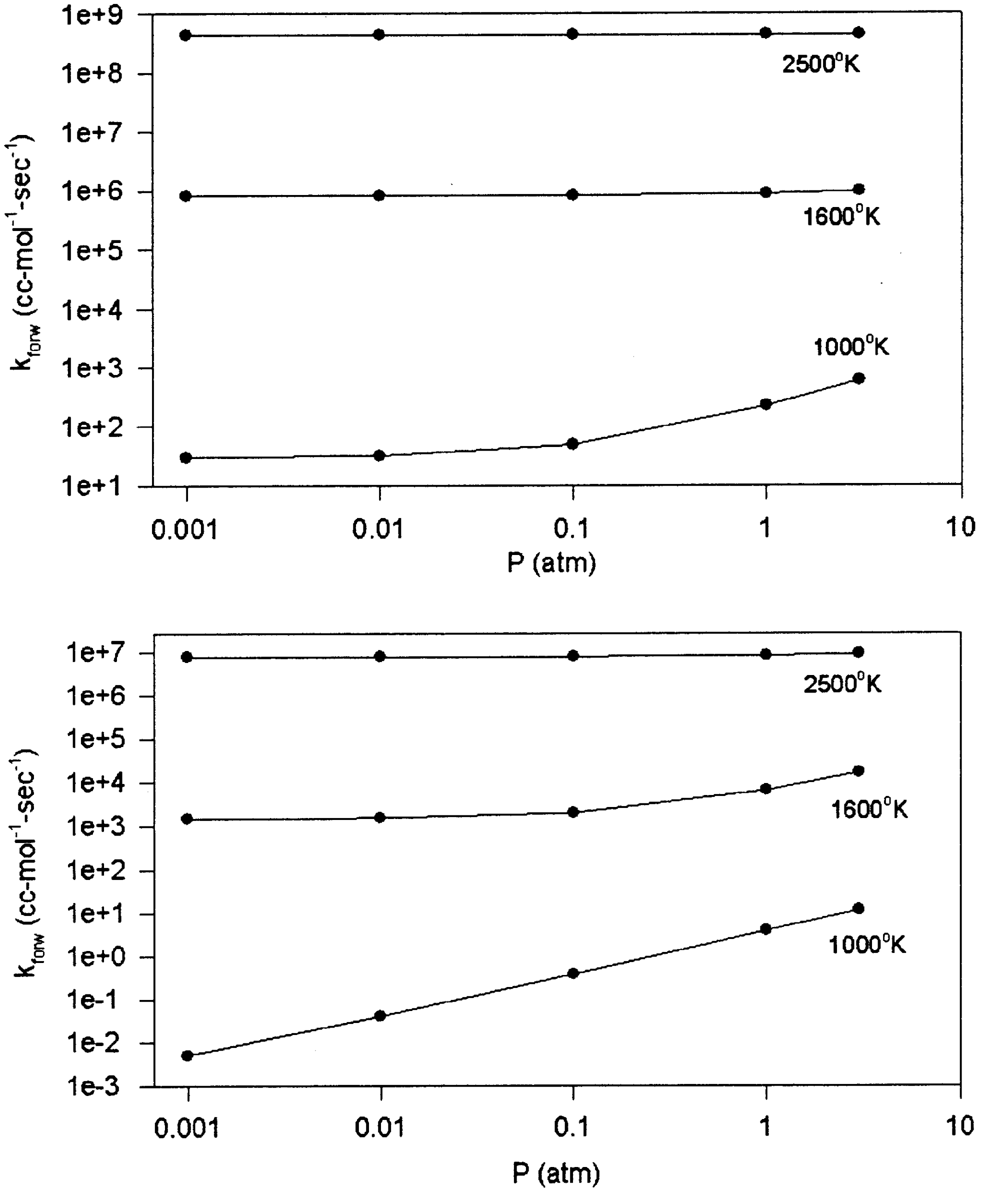
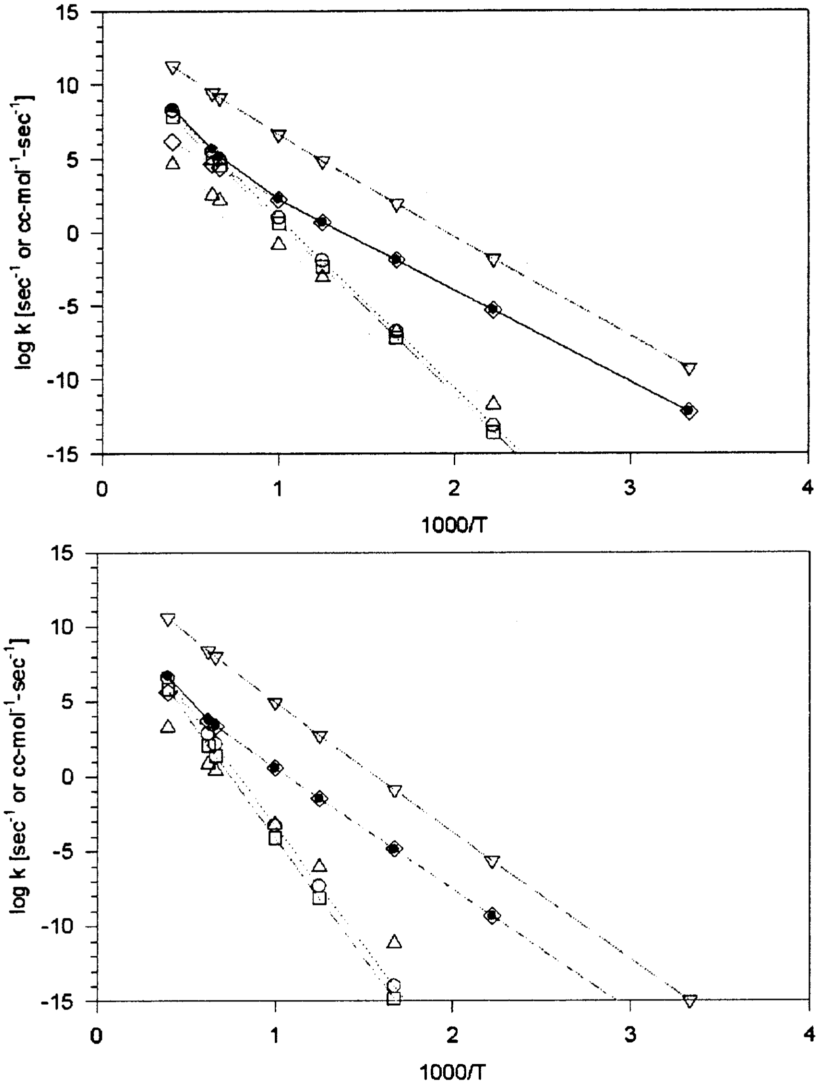


Figure 5.3 Overall forward rate constants, under isothermal conditions, as determined from quantum RRK calculation for HCCH + $^3O_2$ triplet system at temperatures of 1000, 1600 and 2500 K over a pressure range from 0.001 to 10 atm. Top: B3LYP/6-31G(d,p) Bottom: CBS-q//MP2/6-31G(d)



k_{forw}	●
HCCH + $^3O_2$	▽
^{3}•C=COO•	◇
^{3}CYCOO	△
HCO	○
•C=OCHO + H	□

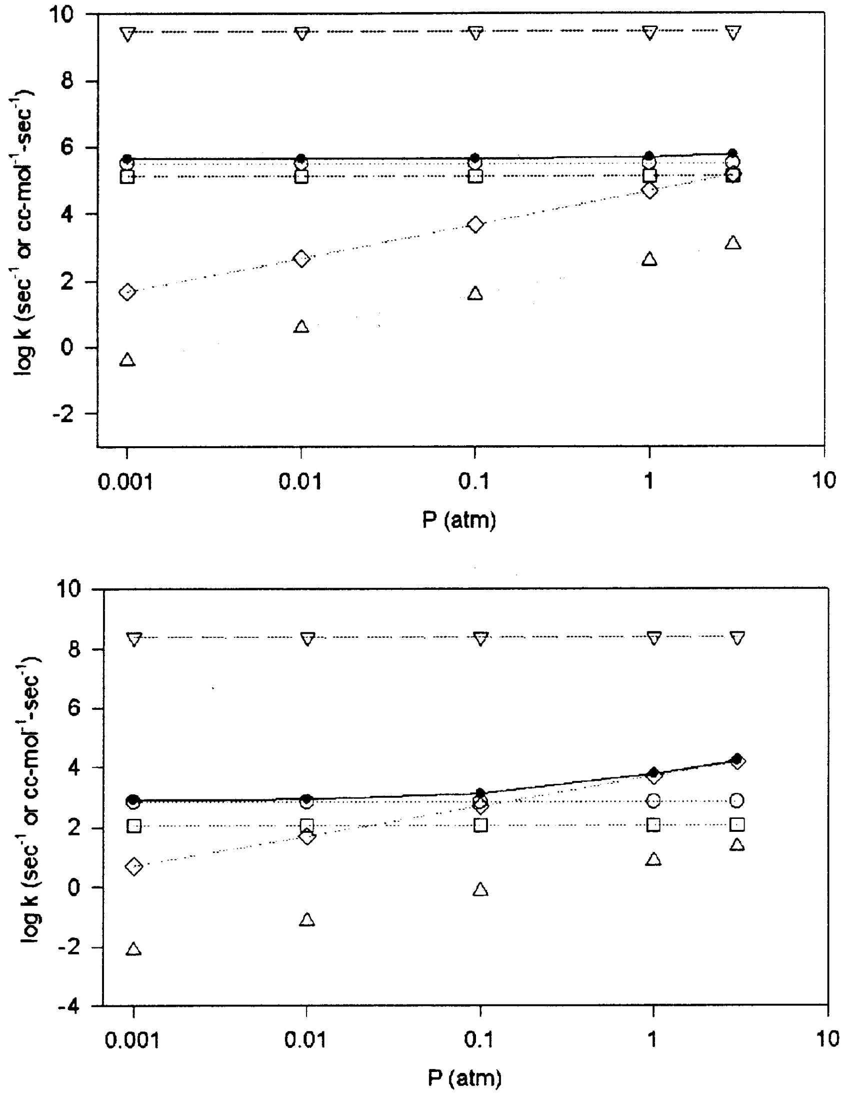
Figure 5.4 Elementary rate constants, as determined by QRRK, for HCCH + $^3O_2$ system under isobaric condition of 1 atm over a temperature range of 300 to 2500 K. Top: B3LYP/6-31G(d,p); Bottom: CBS-q//MP2/6-31G(d)

Dissociation of this adduct, back to reactants, is its dominant reaction path and the dissociation barriers are low; thus reverse reaction proceeds at the high pressure limit. While the adduct formation rate appears significant, it is not important as a stable intermediate, due to its rapid dissociation back to reactants.

Figures 5.5a and 5.5b show rate constants vs. pressure (log-log scale) at T = 1600 K for the B3LYP/6-31G(d,p) and CBS-q//MP2/6-31G(d) calculation data, respectively. The two formyl radicals and hydrogen atom plus glyoxal radical products are the important channels. Rate constant calculations based on B3LYP/6-31G(d,p) estimates show the highest rate constant for these products. Rate constants for CBS-q//MP2/6-31G(d) calculations show rate of stabilization for the triplet peroxy-ethylene biradical becoming important at pressures above 0.1 atm; but as above, stabilized adducts quickly dissociate back to reactants, due to the shallow well.

A CHEMKIN integrator computer code is utilized to calculate the concentration profile of reactants, stabilized adducts and products[145] versus time to 35 milliseconds at several temperatures. Concentration profiles for B3LYP/6-31G(d,p) and CBS-q//MP2/6-31G(d) calculated energies at pressures of 0.013 and 1 atm and temperatures of 1000, 1600 and 2000 K are presented for initial concentration conditions of 5% HCCH, 15% $^3O_2$ and 80% N_2.

Results of the CHEMKIN concentration profiles further confirm that levels of stabilized adducts are low, mole fractions of 10^{-12} and lower. Product sets include formyl radicals and glyoxal radical plus hydrogen atom. Concentration of formyl radicals is about a magnitude greater than that of glyoxal, due to a higher pre-exponential A-factor, a lower activation barrier and the formation of two formyl radicals. Product formation at 1000 K



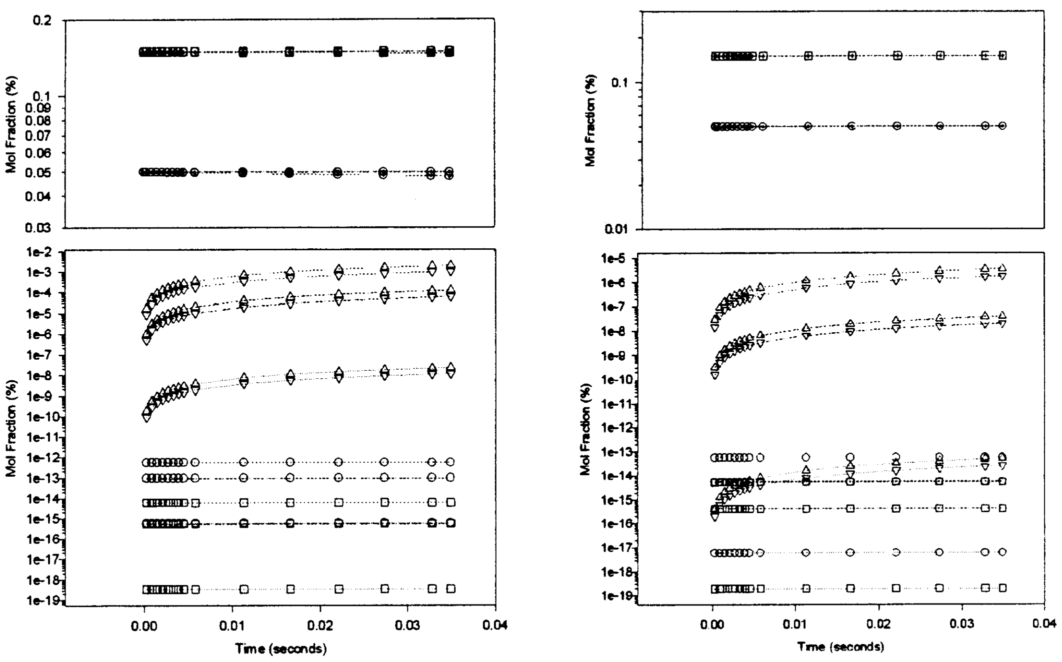
k_{forw}	●
HCCH + $^3O_2$	▽
^{3}•C=COO•	◇
^{3}CYCOO	△
HCO	○
•C=OCHO + H	□

Figure 5.5 Elementary rate constants, as determined by QRRK, for HCCH + $^3O_2$ system under isothermal condition of 1600 K over a pressure range of 0.001 to 10 atm.
Top: B3LYP/6-31G(d,p); Bottom: CBS-q//MP2/6-31G(d)

for all conditions tested result in negligible conversion of acetylene, < 0.04% after 35 milliseconds. Increased product formation as pressure and temperature are increased is observed. CBS-q//MP2/6-31G(d) results do not show significant product yields; at 1 atm and 2000 K, with 0.2% conversion after 35 milliseconds.

Figures 5.6 and 5.7 show concentration profiles determined by CHEMKIN for B3LYP/6-31G(d,p) density functional theory method. The concentration of both stabilized adducts follows similar trends to that of acetylene. At 0.013 atm, acetylene and stabilized adduct concentrations do not change significantly; at 1 atm both concentrations deplete exponentially. This analysis indicates the rate constant for stabilization of chemically activated adducts are significant, but the stabilized adducts are very short lived and undergo rapid reaction. The important overall channels are formation of the product sets. Product formation at 1600 K at 0.013 atm is about 0.2% and 2.6% at 2000 K. Conversion of reactants to products increases significantly at 1 atm due to an increase in amount of O_2. At 1600 K about 10.2% conversion and at 2000 K 80.4% conversion is observed after 35 milliseconds.

Formation of products shows a slight dominance of formyl radical formation over glyoxal radical plus hydrogen atom. The product ratios of formyl radicals to glyoxal radicals with an initial concentration of 15% O_2, 5% HCCH and 80% N_2 system varied from 6:1 to 8:1 over the pressure range of 0.013atm to 1 atm; temperature did not affect product ratio distribution significantly. QRRK analysis show rate of adduct stabilization are important at higher pressures, but CHEMKIN results show that these adducts rapidly react back to reactants and are not important; need not be included in the detailed mechanisms.



(a)

(b)

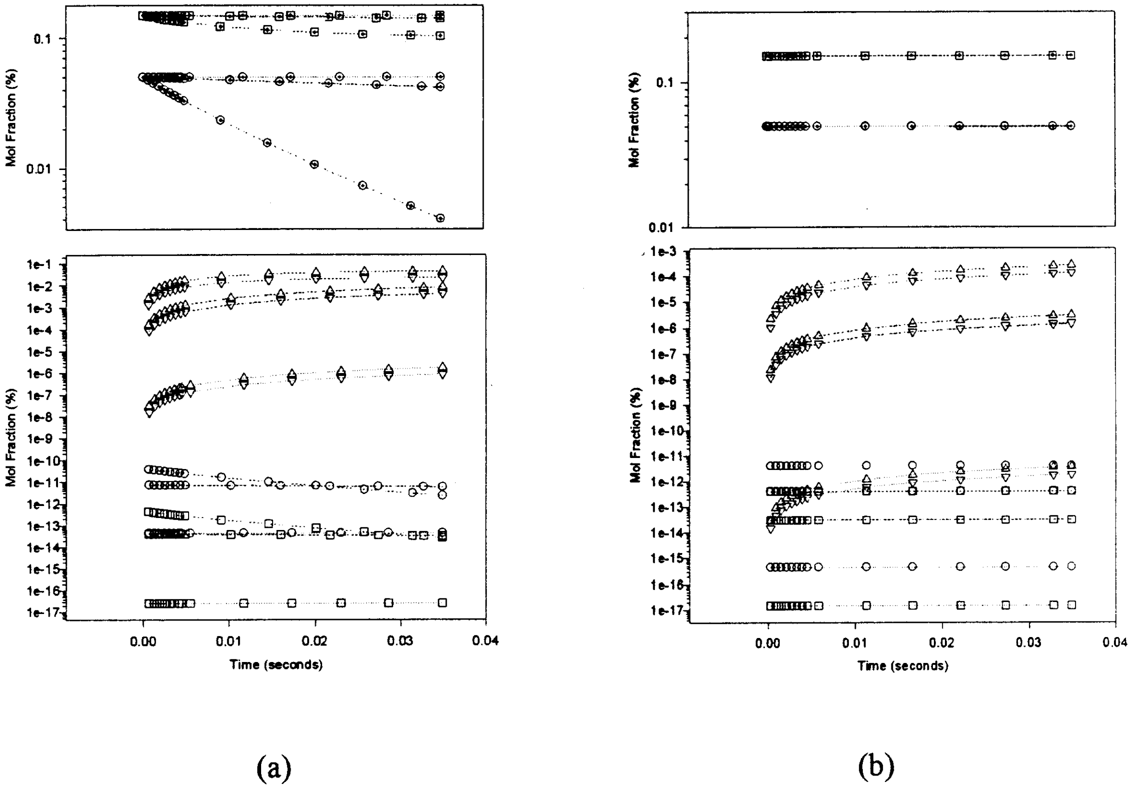
HCCH	⊕
$^3O_2$	⊞
^{3}•C=COO•	○
^{3}CYCOO	□
HCO	△
•C=OCHO + H	▽

—— Temp = 2000 K

- - - - Temp = 1600 K

…… Temp = 1000 K

Figure 5.6 Concentration profiles of reactants, adducts and products vs time for HCCH + $^3O_2$ on triplet surface at P = 0.013 atm and T = 1000, 1600 and 2000 K. Initial concentration of mixture: 15% $^3O_2$, 5% HCCH and 80% N_2. (a) B3LYP/6-31G(d,p); (b) CBS-q//MP2/6-31G(d)



(a)

(b)

HCCH	⊕
$^3O_2$	⊞
^{3}•C=COO•	○
^{3}CYCOO	□
HCO	△
•C=OCHO + H	▽

——— Temp = 2000 K

- - - - - Temp = 1600 K

……… Temp = 1000 K

Figure 5.7 Concentration profiles of reactants, adducts and products for HCCH + $^3O_2$ mechanism as function of time at P = 1.0 atm (isobaric) for T = 1000, 1600 and 2000 K. Initial concentration of mixture: 15% $^3O_2$, 5% HCCH and 80% N_2. (a): B3LYP/6-31G(d,p): (b) CBS-q//MP2/6-31G(d).

Based on *ab initio* and density functional calculation, the two favorable product sets are H + •C=OCHO and HCO + HCO. The estimated overall forward rate constant for HCCH + O_2 → H + •C=OCHO is determined to be $k_f = 3.75x10^{11}T^{1.165}e^{-\frac{51.09\frac{kcal}{mol}}{RT}}$ and for HCCH + O_2 → HCO + HCO the overall forward rate constant is estimated to be $k_f = 6.22x10^{7}T^{1.341}e^{-\frac{51.19\frac{kcal}{mol}}{RT}}$ from B3LYP/6-31G(d,p) at 1 atm over a temperature range from 300 to 2500 K. These forward rate constants are determined from QRRK analysis, based on all three wells, as defined in this triplet system.

5.3.3 $^1O_2$ + Acetylene Path

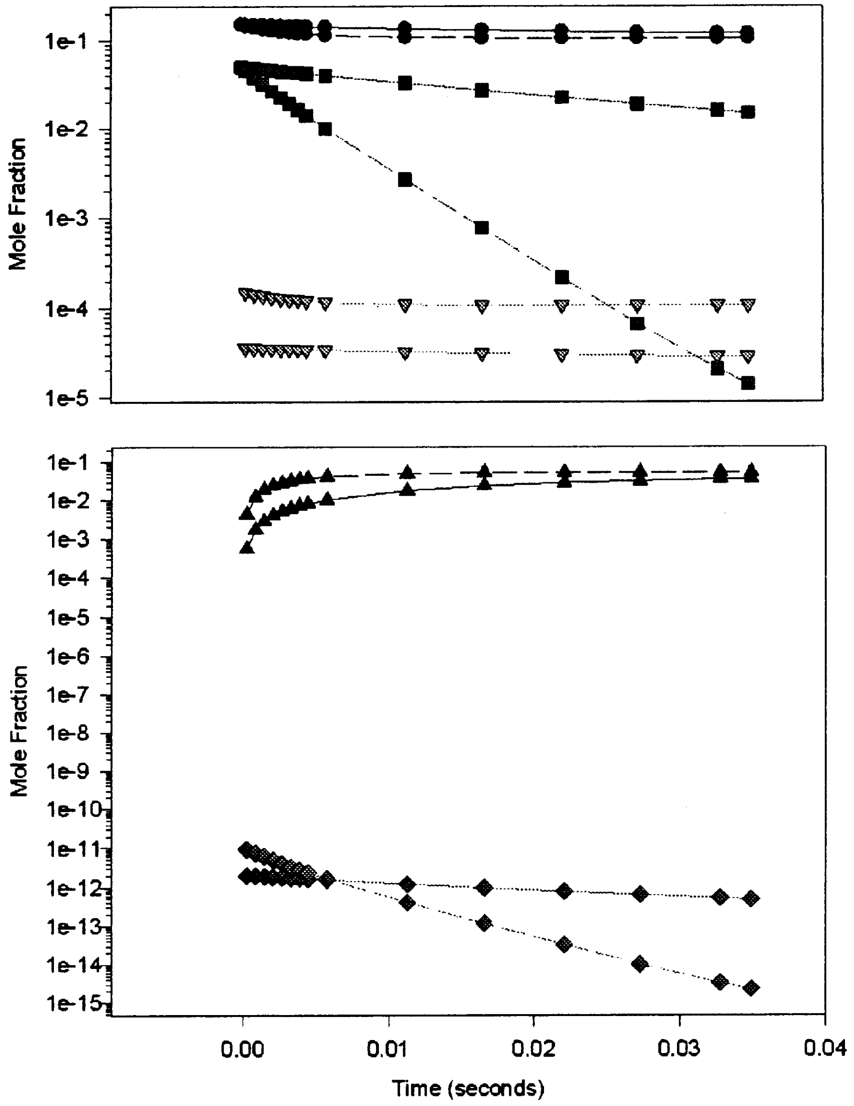
A small mechanism file was generated, based upon rate constants and activation barriers suggested by Benson[17], for pathways in the singlet oxygen addition to acetylene system. The singlet oxygen addition pathway can be reasonably expressed with control by three reaction steps and assuming all reactions, after formation of dioxitene (cyclic C=C-O-O), which are exothermic by over 50 kcal/mol, rapidly go to products. The three controlling reaction steps, along with rate constant expressions are listed as:

Reaction		Rate Constant (cc/mol-sec)	Rxn
$^3O_2 + M$	⇔ $^1O_2 + M$	$k = 10^{13}e^{-\frac{23.0\frac{kcal}{mol}}{RT}}$	B1
$^1O_2$ + HCCH	⇔ ^{1}HC•COO•	$k = 6.95x10^{7}T^{1.8}e^{-\frac{7.6\frac{kcal}{mol}}{RT}}$	B2
^{1}HC•COO•	⇔ (cyclic C=C-O-O)	$k = 2x10^{12}e^{-\frac{6.0\frac{kcal}{mol}}{RT}}$	B3
(cyclic C=C-O-O)	⇔ O=CH-CH=$O^{\neq}$		
	⇔ HCO + HCO (fast)		

E_a in kcal/mol; M = buffer gas

Benson estimated the net forward reaction for the triplet to singlet oxygen conversion and addition of oxygen to acetylene (net **Rxn B1 + B2**) to be $k_f = 2x10^{12}\left(\frac{T}{300}\right)^{1.8} e^{-\frac{30.6\frac{kcal}{mol}}{RT}}$. The pre-exponential A-factor for the subsequent isomerization reaction was not provided by Benson. The estimate A-factor for this isomerization **Rxn B3** at 2 x 10^{12} from calculations of Mebel, *et al.* on vinyl peroxide cyclization with an E_a =6 kcal/mol from Benson.[17,70] Product yields determined from ChemKin results for acetylene oxidation, through this singlet channel proposed by Benson, using **Rxn B1 to B3** above as rate controlling parameters, is shown in Figure 5.8.

B3LYP/6-31G(d,p) calculations have been performed on the singlet peroxy-ethylene biradical and the singlet TS1 to further validate the path proposed by Benson. Comparison of the heat of formation for the singlet peroxy-ethylene biradical, between Benson's estimation technique and DFT calculation show reasonable agreement. Benson reports a ΔH_{rxn} for the net reaction of $^3O_2$ + HCCH + M → ^{1}•OOCH=C•H + M to be about 24 kcal/mol, where 23 kcal/mol is required for the $^3O_2 + M \Leftrightarrow {}^1O_2 + M$ conversion. B3LYP/6-31G(d,p) calculates a ΔH_{rxn} for $^3O_2$ + HCCH → ^{3}•OOCH=C•H as 26.42 kcal/mol. This would suggest the difference between the heat of formation for singlet and triplet peroxy-ethylene biradical is less than 3 kcal/mol difference, as is also suggested by Benson. DFT calculations do not show any significant difference between the triplet peroxy and the singlet peroxy biradical adducts, which are within about 1 kcal/mol, as calculated from B3LYP/6-31G(d,p) and in agreement with estimates by Benson.



$^3O_2$	●
HCCH	■
$^1O_2$	▼
^{1}•C=COO•	◆
OHC=CHO	▲

Figure 5.8 Concentration profiles of reactants, adducts and products for HCCH + $^1O_2$ reaction system vs time as determined by CHEMKIN at 1 atm for T = 1600 and 2000K. Initial concentration of mixture: 15% $^3O_2$, 5% HCCH and 80% N_2.

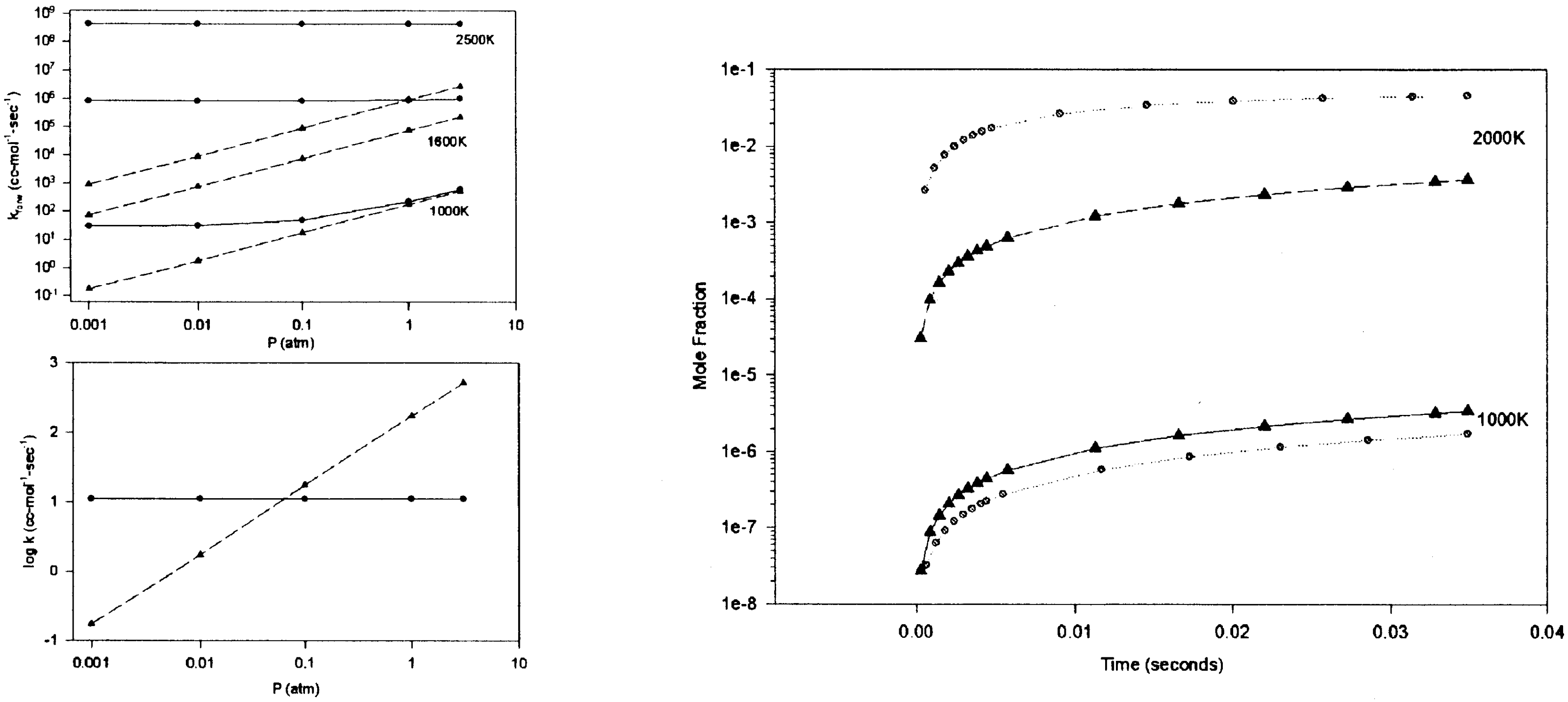
Calculations on the transition state for singlet oxygen addition to acetylene are performed in both B3LYP and QCISD(T) with larger basis sets to see if a lower barrier as recommended by Benson can be found and to ascertain if convergence is obtained. The enthalpy of formation for the singlet TS1 (^{1}TS1) and triplet TS1 (^{3}TS1) are presented in Table 5.3. The variation in ΔH_f(298K) values for ^{1}TS1, based on B3LYP theory, between the smallest and largest basis set is less than 2.5 kcal/mol. The ΔH_f(298K) for ^{1}TS1 is approximately 18 kcal/mol higher than ^{3}TS1 at B3LYP/6-311++G(3df,2p) level of theory and approximately 25 kcal/mol higher than ^{3}TS1 in comparing the two values from QCISD(T) /6-311++G(2df,p)//MP2/6-31G(d) level of theory. The 25 kcal/mol difference between ^{3}TS1 and ^{1}TS1 seems to be near constant in the QCISD(T) calculation with the 6-311++G(2d,p) and 6-311+G(2df,p) basis set calculations, only showing a 1 kcal/mol difference. Increasing the basis set in this calculation will likely not result in further decrease of the calculated barrier.

The barrier for addition of $O_2(^1\Delta)$ to HCCH through ^{1}TS1 is about 25 kcal/mol and $O_2(^3\Sigma)$ addition through ^{3}TS1 is about 5 kcal/mol higher. However, an added energy of 22.5 kcal/mol for conversion of $^3O_2$ + M $\Leftrightarrow$ $^1O_2$ + M is required, which makes the $O_2(^3\Sigma)$ + HCCH +M $\Leftrightarrow$ ^{1}TS1 + M barrier 17.5 kcal/mol higher than $O_2(^3\Sigma)$ + HCCH $\Leftrightarrow$ ^{3}TS1. The calculations suggest that the overall barrier estimated by Benson for the $O_2(^1\Delta)$ addition is at least 48 kcal/mol, relative to $O_2(^3\Sigma)$ + HCCH; this is over 18 kcal/mol higher than Benson's original estimate for the overall reaction barrier. Maranzana, *et al.* have performed calculations and analysis on $O_2(^1\Delta_g)$ addition to ethylene at the B3LYP density functional theory as well as the multireference method CAS-MCSCF/6-31G(d) and CAS-PT2/6-31G(d) levels. They indicate that the barrier for $O_2(^1\Delta_g)$ addition to ethylene is over 16 kcal/mol.[146] The calculated barrier to the diradical formation transition state at the B3LYP/6-311+G(2d,2p) is 16.8 kcal/mol and at CAS-MCSCF/6-31G(d) and CAS-PT2/6-31G(d) are 24.8 and 17.5 kcal/mol, respectively. The agreement between Maranzana, *et al.*'s CAS and density function calculations support, on this similar reaction, the current calculation estimates.

5.3.4 Vinylidene Pathway

Comparison of rate constants between the B3LYP/6-31G(d,p) determined $^3O_2$ + HCCH system and the vinylidene pathway of Laskin and Wang's[72,124], based on their G2//B3LYP/6-31G(d) analysis are shown in Figures 5.9a and 5.9b. Figure 5.9a shows the total forward rate constant, based on QRRK analysis, which includes formation of adducts and products. Figure 5.9b shows the rate constant from reactant to products. The assumption used in determining Laskin and Wang's rate constants is that the isomerization of acetylene is the rate limiting reaction. That is, once vinylidene is formed it immediately reacts with molecular oxygen to products, methylene ($^3CH_2$) and carbon dioxide using spin conservation is choosen as product sets. The enthalpy of formation for vinylidene is 97 kcal/mol determined from the E_a provided by Laskin and Wang and literature value of acetylene.

Further evaluation of the kinetics on the vinylidene path using Laskin and Wang's[72,124] low-pressure limit (second order) rate coefficient. A high-pressure limit rate constant is calculated for the isomerization from literature data and canonical transition state theory. Fall-off is estimated using the current QRRK-modified strong collision analysis on the bimolecular reaction: HCCH + M ⇔ $H_2C{=}C{:}$ + M. The QRRK results



(a)

(b)

(c)

Figure 5.9 Comparison of forward rate constants between Laskin and Wang's vinylidene system and HCCH + $^3O_2$ system – triplet surface. (a) forward rate constant, (b) rate constant to product formation and (c) shows product concentration profiles at 1000 and 2000 K vs time. Symbols: ● = HCCH + $^3O_2$ system and ▲ = Laskin and Wang's vinylidene system.

suggest acetylene isomerization to vinylidene starts to fall off, deviate from low pressure limit above 8 atm at T = 1000 K.

The rate constant for HCCH + ${}^3O_2$ to the initial adduct, as calculated from B3LYP/6-31G(d,p), is faster than acetylene isomerization to vinylidene over the pressure range from 10^{-3} to 3 atm. Further reactions on the triplet surface are, however, rate controlling. Figure 5.9b compares rate constants to the formation of products, i.e. formyl radicals from HCCH + ${}^3O_2$ on the triplet surface (this study) and ${}^3CH_2 + CO_2$ from ${}^1CH_2C$: + ${}^3O_2$, over the pressure range of 10^{-3} to 3 atm. Analysis on the formation of products shows that the vinylidene pathway is more favorable than the ${}^3O_2$ addition and reaction on the triplet surface at 1000 K and pressures above 0.1 atm.

CHEMKIN results show an initial mole fraction of 0.05 HCCH, 0.15 ${}^3O_2$, and 0.80 N_2, at the same temperature and pressure after 34.9 msec residence time, the mole fraction of CO_2 is $4.135\text{x}10^{-6}$, while the formyl radical concentration from reaction on triplet surface is $1.73\text{x}10^{-6}$. This suggests that for low temperature (ca 1000 K) and high-pressure systems, acetylene isomerization is a viable pathway. (Refer to Figure 5.9c).

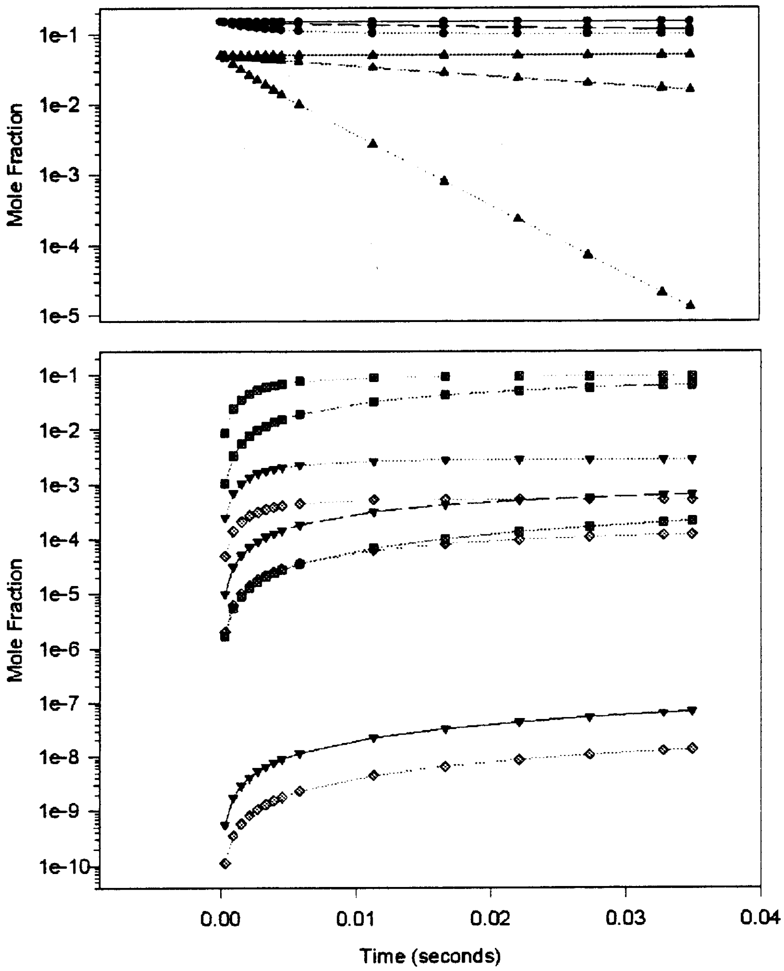
5.3.5 Triplet Biradical Adduct Conversion to a Singlet

An additional reaction process is considered, addition of triplet oxygen to acetylene, forming ${}^3HC\bullet{=}CHOO\bullet$. This triplet biradical adduct is allowed to convert into the singlet biradical through collision, in the ChemKin analysis; *i.e.* ${}^3HC\bullet{=}CHOO\bullet + M \Leftrightarrow {}^1HC\bullet{=}CHOO\bullet + M$, with an estimate $k_f = 10^{13} e^{-\frac{1.02\frac{kcal}{mol}}{RT}}$ cc/mol-s. The assumption of pre-exponential A-factor = 10^{13} cc/mol-s for ${}^3HC\bullet{=}CHOO\bullet + M \Leftrightarrow {}^1HC\bullet{=}CHOO\bullet$ +

M, about 1 in 40 collisions is conservative. The singlet biradical adduct then proceeds to 2 HCO as in Benson's scheme. Overall rate constants, via conversion of the triplet biradical adduct to singlet biradical adduct, at 1 atm as determined by QRRK analysis is $k_f = 2.21x10^7 T^{1.41} e^{-\frac{33.1\frac{kcal}{mol}}{RT}}$ cc/mol-s.

Comparison of product formation between two systems, (i) Benson's HCCH + $^1O_2$ and (ii) the HCCH + $^3O_2$ ⇔ ^{3}Adduct + M ⇔ ^{1}Adduct + M are performed using CHEMKIN and show that the concentrations and initiation rate processes are nearly identical. (Refer to Figures 5.8 and 5.10). The products compared are glyoxal for Benson's HCCH + $^1O_2$ system and formyl radicals for the ^{3}Adduct + M ⇔ ^{1}Adduct + M conversion. The concentration of glyoxal after 34.9 ms is 0.053 mole fraction and for formyl radical products it is 0.096 mole fraction for the same residence time. The doubling of mole fraction concentration for the formyl radical concentration is due to the formation of 2 moles of formyl radical for every mole of glyoxal.

Comparison of forward rate constants from selected literature, the triplet surface reactions system, Benson's proposed system and the system proposed by Laskin and Wang are shown in Figure 5.11. It should be noted that other currently available rate constants for this system are estimated or fitted rate constants on a net reaction of HCCH + O_2 ➔ products, (where the products are chosen by the respective authors[26,32,120-123]) in order to match a set of experimental data. Comparison of the literature rate constants at 1500 K between Miller, *et al.*, Marinov, *et al.* and Hidaka, *et al.* shows a difference of almost one order of magnitude, with steady increase in this difference to nearly two orders of magnitude at 2500 K. Miller, *et al.*'s estimated rate constant is the highest of these.



$^3O_2$	●
HCCH	▲
HCO (via conversion channel)	■
HCO (triplet channel)	▼
•C=OCHO + H	◆

——— Temp = 1000 K
- - - - - - - Temp = 1600 K
·············· Temp = 2000 K

Figure 5.10 CHEMKIN results for acetylene oxidation via triplet to singlet conversion of adduct, ^{3}•C=COO• + M ⇔ ^{1}•C=COO• + M ⇨ products, at 1 atm.

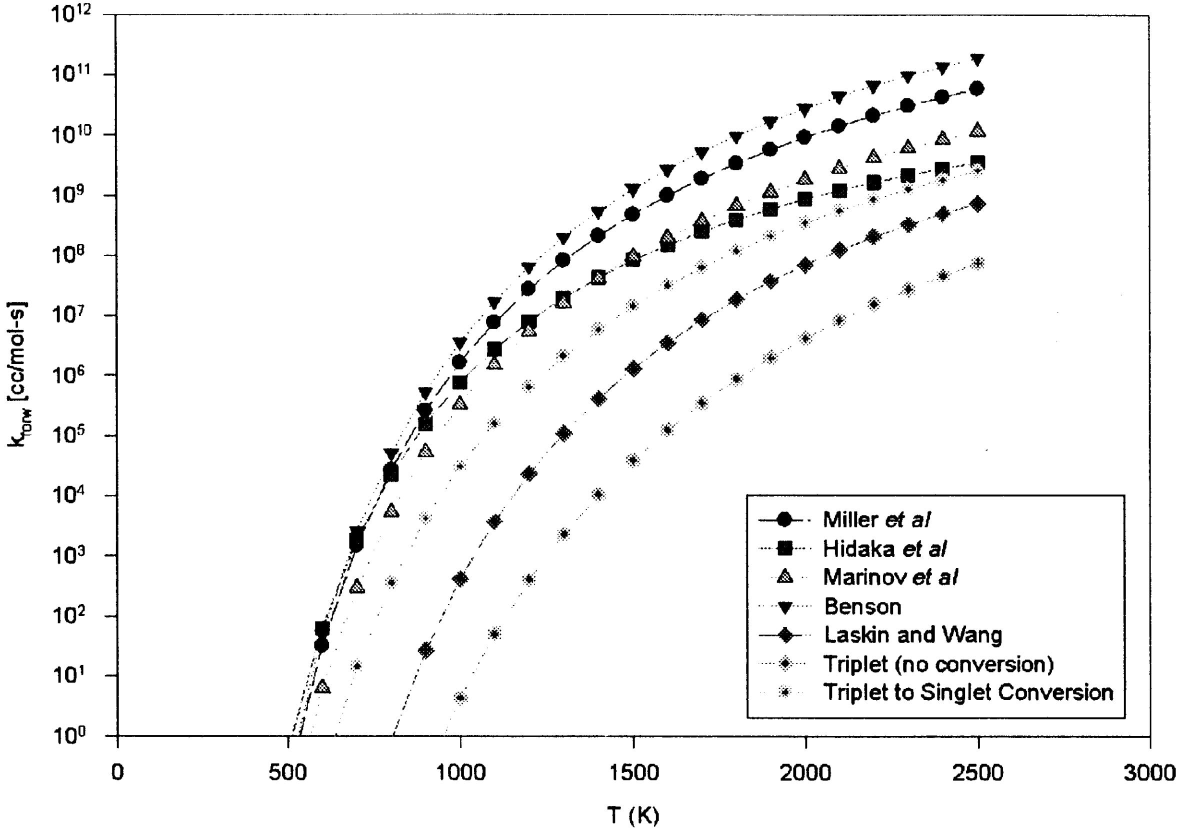


Figure 5.11 Comparison of overall rate constants between previous CHEMKIN modeling of experimental data by Miller, *et al.*, Marinov, *et al.*, Hidaka, *et al.* and with the four proposed chemistry mechanisms of Benson, Laskin and Wang, HCCH + O_2 on triplet surface and the HCCH + O_2 triplet to singlet conversion (^{3}•C=COO• + M ⇔ ^{1}•C=COO• + M).

The net reaction over the triplet surface (with no spin conversion) has the greatest deviation from the literature fitted rate constants; it is almost two orders of magnitude lower than that reported by Hidaka, *et al.* The acetylene oxidation pathway via isomerization to vinylidene, at 2500 K is less than one order of magnitude lower than that reported by Hidaka, *et al.* The reaction over the singlet surface, as proposed by Benson (without the current modifications – *i.e.* inclusion of barriers for additional reaction of this singlet adduct), is slightly over three times higher than that reported by Miller, *et al.* at 2500 K. However, the proposed forward rate constant by Benson, shown in Figure 5.11, is only for the initiation reaction, and does not include barriers for isomerization to products; Benson did not provide estimates of isomerization rate constants. The rate constant for the current proposed pathway, collisional conversion of triplet peroxy-ethylene to singlet peroxy-ethylene biradical, is also slower than the three literature sources. However, it approaches the rate constant of Hidaka, *et al.* with increase in temperature. It is within one order of magnitude at 1500 K of Hidaka, *et al.*'s value and approaches the same asymptote at 2500 K.

5.4 Summary

ab initio, DFT and semi-empirical methods are used to estimate thermodynamic properties and kinetic parameters for the acetylene + oxygen reaction system on the triplet surface. Overall rate constants have been calculated by QRRK analysis for CBS-q//MP2/6-31G(d) and B3LYP/6-31G(d,p) levels of calculation. DFT computational method, B3LYP/6-31G(d,p), provides lowest spin contamination in all adducts, TS1 and TS2. B3LYP/6-31G(d,p) calculates TS3 with a spin contamination of 2.3, while CBS-q//MP2/6-31G(d) reports spin contamination greater than 2.9. QRRK results indicate stabilization rate constant for triplet peroxy-ethylene biradical adduct as significant, but concentration profiles determined by CHEMKIN indicate very little presence of the stabilized adducts due to their rapid reactions and show only product forming channels as important. Spin contamination is a concern and calculation methods leading to reducing $\langle S^2 \rangle$ projections will help clarify the HCCH + O_2 reaction kinetics.

Two reaction processes contribute to initiation of acetylene oxidation: HCCH + $^3O_2$ to form an adduct with conversion of the triplet ^{3}HCCHOO• adduct to singlet via collision and isomerization of HCCH to vinylidene and then further reaction of vinylidene with O_2. Acetylene/vinylidene + O_2 reaction has an activation barrier of 43 kcal/mol and is also a viable pathway at low temperatures and pressures above 0.1 atm. The lowest energy pathway seems to be the $^3O_2$ + HCCH to form the triplet biradical adduct, which converts to the singlet biradical adduct through collision. The calculated overall rate constant from QRRK analysis closely matches the reported rate constant of Hidaka, *et al.* above 2000 K.

CHAPTER 6

DETAILED KINETICS AND THERMOCHEMISTRY OF $C_2H_5 + O_2$: REACTION KINETICS OF THE CHEMICALLY-ACTIVATED AND STABILIZED $C_2H_5OO\bullet$ ADDUCT

6.1 Introduction

Reactions of hydrocarbon radicals with molecular oxygen are important in atmospheric chemistry as well as in combustion processes. The intermediates include energized and stabilized peroxy radicals, both of which can react back to reactants, isomerize or react to new products. The initially-formed energized peroxy radical has multiple reaction possibilities. The $C_2H_5 + O_2$ reaction represents an important model system to explore the kinetic consequences of these reactions; it contains many of the complexities of larger systems, yet is more amenable to higher level electronic structure calculations. An added advantage is that this reaction has been well studied experimentally.[147-154] These experiments will be detailed in the modeling and comparison section.

There have also been several theoretical analyses of this system.[25,29,147,155-160] Wagner, *et al.*[29] have analyzed the $C_2H_5 + O_2$ reaction using variational RRKM theory for ethylene production and ethyl radical loss at pressures and temperatures relevant to the experimental data of Slagle, *et al.*[149,153] Their analysis assumes formation of a chemically-activated adduct, which can react directly through a cyclic (five-member ring) intermediate to a primary hydroperoxy-alkyl radical and then to $C_2H_4 + HO_2$ or be stabilized to $C_2H_5OO\bullet$. Subsequent reaction of the stabilized peroxy back to reactants or forward, over the isomerization barrier, to ethylene + HO_2 is accounted for with an analytical solution to a four-reaction mechanism, which assumes the kinetics depend only on the reactions leading to and including formation of the cyclic intermediate (excludes stabilization of the alkyl-hydroperoxy intermediate). The height of this barrier was adjusted to model the experimental data. Recent high-level *ab initio* calculations[161] have characterized a new concerted elimination path to directly produce C_2H_4 and HO_2 from the initially-formed ethylperoxy adduct. This pathway was not considered in earlier kinetic analyses of the ethyl + O_2 system[29,155], but was included in a recent study.[162] One important aspect of this system is that most of the reaction channels of the energized adduct are higher in energy than the entrance channel, but this new concerted elimination channel is a few kcal/mole lower. This suggests that adduct stabilization is likely over an extended temperature range. Both Kaiser and Clifford, *et al.* recognized the need to consider the kinetic consequences of subsequent thermal dissociation of this adduct in analyzing their experimental data. The dissociation reactions become increasingly important at higher temperatures, where the rate coefficients are larger.

The current study uses electronic structure theory to generate all the input parameters needed to analyze this chemically-activated system. The assessment of whether this approach can accurately predict the temperature and pressure dependence of the various reaction channels is studied. The potential energy surface is calculated at relatively high levels, and the rate coefficients for reactions of the energized adducts are obtained from canonical transition state theory (CTST). The rate coefficient for initial formation of ethylperoxy is calculated using variational transition state theory (VTST). The current study compare two models for collisional deactivation in conjunction with use of a multi-frequency QRRK analysis to estimate *k(E)*. Finally, the current study incorporate the predictions for the individual branching fractions of the energized adducts and those for thermal dissociation of the stabilized adducts into a mechanism to illustrate where it is necessary to account for thermal dissociation. Comparison of model with experiment suggests that this approach, with no adjustments to any of the parameters, permits an accurate description of this system. The results for loss of ethyl and production of ethylene show good agreement with recent experimental data of Kaiser.[147] Good agreement was also obtained for HO_2 production measurements of Clifford, *et al.*[148] The current study also explore the kinetic implications of the direct formation of ethylene and HO_2 from $C_2H_5OO\bullet$.

Since the QRRK rate coefficients are dependent on both temperature and pressure, a conventional CHEMKIN mechanism needs different sets of coefficients for each set of experimental conditions with different P. This is a good example of the utility in using Chebyshev fits[163,164] to capture k(T,P) so that one set of rate coefficients could be used for all conditions. The current study also introduce a modification to the CHEMKIN integrator package[145] to accept rate constants in the Chebyshev polynomial expression. This allows use of a single mechanism to cover a wide range of temperatures and pressures.

6.2 Computational Methods

6.2.1 *Ab Initio* and Density Functional Theory Computations

Molecular properties for reactants, adducts, transition states (TS) and products are estimated by high level CBS-Q[165] ab initio calculations and by density functional theory (DFT). The *ab initio* and DFT calculations are performed using Gaussian94.[55] The hybrid DFT method B3LYP, which combines the three parameter Becke exchange functional, B3, with the Lee-Yang-Parr nonlocal correlation functional, LYP, with a double zeta polarized basis set, 6-31G(d,p), is used to determine the optimized geometry.[129,166] Single point calculations at the complete basis set, composite method - CBS-Q are utilized based on the optimized B3LYP/6-31G(d,p) geometry, denoted as CBS-Q//B3LYP/6-31G(d,p). The DFT calculations are spin-unrestricted Hartree-Fock. Molecular geometries at B3LYP/6-31G(d,p) are fully optimized using the Berny algorithm and redundant internal coordinates.[55] The geometries of the five TS structures in this system are verified by checking for one imaginary frequency, consistency in bond lengths characteristic of a TS and by comparison to data of Schaefer's group.[160,161] Zero-point vibrational energy (ZPVE), vibrational frequencies and thermal correction contributions to enthalpy from harmonic frequencies are scaled in accordance to the scaling factors recommended by Scott and Radom.[62] The inclusion of ZPVE and thermal corrections to the total energies of the species in this system has been applied accordingly.

The enthalpies of adducts in the system are determined by use of isodesmic working reactions with group balance. Fundamental requirements for an isodesmic reaction are conservation of electron pair and chemical bond type.[136] The use of isodesmic reactions is an accurate and desired method for estimating enthalpy of formation. Three isodesmic reactions are employed to determine the enthalpy of formation for the two adducts of interest.

$CH_3CH_2OOH + CH_3OH = CH_3CH_2OH + CH_3OOH$ **(IR1)**

$\mathbf{CH_3CH_2OO\bullet} + CH_3OOH = CH_3OO\bullet + CH_3CH_2OOH$ **(IR2)**

$\mathbf{\bullet CH_2CH_2OOH} + CH_3CH_2OH = CH_3CH_2OOH + CH_2\bullet CH_2OH$ **(IR3)**

The enthalpies of formation for the adducts of interest are the ethylperoxy radical in **IR2** and the hydroperoxy-ethyl radical in **IR3**. The enthalpies of formation for all the other oxy-hydrocarbon species in the respective isodesmic reaction are needed before one can determine the enthalpy of formation of the two desired adducts. **IR1** is utilized to determine the enthalpy of formation for the ethyl-hydroperoxide molecule, which is then used in **IR2** and **IR3** to aid in the determination of the ethylperoxy radical and hydroperoxy-ethyl radical. It is important to note that the enthalpies of the ethylperoxy and hydroperoxy-ethyl radicals are determined independently and on an absolute scale. The difference in these two enthalpy values is ΔH_{rxn} between the two isomers (adducts).

The reaction enthalpies of the TS in this system are determined from the difference in total energies between the calculated TS and the calculated energies of both reactant and product, with ZPVE and thermal corrections included. These energies are designated E_c in the equations below. The enthalpy of formation of the adducts from the isodesmic reaction analysis above is used. The enthalpy of formation for the TS is now determined relative to enthalpy of both isomers, *viz.*

$$\Delta H_{reactant}(TS) = E_C(TS) - E_C(CH_3CH_2OO\bullet)$$

$$\Delta H_{product}(TS) = \left[E_C(TS) - E_C(\bullet CH_2CH_2OOH)\right] + \Delta H_{P-R}$$

$$\Delta H_{P-R} = H_f^{298}(\bullet CH_2CH_2OOH) - H_f^{298}(CH_3CH_2OO\bullet), \text{ from isodesmic analysis}$$

$$\Delta H_{rxn}(TS) = \frac{\Delta H_{product}(TS) + \Delta H_{reactant}(TS)}{2}$$

$$H_f^{298}(TS) = H_f^{298}(CH_3CH_2OO\bullet) + \Delta H_{rxn}(TS)$$

A comparative study of G2[167] vs. CBS-Q on the two adducts in the ethyl radical oxidation system is also performed. The "standard" G2 calculation, using the MP2(FU)/6-31G(d) method to optimize the geometry, is used. Comparison of the two high level – composite *ab initio* methods, G2 and CBS-Q//B3LYP/6-31G(d,p) implies good accuracy of the enthalpy of formation for the two adducts in this system.

A standard statistical mechanical analysis was employed to determine the vibrational, external rotational and translational contributions to entropy and $C_p(T)$.[168] Molecular parameters required in the statistical mechanic analysis are calculated at the B3LYP/6-31G(d,p) level of theory for the optimized geometric structure of the species. Vibrational contributions to entropy and C_p are scaled by the recommended scaling factors from Scott and Radom.[62] Optical isomers and unpaired electrons are also included in the S^{298} and $C_p(T)$ calculations accordingly. Contributions of internal rotation to S^{298} and $C_p(T)$ are incorporated based on the Pitzer-Gwinn formalism.[90]

6.2.2 Calculation of High-Pressure Rate Constants

The high-pressure forward rate constants for most reactions were determined by application of CTST for temperatures from 300 – 2500 K. Forward rate constants from 300 – 2500 K are calculated and fitted by a nonlinear least squares method to the form of a modified Arrhenius rate expression, *i.e.*, $k_{\infty,forw} = A_\infty T^n e^{-\frac{E_a}{RT}}$.

The rate constants for the addition and dissociation reaction for $C_2H_5 + O_2 \Leftrightarrow C_2H_5OO\bullet$ are calculated by VTST at B3LYP/6-31G(d,p) level. The reaction coordinate along the C-O bond length is calculated to determine the total energy (Figure 1). Rate constants are calculated based on the most favorable dissociation pathway along the reaction surface. The addition reaction rate constant is determined by satisfying the detailed balance criteria.

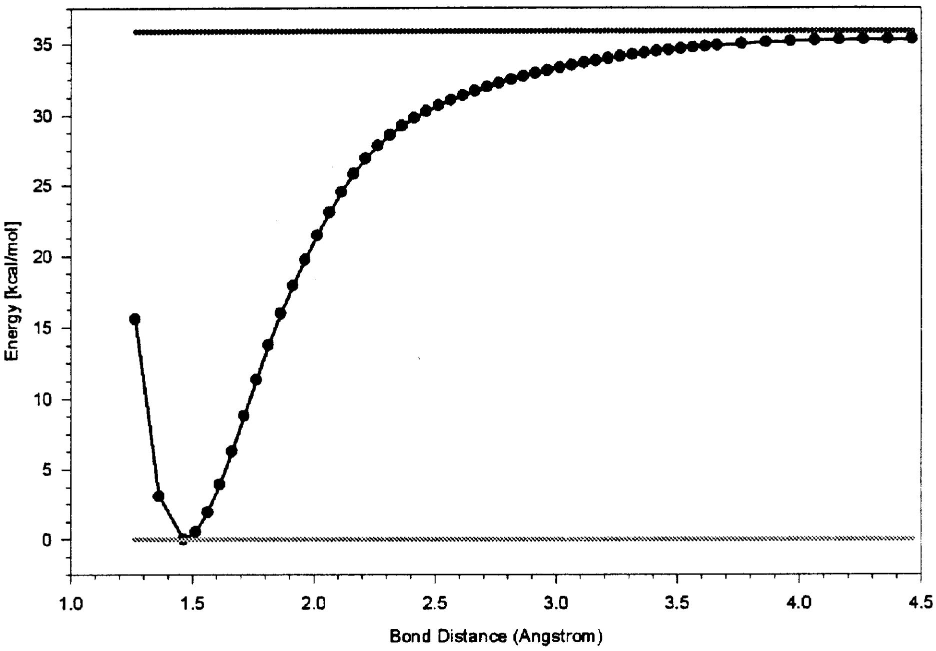


Figure 6.1 Reaction coordinate of the dissociation reaction of $CH_3CH_2OO\bullet$ → C_2H_5 + O_2 as the C-O bond increases.

6.2.3 Kinetic Analysis – Modified Strong Collision and Master Equation

Two approaches are used to calculate the collisional deactivation of the energized adduct: a master equation model and a modified strong collision model. The master equation model (ME) used $<\Delta E>_{down}$ = 830 cal/mole for the collisional deactivation with N_2 as the third body. The modified strong collision model (MSC) of Gilbert, *et al.*[169] was used with $<-\Delta E>_{av}$ = 440 cal/mole for the collisional deactivation with N_2 as the third body. This value is consistent with the $<\Delta E>_{down}$ value used in the master equation analysis.

6.2.4 Calculation of k(T,P)

Kinetic parameters for the bimolecular chemical activation reactions and the subsequent unimolecular thermal dissociation reactions to adducts and product sets are calculated by using a multi-frequency Quantum Rice-Ramsperger-Kassel (QRRK) analysis for *k*(*E*)[60] with the steady state assumption on the energized adduct(s). Both the forward and reverse paths are included for adducts, but product formation is not reversible in the analysis. (Reverse directions of products are incorporated in the subsequent mechanism analysis using CHEMKIN).

The current version of the QRRK computer code utilizes a reduced set of three vibration frequencies which accurately reproduce the molecule (adduct) heat capacity data.[65,170,171] Molecular density-of-state functions are constructed through direct convolution of single frequency density functions on a 10 cm^{-1} grid. The functions corresponding to each reduced frequency is explicitly convolved into a relative density-of-states ($\rho(E)$), which is normalized by the partition function (Q). The inclusion of one external rotation, corresponding to the symmetric top, is incorporated into the calculations by convolving the vibration density function with the proper rotational density function. A detailed description of this and comparisons of the $\rho(E)/Q$ ratios with the direct count $\rho(E)/Q$ ratios are shown to be in good agreement.[65]

6.2.5 Mechanism Construction

To apply the results of the chemical activation and the thermal dissociation analysis for comparison to data, it is necessary to construct an elementary chemical reaction mechanism. This includes all the reactions involved in the chemical activation process, including stabilizations and reactions for thermal dissociation of the stabilized species. Reactions are reversible, and implicitly account for some of the thermal dissociation reactions as the reverse of the forward (chemically-activated) reactions, *e.g.*, $C_2H_5OO\bullet$

dissociation to $C_2H_5 + O_2$ is included as the reverse of $C_2H_5 + O_2 \Leftrightarrow C_2H_5OO\bullet$. Thermal dissociation to products (other than the original reactants $C_2H_5 + O_2$) must be specifically included. Inclusion of other reactions for analysis of the experiments considered in this work, to account for competing processes, such as $HO_2 + HO_2$ … etc are needed. The same reactions used in the experimental analysis are also used in this study.

Since the QRRK rate coefficients are dependent on both temperature and pressure, the conventional approach is to use different sets of rate coefficients at each pressure. An alternative approach is to use Chebyshev polynomials to represent a rate constant expression as a function of both temperature and pressure, as described by Venkatesh, *et al.*[163,164] The temperature-pressure dependent rate coefficients in Chebyshev format for the current system of interest is derived from application of the methodology described by Venkatesh, *et al.* The current mechanism files are derived based on seven temperature functions and three pressure functions to fit the rate coefficients over a 50 x 50 Gauss-Chebyshev grid using a Levenberg-Marquardt algorithm. The current mechanism file is fitted over a temperature range of 250 – 1200 K and a pressure range of 10^{-3} – 100 atm. The CHEMKIN integrator package program[145] has been modified to accept rate coefficients in the Chebyshev format. The idea of having a single CHEMKIN mechanism file capable of determining concentration profiles over a wide temperature and pressure range is appealing; however, the Chebyshev polynomials are still fitted parameters and verification of calculated rate constants should be checked for consistency.

6.3 Results and Discussion

6.3.1 Geometries

Optimized geometric structures for the reactants, transition states, adducts and products are calculated at the B3LYP/6-31G(d,p) level of theory and are listed in Table 6.1. The TS for molecular elimination of ethylene from the ethylperoxy radical (denoted as TS1 in Figure 6.2) has a C-C bond of 1.39Å, considerably shorter than the normal C-C bond length of approximately 1.53Å and slightly longer than the normal C=C bond of 1.34Å. The C-O bond is 2.20Å, approximately 0.8Å longer than the normal C-O bond length. Shortening of the O-O bond to 1.28Å is also observed. The O-H bond length is 1.25Å and the C-H bond is 1.38Å. The spin contamination, <S^2>, is 0.76, which is consistent with the spin for a doublet.

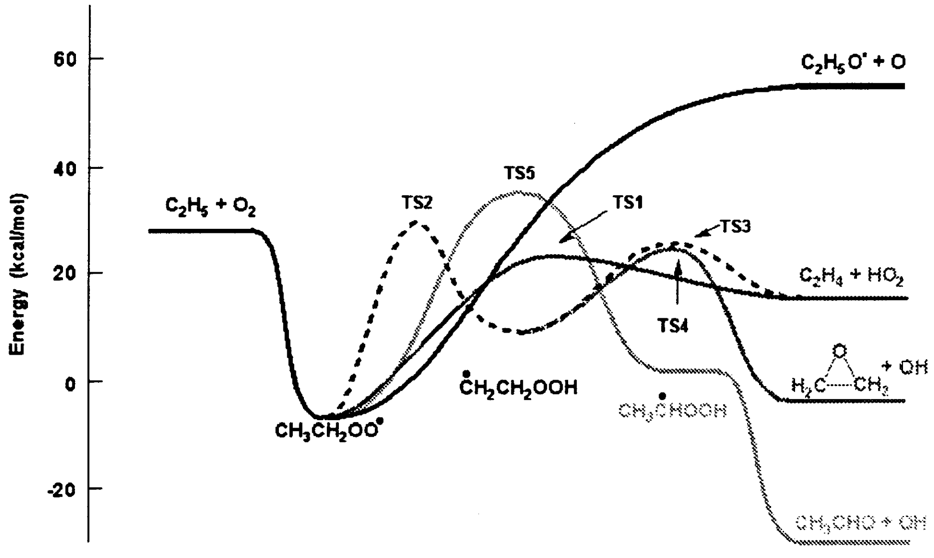
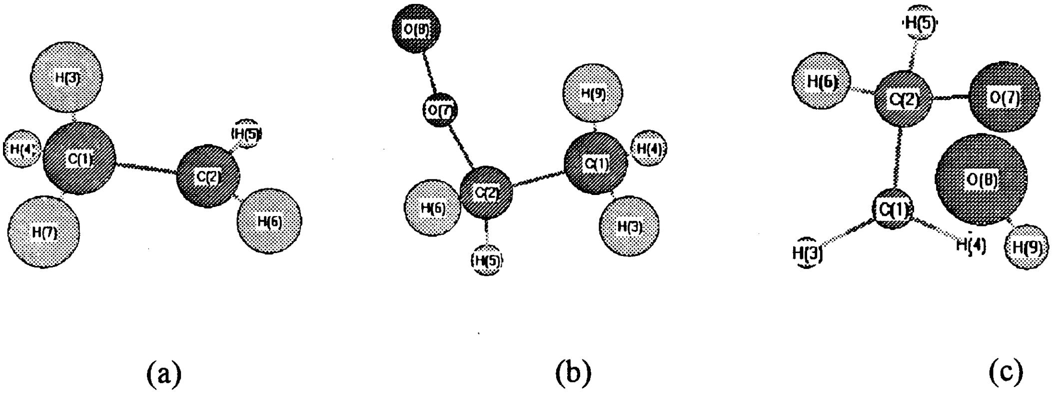


Figure 6.2 Potential Energy Diagram for the $C_2H_5 + O_2$ system calculated at CBS-Q//B3LYP/6-31G(d,p).

Table 6.1 Optimized Geometric Parameters for Species in the Ethyl + O_2 Oxidation System at the B3LYP/6-31G(D,P) Level of Theory

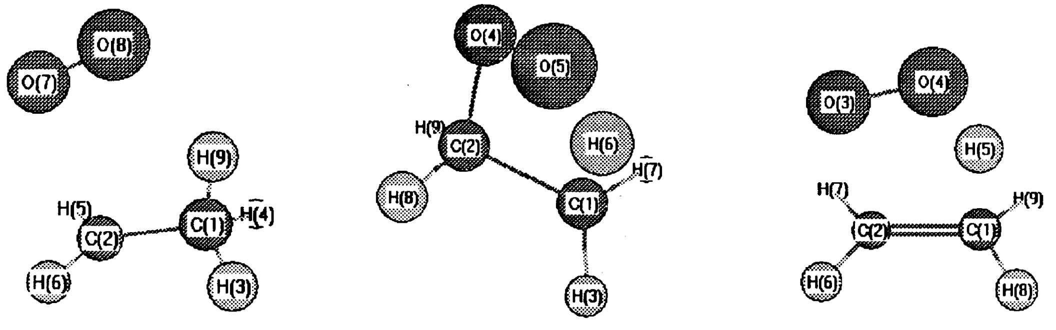


(a) (b) (c)

C_2H_5		$CH_3CH_2OO\bullet$		$\bullet CH_2CH_2OOH$	
Parameter†	Value	Parameter†	Value	Parameter†	Value
r21	1.4886	r21	1.5174	r21	1.4867
r31	1.1041	r31	1.0944	r31	1.0839
r41	1.0959	r41	1.0936	r41	1.0857
r52	1.0848	r52	1.0935	r52	1.1028
r62	1.0848	r62	1.0932	r62	1.0964
r71	1.0959	r72	1.4625	r72	1.4338
a312	112.09	r87	1.3231	r87	1.4545
a412	111.86	r91	1.0926	r98	0.9715
a521	120.93	a312	109.90	a312	121.63
a621	120.92	a412	110.99	a412	119.66
a712	111.86	a521	112.58	a521	111.64
d4123	-119.32	a621	112.35	a621	111.78
d5213	85.12	a721	111.04	a721	113.52
d6213	-84.99	a872	110.97	a872	107.09
d7123	119.31	a912	109.93	a987	100.63
		d4123	-119.96	d4123	-175.60
		d5213	64.40	d5213	107.52
		d6213	-60.12	d6213	-13.42
		d7213	179.93	d7213	-138.25
		d8721	71.18	d8721	70.81
		d9123	119.51	d9872	-100.13

† Parameters: "R" corresponds to atomic distance between respective atoms in Angstroms, "A" parameter is the bond angle in degrees and "D" is the dihedral angle in degrees.

Table 6.1 Optimized Geometric Parameters for Species in the Ethyl + O_2 Oxidation System at the B3LYP/6-31G(D,P) Level of Theory **(Continued)**



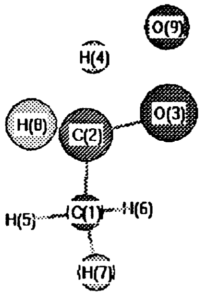
(d) (e) (f)

$T[CC\text{--}OO]^{\neq}$		TS2		TS1	
Parameter†	Value	Parameter†	Value	Parameter†	Value
r21	1.4787	r21	1.5256	r21	1.3849
r31	1.0953	r31	1.0884	r32	2.2040
r41	1.0953	r42	1.4341	r43	1.2778
r52	1.0842	r54	1.4231	r54	1.2480
r62	1.0842	r65	1.1925	r62	1.0843
r87	1.2245	r71	1.0903	r72	1.0843
r91	1.1090	r82	1.0971	r81	1.0888
a312	112.18	r92	1.0958	r91	1.0888
a412	112.18	a312	118.41	a321	96.77
a521	121.29	a421	104.25	a432	98.21
a621	121.30	a542	102.27	a543	98.76
a721	91.25	a654	94.39	a621	121.79
a872	103.41	a712	116.42	a721	121.79
a912	110.85	a821	110.40	a812	118.81
d4123	-122.74	a921	114.77	a912	118.81
d5213	152.12	d4213	-144.62	d4321	-0.03
d6213	-29.18	d5421	45.71	d5432	0.05
d7213	241.42	d6542	-34.12	d6213	94.77
d8721	-0.05	d7123	-142.74	d7213	-94.71
d9123	118.63	d8213	-25.52	d8126	-10.78
r72	2.8625	d9213	99.39	d9126	-159.68

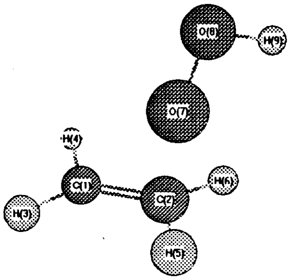
---

† Parameters: "R" corresponds to atomic distance between respective atoms in Angstroms, "A" parameter is the bond angle in degrees and "D" is the dihedral angle in degrees.

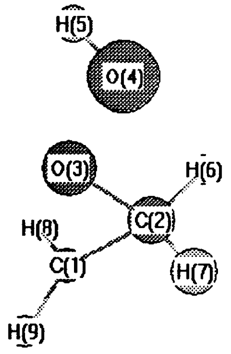
Table 6.1 Optimized Geometric Parameters for Species in the Ethyl + O_2 Oxidation System at the B3LYP/6-31G(D,P) Level of Theory **(Continued)**



(g)



(h)



(i)

TS5		TS3		TS4	
Parameter†	Value	Parameter†	Value	Parameter†	Value
r21	1.500872	r21	1.379152	r21	1.475339
r32	1.3927	r31	1.0848	r32	1.3996
r42	1.3314	r41	1.0848	r43	1.7530
r51	1.0936	r52	1.0857	r54	0.9722
r61	1.0931	r62	1.0859	r62	1.0953
r71	1.0982	r72	1.9080	r72	1.0958
r82	1.0958	r87	1.3932	r81	1.0827
r94	1.2736	r98	0.9744	r91	1.0828
a321	115.81	a312	121.12	a321	82.97
a421	114.14	a412	121.21	a432	107.32
a512	110.98	a521	119.64	a543	93.16
a612	110.51	a621	119.54	a621	115.61
a712	109.91	a721	105.39	a721	116.49
a821	118.67	a872	110.39	a812	120.15
a942	102.70	a987	103.04	a912	120.55
d4213	-96.57	d4123	-171.93	d4321	171.89
d5123	172.50	d5213	-17.13	d5432	-139.04
d6123	50.90	d6213	-169.34	d6213	113.12
d7123	-67.99	d7213	85.01	d7213	-113.59
d8213	140.03	d8721	84.01	d8123	-86.41
d9421	118.80	d9872	82.91	d9123	84.60

---

† Parameters: "R" corresponds to atomic distance between respective atoms in Angstroms, "A" parameter is the bond angle in degrees and "D" is the dihedral angle in degrees.

The TS for isomerization of $C_2H_5OO\bullet$ to $\bullet CH_2CH_2OOH$ is a 5-member ring (denoted as TS2). The oxygen-hydrogen bond length is 1.19Å and the carbon-hydrogen bond is 1.40Å, both slightly longer than the stable O-H bond length, ca. 0.96Å, and the C-H bond length, ca. 1.08Å. The spin contamination is slightly higher than that of TS1 with $<S^2> = 0.81$.

The TS for β-scission of $\bullet CH_2CH_2OOH$ to ethylene + HO_2 (denoted as TS3) shows a C-C bond of 1.38Å and a C-O bond length of 1.91Å. This is also described by Chen and Bozzelli.[71] The TS for the formation of the oxirane + OH products from the hydroperoxy-ethyl adduct (denoted as TS4) has a C-O bond length of 1.40Å and an O-C bond of 1.91Å. The dissociating O-O bond is 1.75Å. Spin contamination for TS3 is 0.78 and for TS4 is 0.81.

The TS for the formation of the acetaldehyde + OH from the $C_2H_5OO\bullet$ adduct via a 4-member ring isomerization on the ipso-carbon (denoted as TS5) shows a C-H bond length 1.33Å and an O-H bond length of 1.27Å. The O-O bond length is 1.50Å, slightly longer than the normal O-O bond length of 1.46Å. Spin contamination for TS5 calculated by B3LYP/6-31G(d,p) is 0.76.

The TS for the $O_2 + C_2H_5 \Leftrightarrow [CC—OO]^\ddagger \Leftrightarrow C_2H_5OO\bullet$ reaction does not exhibit any barrier from the addition reaction, and therefore, one cannot utilize the saddle point requirement for TS calculations. The reaction coordinate for this reaction is determined by incremental increases in the C-O bond distance along the dissociation reaction path, starting with the full geometrically optimized ethylperoxy radical at the B3LYP/6-31G(d,p) level of theory. Calculations are performed over the C-O bond length range of 1.46-4.46 Å in an incremental step size of 0.10Å. Each of the geometric configurations of the "stretched" ethylperoxy radical are fully optimized, with respect to the constraint of the "frozen" C-O bond distance of interest. The spin contamination for the ethyl radical and the $C_2H_5OO\bullet$ radical are 0.75. Spin contamination also begins to deviate from the theoretical spin for a doublet at C-O bond lengths above 2.0Å. The spin contamination at 2.0Å is 0.87, which is slightly higher than the theoretical spin of 0.75 for a doublet. A steady linear increase in the spin contamination value is observed as the C-O bond length is increased from 2.0Å to 3.4Å, *i.e.* for every 0.1Å increase in the C-O bond length, an increase of 0.06 in $<S^2>$ is observed. The spin contamination at 3.4Å is 1.7.

6.3.2 Thermodynamic Properties – ΔH_f^{298}, S^{298} and $C_p(300\text{-}1500K)$

Thermodynamic properties used in the current study are presented in Table 6.2. Entropy and heat capacities are calculated by statistical mechanics, as outlined above. Pitzer-Gwinn's[90] general treatment of hindered internal rotational contributions is used to adjust for entropy and C_p values. (Refer to Table 6.3 for rotational barriers and hindered moments of inertia used in the Pitzer-Gwinn treatment). Entropy and heat capacity for the association TS is also determined from statistical mechanics with scaled frequencies and moments of inertia from each C-O configuration. However, as the C-O bond distance increases, the C-O rotor becomes more of a free-rotor. This difficulty in determining the "changing" contribution is not addressed, but instead the same hindered rotor entropy and C_p contribution used in the stable adduct is utilized in the hindered rotor contribution to S and C_p for the VTST structure species. The hindered rotor

Table 6.2 Thermodynamic Properties of Species in the Ethyl Oxidation System Calculated at CBS-Q//B3LYP/6-31G(d,p)

SPECIES[a]	Hf°_{298}	S°_{298}	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)
C_2H_5	28.6	60.61	12.20	14.64	17.01	19.11	22.62	25.39	29.96
O_2	0	49.01	7.02	7.23	7.44	7.65	8.04	8.35	8.73
$CH_3CH_2OO\bullet$	-6.72	73.82	16.20	19.86	23.34	26.36	31.11	34.63	40.08
TS1	23.76	70.76	17.47	21.62	25.25	28.26	32.82	36.05	40.94
TS2	29.64	68.83	16.38	20.91	24.82	28.01	32.77	36.1	41.04
$\bullet CH_2CH_2OOH$	11.22	81.91	20.25	23.52	26.36	28.72	32.30	35.13	39.67
TS3	27.07	79.06	19.38	22.73	25.55	27.85	31.35	34.11	38.61
TS4	26.51	77.46	19.04	22.52	25.54	28.03	31.86	34.74	39.43
TS5	35.04	73.07	16.99	20.83	24.31	27.26	31.80	35.09	40.03
C_2H_4	12.52	52.47	10.2	12.72	15.02	17	20.14	22.54	26.38
HO_2	3.8	54.73	8.37	8.95	9.48	9.96	10.78	11.43	12.47
Oxirane	-12.57	59.35	11.3	14.74	17.9	20.55	24.57	27.46	
OH	9.49	43.88	7.16	7.08	7.05	7.05	7.15	7.33	7.87
CH_3CHO	-39.18	63.13	13.22	15.71	18.22	20.47	24.22	26.97	

a The notation below the species correlates to the structure shown in Table 6.1.

Table 6.3 Rotational Barriers and Moments of Inertia Parameters Used in the Pitzer-Gwinn Treatment to Determine Hindered Rotor Contribution to Entropy and Cp

Species[a]	Rotational Barrier (kcal/mol)	Moment of Inertia (amu-Å^2)	
CH_3—C•H_2 (1a)	0.16	3.2	1.8
CH_3—CH_2OO•	1.40	3.2	80
CH_3CH_2—OO•	1.26	100	18.5
(1b)			
•CH_2—CH_2OOH	0.16	1.8	100
•CH_2CH_2—OOH	5.40	100	20
•CH_2CH_2O—OH	6.38	100	0.8
(1c)			
[CH_3—yCOOH]$^{\neq}$ (1g)	4.0	3.2	68.7
[CH_2—CH_2OOH]$^{\neq}$	0.16	1.8	100
[CH_2CH_2—OOH]$^{\neq}$	5.40	100	20
[CH_2CH_2O—OH]$^{\neq}$	6.38	100	0.8
(1h)			
T[yCOC—OH]$^{\neq}$ (1i)	6.38	100	0.8

a The notation below the species correlates to the structure shown in Table 6.1 in manuscript; "y" denotes cyclic, e.g. (1g) is a 4-member cyclic COOH, and (1i) is a 3-member cyclic COC.

contribution for both the ethylperoxy adduct and VTST structures at 298K for entropy is 12.09 cal/mol-K and for Cp is 3.28 cal/mol-K.

The enthalpy of formation for reactants, TS, adducts and products are calculated at the CBS-Q//B3LYP/6-31G(d,p) level of theory. The enthalpy of formation for the ethyl radical is well known and generally accepted to be 28.5 ± 0.5 kcal/mol[172] and Marshall recently performed high level *ab initio* calculations at CCSD(T) level of theory and reports 28.8 ± 0.5 kcal/mol.[173] The enthalpy of formation for the ethyl radical used in this study is 28.6 kcal/mol.

6.3.3 Adduct Enthalpy of Formation

Isodesmic reaction analyses are performed on the two adducts in this system, *i.e.* ethylperoxy and the hydroperoxy-ethyl radical, at three different levels of calculation. The composite *ab initio* methods utilized are CBS-Q//B3LYP/6-31G(d,p) and G2 level of calculation. The following illustrates the typical approach utilizing isodesmic reactions to obtain enthalpy of formation values. Two sets of isodesmic reactions are used to determine the enthalpy of formation for the ethylperoxy radical at the CBS-Q//B3LYP/6-31G(d,p) level of theory.

CH_3CH_2OOH	+	CH_3OH	=	CH_3CH_2OH	+	CH_3OOH
-229.8156475		-115.5342428		-154.7628396		-190.5872192
X		-48.0		-56.2		-31.8

$$\Delta E(hartrees) = [(-154.7628396)+(-190.5872192)]-[(-229.8156475)+(-115.5342428)]$$

$$= -0.000168562 hartrees = -0.11\frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{rxn} = -0.11\frac{\text{kcal}}{\text{mol}} = [(-31.8)+(-56.2)]-[(-48)+\text{X}]$$

X = -39.9 kcal/mol

$CH_3CH_2OO\bullet$	+	CH_3OOH	=	$CH_3OO\bullet$	+	CH_3CH_2OOH
-229.182771		-190.5872192		-189.9531084		-229.8156475
Y		-31.8		2.15		-39.9

$$\Delta E(hartrees) = [(-189.9531084) + (-229.8156475)] - [(-229.182771) + (-190.5872192)]$$
$$= 0.001234314 hartrees = 0.77\frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{rxn} = 0.77\frac{\text{kcal}}{\text{mol}} = [(2.15) + (-39.89)] - [(-31.8) + \text{Y}]$$

Y = -6.7 kcal/mol

The ΔH_f^{298} for the ethylperoxy radical, determined by use of isodesmic reactions is -6.7 kcal/mol. This value is in very good agreement with recent publications[25,29,155,156,174] and results in a well depth for ethyl + O_2 to ethylperoxy radical of 35.3 kcal/mole.

The enthalpy results from use of isodesmic reactions are shown in Table 6.4. The enthalpy of formation for the ethylperoxy radical calculated at the CBS-Q//B3LYP/6-31G(d,p) and at G2 level of theory offers similar results, -6.7 and –6.8 kcal/mol, respectively. The calculated value of 11.2 kcal/mol for hydroperoxy-ethyl radical at the CBS-Q//B3LYP/6-31G(d,p) is in agreement with the CBS-q//B3LYP/6-31G(d) value of 11.3 kcal/mol published by Chen and Bozzelli.[71] The same isodesmic reactions at the G2 level of theory results in a value of 10.5 kcal/mol.

Comparison of the two radicals with the different methods of calculation shows that both CBS-Q//B3LYP/6-31G(d,p) and G2 are similar and agree with values reported in the literatures. The difference in energy between G2 and those from literature is less than 0.5 kcal/mol. The CBS-Q analysis is used (as opposed to G2) because of significantly lower spin contamination.

Table 6.4 Enthalpy of Formation for the Two Adducts in This System Determined from Use of Isodesmic Reaction Sets.

Isodesmic Reaction							ΔH_f(kcal/mol)	Method
CH_3CH_2OOH	+	CH_3OH	=	CH_3CH_2OH	+	CH_3OOH	**-39.89**	**CBS-Q//B3LYP/6-31G(d,p)**
CH_3CH_2OOH	+	CH_3OH	=	CH_3CH_2OH	+	CH_3OOH	**-40.06**	**G2**
$CH_3CH_2OO\bullet$	+	CH_3OOH	=	$CH_3OO\bullet$	+	CH_3CH_2OOH	**-6.72**	**CBS-Q//B3LYP/6-31G(d,p)**
$CH_3CH_2OO\bullet$	+	CH_3OOH	=	$CH_3OO\bullet$	+	CH_3CH_2OOH	**-6.77**	**G2**
$\bullet CH_2CH_2OOH$	+	CH_3CH_2OH	=	CH_3CH_2OOH	+	$CH_2\bullet CH_2OH$	**11.22**	**CBS-Q//B3LYP/6-31G(d,p)**
$\bullet CH_2CH_2OOH$	+	CH_3OH	=	CH_3CH_2OOH	+	$C\bullet H_2OH$	**10.49**	**G2**

6.3.4 Reaction Pathways

A reaction path potential energy diagram is illustrated in Figure 6.2 calculated at CBS-Q//B3LYP/6-31G(d,p) level of theory. Addition of the oxygen to ethyl radical forming an energized ethylperoxy adduct.

$C_2H_5 + O_2 \rightarrow CH_3CH_2OO\bullet^*$

There are six possible reactions for this activated adduct

RXN 1)	reverse reaction back to reactants
RXN 2)	stabilization
RXN 3)	direct molecular elimination to $C_2H_4 + HO_2$ (TS1)
RXN 4)	hydrogen shift isomerization to hydroperoxy-ethyl adduct (TS2)
RXN 5)	dissociation of O atom to form an ethoxy radical plus oxygen atom
RXN 6)	H-shift from ipso carbon to form acetaldehyde plus hydroxyl radical (TS5)

RXN 1-3 are important reactions at lower temperature hydrocarbon oxidation. **RXN 4** becomes important after HO_2 addition to ethylene (olefins), reverse direction. **RXN 3** has an activation barrier of 30.5 kcal/mol, about 4.8 kcal/mol below the ground state starting energy of the reactants. This transition state leads directly to $C_2H_4 + HO_2$ products. **RXN 4** has a barrier of 36.3 kcal/mol, or about 1 kcal/mol above the reactants $C_2H_5 + O_2$.

The thermodynamic properties for ethoxy radical in **RXN 5** were estimated from group additivity and use of hydrogen bond increment method.[88,130] The products ethoxy + O are estimated to have an endothermicity of over 25 kcal/mol above the reactants and the rate constants at low temperatures would not be significant compared to the other channels, but it is important at high temperatures.

The sixth possible channel, **RXN 6**, for the fate of the activated ethylperoxy adduct is the formation of an aldehyde. The activated ethylperoxy adduct crosses over TS5, which then undergoes OH elimination to form acetaldehyde. The barrier required is 41.7 kcal/mol or 6.4 kcal/mol above the reactants.

The energized hydroperoxy-ethyl adduct can undergo 4 different reactions: reverse reaction back to ethylperoxy radical, stabilization, β-scission to C_2H_4 + HO_2 products or react through a 3-member ring transition state to form oxirane + hydroxyl. The reverse reaction to ethylperoxy radical through TS2 has a barrier of about 18.5 kcal/mol. The transition state to form C_2H_4 + HO_2 (TS3) is about 0.5 kcal/mol higher than that to form oxirane + OH (TS4), based on CBS-Q//B3LYP/6-31G(d,p) level of theory. Both TS3 and TS4 are below the reactants.

6.3.5 High-pressure Limit Arrhenius Rate Parameters (k_∞)

High-pressure limit kinetic parameters in the form of modified Arrhenius rate parameters are included in Table 6.5 for both forward and reverse reactions. The rate constants are derived from the thermodynamic properties, which consists of enthalpy calculated at the CBS-Q//B3LYP/6-31G(d,p) and entropy and heat capacity values from frequencies and structures at B3LYP/6-31G(d,p) level of theory.

The rate constants for the addition and dissociation reaction for $C_2H_5 + O_2 \Leftrightarrow C_2H_5OO\bullet$ are calculated by VTST at B3LYP/6-31G(d,p) level of theory. The reaction coordinate along the C-O bond length is calculated to determine the respective energies. Refer to Figure 6.1. Rate constants are calculated based on the dissociation path. The addition reaction rate constant is determined by satisfying the detailed balance criteria.

Table 6.5 Reactions and Rate Constants Used to Build the Current Mechanism to Model Ethyl + O_2 Oxidation

	Reaction	**A (cc/mol-s or 1/s)**	**n**	**Ea (cal/mol)**	**comments**
T5-1	$Cl_2 + h\nu \rightarrow Cl + Cl$		Adjust to fit ethane decay		
T5-2	$Cl + C_2H_6 \rightarrow C_2H_5 + HCl$	5.18×10^{13}	0.0	225.	a, e
T5-3	$C_2H_5OO\bullet + C_2H_5OO\bullet \rightarrow CH_3CH_2O\bullet + CH_3CH_2O\bullet + O_2$	3.23×10^{10}	0.0	248.38	c
T5-4	$C_2H_5OO\bullet + C_2H_5OO\bullet \rightarrow CH_3CHO + CH_3CH_2OH + O_2$	1.64×10^{10}	0.0	248.37	c
T5-5	$C_2H_5OO\bullet + HO_2 \rightarrow CH_3CH_2OOH + O_2$	1.62×10^{11}	0.0	-1987.	b
T5-6	$CH_3CH_2OOH \rightarrow CH_3CH_2O\bullet + OH$	2.5×10^{13}	0.0	37700.	b
T5-7	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.87×10^{12}	0.0	1540.	d
T5-8	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	4.68×10^{12}	0.0	2030.	b
T5-9	$CH_3CH_2O\bullet + O_2 \rightarrow CH_3CHO + HO_2$	3.6×10^{10}	0.0	1090.	b
T5-10	$C_2H_5 + O_2 \rightarrow C_2H_5OO\bullet$	2.94×10^{13}	-0.44	0.0	f
T5-11	$C_2H_5OO\bullet \rightarrow C_2H_5 + O_2$	2.46×10^{18}	-1.07	35320.	f
T5-12	$C_2H_5OO\bullet \rightarrow \bullet CH_2CH_2OOH$	7.90×10^{6}	1.79	35820.	f
T5-13	$\bullet CH_2CH_2OOH \rightarrow C_2H_5OO\bullet$	1.17×10^{7}	1.04	17980.	f
T5-14	$C_2H_5OO\bullet \rightarrow CH_3CHO + OH$	1.32×10^{9}	1.37	41590.	f
T5-15	$C_2H_5OO\bullet \rightarrow C_2H_4 + H_2O$	8.80×10^{5}	2.24	29610.	f
T5-16	$C_2H_5OO\bullet \rightarrow CH_3CH_2O\bullet + O\bullet$	2.98×10^{15}	-0.09	61600.	f
T5-17	$\bullet CH_2CH_2OOH \rightarrow C_2H_4 + HO_2$	1.28×10^{11}	0.52	16150.	f
T5-18	$\bullet CH_2CH_2OOH \rightarrow H_2(COC)H_2 + OH$	1.32×10^{10}	0.72	15380.	f

a Pilgrim, J. S., McIlroy, A. and Taatjes, C.A., *J. Phys. Chem. A*, **1997**, 1973-1880

b Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Rossi, M.J., Troe, J., *J. Phys. Chem. Rev. Data*, **1997**, 26, 521

c Wallington, T.J., Dagaut, P., Kurylo, M.J., *Chem. Rev.*, **1992**, 92, 667

d Baulch, D.L.; Cobos, C.J.; Cox, R.A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J.A.; Pilling, M.J.; Troe, J.; Walker, R.W.; Warnatz, J., *J. Phys. Chem. Ref. Data 21*, **1992**, 411-429

e Clifford, E.P., Farrel, J.T., DeSain, J.D. and Taatjes, C.A., *J. Phys. Chem. A*, **2000**, 11549-11560

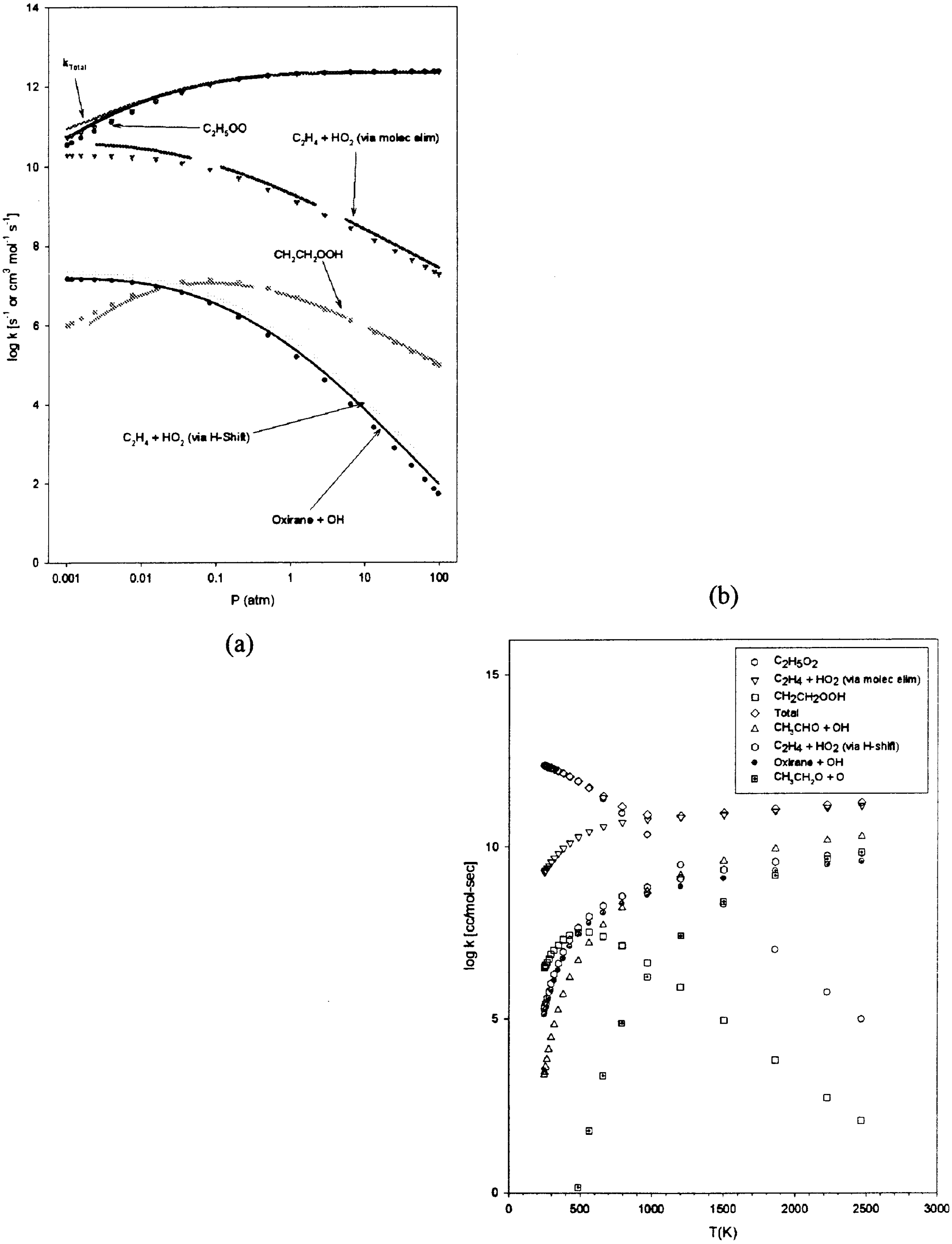
f High pressure limit rate constant determined in current study.

The dissociation reaction rate constant is calculated to be $k_{\infty,diss} = 2.46 \times 10^{18} T^{-1.07} e^{-\frac{35.32 kcal/mol}{RT}}$ and the addition reaction to be $k_{\infty,addn} = 2.94 \times 10^{13} T^{-0.44}$, with no barrier for the addition path.

6.4 Comparison of Modified Strong Collision Assumption Vs. Master Equation Results

6.4.1 Major Channels

Both master equation and modified strong collision treatments of collisional deactivation were employed in this analysis. The predicted effects of pressure (at 297K) are compared in Figure 6.3a. Both treatments give nearly identical results. Stabilization is the dominant reaction over the entire range, even at pressures as low as 0.001 atm. The only other channel of importance at this low temperature is the concerted elimination pathway to produce C_2H_4 + HO_2 **(RXN 3)**. This pathway is predicted to decrease with increased pressure above about 0.01 atm. This decrease in rate coefficient with pressure is due to the increasing importance of collisional stabilization, which results in deactivation of the energized adduct before the concerted elimination can occur.



(a)

(b)

Figure 6.3 Calculated chemical activation rate constants (a) T = 297K : Symbols = MSC results and lines = ME results, (b) P = 0.5 atm (ME).

6.4.2 Minor Channels

For the minor channels, the qualitative behaviour is as expected. Stabilization of the hydroperoxy-ethyl adduct rate goes through a maximum near 0.1 atm. The maximum can be attributed to the fact that the barrier heights of TS3 (formation of C_2H_4 + HO_2) and TS4 (formation of oxirane + hydroxyl radical) are lower than that of TS2 (reverse isomerization to ethylperoxy radical). At low pressures, some of the energized $C_2H_5OO\bullet$ adduct can isomerize to $\bullet CH_2CH_2OOH^*$ prior to stabilization, but the subsequent rate of stabilization of $\bullet CH_2CH_2OOH^*$ in the low-pressure environment is slower than the rate through TS3 and TS4, so the overall rate for stabilization remains low. As pressure increases, stabilization (primarily $C_2H_5OO\bullet$) becomes more important. But continued increases in pressure diminish the isomerization rate, leading to a decrease in the stabilization rate of rate coefficient of C•CCOH. The similar rate coefficients for formation of oxirane and ethylene (via the hydrogen shift) reflect similar barriers and A-factors for these two channels. This conclusion is similar to that of Green[156] and Shen, *et al.*[159] At this low temperature, the reaction to form ethoxy + O is negligible, due to the high endothermicity. A possible conclusion from other modelling studies on the system that a more important path for the $\bullet CH_2CH_2OOH$ formation is HO_2 addition to ethylene.[71]

Figure 6.3b illustrates the results of the master equation predictions for the temperature dependence of the various reaction channels at a fixed pressure of 0.5 atm. The stabilization channel is predicted to dominate at temperatures below approximately 750K. Above this temperature, the concerted elimination becomes the dominant pathway. As temperature is increased, the rate through other channels begins to increase, while the stabilization rate decreases. Formation of acetaldehyde becomes more rapid at higher temperatures, about one order of magnitude slower than the direct molecular elimination channel to form ethylene plus HO_2 at about 2000K. At the higher temperatures, there is sufficient energy for the energized adduct to overcome the high barrier associated with the 4-membered ring TS. The ethoxy radical channel is not important at low temperatures, but rate constant increases rapidly as temperature increases. At 2000K, the rate constant to form ethoxy radical is less than 2 orders of magnitude slower than the direct molecular elimination channel.

Figure 6.4 shows the rate coefficient for stabilization of $C_2H_5OO\bullet$ as a function of both temperature and pressure. A complex temperature-pressure dependence on the stabilization rate constant is apparent. The stabilization rate constant is seen to scale linearly with pressure at temperature greater than 1200 K.

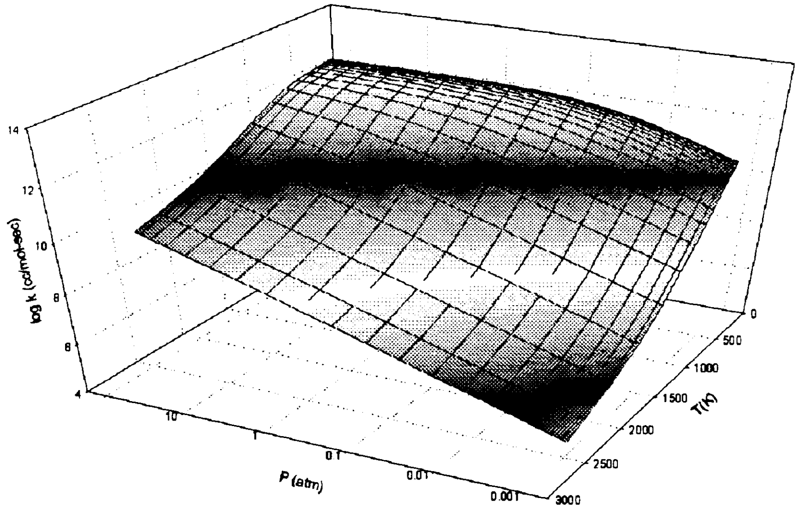


Figure 6.4 Surface plot of stabilization rate constant for $CH_3CH_2OO\bullet$ as function of temperature and pressure calculated by QRRK with modified strong collision

The rate constant for formation of ethylene + HO_2 via molecular elimination is shown in Figure 6.5. Note the predicted lack of pressure dependence at high temperature, above 1500K. Two channels are competing here: dissociation back to $C_2H_5 + O_2$ and molecular elimination to $C_2H_4 + HO_2$. Collisional stabilization is unimportant even at 100 atm. The predicted rate constants at low temperatures exhibit a negative pressure dependence, consistent with many experimental studies. Kaiser observed a less pronounced pressure dependence on C_2H_4 formation at higher temperatures, with stronger pressure dependence at lower temperatures,[147] similar to the predictions.

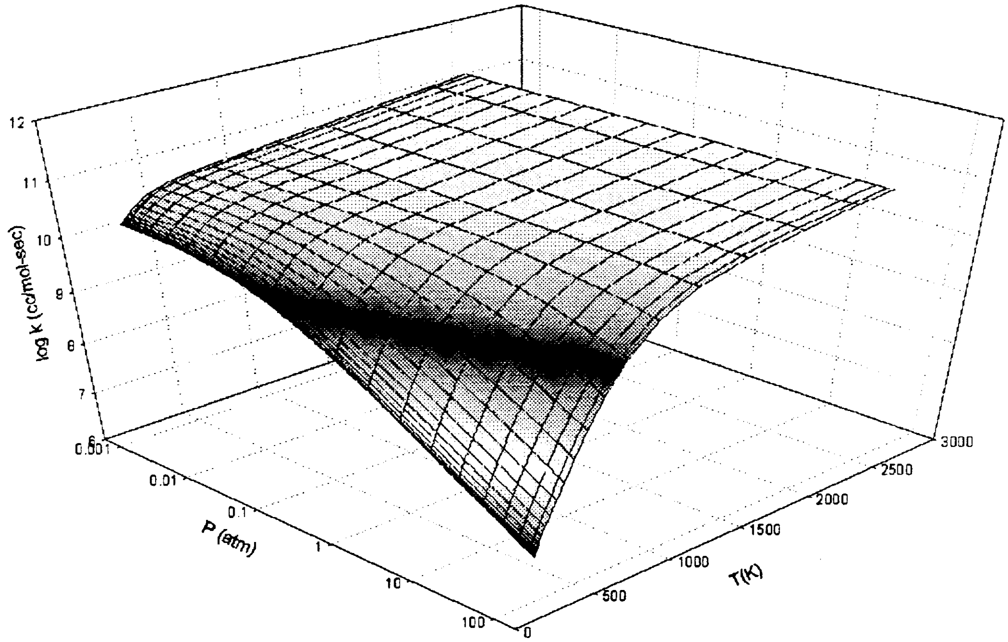


Figure 6.5 Surface plot of direct molecular elimination rate constant for $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ as function of temperature and pressure calculated by QRRK with modified strong collision.

6.4.3 Comparison to Experimental Results

As indicated earlier, it is necessary to combine the chemical activation with thermal activation reactions that account for the subsequent thermal dissociation of the stabilized adducts. It is also necessary to include reactions of important products that control or limit reverse processes. In Table 6.5, Reactions **T5-1** to **T5-9** are included in the mechanism to account for secondary reactions. These same reactions were used in the earlier experimental analysis by Kaiser and by Clifford, *et al.* The pressure-dependent reactions included in the mechanism are calculated in this work. These rate coefficients are listed in the Chebyshev form. For comparison to the data, two mechanisms are used: master equation and modified strong collision. Both included reactions **T5-1** to **T5-9**, with one using the master equation predictions and the other the modified strong collision predictions. All comparisons with experimental data are done using the Chebyshev form of the rate constants, unless explicitly stated that the "conventional" form is also used.

6.4.4 Ethylene Yield

Comparison of the two different collisional models, *i.e.* modified strong collision and master equation, with Kaiser's experimental UV reactor data[147] at 298 K are shown in Figure 6.6.[147] The two mechanisms are used in the CHEMKIN integrator package to determine the ethylene concentration.[145] Figure 6.6 shows the comparison of the two predictions to Kaiser's experimental data for the effect of pressure on the ethylene yield. The error bars on Kaiser's data are based on secondary consumption corrections that Kaiser estimated to be < 12%. Both models show reasonable agreement with Kaiser's experimental data, and properly capture the dramatic drop in yield with increasing pressure. At the higher pressures, the dominant product is formation of the stabilized $C_2H_5OO\bullet$ adduct (*cf.* Figure 3a) which does not dissociate at 298K.

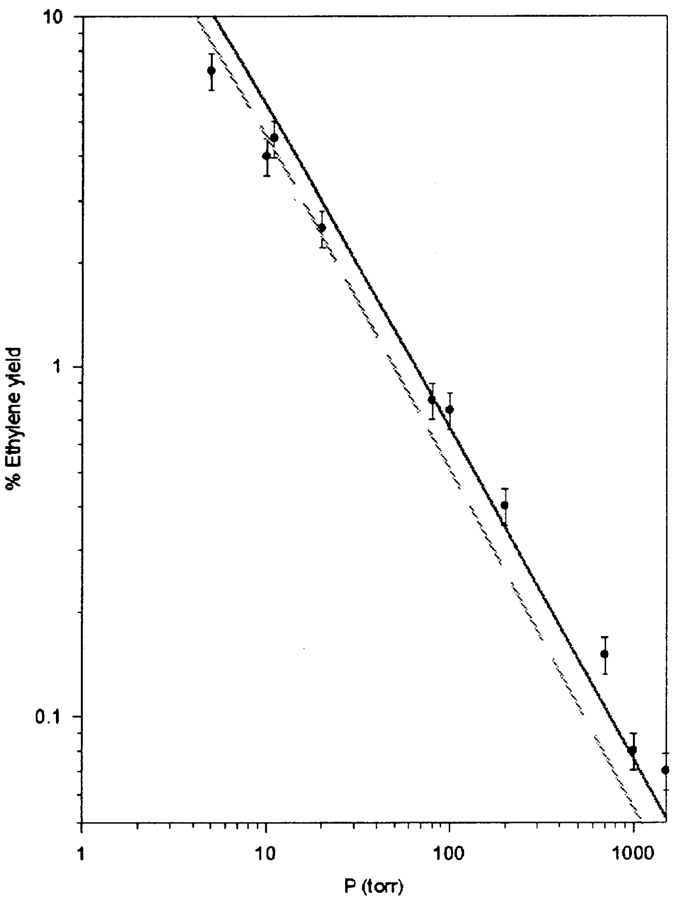
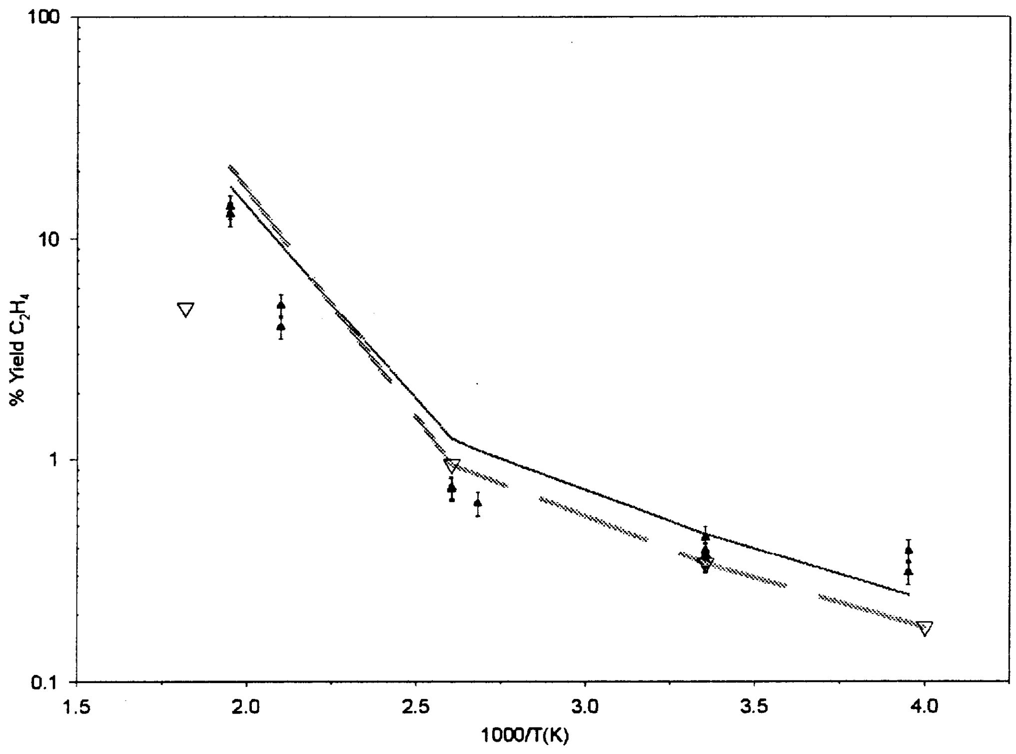


Figure 6.6 Comparison of the pressure effect on C_2H_4 yield at 298 K. Data from Kaiser. ME = Solid line; MSC = Dashed line.

Comparisons of the predicted and observed temperature dependence of the ethylene yield, at a constant density of 4.8 x 10^{18} molecules/cm^3, are shown in Figure 6.7. Both methods produce reasonable agreement with the experimental data, especially the increase in temperature dependence at higher temperatures. The results for the MSC model are calculated based on the "conventional" CHEMKIN mechanism file format, *viz.*

the non-Chebyshev polynomial formalism. The results for the ME model presented in Figure 6.7 are calculated based on the Chebyshev polynomial formalism for the CHEMKIN mechanism.

At low temperatures, it is possible to compute the ethylene yield directly by taking the ratio of the sum of the predicted rate coefficients for "direct", *i.e.* chemically-activated, ethylene production to the total predicted "direct" rate coefficient. The temperature is sufficiently low that any contribution from dissociation of the stabilized adduct is insignificant. However, as the temperature is increased and the thermal dissociation rate coefficient increases, it is necessary to include the effects of thermal dissociation of the adduct. The growing importance of the dissociation pathway can be seen in Figure 6.7 by the difference between the "direct" ethylene yield, based on the MSC model, and the predictions using the mechanism. Below 400K, results from the "direct" and CHEMKIN produce identical results, but at higher temperatures the "direct" ethylene yield is less than the numerical integration results, as the dissociation reactions become important. There are two important dissociation channel of $C_2H_5OO\bullet$, C_2H_4 + HO_2 and $C_2H_5 + O_2$, both need to be considered.



Fiugre 6.7 Comparison of Kaiser's data at a constant molecular density of 4.8 x 10^{18} molecule/cc with ME and MSC models. Circle = Kaiser; Dash line = MSC; Solid line = ME. Inverted triangles show the predicted yield from only the "direct" chemical activation pathway using the MSC model.

6.4.5 HO_2 Yield

Experimental data on HO_2 production from Clifford, *et al.*[148], using laser photolysis, are also compared with the current ME and MSC models. The experiments were carried out from 298 – 700K at a constant molecular density of 1.1 x 10^{18} cm^{-3}. Clifford, *et al.* present two types of HO_2 concentration yield: total and prompt HO_2 yield. An accurate account of the HO_2 yield has to take into consideration not only the formation of HO_2, but also the amount of HO_2 that is consumed in other reactions, *i.e.* the HO_2 self reaction and reaction with the ethylperoxy radical. Figure 6.8 illustrates an example of the HO_2 concentration profile from CHEMKIN using the MSC mechanism expressed in the "conventional" CHEMKIN mechanism format; CHEMKIN results using the ME mechanism are similar and omitted for clarity.

Predicted HO_2 concentrations, represented by the black circles in Figure 6.8, show a rapid rise in HO_2 followed by a slower decay before reaching steady state. The shape of this curve is similar to the actual experimental time-resolved infrared FM signal for HO_2 reported by Clifford, *et al.* Correction of this data for the HO_2 self reaction, (achieved by omitting reaction **T5-7**) which Clifford, *et al.* term "raw" HO_2, shows slightly higher initial HO_2 formation followed by a slow increase, also consistent with Clifford, *et al.*'s interpretation. Further correction for the ethylperoxy radical reaction with HO_2 (omitting reaction **T5-5**) shows an even higher HO_2 formation. This upper curve represents the expected evolution of HO_2 with time, under conditions where there are no HO_2 destruction reactions. Note there is a "prompt" production of HO_2 at very early time, representing formation directly from the initially formed *energized* ethylperoxy radical. This is followed by a much slower rise, and this can be attributed to the slower production of HO_2 from the *stabilized* ethylperoxy radical. Clifford, *et al.* accounted for the secondary reactions of HO_2 by comparing their observed HO_2 production to that obtained using $\bullet CH_2OH$ from methanol as a reactant, since the HO_2 yield from $\bullet CH_2OH$ is expected to be unity. Calculations from this study to determine the HO_2 yields is obtained in a similar manner.

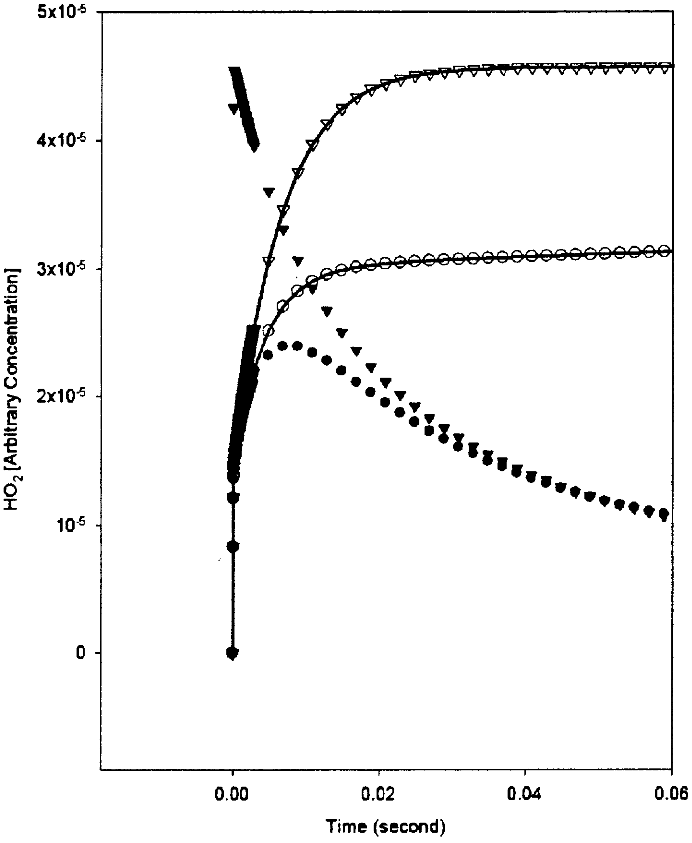


Figure 6.8 Transient HO_2 concentration profile calculated by CHEMKIN. Upside-down triangle = $CH_3OH/Cl_2/O_2$ reference reaction set. Solid circle = total HO_2 concentration with the complete mechanism. Line with circle = $HO_2 + HO_2$ reaction omitted. Line with upside-down triangle = $HO_2 + HO_2$ and $HO_2 + CH_3CH_2OO$● reactions omitted.

A comparison of the "prompt" HO_2 yield between Clifford, *et al.*'s experimental data, at a constant total molecular density of 1.1 x 10^{18} molecule-cm^{-3}, and the numerical integration results from the ME and MSC mechanisms is shown in Figure 6.9. The results using both master equation and modified strong collision treatments are similar and slightly lower than observed.

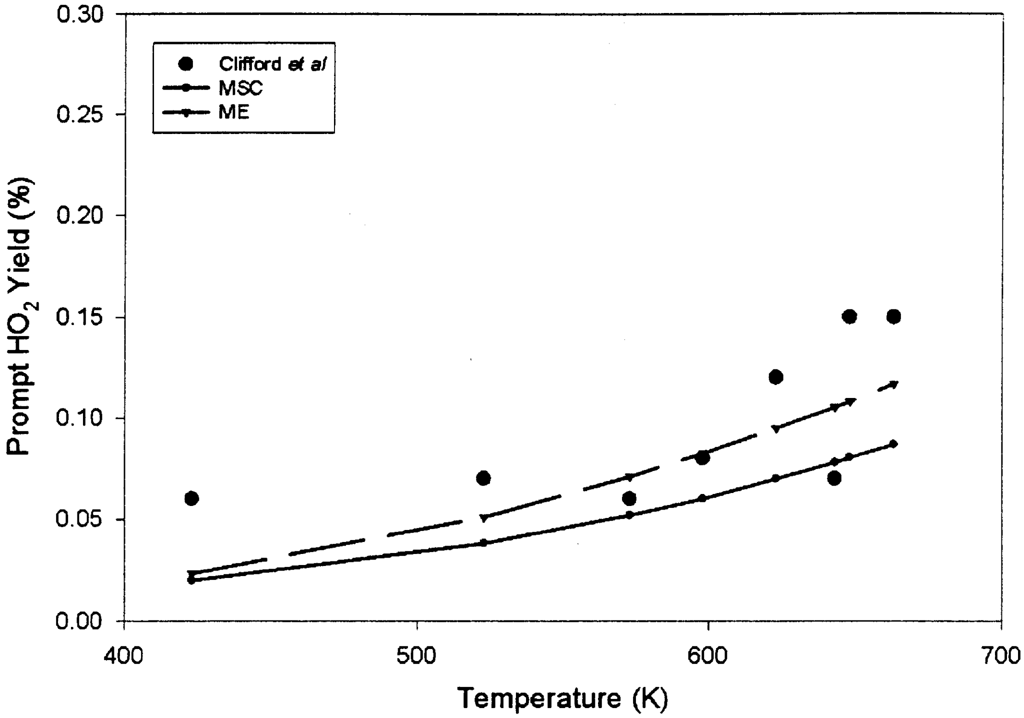


Figure 6.9 Comparison of formation of "prompt" HO_2 between Clifford, *et al.*'s experimental data and predictions using the mechanisms.

Figure 6.10 compares the predicted "total" HO_2 yield as a function of temperature to that measured by Clifford, *et al.* The results from both the ME and MSC are similar and agree very well with the observations of Clifford, *et al.* Particularly encouraging is the correct prediction of the observed rapid increase near 600K. At the higher temperatures, only a small fraction of the total HO_2 is predicted to come directly for the energized adduct; the dominant pathway is dissociation of the initially stabilized adduct. Failure to account for this dissociation in the mechanism would lead to a substantial error.

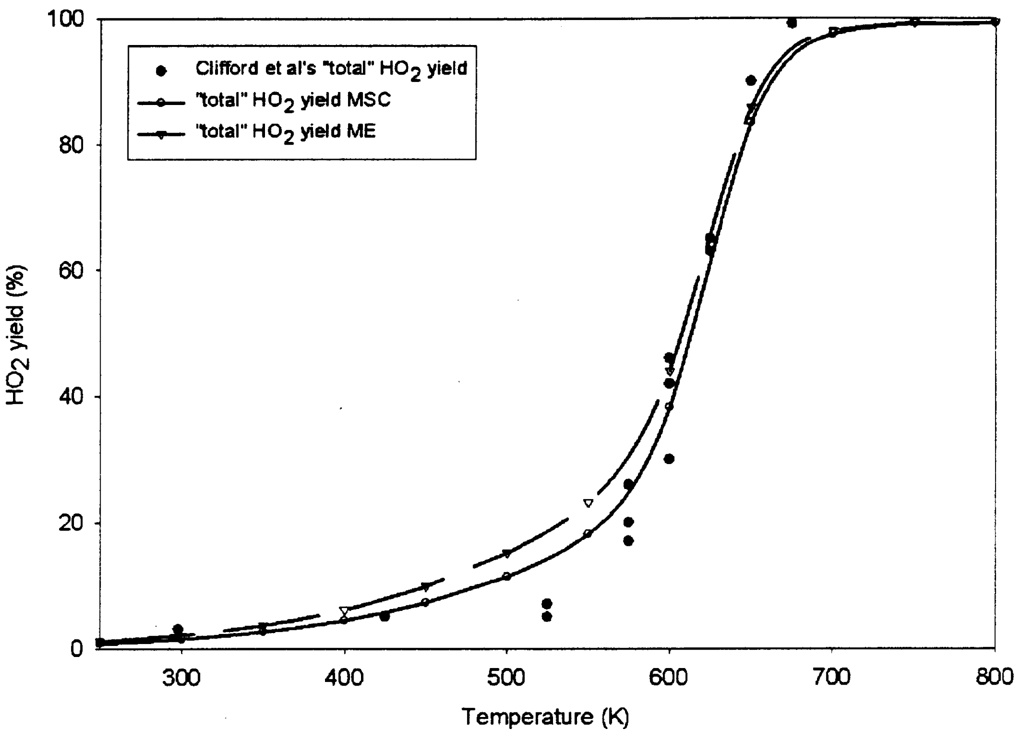


Figure 6.10 Comparison of master equation and modified strong collision model predictions with data for "total" HO_2 formation.

6.5 Kinetic Implications for Low Temperature Ignition

The conventional approach to describe low-temperature ignition kinetics, especially the region of negative temperature coefficient, considers the following reactions[175]:

R• + O_2 ⇆ ROO•	(KIN1)
ROO• + RH → ROOH + R•	(KIN2)
ROOH → RO• + •OH (Branching)	(KIN3)
ROO• → R'•COOH	(KIN4)
R•OOH → yRO + •OH	(KIN5)
R'•COOH + O_2 → (Branching)	(KIN6)

(R• is an alkyl radical, RO• is an alkoxy radical and yRO is generally a cyclic ether. R•OOH is often written as QOOH, but for clarity the R•COOH notation is used to emphasize the free radical character of this species.) If the temperature is sufficiently low that the equilibrium in **KIN1** is shifted to the right, the subsequent reactions of RO_2

can lead to the chain-branching (**KIN3** and **KIN6**) needed for ignition. However, as the temperature rises, the equilibrium in **KIN1** shifts to the left, reducing the RO_2 concentration and thus slowing down the overall rate, *i.e.*, producing a negative temperature coefficient of reaction rate. Particularly noteworthy in this mechanism is the importance of the isomerization reaction (**KIN4**); without this, chain branching via **KIN6** cannot occur. In ethane oxidation, the *newly-identified* direct pathway for production of ethylene and HO_2 from ethylperoxy is much faster than **KIN4**. This competing fast reaction necessarily reduces the amount of R'•COOH that can be produced via **KIN4**. (One specific illustration is shown in Figure 3b, where $\bullet CH_2CH_2OOH$ is approximately three orders of magnitude lower than $C_2H_5OO\bullet$.) Thus the amount of chain branching via **KIN6** will be substantially reduced. Although more complex fuels might well have lower barriers to isomerization [by having the internal hydrogen transfer proceed through a less strained ring (6- or 7- vs. 5-member) or by abstracting secondary or tertiary hydrogens rather than the primary hydrogens in ethyl], the possibility of concerted elimination of HO_2 from RO_2 in these fuels will generally result in formation of less R•COOH this will reduce the overall branching rates. Thus there is a need to revisit these systems to see if new branching pathways are needed to accurately describe low-temperature ignition.

6.6 Conclusions

Thermodynamic properties for the reaction system of ethyl radical plus molecular oxygen have been calculated by the *ab initio* composite method, G2 and CBS-Q//B3LYP/6-31G(d,p). The enthalpies calculated by CBS-Q//B3LYP/6-31G(d,p) shows that the molecular elimination transition state is lower than the reactants by 4.8 kcal/mol, and that the hydrogen shift transition state is higher than the reactants by about 1 kcal/mol. The association and dissociation reaction rate constants are determined by VTST and detailed balance criteria. The other high-pressure rate constants are determined from canonical transition state theory. This reaction system was analyzed in terms of both the initial product distribution resulting from the reactions of the *energized* $C_2H_5OO\bullet$ adduct and the subsequent thermal dissociation of the *stabilized* $C_2H_5OO\bullet$ adduct. This analysis was performed by using a QRRK formalism for *k(E)* coupled with either a modified strong collision model (MSC) or a master equation model (ME) to account for collisional deactivation. These models used unadjusted input parameters based exclusively on electronic structure calculations with adduct enthalpies from isodesmic working reactions. Comparison of predictions from these models to experimental observations for both ethylene and HO_2 yields were generally very satisfactory, with little differences in the MSC and ME predictions.

The utility of a Chebyshev formalism to represent both the temperature and pressure dependence of the rate coefficients for use within a CHEMKIN mechanism was demonstrated. The Chebyshev polynomial mechanism is a promising method to model complex pressure dependent systems.

CHAPTER 7

THERMOCHEMISTRY, REACTION PATHS AND KINETICS ON THE HYDROPEROXY-ETHYL RADICAL REACTION WITH O_2: NEW CHAIN BRANCHING REACTIONS IN HYDROCARBON OXIDATION

7.1 Introduction

The conventional approach to describe low-temperature ignition kinetics, especially in the negative temperature coefficient regime, considers the following reactions of peroxy species[175]:

$R\bullet + O_2 = ROO\bullet$ **(R1)**
$ROO\bullet + RH \rightarrow ROOH + R\bullet$ **(R2)**
$ROOH \rightarrow RO\bullet + \bullet OH$ Branching ($E_a \sim$ Bond Energy, ~ 44 kcal/mol) **(R3)**
$ROO\bullet \rightarrow R'\bullet CH_2OOH$ **(R4)**
$R'\bullet CH_2OOH \rightarrow Cy\text{-}R'CO + OH$ **(R5)**
$R'\bullet CH_2OOH + O_2 \rightarrow R'OO\bullet CH_2OOH \rightarrow R'(OOH)CH(=O) + OH$ **(R6a)**
$R'(OOH)CH(=O) \rightarrow R'(O\bullet)CH(=O) + OH$ Branching $E_a \sim 44$ kcal/mol **(R6b)**

$R\bullet$ is an alkyl radical, $RO\bullet$ is an alkoxy radical and Cy-R'CO is a cyclic ether. $R'\bullet CH_2OOH$ is often written as QOOH; for the purpose of clarity the $R'\bullet CH_2OOH$ notation is used to emphasize the free radical character of this species. Reaction **(R4)** is written slightly differently than Walker,[175] to distinguish radical formation on the carbon bonded to peroxide versus other carbons; the radical formed is not on the peroxide carbon. If the temperature is sufficiently low that the equilibrium in **(R1)** is shifted to the right, the subsequent reactions of $ROO\bullet$ can lead to the chain branching needed to model ignition and cool flames **(R3** and **R6)**. However, as the temperature rises, the equilibrium in **(R1)** shifts to the left, reducing the $ROO\bullet$ concentration and $R\bullet$ conversion. This slows the overall oxidation rate, and produces a negative temperature coefficient for conversion of alkanes. The isomerization in reaction **(R4)** is important because it is needed for chain branching. The alkyl radical which is formed reacts further with O_2 (**R6a and R6b** above exemplified for ethyl in this study).

$\bullet CH_2CH_2OOH + O_2 \Rightarrow [\bullet OOCH_2CH_2OOH]^*$ (R7)
$[HOOCH_2CH_2OO\bullet]^* \Rightarrow [HOOCH_2CH_2OO\bullet]$ (stabilization) (R8)
$[HOOCH_2CH_2OO\bullet] \Rightarrow [HOOCH_2C\bullet HOOH]^* \Rightarrow HOOCH_2CH(=O) + OH$ (R9)
$HOOCH_2CH(=O) \Rightarrow \bullet OCH_2CH(=O) + OH$ (Branching) **(R10)**

One should note that $\bullet CH_2OOH$ and $RC\bullet H_2OOH$ rapidly dissociate to $CH_2=O$ + OH (and $RCH_2=O$ +OH) with no barrier; because the carbonyl bond formed is so much stronger (*ca* 80 kcal/mol) than the peroxide (RO—OH, *ca* 45 kcal/mol) bond cleaved.

In this study the composite CBS-Q and G3(MP2) calculations to estimate enthalpies of the adduct and transition states in the hydroperoxy-ethyl + O_2 reaction system are used. Two reaction paths, which have lower energies than the (entrance channel) are found: a direct elimination to HO_2 plus $H_2C=CHOOH$ and a 1,4 hydrogen shift (5-member ring) transition state structure to $(HOOCH_2C\bullet HOOH)^*$, which immediately dissociates to $HOOCH_2CH(=O)$ + OH. The direct HO_2 elimination is a new reaction path not previously considered in this di-peroxy system; the vinyl-hydroperoxide formed ($H_2C=CHOOH$) dissociates rapidly with an E_a of about 22.5 kcal/mol, leading to low energy chain branching channel. The hydrogen shift and direct HO_2 elimination path are found to have similar kinetics. Relative to the 5 member ring H-shift in the ethyl-peroxy radical, the hydrogen shift is found to have a more important role in this hydroperoxide-peroxy system, because the peroxy oxygen is abstracting from a weak C—H bond on R—CH_2OOH. The H-shift path also results in some chain branching because the $HOOCH_2CH(=O)$ formed is chemically activated and a fraction dissociates to OH + formyl-methoxy radical, before stabilization.

A third path to chain branching is also apparent: chemical activation association of the hydroperoxy-ethyl + O_2, which has 35 kcal/mol of energy relative to the stabilized adduct, results in a diradical •OCH_2CH_2OO• + OH from hydroperoxide O—O bond cleavage. This is about 9 kcal/mol above entrance channel, but has a loose transition state structure.

7.2 Calculation Methods

7.2.1 Thermodynamic Properties

Molecular properties for reactants, adducts, transition states (TS) and products are estimated by the composite CBS-Q[165] and by G3(MP2)[176] methods using Gaussian94.[55] The hybrid DFT method B3LYP, with a double zeta polarized basis set, 6-31G(d,p), is used to determine the optimized geometry for CBS-Q calculations,[129,166] denoted as CBS-Q//B3LYP/6-31G(d,p), and MP2(full)/6-31G(d) is used for G3(MP2). The DFT calculations are spin-unrestricted Hartree-Fock. Molecular geometries are fully optimized using the Berny algorithm and redundant internal coordinates.[55] Confirmation of TS structures is verified by checking for a single imaginary frequency and its motion, plus evaluation of the optimized TS structures. The spin contamination for all three saddle point TS's is 0.76, in the B3LYP/6-31G(d,p) calculations, in reasonably close agreement with the theoretical spin value of 0.75.

Statistical mechanics is employed to determine the vibration, external rotational and translational contributions to entropy and Cp(T). Molecular parameters required in the statistical mechanics analysis are calculated at the B3LYP/6-31G(d,p) level of theory for the optimized geometric structure of the species. Zero-point vibration energy

(ZPVE), vibration frequency and thermal contributions to enthalpy from harmonic frequencies are scaled in accordance to the factors recommended by Scott and Radom.[62] Contributions from optical isomers and unpaired electrons are included in the S^{298} calculations accordingly. The active carbon site has chiral characteristics, in addition to presence of optical isomers from the hydroperoxy group. The hydroperoxy being formed in the ring (TS) does not contribute to a second optical isomer, since it is part of the chiral characteristic. Contributions of internal rotation to S^{298} and Cp(T) are incorporated based on the Pitzer-Gwinn formalism.[90]

7.2.2 Determination of Rate Constants

The high-pressure limit rate constants are determined by application of macrocanonical transition state theory for temperatures from 250 – 2500 K. The rate constants are fitted by a nonlinear least-squares method to the form of a modified Arrhenius rate expression, $k_{\infty,forw} = A_{\infty}T^{n}e^{-\frac{E_a}{RT}}$, to obtain the parameters: A_{∞}, n and E_a. The reported rate constants are derived from the enthalpy of formation calculated at the CBS-Q//B3LYP/6-31G(d,p) level of theory and entropy and heat capacity values at B3LYP/6-31G(d,p) level of theory. The CBS-Q analysis is used, as opposed to G3(MP2), because of significantly lower spin contamination in several species. The rate constant for the $\bullet CH_2CH_2OOH + O_2 \Leftrightarrow HOOCH_2CH_2OO\bullet$ reaction is estimated based on the variational transition state theory for ethyl + O_2.[177] The dissociation (reverse rate constant) is based on microscopic reversibility. The rate constant for

$$HOOCH_2CH_2OO\bullet \Leftrightarrow OH + \bullet OCH_2CH_2OO\bullet \qquad \textbf{(R11)}$$

is estimated from ΔH_{rxn} and literature values for the A factor of O—O bond cleavage in hydroperoxides.[178]

This overall $\bullet CH_2CH_2OOH + O_2 \Leftrightarrow HOOCH_2CH_2OO\bullet$ reaction process is complex, involving several competitive reactions of the energized and stabilized adduct: which has 4 forward paths plus a reverse reaction with a loose transition state, all at competitive energies. In addition stabilization and one higher energy isomerization with a tight transition state are present. A weak (*ca* 1 kcal/mol well) hydrogen bonding conformer of the adduct is also present.

Kinetic parameters describing product formation from the bimolecular chemical activation association process and the unimolecular thermal dissociations are estimated using a multi-frequency quantum Rice-Ramsperger-Kassel (QRRK) analysis for $k(E)$[60,179-181] with the steady state assumption on the energized adduct and master equation analysis[116,182,183] for fall-off. Chang, *et al.*[60,63] described a modified QRRK analysis that is used in this paper.

7.3 Results and Discussion

7.3.1 Structures

Table 7.1 lists the optimized structure parameters from the B3LYP/6-31G(d,p) level of theory. Figure 7.1 shows an overall energy diagram of the reaction paths. The lowest energy conformer – a cyclic hydrogen bonded intermediate is 0.85 and 1.02 kcal/mol lower in energy than the more linear alkyl like structure calculated at B3LYP/6-31G(d,p) and UHF/6-31G(d), respectively.

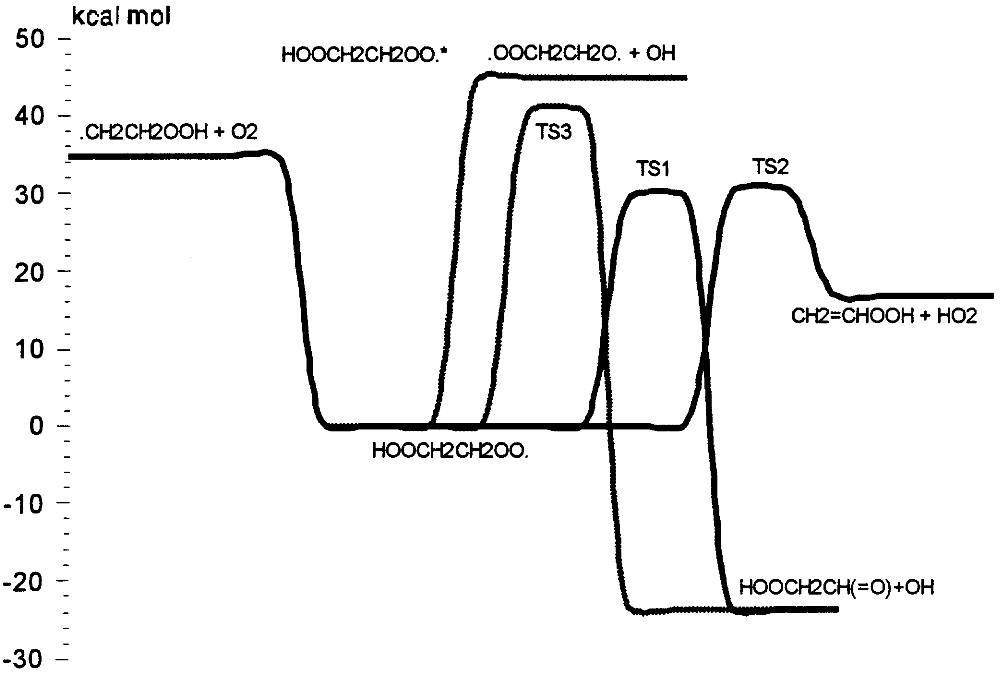
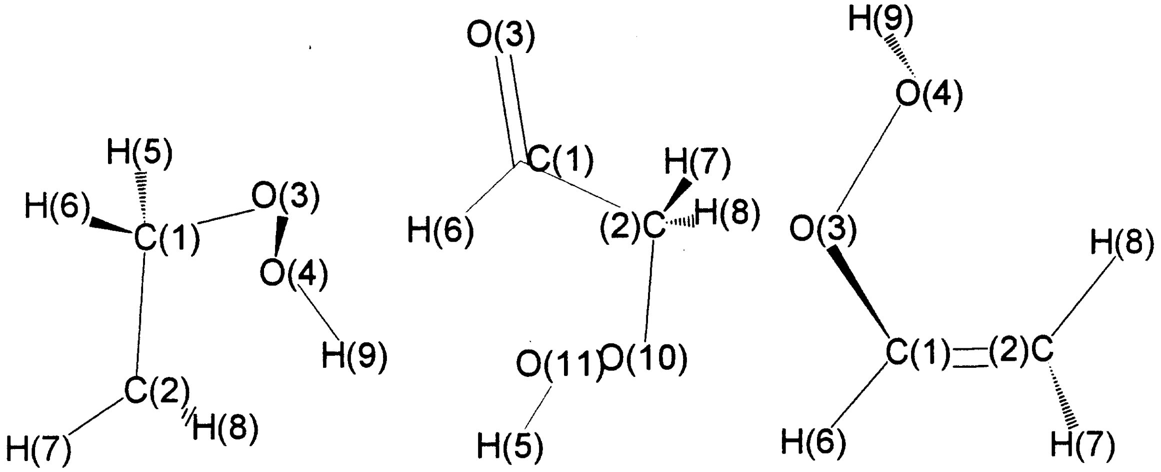


Figure 7.1 Potential Energy Diagram for the •CH_2CH_2OOH + O_2 system calculated at B3LYP/6-31G(d,p).

7.3.2 Hydrogen Shift Isomerization (5 member ring) - TS1

The TS for the hydrogen shift of $HOOCH_2CH_2OO$• to $HOOCH_2CH(=O)$ + OH, via a 5-member ring, (TS1) forms an unstable $HOOCH_2C$•HOOH, which rapidly dissociates (elimination of OH) to form the hydroperoxy-acetaldehyde + OH product. This second reaction (after the H-shift) is similar to the instability in the hypochlorite-methyl radical, where •CH_2O—Cl dissociation to lower energy products CH_2O + Cl exhibits no barrier.[184] The structure of TS1 infers the start of the second reaction step, elimination of OH from the hydroperoxy on the β-carbon, since the C—O bond length is 1.37Å, which is slightly shorter than the normal C—O bond length of 1.46Å.[185] This suggests that TS1 continues through an unstable dihydroperoxy-ethyl radical structure, which quickly

Table 7.1 Optimized Geometric Parameters for Species in the Hydroperoxy-Ethyl + O_2 Oxidation System at the B3LYP/6-31G(d,p) Level of Theory

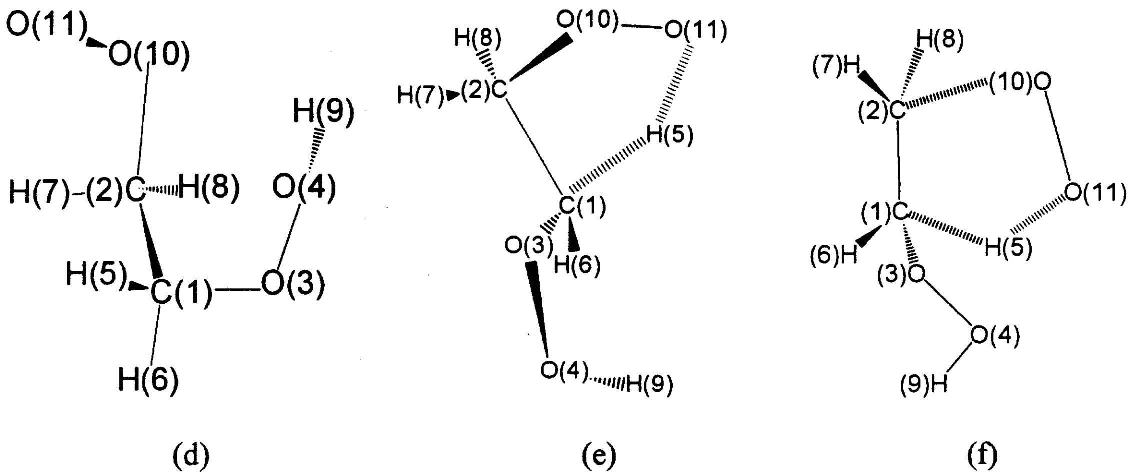


(a) (b) (c)

•CH_2CH_2OOH		$HOOCH_2CH(=O)$		$H_2C=CHOOH$	
Parameter†	Value	Parameter†	Value	Parameter†	Value
r21	1.4867	r21	1.5225	r21	1.3294
r31	1.4338	r31	1.2083	r31	1.3715
r51	1.1028	r61	1.1126	r61	1.0873
r61	1.0964	r72	1.0971	r72	1.0825
r72	1.0839	r82	1.0981	r82	1.0810
r82	1.0857	r102	1.4116	r43	1.4477
r43	1.4545	r1110	1.4669	r94	0.9725
r94	0.9715	r511	0.9708	a431	110.61
a431	107.08	a721	110.17	a721	118.94
a721	121.63	a821	109.09	a821	122.06
a821	119.65	a1021	112.47	a312	128.85
a312	113.51	a312	123.20	a612	124.20
a512	111.64	a612	114.24	a943	99.97
a612	111.78	a11102	104.30	d9431	105.50
a943	100.62	a51110	99.07	d4312	-2.24
d9431	-100.13	d111021	-68.62	d6123	179.93
d4312	70.81	d511102	145.97	d7213	-179.85
d8217	-175.59	d82110	115.43	d8213	1.20
d3127	-138.25	d72110	-125.68		
d5127	107.51	d31210	-193.36		
d6127	-13.42	d61210	-15.04		

† Parameters: "r" corresponds to atomic distance between respective atoms in Angstroms, "a" parameter is the bond angle in degrees and "d" is the dihedral angle in degrees.

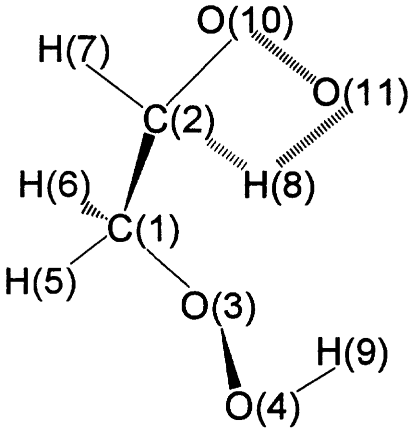
Table 7.1 Optimized Geometric Parameters for Species in the Hydroperoxy-Ethyl + O_2 Oxidation System at the B3LYP/6-31G(d,p) Level of Theory **(Continued)**



(d) (e) (f)

$HOOCH_2CH_2OO$•		TS1		TS2	
Parameter†	Value	Parameter†	Value	Parameter†	Value
r21	1.5226	r21	1.5338	r21	1.3899
r31	1.4205	r31	1.3720	r31	1.4008
r51	1.0946	r61	1.0923	r61	1.0944
r61	1.0969	r72	1.0946	r72	1.0827
r72	1.0933	r82	1.0977	r82	1.0831
r82	1.0932	r102	1.4226	r102	2.1554
r102	1.4593	r43	1.4519	r43	1.4673
r43	1.4515	r94	0.9722	r94	0.9713
r94	0.9735	r1110	1.4274	r1110	1.2730
r1110	1.3255	r511	1.2521	r511	1.2719
a721	111.53	a721	114.79	a721	120.58
a821	111.08	a821	109.21	a821	120.52
a1021	111.46	a1021	102.68	a1021	97.48
a431	107.72	a431	108.36	a431	107.11
a312	112.71	a312	111.68	a312	115.06
a512	110.64	a612	117.54	a612	119.67
a612	108.66	a11102	103.06	a11102	99.23
a11102	111.18	a943	99.26	a943	99.48
a943	101.56	a51110	92.92	a51110	98.40
d111021	-75.73	d111021	47.36	d9431	121.50
d9431	272.07	d9431	223.81	d111021	-2.09
d4312	83.99	d4312	198.65	d4312	142.18
d6128	-66.54	d511102	323.72	d511102	0.18
d82110	115.52	d72110	243.75	d72110	-96.23
d72110	-120.54	d82110	119.02	d82110	97.14
d31210	-66.08	d31210	209.34	d31210	-108.46
d51210	57.93	d61210	75.86	d61210	108.86

Table 7.1 Optimized Geometric Parameters for Species in the Hydroperoxy-Ethyl + O_2 Oxidation System at the B3LYP/6-31G(d,p) Level of Theory **(Continued)**



(g)

TS3	
Parameter[†]	Value
r21	1.5142
r31	1.4121
r51	1.0981
r61	1.0999
r72	1.0954
r82	1.3317
r102	1.3890
r1110	1.5090
r43	1.4543
r94	0.9762
a721	118.03
a1021	116.33
a431	107.44
a312	113.50
a512	109.72
a612	109.39
a11102	88.92
a943	99.70
a8210	85.70
d9431	-96.60
d111021	-109.00
d4312	66.90
d72110	141.99
d61210	-73.53
d51210	-192.47
d31210	41.58
d821011	2.08

dissociates by breaking the weak (ca 45 kcal/mol) hydroperoxy bond while forming the stronger (*ca* 80 kcal/mol) carbonyl bond.

7.3.3 Direct Molecular (HO_2) Elimination – TS2

The TS for the direct molecular elimination channel (denoted as TS2) has a breaking C—O bond length of 2.16Å, and forming OO—H bond length of 1.27 Å and a breaking C—H bond length of 1.36 Å. The long C—O and OO—H bonds, the shorter O—O and C—C bonds, and near planar ethylene structure decisively determine this as the HO_2 molecular elimination TS.

7.3.4 Hydrogen Shift (4 member ring) TS3

The third TS (denoted as TS3) is a 4-member ring H-shift from the ipso-carbon to the peroxy oxygen. The C—H bond length in TS3 is 1.33 Å, and the O—H bond length is 1.27 Å. Again the C—O bond (1.39 Å) is shorter and the O—O bond (1.51 Å) is longer than normal, which infers the start of the OH elimination as in TS1. This transition state structure continues to react (eliminate OH) and form the strong carbonyl bond in hydroperoxy-acetaldehyde + OH. TS3 passes through a dihydroperoxy-ethyl radical structure, identical to TS1.

7.3.5 Diradical + OH Channel ($HOOCH_2CH_2OO\bullet \Leftrightarrow OH + \bullet OCH_2CH_2OO\bullet$)

The RO—OH bond energy in alkyl hydroperoxides is ca 44.5 kcal/mol, which is only ca 9 kcal/mol above the entrance channel of the hydroperoxy-ethyl + O_2. This channel is included in the chemical activation and dissociation reactions; because the molecule is relatively large and the bond cleavage has a loose transition state structure. Reints, *et al.*[178] report a generic Arrhenius A-factor for alkyl RO—OH dissociation of 3 x 10^{15} sec^{-1}, while Chen, *et al.*[71] use 4.5 x 10^{15} sec^{-1}. This is used in the current analysis as an estimate, plus perform a sensitivity study showing results from increase and decrease of this A-factor by a factor of 3.3.

7.3.6 Thermodynamic Properties

The enthalpy of formation of the hydroperoxy-ethylperoxy radical, is calculated by isodesmic reaction analysis[136] with B3LYP/6-31G(d,p) and CBS-Q//B3LYP/6-31G(d,p) *ab initio* calculations to be -24.01 and -23.89 kcal/mol, respectively. (Refer to Table 7.2) This is about 35 kcal/mol below the entrance channel and nearly identical to the well for ethyl radical + O_2. The thermodynamic properties of reactants, TS's and products of this system are listed in Table 7.3. TS1 and TS2 are very close in energy (within *ca* 1 kcal/mol) and both are over 4 kcal/mol below the entrance channel. B3LYP/6-31G(d,p) and G3(MP2) calculate TS2 to be slightly lower in energy than TS1: but CBS-Q//B3LYP/6-31G(d,p) calculates TS1 slightly lower in energy than TS2, see Table 7.4. The 42.24 kcal/mol barrier of TS3 makes this channel unimportant.

7.3.7 Reaction Paths and High-pressure Limit Rate Constants

The 2 hydroperoxy-ethyl radical undergoes addition with oxygen to form an energized 2-hydroperoxy-ethylperoxy radical, with no barrier and a 35.23 kcal/mol well depth at B3LYP/6-31G(d,p). CBS-Q//B3LYP/6-31G(d,p) determines this well depth to be 35.11 kcal/mol. The adduct (energized and stabilized) can undergo four possible reactions,

Table 7.2 Isodesmic Working Reactions for CBS-Q//B3LYP/6-31G(d,p) and B3LYP/6-31G(d,p) Analysis on Enthalpy of the Hydroperoxy-Ethylperoxy Adduct.

CBS-Q//B3LYP/6-31G(d,p)

$HOOCH_2CH_2OOH$	+	C_2H_6	=	CH_3CH_2OOH	+	CH_3CH_2OOH
-380.0054538		-79.62475631		-229.8156475		-229.8156475
X		-20.4[a]		-39.89[b]		-39.89[b]

X = -58.7 kcal/mol

$HOOCH_2CH_2OO\bullet$	+	CH_3CH_2OOH	=	$CH_3CH_2OO\bullet$	+	$HOOCH_2CH_2OOH$
-379.3699627		-229.8156475		-229.182771		-380.0054538
Y		-39.89[b]		-6.72[b]		-58.7

Y = -23.89 kcal/mol

B3LYP/6-31G(d,p)

$HOOCH_2CH_2OOH$	+	C_2H_6	=	CH_3CH_2OOH	+	CH_3CH_2OOH
-380.4196807		-79.76083203		-230.0904115		-230.0904115
X		-20.4		-39.89[b]		-39.89[b]

X = -59.19 kcal/mol

$HOOCH_2CH_2OO\bullet$	+	CH_3CH_2OOH	=	$CH_3CH_2OO\bullet$	+	$HOOCH_2CH_2OOH$
-379.7921956		-230.0904115		-229.466121		-380.4196807
Y		-39.89[b]		-6.72[b]		-58.7

Y = -24.01 kcal/mol

a: CRC Handbook of Chemistry and Physics, 63rd Ed., CRC Press, Inc. 1974

b: Based on CBS-Q//B3LYP/6-31G(d,p) calculation with isodesmic working reactions. Refer to Sheng, C., Bozzelli, J.W., Dean, A.M., "Second Joint Meeting of the U.S. Sections of the Combustion Institute: Western States, Central States, Eastern States", Oakland, CA, 2001

Table 7.3 Thermodynamic Properties of Species in the 2 Hydroperoxy-Ethylperoxy Oxidation System Calculated at CBS-Q//B3LYP/6-31G(d,p)

SPECIES	Hf°_{298}	S°_{298}	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)
$\bullet CH_2CH_2OOH$	11.22	83.28	20.25	23.52	26.36	28.72	32.30	35.13	39.67
O_2	0	49.01	7.02	7.23	7.44	7.65	8.04	8.35	8.73
$HOOCH_2CH_2OO\bullet$	-23.89	90.67	25.00	30.45	34.92	38.41	43.27	46.48	51.14
TS1	5.84	85.96	23.94	29.63	34.43	38.23	43.51	46.90	51.56
TS2	6.54	87.40	25.36	30.89	35.46	39.05	44.01	47.19	51.63
TS3	16.78	89.05	24.42	30.21	34.86	38.46	43.38	46.54	50.92
$HOOCH_2CH(=O)$	-57.06	83.24	21.07	25.20	28.66	31.42	35.31	37.90	41.61
$H_2C=CHOOH$	-10.87	73.59	17.67	21.58	24.80	27.33	30.83	33.16	36.61
HO_2	3.25	54.73	8.37	8.95	9.48	9.96	10.78	11.43	12.47
OH	8.96	43.88	7.16	7.08	7.05	7.05	7.15	7.33	7.87

Units: Enthalpy in kcal/mol, Entropy in cal/mol-K, Cp in cal/mol-K

Table 7.4 Comparison of Activation Barriers, Relative to the Hydroperoxy-Ethylperoxy Adduct, to the Molecular Elimination and the 5-Member Ring Hydrogen Shift Transition State; CBS-Q//B3LYP/6-31G(d,p), B3LYP/6-31G(d,p) and G3(MP2)

	TS1 (5-member ring HS)	TS2 (molecular elimination)
B3LYP/6-31G(d,p)	29.05	28.25
CBS-Q//B3LYP/6-31G(d,p)	29.72	30.43
G3(MP2)	31.19	29.08
G3(MP2) (using B3LYP/6-31G(d,p)	31.26	31.27

Units: kcal/mol

with the high-pressure limit rate constants shown in Table 7.5. The reactions are:

R(-11) Dissociation back to reactants: $\bullet CH_2CH_2OOH + O_2 \Leftrightarrow HOOCH_2CH_2OO\bullet$

R12 5-member ring hydrogen shift forming an unstable dihydroperoxy-ethyl radical that rapidly *β* -scissions to hydroperoxy-acetaldehyde plus OH. (TS1) $(HOOCH_2CH_2OO\bullet) \rightarrow [HOOCH_2C\bullet HOOH] \rightarrow HOOCH_2CH(=O) + OH$ via H-shift)

The typical O—O bond energy in a hydroperoxide ~ 45 kcal/mol, which is lower than the ~ 80 kcal/mol gained in the new π-bond of the C=O moiety. This reaction, over the H shift transition state, has some 54 kcal/mol excess energy over the product set $HOOCH_2CH(=O) + OH$. A significant fraction of the $HOOCH_2CH(=O)$ has sufficient energy to cleave the RO-OH bond (45 kcal/mol) resulting in a second OH + a formyl methoxy radical (CH(=O)CH3O•). This is a new chain branching step; with the last step a function of both pressure and temperature.

R13 Molecular elimination, through a 5-member ring, to form a hydroperoxy-ethylene molecule ($H_2C{=}CHOOH$) plus HO_2. (TS2) $(HOOCH_2CHOO\bullet) \rightarrow H_2C{=}CHOOH + HO_2$

R14 4-member ring hydrogen transfer on the ipso carbon forming an unstable dihydroperoxy-ethyl radical that rapidly *β*-scissions to hydroperoxy-acetaldehyde plus OH. (TS3) This $HOOCH_2CH(=O)$ is also chemically activated; but with more energy, than **R12.**

R15 Cleavage of the weak hydroperoxide O-O bond in the energized $[HO\text{-}OCH_2CH_2OO\bullet]^*$ adduct to form a diradical + OH. $\bullet CH_2CH_2OOH + O_2 \Leftrightarrow [HOOCH_2CH_2OO\bullet]^* \rightarrow \bullet OCH_2CH_2OO\bullet + OH$

The two isomerization channels, **R12** and **R14**, both react to a dihydroperoxy-ethyl radical, which is unstable; it undergoes rapid *β*-scission, with no barrier, cleaving the weak RC•O—OH bond and forming a strong carbonyl bond, resulting in 2-hydroperoxy-acetaldehyde plus OH radical. (Figure 7.1). **R14** is not important because of its' higher barrier.

Table 7. 5 High-Pressure Limit Rate Constants. Rate Constants Expressed as $k_{forw} = A\ T^n \exp(-E_a/RT)$.

Reaction (#)		A†	n	Ea	comment
$\bullet CH_2CH_2OOH + O_2 \rightarrow HOOCH_2CH_2OO\bullet$	(11)	8.82E+09	1.12	0.0	a
$HOOCH_2CH_2OO\bullet \rightarrow \bullet CH_2CH_2OOH + O_2$	(-11)	4.24E+23	-0.99	36.14	b
$HOOCH_2CH_2OO\bullet \rightarrow HOOCH_2CH(=O) + OH$ (HS)	(12)	1.61E+02	3.27	27.71	c
$HOOCH_2CH_2OO\bullet \rightarrow H_2C{=}CHOOH + HO_2$ (ME)	(13)	8.63E+01	3.51	28.46	c
$HOOCH_2CH_2OO\bullet \rightarrow HOOCH_2CH(=O) + OH$ (ipso)	(14)	1.75E+03	3.19	38.90	c
$HOOCH_2CH_2OO\bullet \rightarrow \bullet OCH_2CH_2OO\bullet + OH$	(15)	3.0E15	0.0	43.5	d

† Units: Rate constants in cc/mol-sec or 1/sec; Ea in kcal/mol.

a Used the rate constant from ethyl + $O_2 \rightarrow CH_3CH_2OO\bullet$

b Rate constant determine by satisfying the detailed balance criteria with current thermodynamic data

c Rate constants calculated by canonical transition state theory. "HS" denotes through TS1, "ME" denotes through TS2 and "ipso" denotes through TS3.

d Estimated pre-exponential A-factor from Reints *et al.* Ea is estimated by ΔH_{rxn} between products and reactants.

7.3.8 General Kinetic Implications

There are two low energy channels **(R12 and R13)**; both have similar rate constants and both result in low energy chain branching from chemical activation reactions of hydroperoxy alkyl radical associations with O_2 and from thermal activation reactions of the stabilized peroxy adduct.

The hydroperoxy-ethylene from HO_2 elimination **(R13)** results in an important new chain branching channel, where the Ea reaction is ~ 22.5 kcal/mol. This is one half the value of conventional chain branching activation energies. The vinyl hydroperoxide undergoes rapid unimolecular dissociation, breaking the weak O—O bond to form an OH plus vinoxy radical.[186-188]

$$CH_2{=}CHOOH \rightarrow CH_2{=}CHO\bullet + OH \leftrightarrow \bullet CH_2\text{-}CH(=O) + OH$$
$$\Delta H_{rxn} = 22.5\ \text{kcal/mol}^{188}$$

The vinyl hydroperoxide is probably formed with sufficient energy in moderate temperature combustion reactions to dissociate immediately; and even at thermal conditions it only has a short (several seconds) lifetime. This is a new, low energy, chain branching reaction and further studies is anticipated to learn and understand the implications of including this reaction in low to moderate temperature hydrocarbon and oxy-hydrocarbon oxidation systems and in oxidation of lubricating oils. A lower energy resonance structure of the vinoxy radical is the formyl-methyl radical; it will further react with O_2 or undergo unimolecular isomerization / dissociation reactions.

The $HOOCH_2CH(=O)$ formed from **R12** is chemically activated. It can dissociate before stabilization, or the stabilized molecule can undergo dissociation of the hydroperoxide bond to R(O●)CH(=O) + OH, which is the conventional chain branching path, Ea ~ 44 kcal/mol **(R3)**. The alkoxy-acetaldehyde radical can *β*-scission to either a di-aldelyde (glyoxal) + H atom or to a formyl radical plus formaldehyde. **R3** has been considered important in recently published mechanisms, where the barrier was reduced to 37 kcal/mol for a better mechanism fit to data.[189,190] The estimation of the pre-exponential A-factor for the cleavage of the O—O bond from ROOH → RO● + OH is 4.5×10^{15} sec^{-1}.[191,192]

It is surprising to find the barrier for the hydrogen shift to the peroxy radical from the *beta*-carbon to be low, 29.72 kcal/mol, and similar to the HO_2 elimination barrier, 30.43 kcal/mol. This hydrogen transfer barrier is significantly lower than the isomerization barrier of ethyl-peroxy to hydroperoxy-ethyl, *i.e.* 36.36 kcal/mol.[25,161,177] The reason for this low barrier is the very weak C—H bond energy on the hydroperoxide carbon, where the TST appears to recognize the lower energy, final products.[184] The hydrogen transfer path (TS1) continues to lower energy products, and it also moves the hydroperoxy-ethyl radical out of the ethyl + O_2 quasi-equilibrium system; which serves to accelerate oxidation.

7.3.9 Kinetic Analysis on Chemical Activation C•COOH + O_2 Reaction System

Rate constants calculated by QRRK analysis for *k(E)* with master equation for fall-off over a temperature range of 250-2500K and a pressure range of 0.001-100 atm are performed. Nitrogen is used as the collision bath gas with a ΔE_{down} of 830 cal/mol. The CBS-Q//B3LYP/6-31G(d,p) parameters are shown in Figure 7.2 for log rate constant versus log pressure at 800 K. This constant temperature analysis shows that stabilization is still increasing as pressure approaches 100 atm. The overriding reaction channels of the chemically activated adduct are stabilization at low T and high pressure, and dissociation of the adduct back to reactants. The molecular elimination to vinyl-hydroperoxide plus HO_2, is the dominant product channel, but only factor of 1.8 faster than the low energy H-shift reaction and, surprisingly, only a factor of 3.5 faster than the higher energy chemical activation chain branching di-radical + OH product set at 1 atm. The formation rate of hydroperoxy-acetaldehyde plus OH, via the 4-member ring ipso-carbon H-shift is slower than the 5-member ring H-shift by over two orders of magnitude and is not important at lower temperatures. The 5-member ring hydrogen shift and the molecular elimination channel are faster than the stabilization rate below 0.01 atm in the chemical activation reaction. The dissociation kinetics of the chemically activated $HOOCH_2CH(=O)$ adduct from the H shift reactions will be treated in a future study.

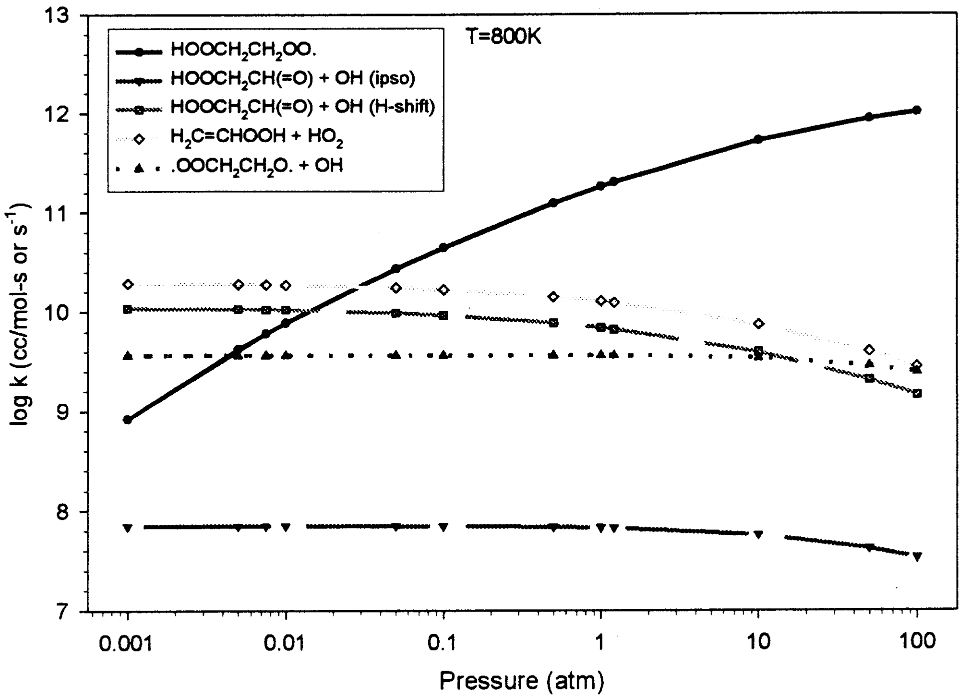


Figure 7.2 Rate Constants vs. Pressure at T = 800K.

A plot of rate vs. temperature at 1.0 atm in Figure 7.3, shows complex temperature dependence. The stabilization rate constant for the hydroperoxy-ethylperoxy adduct is more important than product formation below 1000K. The molecular elimination and the 5-member ring H-shift channels are the most dominant products up to 800K. The biradical + OH channel increases in importance with increase in temperature, and is near equal the HO_2 elimination channel at 1000K. It is the most important product at higher T. Formation of hydroperoxy-acetaldehyde plus OH, via the 4-member ring ipso-carbon H-shift is the least important channel.

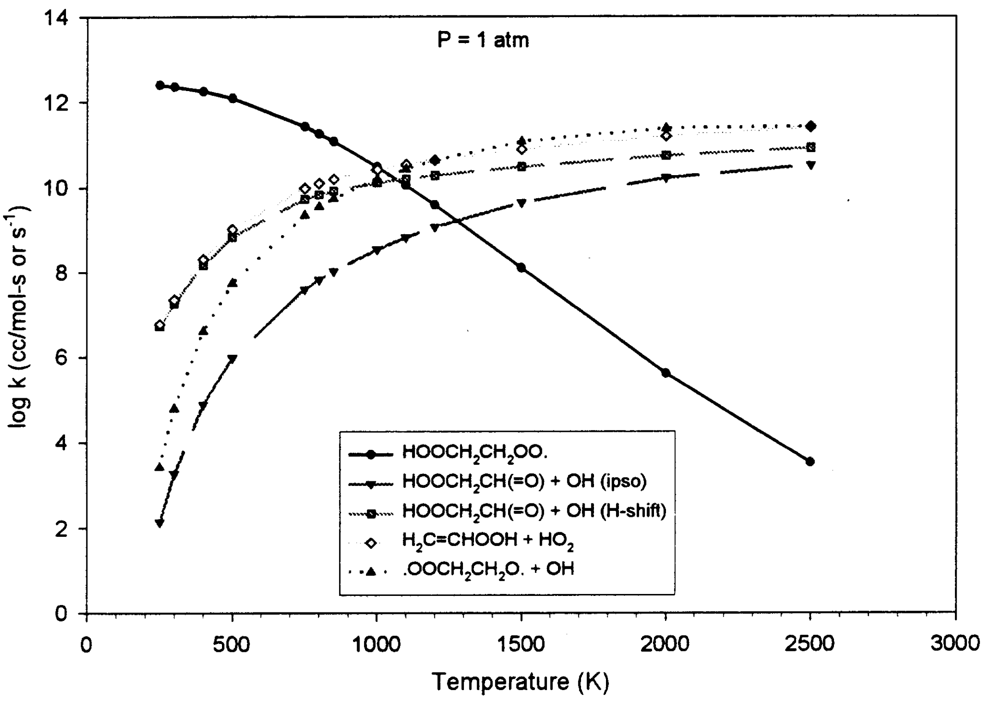


Figure 7.3 QRRK Rate Constants at P = 1.0 atm.

7.3.10 Kinetic Analysis on Thermal Dissociation of $HOOCH_2CH_2OO\bullet$ Adduct

It is important to analyze the adduct dissociation due to the importance of stabilization. Dissociation rate constants at 800 K over a pressure range of 10^{-3} to 100 atm are illustrated in Figure 7.4. Dissociation to hydroperoxy-ethyl radical + O_2 is the most important channel, with HO_2 elimination and the H-shift isomerization channels showing a slight increase in rate constant with pressure. Dissociation of the stabilized adduct to the biradical + OH is increasing in importance with pressure.

Figure 7.5a and 7.5b illustrate dissociation rates at constant pressures of 0.0075 and 1.21 atm vs. temperature. At 0.0075 atm pressure dissociation to hydroperoxy-ethyl radical + O_2 and the two similar barrier channels, HO_2 elimination and the H-shift isomerization, are all of similar importance. Above 1000 K, these two product channels dominate. As pressure is increased to 1.21 atm, the reverse reaction to hydroperoxy-ethyl radical + O_2 is the dominant channel below 1500 K.

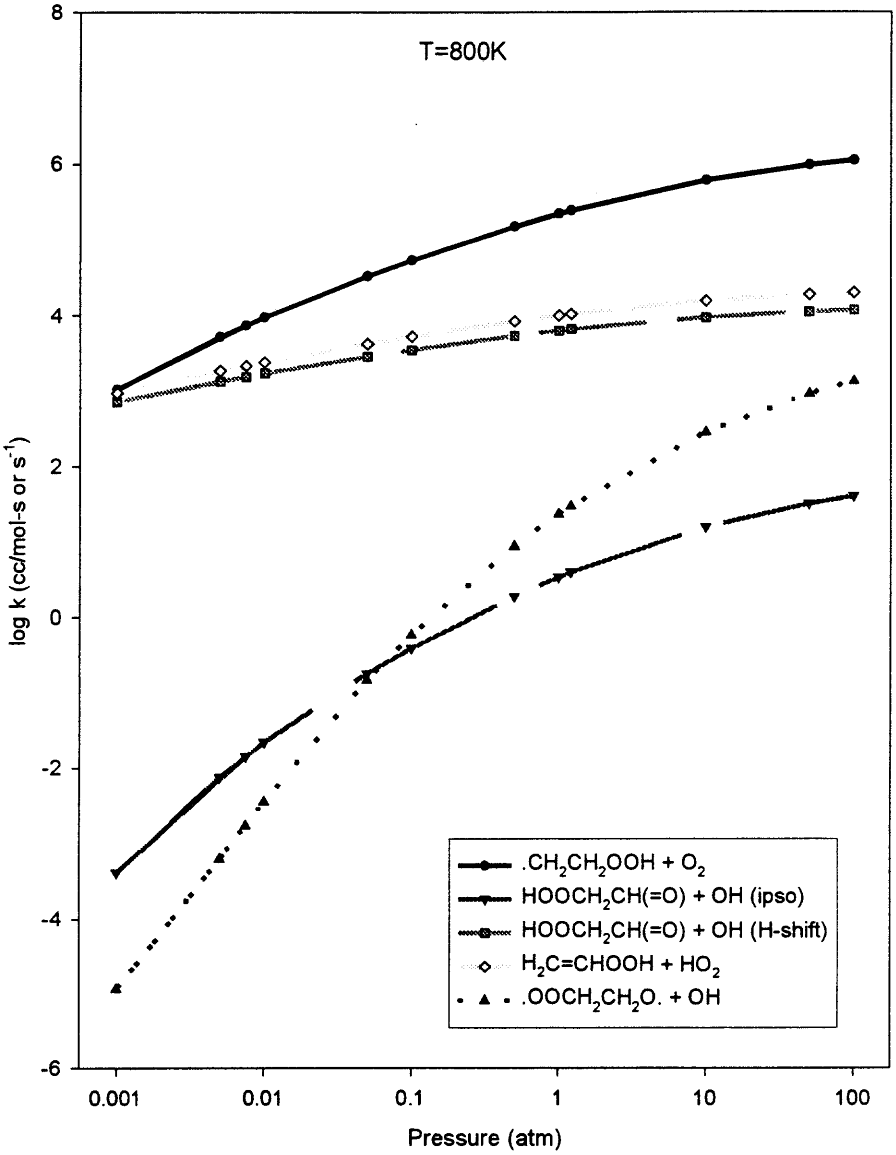
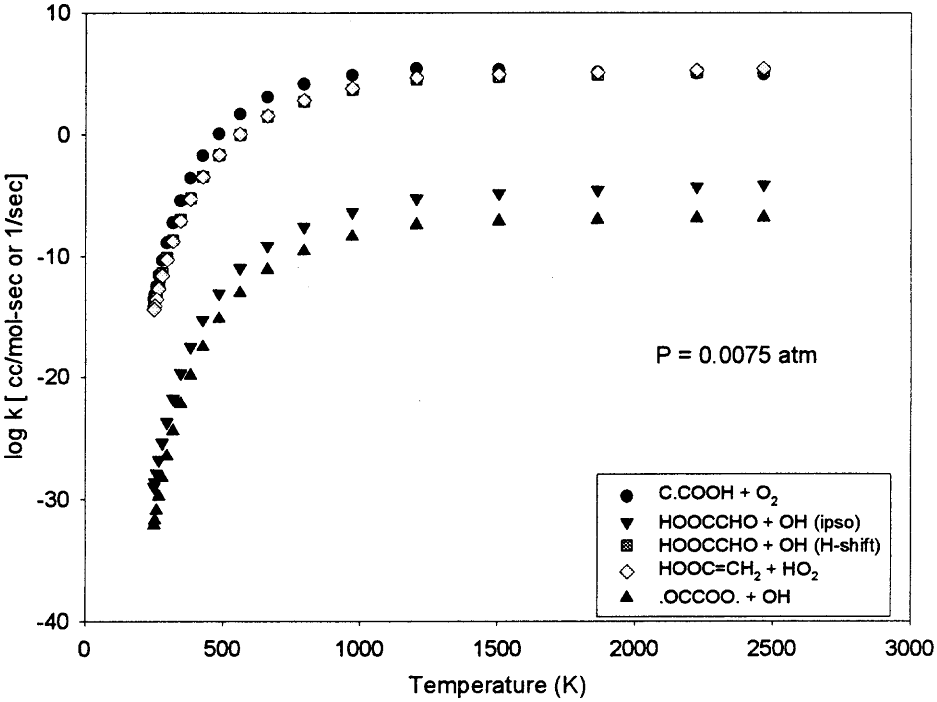


Figure 7.4 Dissociation rate constants for hydroperoxide ethyl peroxy radical calculated by QRRK with master equation analysis at isothermal conditions of T = 800 K



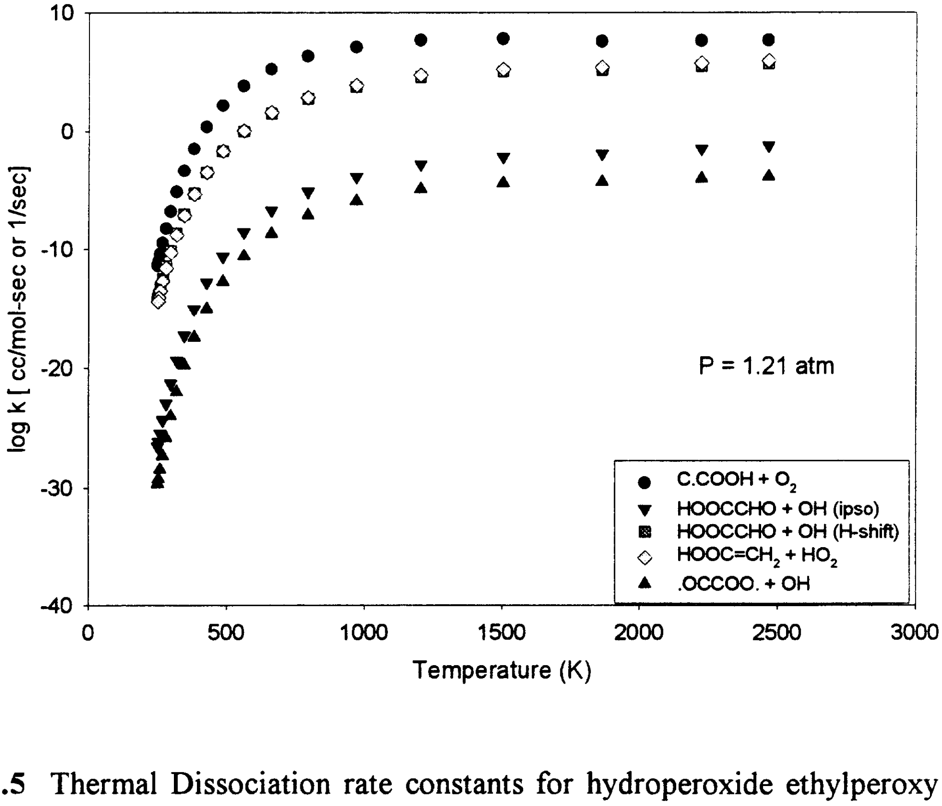


Figure 7.5 Thermal Dissociation rate constants for hydroperoxide ethylperoxy radical calculated by QRRK with master equation analysis at isobaric conditions. Top 0.0075 atm, bottom = 1.21 atm.

7.3.11 Sensitivity to R15

Figure 7.6 illustrates the sensitivity of **R15** relative to the HO_2 elimination channel vs temperature when the Arrhenius A-factor is varied by +/- factor of 3.3 in the chemical activation system at low pressure. The HO_2 elimination and H-shift dominate below 1000 K but the importance of this diradical increases with temperature and pressure.

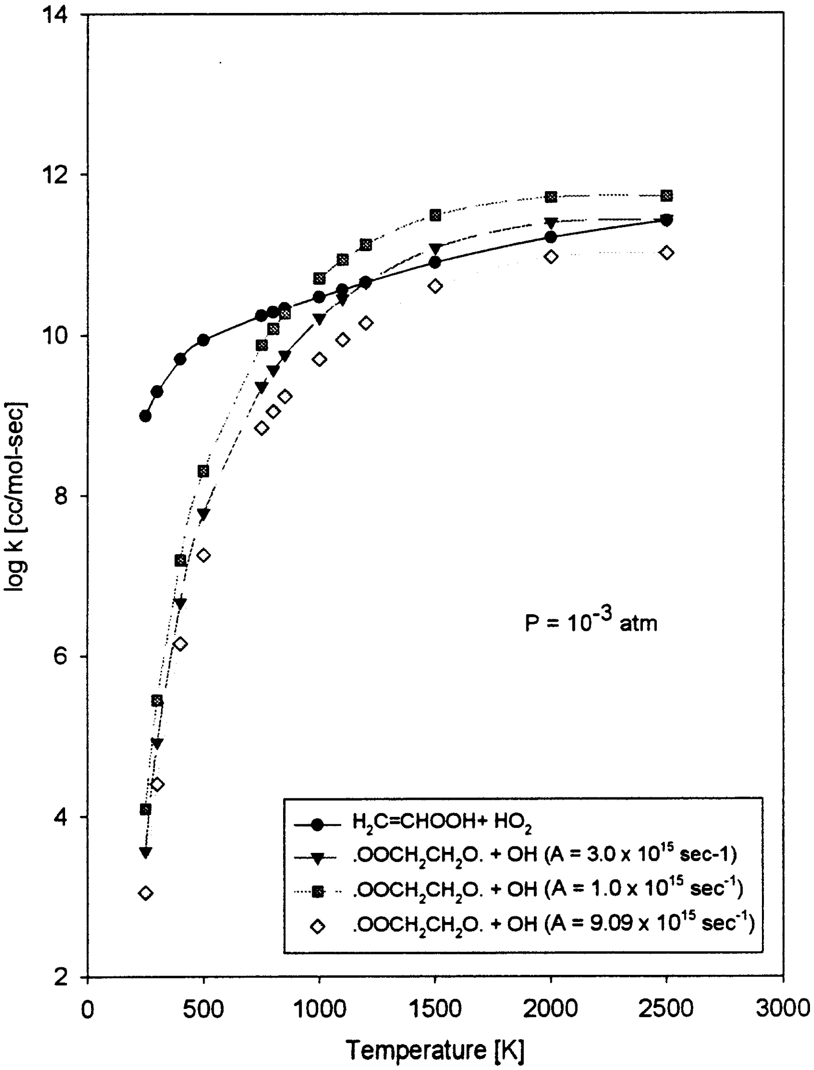


Figure 7.6 Sensitivity analysis of $\bullet OCH_2CH_2OO\bullet$ + OH channel. The molecular elimination channel is used as the reference comparison to the di-peroxy system.

7.3.12 Formation of Hydroperoxy – Alkyl Radicals

If these newly proposed reactions are to be important in combustion and thermal oxidation systems; the paths for formation of the hydroperoxy-alkyl radical reactants need to occur. These are formed via two general mechanisms in combustion and other thermal oxidation systems. One via isomerization (H-shift) of peroxy radicals, particularly on hydrocarbons where 6 and 7 member H-shift ring transition states can occur. These larger rings have lower ring strain and thus lower barriers to the H-shift reactions. The second path is HO_2 radical addition to olefins.[71]

$$HO_2 + RCH{=}CH_2 \Leftrightarrow RC{\bullet}H\text{-}CH_2OOH \quad \text{or} \quad RCH(OOH)\text{-}C{\bullet}H_2$$

7.4 Summary

Thermochemical and kinetic parameters on the 2 hydroperoxy-ethyl radical reaction with molecular oxygen are determined for the first time. The standard enthalpy of formation for the hydroperoxide-ethylperoxy adduct is –23.89 kcal/mol and the reaction well depth is 35 kcal/mol. The activation barrier for the molecular elimination channel and the five-member ring hydrogen shift channels are calculated by CBS-Q//B3LYP/6-31G(d,p) {G3(MP2)} to be 30.43 {29.08} and 29.72 {31.19} kcal/mol. These barriers are 4 to 6 kcal/mol below the energy of the reverse reaction. The low barrier for the 5-member ring isomerization reaction, some 7 kcal/mol lower than in the ethyl-peroxy system, is a result of the low C—H bond energies on the carbon bonding to the peroxide.

Chemical activation analysis on the reaction system shows prompt formation of: (i) a HO_2 molecular elimination plus vinyl hydroperoxide, where the the vinyl hydroperoxide has a weak (22 kcal/mole) $CH_2{=}CHO\text{—}OH$ bond and rapidly undergoes unimolecular dissociation to formyl methyl plus OH radicals (ii) an intramolecular hydrogen transfer (5-member ring) to 2 hydroperoxide acetadehyde + OH, where the $HOOCH_2CH(=O)$ formed is chemically activated and a significant fraction dissociates to OH + formyl-methoxy radical, before stabilization and (iii) a third new reaction path – cleavage of the weak peroxide bond to form a bi-radical + OH. The bi-radical + OH formation (**R15**) may have more importance in larger hydrocarbon radical systems, where the H-shift isomerizations to form hydroperoxide alkyl radicals have 6 and 7 member rings with low energy barriers. These larger molecules are also closer to the high-pressure limit.

Thermal dissociation of the stabilized adduct shows that the reverse reaction back to reactants is the dominant reaction below 1500 K at 1 atm; but HO_2 elimination and 5-member ring H-shift (**R12** and **R13**), become competitive under lower pressure and temperature conditions.

The intramolecular H-transfer and HO_2 elimination reactions, **R12**, and **R13** have similar barriers and rate constants; they are important reactions in both chemical activation and in unimolecular dissociation; they move the hydroperoxy-ethyl radical out of the ethyl + O_2 quasi-equilibrium and both lead to chain branching. Pressure effects on the rate constants of **R12** and **R13** are relatively small.

The overall (major flux) reaction paths are stabilization and reverse reaction to hydroperoxy-ethyl + O_2. This forward / reverse reaction process results in a quasi-equilibria and allows the chain branching reaction steps to exhibit a strong and perhaps controlling influence under some conditions in hydrocarbon oxidation.

CHAPTER 8

DEVELOPMENT OF A PRESSURE DEPENDENT REACTION MODEL FOR METHANE/METHANOL MIXTURES UNDER PYROLYTIC AND OXIDATIVE CONDITIONS AND COMPARISON WITH EXPERIMENT

8.1 Introduction

Oxygenated hydrocarbons play an important role in both industrial and environmental chemistry. Alcohols, such as methanol and ethanol, are in use as alternative motor fuels and as additives to conventional transportation fuels to improve performance. Ethers, such as methyl tert-butyl ether (MTBE), are in use as oxygen additives as anti-knock components in gasoline and other ethers are being considered as additives for diesel fuels.

The oxidation and pyrolysis of gas phase methanol has been reported in a number of studies over the past half century by experimental methods, which range from laser induced fluorescence, diffusion flame, shock-tube and static or flow reactors.[34,193-204]

Norton and Dryer performed methanol oxidation experiments using a turbulent flow reactor at equivalence ratios in the range from 0.6 to 1.6 and initial temperatures from 1025 to 1090K at atmospheric pressure.[33] They also presented a kinetic mechanism for methanol pyrolysis which matched multiple sets of experimental data from static, flow, and shock tube reactors, covering temperatures of 973 to 1993K and pressures of 0.3 to 1 atmosphere.[34,203] They indicated that the fuel decomposition reaction $CH_3OH \rightarrow CH_2OH + H$, previously included only in mechanisms for high temperature conditions, also has a significant effect at low temperatures through the reverse radical recombination reaction. They also reported that the reaction $CH_3O + CO \rightarrow CH_3 + CO_2$ rather than $CH_3OH + H \rightarrow CH_3 + H_2O$, was the major source of CH_3 at low temperatures and the reverse of CH_3 + OH → CH_2OH + H was important to CH_3 production at high temperatures.

Held and Dryer published additional results on a methanol oxidation mechanism for static reactor, flow reactor, shock tube reactor and laminar flames for temperatures from 633 to 2050K over a pressure range of 0.26 to 20 atm.[24] Their mechanism is primarily from Yetter, *et al.*,[205] Hochgreb and Dryer[206] and Norton and Dryer[33] with modifications. Held and Dryer report, through sensitivity analysis, that methanol oxidation was found to be very sensitive to kinetics of hydroperoxy radical. While the pressure and temperature range is large the mechanism only includes fall-off analysis for four reactions.

The CH_2OH radical is an important first product from varied abstraction reactions on methanol. Important elementary reactions of CH_2OH with molecular and atomic oxygen in the methanol oxidation system were studied by Grotheer, *et al.*[204] using a direct discharge flow reactor over temperature range from 298 to 673K at pressures around 1 mbar. Radical profiles were monitored by a low-energy electron impact ionization mass spectrometer. The rate coefficient was measured for the CH_2OH + O reaction. A strong non-Arrhenius behavior for CH_2OH + O_2 reaction was reported.

Three different wide range of experimental conditions were performed previously by Wen-chiun Ing[207] at New Jersey Institute of Technology: methanol pyrolysis, methanol oxidation and methanol/methane oxidation. Mixtures of methanol and methane are studied over varied pressure and temperature range to assess effects of methanol as an additive in motor vehicle fuels. This data will serve as a basis, along with that in the literature, on the validation of the pressure dependent model for methanol and methane oxidation and pyrolysis. The current model will allow evaluation and simulation of methanol combustion under atmospheric conditions as well as in compression engines or turbines, where pressures are very different from atmospheric.

The mechanism presented in this current study includes about 200 pressure dependent reaction steps, which exhibit significant pressure dependence in the pressure and temperature range of these experiments, and are represented in Chebyshev polynomial form over a pressure range from 0.001 - 100 atm and a temperature range of 250 – 2500K. Included in the mechanism are pressure effects on important unimolecular and bimolecular reactions plus negative temperature dependence and pressure effects on hydrocarbon (HC) and oxy-hydrocarbon (OHC) species reactions that account for observations by Grotheer, *et al.*[204] Pathways for formation and oxidation of higher molecular weight products, such as C_2 hydrocarbons and methyl-ethers, which are observed in this study, are also included.

8.2 Description of Experimental Setup

The reactor used in Ing's experiments is a 6mm ID (12mm OD) quartz tube, which is housed within a 75 cm length of three-zone clamshell 3 cm ID electric tube furnace equipped with three independent Omega Model CN-310 digital temperature controllers. A Neon Controls BPS 26G2501, 200 psi back pressure regulator is used to maintain the desired pressure within the reactor. (Refer to Figure 8.1 for experimental setup).

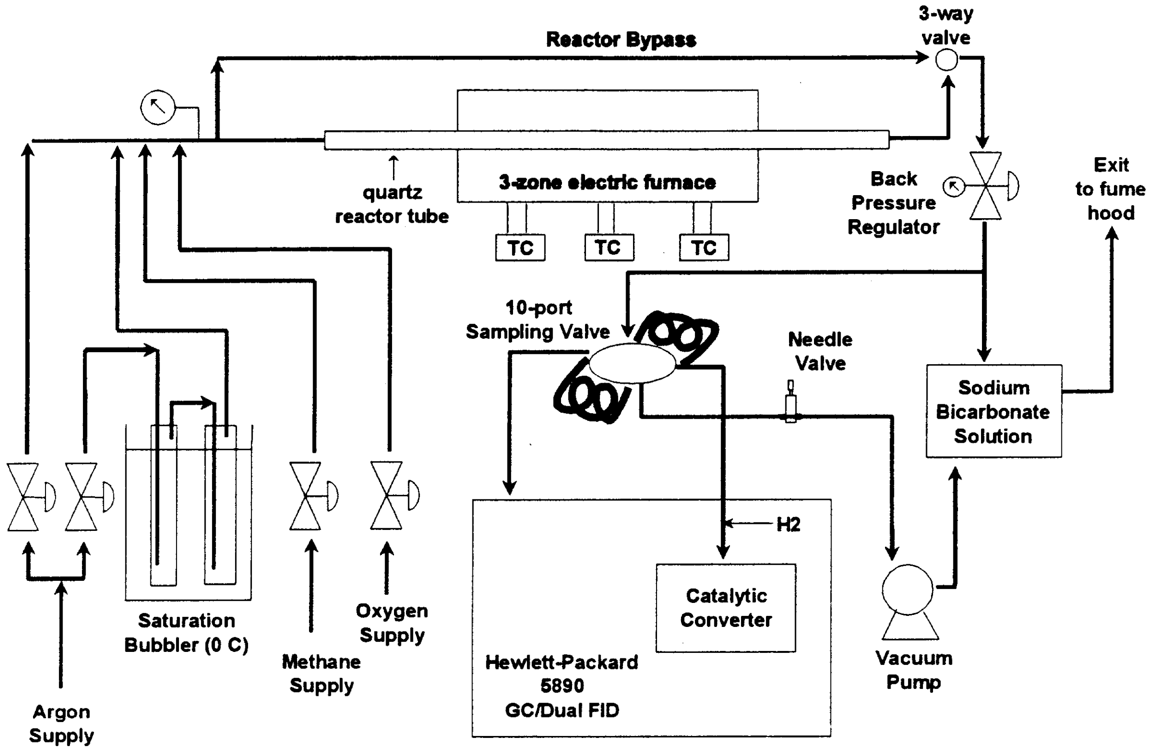


Figure 8.1 Schematic diagram of Ing's methanol/methane experiment.

Temperature profiles for the reactor are obtained at each flow using a type K thermocouple probe that moves axially across the 75 cm length reactor. Thermocouple error caused by radiation from furnace wall is minimized by using a grounded sheath and with a representative flow of inert. The darkened outside surface of the quartz tube reactor serves as a second radiation shield. Temperature control resulted in temperature profiles isothermal to within ± 5°K over 80 - 85% of the furnace length for each temperature. Temperature gradients of 500°K in 5 cm occur at the inlet and outlet of the reactor. Uncertainty in absolute temperature measurements is estimated to be ± 1% (*i.e.* ± 8-12°K), but relative temperatures are measured to within ± 5°K.

Methanol is reagent grade supplied by Aldrich Co. Methane and argon gases are filtered for removal of O_2, H_2O, and hydrocarbon impurities before entering the reactor system. Oxygen is filtered for H2O and hydrocarbons. All gases are from Praxair

(Liquid Carbonic). The carrier gas (argon) is passed through a saturation bubbler, which contains liquid methanol held at 273°K using an ice bath. A second argon flow stream is used as make-up gas in order to achieve the desired reactant ratio. Methane and oxygen are added to the CH_3OH/Ar flow as required. All four gas streams (argon, make-up argon, oxygen and methane) are controlled by a Union Carbide LINDE® Model FM-4550 mass flowmeter-flowcontroller with four independent mass flow control modules. Four channels are calibrated to indicate 0-100% range of the desired gases.

The mixed reactants (feed mixture) are preheated to about 373°K to prevent condensation and improve reactor temperature control. The reactants can either flow through the reactor or flow directly to a GC sampling valve, via a bypass line. The bypass is used to determine the initial concentration of reactants prior to entry through the high temperature reactor.

Gas samples are drawn through the sampling line by means of a mechanical vacuum pump with a constant flow rate of 30 cm^3/min, where pressure in the sample loop is controlled. A HP-5890 Series II gas chromatograph (GC) with two flame ionization detectors (FID) is used on-line for analysis. The bulk of the effluent is passed through a sodium bicarbonate ($NaHCO_3$) flask for neutralization before being released to a fume hood.

A HP-5890 Series II GC with two FIDs is used on-line to determine the concentration of reactants and products. A ten-port VALCO gas sampling valve is employed to introduce the gas samples into the GC columns. Two columns, one packed and one capillary, are used to perform the chromatographic separations. A 6’ × 1/8” stainless steel column is packed with 50% 80/100 Poropak T and 50% 80/100 Poropak Q for the separation of CO, CO_2 and light hydrocarbons. A 90 m × 0.53 mm Hewlett-Packard fused silica capillary column is used for heavier hydrocarbon and oxy-hydrocarbon separation. The gas samples pass through two sampling loops, 1.0 cm^3 and 0.25 cm^3, at a constant flow rate of 30 cm^3/minute, and are injected into the packed and capillary column, respectively.

A catalytic converter is connected in series after the packed column in order to increase the accuracy in quantitative analysis of CO and CO_2. The catalyst consists of 5% 80/100 ruthenium on alumina. After CO and CO_2 are separated by the packed column, just prior to entering the catalytic converter, it will mix with 15 cm^3/min H_2 gas, coming from a tee. The catalytic converter will convert the mixture to methane, which can be detected by the FID for high sensitivity. The chromatogram peaks are analyzed with two HP 3396A integrators.

Product identifications are verified by a HP 5899A GC/Mass Spectrometry, with a HP 90 m × 0.53 mm fused silica capillary columns (same type as the one used in the on-line GC system). Batch samples of reactor gas drawn from the reactor are collected into an evacuated 25 cm^3 stainless steel sample cylinders for later analysis.

Methanol pyrolysis experiments are all performed under isothermal condition at 1073°K, with varying concentrations of CH_3OH over a pressure range from 1 to 10 atm. Experimental data on the decomposition of methanol in presence of oxygen and argon were obtained for both fuel lean ($\phi = 0.75$) and stoichiometric ($\phi = 1.0$) conditions over a temperature range from 873 to 1073°K and a pressure range of 1 to 5 atm. Initial CH_3OH mole fraction for both fuel lean and stoichiometric conditions are 0.0078. All methanol/methane oxidation experiments are carried out under overall stoichiometric conditions. Experimental data for methanol/methane oxidation experiments at two different temperatures and pressure combination conditions are collected: either 873°K and 5 atm or 1073 and 1 atm. Various methanol/methane concentration ratios, ranging from 0:2 to 2:0, were studied for each of the two temperature/pressure conditions. All experimental data were monitored over a residence time from 0.1 to 2.0 seconds.

8.3 Computational Methods

A pressure dependent mechanism for CH_3OH/CH_4 system has been developed; it consists of about 150 species and 450 elementary reaction steps, with over 200 elementary reactions being pressure dependent. Pathways for formation and oxidation of higher molecular weight products, such as C_2 hydrocarbons and methyl-ethers, which are observe, are also included. Thermodynamic properties of species are from literature, theoretical and estimation techniques, such as group additivity,[88] hydrogen bond increment (HBI) [130,208] and *ab initio* or density function calculations. The HBI group technique is based on known thermodynamic properties of the parent molecule and calculated changes that occur upon formation of a radical, via loss of a H atom. The HBI group incorporates evaluated carbon hydrogen (C-H) bond energies, for ΔH_{298} of the respective radical, and changes that result from loss or changes in vibrational frequencies, internal rotation, symmetry and spin degeneracy when a hydrogen atom is removed from the specific carbon site. Entropies and $C_p(T)$ values are from use of HBI.

8.3.1 *Ab initio* and Density Functional Theory Computations

The molecular properties for the explicit CH_3OH dissociation system, including methanol, transition states (TS) and products, are determined by the high level composite CBS-APNO *ab initio* calculations. The *ab initio* calculations are performed using Gaussian94.[55] The CBS-APNO calculations are performed in accordance to the method outlined by Montgomery, *et al.*[209] Vibrational frequencies, ZPVE and thermal correction contributions are calculated at the HF/6-311G(d,p) level of theory, with scaling factors consistent with the recommended values by Scott and Radom.[62] The optimized geometry is calculated at the QCISD/6-311G(d,p) level of theory. Figure 8.2 illustrates the potential energy diagram of the CH_3OH subsystem

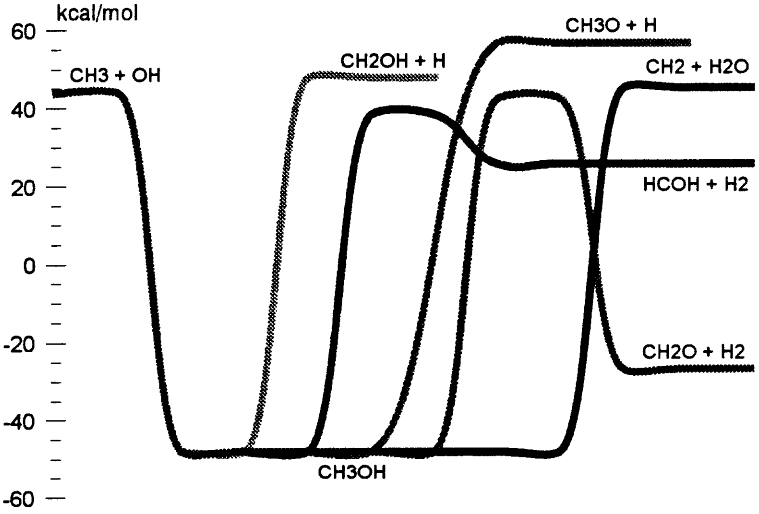


Figure 8.2 Potential energy diagram of CH_3 + OH calculated at CBS-APNO.

The three channels in the CH_3OH system that do not exhibit conventional transition state structures are calculated from variational transition state theory (VTST). The thermodynamic properties of the complexes along the reaction coordinate of these three channels in the CH_3OH system are determined by the composite CBS-Q method utilizing the optimized geometry from B3LYP/6-31G(d,p). The optimized geometries of the complexes along the respective reaction coordinate are determined by holding the respective dissociating bond distance constant in increments of 0.1Å starting from the stable ground state of methanol to a bond distance that corresponds to the total energy equivalent to the sum of the total energy of the respective dissociated products. The optimized geometries of the complexes are calculated by the hybrid DFT method B3LYP, which combines the three parameter Becke exchange functional, B3, with the Lee-Yang-Parr nonlocal correlation functional, LYP, with a double zeta polarized basis set, 6-31G(d,p).[129,166] Single point calculations at the complete basis set, composite method — CBS-Q[125] are utilized based on the optimized B3LYP/6-31G(d,p) geometry, denoted as CBS-Q//B3LYP/6-31G(d,p).[59,129,166] The DFT calculations are spin-unrestricted Hartree-Fock. Molecular geometries at B3LYP/6-31G(d,p) are fully optimized using the Berny algorithm and redundant internal coordinates.[55] Zero-point vibrational energy (ZPVE), vibrational frequencies and thermal correction contributions to enthalpy from harmonic frequencies are scaled in accordance to the scaling factors recommended by Scott and Radom.[62] The inclusion of ZPVE and thermal corrections to the total energies of the species in this system has been applied accordingly.

The enthalpies of the two biradicals in the system are determined by use of isodesmic working reactions with group balance. Fundamental requirements for an isodesmic reaction are conservation of electron pair and chemical bond type.[136] The use of isodesmic reactions is an accurate and desired method for estimating enthalpy of formation. Two isodesmic reactions are employed to determine the enthalpy of formation for the two biradicals of interest in the CH_3OH sybsystem.

$$ {}^1\mathbf{CH_2} + CH_4 = CH_3 + CH_3 \qquad \textbf{(IR1)} $$

$$ {}^1\mathbf{HCOH} + CH_4 = CH_3OH + {}^1CH_2 \qquad \textbf{(IR2)} $$

The enthalpies of formation of the biradicals of interest are shown in **IR1** and **IR2** in bold. The enthalpies of formation for all the other oxy-hydrocarbon species in the respective isodesmic reaction are needed before one can determine the enthalpy of formation of the two desired biradicals. **IR1** is utilized to determine the enthalpy of formation for the singlet methylene biradical, which is then used in **IR2** to aid in the determination of the singlet HCOH biradical.

Conventional statistical mechanics analysis was employed to determine the vibrational, external rotational and translational contributions to entropy and $C_p(T)$.[210] Molecular parameters required in the statistical mechanic analysis are calculated at the B3LYP/6-31G(d,p) level of theory for the optimized geometric structure of the species. Vibrational contribution for entropy and C_p are scaled correspondingly to the recommended scaling factors from Scott and Radom.[62] Unpaired electrons are also included in the S^{298} and $C_p(T)$ calculations accordingly. Contributions of internal rotation to S^{298} and $C_p(T)$ are incorporated based on the Pitzer-Gwinn formalism.[90]

8.3.2 Calculation of High-Pressure Rate Constants

Abstraction reaction rate constants are not pressure dependent and are usually taken from evaluated literature when available. If estimation is required, a generic reaction is utilized as a model and adjusted for steric effects.[36] Evans-Polanyi analysis is used on the reaction in the exothermic direction to estimate the energy of activation (E_a) for rate constant.

The high-pressure limit rate constant for combination is obtained from literature or estimated from known generic reactions. Both elimination and dissociation reactions utilize similar technique to arrive at its respective rate constants. The reverse of high-pressure reaction (addition or combination) parameters is determined from microscopic reversibility.

The high pressure forward rate constants in the CH3OH subsystem are determine by application of macrocanonical transition state theory (CTST) for temperatures from 300 – 2500 K. Forward rate constants from 300 – 2500 K are calculated and fitted by a nonlinear least squares method to the form of a modified Arrhenius rate expression, *i.e.*

$$k_{\infty,forw} = A_{\infty}T^{n}e^{-\frac{E_a}{RT}}.$$

The rate constants for the three combination and dissociation reaction in the CH_3OH system are calculated by variational transistion state theory (VTST), with thermochemical properties determine at the CBS-Q//B3LYP/6-31G(d,p) level of theory. The reaction coordinate along the respective dissociating bond length is calculated based on the most favorable dissociation pathway along the respective reaction surface. The combination reaction rate constant is determined by satisfying the microscopic reversibility criteria.

8.3.3 Kinetic Analysis – Modified Strong Collision and Master Equation

Pressure and temperature dependent rate constants are determined by a modified quantum RRK (QRRK) formalism for *k(E)*. Two methods to analyze the collisional deactivation of the energized adduct are used: master equation analysis and the modified strong collision model. The master equation analysis used in this study, uses a $<\Delta E>_{down}$ of 830 cal/mole for the collisional deactivation with N_2 as the third body. The second fall-off analysis method used is the modified strong collision approach (beta collision) of Gilbert, *et al.*[137] A $<-\Delta E>_{av}$ of 440 cal/mole is employed for the collisional deactivation with N_2 as the third body in the modified strong collision model, to ensure consistency in the third body collisional energy with the master equation analysis.

Chang, *et al.*[60,63] described a modified QRRK analysis that is used in this paper. It is shown to yield reasonable results and provides a framework by which the effects of temperature and pressure can be evaluated in complex reaction systems. The current version of the QRRK computer code utilizes a reduced set of vibration frequencies which accurately reproduce the molecule (adduct) heat capacity data. Molecular density-of-state functions are constructed through direct convolution of single frequency density functions on a 10 cm^{-1} grid. The functions corresponding to each reduced frequency is explicitly convolved into a relative density-of-states ($\rho(E)$), which is normalized by the partition function (Q). The inclusion of one external rotation, corresponding to the symmetric top, is incorporated into the calculations by convolving the vibration density function with the proper rotational density function. A detailed description of this and comparisons of the $\rho(E)/Q$ ratios with the direct count $\rho(E)/Q$ ratios are shown to be in good agreement.[65] Nonlinear Arrhenius effects resulting from changes in the thermodynamic properties of the respective TS, relative to the adduct, with temperature are incorporated using a two parameter Arrhenius pre-exponential A-factor (A, n) in the form of AT^n.

Reduced sets of three vibration frequencies and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter[170,211] and Bozzelli, *et* *al.*[65] These have been shown by Ritter to accurately reproduce molecular heat capacities, Cp(T), and by Bozzelli, *et al.* to yield accurate ratios of density-of-states to partition coefficient, $\rho(E)/Q$.

Master equation analysis is used for fall-off in this analysis as described by Sheng, *et al.*[64] and follows Gilbert and Smith.[116] The method to determine the density of state functions is as described above. Chemical activation is treated by a steady state analysis; the reactant channel provides a continuous input while the product and stabilization channels provide steady outputs. Multiple isomerization channels for the activated adduct is treated by a modified method proposed by Carter and Tardy[212] which treats the solution by solving a successions of 2x2 matrix equations that consists of sub matrices. The collision model is based on an exponential down model that describes the collision probability. The frequency of collision between the adduct and bath gas is described by the standard Lennard-Jones model. Unfortunately, a time-independent master equation solution for dissociation that allows for multiple isomerization is not included[116]; unimolecular dissociation reactions are treated as irreversible channels and solved separately. Reversibility of the isomers are taken into consideration by the numerical integrator package CHEMKIN.[87]

8.3.4 Pressure Dependent CHEMKIN Mechanism

Both the modified strong collision and master equation codes incorporate a temperature and pressure dependent output formalism for the rate constants, in the form of an N x M Chebyshev polynomial expression. The temperature-pressure dependent rate coefficients in Chebyshev format for the current system of interest are derived from application of the methodology described by Venkatesh, *et al.*[163,164] The current mechanism file is fitted over a temperature range of 250 – 2500 K and a pressure range of 10^{-3} – 100 atm with seven temperature functions and three pressure functions, *i.e.* a 7 x 3 Chebyshev polynomial expression. CHEMKIN is used to integrate the linear differential equations for specie concentrations versus time of reaction.[87] The CHEMKIN interpreter is modified to accept the N x M Chebyshev polynomial formalism of rate constant. The use of a Chebyshev polynomial formalism for the temperature and pressure dependent rate expression, offers the major advantage in that only one mechanism file is needed that can run multiple temperature/pressure conditions in CHEMKIN.

The current modified CHEMKIN code expresses the Chebyshev series[213,214] in the inverse temperature and logarithm of pressure as the approximation of the logarithm of the rate coefficients. A $d \times d$ Gauss-Chebyshev grid is taken to fit N×M Chebyshev polynomials using the Levenberg-Marquardt regression algorithm for the reaction systems of interest, where N and M denote the respective temperature and pressure i^{th} and j^{th} term and are predefined for different orders of accuracy. The logarithm of the rate coefficient is thus approximated as,

$$\log k(\widetilde{T},\widetilde{P}) = \sum_{i=1}^{N}\sum_{j=1}^{M} a_{ij}\varphi_i(\widetilde{T})\varphi_j(\widetilde{P})$$

The user specifies the size of the Gauss-Chebyshev grid. The current mechanism utilizes a 50x50 Gauss-Chebyshev grid. A typical 7×3 Chebyshev expression of rate constant in CHEMKIN would be,

```
HCO + O2  (+M)  <=> HCQ.*O  (+M)          1.00E+00     .000        0. ! ING341
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0438E+01  2.1076E+00 -2.1625E-01 -1.5689E+00/
    CHEB/  3.9500E-01  2.0033E-01 -6.9226E-01  2.4277E-02  2.9829E-02/
    CHEB/ -2.8569E-01 -1.9522E-02 -8.6222E-03 -1.0518E-01 -1.1326E-02/
    CHEB/ -7.5687E-03 -3.2695E-02 -3.4330E-03 -2.8109E-03 -6.8658E-03/
    CHEB/ -4.4532E-04 -5.6770E-04/
```

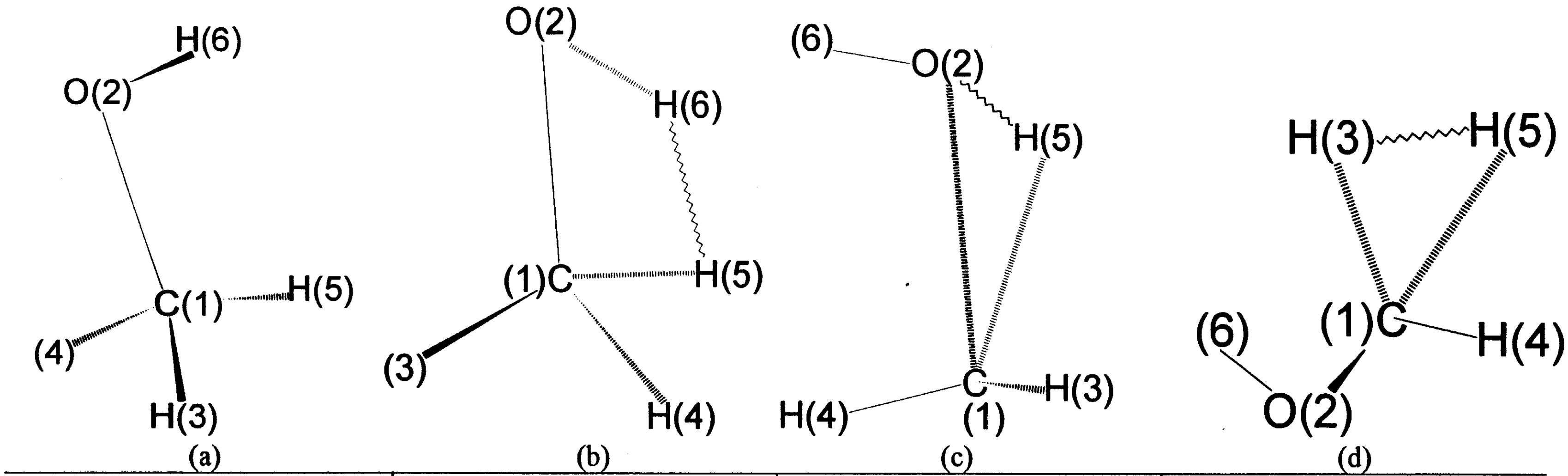
The first line provides the reaction information and the dummy rate constant expression in the Arrhenius expression, followed by a comment after the "!" mark. The dummy rate constant is not used in determining the rate constant of the reaction, but is required to be non-zero. The second line denotes the keyword "LOW / 1.0 0.0 0.0 /", which is used for fall-off parameters. The numerical values expressed here do not contribute to computation of the rate constant. Both the "pseudo" rate coefficient and the second line are done to minimize modifications from the original CHEMKIN code. The keyword "CHEB" denotes a rate coefficient expression in the Chebyshev polynomial format. A series of subroutines in the CHEMKIN library files are modified to accept the keyword "CHEB." The "7 3" are the "N" and "M" terms of the Chebyshev polynomials. The following coefficients (21 coefficients for a 7x3 Chebyshev expansion) correspond to the "a_{ij}" coefficients that represent the rate constant over a wide temperature and pressure range.

8.4Results And Discussion

8.4.1 Optimized Geometries of the CH_3OH Subsystem

The optimized geometry calculated by the prescribed CBS-APNO[209] method, QCISD/6-311G(d,p),[215] is shown in Table 8.1. Determination of the activated complex or transition states (TS) consists of an imaginary frequency and analysis of the geometric structure.

Table 8.1 Optimized Geometry Calculated at the QCISD/6-311G(D,P) Level of Theory for the CH_3OH System

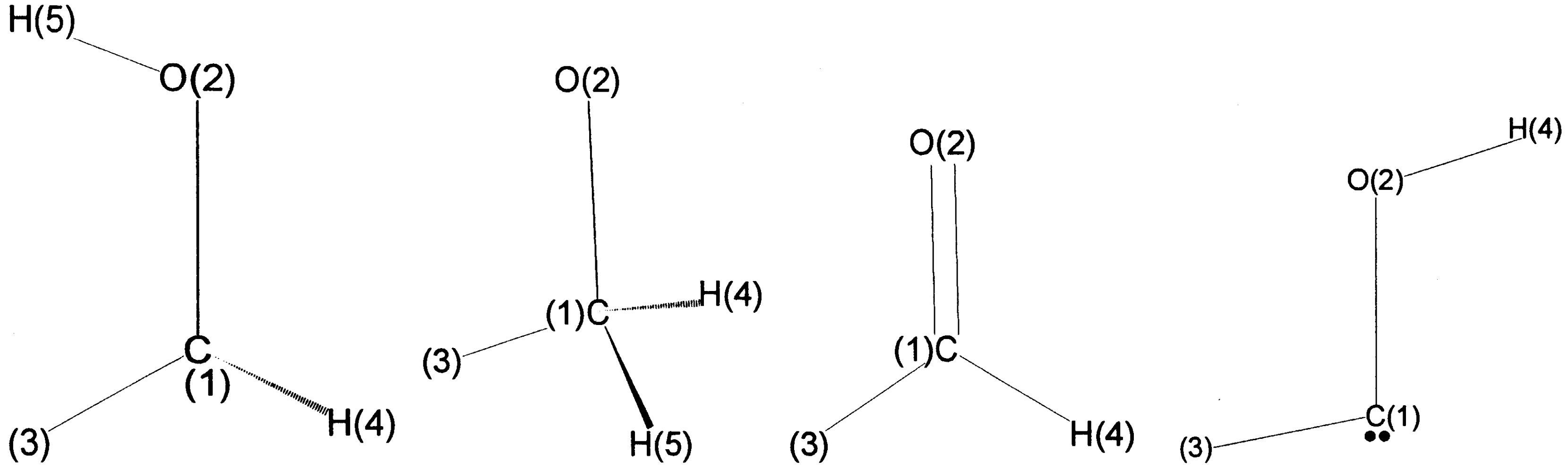


(a) (b) (c) (d)

CH_3OH		TS [CH_2OxH_2]		TS [CH_2xH_2O]		TS [HCOHxH_2]	
Parameter[†]	Value	Parameter[†]	Parameter[†]	Parameter[†]	Value	Parameter[†]	Value
R21	1.417547	R21	1.322864	R21	1.881842	R21	1.348582
R31	1.099689	R31	1.103625	R31	1.096920	R31	1.338209
R41	1.092881	R41	1.103625	R41	1.099310	R41	1.104309
R51	1.099690	R51	1.449977	R52	1.064410	R53	0.872592
R62	0.956922	R65	0.984260	R62	0.963036	R62	0.959971
A312	112.315654	A312	120.108987	A312	96.528451	A312	114.831362
A412	106.957197	A412	120.109021	A412	99.179145	A412	107.002123
A512	112.315599	A512	107.166999	A521	48.005093	A531	103.347867
A621	106.712384	A651	59.298010	A621	102.139719	A621	106.587653
D4123	118.555388	D4123	147.628287	D4123	251.024374	D4123	113.127995
D5123	237.110825	D5123	253.814137	D5213	237.426978	D5312	73.688300
D6213	61.443617	D6512	.000000	D6213	141.610898	D6213	74.041484

[†] **Parameters: "R" corresponds to atomic distance between respective atoms in Angstroms, "A" parameter is the bond angle in degrees and "D" is the dihedral angle in degrees.**

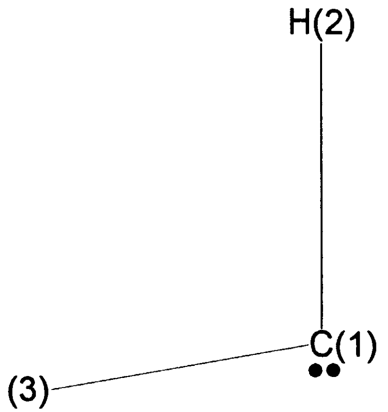
Table 8.1 Optimized Geometry Calculated at the QCISD/6-311G(D,P) Level of Theory for the CH_3OH System **(Continued)**



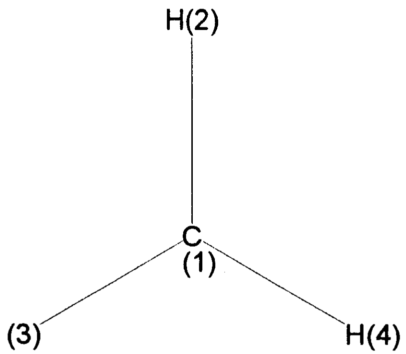
(e) (f) (g) (h)

CH_2OH		CH_3O		CH_2O		HCOH	
Parameter[†]	Value	Parameter[†]	Value	Parameter[†]	Value	Parameter[†]	Value
R21	1.370547	R21	1.379202	R21	1.206146	R21	1.317594
R31	1.088078	R31	1.099666	R31	1.108167	R31	1.118114
R41	1.083449	R41	1.105744	R41	1.108167	R42	0.963548
R52	0.957927	R51	1.099667	A312	122.197483	A312	101.806920
A312	118.253230	A312	112.738655	A412	122.197408	A421	107.019088
A412	112.856068	A412	105.253819	D4123	179.999568	D4213	180.000062
A521	107.597490	A512	112.738616				
D4123	146.920028	D4123	116.578750				
D5213	28.717385	D5123	233.157384				

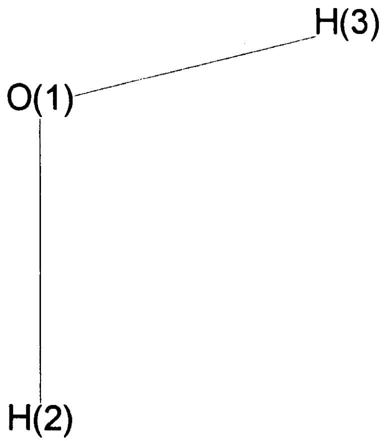
Table 8.1 Optimized Geometry Calculated at the QCISD/6-311G(D,P) Level of Theory for the CH_3OH System **(Continued)**



(i)



(j)



(k)

$^1CH_2$		CH_3		H_2O	
Parameter†	Value	Parameter†	Value	Parameter†	Value
R21	1.1164	R21	1.082667	R21	0.9574
R31	1.1164	R31	1.082666	R32	0.9574
A312	101.0004	R41	1.082666	A321	102.6892
		A312	120.000006		
		A412	119.999980		
		D4123	179.999572		

The TS for molecular elimination of hydrogen molecule from the methanol (denoted as TS1) has a C-O bond of 1.32Å, shorter than the normal C-O bond length of approximately 1.40Å and slightly longer than the normal C=O bond of 1.22Å.[216] B3LYP/6-31G(d,p) calculates the C-H bond as 1.46Å and QCISD/6-311G(d,p) calculates this bond to be 1.45Å, approximately 0.4Å longer than the normal C-H bond length. The O-H bond length calculated at B3LYP/6-31G(d,p) is 1.40Å, whereas the normal O-H bond length should be about 0.96 Å. QCISD/6-311G(d,p) shows that the H-H bond forming is about 0.98Å; the normal H-H bond is about 0.74Å.

The second TS is this subsystem is the dissociation to form water and the singlet methylene biradical. The reverse is an insertion reaction of the $^1CH_2$ into H_2O. The C-O bond distance in the TS at B3LYP/6-31G(d,p) is 1.92Å and at QCISD/6-311G(d,p) is 1.88Å. Both computed distances are significantly larger than the normal C-O bond length of 1.4Å. The O-H bond forming at QCISD/6-311G(d,p) is about 1.06 Å and at B3LYP/6-31G(d,p) is 0.99 Å, slightly longer than the stable O-H bond length of 0.96 Å. The C-H bond distance at QCISD/6-311G(d,p) is 1.41Å and at B3LYP/6-31G(d,p) is 1.72Å, the normal C-H bond distance is 1.08Å.

The third TS forms a hydrogen molecule and a singlet HCOH biradical (TS3). The C-O bond length contracts slightly from the 1.42Å to about 1.34Å. There are two C-H bond lengths of interest in TS3. Both C-H bond lengths are not the same, although both are dissociating from the carbon atom. QCISD/6-311G(d,p) reports the two dissociating C-H bond lengths as 1.34 Å and 1.76Å. B3LYP/6-31G(d,p) determine the two dissociating C-H bond length as 1.31 Å and 1.82Å. The forming H-H bond distance computed by B3LYP/6-31G(d,p) is 0.89 Å and at QCISD/6-311G(d,p) is 0.87Å.

The methanol subsystem also exhibits three channels where there are no barriers from the addition reaction: CH_3 + OH, CH_3O + H and CH_2OH + H. Since these reaction do not exhibit any barrier from the addition reaction, and therefore, one cannot utilize the saddle point requirement for TS calculations. Variational transition state theory (VTST) calculations on these three channels are performed at the CBS-Q level with the optimized geometry from B3LYP/6-31G(d,p). The reaction coordinate for these channels are determined by incremental increase in the bond distance of interest along the dissociation reaction path, starting with the full geometrically optimized methanol specie at the B3LYP/6-31G(d,p) level of theory. Single point calculation are then performed at the high level composite method of CBS-Q. Frequencies, ZPVE and thermal correction are determine at the B3LYP/6-31G(d,p) level. Enthalpy of formation are determine by the composite CBS-Q//B3LYP/6-31G(d,p)

Construction of the reaction coordinate for the three VTST channels is based on calculated parameters at incremental increases in the appropriate bond distance by 0.10 Å. The VTST calculation performed for the CH_3 + OH consists of varying the C-O bond length from 1.22 - 3.72Å in incremental steps of 0.10Å. Full optimized geometric structures of the CH_3—OH complexes along this reaction coordinate are optimized by B3LYP/6-31G(d,p). Single point calculation of these complexes are then calculated by CBS-Q method. The CH_3O + H channel, calculation of complexes along this reaction coordinate consists of changing the O-H bond distances from 0.67 – 4.47Å. The C-H bond length along the reaction path of the CH_2OH + H channel range from 0.99 – 3.89 Å. Entropy and Cp are determine at the B3LYP/6-31G(d,p) level of theory and enthalpy of formation at the CBS-Q//B3LYP/6-31G(d,p). No spin contamination is observed for the

the complexes. The theoretical spin contamination for this singlet system should be "zero", as was reported from the ab initio and DFT computations.

8.4.2 Thermodynamic Properties – ΔH_f^{298}, S^{298} and C_p(300-1500K)

Thermodynamic properties used in the current study are presented in Table 8.2. The current study uses the thermodynamic properties determine by the CBS-APNO method because both the CBS-APNO method and B3LYP/6-31G(d,p) did not have spin contamination and CBS-APNO is a higher theoretical level of computation. Entropy and heat capacities are calculated by statistical mechanics, as outlined above, with adjustment of frequency by scaling factors recommended by Scott and Radom.[62] Pitzer-Gwinn's[90] general treatment of hindered internal rotational contributions is used to adjust for the entropy and C_p values from the rotors.

The hinder rotor contributions for the complexes for the three VTST channels were treated by a modification of the Pitzer-Gwinn's method. All three channels have a rotor along the C—O bond. The hinder rotor contribution for transition state structures along the H—CH_2OH path, is treated by the Pitzer-Gwinn's general treatment. The only rotor in this system is not directly affected by the "stretching" of the C—H bond. The complexes along the CH_3—OH and CH_3O—H path are treated by a direct relationship between the total energy calculated and the sum total of the linear interpolation based on the hinder rotor contribution of the ground state CH_3OH and a free-rotor. The method is described by the following equations

$$\varphi = \frac{E_i - E_R}{E_p - E_R}$$

$$G_i = G_R + (G_P - G_R) \times \varphi$$

Table 8.2 Thermodynamic Properties for the CH_3OH System Calculated at the CBS-APNO Level of Theory.

SPECIES	Hf°_{298}	S°_{298}	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)
CH2SISO1	102.47	45.21	8.03	8.22	8.49	8.82	9.52	10.23	11.6
CH2T	94.15	46.69	8.16	8.46	8.77	9.07	9.66	10.25	11.51
CH2O	-26.08	52.19	8.26	8.95	9.86	10.83	12.62	14.09	16.47
CH2OH	-3.49	58.564	10.621	11.796	13.033	14.161	16.043	17.529	20.164
CH3	34.96	46.85	9.62	10.18	10.79	11.4	12.61	13.75	15.95
CH3O	5.26	54.26	9.25	10.75	12.32	13.78	16.23	18.14	21.25
CH3OH	-48	57.44	9.8	11.33	13.143	14.903	17.923	20.313	24.333
H2O	-57.8	45.07	7.95	7.95	7.95	7.97	8.07	8.3	9.15
HCOHISO1	25.82	56.983	9.784	10.203	10.85	11.538	12.803	13.845	15.677
TS1	42.49	55.62	9.33	11.2	13.26	15.21	18.51	21	24.79
TS2	38.46	60.12	10.48	12.3	14.153	15.813	18.473	20.473	23.693
TS3	35.63	57.27	11.43	13.4	15.15	16.67	19.13	21.06	24.34
OH	8.96	43.88	7.16	7.08	7.05	7.05	7.15	7.33	7.87
H2	0	31.21	6.9	6.95	6.99	7.02	7.1	7.21	7.72
*H	52.1	27.39	4.97	4.97	4.97	4.97	4.97	4.97	4.97

where,

E_i = total energy of the complex
E_R = total energy of the reactant/methanol
E_P = total energy of the sum of the products
G_i = hinder rotor contribution for the complex
G_R = hinder rotor contribution for the CH_3—OH rotor
G_P = hinder rotor contribution for free rotor

The calculated hinder rotor contribution for the complexes are then taken into account for the entropy and heat capacity values. Although the final products of this system do not have hinder rotors, the rotor within the complexes still needs to be taken into consideration.

The enthalpy of formation for reactants, TS, adducts and products are calculated at the CBS-APNO level of theory. The enthalpy of formation for methanol is well known and generally accepted to be –48.0 kcal/mol, and is, therefore, chosen as the reference.

8.4.3 Adduct Enthalpy of Formation

Isodesmic reaction analyses are performed on the two biradicals in this system, *i.e.* $^1CH_2$ and ^1HCOH, by the composite *ab initio* method CBS-APNO. The following illustrates the typical approach utilizing isodesmic reactions to obtain enthalpy of formation values.

$^1CH_2$	+	CH_4	=	CH_3	+	CH_3
-39.110152		-40.465122		-39.799533		-39.799533
X		-17.895		34.82		34.82

$$\Delta E(hartrees) = [(-39.799533) + (-39.799533)] - [(-39.110152) + (-40.465122)]$$

$$= -0.023792 hartrees = -14.92971792 \frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{rxn} = -14.92971792 \frac{\text{kcal}}{\text{mol}} = [(34.82) + (34.82)] - [(-17.895) + \text{X}]$$

$$X = 102.47 \frac{\text{kcal}}{\text{mol}}$$

^{1}**HCOH**	+	CH_4	=	CH_3OH	+	$^1CH_2$
-114.385809		-40.465122		-115.666623		-39.110152
X		-17.895		-48		102.47

$$\Delta E(hartrees) = [(-115.666623) + (-39.110152)] - [(-114.385809) + (-40.465122)]$$

$$= 0.074156 hartrees = 46.53363156 \frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{rxn} = 46.53363156 \frac{\text{kcal}}{\text{mol}} = [(-48.0) + (102.47)] - [(-17.895) + X]$$

$$X = 25.82 \frac{\text{kcal}}{\text{mol}}$$

Walch reports the difference in enthalpy between the triplet and singlet methylene to be 9.0 kcal/mol using complete-active-space self-consistent-field (CASSCF) / internally contracted configuration-interaction (CCI), *ab initio* calculations.[30] The current study also include the computed triplet methylene biradical and determine the difference in enthalpy between the singlet and triplet biradical at the CBS-APNO level of theory to be 8.99 kcal/mol, in good agreement with Walch.

8.5 Reaction Pathways

8.5.1 Methanol Subsystem

The initial decomposition steps of methanol, via six different channels, are analyzed and are presented. The barriers for $^1HCOH + H_2$, $^1CH_2 + H_2O$ and $CH_2O + H_2$ channels are calculated at CBS-APNO level of theory using Gaussian 94.[55] The sum of enthalpies for the respective product sets are compared with data from the study of Walch[30] and Harding, *et al.*[217] (Refer to Table 8.3). Harding, *et al.*'s data are calculated at the RMP4/6-31G(d,p) level of theory and Walch's data are derived using complete-active-space self-consistent-field (CASSCF) / internally contracted configuration-interaction (CCI), *ab initio* calculations.

Table 8.3 Comparison of Enthalpies in the CH_3OH System with Literature Data.

	CBS-APNO	Walch	Harding, *et al.*
CH_3OH	0	0.0	0.0
$CH_3O + H$	104.1		
$CH_2OH + H$	95.1		
$^1CH_2 + H_2O$	91.8	88.8	94.9
$^3CH_2 - {}^1CH_2$	-8.99	-9.0	
$CH_3 + OH$	90.5		
$^1HCOH + H_2$	72.8	71.1	71.1
$CH_2O + H_2$	20.1	18.1	16.4
TS $[H_2CO\cdots H_2]^\ddagger$	90.7	91.9	96.5
TS $[HCOH\cdots H_2]^\ddagger$	86.5	85.0	91.0
TS $[^1CH_2\cdots H_2O]^\ddagger$	83.6	82.3	84.6

The enthalpy for the transition state of $^1CH_2$ + H_2O channel, as reported also by Walch and Harding, *et al.*, is lower than the enthalpy of $^1CH_2$ + H_2O. The CH_3OH dissociation barrier, through the $^1CH_2$ + H_2O channel, in the current mechanism utilizes the difference in enthalpy between CH_3OH and $^1CH_2$ + H_2O. The reverse of $^1CH_2$ + H_2O channel does not have a barrier. The high-pressure limit for this dissociation channel is still calculated form canonical transition state theory, but based on an excited state of TS that has the same enthalpy as the enthalpy of $^1CH_2$ + H_2O. Entropy of the TS is also determined at the same energy level as the excited TS. The barriers of the reverse for ^1HCOH + H_2 and CH_2O + H_2 channels are calculated as –4.0 and 0.2 kcal/mol with respect to the energy level of CH_3 + OH channel. The rate constants for the three channels that do not have a saddle point are calculated by VTST from the dissociation of methanol. The high-pressure limit rate constants are shown in Table 8.4.

Table 8.4 High-Pressure Rate Constant Parameters Based on CBS-APNO and CBS-Q//B3LYP/6-31G(d,p)

Reaction	A	n	Ea (kcal/mol)	comments
$CH_3 + OH \rightarrow CH_3OH$	3.31E6	2.08	-1.76	a
$CH_3OH \rightarrow CH_3 + OH$	3.26E10	2.05	90.35	b
$CH_3OH \rightarrow CH_2OH + H$	1.64E7	2.55	91.95	b
$CH_3OH \rightarrow CH_3O + H$	1.19E7	2.39	99.61	b
$CH_3OH \rightarrow CH_2O + H_2$	1.10E9	1.28	90.23	c
$CH_3OH \rightarrow {}^1HCOH + H_2$	2.03E10	1.22	86.41	c
$CH_3OH \rightarrow {}^1CH_2 + H_2O$	2.87E11	1.60	92.54	d

a Microscopic reversibility
b Variational transition state theory calculation, based on CBS-Q//B3LYP/6-31G(d,p)
c Canonical transition state theory calculation, based on CBS-APNO.
d Adjusted canonical transition state theory calculation – thermochemical properties of the transition state taken at the corresponding energy level of the sum of the products.

The unimolecular dissociation shows that CH_3 + OH channel is dominant at moderate temperature (ca 1000°K) and $^1HCOH + H_2$ channel becomes important when temperature increases. After the initial decomposition of methanol, two H atom abstraction reactions are found to be the most significant to form CH_2OH and CH_3O radicals.

$$CH_3OH + H \rightarrow CH_2OH + H_2$$
$$CH_3OH + H \rightarrow CH_3O + H_2$$

There are no well-accepted rate coefficients for CH_3OH + H abstractions available. Warantz's data are adopted in Norton's mechanism and this study.[218] The ratio for forming CH_2OH to CH_3O is 4:1 and is temperature sensitive. The CH_2OH and CH_3O radicals decompose, via beta scission, to form formaldehyde:

$$\begin{aligned} &CH_2OH + M \rightarrow CH_2O + H + M \\ &CH_3O + M \rightarrow CH_2O + H + M \end{aligned}$$

These two unimolecular decomposition reactions are pressure dependent and are analyzed by QRRK analysis. Formaldehyde, an important intermediate, decays primarily by a H abstraction reaction: $CH_2O + H \rightarrow HCO + H_2$. The decomposition reaction of $HCO + M \rightarrow CO + H + M$ is found to be the dominant channel to form carbon monoxide, the final product undergoing pyrolysis.[219]

8.5.2 Methanol Oxidation

After methanol decomposition occurs, the following reactions play the important roles for methanol decay under oxidation condition and intermediate temperature. In contrast to pyrolysis where H abstraction is important, CH_3OH + OH is the critical reaction responsible for methanol decay. An important source of hydroxyl radical in the CH_3OH + OH abstraction reaction is from the hydroperoxy radical plus hydrogen atom to form two hydroxyl radicals.

$$\begin{aligned} &CH_3OH + OH &&\rightarrow &&CH_2OH / CH_3O + H_2O \\ &CH_3OH + HO_2 &&\rightarrow &&CH_2OH / CH_3O + H_2O \\ &CH_3OH + H &&\rightarrow &&CH_2OH / CH_3O + H_2 \end{aligned}$$

The reaction of CH_2OH radical with O_2 to form formaldehyde and hydroperoxy radical is the most important reaction for the production of the consequential intermediate, formaldehyde.

$CH_2OH + O_2 \rightarrow [\bullet OOCH_2OH]\#$ $\rightarrow .OCH_2OH + O$
$\rightarrow [HOOC\bullet HOH]\# \rightarrow HCO_2H + OH$
$\rightarrow [CH_2O...HOO\bullet]\# \rightarrow CH_2O + HO_2$
$\rightarrow [HOOCH_2O\bullet]\# \rightarrow CH_2O + HO_2$
$\rightarrow CH_2OH + O_2$ (Reverse - Null Reaction)
$\rightarrow \bullet OOCH_2OH$ (Stabilization)

There are two pathways to form $CH_2O + HO_2$. One pathway is through the addition of the O_2 onto the radical site on carbon, and through a 5-member ring isomerization step, beta-scissions to form $CH_2O + HO_2$. The second pathway is the direct abstraction of H from the hydroxyl group by the O_2, via $[CH_2O...HOO\bullet]^{\#}$, a hydrogen-bonded complex. The rate constant for the isomerization pathway is about two orders of magnitude slower than the pathway via hydrogen-bonded complex and reported experimental data at low pressure and temperature. The dominance of hydrogen-bonded channel is why the experimental kinetic data cannot be explained through the first route unless the inclusion of the hydrogen-bonded complex $CH_2O..HOO\bullet$ is incorporated into the reaction system.[22]

The formation of $CH_2O + HO_2$ via isomerization of $CH_2(OH)OO\bullet$ and $CH_2O..HOO\bullet$ adduct is the dominant channel for pressures < 1 atm and temperature < 2000°K. The stabilization adduct of $H_2C(OO\bullet)OH$ formation is important for pressures > 3 atm at 298°K and for pressures > 25 atm at 900°K, but this adduct rapidly reacts to HO2 + CH2O. The formic acid adduct is only important above 2000°K.

Formaldehyde then decays mostly by the reaction of $CH_2O + OH \rightarrow HCO + H_2O$. The decomposition reaction of $HCO + M \rightarrow CO + H + M$ is found to be the dominant channel to form carbon monoxide and $CO + O + M \rightarrow CO_2 + M$ to form final product of carbon dioxide.

8.5.3 Methanol Addition to Methane Oxidation Reactions

The comparison of methane and methanol oxidation can be described in three stages: initiation, propagation and oxidation. During initiation, formation of key radicals is determined by the most favorable thermochemical kinetic of the respective elementary reaction. Several channels of CH_3OH unimolecular decomposition are much lower in energy than CH_4 and, therefore, faster than CH_4 decomposition.

$CH_3OH \rightarrow CH_3 + OH \quad \Delta H_{rxn} = 92$ kcal/mol
$\rightarrow HCOH + H_2 \quad \Delta H_{rxn} = 71$ kcal/mol
$\rightarrow {}^1CH_2 + H_2O \quad \Delta H_{rxn} = 92$ kcal/mol
$\rightarrow CH_2O + H_2 \quad \Delta H_{rxn} = 74$ kcal/mol
$CH_4 \rightarrow CH_3 + H \quad \Delta H_{rxn} = 103$ kcal/mol

Abstraction of H atom radicals from CH_3OH is also more favorable than from CH_4: H–CH_2OH has a lower bond energy (97 kcal/mol) than H–CH_3 (105 kcal/mol). CH_2OH forms easier than CH_3 (from CH_4) by decomposition as well as through abstraction reactions. CH_2OH also has a much more rapid unimolecular decomposition channel relative to CH_3.

$CH_3 \rightarrow CH_2 + H \quad \Delta H_{rxn} = 108$ kcal/mol
$CH_2OH \rightarrow CH_2O + H \quad \Delta H_{rxn} = 30$ kcal/mol

Therefore, propagation reactions in CH_3OH oxidation occur more rapidly than CH_4 oxidation. Methyl oxidation, $CH_3 + O_2$, is much slower than $CH_2OH + O_2$. The difference between $CH_2OH + O_2$ and $CH_3 + O_2$ reaction system is that $CH_2OH + O_2$ has a low energy exit channel to $CH_2O + HO_2$, which explains the faster $CH_2OH + O_2$ reaction. That is, the barrier is below the energy level of initial $CH_2OH + O_2$.

CH_3 is the initial radical intermediate in CH_4 oxidation. The major reaction of CH_3 at low CH_3 concentration is reaction with O_2. CH_3 reacts with O_2 to form the $[CH_3OO]^*$ complex. The $[CH_3OO]^*$ complex undergoes four reactions: stabilization, formation of CH_3O + O, isomerize to $[CH_2OOH]^*$ and the reverse reaction. The $[CH_2OOH]^*$ isomer can also isomerize back to $[CH_3OO]^*$, stabilize or form the products CH_2O + OH. CH3OO can also react with CH3 to form two methoxy radicals.

High-pressure limit input parameters for the CH_3 + O_2 combination reaction to form the $[CH_3OO]^*$ complex, are taken from Cobos, *et al.*[220] The input parameters for dissociation of the complex back to reactants are calculated by microscopic reversibility over the temperature range 298 to 2000°K. Parameters for the CH_3O + O product channel are obtained from an estimate of 5.0×10^{13} $cm^3mol^{-1}s^{-1}$ for the high-pressure recombination rate constant via microscopic reversibility. The pre-exponential A factor for isomerization is taken from Transition State Theory with loss of one rotor ($\Delta S^{\ddagger} = -4.3$ cal/mol) and a degeneracy of 3. The activation energy is estimated as the sum of reaction enthalpy, ring strain (26 kcal/mol) and H abstraction (6 kcal/mol). The A-factor of the exit channel, CH_2O + OH, is calculated from microscopic reversibility, with the reverse taken as the addition of OH to CH_3CHO from Semmes, *et al.*[221] with an E_a estimated as 2 kcal/mol from the intrinsic activation energy expected for OH addition.

8.6 Formation of C_2 Species

8.6.1 $C_2H_5 + O_2$

The current mechanism also includes the kinetics of several C_2 species. The formation of C_2 species is from the combination of two methyl radicals to form ethane.[222] Abstraction of hydrogen from ethane by radicals from the radical pool forms ethyl radicals. The ethyl oxidation system used in the current mechanism is from Sheng, *et al.*, which is developed at the CBS-Q//B3LYP/6-31G(d,p) level of theory.[64] The dominant products in this products in this system is the formation of C_2H_4 + HO_2. This system is initiated by the addition of oxygen to the radical site on the ethyl radical forming an activated ethylperoxy adduct. The activated ethylperoxy adduct can undergo several channels: stabilization, isomerization and molecular elimination are the important channels. The isomerization channel forms a hydroperoxy-ethyl radical which can β-scission to form C_2H_4 + HO_2 or undergo a 3-member ring transition state and dissociate to form dioxirane plus OH. The molecular elimination channel to directly form C_2H_4 + HO_2 has a transition state below the entrance channel.

8.6.2 $C_2H_3 + O_2$

Vinyl radicals can be formed from hydrogen abstraction reactions from radicals on ethylene molecule. Ethylene can be formed from β-scission reaction of ethyl radicals to ethylene plus hydrogen atom. Ethylene can also be formed by the oxidation of ethyl radical + O_2, as discussed above. The vinyl oxidation system is obtained from Chang, *et al.*[60] This vinyl oxidation subsystem includes 5 possible stabilized adducts with multiple exit channels. Also included is the formation of the 3-member ring dioxiranyl radical, which has recently been recognized to be an important channel.[138,139] This subsystem is initiated by the addition of oxygen onto the radical site on the vinyl radical forming a vinyl-peroxy radical. The lowest energy process is peroxy radical attack on the ipso carbon, forming a di-oxirane methylene radical, which then isomerizes through an epoxide and cleaves the weak peroxy O—O bond. A further beta scission, preferring to maintain the ether linkage due conjugation, opens this epoxide ring to form the H_2C•-O-CHO isomer. This isomer beta scissions to form CH_2O + HCO before stabilization can occur. This sequence, although the lowest in energy, starts with a relatively tight transition state to form the 3-member ring. A higher energy, but looser, transition state is associated with dissociation of the peroxy radical to form C•CHO (vinoxy) + O. [Vinoxy is written in its more stable resonance form as a carbon-centered radical.] The energetics of this pathway is lower than usual for O-O bond breaking, since the vinoxy radical is resonantly stabilized and the well depth for vinyl + O2 is very deep – 45 kcal/mol. The peroxy radical can also undergo a concerted elimination to form acetylene + HO_2, isomerize via a hydrogen atom shift to form the vinyl hydroperoxide radical—which can then undergo beta-scission to form acetylene + HO_2 (the same products formed via the concerted HO_2 elimination from vinylperoxy), form ketenyl radical plus OH, or isomerize to form a 4-member ring—which then can ring open to form product pairs such as HCO + H_2CO or H + glyoxal, or redissociate to reactants.

8.6.3 $CH_3C{\bullet}O + O_2$ and $\bullet CH_2CHO + O_2$

These two subsystems are obtained from Lee and Bozzelli where thermochemical and kinetic properties are calculated at CBS-Q level of theory.[223] Both reaction systems initiate by the addition of oxygen onto the radical site forming a peroxy radical. One product set resulting from both systems is the formation of $CH_2CO + HO_2$. In both oxidation systems, the $CH_2CO + HO_2$ products can be formed through two channels; direct molecular elimination from the activated peroxy radical or via β-scission of the hydroperoxy radical formed from isomerization. The activated peroxy radical specie can stabilize or undergo direct molecular elimination or isomerize to a hydroperoxy radical. The hydroperoxy radical can then beta-scission to the $CH_2CO + HO_2$ product set. The other channel the hydroperoxy radical, resulting from the $CH_3C\bullet O$ + O_2 subsystem, can undergo is ring closure to form a carbonyl-oxirane specie plus OH. In the $\bullet CH_2CHO$ + O_2 subsystem, the hydroperoxy ethyl-aldehyde radical can also undergo a fast reaction, albeit complex, to form the product set consisting of OH + CO + H_2CO.

8.6.4 CH_3 + CH_3

The recombination reaction of two methyl radicals form an activated ethane molecule, with no barrier. The ethane molecule can stabilize, undergo simple dissociation (reverse reaction) or undergo two other reaction pathways. The first is a simple dissociation to form the ethyl radical plus hydrogen atom. The second channel is a molecular elimination channel, via a four member ring transition state, to form ethylene plus hydrogen molecule. The ethyl radical formed in this pathway, can also undergo addition reaction with O_2; this reaction pathway is explained above.

8.6.5 CH_3-O-CH_2 + O_2

The dimethyl-ether oxidation reaction used in this study is taken from the study by Yamada.[224] This oxidation system consists of two wells. The addition of oxygen molecule to dimethyl-ether forms an activated dimethyl-ether peroxy radical which can stabilize, undergo dissociation (reverse reaction) or isomerize to form $\bullet CH_2$-O-CH_2-OOH radical through a 6-member ring transition state. The $\bullet CH_2$-O-CH_2-OOH adduct can also undergo a reverse isomerization back to CH_3-O-CH_2-OO$\bullet$ radical or undergo a complex dissociation pathway to yield two formaldehyde molecule plus OH.

8.7 Comparisons of Model with Experimental Results

Only one pressure dependent CHEMKIN mechanism file is used to model all experimental concentration profiles under three different reaction systems (*i.e.* methanol pyrolysis, methanol oxidation and mixture of methanol and methane oxidation), at various temperatures and pressures. Methanol oxidation experiments are performed for both fuel lean and stoichiometric conditions. Controlled ratios of methane to methanol mixtures are conducted under stoichiometric conditions.

Methanol pyrolysis comparisons between the model with experimental results at 1 and 3 atm are illustrated in Appendix A, Figures A1 and A2. Good agreement for reactant decay and main product formations at 1 atm are observed. At 3 atm, the model results prediction is a slightly faster than experimental data. Methane formations are under predicted at both conditions. The model predicts faster decay of methanol than experimental at higher pressure. Formation of CO is higher in the model than experiment at 3 atm pressure. At 1 atm pressure, the model fits the experimental CO concentration well.

Comparisons of the methanol oxidation model and the experimental results at 873K and 5 atm for two equivalence ratios: stoichiometric ($\phi = 1$) and fuel lean ($\phi = 0.75$), are in illustrated in Figures A3 and A4. These show reasonable agreement for reactant decay and main products formation. The model is able to capture and predict the trend in formaldehyde formation. Reaction changes in methanol conversion and the intermediates or products profiles under conditions of excess oxygen (equivalence ratio = 0.75) are small relative to those illustrated at stoichiometric conditions throughout all temperatures and pressures studied, in both the experimental data and model predictions.

Comparison of methanol oxidation at 3 atm, shows the modeling result is a little slower than the observed experimental data, albeit the trends in concentration profiles of both major and minor products are predicted by the model. Figure A5 shows a time delay of 0.15 second for modeling result relative to experimental data. In general, there is a longer time delay for the model compared with experimental data at lower pressures. At lower pressure and temperature, decay will occur at longer residence times, which are unfortunately, out of the flow range of the flow controller used in this study.

The effects on the reactants' concentration profiles at various methane/methanol mixture ratios were performed. Concentration profiles of reactants, major and minor products from the model and experimental results are shown in Figures A6 and A7. The experimental conditions for both plots are at 873°K, 5 atm and equal initial concentrations of methane and methanol, with a fuel equivalence ratio of unity. The initial methane concentration in Figure A6 is 0.78% and in Figure A7 it is 0.39%. Agreements between model and experimental data on methane and methanol predictions are relatively well matched. The model predicts methanol reacts slightly faster than experimental data. The model under predicts carbon monoxide at both conditions, while carbon dioxide is over predicted. Formaldehyde formation between the model and experimental data has very good agreement. The model is able to predict a maximum inflection point in the concentration profile, which is observed in the experimental data as well. Trace product concentrations of ethane and ethylene, as predicted by the model, are higher than expected compared to experimental data.

Comparison of the current Chebyshev CHEMKIN mechanism file with recent experimental data on methanol oxidation from Held and Dryer's flow reaction are shown in Figures A8 – A12.[24] The uniqueness of Held and Dryer's data is that the oxidation data are provided at high pressures, up to 20 atm. This provides an opportunity to test this single CHEMKIN mechanism file with available experimental data over large pressure differences. Held and Dryer claimed the data they provided has an uncertainty in the absolute "zero time" and a time shift is needed for them to model the data.[24] Held and Dryer's flow reactor is also not performed under isothermal conditions, in some cases a rise in temperature of 50K is observed. The results from the current model are presented under isothermal conditions at the initial temperature provided by Held and Dryer.

Comparison of experimental data with the current model at 1043K with a pressure of 1 atm and a $\phi = 0.86$, the results are shown in Figure A8. The methanol and oxygen concentration in the model decays faster than in the experiment. A higher concentration of H_2 from the model is also seen. The model is able to predict the rapid changes in concentration with H_2O, CO, H_2 and CO_2, seen in the experimental data.

The second set of Held and Dryer's experimental data were at a higher pressure and lower temperature: T = 949K and P = 2.5 atm. (Refer to Figure A9) The predictions from the model for all the major species CH_3OH, O_2, H_2O, H_2, CO and CO_2 are in agreement with the experimental data.

The high pressure data are presented in Figures A10 – A12. Data presented in Figure A10 are performed at 10 atm, 810 K and a fuel equivalence ratio, ϕ, of 0.42. The overall formation and consumption of the major species reported are well characterized by the current model. The initial formation of H_2O is in agreement with the experimental data, at longer reaction times, the model under-predicts the H_2O concentration.

Comparison of model with experiments performed at 15 atm, 783 K and $\phi = 1.04$ is illustrated in Figure A11. The model agrees well with the experimental data, however, at long reaction times, H_2O concentration is under-predicted by the model. Figure A12 shows the comparison at 15 atm, and 781 K, similar to conditions in Figure A11, but at a higher fuel equivalence ratio at 2.59. The trends in the consumption and formation of reactant and products are well characterized by the current model. The model slightly over-predicts the final consumption of CH_3OH. The final concentration of CO is under-predicted by the model and the final concentration of H_2 is over-predicted by the model.

The comparisons of the "minor" products in this system, i.e. formaldehyde and formic acid, for all 5 conditions performed by Held and Dryer did not match exactly. The major pathway for formation of formic acid used in the current model first forms a methanoic-oxy radical from HCO + HO_2. The methanoic-oxy radical undergoes abstraction reactions with CH_3OH and CH_4 to form methanoic acid. However, the kinetics for the formation of formic acid is estimated by homologous reaction sets and not from CTST. A more rigorous treatment in obtaining better rate constants is recommended. Accurate experimental measurements of formaldehyde and formic acid are also difficult. This is due to the nature of formaldehyde and formic acid, which rapidly decays even while in transit through sampling lines.

The comparison of results with Held and Dryer, although do not show exact matches for all the cases presented, is encouraging. The current mechanism is able to predict and match all the consumption and formation trends of the major species over a wide pressure difference. All the comparisons with Held and Dryer's data are done with a single CHEMKIN mechanism file, which has over 200 rate coefficients for both the pressure and temperature dependence represented by a Chebyshev formalism. The methodology involved: fall-off analysis for chemical activation and unimolecular dissociation rate constants including quantum RRK analysis for k(E), is based on fundamental principles of thermochemistry and kinetics. The results from the comparison with experimental data over large pressure differences provides positive reinforcement the validity of the current method adopted to represent both temperature and pressure dependent rate coefficients in a single detail kinetic mechanism.

8.8 Conclusion

A single unified mechanism file capable of handling multiple pressures ranging from 10^{-2} to 100 atm over a temperature range of 250 to 2500°K has been constructed that can be used by the CHEMKIN integrator computer code. The pressure dependent reactions in the mechanism are based on fundamental principles of thermochemical kinetics. The mechanism file is expressed in a 7×3 Chebyshev polynomial set, and a driver for CHEMKIN has been developed that can interpret this Chebyshev data set.

Experimental data and a kinetic model has been developed and tested for various types of reaction system (*i.e.* pyrolysis, fuel lean, stoichiometric and fuel additive) at different system conditions (temperature, pressure and initial fuel concentration). Comparison between experimental and the kinetic model shows relatively good agreement and encouraging for this first mechanism. This mechanism can serve as a basis for future pressure dependent mechanism development studies on other higher molecular weight hydrocarbon and oxy-hydrocarbon system.

CHAPTER 9

AB INITIO CALCULATIONS AND KINETIC ANALYSIS OF CH_3NH_2, $CH_3N{\bullet}H + O_2$ AND $C{\bullet}H_2N{\bullet}H_2 + O_2$ SYSTEMS

9.1 Introduction

Monomethyl-amine (CH_3NH_2) is chosen as a surrogate molecule in this study to represent the fuel bound nitrogen. Literature sources show very limited experimental kinetic and thermochemical data are available for gas phase methylamine and the intermediate products resulting from its breakdown. Reaction analysis on unimolecular dissociation, abstraction of the amine and methyl hydrogen's by the radical pool (H, OH, O, CH_3, NH_2, and HO_2 radicals) and thermochemistry of the intermediates are not well established.[43,225] Thermochemical and kinetic analysis is also needed on the reaction pathways of the intermediate radicals and their reactions with O_2.

The most recent experimental study on methylamine thermal oxidation in a flow reactor by the research group of Robert Hesketh who is currently at Rowan University, Glassboro, NJ.[41] This study also developed a detailed reaction mechanisms for the methyl amine oxidation; but did not include detailed analysis or pressure dependence (fall off) of methyl amine dissociations (initiation) or chemical activation association reactions with by the radical species produced from loss of H atoms of the parent molecule reacting with O_2. Mao and Barat[37,61] did perform these more detailed analysis; but knowledge of the thermochemistry on the $C{\bullet}H_2NH_2$ and $CH_3N{\bullet}H$ radicals and the corresponding peroxy radicals and on the peroxy radical reaction paths has changed over the past 7 years.

Earlier studies on methyl amine oxidation are those of Jolley, *et al.*,[41,226] in the middle 1930's using batch reactors, and of the Cullis's research group[227-229] in the 1950s; Cullis also studied pyrolysis of methylamine.[227] A more recent study is that of Basevich in 1983, where he had a flow reactor with initialtion via reaction with Oxygen atoms, then subsequent reactions of both O atoms and O_2 with the initial products. Basevich[230] decided the CH_3NH—H bond reacted first, via O atom abstraction to form OH, in this CH_3NH_2 system.

The research group of Gardiner, *et al.*[225,231] studied methylamine thermal decomposition and oxidation respectively in shock tube experiments, with the reaction mechanisms developed mostly by empirical fit to model the data obtained. Lifshitz also studies the oxidation and ignition of methylamine / oxygen mixtures in a shock tube reactor from 1000 to 1300K, where mechanism from earlier studies of the Gardiner group were modified to model the data.

As noted above, accurate thermochemistry of methylamine radical and on the corresponding $CH_3NHOO\bullet$ and $\bullet OOCH_2NH_2$ peroxy radicals has not been available to these early researchers. One illustration, for example, is that the NH_2CH_2—H bond is now known to be ca 92 to 93 kcal/mole, while the CH_3NH—H bond is significantly stronger 101 to 102 kcal/mole. Thus the assumptions of Basevich, *et al.* on the initial reaction and intermediate are incorrect. The development and fits of the mechanism's to the experimental data is and was highly valuable and of importance to further work in fuel bound nitrogen chemistry; because of the importance of NOx in the environment.

Complete analysis would include thermochemistry, kinetic parameters, chemical activation and fall-off for pressure is needed on the unimolecular dissociation reactions, abstraction of the C—H and N—H's by the radical pool. The thermochemistry includes intermediate radicals: $C{\bullet}H_2NH_2$, $CH{=}N{\bullet}H$, $CH_2{=}NH({=}O)$, $C{\bullet}H{=}NHO$, $C{\bullet}H{=}NH$, and peroxy radicals formed via reactions of these radicals with O_2; plus isomers and isomers of the O_2 adducts. Kinetics includes thermochemistry plus four to five transition states (TS) for each system describing isomerization, and dissociations of these intermediate and oxygen adducts. These projects would result in several full journal publications; it is estimated that this comprises the major component of work in a separate PhD study. This is recommended to be important future research projects. The study would then need to test the mechanism against a number of experimental data sets in the literature. The current investigation is a more limited analysis using a detailed analysis of methylamine dissociation and the methyl and amine radical reactions with O_2 plus a recently published detailed reaction mechanism, which includes the breakdown products from the above reactions.

It is fortunate that there is the opportunity to start out in the development of a mechanism using a reasonably accurate evaluation on the thermochemistry of the initial reactions in thermal pyrolysis and oxidation. It is, however, unfortunate that there is so much work needed in the further reactions – work involving even further thermochemistry analysis with both chemical activation and unimolecular dissociation reaction analysis plus a pressure dependent anslysis on many system.

There are two significant, recent studies on the CH_2NH_2 radical, one by D.D.M. Weyner, *et al.*[45] and by Radom's research group[232] providing results of high level ab initio calculations for the $C{\bullet}H_2NH_2$ radical showing the bond energy of 91.8 +/- 2 kcal/mole. Melius has also calculated the CH_3NH.radical with a bond energy of *ca* 103 kcal/mole.[44] Jursic[42] also calculated this bond energy with a range of 98 to 108 kcal/mole. The value from Melius is chosen. These values for $\Delta H_{f(298)}$ from these studies on the two radicals are selected.

The research group of Mats Johnson has estimated the $\bullet OOCH_2NH_2$ peroxy species as having a well depth of 28.7 to 36.9 kcal/mole and using *ab initio* calculations with heats of atomization (not isodesmic reaction analysis).[233] This is a significant range in well depth and the value needs to be more accurately determined to estimate the kinetics of $C\bullet H_2NH_2 + O_2$ reaction rate constants and paths. Survey of currently available literature sources do not show any high level study on the Amine radical –OO well depth, $CH_3N\bullet H + O_2 \Leftrightarrow CH_3NH—OO\bullet$.

The enthalpies of these species are calculated in the current study to obtain accurate well depth, which are needed for chemical activation analysis. Hydroperoxides and peroxy radicals are from current calculations. Other thermochemical properties for this system are from literature sources, where available, but mostly from computational methods, such as THERM[53], MOPAC[133] and Gaussian 94.[55] Density functional theory calculations at the B3LYP/6-31G(d,p)[58,129] level and the composite G2(MP2)[167] have been performed on the species in the complex reaction system for $CH_3N\bullet H + O_2$ and $C\bullet H_2NH_2 + O_2$: the results calculated from Gaussian94 (*i.e.* vibrational frequencies, moments of inertia, zero point vibrational energy, thermal correction to enthalpy, total energies at 0 K and total energies at 298 K) for these two oxidation system are shown in Table 9.1. Examples from two results from the G2(MP2) level of calculation are presented below.

Table 9.1 Vibrational Frequencies (cm^{-1}) for Species in Ethyl Oxidation System Calculated at B3LYP/6-31G(d,p) Level of Theory

Species	Frequencies$^{\#}$							Moment of Inertia (GHz)
CH_3NH_2	327.6	857.2	981.3	1067.8	1182.2	1358.2	1473.0	103.0
	1512.8	1532.1	1674.8	2966.2	3072.4	3112.5	3491.4	22.7
	3574.1							21.9
$CH_3N\bullet H$	261.6	957.4	1013.7	1047.1	1348.4	1407.6	1494.3	124.2
(1a)	1500.7	2960.5	3000.4	3106.9	3366.6			25.3
								24.2
$CH_3NHOO\bullet$	46.9	234.3	414.7	534.6	701.1	971.0	1011.4	23.4
(1b)	1136.2	1185.6	1265.7	1446.2	1467.6	1491.4	1522.7	5.2
	3024.7	3112.4	3145.8	3452.5				5.0
$\bullet CH_2NH(OOH)$	101.5	182.6	267.1	381.5	508.2	607.2	650.7	25.4
(1c)	876.6	911.7	1147.7	1235.1	1357.0	1445.6	1489.6	4.9
	3164.1	3288.2	3512.6	3727.6				4.7
$CH_2{=}NH$	1079.1	1094.7	1171.4	1379.4	1508.0	1732.9	3027.1	197.4
(1d)	3130.7	3428.6						34.8
								29.5
$\bullet CH_2NH({=}O)$	571.6	700.7	770.8	993.2	1080.7	1311.2	1460.6	75.8
(1e)	1507.0	1693.4	3199.9	3265.2	3332.8			11.7
								10.2
$CH_3N\bullet OOH$	108.9	163.7	180.8	330.3	546.7	904.5	989.3	41.4
(1f)	1058.1	1103.7	1202.1	1430.2	1455.2	1481.8	1493.9	4.6
	3014.1	3072.6	3150.9	3652.6				4.2
$CH_3N{=}O$	169.7	573.6	840.1	967.3	1157.1	1378.2	1465.3	60.7
(1g)	1465.8	1681.5	3034.2	3118.8	3152.3			11.4
								10.2

The frequencies reported are not scaled. Imaginary frequencies are denoted by "(*i*)."

Thermochemical kinetic parameters are estimated from literature and from techniques, such as homologous reactions and Evans-Polanyi relationship; in addition to MOPAC, *ab initio*, density functional and group additivity.

9.2 Isodesmic Working Reaction Sets

Isodesmic reaction analyses are performed on the two adducts in this system, *i.e.* C•H_2NH_2 and the •$OOCH_2NH_2$. The composite *ab initio* method is at the G2 level of calculation using the optimized geometric structure determine at the MP2(full)/6-31G(d) level of calculation. The reference enthalpy of formation for the stable molecules, C_2H_6 and CH_3NH_2, are from literature[234] and the radicals are obtained from Sheng, *et al.*[64] The following illustrates the approach utilizing isodesmic reactions to obtain enthalpy of formation values.

Species	*C•H_2NH_2*	+	C_2H_6	=	CH_3NH_2	+	C_2H_5
E (hartrees)	-95.011709		-79.625251		-95.660138		-78.963182
H_f(298K)	*X*		-20.24		-5.49		28.6

E values are from G2(MP2) level of theory

$$\Delta E(hartrees) = [(-95.660138) + (-78.963182)] - [(-95.011709) + (-79.625251)]$$

$$= -0.01364 hartrees = 8.56 \frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{rxn} = 8.56 \frac{\text{kcal}}{\text{mol}} = [(-5.49) + (28.6)] - [X + (-20.24)]$$

X = **34.79 kcal/mol**

The ΔH_f(298K) for C•H_2NH_2 calculated from isodesmic working reactions using total energies determined at the G2(MP2) level of theory is 34.79 kcal/mol. THERM[53] estimates the enthalpy of formation for C•H_2NH_2 radical to be 36.26 kcal/mol. Brinck, *et al.*[233] reports a value of 37.11 kca/mol at the G2MS[235] level of theory. The enthalpy of formation for the peroxy-methyl-amine radical is based on the following isodesmic working reaction set.

Species	*$\bullet OOCH_2NH_2$*	+	C_2H_6	=	CH_3NH_2	+	$CH_3CH_2OO\bullet$
E (hartrees)	-229.182771		-79.625251		-95.660138		-229.1702082
H_f(298K)	***Y***		-20.24		-5.49		-6.72

E values are from G2(MP2) level of theory

$$\Delta E(hartrees) = [(-95.660138) + (-229.1702082)] - [(-145.211921) + (-79.625251)]$$

$$= 0.006825846 hartrees = 4.28 \frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{rxn} = 4.28 \frac{\text{kcal}}{\text{mol}} = [(-5.49) + (-6.72)] - [Y + (-20.24)]$$

***Y* = 3.75 kcal/mol**

The ΔH_f(298K) for $\bullet OOCH_2NH_2$ calculated from isodesmic working reactions using total energies determined at the G2(MP2) level of theory is 3.75 kcal/mol. THERM estimates the enthalpy of formation for $\bullet OOCH_2NH_2$ to be 1.87 kcal/mol. The enthalpy of formation determine by G2(MP2) with isodesmic working reactions are used in this study. The thermodynamic properties for the CH_3NH_2, $CH_3N\bullet H$ + O_2 and $C\bullet H_2NH_2$ + O_2 system are listed in Table 9.2.

Table 9.2 Thermodynamic Properties Used in the CH_3NH_2, $CH_3N{\bullet}H + O_2$ and $CH_2N{\bullet}H_2 + O_2$ Study

SPECIES	Hf°_{298}	S°_{298}	Cp(300)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)	Comment
$C{\bullet}H_2NH_2$	36.26	57.92	13.01	14.95	16.82	18.26	20.75	22.64	25.99	a
$CH_3N{\bullet}H$	43.26	59.67	11.13	13.16	15.1	16.77	19.42	21.44	25.17	a
CH_3NH_2	-5.5	57.98	12.01	14.38	16.73	18.86	22.44	25.26	0	b
$HOOC{\bullet}H_2NH_2$	4.67	77.25	19.17	22.42	25.08	27.2	30.57	33.14	0	a, c
${\bullet}OOCH_2NH_2$	1.87	74.74	18.22	21.64	24.44	26.74	30.35	33.07	0	a
$H_2C{=}NH$	21.85	55.94	9.12	10.7	12.29	13.84	16.62	18.56	21.38	b
CH_2NHO	14.11	59.69	11.59	14.08	16.32	18.32	21.2	23.39	26.84	d
$HOOCH_2N{\bullet}H$	14.77	79.86	19.03	22.28	24.9	26.95	30.03	32.3	0	a
$H_2NO{\bullet}$	15.9	55.7	9.29	10.39	11.36	12.22	13.67	14.84	16.78	b
$CH_3N{=}O$	18.5	62.62	12.19	14.2	16.13	17.85	20.63	22.72	26.1	d
NH_2CHO	-46.66	64.47	13.74	15.73	17.82	19.43	21.82	23.87	0	b
$CH_2{=}NH$	21.85	55.94	9.12	10.70	12.29	13.84	16.62	18.56	21.38	e
$C{\bullet}H_2NH_2$	34.79	59.11	12.18	14.33	16.23	17.81	20.40	22.44	25.80	f
${\bullet}OOCH_2NH_2$	3.75	74.56	18.37	21.92	24.74	27.01	30.38	32.80	36.53	f
$CH_3NHOO{\bullet}$	35.72	74.026	18.015	21.835	24.916	27.332	30.875	33.338	36.973	f

Units: Enthalpy [=] kcal/mol; S [=] cal/mol-K; Cp [=] cal/mol-K.

a: THERM b: Dean, A.M.; Bozzelli, J.W.; "Combustion of Nitrogen Chemistry"; Gas-Phase Combustion Chemistry, Gardiner, Jr., W.C. (Editor), Springer-Verlag, NY, 2000. c: This molecular specie is not stable, see text for details. The thermodynamic properties are presented for completeness. d: MOPAC, PM3 e: Melius, C., website: http://z.ca.sandia.gov/~melius/. f: this study.

9.3 CH_3NH_2

The unimolecular dissociation of monomethyl-amine has four channels: one molecular elimination channel and three simple dissociation channels, where reverse (association) has no barrier. The potential energy diagram is shown in Figure 9.1. The barrier for the molecular elimination channel ($CH_3NH_2 \rightarrow CH_2{=}NH + H_2$) is estimated to be similar to the molecular elimination of $C_2H_6 \rightarrow C_2H_4 + H_2$. This estimated barrier is to be 102.5 kcal/mol, based on the TS calculations from Gordon, *et al.*[236,237] The dissociation barriers are estimated to be equal to the enthalpy of reaction. The enthalpy of formation for CH3N•H is determined from THERM since experimental or literature data on species with radical site on nitrogen are not available.

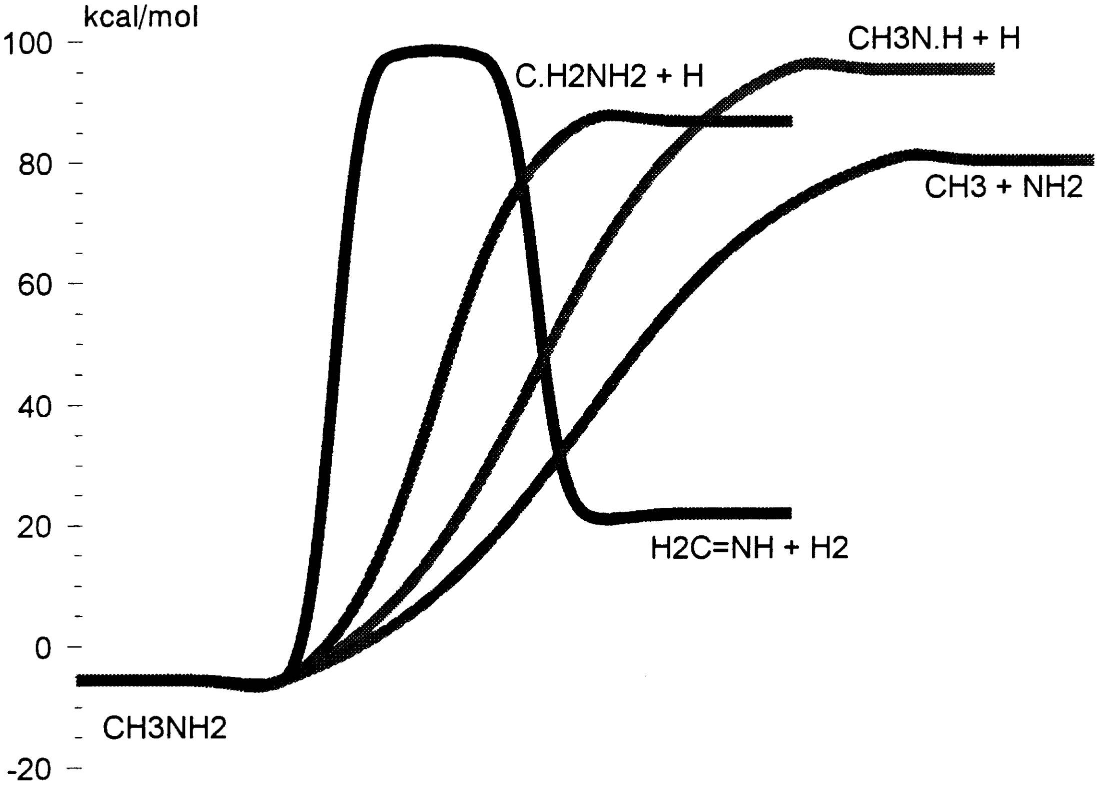


Figure 9.1 Potential energy diagram for dissociation of CH_3NH_2

The pre-exponential A-factors for simple dissociation reactions are obtained from Dean and Bozzelli.[36] The high-pressure limit rate constants are shown in Table 9.3. The CH_3—NH_2 bond cleavage is lowest energy path at 84.6 kcal/mol. The methyl C—H bond dissociation is next lowest at 92.3 kcal/mol and the amine N—H bond is highest simple dissociation reaction at 103 kcal/mol; these two association/dissociation reactions are assumed to have an activation barrier equal to the ΔH_{rxn}. Enthalpy of reaction is determined from the G2(MP2) calculations in this study. The H_2 elimination has a tight TS and a higher E_a than the three dissociation reactions and will be unimportant.

A multi-frequency QRRK analysis to determine *k(E)* with master equation analysis for collisional deactivation is utilized to determine the rate coefficients for the chemical activation and thermal dissociation. This analysis is described in detail in Chang, *et al.* and Sheng, *et al.*'s publications.[60,64] Figure 9.2 illustrates the thermal dissociation rate constants at 1 atm pressure over a temperature range from 300 – 3000 K and Figure 9.3 shows the rate constant at 1200 K over a pressure range of 10^{-4} to 100 atm. Figure 9.2 shows that at 1 atm, the dissociation path to form $CH_3 + NH_2$ is dominant over the entire temperature range of 300 – 3000 K. The dissociated products $C{\bullet}H_2NH_2 + H$ is of minor importance, being slower than $CH_3 + NH_2$ by about 3 orders of magnitude. The dissociation channels to $CH_3N{\bullet}H + H$ and the molecular elimination channel are unimportant, being over 10 orders of magnitude slower than $CH_3 + NH_2$. Results at 1200 K are shown in Figure 9.3 and the most important channel is the $CH_3 + NH_2$, especially at low pressures, at 10^{-4} atm, $CH_3 + NH_2$ is faster than $C{\bullet}H_2NH_2 + H$, the next fastest reaction, by over 8 orders of magnitude. Figure 9.3 also indicate that all four channels are in the fall-off regime over the pressure range of 10^{-4} to 100 atm. At pressure above 1 atm, $C{\bullet}H_2NH_2$ + H channel becomes of minor importance about 3 orders of magnitude slower than $CH_3 + NH_2$, and becoming more important as pressure increases.

Table 9.3 High-Pressure Limit Rate Constants

Reaction	A	n	Ea (kcal/mol)	comments
Dissociation of CH_3NH_2				
$CH_3 + NH_2 \rightarrow CH_3NH_2$	2.3E13		0.	a
$CH_3NH_2 \rightarrow CH_3 + NH_2$	1.2E16		84.6	a
$CH_3NH_2 \rightarrow C{\bullet}H_2NH_2 + H$	2.0E15		92.3	a, b
$CH_3NH_2 \rightarrow CH_3N{\bullet}H + H$	1.8E15		103.4	a, b
$CH_3NH_2 \rightarrow H_2C{=}NH + H_2$	4.9E13		103.5	a
Abstraction Reactions				
$CH_3NH_2{+}H \rightarrow C{\bullet}H_2NH_2{+}H_2$	5.60E+08	1.5	5.46	a
$CH_3NH_2{+}O \rightarrow C{\bullet}H_2NH_2{+}OH$	4.00E+08	1.5	5.20	a
$CH_3NH_2{+}OH \rightarrow C{\bullet}H_2NH_2{+}H_2O$	3.60E+06	2.0	0.24	a
$CH_3NH_2{+}CH3 \rightarrow C{\bullet}H_2NH_2{+}CH_4$	1.50E+06	1.9	9.17	a
$CH_3NH_2{+}NH_2 \rightarrow C{\bullet}H_2NH_2{+}NH_3$	2.80E+06	1.9	5.49	a
$CH_3NH_2{+}H \rightarrow CH_3N{\bullet}H{+}H_2$	4.80E+08	1.5	9.71	a
$CH_3NH_2{+}O \rightarrow CH_3N{\bullet}H{+}OH$	3.30E+08	1.5	6.35	a
$CH_3NH_2{+}OH \rightarrow CH_3N{\bullet}H{+}H_2O$	2.40E+06	2.0	0.45	a
$CH_3NH_2{+}CH_3 \rightarrow CH_3N{\bullet}H{+}CH_4$	1.60E+06	1.9	8.84	a
$CH_3NH_2{+}NH_2 \rightarrow CH_3N{\bullet}H{+}NH_3$	1.80E+06	1.9	7.14	a
$CH_3N{\bullet}H + O_2$				
$CH_3N{\bullet}H + O_2 \rightarrow CH_3NH(OO{\bullet})$	2.8E15	-2.5	0.	a, c
$CH_3NH(OO{\bullet}) \rightarrow CH3N{\bullet}H + O_2$	2.43E31	-5.81	15.1	d
$CH_3NH(OO{\bullet}) \rightarrow H_2CNHO + OH$	4.E12		33.51	e
$CH_3NH(OO{\bullet}) \rightarrow H_3CN{=}O + OH$	8.E12		37.0	e
$CH_3NH(OO{\bullet}) \rightarrow CH_2{=}NH + HO_2$	8.80E+05	2.24	29.61	f
$C{\bullet}H_2NH_2 + O_2$				
$CH_2NH_2 + O_2 \rightarrow {\bullet}OOCH_2NH_2$	2.11E13			g
${\bullet}OOCH_2NH_2 \rightarrow C{\bullet}H_2NH_2 + O_2$	2.55E+04	4.10	31.05	h
${\bullet}OOCH_2NH_2 \rightarrow HOOCH_2N{\bullet}H$	2.E12		36.0	i
${\bullet}OOCH_2NH_2 \rightarrow NH_2CHO + OH$	4.E12		46.0	j
${\bullet}OOCH_2NH_2 \rightarrow CH_2O + H_2N{=}O$	4.E12		46.3	j
${\bullet}OOCH_2NH_2 \rightarrow H_2C{=}NH + HO_2$	8.80E+05	2.24	31.61	k
$HOOCH_2N{\bullet}H \rightarrow {\bullet}OOCH_2NH_2$	1.17E+12	-0.16	18.30	h
$HOOCH_2N{\bullet}H \rightarrow H_2C{=}NH + HO_2$	1.28E+11	0.52	16.15	l

(a) Dean, A.M.; Bozzelli, J.W., "Gas-Phase Combustion Chemistry"; Gardiner, W.C. (Editor), Verlag-Springer, 2000. (b) Ea calculated based on G2(MP2) energy using isodesmic working reaction sets. (c) Estimated using $NH_2 + O_2$. (d) A-factor fitted from Af/Ar ratio, Ea = ΔHrxn. (e) The isomer formed is unstable and immediately dissociates to form products. (f) Estimated A-factor to be similar to molecular elimination of $C_2H_5OO{\bullet} \rightarrow C_2H_4 + HO_2$ (g) Masaki, A; Tsunashima, S.; Washida, N.; JPC, 99, 1995. (h) Rate constant determine from microscopic reversibility. (i) Ea is estimated to be 36 kcal/mol. (j) A-factor estimated from isomerization of 4-member ring. (k) Estimated A-factor to be similar to molecular elimination of $C_2H_5OO{\bullet} \rightarrow C_2H_4 + HO_2$; Ea to be 2 kcal/mol higher than reference reaction. (l) Estimate rate constant to be similar to hydrogen shift of $C_2H_5OO{\bullet} \rightarrow {\bullet}CH_2CH_2OOH$.

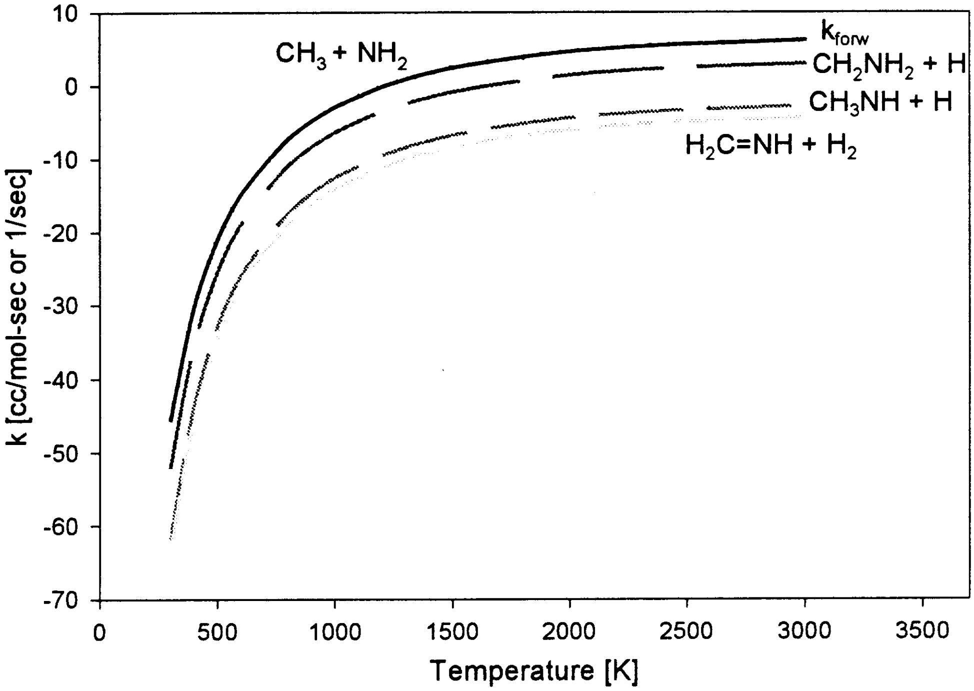


Figure 9.2 Thermal dissociation of CH_3NH_2 at 1 atm

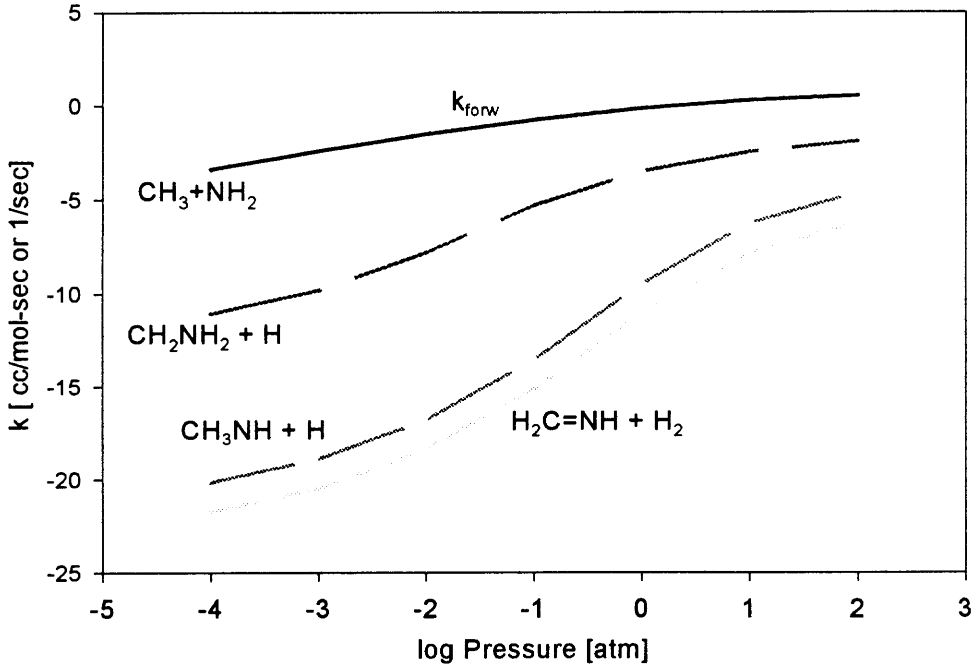


Figure 9.3 Thermal dissociation of CH_3NH_2 at 1200 K

9.4 Abstraction of Hydrogen from CH_3NH_2 by Radicals

The formation of $CH_3N{\bullet}H$ and $C{\bullet}H_2NH_2$ can also occur by abstraction reactions by radical species in the radical pool, *i.e.* H, O, OH, CH_3 ... etc. The abstraction reaction rate constants used in the current analysis are estimated from procedures published by Dean and Bozzelli.[36] The rate constants are presented in the form A T^m exp (-E/RT) in Table 9.3.

9.4.1 $CH_3N{\bullet}H + O_2$

Reaction of oxygen with $CH_3N{\bullet}H$ forms an adduct that has a shallow well, with a reverse barrier of only *ca* 13 kcal/mol. The H_f(298K) of this peroxy adduct is calculated from G2(MP2) level of theory, relative to the ${\bullet}OOCH_2NH_2$ adduct (non isodesmic reaction analysis), to be 35.5 kcal/mol. This shallow well is similar to that for NH_2 radical reaction with O_2, which only has a 6 kcal/mol well depth. The methyl group here increases the well depth by factor of two, to 13 kcal/mol. The potential energy diagram of this oxidation system is shown in Figure 9.4. The pre-exponential A-factor for the association rate constant is estimated to be similar to that of NH_2 + O_2, $k = 2.83 \times 10^{15} T^{-2.5}$, with no barrier. The reverse reaction rate is estimated from microscopic reversibility for an activation barrier equal to the enthalpy of reaction. The hydrogen transfer reaction (isomerization) moving a hydrogen from the methyl to the peroxy will form the $C{\bullet}H_2NH(OOH)$, through a 5 member ring TS. DFT calculation at the B3LYP/6-31G(d,p) for the $C{\bullet}H_2NH(OOH)$ specie shows that this radical is not stable and immediately dissociates to the products $H_2C{=}NHO$ + OH.[35] It is interesting to note that $CH_2{=}NH({=}O)$ has five bonds (2 double + 1 single) on the nitrogen. Here the two electrons which are normally in the nitrogen lone pair orbital, are in π orbitals for π-bonding. The bonding on nitrogen-oxygen species is often complex and detailed study of the enthalpies, structures and TS of nitrogen-carbon-oxygen-hydrogen molecules are also complex.

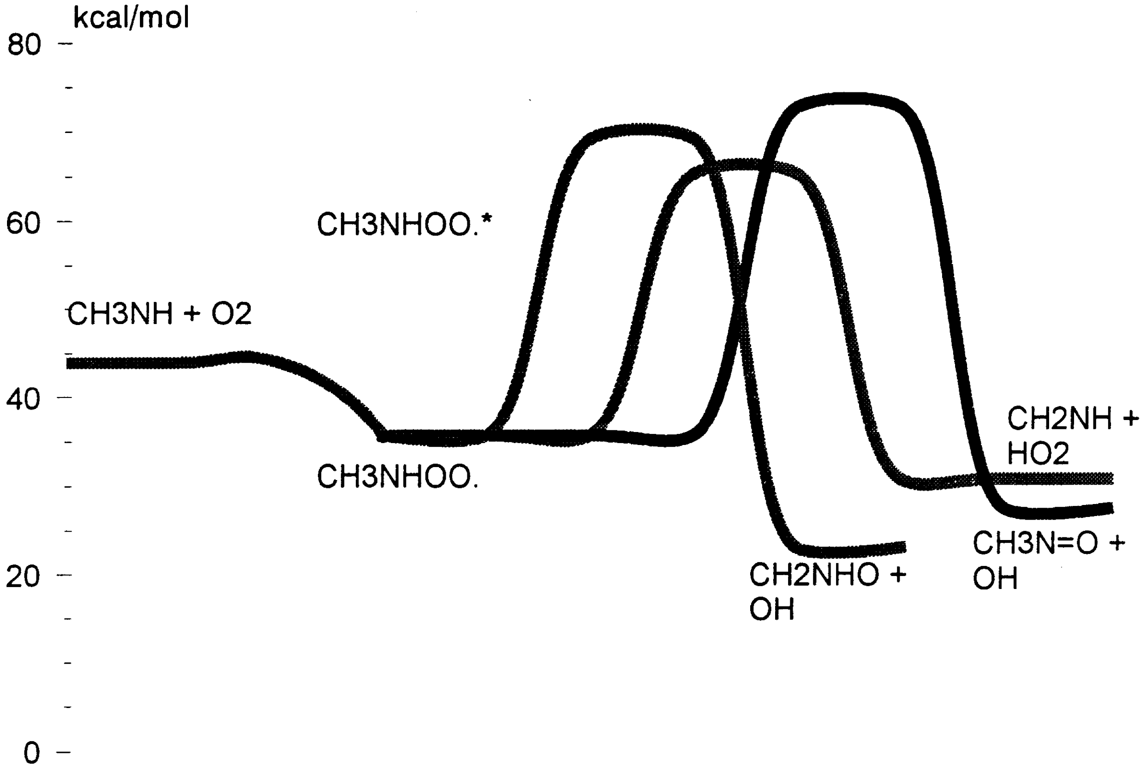


Figure 9.4 Potential energy diagram for $CH_3N\bullet H + O_2$

For the kinetic parameters, the pre-exponential A-factor is estimated by the loss of 2 rotors with a reaction degeneracy of 3, and the activation barrier is estimated from ΔH_{rxn} + 5-member ring strain + $E_{abstraction}$. The second isomerization channel in this system is a hydrogen shift through a 4-member ring on the ipso nitrogen to form $CH_3N\bullet(-OOH)$. An HOO- bonded to a nitrogen with a radical site is expected to behave similarly to $CH_3C\bullet H(-OOH)$,[188] where the weak peroxide $CH_3N\bullet O—OH$ bond will readily break to form the more stable product set $CH_3N{=}O + OH$. The intermediate "unstable" (quasi-stationary point species), $C{\bullet}H_2NHOOH$ and $CH_3N{\bullet}OOH$, are not shown on the potential energy diagram in Figure 9.4. The high-pressure limit rate constants for this oxidation system are shown in Table 9.3.

Figures 9.5 illustrates the rate constants for the chemical activation of $CH_3N{\bullet}H$ + O_2 at 1 atm from 300 – 3000 K and Figure 9.6 illustrates the rate constants at 1200 K over a pressure of 10^{-4} – 100 atm. At 1 atm, the reverse reaction is the fastest, and the rate of stabilization decreases as temperature increases. The well depth of only 13 kcal/mol, *i.e.* a very shallow well, results in little stabilization and predominantly reaction is in the reverse direction. The rate for the two other product channels, CH_2NHO + OH and $H_3CN{=}O$ + OH, increases with temperature, but even at 2000 K it is still 3 orders of magnitude slower than the reverse reaction. At 1200 K, the predominant reaction is the reverse reaction back to $CH_3N{\bullet}H$ + O_2. Rate of stabilization is slower than reverse by three orders of magnitude at 10 atm. Figure 9.7 shows the dissociation of the stabilized adduct at 1200 K over a pressure range of 10^{-4} – 100 atm. The dissociation of the stabilized adduct is nearly completely back to $CH_3N{\bullet}H$ + O_2, result of the low 13 kcal/mol barrier and loose transition state where the pre-exponential A-factor is 9.56 x 10^{13} sec^{-1} at 1000 K.

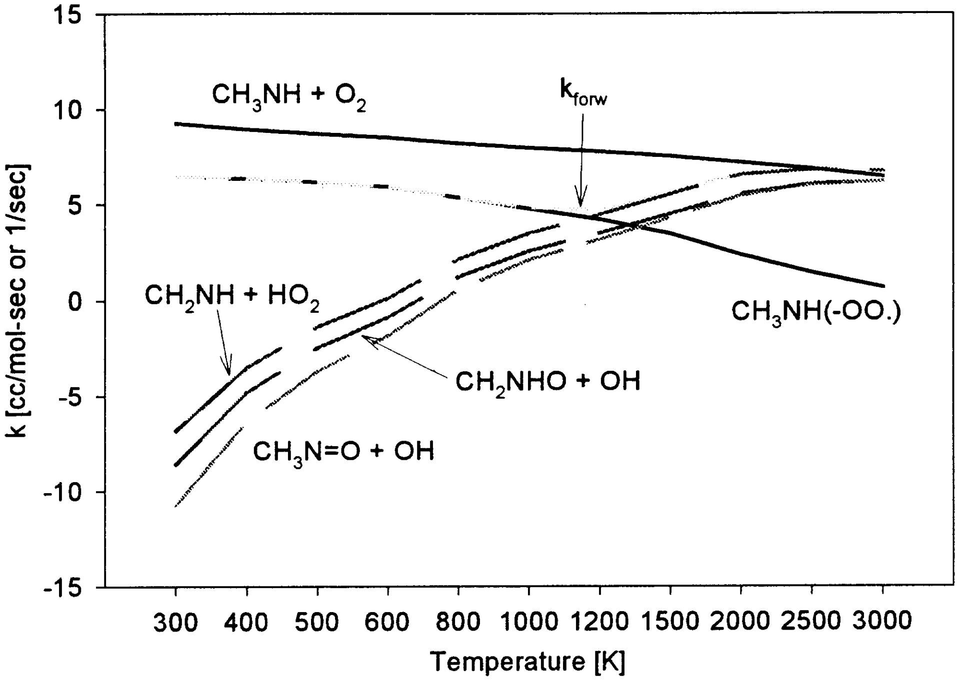


Figure 9.5 Chemical activation of $CH_3N{\bullet}H + O_2$ at 1 atm

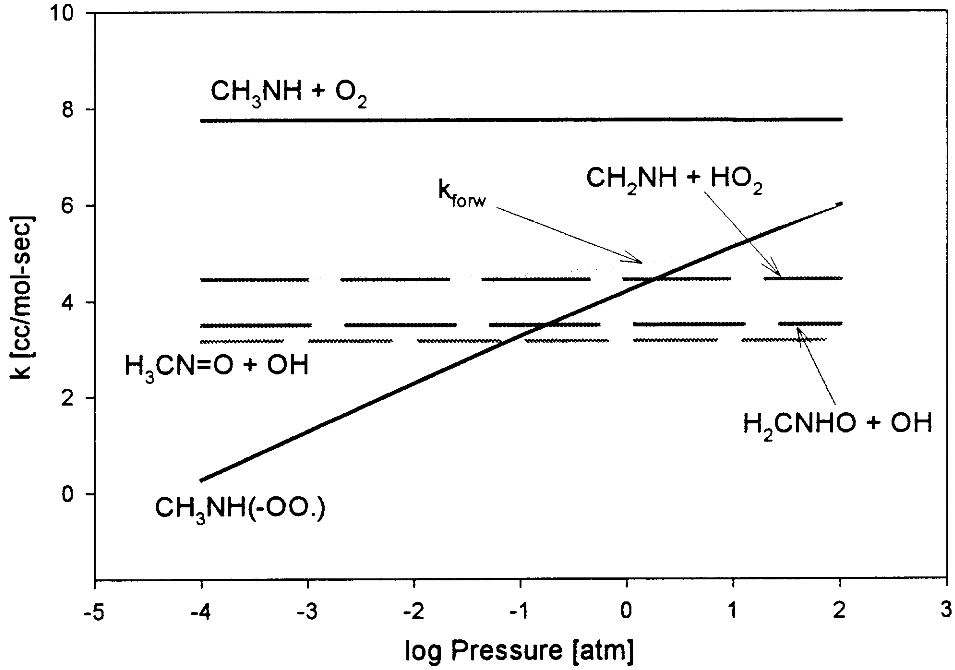


Figure 9.6 Chemical activation of $CH_3N{\bullet}H + O_2$ at 1200 K

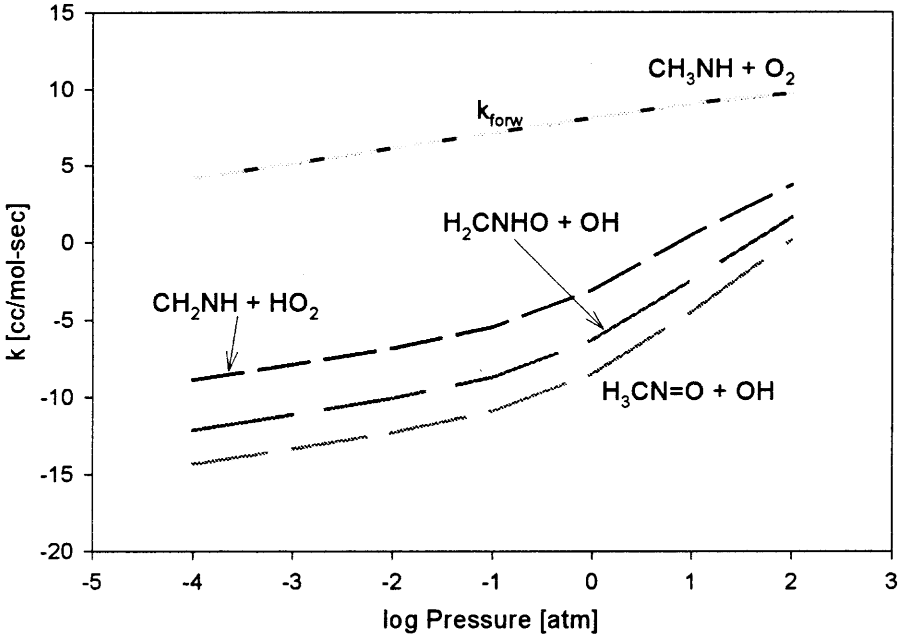


Figure 9.7 Thermal l dissociation of the $CH_3NHOO\bullet$ at 1200 K

9.4.2 $C\bullet H_2NH_2 + O_2$

The H_f(298K) for the $\bullet OOCH_2NH_2$ adduct is determined by isodesmic working reaction analysis at the G2(MP2) level of theory. The reaction of the $C\bullet H_2NH_2$ intermediate with O_2 forms an activated peroxy-methylamine adduct, $\bullet OOCH_2NH_2$* with a 31 kcal/mol well depth, as determined in this study. This adduct can undergo four different reactions, plus reverse dissociation back to reactants in both its chemically activated and stabilized states. The potential energy diagram is illustrated in Figure 9.8. The activated adduct can undergo a hydrogen shift via a 5-member ring from a hydrogen on the amine to form a $HOOCH_2N\bullet H$ isomer, which is 11 kcal/mol endothermic.

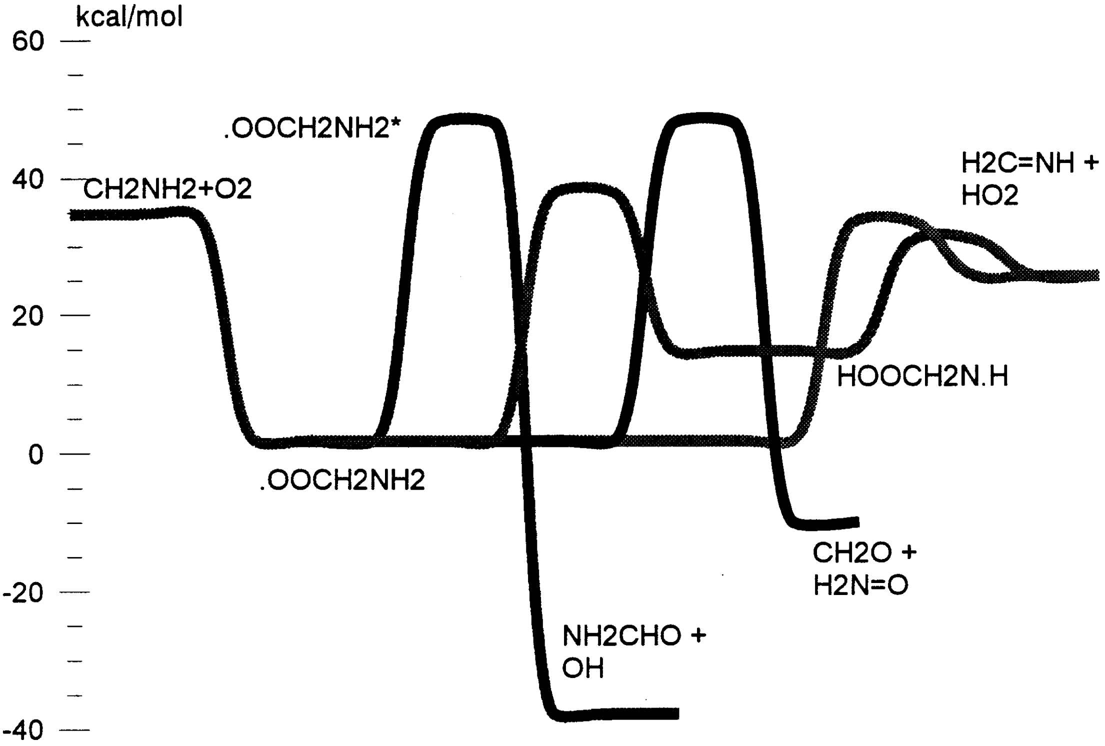


Figure 9.8 Potential energy diagram for $C\bullet H_2NH_2 + O_2$

The activated peroxy adduct can also form $H_2C=NH + HO_2$ directly via molecular elimination which is 27 kcal/mol endothermic and has a barrier of 31 kcal/mol. This is the lowest energy channel for the adduct $\bullet OOCH_2NH_2$, but it has a tight TS, resulting in a lower pre-exponential A-factor than the reverse dissociation.

A third intramolecular reaction of $\bullet OOCH_2NH_2$ is a hydrogen shift on the ipso carbon, through a 4-member ring, to form hydroperoxy bonded to a carbon with a radical site. This "type" of specie has been shown to be unstable by Sebbar, *et al.*[188] and Bozzelli and Jung[184]; it rapidly dissociates to an aldehyde plus OH.[188]

The peroxy radical can also form a bond directly to the nitrogen lone pair, forming a 4-member cyclic COON, followed by breaking the weak peoxide O-O bond forming a biradical. Based on the G2(MP2) calculation (relative to the $\bullet OOCH_2NH_2$

adduct), this biradical is 20.3 kcal/mol above the $\bullet OOCH_2NH_2$ adduct and about 22 kcal/mol below the estimated TS. This "unstable" intermediate is not shown on the potential energy diagram. This biradical specie is expected to quickly break the C – N bond to form formaldehyde plus $H_2NO\bullet$, in favor of gaining a strong C=O bond.

The $HOOCH_2N\bullet H$ adduct, formed from a 5-member ring hydrogen shift of the $\bullet OOCH_2NH_2$ adduct can also undergo reverse reaction back to $\bullet OOCH_2NH_2$ requiring to overcome an activation barrier of 18.3 kcal/mol or β-scission to $H_2C{=}NH + HO_2$, which is 16 kcal/mol endothermic.

The high-pressure limit rate constants are presented in Table 9.3. The rate constants calculated by QRRK with master equation analysis for fall-off are shown in Figures 9.9 and 9.10. Figure 9.9 illustrates the rate constants of $C\bullet H_2NH_2 + O_2$ at 1 atm over the temperature range of 300 – 3000 K. At temperatures below 1200 K, stabilization is dominant, but above 1200 K, formation of $H_2C{=}NH + HO_2$, via molecular elimination becomes the dominant path and at 1800 K, the molecular elimination path is about 3 orders of magnitude faster than stabilization.

Figure 9.10 shows the system at 1200 K, over a pressure range of 10^{-4} – 100 atm. The molecular elimination channel is the most important channel below 1.0 atm. Above 1.0 atm, stabilization becomes important. Thermal dissociation of the $\bullet OOCH_2NH_2$ adduct at 1200 K over a pressure range of 10^{-4} – 100 atm is illustrated in Figure 9.11. The most important reaction is the reverse reaction back to $C\bullet H_2NH_2 + O_2$, due to the high pre-exponential A-factor for this simple dissociation relative to tight TS structures of isomerization reactions. The molecular elimination channel is about 5 orders of magnitude slower than the reverse dissociation reaction over the entire pressure range shown.

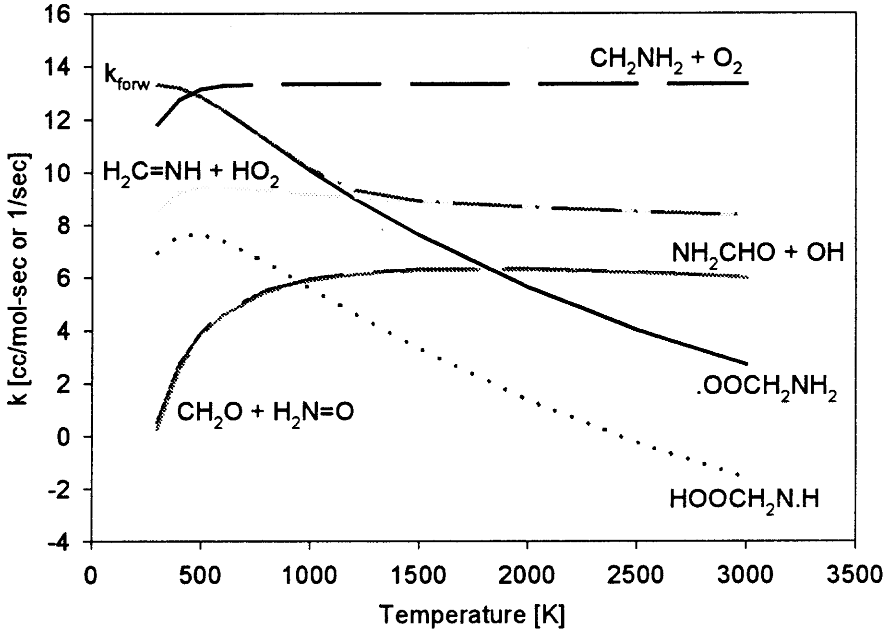


Figure 9.9 Chemical activation of $C{\bullet}H_2NH_2 + O_2$ at 1 atm

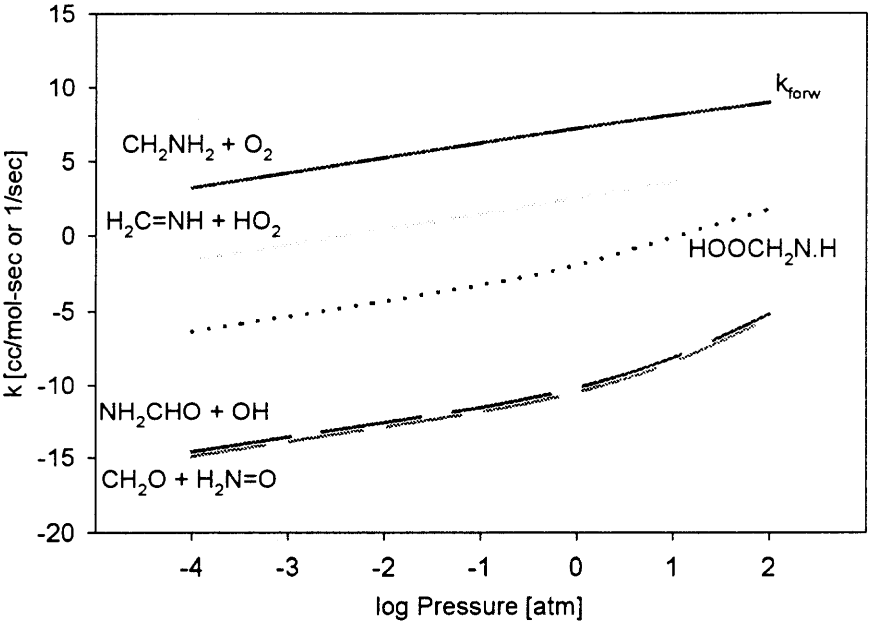


Figure 9.10 Chemical activation of $C{\bullet}H_2NH_2 + O_2$ at 1200 K

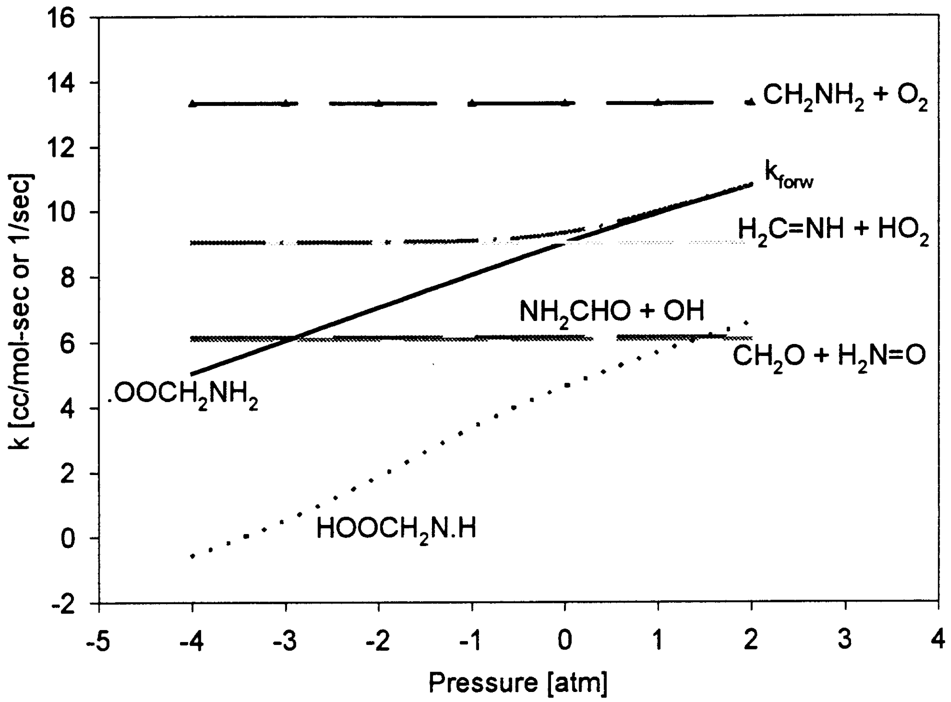


Figure 9.11 Thermal dissociation of •$OOCH_2NH_2$ at 1200 K

CHAPTER 10

COMPARISON OF A DETAILED ELEMENTARY KINETIC MODEL IN A PSR-PFR-PFR CONFIGURATION WITH EXPERIMENTAL DATA OBTAINED FROM A PILOT SCALE INCINERATOR

10.1 Determination of Fuel Composition Used in the Model

The fuel components used in the model consist of CH_3OH, C_2H_4, C_2H_6 and CH_3NH_2. The procedure to determine the initial molar composition utilizes the experimental data of the pilot scale incinerator runs to derive a molar fuel composition for the model that correlates as closely to the experiment fuel as possible. Initial "guess" mass fractions (of the total fuel) of 0.25 for each of CH_3OH, C_2H_4 and C_2H_6 and 0.05 for CH_3NH_2 are assigned; this leaves H_2O forming 0.2 of the total (fuel / feed) mass fraction. The total mass of fuel consumed for each run, as known from the experimental data on fuel feed rate, can be converted to mass fraction of the individual "model" components and their mass feed rate. Here water is excluded, as it is assumed to evaporate during the ignition of the solid fuel. The total fuel feed rate from experimental data is determine by the following formula,

$$feed\_rate = \frac{0.8 \times (total\_weight\_of\_fuel\_feed) - (weight\_of\_ash)}{time}$$

In the "weight of ash", one also needs to discount the 9% incombustible (8% metal and 1% inert). The "time" in the denominator refers to the total time when solid fuel has been supplied to the incinerator, *i.e.* it excludes warm-up and shut down time when solid fuel are not fed into the incinerator. The mole fractions for CH_3OH, C_2H_4, C_2H_6 and CH_3NH_2 are calculated from the experimental fuel mass feed rate for each experiment run. An average (overall) mole fraction is determined for the "model" fuel.

Based upon the fuel analysis performed on the synthetic fuel pellets, in accordance to the ASTM E778-87 test procedure,[238] nitrogen was determine to make up 0.42% of the mass of the fuel.[239] Nitrogen balance is satisfied by adjusting the initial molar concentration of CH_3NH_2 to consist of 0.42% mass fraction of nitrogen in the fuel, *viz.*

$$x_N = 0.0042 = \frac{m_{CH_3NH_2} \times \left(\dfrac{14gN}{mol\_CH_3NH_2} \right)}{\sum m_i \times MW_i}$$

where x_i denotes mass fraction, m_i is the mole fraction and MW_i is the respective molecular weight of the specie. To minimize the iterative calculations needed, the increase/decrease in the methylamine mole fraction will result in a decrease/increase in the ethane mole fraction to maintain the total mole fraction of 1.0 in the "model" fuel. Ethane is chosen, as oppose to ethylene, because ethane and methylamine have similar molecular weight, *i.e.* methylamine is 31 g/mol and that of ethane is 30 g/mol. The resulting "model" fuel composition used in the model fuel is shown in Table 10.1. The actual nitrogen mass fraction in the "model" fuel is then determined by the following,

$$x_N = 0.0115 \times \frac{\left(\dfrac{14gN}{mol\_CH_3NH_2} \right)}{\left(\dfrac{31g}{mol\_CH_3NH_2} \right)} = 0.0052 = 0.52\%$$

Table 10.1 Initial Fuel Composition Used in the Model

Species	Mole Fraction	Mass Fraction
CH_3OH	0.2104	0.2527
C_2H_6	0.2639	0.2971
C_2H_4	0.2404	0.2527
CH_3NH_2	0.0099	0.0115
H_2O	0.2754	0.1860

10.2 Determination of a Global Overall Heat Transfer Coefficient

The current reactor model configuration consists of a perfectly stirred reactor (PSR) followed by two plug flow (PFR reactors) each with different heat transfer coefficient; this configuration will be designated as PSR-PFR1-PFR2. The PSR will correlate to the primary combustion chamber (PCC) in the pilot scale, PFR1 will correlate to the glycol heated portion of the secondary combustion chamber (SCC) and PFR2 will correlate to the SCC will correlate to the cool-down stage of the combustion process, *i.e.* after the glycol heated annular pipe and before the heat exchanger. The volume of the PCC is 90538 cm^3, and the volume for the glycol heated SCC is 97814 cm^3 and the cool-down stage has a volume of 167314 cm^3. These volumes correspond to PSR, PFR1 and PFR2, respectively. The PSR is assumed to be an isothermal reactor. This is to simulate the actual pilot scale incinerator condition when steady state is reached, and the primary combustion chamber temperature is constant. An overall heat transfer coefficient for PFR1 and PFR2 is calculated from the following equation,

$$\Delta H = (U\ A)\ \Delta T$$

Total heat, ΔH, is calculated from the feed rate and the higher heating value of the fuel, *i.e.* 4570 cal/g. The overall heat transfer coefficient per unit area, U, and A is the heat conduction surface area. For a PFR, the overall heat transfer term is expressed in terms of heat transfer area per volume of reactor, *viz.* (Ua) ΔT dV. The temperature inside PFR1 is calculated as the average between PCC and at the end of the SCC and the temperature inside PFR2 is calculated as the average temperature between the beginning and end of the cool-down stage. The ambient temperature is 25 C. The average heat transfer coefficient, (UA), for PFR1 is calculated to be 11.21 cal/sec-K and for PFR2 to be 13.17 cal/sec-K. The heat transfer coefficient, (Ua), per 1000 cm^3 volume of reactor for PFR1 is 0.071 cal/s-K and PFR2 is 0.083 cal/s-K.

10.3 Determination of the Equivalence Ratio

The over-fire air (OFA) is determined directly from the readings taken from a Dwyer flowmeter. The pressure in the OFA line is determine from a pressure gauge attached in-line and is 35 psig. The under fire air (UFA) is calculated based on a Dwyer magnahelic differential pressure gauge. The steady state macroscopic mechanical energy balance, with assumption of turbulent flow, incompressible fluid, negligible friction and work is applied to determine the volumetric airflow in UFA.[52] The equation is then represented by the following,

$$\Delta\frac{1}{2}\langle\bar{v}\rangle^2 = \int_{P_1}^{P_2}\frac{1}{\rho}dP$$

where $\langle\bar{v}\rangle$ is the average velocity, ρ is the density and P is pressure. The UFA flows through a 3 inch diameter duct and the UFA volumetric flow rate can be determine by the following equation,

$$Q = Area \times \langle\bar{v}\rangle$$

The ambient conditions are 25 C and 1 atm and the molar air composition of 0.79 N_2 and 0.21 O_2 is used. The calculated molar flow rate of N_2 and O_2 at different OFA and UFA settings are presented in Table 10.2.

Table 10.2 Volumetric Flow Rate of N_2 and O_2 at Different OFA and UFA Settings

OFA	3 SCFM	5 SCFM	7 SCFM
N_2	9.22	15.37	21.52
O_2	2.45	4.09	5.72

UFA	0.25 inches H_2O	0.3 inches H_2O	0.6 inches H_2O
N_2	47.62	48.29	67.34
O_2	12.66	12.84	17.90

The equivalence ratio is the ratio of the experimental fuel-to-oxidant ratio to the stoichiometric fuel-to-oxidant ratio, *viz.*

$$\Phi = \frac{\left(\frac{fuel}{oxidant}\right)_{actual}}{\left(\frac{fuel}{oxidant}\right)_{stoichiometric}}$$

Three different fuel equivalence ratios are used in the model study,

a. base upon the molar flow rate of the "model" fuel (Table 10.1).

b. base upon the experimental O_2 reading from experimental data.

c. base upon assuming all the mass consumed in experiment is composed of cellulose, $C_6H_{10}O_5$.

The different fuel equivalence ratios will be denoted as ϕ_a, ϕ_b and ϕ_c, respectively.

10.4 Numerical Integrated Solutions of the Model

The program INFERNO2,[49] which is base on the ChemKin II[87] integrator package, calculates the concentration profile for a PSR-PFR1-PFR2 configuration. The mechanism file used consists of over 180 species and over 900 elementary reactions. Inclusive in the mechanism file are the C_1 and C_2 hydrocarbon oxidation systems discussed previously, as well as 370 reactions for the nitrogen system.[36] Three different experimental data sets are used and calculated for the three different equivalence ratio. The three different experimental data sets are referred to the dates when the experiments are performed, *e.g.* Dec. 10, 1998.

Table 10.3 Volumetric Flow Rate for the Fuel Used in INFERNO2

Dec. 10, 1998	219 cm^3/sec
Nov. 9, 1999	283.7 cm^3/sec
Nov. 9, 1999	248 cm^3/sec

The concentration profile determine from INFERNO2 for the Dec. 7, 2000 conditions at $\Phi_a = 0.40$ is shown in Figure 10.1. According to the results from INFERNO2, the O_2, is consumed and CO_2 and NO are formed mainly in the PSR. The concentration of these three components do not change throughout PFR1 and PFR2, and the results are shown in Table 10.4. Both CO and C_2H_6 undergo drastic decrease in concentration, upon entering PFR1. The CO concentration decreases from 56 ppm to 0.15 ppm within the first 2000 cm^3 of PFR1, less than 2% of the total PFR1 volume. The C_2H_6 concentration drops from 0.5 ppm to 1.5×10^{-11} ppm within the first 2000 cm^3 of PFR1. The NO_2 concentration, initially drops during the first 2000 cm3 of PFR1, but slowly increases in concentration afterwards and continues to slowly increase until reaching PFR2 when the concentration of NO_2 plateaus of approximately 2 – 5 ppm. The other hydrocarbon species, *i.e.* CH_4, C_2H_2 and C_2H_4, slowly decreases along PFR1 and PFR2.

Comparison of the results from the model, as calculated by INFERNO2, on the three different equivalent ratio cases, with the experimental data are shown in Table 10.4. For all three dates, comparison of O_2 concentration is best matched between Φ_a and Φ_b (0.4 – 0.7) and for the given fuel composition used in the model. Comparison of the NO and

NOx experimental data with the model show the data are in the same range, varying from 100 – 200 ppm, with less than 50 ppm difference. Particularly worth noting is the ratio of NO:NOx. The average NO:NOx ratio for experimental data is 0.97, and the average NO:NOx ratio for the nine model results is 0.98. Compared with experimental data, the model predicts the hydrocarbon species of interest, *i.e.* CH_4, C_2H_2 and C_2H_4, to be near completely oxidized, while experimental data shows trace ppm concentration levels. The model predicts less than 1 ppm concentration, while the experimental datum is about 15 ppm.

The significant under-prediction of the hydrocarbons suggests that future studies include analysis of dead zones and incomplete mixing sections of the incinerator. Additional reactor configurations or by-pass flows may also be considered as needed, to describe the measured HC levels.

10.5 Summary

A pilot scale incinerator has been constructed, tested and run; and an on-line sampling train capable of taking *in situ* data has been established. The continuous on-line analytical instruments include a CO analyzer, an NO/NOx analyzer and an O_2 analyzer. Temperatures at five different locations along the incinerator process are determine by type K and type R thermocouples (the type R thermocouple is located at the end of SCC). National Instruments' LabView software is used to collect the data readings and store it onto electromagnetic media in a personal computer. In addition, two gas chromatographs with flame ionization detector are used to determine specific hydrocarbon and total hydrocarbon concentrations. Chromatograms are stored onto a second personal computer

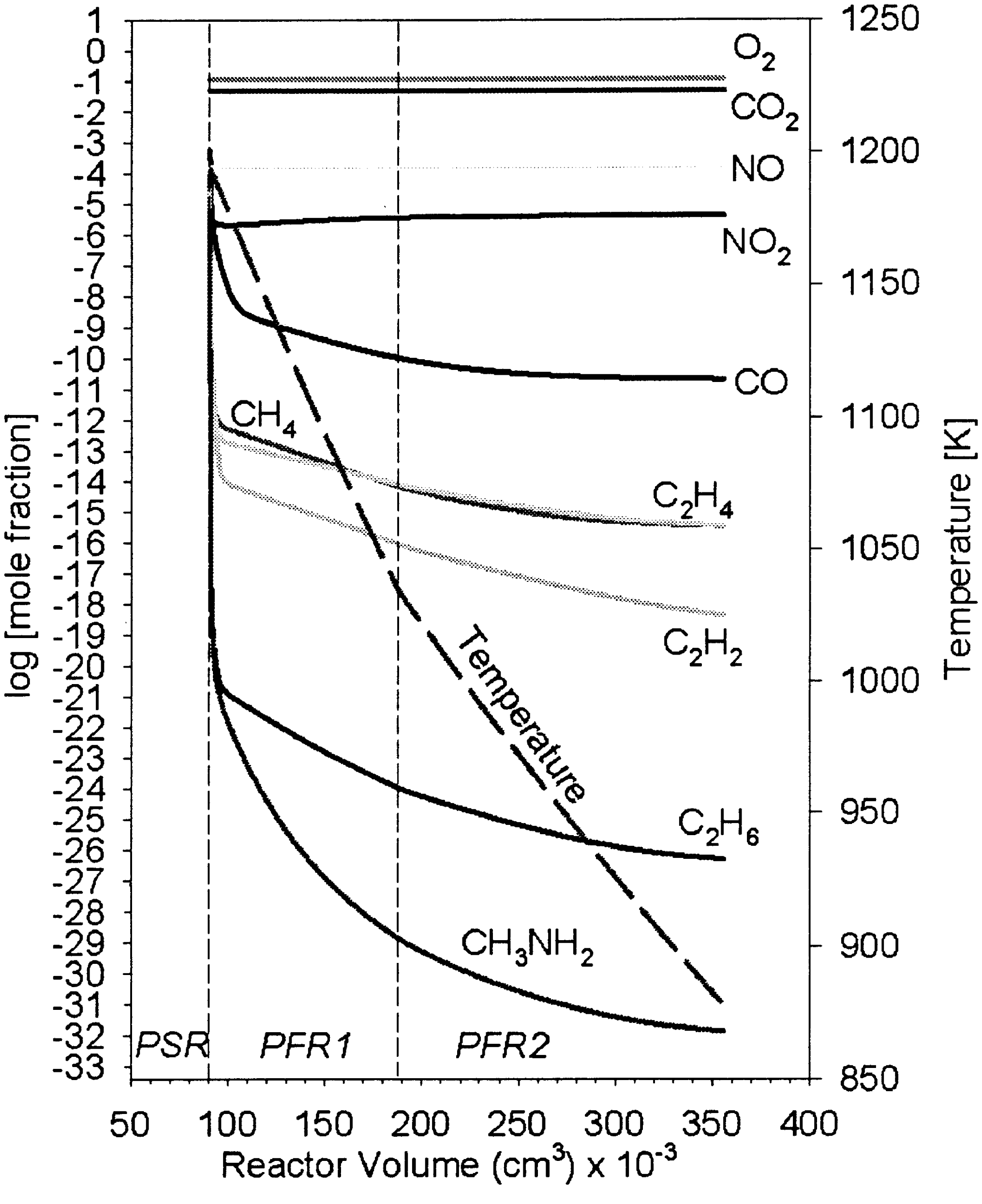


Figure 10.1 Modeling results from INFERNO2 based on the calculated input parameters for Dec. 7, 2000 at $\Phi_a = 0.40$

Table 10.4 Comparison of Experimental Data with Results Calculated from INFERNO2.

Incinerator Data at Steady-State

	Dec 10, 1998	Nov 9, 1999	Dec 7, 2000
CO (ppm)	20.5	46.1	2.4
O_2 (%)	7.5	7.61	6.5
NO (ppm)	153	99.2	189
NO_X (ppm)	156	101.1	198
CH_4 (ppm)	1.4	0.2	0.08
$C_2H_4 + C_2H_2$ (ppm)	53.6	2.9	N/D
Total HC (ppm)	N/D	N/D	15.73
CO2 (%)	N/D	N/D	N/D

N/D = No Data

Model data at steady-state Dec 10, 1998

	$\Phi_a = 0.44$	$\Phi_b = 0.64$	$\Phi_c = 0.23$
CO (ppm)	2.9E-5	3.9E-5	3.1E-5
O_2 (%)	11.0	6.9	15.7
NO (ppm)	134.4	127.8	103.5
NO_X (ppm)	134.5	130.3	105.9
CH_4 (ppm)	1.3E-9	1.2E-9	1.6E-9
$C_2H_4 + C_2H_2$ (ppm)	2.2E-9	1.2E-9	3.7E-9
Total HC (ppm)	0.18	0.12	0.22
CO_2 (%)	5.5	7.8	2.9

Model data simulating condition of Nov. 9, 1999

	$\Phi_a = 0.44$	$\Phi_b = 0.64$	$\Phi_c = 0.30$
CO (ppm)	3.3E-5	3.8E-5	3.9E-5
O_2 (%)	11.1	7.0	14.2
NO (ppm)	136.1	134.0	118.7
NO_X (ppm)	139.1	136.5	121.3
CH_4 (ppm)	8.3E-10	6.5E-10	1.1E-9
$C_2H_4 + C_2H_2$ (ppm)	1.37E-9	6.4E-10	2.2E-9
Total HC (ppm)	0.18	0.12	0.22
CO_2 (%)	5.4	7.7	3.8

Model data simulating condition of Dec. 7, 2000

	$\Phi_a = 0.40$	$\Phi_b = 0.69$	$\Phi_c = 0.24$
CO (ppm)	2.6E-5	2.0E-5	6.9E-5
O_2 (%)	11.9	6.0	15.5
NO (ppm)	174	129.7	137.2
NO_X (ppm)	178.4	132.7	140.3
CH_4 (ppm)	3.9E-10	2.9E-10	6.9E-10
$C_2H_4 + C_2H_2$ (ppm)	4.1E-10	2.9E-10	9.9E-10
Total HC (ppm)	0.19	0.18	0.24
CO_2 (%)	5.0	8.2	3.0

disk, via an analog-to-digital ChromServer, and the chromatograms are interpreted by the software PC MiniChrom from Thermo LabSystems.

Detailed thermochemical properties and kinetic parameters for the complex reaction systems of acetylene isomerization to vinylidene and acetylene oxidation with O_2, for ethyl radical reaction with O_2, ethylhydroperoxide-2 yl radical reaction with O_2 and methanol dissociation system has been investigated and the results reported. The thermodynamic properties determine by density functional theory, B3LYP, and/or *ab initio* composite methods, CBS-Q and G2(MP2). Transition state structures are also determine by density functional theory and/or *ab initio* methods and the high-pressure limit rate constants for each elementary reaction are determine from canonical transition state theory. Variational transition state theory and microscopic reversibility are used to determine the forward and reverse high-pressure limit rate constants for association and dissociation reactions, where there are no saddle points. Comparisons of each system are compared with and are shown to be in agreement with the experimental data.

Comparison of a C1 – C2 hydrocarbon mechanism, inclusive of the current elementary reaction systems, in addition to a nitrogen mechanism to model data from the pilot scale incinerator is also performed. The composite mechanism consists of over 900 elementary reactions, with almost 200 species. A model fuel composed of CH_3OH, C_2H_4, C_2H_6 and CH_3NH_2 is used to simulate the complex synthetic solid waste fuel pellet used in the incinerator operations.

The O_2 concentration from the model prediction is in close agreement with the experimental O_2 data. The model predictions for the NO and NOx readings are within 30 ppm of the experimental data. Comparison of the NO to NOx ratio; the model predicts an average 0.98, and the ratio from the experiment yield an average 0.97, in excellent agreement. The model underpredicts the CO concentration, predicting nearly complete conversion of CO to CO_2. The experimental data reports data ranging from 2 – 46 ppm range. For hydrocarbon species in the system, the model predicts near complete conversion of total hydrocarbons and CO. The model predicted total hydrocarbon concentration range to be 3 – 8 ppm for the 3 different equivalence ratio conditions. Experimental data reports a total hydrocarbon concentration of about 16 ppm.

10.6 Future Work

The methylamine mechanism has not been extensively studied either experimentally or from a detail computation chemistry and thermochemical kinetic analysis. Accurate thermodynamic properties of the reactants, adducts, transition states and products in the complex CH_3NH_2, $C{\bullet}H_2NH_2 + O_2$ and $CH_3N{\bullet}H + O_2$ systems could be determined from computational chemistry. High-pressure limit rate constants for reactions that have a distinct saddle point, such as isomerization and molecular elimination reactions, could be determined from canonical transition state theory base on *ab initio* or density functional theory calculations on the saddle point structures. For reactions in this system where there are no saddle points, such as dissociation and association reactions, variational transition state theory could be applied to determine the reaction rate across the potential surface.

The second O_2 addition to $C{\bullet}H_2CH_2OOH$ radical also leads to suggest the potential of three new chain branching reactions. Analysis of C_1 – C_2 mechanisms with these chain branching reactions has not been studied previously and only findings illustrate three new, low energy, chain branching reaction paths. This will be important in low temperature combustion and thermal oxidation of hydrocarbon lubricants. Further ChemKin studies on this system to verify if this system could be an important chain branching reaction to help explain low temperature ignition systems.

Considering the complexity of the fuel matrix, combined with the dynamics of the incinerator, the proposed simplified model fuel coupled with detail chemical kinetic was able to provide good comparable results for the O_2, NO and NOx at comparable equivalence ratios. The under-prediction in the hydrocarbon concentrations by the model is unclear. Further analysis on the reactor configuration would perhaps help clarify if a PSR-PFR1-PFR2 in series is sufficient to model such a dynamic process. Suggestions of more complex reactor configurations include parallel reactor configurations. For a three reactor configuration, some parallel configurations can include (PSR/PSR)-PFR1 and (PSR/PFR1)-PFR2. Increasing the number of reactors to include multiple parallel and series configuration may improve the model, but also will imply more complicated computation to solution. Incorporation of "dead zones" in the reactor configuration can also help explain the differences between the model and experimental results. Construction and calculation of a successful complex reactor configuration, which includes "dead zones" in a multi-parallel configuration, may also offer some insight into the dynamics of the incinerator.

APPENDIX A

COMPARISON OF PRESSURE DEPENDENT MODEL WITH EXPERIMENTAL DATA

Concentration profiles determined by CHEMKIN for the pressure dependent model is compared with the methanol/methane experimental data described in Chapter 8.

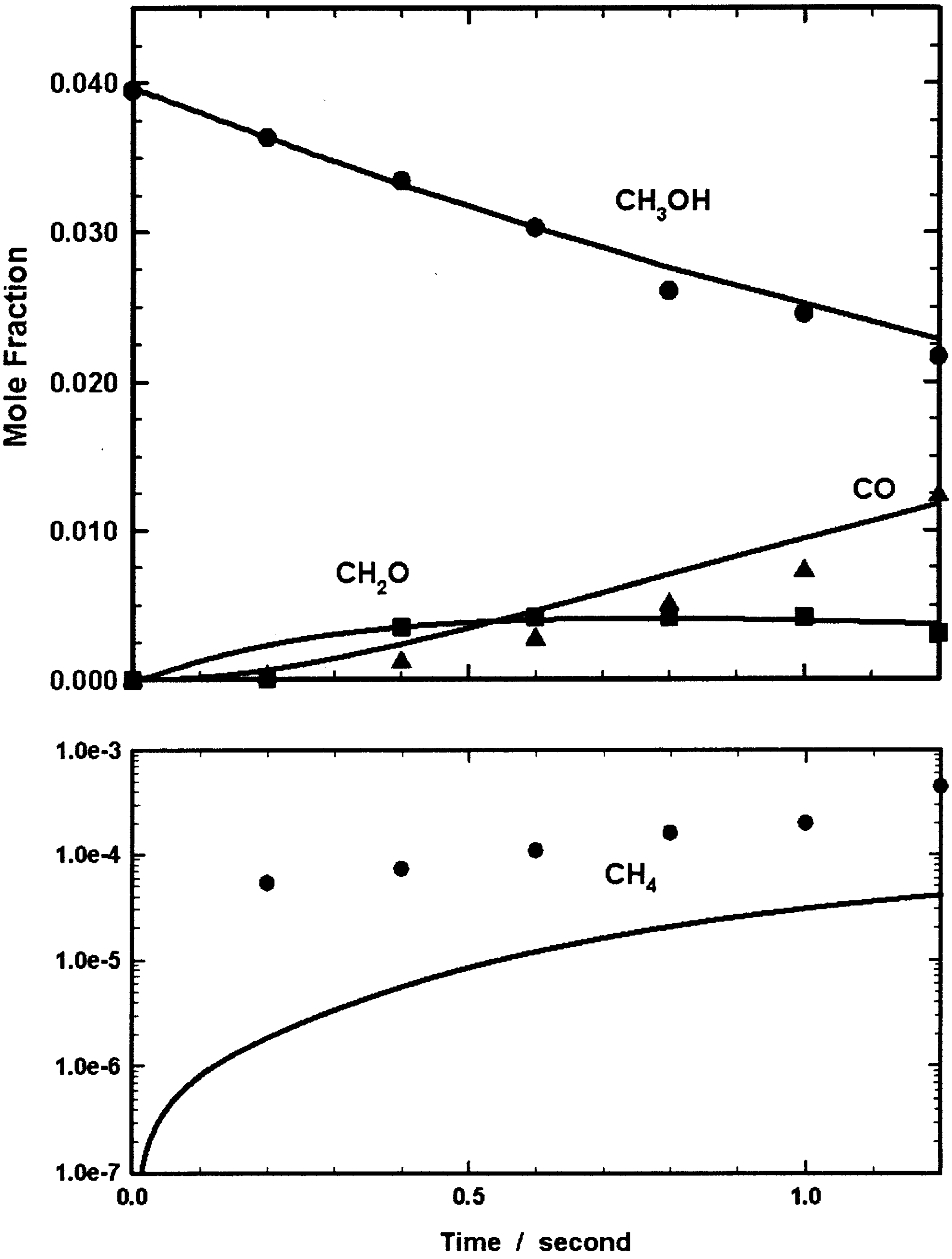


Figure A1 Comparison of model and experimental data for methanol pyrolysis at 800 C, 1 atm and initial methanol mole fraction of 3.95%.

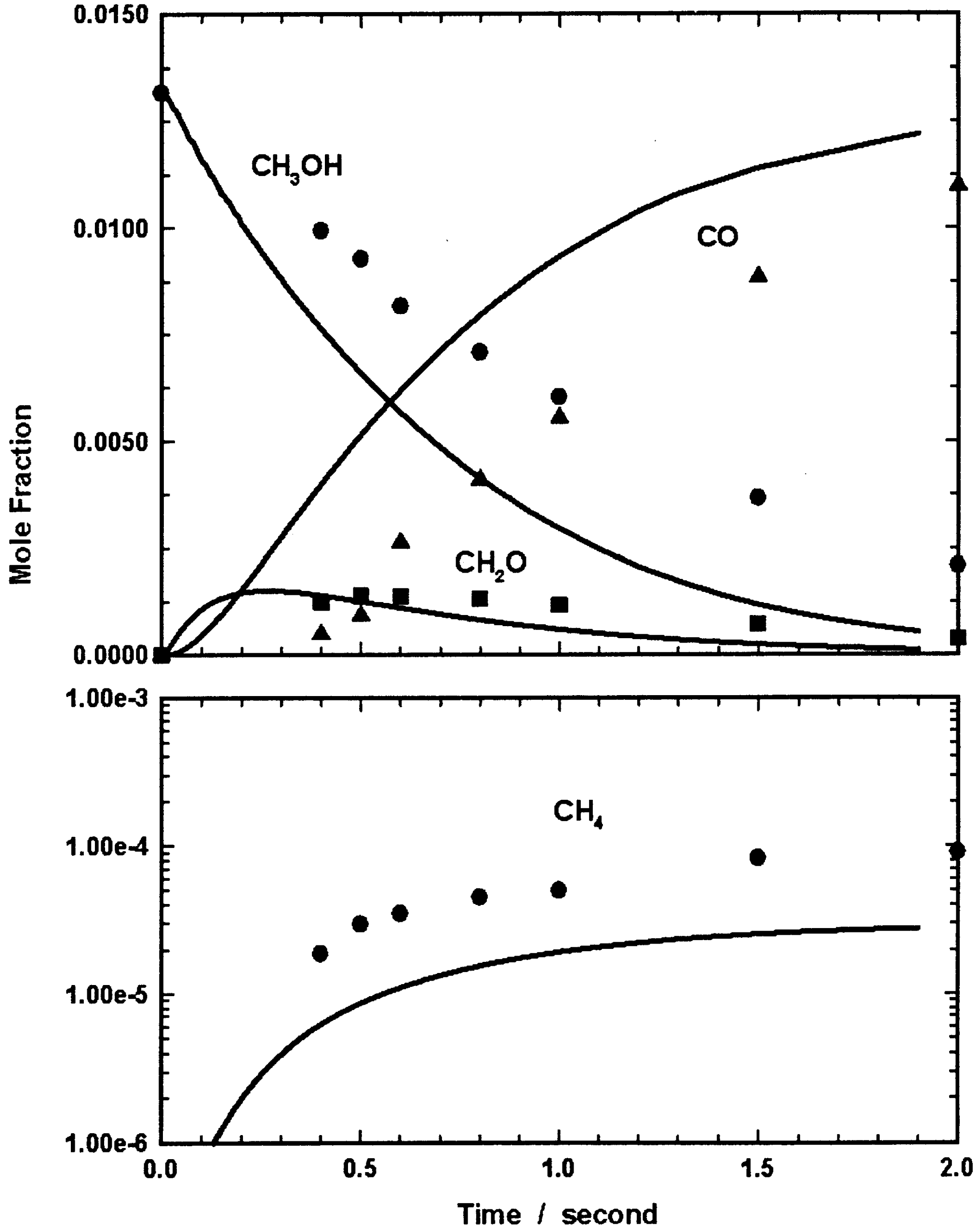


Figure A2 Comparison of model and experimental data for methanol pyrolysis at 800 C, 3 atm and initial methanol mole fraction of 1.317%.

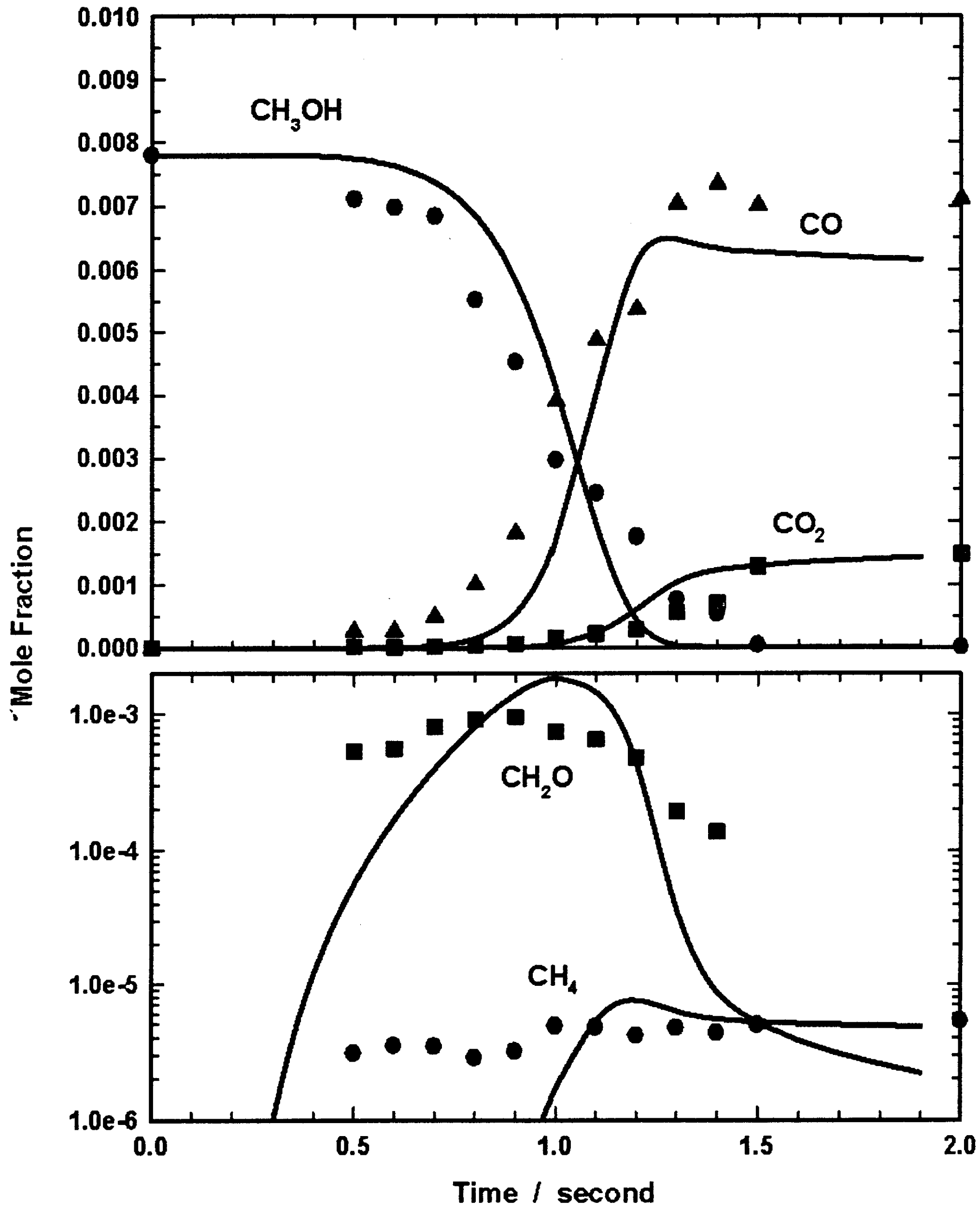


Figure A3 Comparison of model and experimental data for methanol oxidation at 873 K, 5 atm, $\phi = 1.0$ and initial methanol mole fraction of 0.78%.

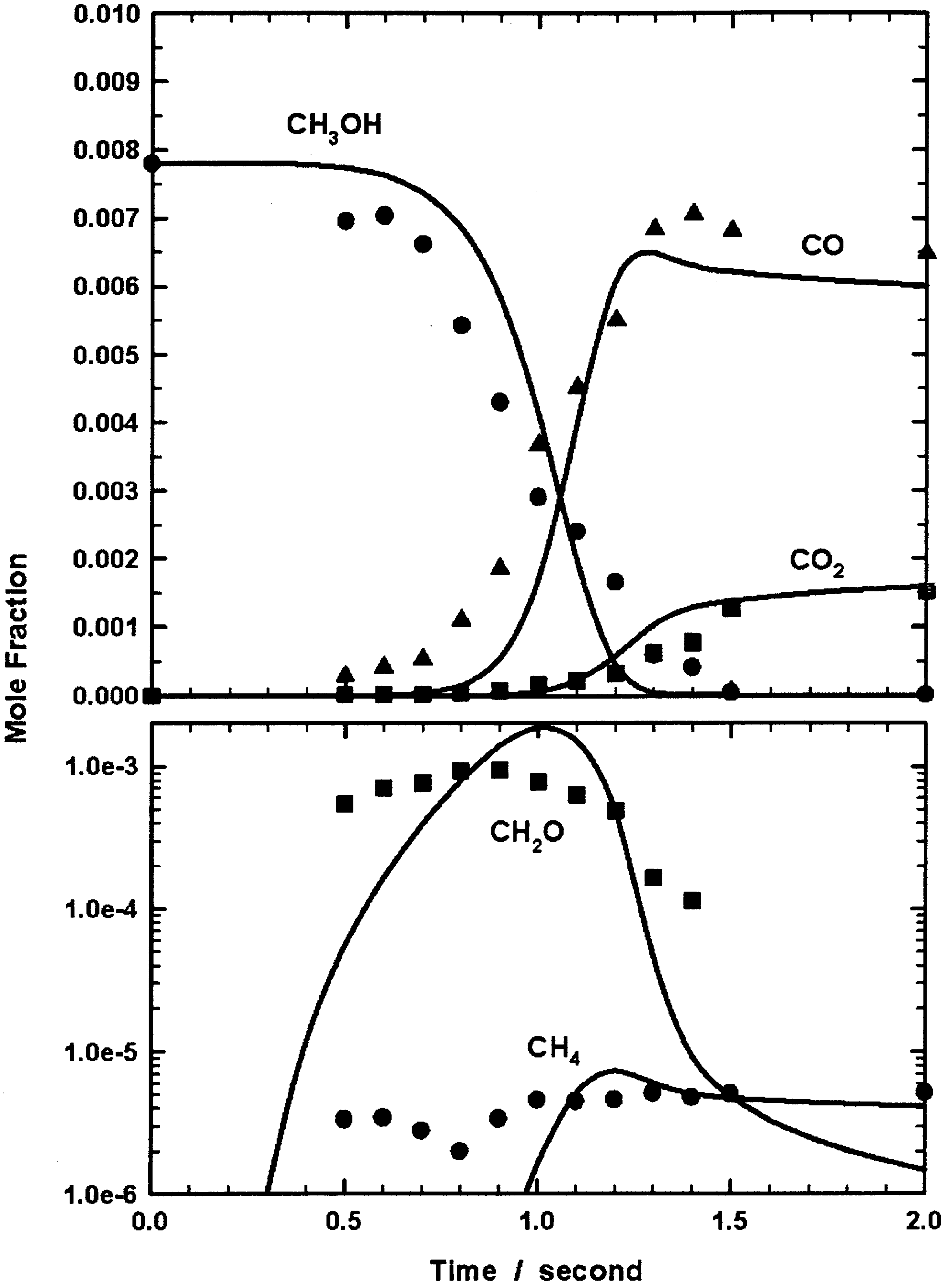


Figure A4 Comparison of model and experimental data for methanol oxidation at 873 K, 5 atm, $\phi = 0.75$ and initial methanol mole fraction of 0.78%.

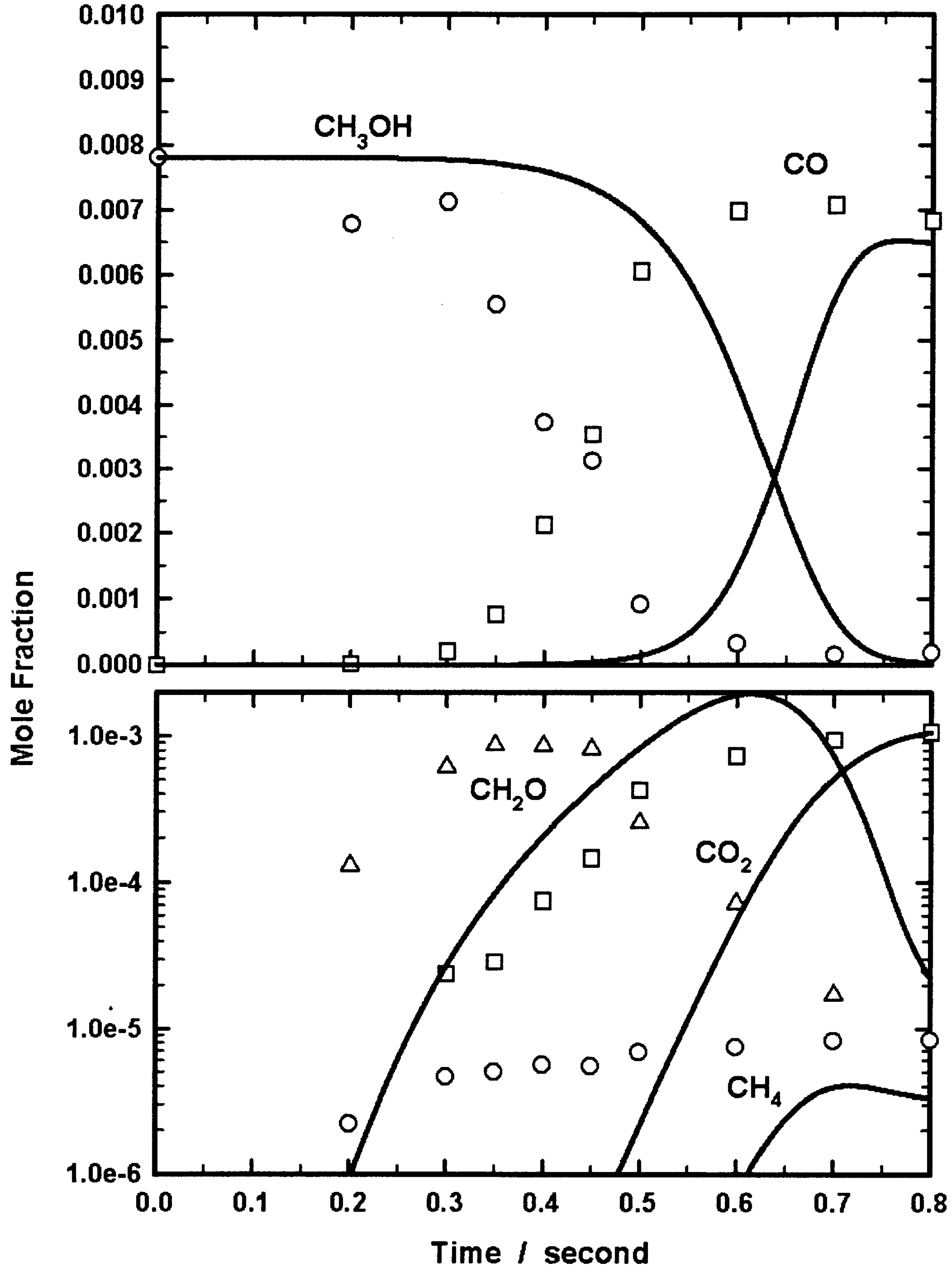


Figure A5 Comparison of model and experimental data for methanol oxidation at 973 K, 3 atm, ϕ = 1.0 and initial methanol mole fraction of 0.78%.

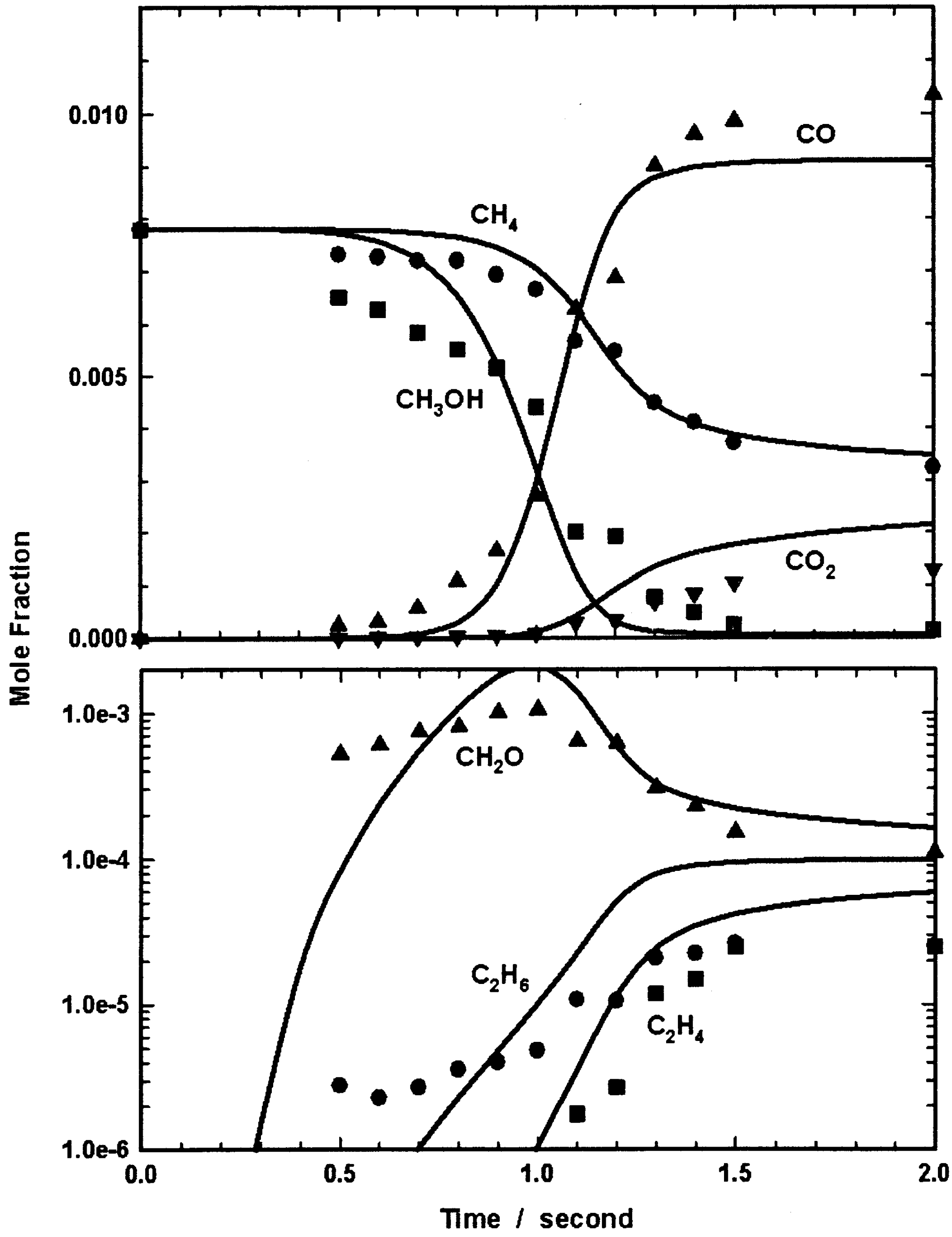


Figure A6 Comparison of model and experimental data for methane/methanol mixture oxidation at 973 K, 3 atm, $\phi = 1.0$ and $X_0(CH_4) = 0.78\%$, $X_0(CH_3OH) = 0.78\%$.

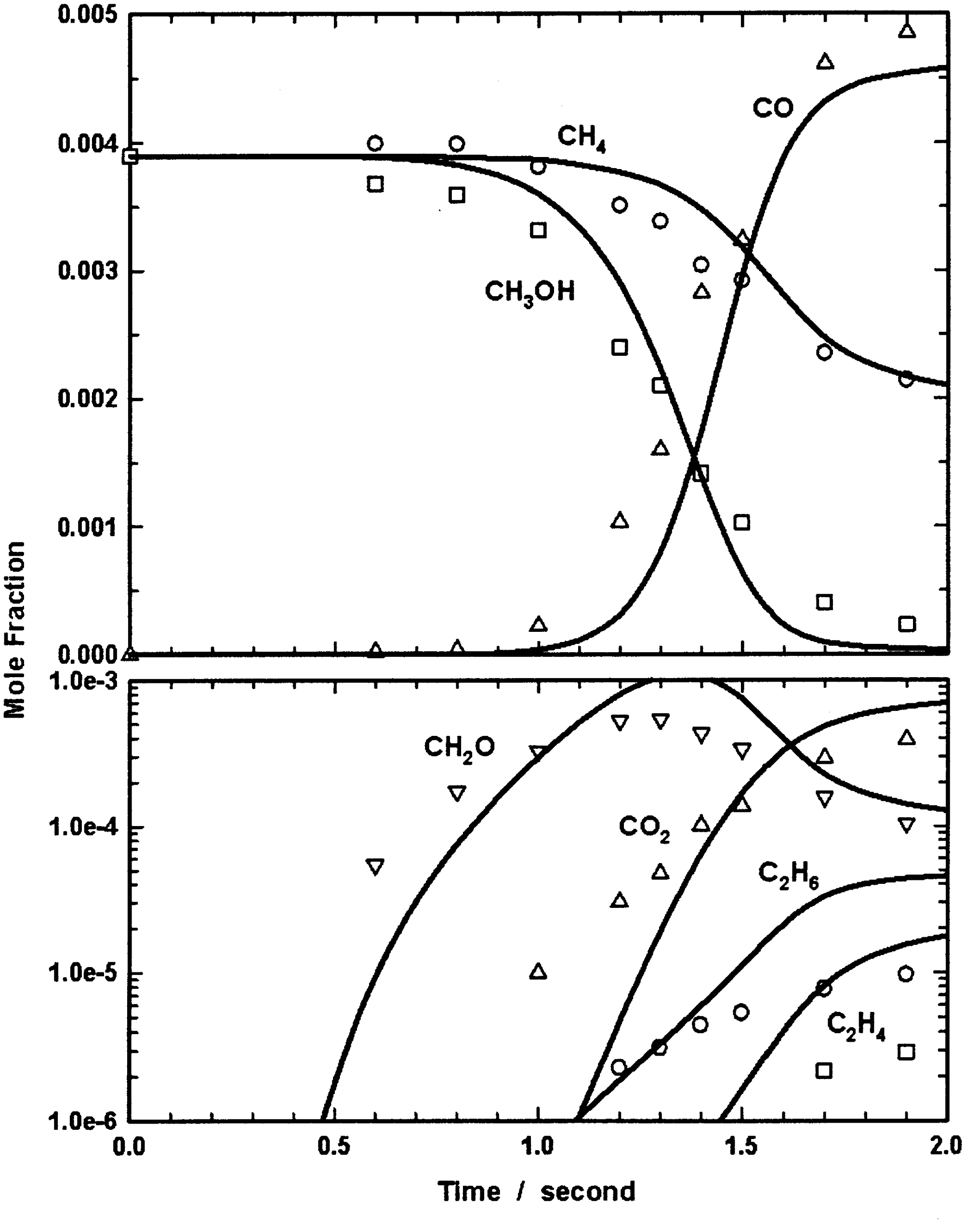


Figure A7 Comparison of model and experimental data for methane/methanol mixture oxidation at 873 K, 5 atm, $\phi = 1.0$ and $X_0(CH_4) = 0.39\%$, $X_0(CH_3OH) = 0.39\%$.

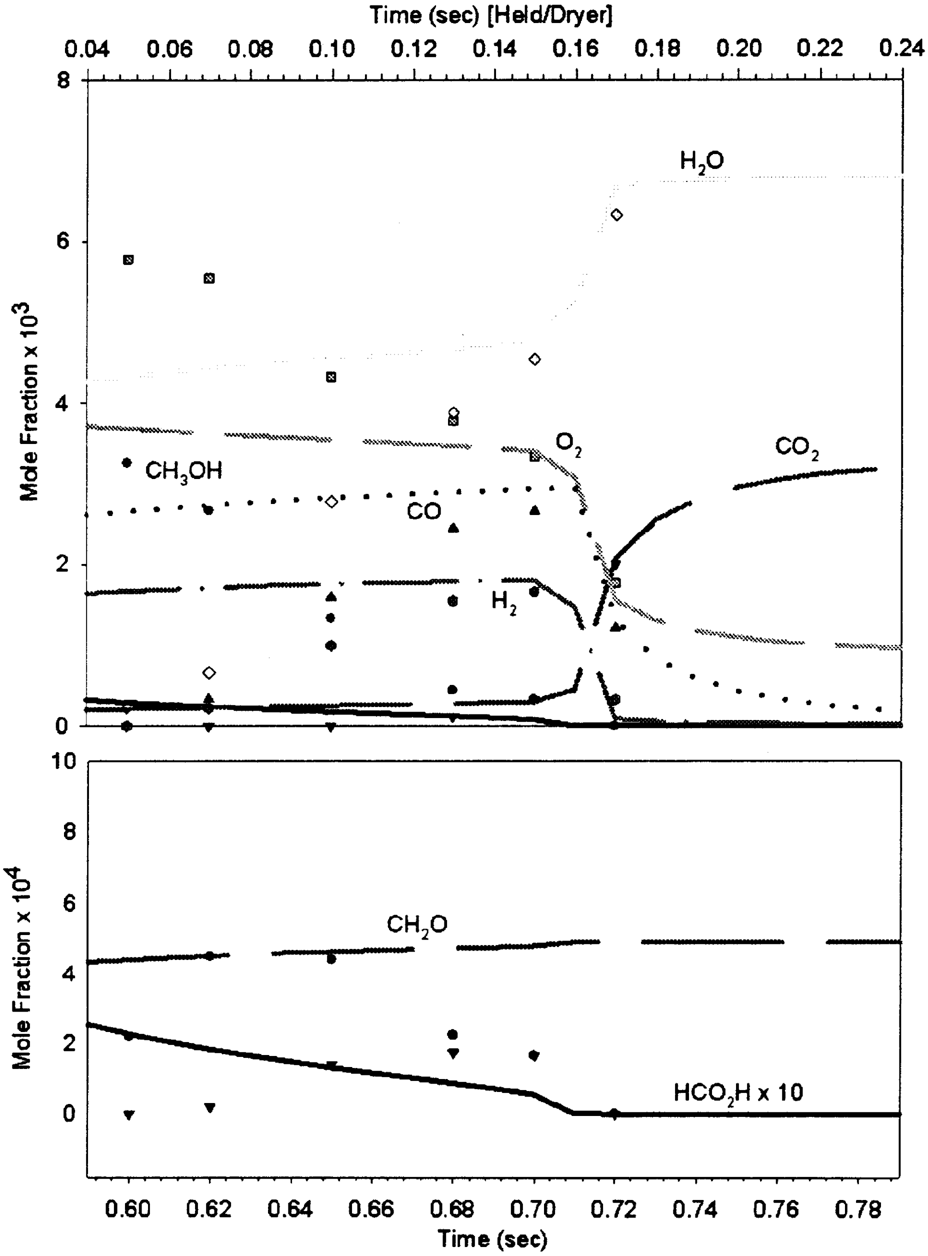


Figure A8 Comparison of model and experimental data from Held/Dryer at 1043 K, 2.1 atm, $\phi = 0.86$ and $X_0(CH_3OH) = 0.00344$

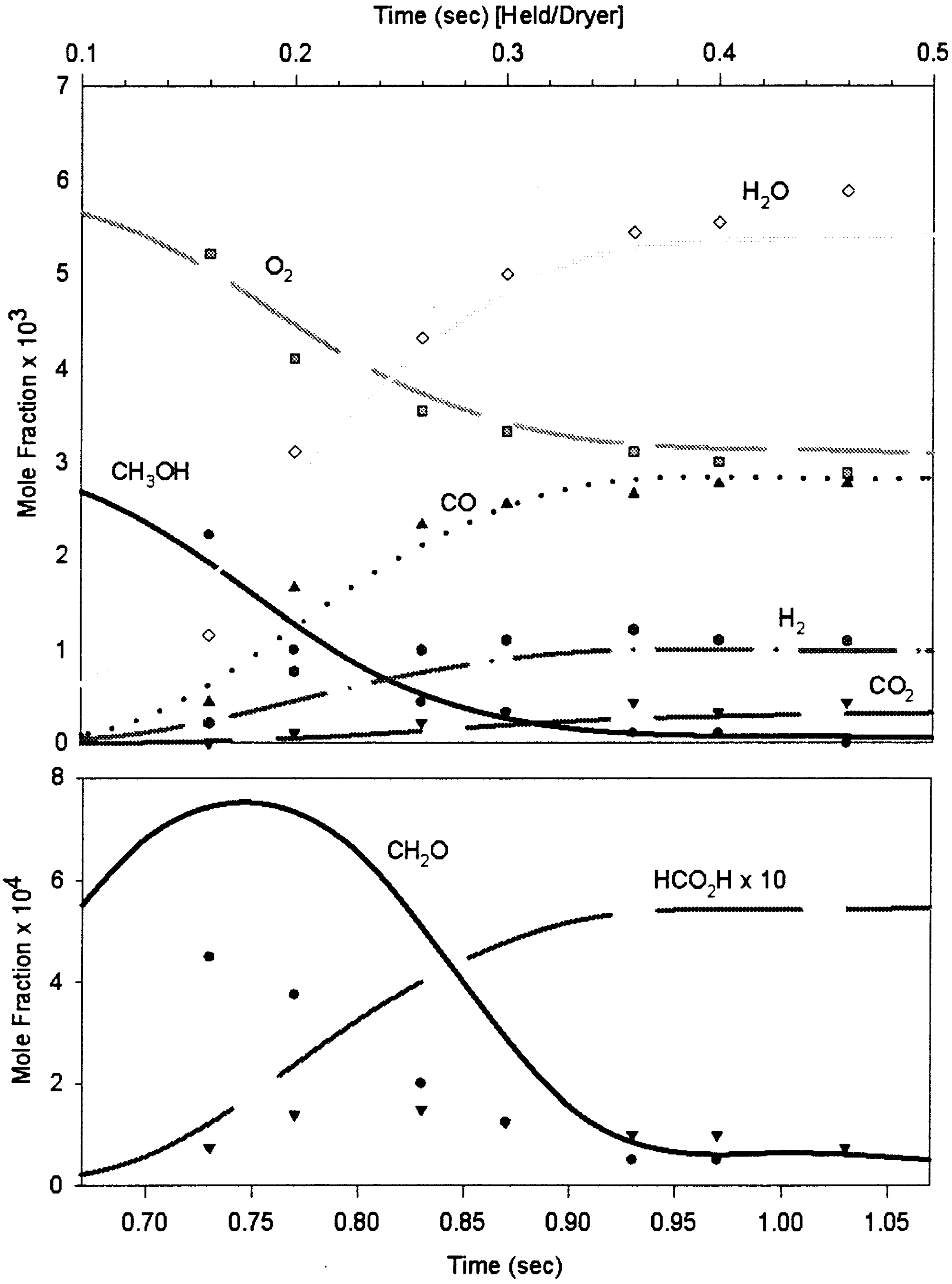


Figure A9 Comparison of model and experimental data from Held/Dryer at 949 K, 2.5 atm, $\phi = 0.83$ and $X_0(CH_3OH) = 0.00333$

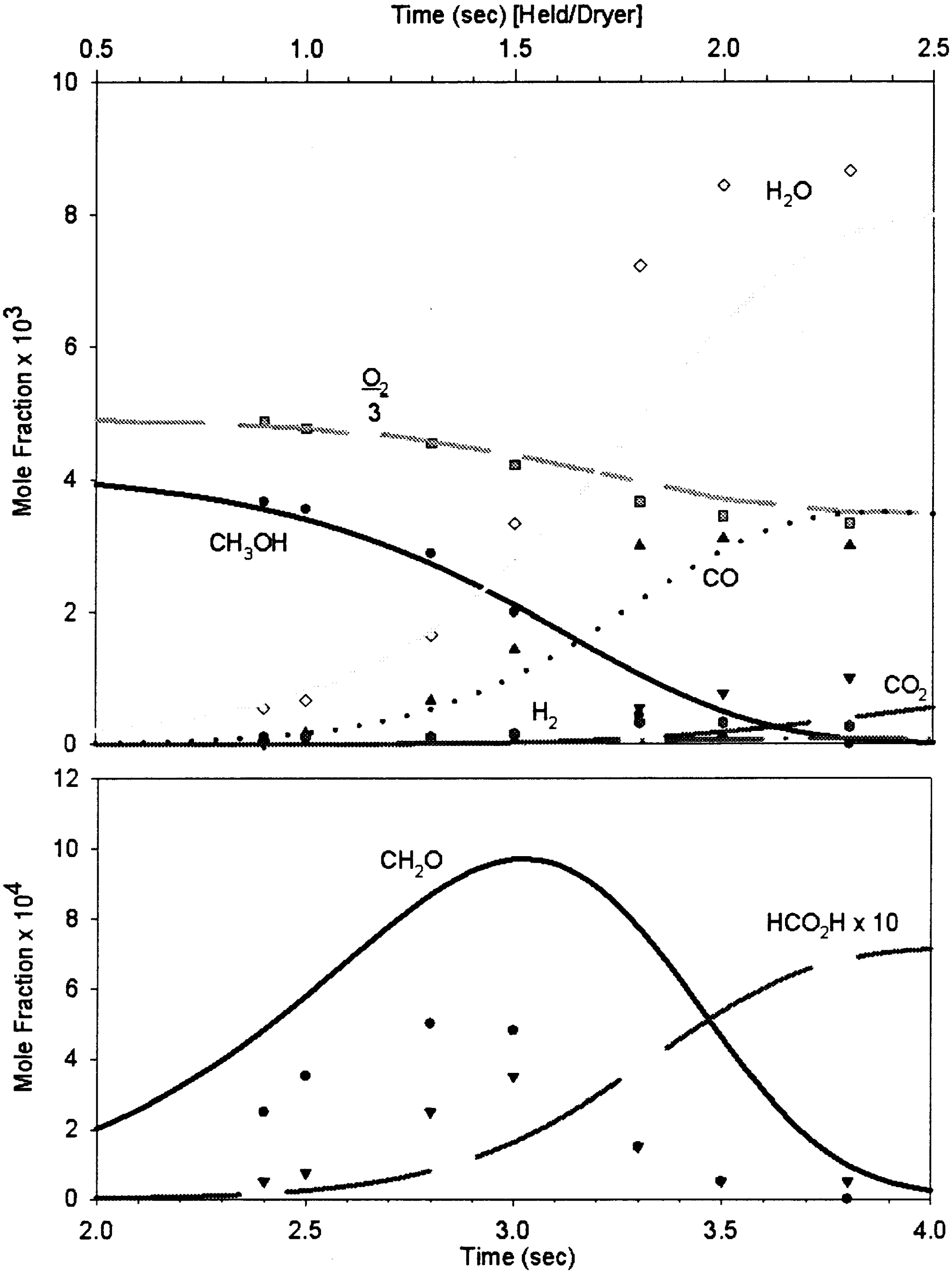


Figure A10 Comparison of model and experimental data from Held/Dryer at 810 K, 10.0 atm, $\phi = 0.42$ and $X_0(CH_3OH) = 0.00415$

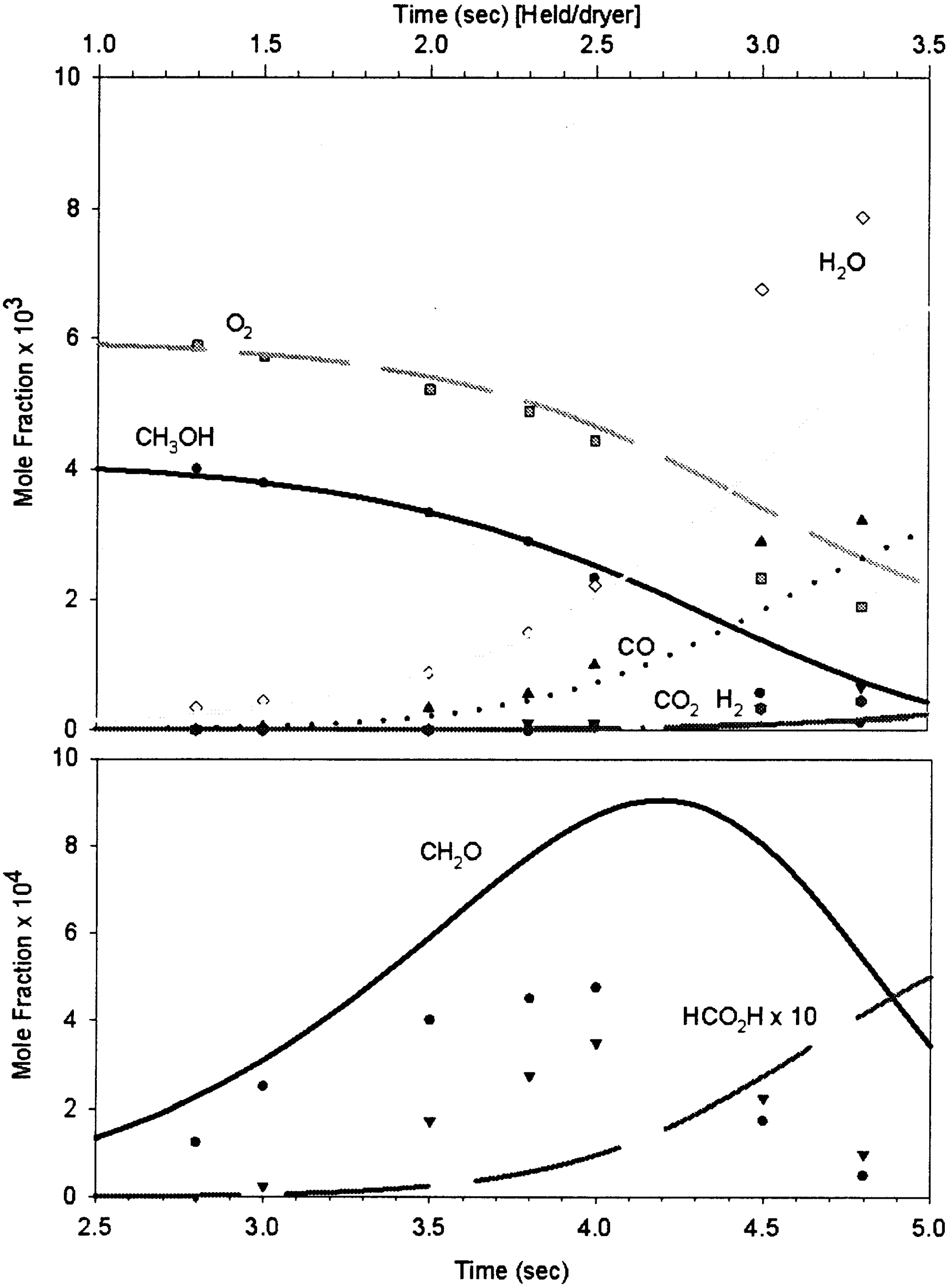


Figure A11 Comparison of model and experimental data from Held/Dryer at 783 K, 15.0 atm, ϕ =1.04 and $X_0(CH_3OH)$ = 0.00415

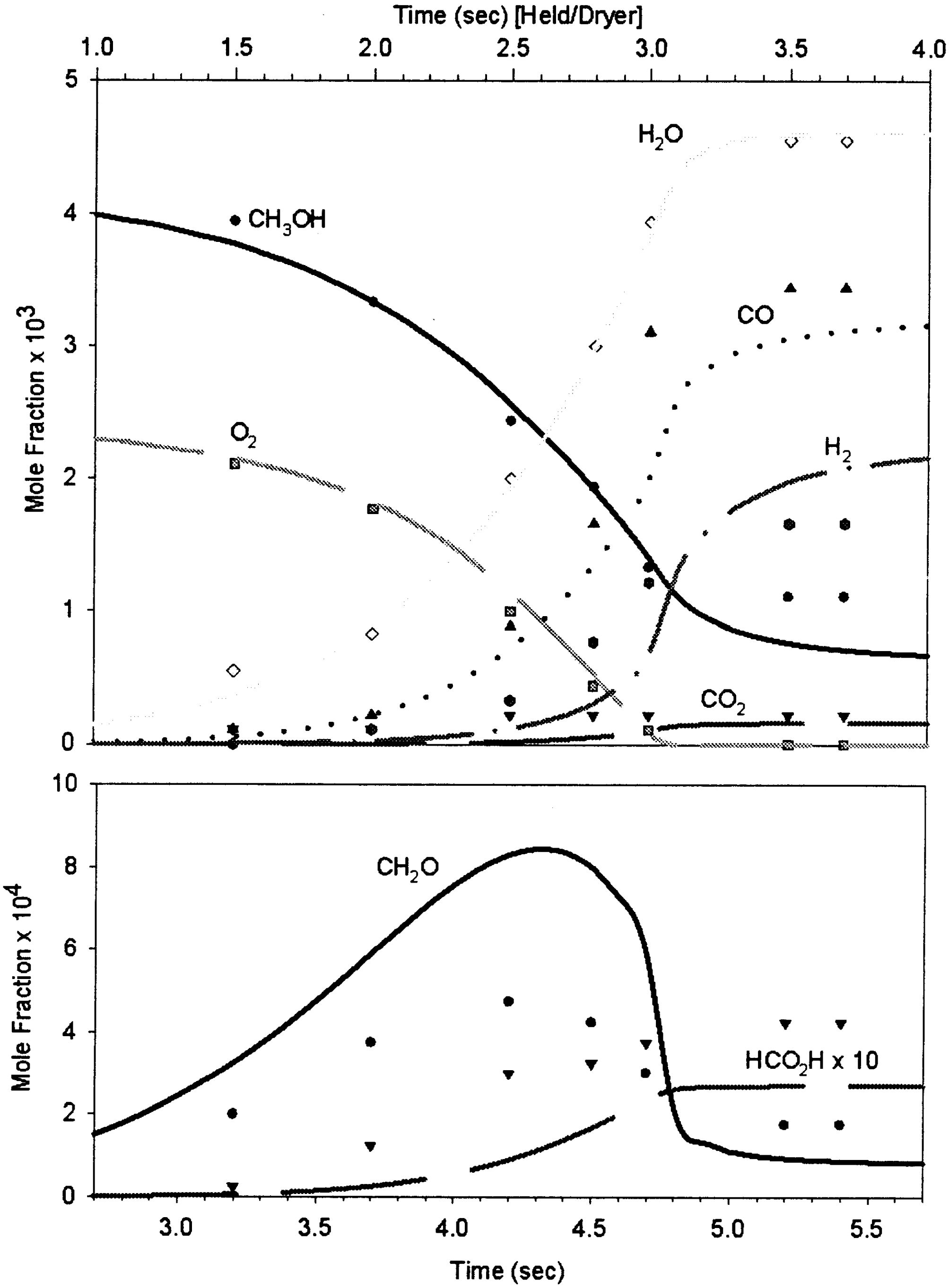


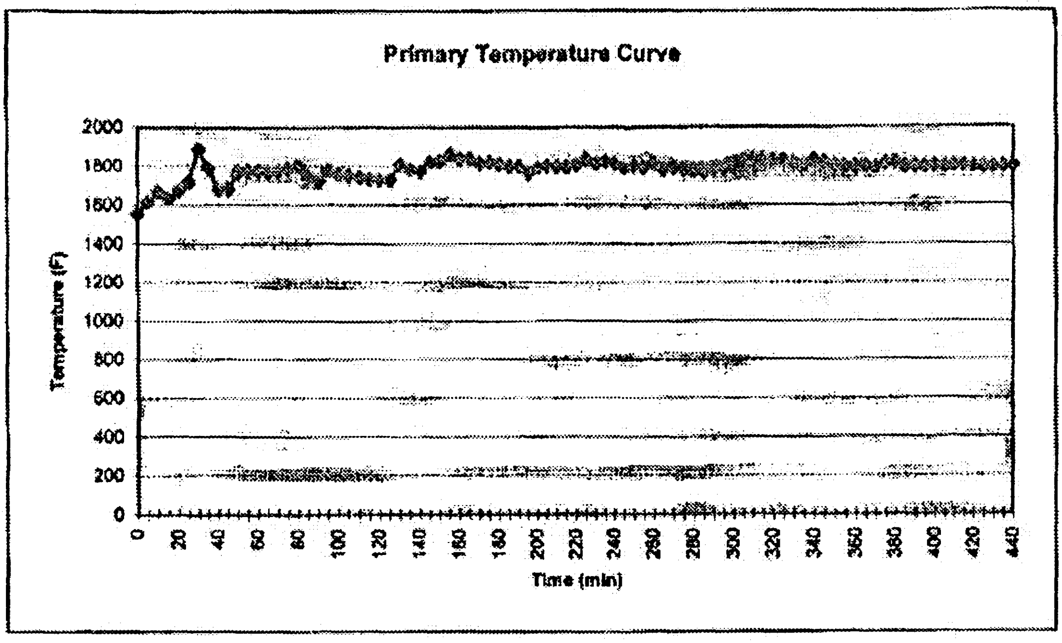
Figure A12 Comparison of model and experimental data from Held/Dryer at 781 K, 15.0 atm, ϕ =2.59 and $X_0(CH_3OH)$ = 0.00415

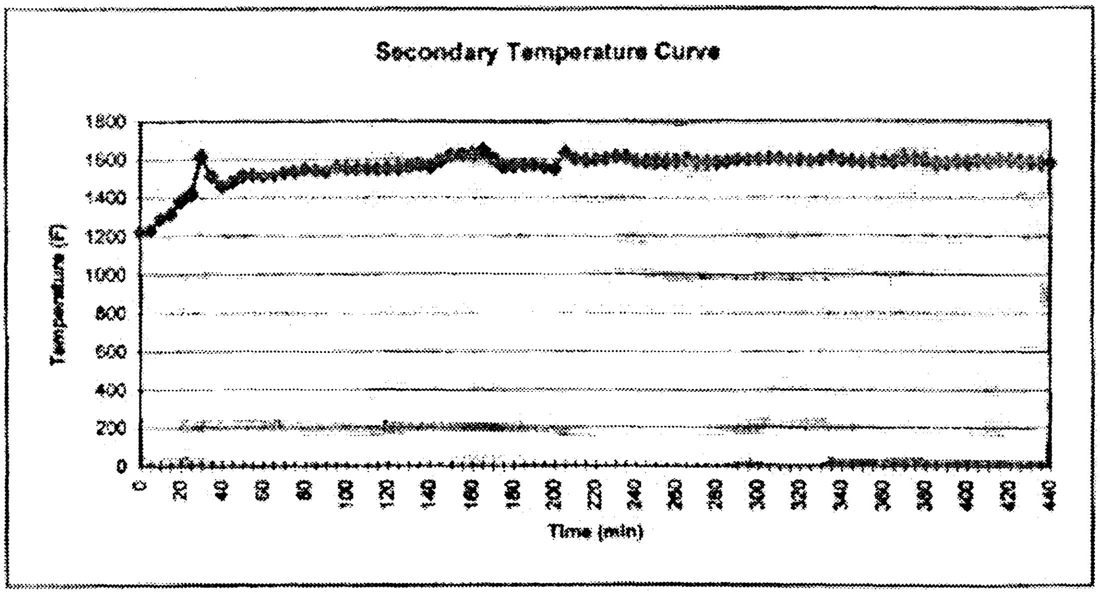
APPENDIX B

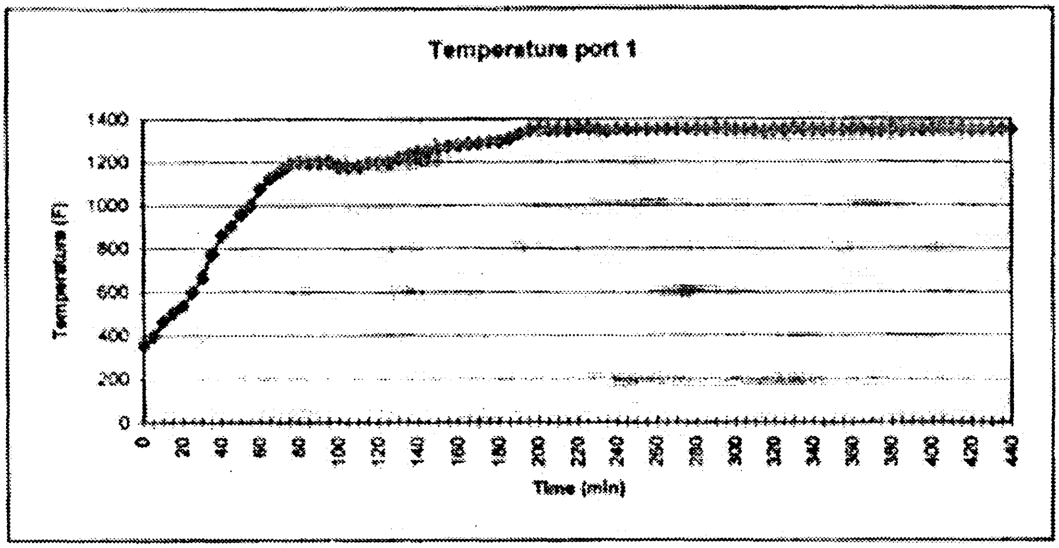
EXPERIMENTAL DATA FROM PILOT SCALE INCINERATOR

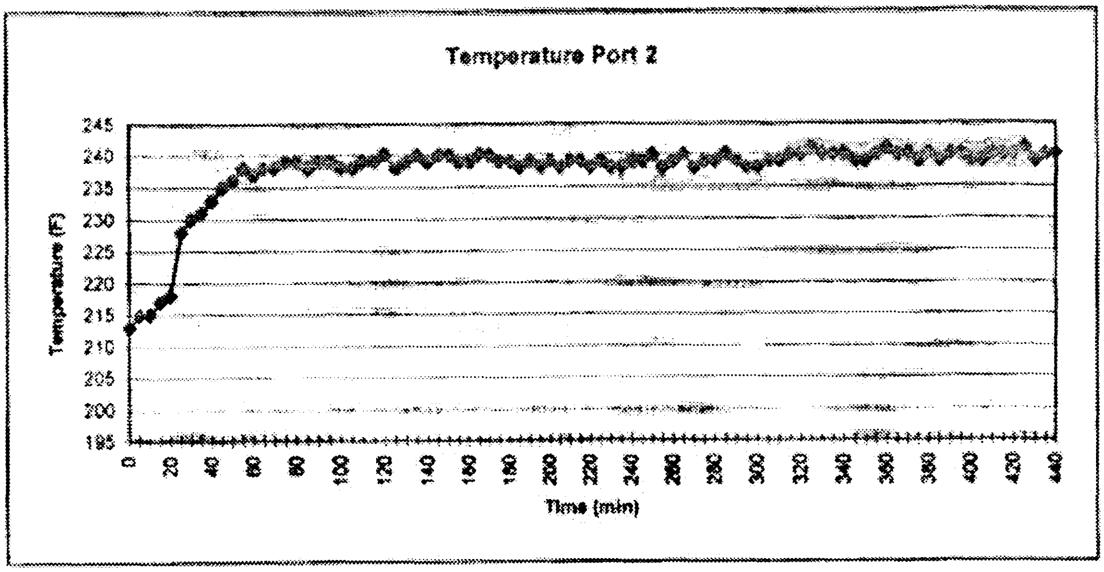
Experimental data real time data acquired from the pilot scale incinerator for the run performed on the following dates: Dec. 10, 1998; Feb. 11, 1999; Aug. 26, 1999, Sept. 14, 1999 and Nov. 9, 1999.

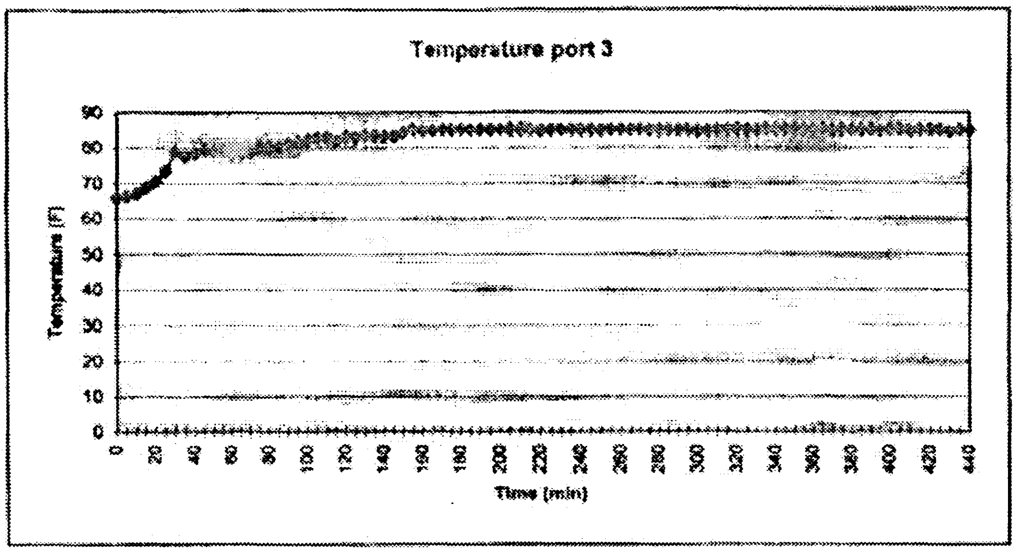
Raw experimental data obtained from the pilot scale incinerator on Dec 10, 1998.

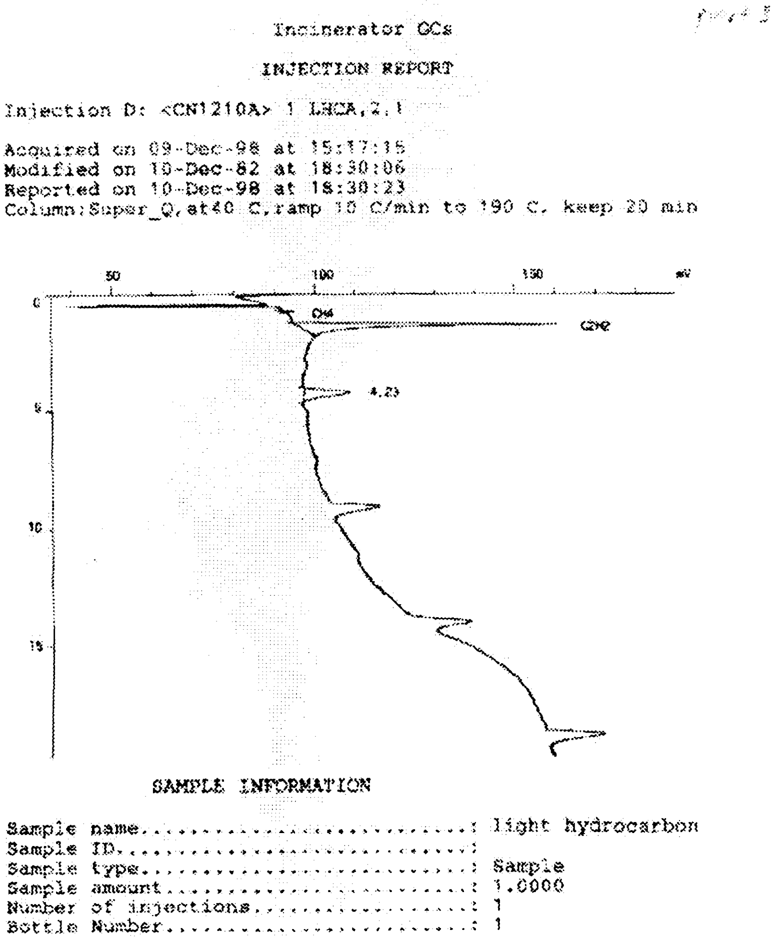





Temperature port 1
1400
1200
1000
800
600
400
200
0
Temperature (F)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
Time (min)


Temperature Port 2
245
240
235
230
225
220
215
210
205
200
195
Temperature (F)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
Time (min)





page 3

Incinerator GCs

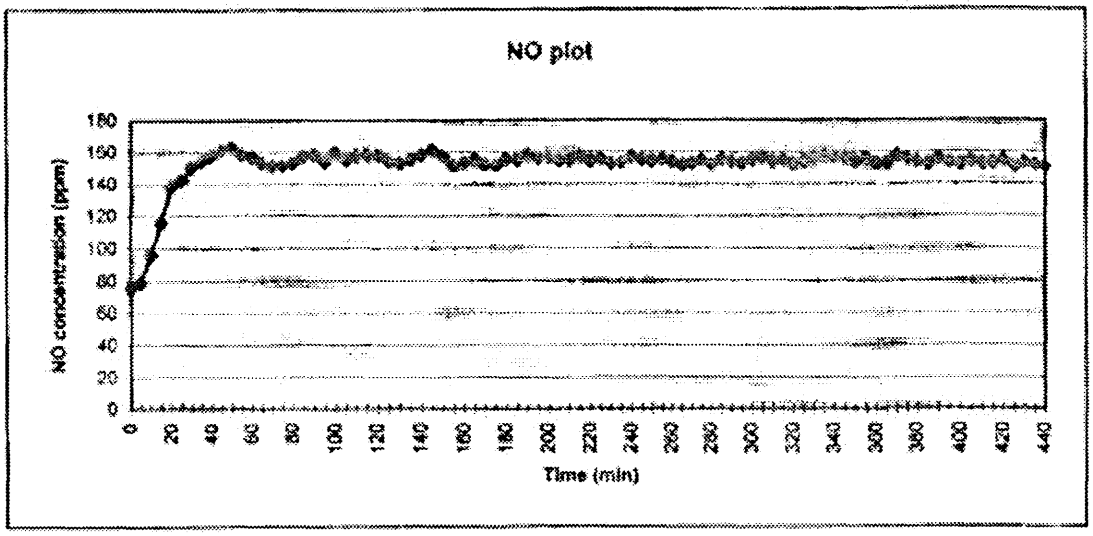
INJECTION REPORT

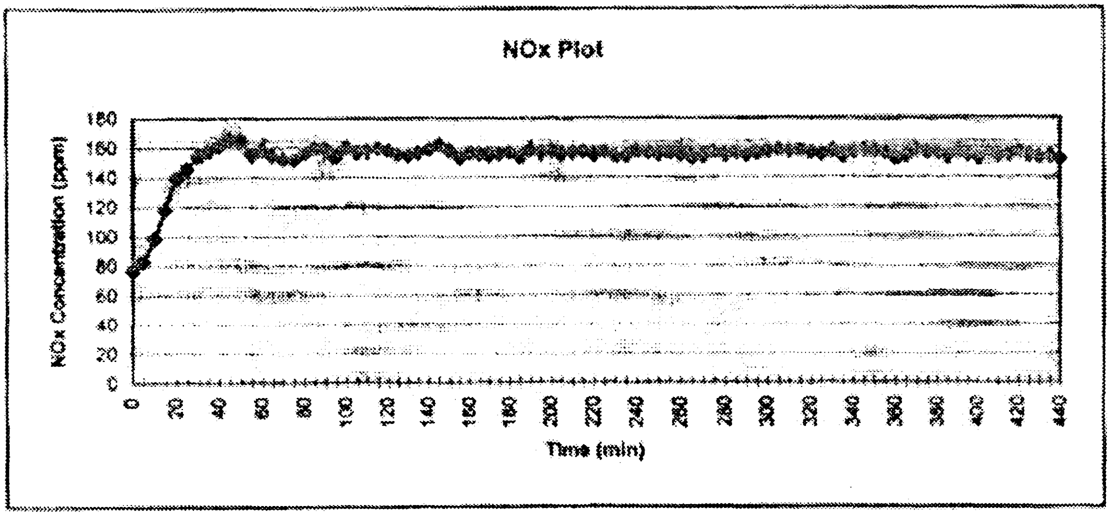
Injection D: <CN1210A> 1 LHCA,2,1

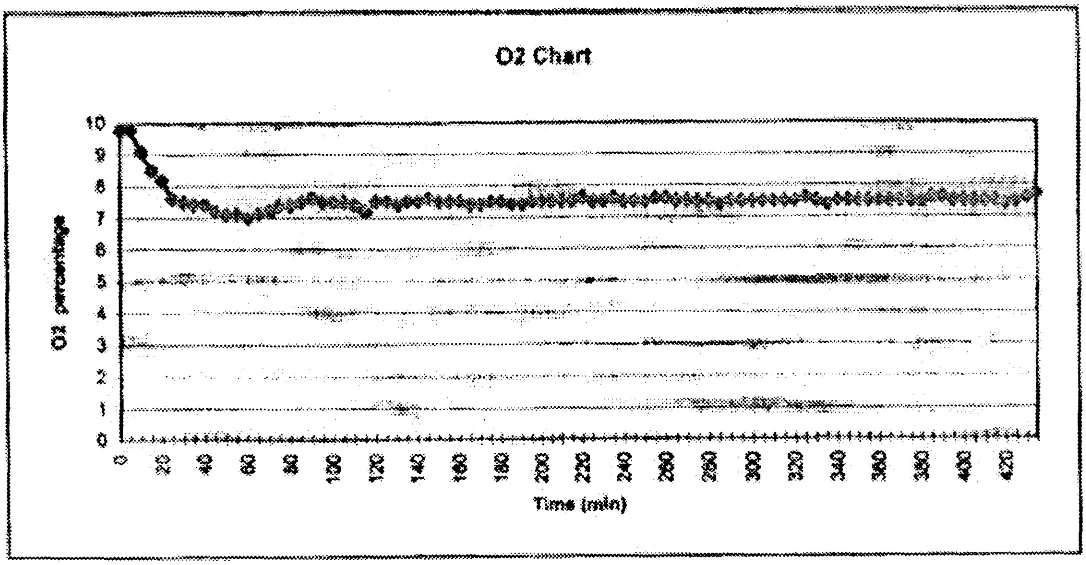
Acquired on 09-Dec-98 at 15:17:15
Modified on 10-Dec-82 at 18:30:06
Reported on 10-Dec-98 at 18:30:23
Column:Super_Q,at40 C,ramp 10 C/min to 190 C, keep 20 min

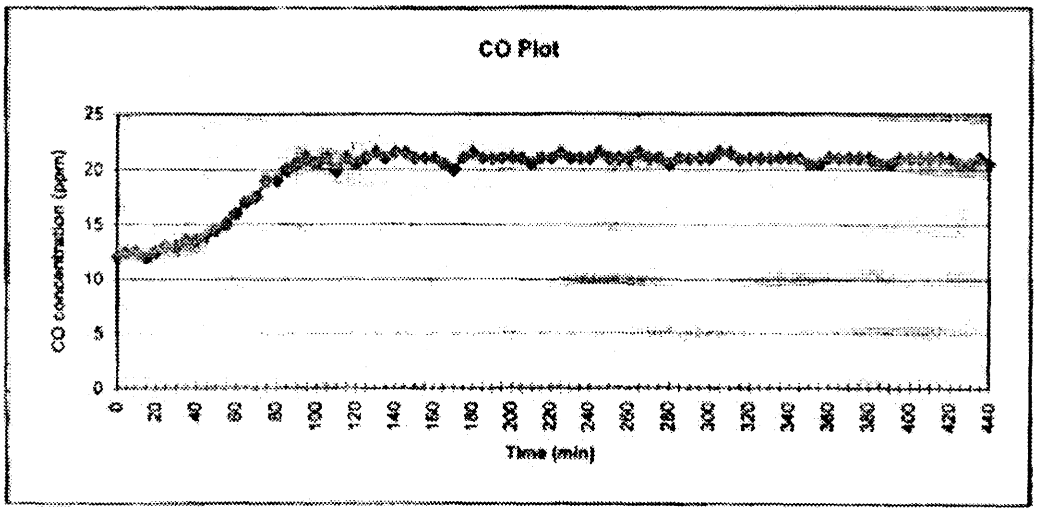
SAMPLE INFORMATION

Sample name..............................: light hydrocarbon
Sample ID................................:
Sample type..............................: Sample
Sample amount............................: 1.0000
Number of injections.....................: 1
Bottle Number............................: 1

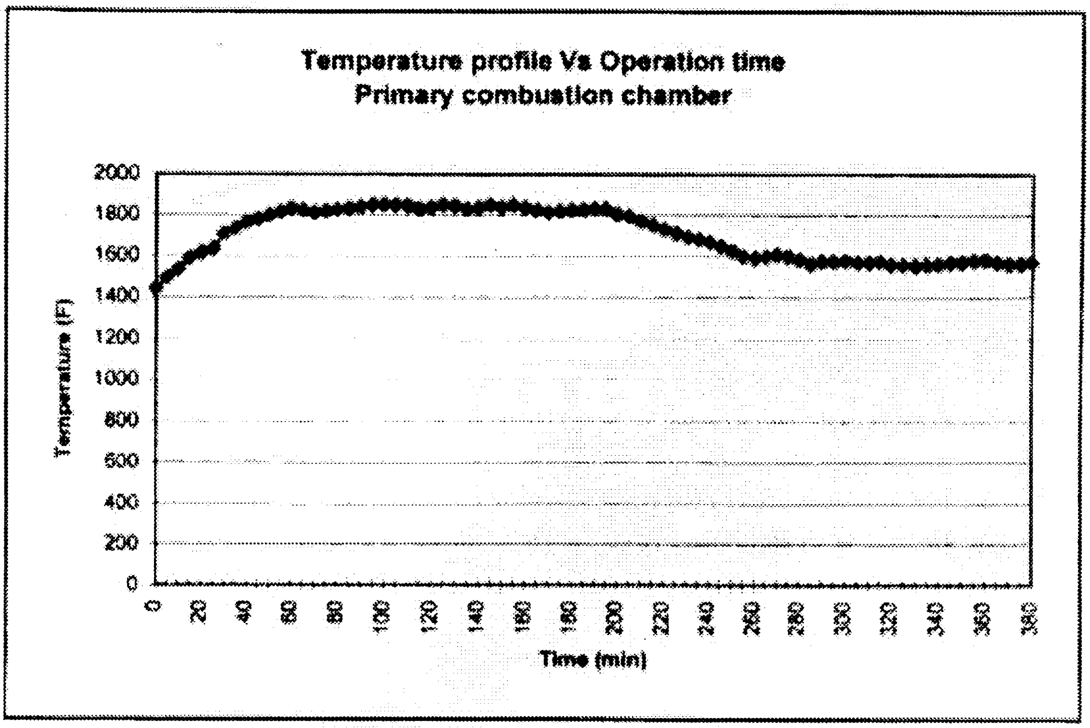

NO plot
NO concentration (ppm)
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
Time (min)

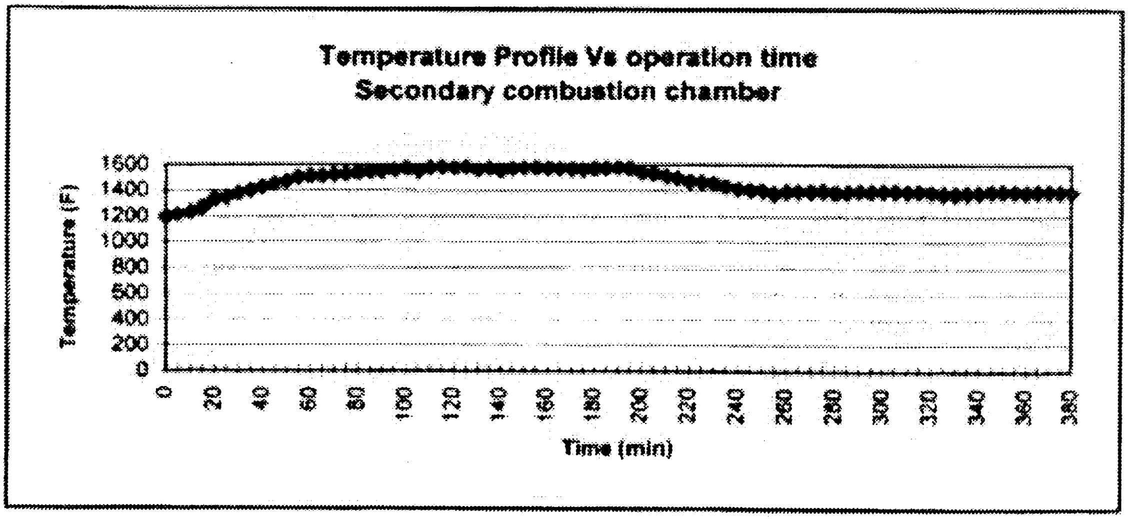

NOx Plot
NOx Concentration (ppm)
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
Time (min)

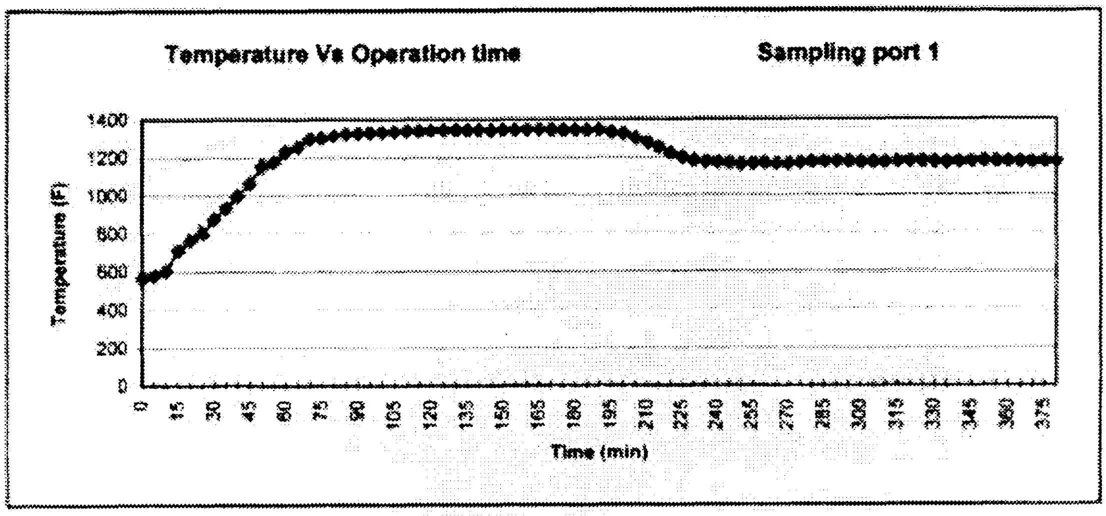

O2 Chart
O2 percentage
10
9
8
7
6
5
4
3
2
1
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
Time (min)


CO Plot
CO concentration (ppm)
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
Time (min)

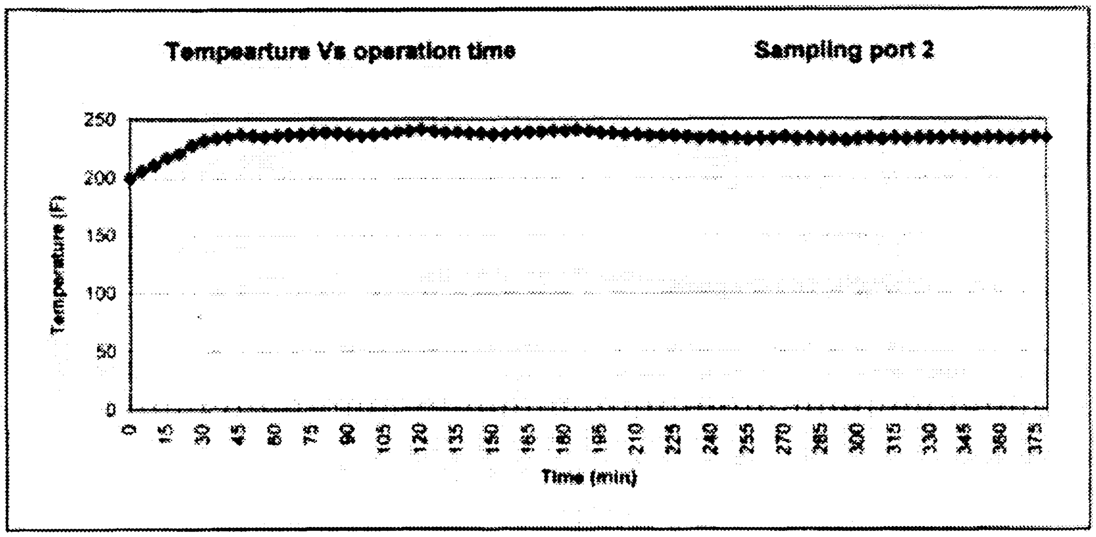
Raw experimental data obtained from the pilot scale incinerator on Feb 11, 1999.



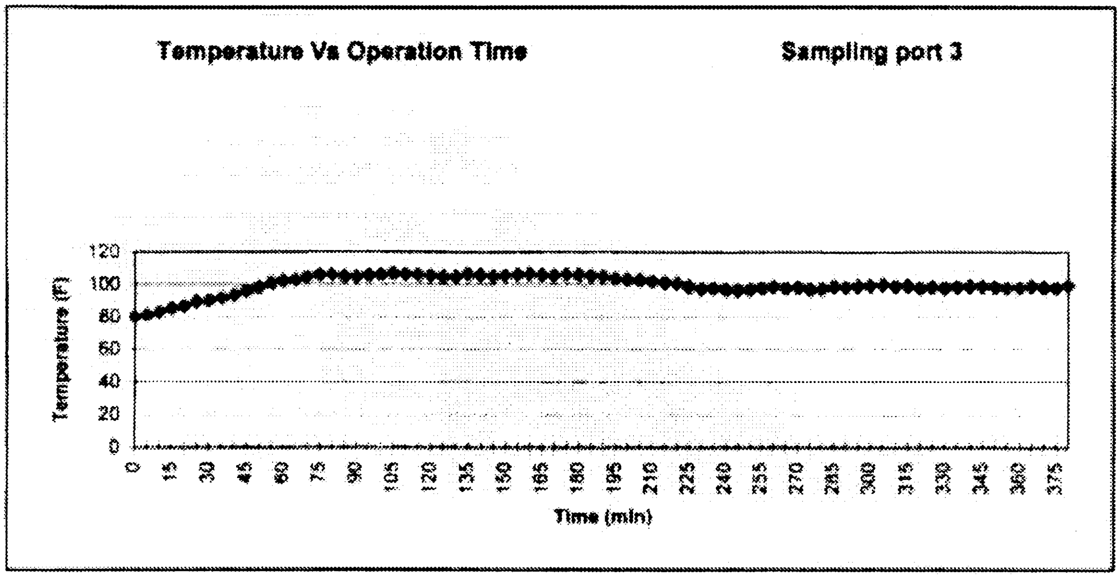


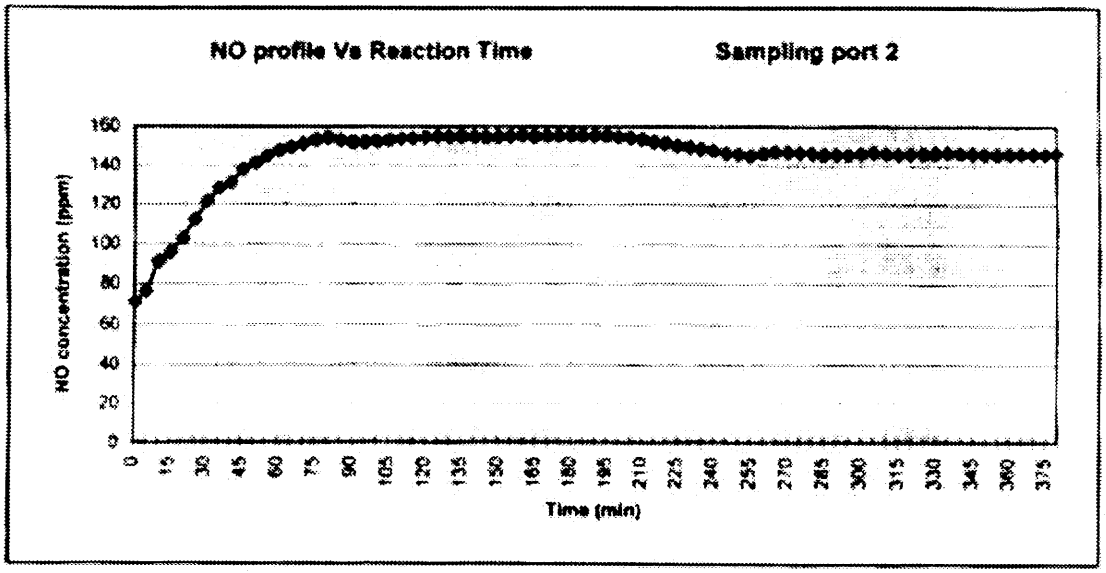


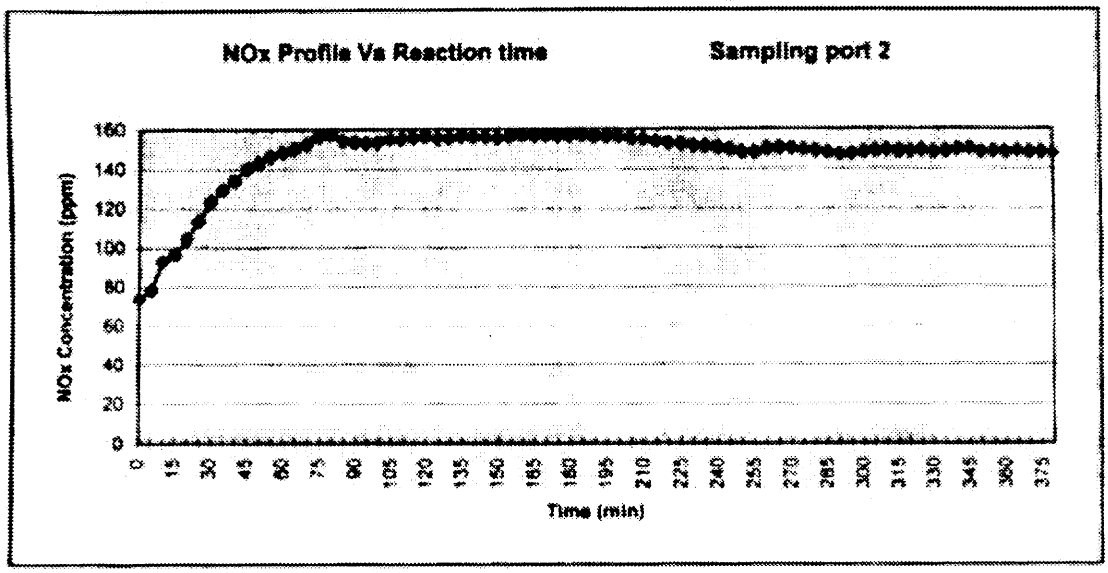
Temperature Vs Operation time
Sampling port 1
Temperature (F)
0
200
400
600
800
1000
1200
1400
Time (min)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
345
360
375

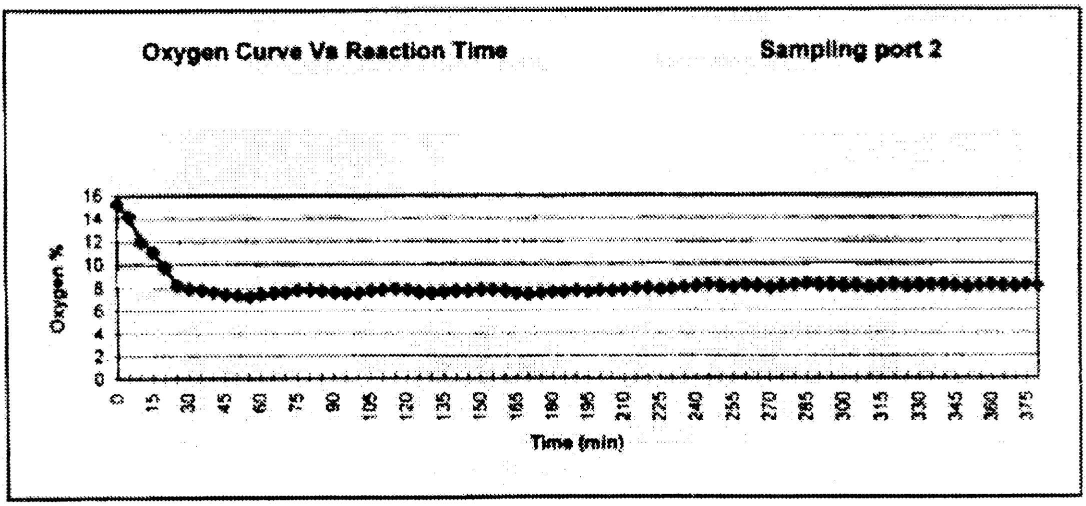


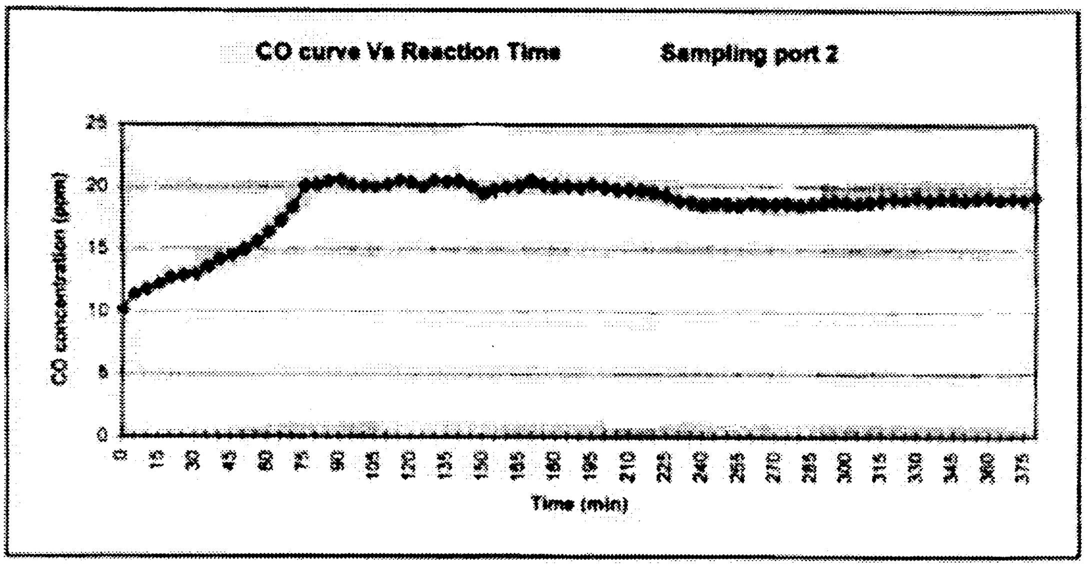
Tempeartura Vs operation time
Sampling port 2
Temperature (F)
0
50
100
150
200
250
Time (min)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
345
360
375


Temperature Vs Operation Time
Sampling port 3
Temperature (F)
0
20
40
60
80
100
120
Time (min)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
345
360
375

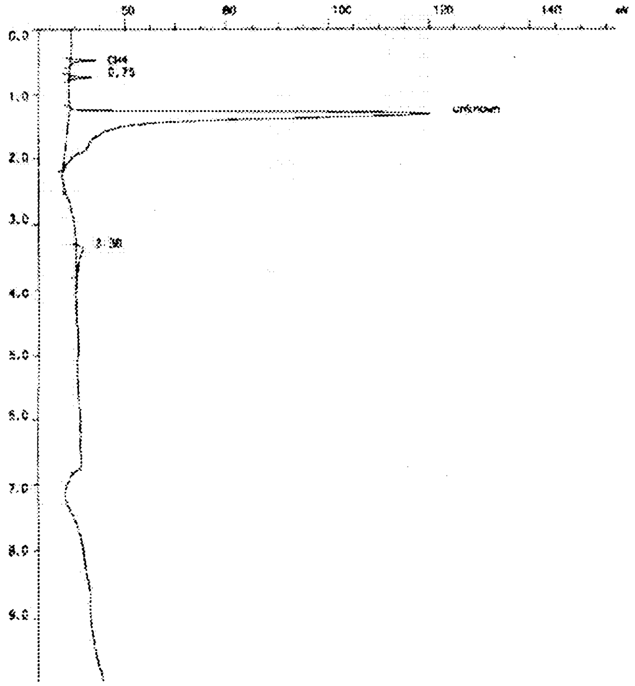

NO profile Vs Reaction Time
Sampling port 2
NO concentration (ppm)
0
20
40
60
80
100
120
140
160
Time (min)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
345
360
375


NOx Profile Vs Reaction time
Sampling port 2
NOx Concentration (ppm)
0
20
40
60
80
100
120
140
160
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
345
360
375
Time (min)

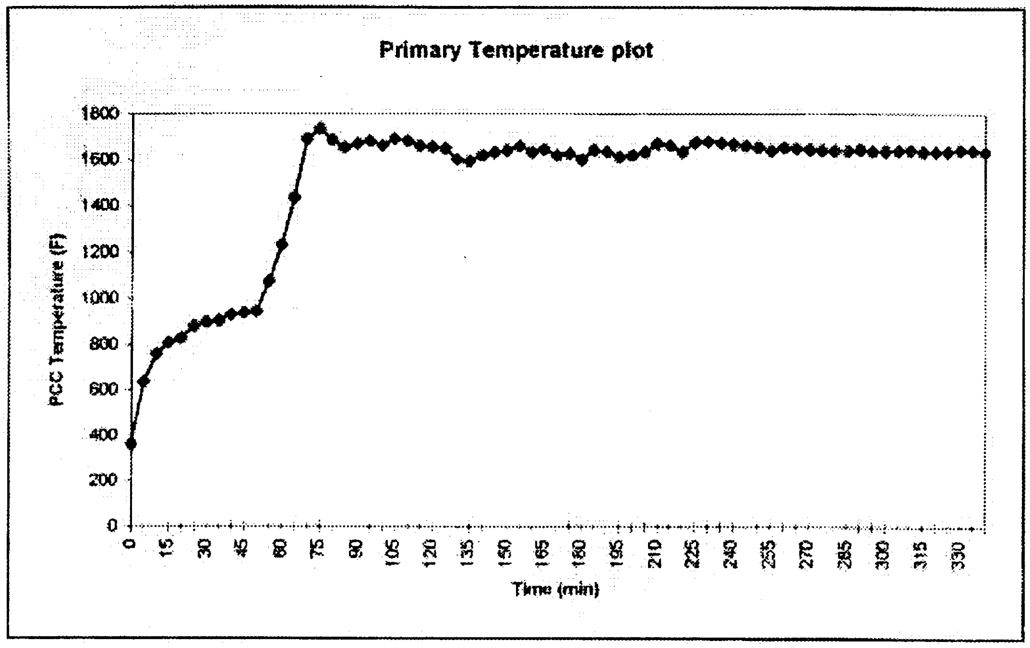

Oxygen Curve Vs Reaction Time
Sampling port 2
Oxygen %
0
2
4
6
8
10
12
14
16
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
345
360
375
Time (min)

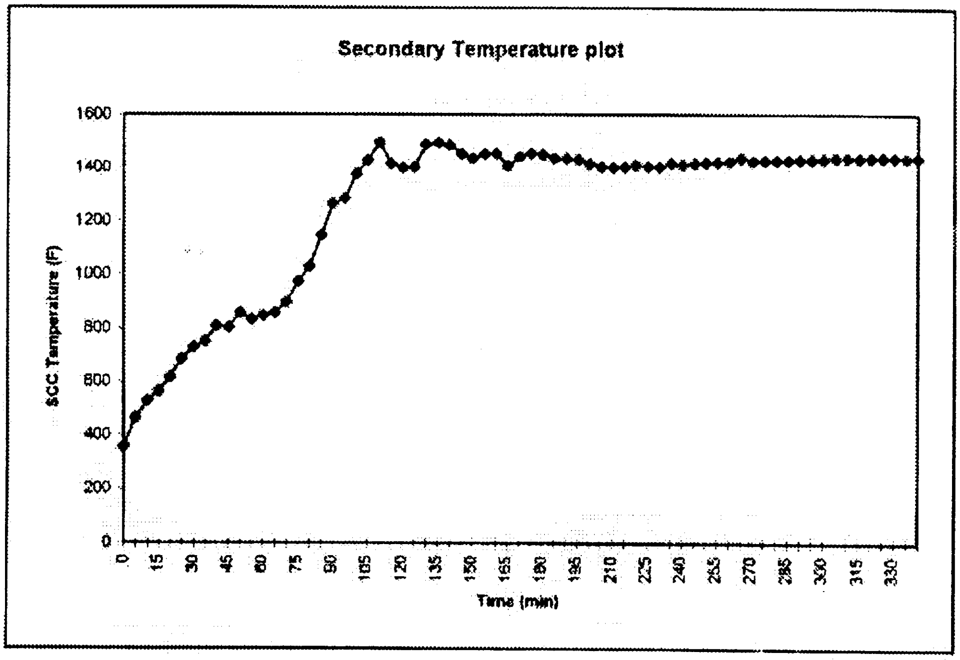


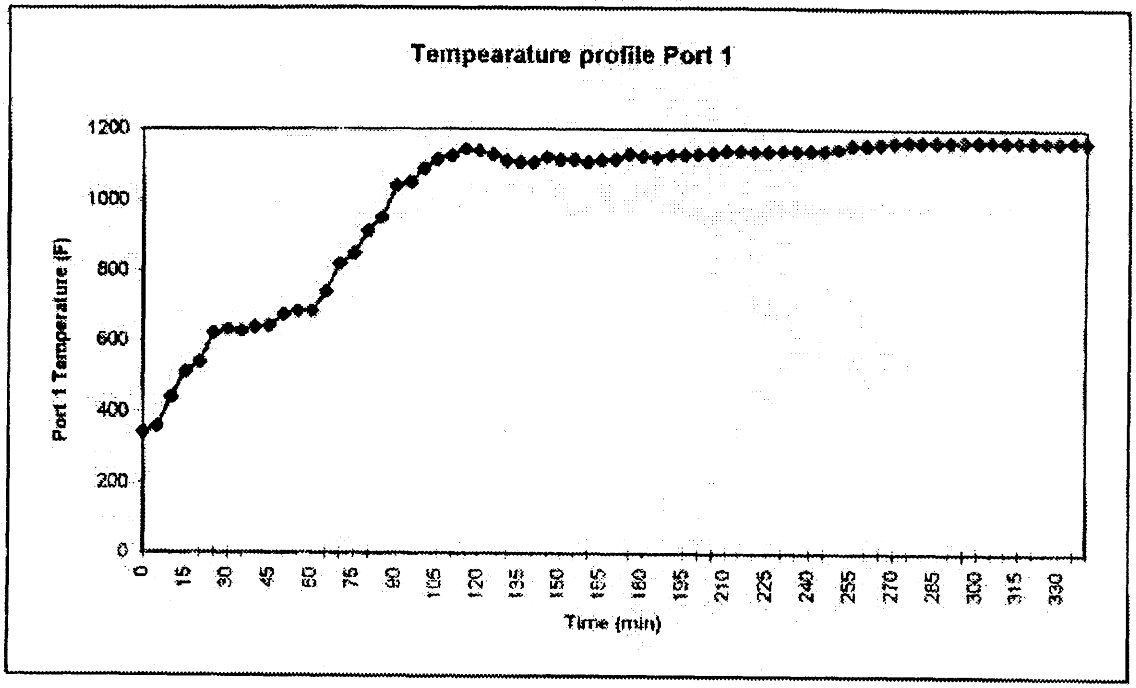
```
                    Incinerator GCs

                    INJECTION REPORT

Injection D: <CN0211A> 1 BFSSA,9,1

Acquired on 05-Feb-99 at 10:02:32
Modified on 05-Feb-99 at 12:26:54
Reported on 05-Feb-99 at 12:27:09
Column:Super-Q, at 40 C,ramp 10 C/min to 190 C,keep 5min.
```

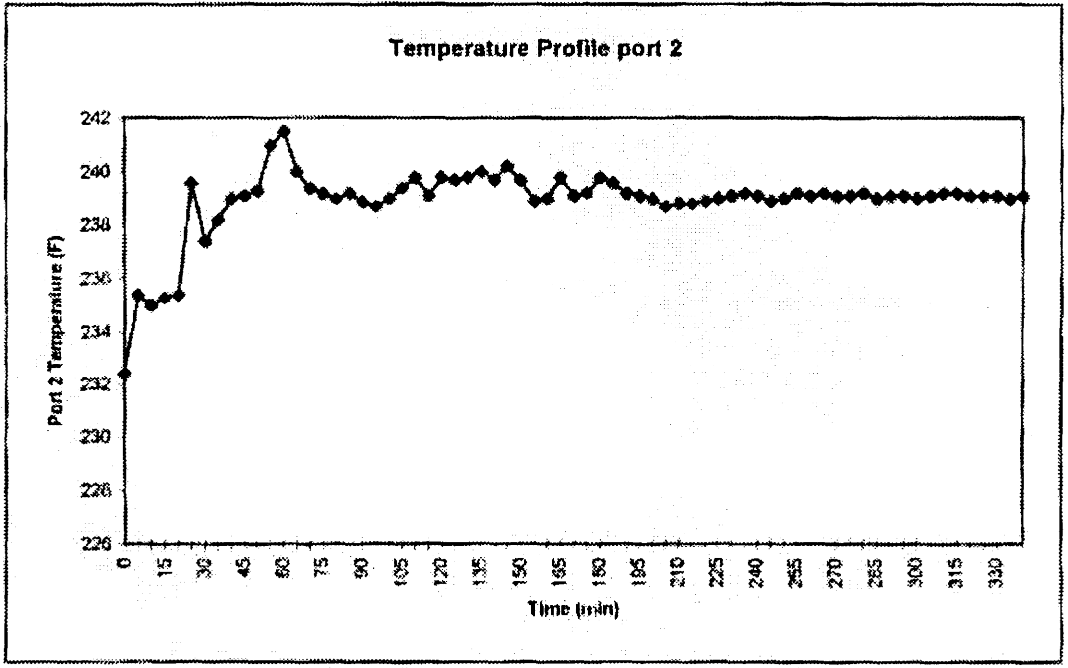


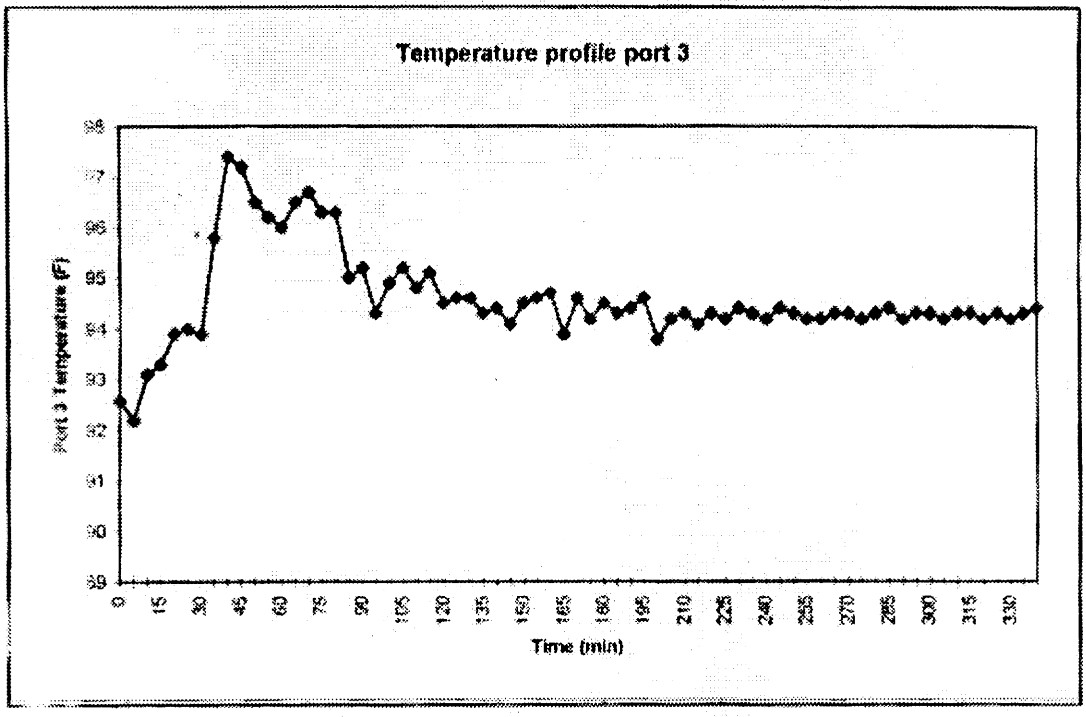
Raw experimental data obtained from the pilot scale incinerator on Aug 26, 1999.

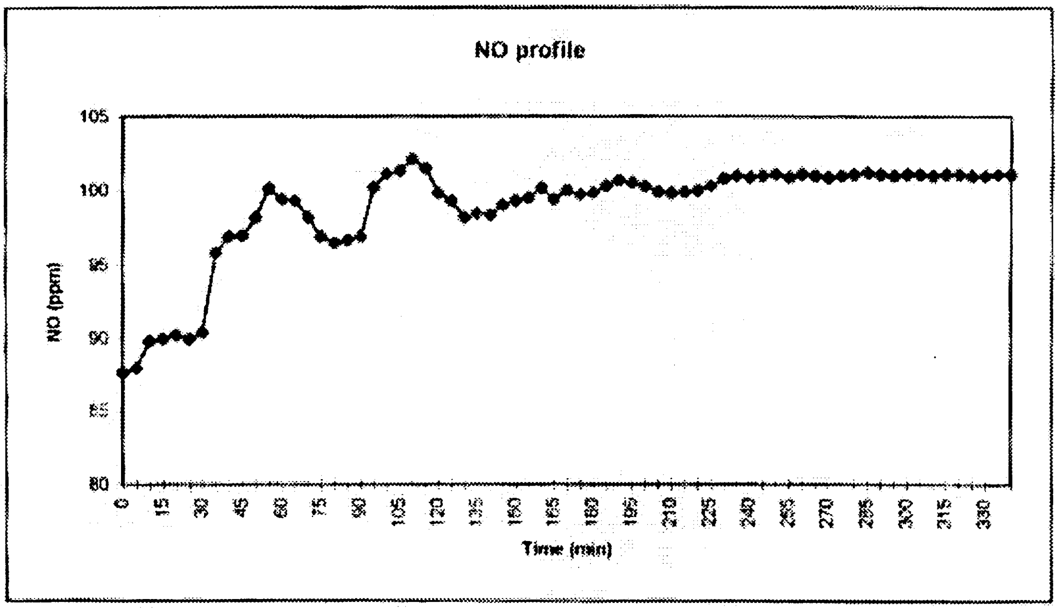


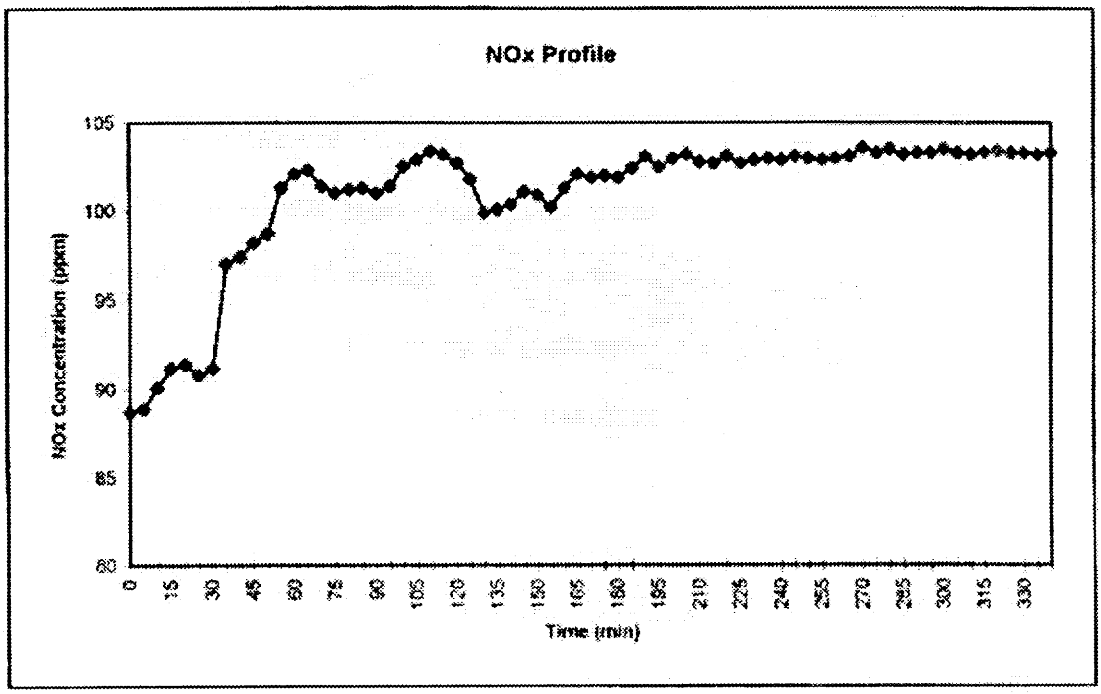


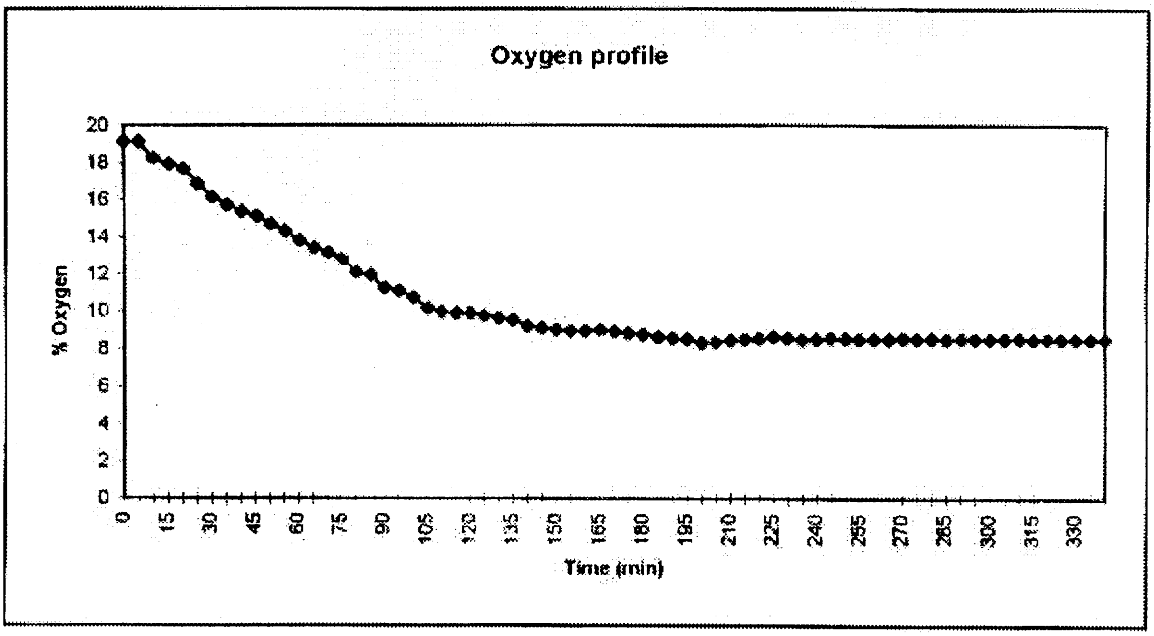

Tempearature profile Port 1
Port 1 Temperature (F)
1200
1000
800
600
400
200
0
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)

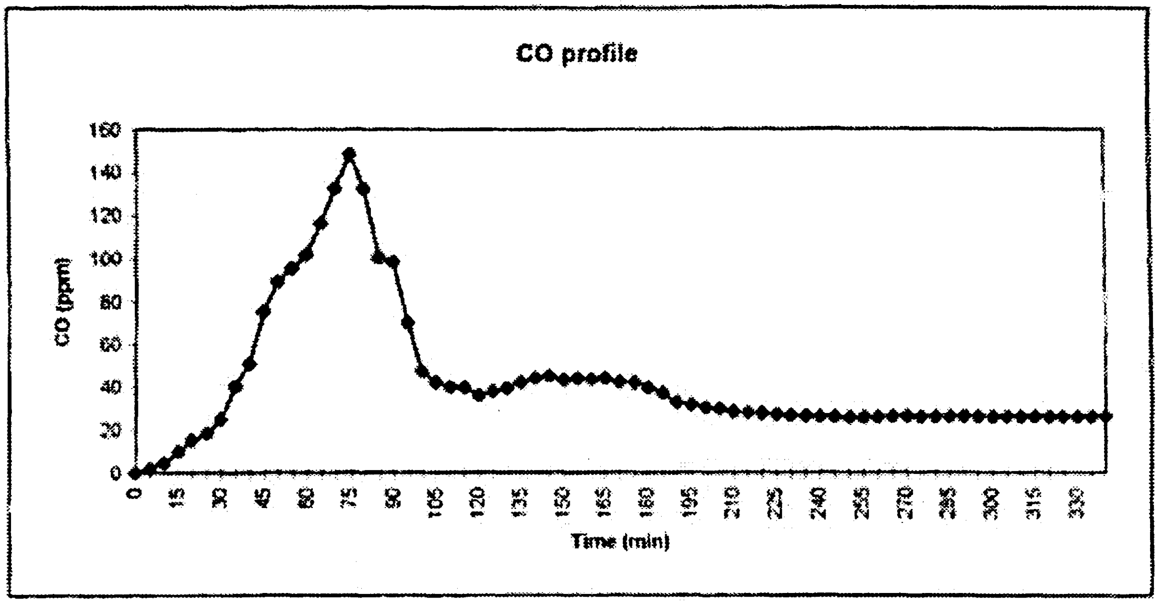

Temperature Profile port 2
Port 2 Temperature (F)
242
240
238
236
234
232
230
228
226
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)


Temperature profile port 3
Port 3 Temperature (F)
98
97
96
95
94
93
92
91
90
89
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)


NO profile
NO (ppm)
105
100
95
90
85
80
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)


NOx Profile
105
100
95
90
85
80
NOx Concentration (ppm)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)


Oxygen profile
20
18
16
14
12
10
8
6
4
2
0
% Oxygen
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)



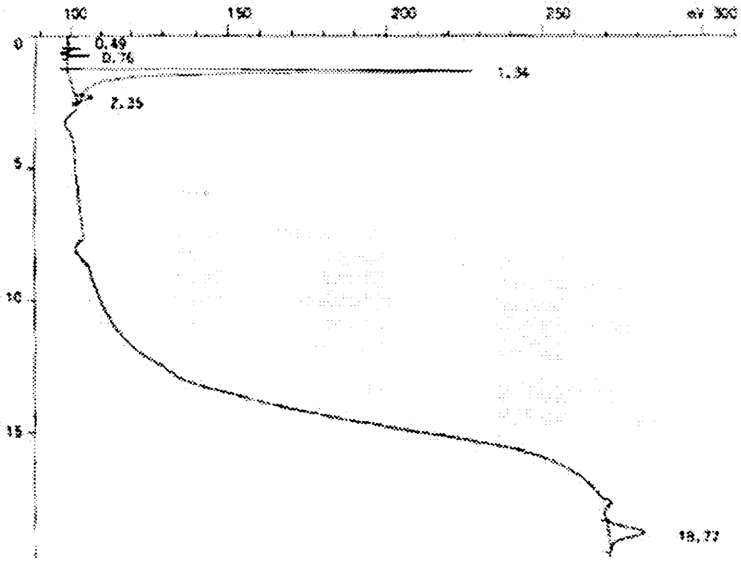
FC Minichrom

LONG PLOT

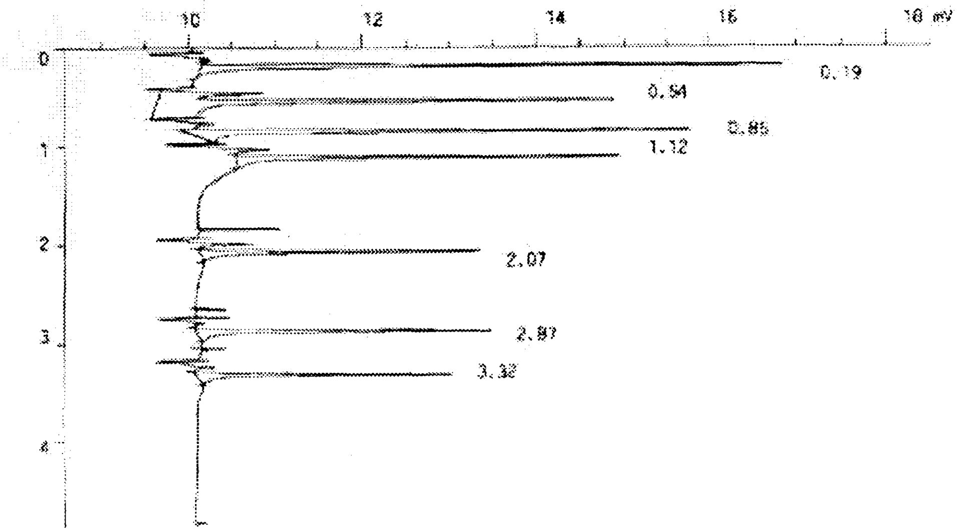
Injection D: <CNLHC>) LHC0826A,11,1

Column:Super-Q, at 40 C,ramp 10 C/min to 190 C,Keep 5min.

Acquired on 04-Aug-99 at 02:43:10
Reported on 10-Sep-99 at 17:51:10

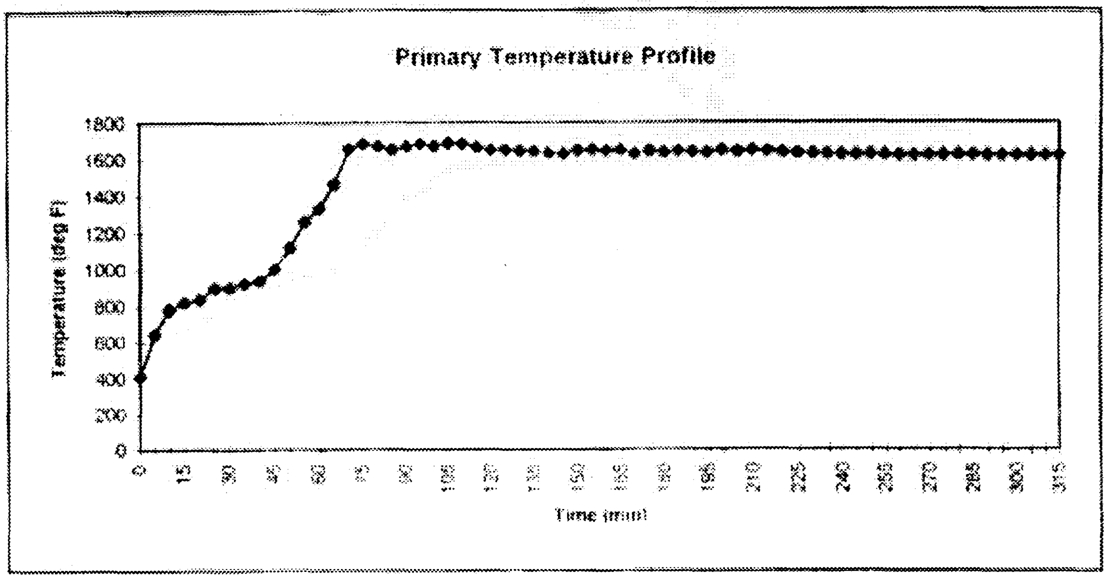


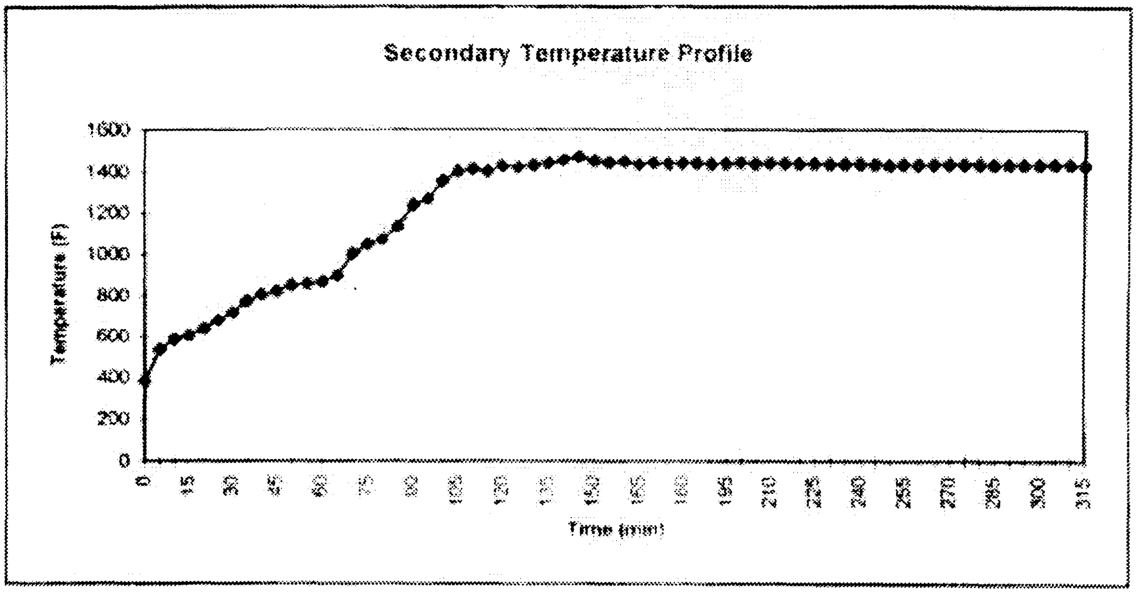
```
                    PC Minichrom

                  INJECTION REPORT

Injection D: <CNTHC> 3 THC0826A,35,1

Acquired on 04-Aug-99 at 03:19:14
Modified on 18-Aug-83 at 19:12:12
Reported on 05-Oct-99 at 12:27:23
FID Temp.: 270 C, Oven Temp.: 80 C, sample loop: empty
```

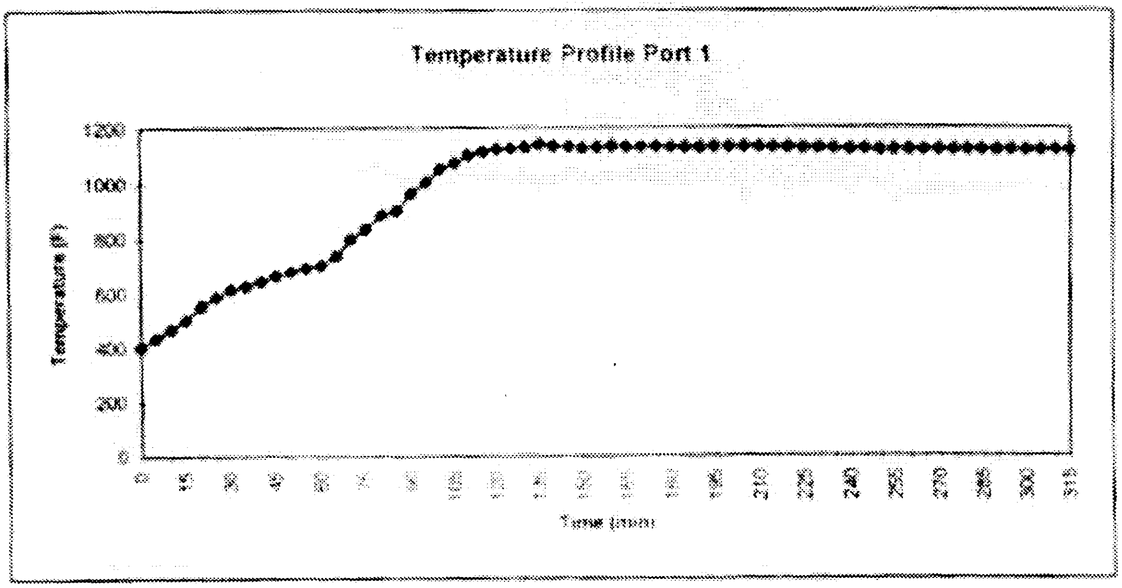


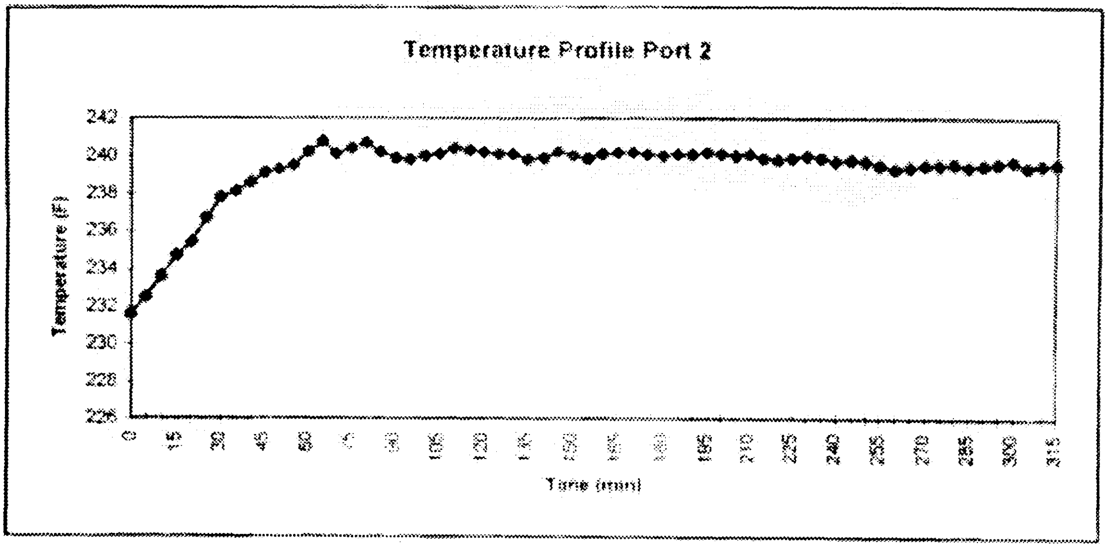
```
              PEAK INFORMATION

Peak  RT mins   Hght  uV      Area  uVs
   1    0.187     6705          12390
   2    0.544     5258          17553
   3    0.853     5824          10482
   4    1.120     4378           7459
   5    2.069     3191           5351
   6    2.875     3387           5647
   7    3.317     2920           4851

Total            31663          63733
Residual             0              0
```

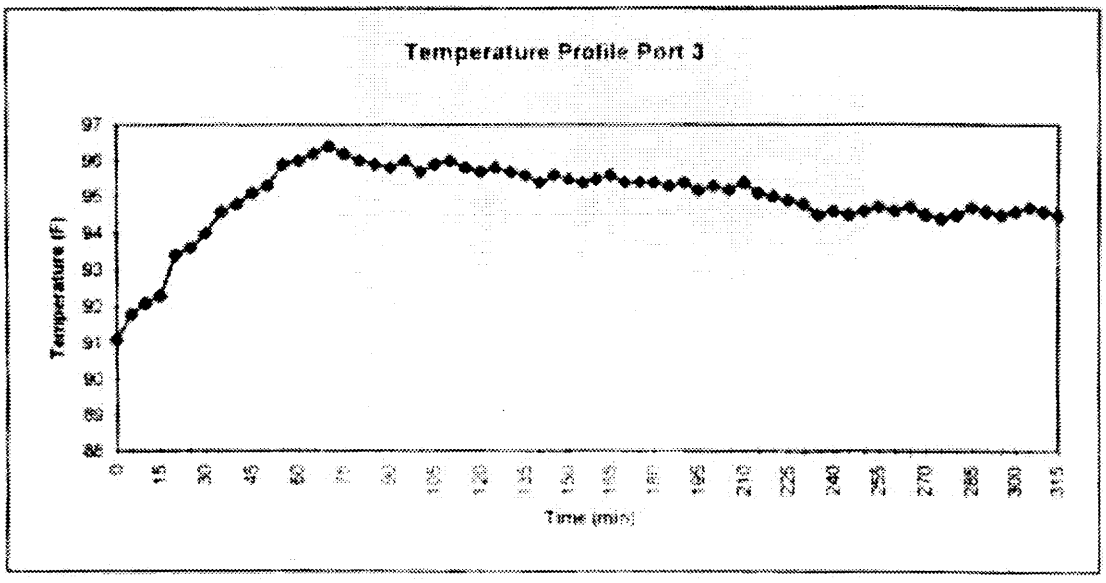
Raw experimental data obtained from the pilot scale incinerator on Sept. 14, 1999.

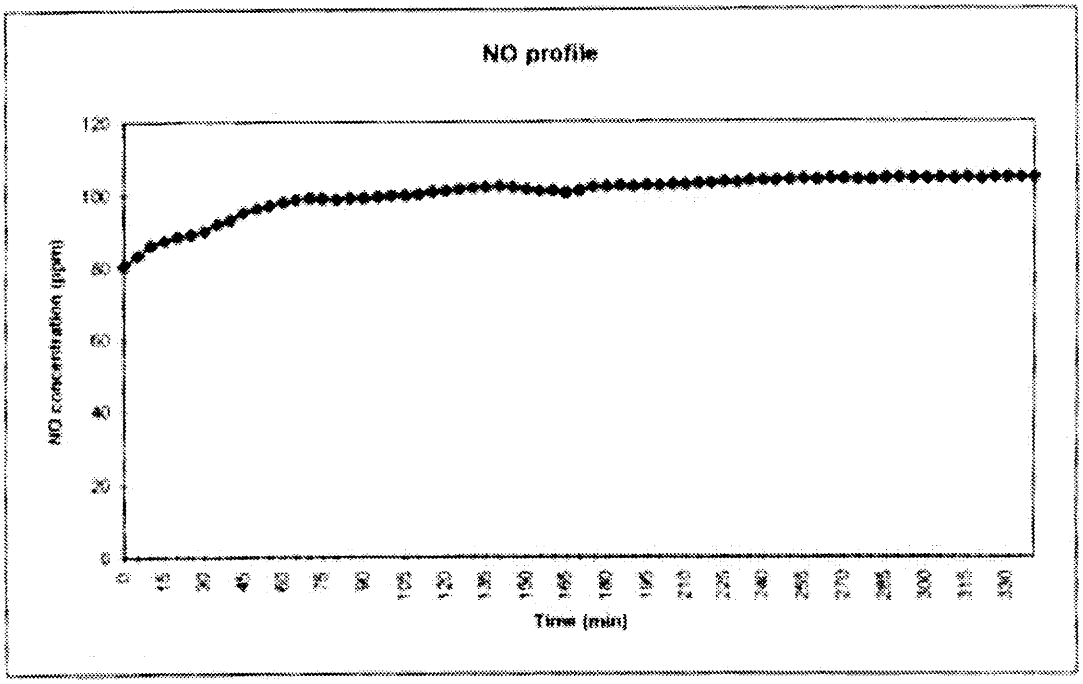


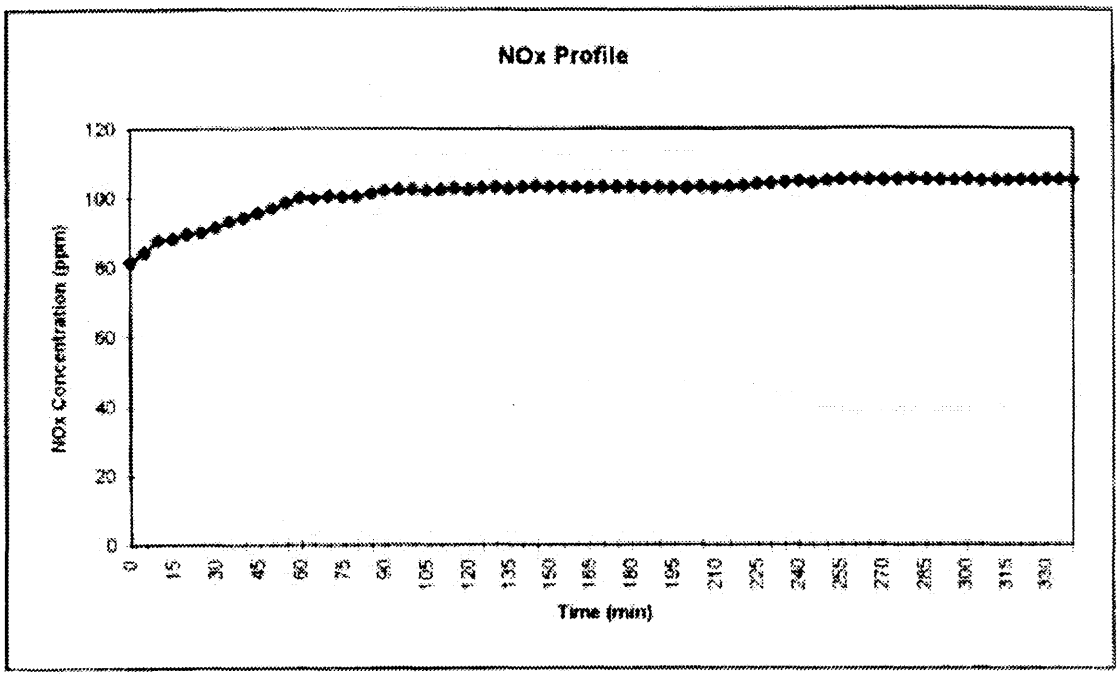


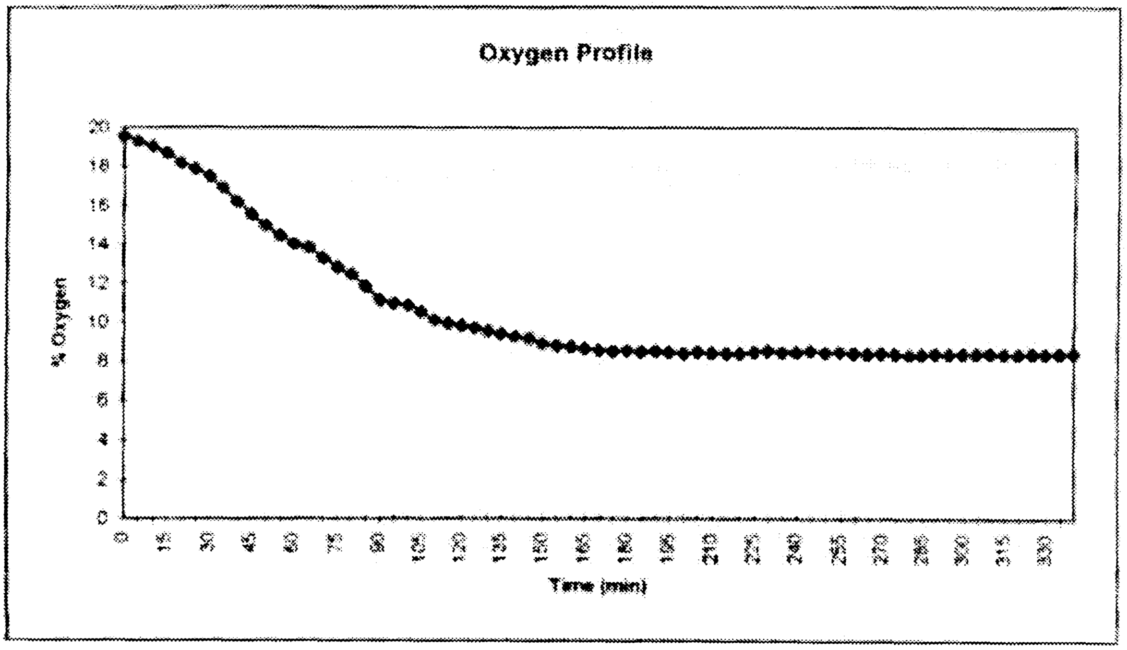

Temperature Profile Port 1
Temperature (F)
1200
1000
800
600
400
200
0
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
Time (min)

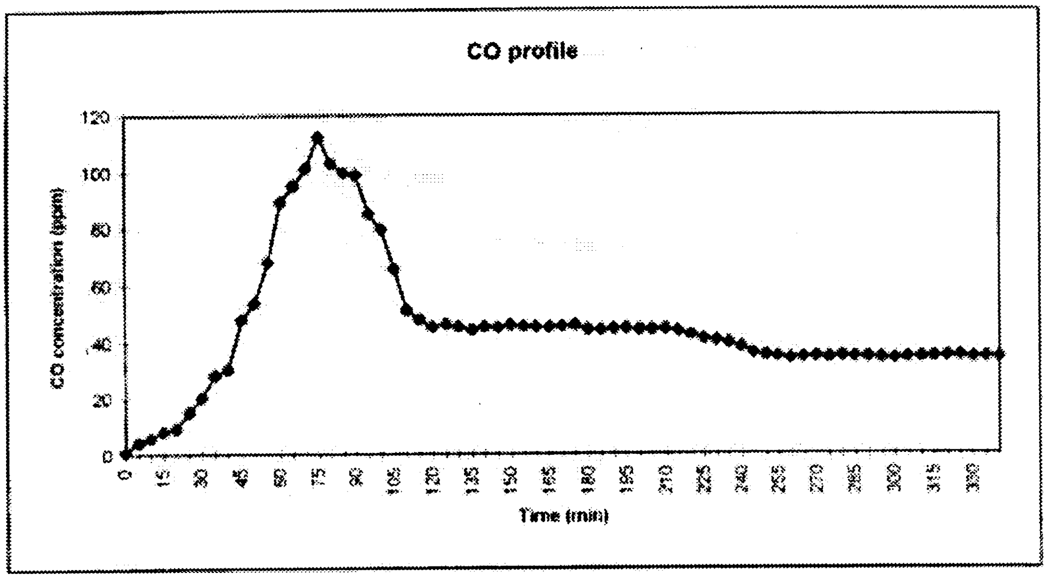

Temperature Profile Port 2
Temperature (F)
242
240
238
236
234
232
230
228
226
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
Time (min)


Temperature Profile Port 3
Temperature (F)
97
96
95
94
93
92
91
90
89
88
Time (min)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315

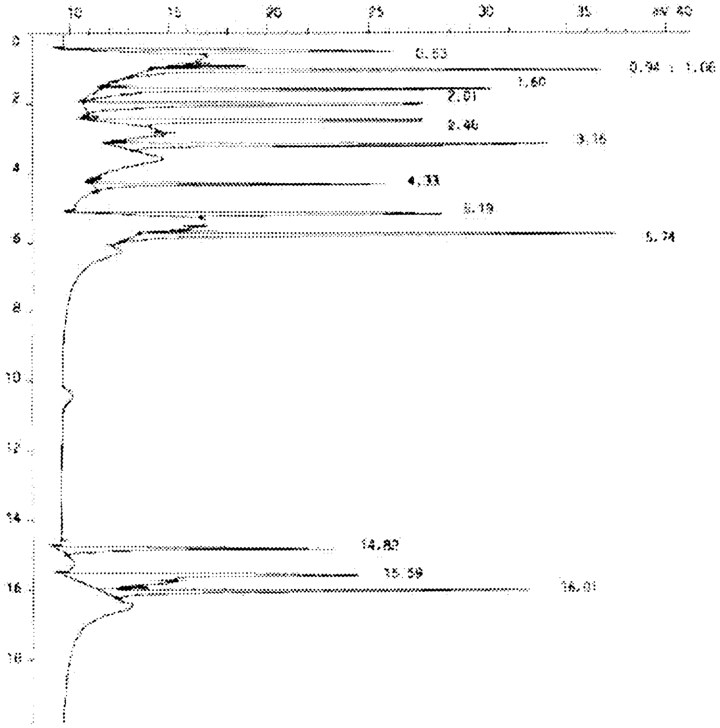

NO profile
NO concentration (ppm)
120
100
80
60
40
20
0
Time (min)
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330


NOx Profile
NOx Concentration (ppm)
120
100
80
60
40
20
0
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)

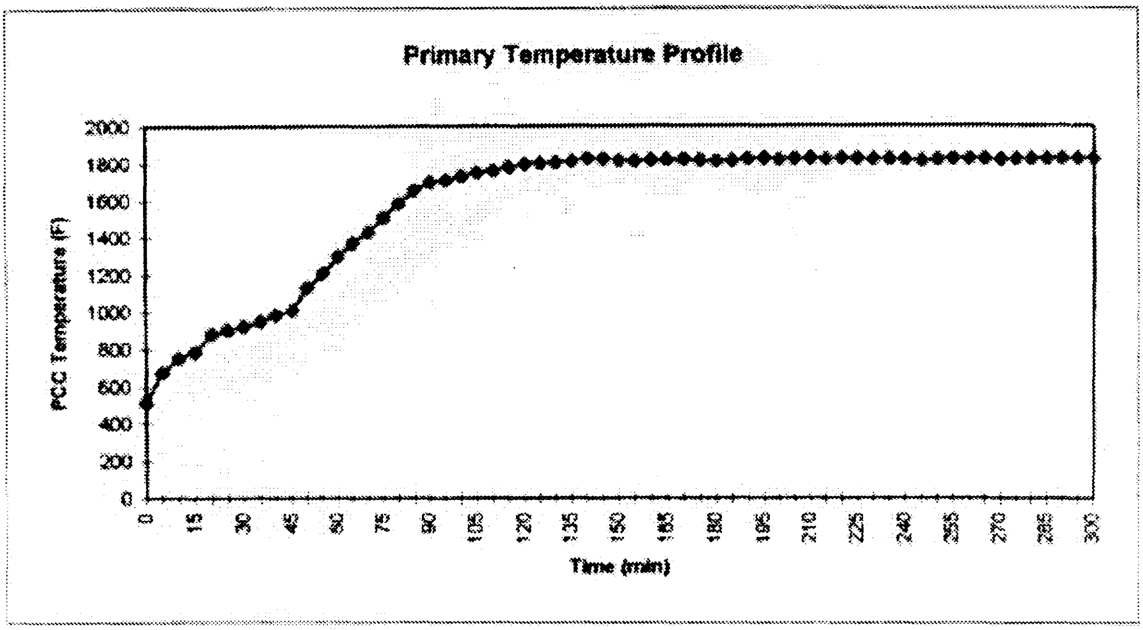

Oxygen Profile
% Oxygen
20
18
16
14
12
10
8
6
4
2
0
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
315
330
Time (min)

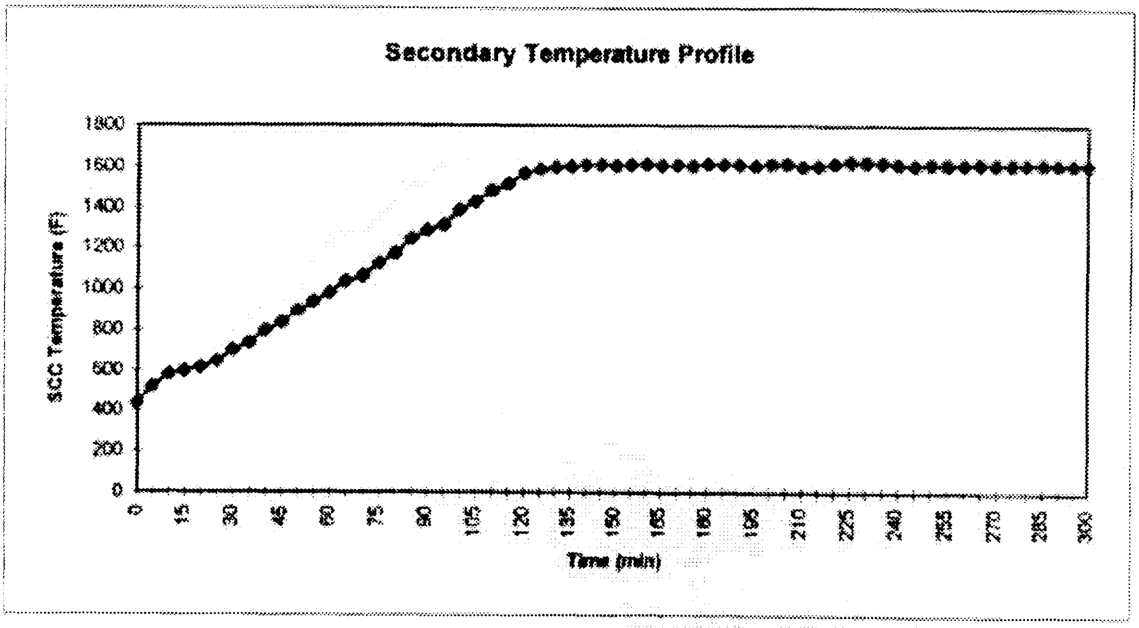


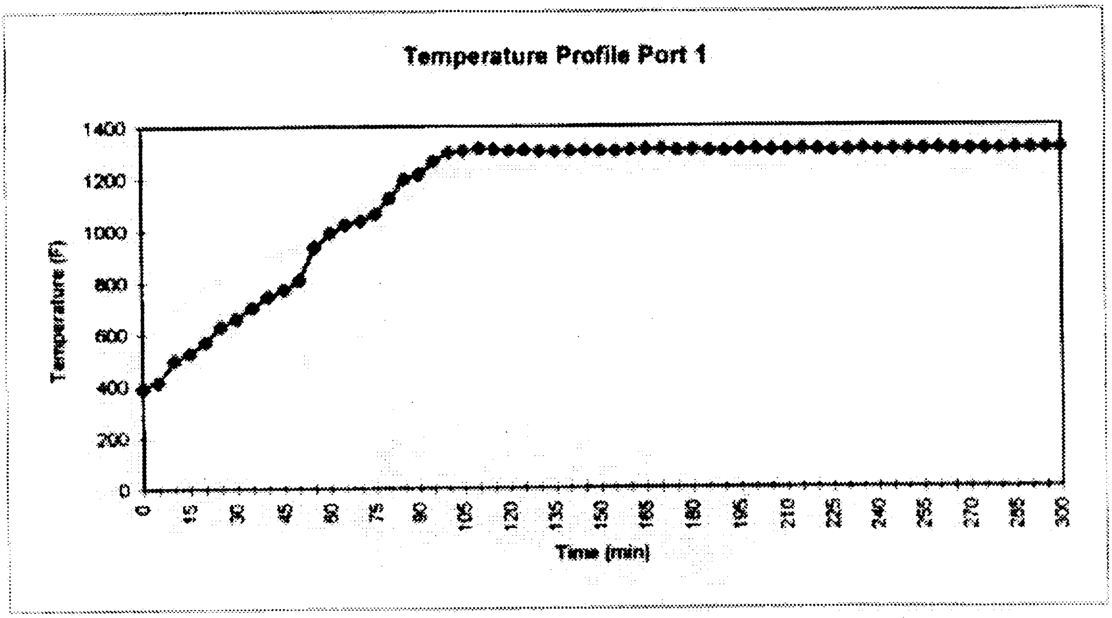
```
PC Minichrom

INJECTION REPORT

Injection D: <CNTHC> 3 THC0914A,7,1

Acquired on 14-Sep-99 at 16:41:46
Modified on 17-Sep-83 at 13:29:58
Reported on 05-Oct-99 at 10:48:57
FID Temp.: 270 C, Oven Temp.: 80 C, sample loop: empty
```

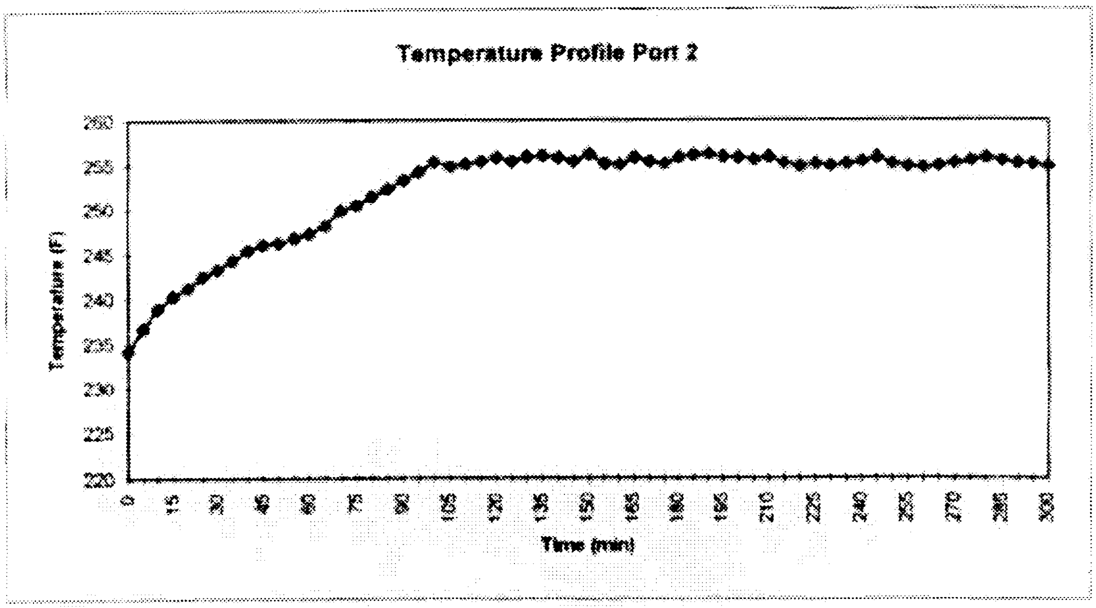


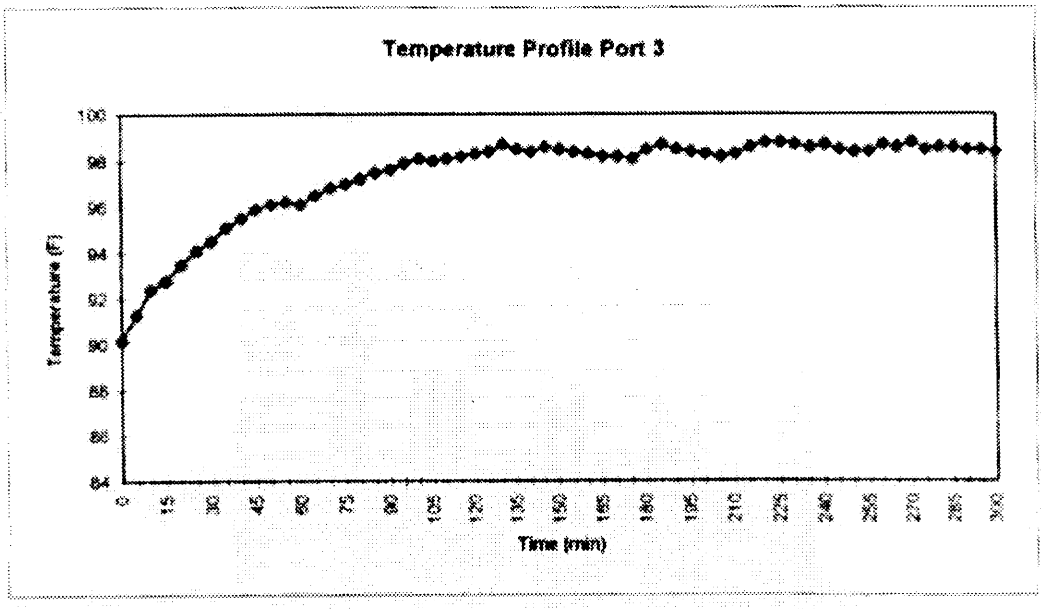
Raw experimental data obtained from the pilot scale incinerator on Nov 9, 1999.

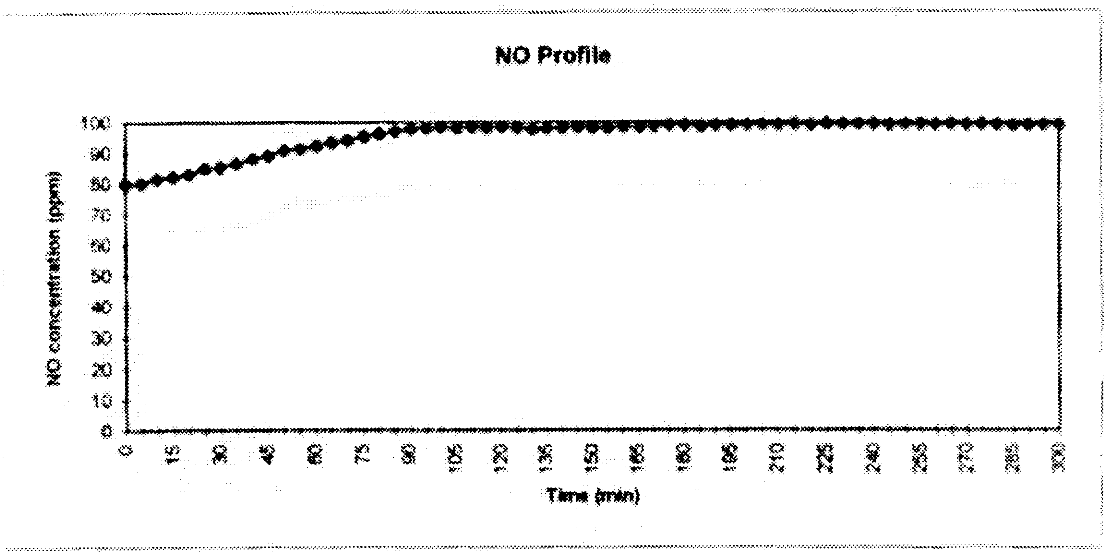


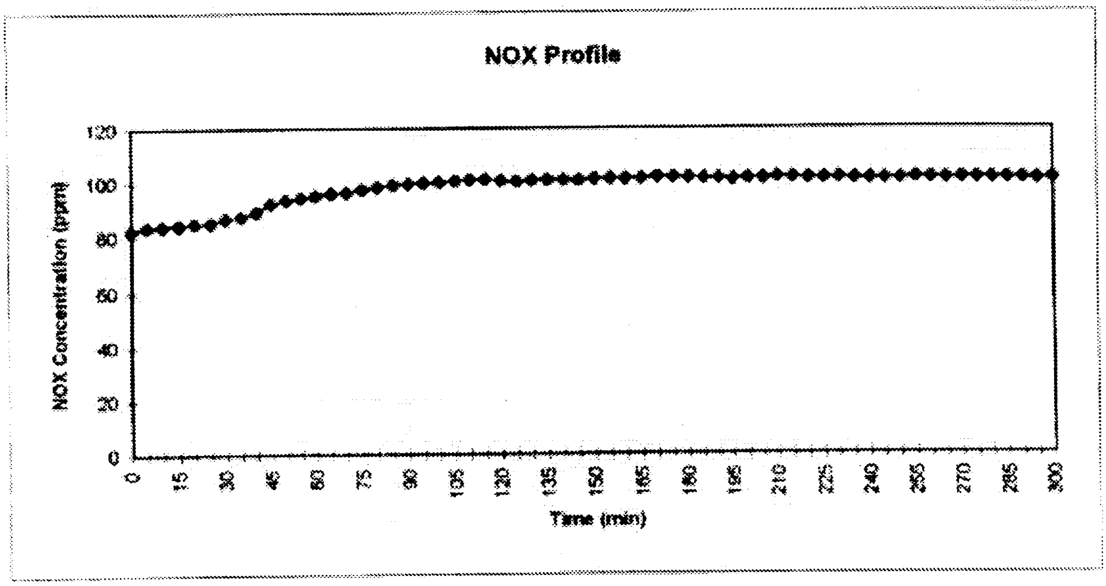


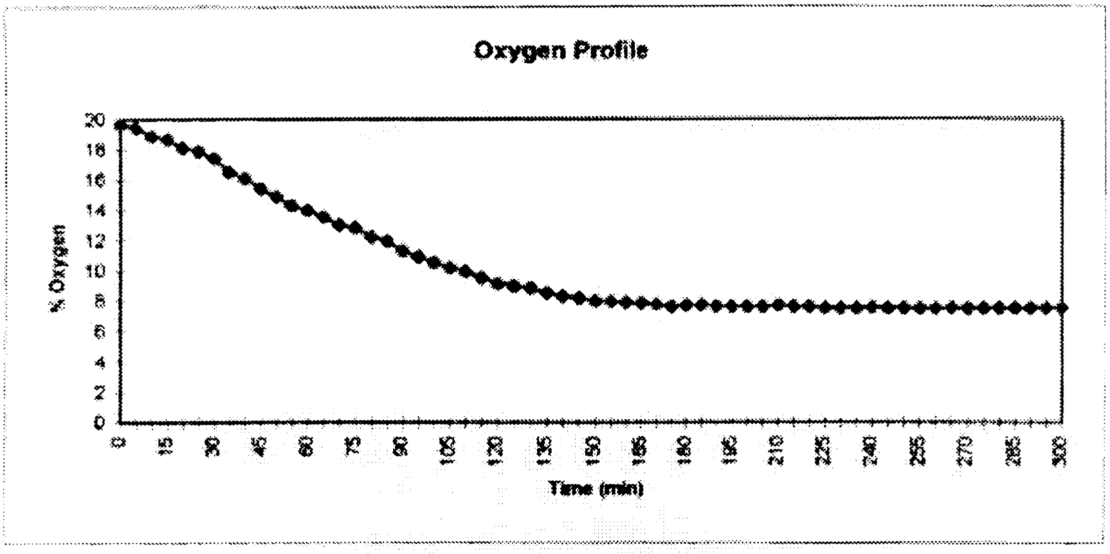

Temperature Profile Port 1
Temperature (F)
1400
1200
1000
800
600
400
200
0
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
Time (min)

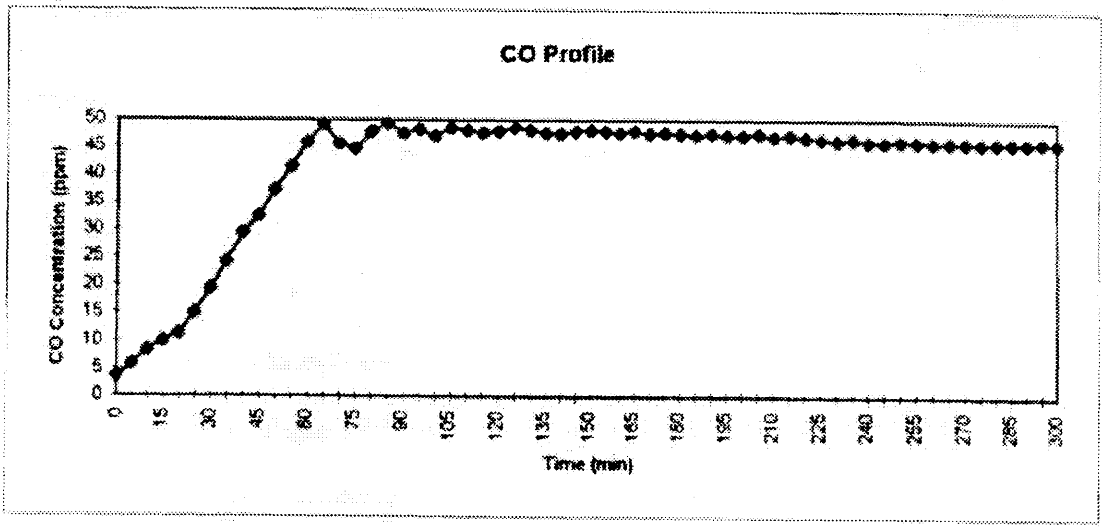

Temperature Profile Port 2
Temperature (F)
260
255
250
245
240
235
230
225
220
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
Time (min)


Temperature Profile Port 3

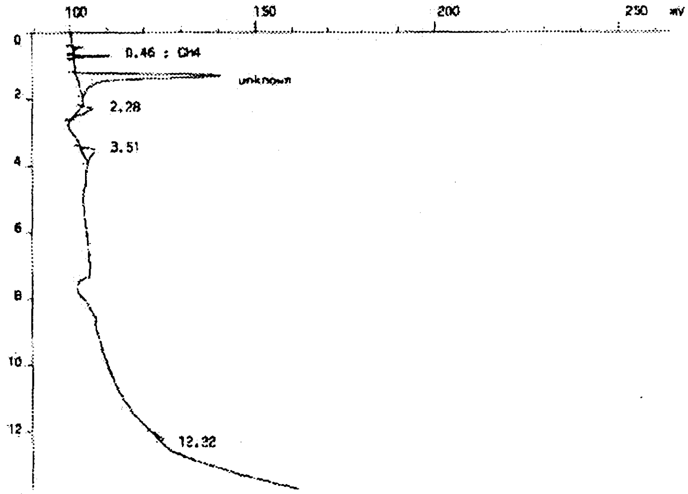

NO Profile


NOX Profile
NOX Concentration (ppm)
0
20
40
60
80
100
120
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
Time (min)


Oxygen Profile
% Oxygen
0
2
4
6
8
10
12
14
16
18
20
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
255
270
285
300
Time (min)



```
                    PC Minichrom

                  INJECTION REPORT

Injection D: <CNLHC> 1 LHC1109A,!0,1

Acquired on 08-Nov-99 at 05:14:29
Modified on 08-Nov-83 at 05:29:54
Reported on 08-Nov-99 at 05:30:57
Column:Super-Q, at 40 C,ramp 10 C/min to 190 C,keep 5min.
```



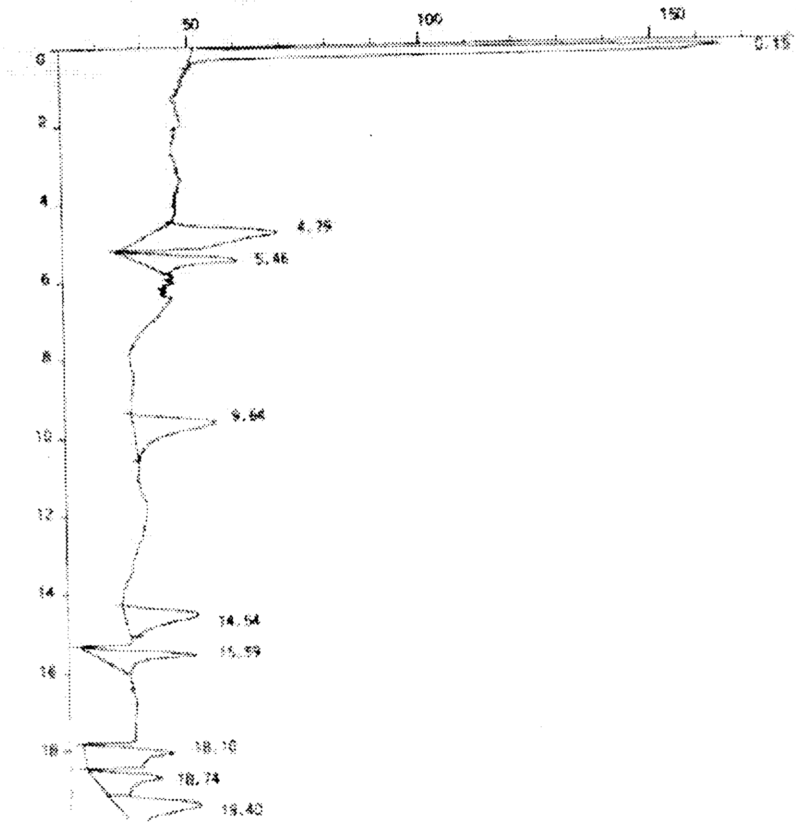
```
          PEAK INFORMATION

Peak          RT mins  Hght uV      Area uVs          ppm Peak n
   1            0.459     3185         10123        0.000
   2            0.725    10199         24968        0.224 CH4
   3            1.291    39178        401059        2.861 unknow
   4            2.283     3621         48650        0.000
   5            3.515     3601         51860        0.000
   6           12.219     1239         11871        0.000

Total                    61022        548531        3.084
Residual                     0             0        0.000
```

PC Minichrom

INJECTION REPORT

Injection D: <CNTHC> 3 THC1109A,10,1

Acquired on 08-Nov-99 at 04:57:51
Modified on 23-Dec-83 at 04:56:48
Reported on 23-Dec-99 at 04:59:33
FID Temp.: 270 C, Oven Temp.: 80 C, sample loop: empty



APPENDIX C

INPUT FILES FOR SMCPS

Input files to the program SMCPS for the molecular species that are presented in this dissertation.

SMCPS input files for the $C_2H_5 + O_2$ system

```
NAME (name of molecule)
C2H5

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098
ROTOR
1    number of internal rotors

MOLECULAR WT
29.03913

OPTICAL ISOMER
1

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
28.6

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
103.49857    22.68020    21.02581

SYMMETRY
3

NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
15
 122.2104              464.0297              813.6975
 983.9569             1071.1841             1198.9046
1412.8064             1480.8467             1496.3710
1496.8882             2963.7353             3056.0519
3102.2922             3160.7820             3262.3294
```

```
NAME (name of molecule)
CCOO

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
2    number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
1

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
-6.055658955

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
17.64590     5.64663     4.86165

SYMMETRY
3

NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
  113.4625             236.0504             358.1303
  528.8224             801.7790             849.5483
 1000.9112            1102.3930            1163.2387
 1209.1766            1309.4074            1380.9676
 1419.6400            1493.7845            1499.6305
 1519.0534            3059.0919            3077.3380
 3129.0971            3136.0663            3154.3323
```

```
NAME (name of molecule)
TYCCQHS

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
1    number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
30.98940909

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
 13.80300     7.73280     5.62039

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
-2227.3619             277.0958              436.7461
  551.3194             688.3236              873.0155
  905.4756             913.2161              970.2090
 1050.2974            1108.3649             1170.7365
 1247.2155            1350.4538             1467.8252
 1509.5858            1737.5917             3038.2823
 3097.6316            3120.8223             3216.2611
```

```
NAME (name of molecule)
CJCOOH

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
3    number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
11.57401862

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
16.07642     5.74828     4.86523

SYMMETRY
1

NON-LINEAR

FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
 132.5085              162.9791              221.1415
 359.3380              461.4223              559.1266
 841.6484              872.2693              965.6320
1067.3019             1141.4258             1273.4955
1364.5671             1379.2652             1459.4444
1476.5466             2987.1331             3069.8579
3160.6945             3272.0522             3745.3915
```

```
NAME (name of molecule)
CJCOOH

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
3   number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
11.57401862

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2   choice of moment of inertia units
16.07642     5.74828     4.86523

SYMMETRY
2

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
 132.5085              162.9791              221.1415
 359.3380              461.4223              559.1266
 841.6484              872.2693              965.6320
1067.3019             1141.4258             1273.4955
1364.5671             1379.2652             1459.4444
1476.5466             2987.1331             3069.8579
3160.6945             3272.0522             3745.3915
```

```
NAME (name of molecule)
TCJCXQ

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
3   number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
27.65115753

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2   choice of moment of inertia units
17.77077     4.32924     4.04617

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
-526.5129              79.8781              218.9425
 299.8005             427.3334              457.1320
 815.2165             830.4155              930.4711
1020.0714            1068.0481             1244.7631
1270.9697            1388.6002             1475.5431
1564.8913            3150.5791             3167.3367
3232.8582            3266.4508             3674.4634
```

```
NAME (name of molecule)
TCYCOOH

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
2    number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
3

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
35.98721741

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
20.56639     5.17032     4.84130

SYMMETRY
3

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
-1832.6095            129.1188              207.7203
  414.7054            657.0614              783.4557
  818.4534            919.2283             1065.5781
 1119.5797           1129.5596             1171.0456
 1366.5968           1418.5232             1487.7595
 1493.8673           1965.5162             3032.7213
 3078.7016           3107.3680             3144.7165
```

```
NAME (name of molecule)
TYCCXQ

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
1    number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
24.86822229

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
14.67621     5.59606     4.28511

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
-1069.8711              216.3894              365.8003
  474.2397              523.8965              628.0752
  833.0654              897.0281             1004.8182
 1038.1396             1229.6467             1295.4490
 1327.1358             1356.2287             1479.9587
 1586.6620             1626.8439             3124.1674
 3179.8189             3205.1048             3270.1512
```

```
NAME (name of molecule)
TYCOCXOH

COMMENTS:
CBS-Q//B3LYP/6-31G(d,p)

TEMPERATURE
20    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

ROTOR
2    number of internal rotors

MOLECULAR WT
61.02895

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
26.953512

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
26.63204     4.48611     4.08337

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
 21
-764.9922              79.2887              125.0656
 256.2316             399.1948              504.7431
 756.7186             837.9449              938.0499
1011.7768            1171.9420             1178.6505
1203.7775            1317.4739             1482.9512
1550.3201            3043.1996             3099.6384
3187.5648            3305.1786             3776.8191
```

SMCPS input files for the CH_3OH system

```
NAME (name of molecule)
CH3OH

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398   598 298   1098 498     (Values of temperature to be read)
ROTOR
1    number of internal rotors

MOLECULAR WT
32.02621

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
-48

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 4  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
127.4730716  24.8852584  24.0038825

SYMMETRY
3

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
12
342.5065               1159.8767               1179.3836
  1277.1001               1488.8914               1615.2998
  1618.9160               1630.3432               3140.5052
  3184.9008               3256.7811               4186.3856
```

```
NAME (name of molecule)
CH2OH

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
1    number of internal rotors

MOLECULAR WT
31.02621

OPTICAL ISOMER
1

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
-4.08720494


STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 3  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
190.4699859     29.8159149     26.1385673

SYMMETRY
2

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
9
414.0067              800.2158              1146.3787
1279.4862             1469.4933              1606.1184
3244.2520             3381.0609              4189.4661
```

```
NAME (name of molecule)
CH2S

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
0    number of internal rotors

MOLECULAR WT
14.01565

OPTICAL ISOMER
1

MULTIPLICITY
1      multiplicity of molecular specie of interest

HF298
102.4653454



STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8              (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
580.7349411    337.8758534    213.6011410

SYMMETRY
2

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
3
1501.7912              3097.0230              3157.6662
```

```
NAME (name of molecule)
CH2T

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
0    number of internal rotors

MOLECULAR WT
14.01565

OPTICAL ISOMER
1

MULTIPLICITY
3       multiplicity of molecular specie of interest

HF298
94.15



STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1       (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
1548.3668759    255.3090330    219.1702222

SYMMETRY
2

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
3
1201.8177              3264.0078              3474.7790
```

```
NAME (name of molecule)
CH3

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
0    number of internal rotors

MOLECULAR WT
  15.02348

OPTICAL ISOMER
1

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
34.82

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1 H 3
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
  285.2011929    285.2011516    142.6005861

SYMMETRY
6

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
6
 375.3193              1512.3427              1512.3457
 3227.4318              3407.6231              3407.6377
```

```
NAME (name of molecule)
CH3O

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
0    number of internal rotors

MOLECULAR WT
31.02621

OPTICAL ISOMER
1

MULTIPLICITY
2       multiplicity of molecular specie of interest

HF298
4.66467703

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 3  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8                (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
156.9823553     27.5561503     27.4109625

SYMMETRY
3

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
9
819.1875              1096.3967              1203.3555
1555.8462              1556.4608              1638.1783
3138.1509              3201.0433              3219.9325
```

```
NAME (name of molecule)
H2O

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
1    number of internal rotors

MOLECULAR WT
18.01056

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
-57.8



STOICHIOMETRY (in form of "atom x" "number of atom x")
H 2  O  1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
    789.3795932    448.5214308    286.0112866

SYMMETRY
2

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
3
1752.0109             4141.2055             4235.8779
```

```
NAME (name of molecule)
HCOH

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398   598 298   1098 498      (Values of temperature to be read)
ROTOR
1    number of internal rotors

MOLECULAR WT
    30.01056

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
25.82199595


STOICHIOMETRY (in form of "atom x" "number of atom x")
C  1 H 2  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8                (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1       (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
286.0627734     36.3819057     32.2768820

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
6
1131.8295              1330.0074              1445.4824
1629.4820              3067.6561              4112.8423
```

```
NAME (name of molecule)
CH2O

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
0    number of internal rotors

MOLECULAR WT
    30.01056

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
-26.67407265



STOICHIOMETRY (in form of "atom x" "number of atom x")
C  1 H 2  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8                (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
285.1205364     38.7172216     34.0882887

SYMMETRY
2

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
6
1337.5184              1372.3532              1656.9104
2006.7950              3091.5896              3159.7720
```

```
NAME (name of molecule)
TS1

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398   598 298  1098 498      (Values of temperature to be read)
ROTOR
1    number of internal rotors

MOLECULAR WT
32.02621

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
42.4932171


STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 4  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1       (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
102.7501223     27.8175701     25.6573951

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
12
-2385.3019             905.8903              1060.0082
1270.3235             1295.5652             1356.0049
1596.5750             1637.7541             2156.3662
2378.2498             3152.9330             3217.2507
```

```
NAME (name of molecule)
TS2

COMMENTS:
CBS-APNO

TEMPERATURE
6    (Number of temperature to be read in)
1  398  598 298  1098 498     (Values of temperature to be read)
ROTOR
2    number of internal rotors

MOLECULAR WT
32.02621

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
38.45895531



STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 4  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8                (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
96.9123008     24.9624254     23.3225884

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
12
 -1270.5891              622.3196              819.5224
 1093.0199              1140.1530             1266.8980
 1403.3584              1539.7751             1786.7812
 3101.8633              3217.9013             4166.2378
```

```
NAME (name of molecule)
TS3

COMMENTS:
CBS-APNO

TEMPERATURE
20    (Number of temperature to be read in)
1 50 100 150 200 250 298 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500
(Values of temperature to be read)
ROTOR
1    number of internal rotors

MOLECULAR WT
32.02621

OPTICAL ISOMER
1

MULTIPLICITY
1       multiplicity of molecular specie of interest

HF298
35.62951272


STOICHIOMETRY (in form of "atom x" "number of atom x")
C 1  H 4  O 1
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
8               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib)
0.8  1.2  1.1      (include decimal input)

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
134.8174049     16.9961064     16.3900576

SYMMETRY
1

NON-LINEAR


FREQ (The format for the frequencies is not important.  Units are cm-1)
12
-1715.9436              530.9497              553.3872
861.8992             1116.5935             1247.4180
1517.0757             1541.9227             2453.1009
3251.4901             3349.5686             4154.0114
```

SMCPS input files for the hydroperoxy-ethyl + O_2 system

```
NAME (name of molecule)
QCCQJ

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
5.90058      2.62927      2.10976

FREQ (The format for the frequencies is not important.  Units are cm-1)
27
  80.0927                110.2595                158.0035
 277.1760                332.0784                419.6598
 488.6324                559.2916                820.6392
 867.3868                921.5991               1008.1988
1062.1885               1127.3439               1170.7651
1281.0893               1296.3463               1377.1661
1393.5698               1401.3231               1459.8788
1475.0923               3053.4105               3078.7599
3115.7766               3147.8323               3722.1299



MOLECULAR WT
93.01878

OPTICAL ISOMER
2

MULTIPLICITY
2       multiplicity of molecular specie of interest

SYMMETRY
1

NON-LINEAR


STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O  4
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR   (Uses Scott & Radom's scaling factors)
18                (integer input)

rem USCALING FACTOR   (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

HF298
-19.81


TEMPERATURE
10     (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

COMMENTS:
rb3lyp/6-31gdp


ROTOR
4   number of internal rotors
```

```
NAME (name of molecule)
TQYCCQS

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
9.82914     1.80218     1.63758

FREQ (The format for the frequencies is not important.  Units are cm-1)
27
-1944.0655              83.7545              102.8373
  166.4490             246.5620              355.1433
  432.1545             572.2374              665.5103
  851.9981             906.0094              934.9568
  990.3567            1031.9323             1142.6910
 1177.7069            1210.6429             1247.2861
 1315.9311            1386.7587             1411.4639
 1498.7662            1775.8575             3036.3608
 3109.7341            3127.1794             3760.2729


MOLECULAR WT
93.01878

OPTICAL ISOMER
4

MULTIPLICITY
2       multiplicity of molecular specie of interest

SYMMETRY
1

ROTOR
3   number of internal rotors

NON-LINEAR

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O  2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

HF298
-5.45


TEMPERATURE
10    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

COMMENTS:
b3lyp/6-31gdp
```

```
NAME (name of molecule)
TQYCCQE

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
5.82819     2.24737     1.75028

FREQ (The format for the frequencies is not important.  Units are cm-1)
27
-1106.3303              88.1780              149.5404
  182.8281             195.4325              367.2320
  377.6692             483.7977              522.1100
  663.8372             809.1175              848.7265
  925.9543             985.2962             1034.5224
 1164.9298            1251.1695             1304.2169
 1360.9856            1368.5632             1408.8230
 1560.4378            1609.2910             3091.3089
 3193.7723            3294.0608             3761.9325


MOLECULAR WT
93.01878

OPTICAL ISOMER
4

MULTIPLICITY
2       multiplicity of molecular specie of interest

SYMMETRY
1

ROTOR
3   number of internal rotors

NON-LINEAR

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O  2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

HF298
-5.45


TEMPERATURE
10    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

COMMENTS:
b3lyp/6-31gdp
```

```
NAME (name of molecule)
TQCYCQ

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
5.62050     2.97413     2.27467

FREQ (The format for the frequencies is not important.  Units are cm-1)
27
-1820.5020               111.0329               152.8012
  207.8920               268.7085               420.5832
  481.8726               608.5390               684.1666
  795.7466               829.8911               896.4484
  904.2059              1033.1536              1089.0435
 1109.0848              1147.1510              1276.3169
 1348.5754              1390.0917              1425.0044
 1462.4183              1960.5319              3018.7586
 3069.0831              3092.2572              3679.2356



MOLECULAR WT
93.01878

OPTICAL ISOMER
4

MULTIPLICITY
2       multiplicity of molecular specie of interest

SYMMETRY
1

ROTOR
4   number of internal rotors

NON-LINEAR

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 5  O  2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

HF298
-5.45


TEMPERATURE
10    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

COMMENTS:
b3lyp/6-31gdp
```

```
NAME (name of molecule)
QCCHO

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
13.66831     2.93933     2.62830

FREQ (The format for the frequencies is not important.  Units are cm-1)
21
  76.4357               143.3936               169.9619
 298.2332               419.5897               571.7434
 729.0566               897.6984              1038.0399
1075.2227              1108.8054              1253.0027
1338.7665              1397.1282              1411.8667
1444.0649              1843.0614              2910.8591
3040.7069              3093.1563              3776.6411




MOLECULAR WT
76.01604

OPTICAL ISOMER
2

MULTIPLICITY
1       multiplicity of molecular specie of interest

SYMMETRY
1

NON-LINEAR


STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 4  O  3
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

HF298
-45.29


TEMPERATURE
10    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

COMMENTS:
b3lyp/6-31gdp


ROTOR
3   number of internal rotors
```

```
NAME (name of molecule)
QCDC

MOMENT (1)=10 e-40 g*cm^2  (2)=GHz  (3)=amu-Bohr^2 (4)=amu-Angstrom^2
2    choice of moment of inertia units
18.53739     6.60366     4.94544

FREQ (The format for the frequencies is not important.  Units are cm-1)
18
 166.5426              243.0778              324.6857
 620.2303              712.6893              849.0511
 897.7788              974.1802              976.0074
1158.5822             1325.6640             1385.1439
1432.0844             1727.8291             3189.5412
3206.2063             3296.8115             3741.6925




MOLECULAR WT
60.02113

OPTICAL ISOMER
2

MULTIPLICITY
1       multiplicity of molecular specie of interest

SYMMETRY
1

ROTOR
2   number of internal rotors

NON-LINEAR

STOICHIOMETRY (in form of "atom x" "number of atom x")
C 2  H 4  O  2
(do not put any comments on same line as stoichiometry info)
(The stoichiometry is NOT sorted.  Will write to *.lst file as is).

RSCALING FACTOR  (Uses Scott & Radom's scaling factors)
18               (integer input)

rem USCALING FACTOR  (User define scaling factors: ZPE, Hvib, Svib, Cpvib)
0.8  1.2  1.1  0.9    (include decimal input)

HF298
-5.45


TEMPERATURE
10    (Number of temperature to be read in)
1 298 398 498 598 698 798 898 998 1098 1198 1298 1398 1498 1598 1698 1798 1898 1998 2098

COMMENTS:
b3lyp/6-31gdp
```

APPENDIX D

HINDERED-ROTOR CONTRIBUTION CALCULATED BY VIBIR

Calculated hindered-rotor contribution to entropy and heat capacity based on the Pitzer-Gwinn formalism for the molecular species that are presented in this dissertation.

Hindered-rotor for the species in HCCH + O_2 system

```
H-C(OO.)=C .-H
                                    S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000   Cp1500
+ 1 x rotor _ H(C@=C .)H-OO.  :     5.769    2.317    2.200    2.008    1.829    1.562    1.396    1.190
Total Increment of Vibration plus Internal Rotation:
                                   5.769    2.317    2.200    2.008    1.829    1.562    1.396    1.190

H-(COO)-C:-H
                                    S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000   Cp1500
+ 1 x rotor _  H(COO)-C:H {CH :   4.651    2.224    2.051    1.841    1.672    1.437    1.304    1.140
Total Increment of Vibration plus Internal Rotation:
                                   4.651    2.224    2.051    1.841    1.672    1.437    1.304    1.140

H-C.(-O)-C(=O)-H
                                    S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000   Cp1500
+ 1 x rotor _ HC .(sO)-C( dO)H :   6.511    1.975    1.697    1.502    1.376    1.222    1.145    1.065
Total Increment of Vibration plus Internal Rotation:
                                   6.511    1.975    1.697    1.502    1.376    1.222    1.145    1.065

.C(=O)-C(=O)-H
                                    S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000   Cp1500
+ 1 x rotor _ .C( dO)-C( dO)H  :   6.511    1.975    1.697    1.502    1.376    1.222    1.145    1.065
Total Increment of Vibration plus Internal Rotation:
                                   6.511    1.975    1.697    1.502    1.376    1.222    1.145    1.065

H(=C.-H)-OO.
                                    S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000   Cp1500
+ 1 x rotor _  H(CdC.H)-OO.  { :   5.769    2.317    2.200    2.008    1.829    1.562    1.396    1.190
Total Increment of Vibration plus Internal Rotation:
                                   5.769    2.317    2.200    2.008    1.829    1.562    1.396    1.190

H-(COO)-C:-H
                                    S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000   Cp1500
+ 1 x rotor _  H(COO)-C:H {CH :   4.651    2.224    2.051    1.841    1.672    1.437    1.304    1.140
Total Increment of Vibration plus Internal Rotation:
                                   4.651    2.224    2.051    1.841    1.672    1.437    1.304    1.140
```

Hindered-rotor for the species in $C_2H_5 + O_2$ system

```
H3-C-C .-H2
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _     CH3-CH2 :   4.757   0.999   0.996   0.995   0.994   0.993       0.993   0.994
Total Increment of Vibration plus Internal Rotation:
                                    4.757   0.999   0.996   0.995   0.994   0.993      0.993   0.994

H3-C-(COO.)-H2
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _ C-COO . {CH3-C2 :   5.337   1.543   1.408   1.308   1.237   1.144   1.095   1.041
+ 1 x rotor _ CC-OO . {RCC-OO :   6.894   1.739   1.488   1.341   1.244   1.140   1.091   1.038
Total Increment of Vibration plus Internal Rotation:
                                   12.231   3.282   2.896   2.648   2.481   2.284   2.185   2.079

H3C-Y(COOH)H
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _ C- Y(COOH) {CH3 :   5.041   1.735   1.660   1.536   1.430   1.287   1.196   1.092
Total Increment of Vibration plus Internal Rotation:
                                    5.041   1.735   1.660   1.536   1.430   1.287   1.196   1.092

H2C.-CH2-O-OH
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _ H2C .-CH2OOH {R :   5.188   0.998   0.996   0.994   0.993   0.994       0.994   0.994
+ 1 x rotor _ H2C.CH2-OOH {  R :   6.110   2.321   2.194   1.999   1.819   1.553   1.389   1.186
+ 1 x rotor _ H2C.CH2O-OH {  R :   2.905   2.244   2.249   2.122   1.965   1.693   1.501   1.253
Total Increment of Vibration plus Internal Rotation:
                                   14.204   5.563   5.438   5.116   4.777   4.240   3.884   3.433

H3C-C.H-O-OH
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _ CH3-CHOOH {  CH3 :   5.337   1.543   1.408   1.308   1.237   1.144   1.095   1.041
+ 1 x rotor _ H3CC .-OOH {RCC :   6.894   1.739   1.488   1.341   1.244   1.140   1.091   1.038
+ 1 x rotor _ H3CC.O-OH {  RCH :   2.905   2.244   2.249   2.122   1.965   1.693   1.501   1.253
Total Increment of Vibration plus Internal Rotation:
                                   15.136   5.526   5.145   4.771   4.446   3.978   3.686   3.332

Y(COC)-OH
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _   Y(COC)-OH {IPR :   4.295   1.159   1.093   1.059   1.040   1.021   1.012   1.001
Total Increment of Vibration plus Internal Rotation:
                                    4.295   1.159   1.093   1.059   1.040   1.021   1.012   1.001

H3-CHO
                                     S298    Cp300    Cp400    Cp500    Cp600    Cp800   Cp1000  Cp1500
+ 1 x rotor _ H3-CHO {CH3-C  . :   5.608   0.000    0.000   0.000    0.000   0.000    0.000    0.000
Total Increment of Vibration plus Internal Rotation:
                                    5.608   0.000    0.000   0.000    0.000    0.000    0.000    0.000
```

Hindered-rotor for the species in C_2H_4OOH + O_2 system

```
HO-OCCOOH
                                     S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ {rch2-oh/ch3o  - :   2.388   1.619   1.917   2.095   2.185   2.165   2.036   1.670
Total Increment of Vibration plus Internal Rotation:
                                    2.388   1.619   1.917   2.095   2.185   2.165   2.036   1.670

HOO-CCOOH
                                     S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ {ph-ooh/cc-  ooh :   5.234   2.109   2.238   2.307   2.319   2.187   1.992   1.602
Total Increment of Vibration plus Internal Rotation:
                                    5.234   2.109   2.238   2.307   2.319   2.187   1.992   1.602

HOOC-COOH
                                     S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ {hooch2-  ch2ooh :   6.279   2.304   2.290   2.158   1.997   1.717   1.518   1.263
Total Increment of Vibration plus Internal Rotation:
                                    6.279   2.304   2.290   2.158   1.997   1.717   1.518   1.263

OO-CCOOH
                                     S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ {ph- oo/rcc-oo} :    3.612   1.869   1.875   1.769   1.644   1.448   1.322   1.156
Total Increment of Vibration plus Internal Rotation:
                                    3.612   1.869   1.875   1.769   1.644   1.448   1.322   1.156
```

Hindered-rotor for the species in CH_3OH system

```
H3COH
                                    S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ H3C-OH {ch3-oh :   3.781   1.383   1.254   1.187   1.139   1.082   1.053   1.021
Total Increment of Vibration plus Internal Rotation:
                                   3.781   1.383   1.254   1.187   1.139   1.082   1.053   1.021

H3COHN
                                    S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ H3C-OH {ch3-oh :   4.180   0.990     0.990  0.993    0.993   0.993   0.993    0.993
Total Increment of Vibration plus Internal Rotation:
                                   4.180   0.990    0.990  0.993    0.993   0.993   0.993    0.993

CH2OH
                                    S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ H2Cj-OH {ch2-  x :   3.734   1.461   1.316   1.223   1.161   1.093   1.059   1.024
Total Increment of Vibration plus Internal Rotation:
                                   3.734   1.461   1.316   1.223   1.161   1.093   1.059   1.024

HCOH
                                    S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ HC-OH { approx   :   3.303   1.554   1.363   1.250   1.178   1.103   1.065   1.027
Total Increment of Vibration plus Internal Rotation:
                                   3.303   1.554   1.363   1.250   1.178   1.103   1.065   1.027

CH2OHN
                                    S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ H2Cj-OH {ch2-  x :   4.037   0.993     0.993  0.993    0.993   0.993   0.993    0.993
Total Increment of Vibration plus Internal Rotation:
                                   4.037   0.993    0.993   0.993   0.993   0.993   0.993    0.993

HCOHN
                                    S298   Cp300   Cp400   Cp500   Cp600   Cp800  Cp1000  Cp1500
+ 1 x rotor _ HC-OH { approx   :   3.645   0.993     0.993  0.993    0.993   0.993   0.993    0.993
Total Increment of Vibration plus Internal Rotation:
                                   3.645   0.993    0.993   0.993   0.993   0.993   0.993    0.993
```

APPENDIX E

INPUT FILES FOR QRRK ANALYSIS WITH MASTER EQUATION ANALYSIS FOR FALL-OFF

Individual input files to calculate rate constants based on QRRK analysis with master equation analysis for fall-off for the reaction systems discussed in this dissertation.

HCCH + O_2

```
05/16/98 HCCH +  O2(3) rxn with CBS-q//MP2/6-31g*   calc
chemact
dissoc
FITRANGE    (uncomment if want modified Arrhenius fits)
fitglobal
CHEB
       7 3 300.  2500. 1.e- 3  1.e+2  20
temp
8  300. 450. 600 . 800. 1000 . 1500. 1600 . 2500.
pres
5 0.001 0.01 0.1 1 . 3. 10 . 30. 60 . 100.
INPUT (A,  n ,alpha, E kcal      k=AT^nexp(- alpha*T) exp(-E/RT) )
2.6814e7  1.88256  0.0  37.169
Mass
58.
PARAMETERS  ( Angstrom, K)
3.62    436.3  !double check correct values
COLLIDER (take user's data if   collider name started with a '!')
   N2
   1. 28.0 3.621 97.5 400.
INT   (integration interval in kcal)
   0.5
WELL 1
   CJ*COOJ
   FREQ
   3    398.5  4.149
         1143.9  5.228
         3380.6  2.123
REACTANT
   C2H2+O2
   1.4345e12  .51519  0.0  2.05
   ISOMER
      CYCOO
      5.5042e11  . 36113  0.0  25.678
END
WELL 2
   CYCOO
   FREQ
   3    446.9  4.349
         1211.5  5.12
         3296.6  2.031
ISOMER
   CJ*COOJ
     8.8974e11  . 4382  0.0  20.932
   ISOMER
   HCJOJCHAB
      1.502e12  . 38717  0.0  31.092  !TS to get over TS3
WELL 3
   HCJOJCHAB
   FREQ
   3    400.6  3.936
        1320.1  5.402
        3114.3   2.162
   ISOMER
   CYCOO
    5.4167E10  0.70694   0.0   118.36
   PRODUCT
      CJ*OCHO + H
       1.0E13  0.0   0.0   26.37  !Estimate with Ea=dHrxn + 2 from CBS-q
   PRODUCT
      HCO + HCO
       2.5e13  0.0   0.0  14.71  !NIST result Ben/  kny 92 w/  Ea=dHrxn + 5.7
   END
TAG
comments: All 3  param input based on TST.  2 prod (well 3) base on    estim. tech.
```

```
4/27/99 HCCH + O2(3) -> (3) adduct -> (1) adduct
dissoc
chemact
temp
6  600. 800. 1000 . 1500. 2000 . 2500.
pres
7  0.001 0.01 0.1 1.  10. 50  . 100.
NOrot   (no internal rotor)
FITRANGE    (uncomment if want modified Arrhenius fits)
INPUT (A,  n ,alpha, E kcal      k=AT^nexp(- alpha*T) exp(-E/RT) )
2.6814e7  1.88256  0.0  29.279
Mass
58.
PARAMETERS  ( Angstrom, K)
3.62    436.3  !double check correct values
COLLIDER (take user's data if   collider name started with a '!')
   N2
   1. 28.0 3.621 97.5 400.
 EXP (temperature exponent to alpha,    alpha= alpha(300)*(T/300)^N )
  0.01
INT   (integration interval in kcal)
   0.5
WELL 1
   HCJCOOJAB
   FREQ
   3    398.5  4.149
         1143.9  5.228
         3380.6  2.123
   REACTANT
   HCCHAB+O2AB
   1.4345e12  .51519  0.0  3.3102
   ISOMER
      CYCOOAB
      5.5042e11  . 36113  0.0  15.298
   ISOMER
      CJCOOJS
      1.0e13  0.0   0.0  1.02      # singlet adduct  4/27/99
WELL 2
   CYCOOAB
   FREQ
   3    446.9  4.349
         1211.5  5.12
         3296.6  2.031
   ISOMER
   HCJCOOJAB
     8.8974e11  . 4382  0.0  2.522
   ISOMER
   HCJOJCHAB
     1.5019E12   0.38717   0.0  12.062
   END
WELL 3
   HCJOJCHAB
   FREQ
   3    400.6  3.936
       1320.1  5.402
       3114.3   2.162
   ISOMER
   CYCOOAB
    5.4167E10  0.70694   0.0   107.71
   PRODUCT
      CJDOCHOAB + H
      1.0E13  0.0   0.0   26.37      #Estimate with   Ea=dHrxn + 2 from CBS-q
   PRODUCT
      HCOAB + HCOAB
      2.5e13  0.0   0.0  26.32     #NIST result Ben/  kny 92 w/  Ea=dHrxn + 5.7
WELL 4
   CJCOOJS
   FREQ
   3  423.7  5.482
      1116.5   3.795
      3169.0 2.222
   ISOMER
      HCJCOOJAB
      7.5288E12  0.0   0.0  0.0      # triplet adduct
   PRODUCT
```

```
   HCOAB + HCOAB     #YCCOO4
      2.0E12  0.0   0.0  6.0      #4 member cyclic
   END
TAG
comments: All 3  param input based on TST.
```

Isomerization of HCCH to vinylidene.

```
5/1/99 HCCH -> h2cc :      b3lyp/6-31g*  calc
FITRANGE    (uncomment if want modified Arrhenius fits)
temp
3  300.  1000. 1500  . 2000.  2500.
pres
7    1.  2.  3.  5. 6.  8. 10  . 100. 1000.
NOrot   (no internal rotor)
dissoc
Mass
26.
PARAMETERS  ( Angstrom, K)
3.62    436.3  !double check correct values
COLLIDER (take user's data if   collider name started with a '!')
   N2
   1. 28.0 3.621 97.5 400.
 EXP (temperature exponent to alpha,    alpha= alpha (300)*(T/300)^N )
  0.01
INT   (integration interval in kcal)
   0.5
FREQ
3    587.0     2.173
    1021.7      2.224
    3341.1   2.603
WELL 1
   HCCH
   PRODUCT
   H2CCJJ
   1.9618e14  0.07395  0.0  42.983
END
TAG
comments: All 3  param input based on TST.
```

$C_2H_5 + O_2$

```
6/29/01  updated  cco + o rate    amd
# 6/28/01  updated k  assocn and k associated with change in   c.coo thermo
# 10/5/00 repeat with lower delta e av to try to get alpha=830     amd
KFIT   (uncomment if want modified Arrhenius fits)
CHEB
  7 3 250.  2500. 1.e-3 1.e+2 50
temp
9  250.  300.    400.  500.  750.  1000. 1500   . 2000. 2500.
pres
6  0.001 0.01 0.1 1. 10. 100.
COLLIDER ( mass  ,sigma, e/k)
28.0  3.62  97.5     (N2)
chemact
dissoc
Ehead
100.
PARAMETERS  ( mass, sigma, e/k)
61.  4.940  450.00
DELTA  (E)
830.   0 .   (taken from literature average)
INT   (integration interval in kcal)
   0.5
INPUT (A,  n ,alpha, E kcal      k=AT^nexp(- alpha*T) exp(-E/RT) )
 2.9436E+13  - .44354  0.0    0.0000E+00 #based on CC+OO -> VTST    addn rxn
#1.0613E+ 12   0.0    0.0    -5.0181E-01  #based on CC+OO -> VTST    addn rxn
#  1.6578E+11   . 24732    0.0   -7.1866E-01  #  mechinfo 3 param fit
# 3.8088E+12   - .14072   0.0    0.0000E+00  #  mechinfo 2  param fit
WELL 1
   CCOO
   FREQ
   3  372.9   4.134
     1255.5  10.527
     3052.9   5.338
   REACTANT
     C2H5 + O2
     2.4614E+18    - 1.06998  0.0   35.320   #based on VTST   dissoc  calc
   ISOMER
     CJCOOH
      7.9026E+ 06      1.78500   0.0  35.829
   PRODUCT
     CCHO + OH
     1.3169E+ 09  1.36595    0.0   41.591   #assuming shift rate-limiting
   PRODUCT
     C2H4(ho2/e) + HO2
     8.8006E+ 05         2.24329    0.0      29.613
   PRODUCT
     CCOJ   +  O
     2.98E+15     - 0.090  0.0    61.6      #    mechinfo fit 300-3000 kr=2e13 ERR=   4.33 %
   END
WELL 2
   CJCOOH
   FREQ
3    289.3   6.101
    1161.4   8.165
    3179.1   5.234
   ISOMER
      CCOO
      1.1741E+ 07   1.03838    0.0    17.979
PRODUCT
      C2H4 + HO2
      1.2829E+11     . 51856    0.0   16.153
PRODUCT
      YCOC + OH
      1.3200E+10     . 71630    0.0    15.382
END
TAG
N2(830)
comments: 10/5/00 lower Delta E down   amd
```

Hydroperoxy-ethyl radical + O_2

```
10/25/ 00  latest AMD  Edown value, T=250-2000K for   ccoo manuscript
KFIT   (uncomment if want modified Arrhenius fits)
CHEB
  7 3 250.  2500. 1.e-3 1.e+2 50
temp
13  250. 300. 400.  500.  750  . 800. 850 . 1000. 1100 . 1200.  1500 . 2000. 2500.
pres
12  0.0075 0.001 .005 0.01 0.05  0.1 0.5  1. 1.21 10   . 50. 100.
COLLIDER ( mass  ,sigma, e/k)
28.0  3.62  97.5     (N2)
chemact
dissoc
PARAMETERS  ( mass, sigma, e/k)
61.  4.940  450.00
DELTA  (E)
830.   0 .   (taken from literature average)
INT   (integration interval in kcal)
   0.5
INPUT (A,  n ,alpha, E kcal     k=AT^nexp(- alpha*T) exp(-E/RT) )
2.9436E+13   - .44354   0.0    0.0000E+00  # using current CC+O2 value 1/2001
# 8.8211E+ 09    1.12152  0.0     0.0  #based on MR from VTST of CCOO   dissoc rxn
WELL 1
   QCCQJ
   FREQ
   3    386.8  9.617
        1187.1  11.886
        3390.9  3.496
   # 1   893.1  25.000
   REACTANT
     CJCOOH + O2
     8.2044E+22   - 2.45484  0.  35.080     #base on   Af/Ar
   PRODUCT
     QCCHO +  OH(ipso)
     1.7529E+ 03   3.18819   0.  3.8896E+01
   PRODUCT
     QCCHO +  OH(5 ring HS)
     1.6053E+ 02  3.26740  0.  2.7711E+01
   PRODUCT
     QCDC + HO2
     8.6226E+ 01    3.51265   0.  2.8455E+01
   PRODUCT
     OH+JOCCOOJ
     3.0E15 0.  0.  43.5
   END
TAG
N2(830)
comments:
```

CH_3OH

```
rxn pathway for ch3oh -> prod  (Base on   cbs-apno for all specie)
KFIT
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
4  290.  473.  700.  298.
pres
9  0.01  0.03 0.05  0.075 0.1 0.3  0.5 0.75  1.0
COLLIDER (take user's data if   collider name started with a '!')
28.  3.798   71.4  # N2  Reid,Prausnitz Sherwood 3rd Ed.
chemact
dissoc
PARAMETERS  ( mass, Angstrom, K)
32.04  3.626  481.8  # CH3OH   Reid,Prausnitz Sherwood 3rd Ed.
DELTA  (E)
830.   0 .   (taken from CCOO  calc done by AMD 9/28/2001)
INT   (integration interval in kcal)
   0.5
INPUT (A,  n ,alpha, E kcal      k=AT^nexp(- alpha*T) exp(-E/RT) )
   3.3134E+ 06  2.07646   0.0  -1.7551  #MR from    recomb VTST  calc
WELL 1
   CH3OH
   FREQ
   3          394.6        .885
             1473.4       6.765
             3493.0       3.849
   REACTANT
     CH3 + OH
     3.2591E+ 10  2.05451  0.0  90.347   #based on VTST    calc
   PRODUCT
     CH2O + H2
     1.1004E+ 09  1.28149  0.0  90.233  #based on TS1 via CTST
   PRODUCT
     CH3O + H
     1.1908E+ 07  2.38792  0.0  99.614  #based on VTST    calc
   PRODUCT
     CH2OH + H
     1.6369E+ 07  2.54513  0.0   91.951  #based on VTST    calc non- intperpolate
   PRODUCT
     CH2S + H2O
     3.8735E+ 11  1.60030  0.0  92.538  #TS3B readjust S to match H(T)=0
   PRODUCT
     HCOH + H2
     2.0299E+ 10   1.22342   0.0   86.411  #base on TS2/isodesmic HCOH     calc CTST
   END
TAG
comments: CBS-APNO; VTST@CBS-Q//B3LYP/6-31G(   d,p) & MicroRev;  Thermkin
```

$CH_2OH + O_2$

```
11/15/01 Using Jeff's input parameters for CH2OH+O2 in    PhD dissertation
chemact
dissoc
KFIT
# showshape
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
4  298.  400.  500.  600.  800.  1000.  1500.  2000.
pres
3  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER (mass),  sigma(A), e/k(K)
         28.   3.798    71.4
# Rot       (external rotor included)
PARAMETERS (mass),  sigma(A), e/k(K)
63.04  4.83  488.   #  Ing's original
delta (E)
   800.  0 . #Ing's original   (830.0 from CCOO calc done by AMD 9/28/2001)

INT   (integration interval in kcal)
   0.5
#EHEAD integration stops at  Ehead + highest barrier,   def. 75 kcal
# 75
INPUT
 3.E12  0.  0.  0.  #NIST avg k

WELL 1
CQ.H2OH
  FREQ
     3   250.0  4.426
        1134.5  3.544
        2390.7  6.030
   REACTANT
      CH2OH+O2
      1.2610E+18  - 1.33507  0.0  35.1  # Ea from Dibble; A, n using  Af/Ar = ca 1e14
   ISOMER
      CH2OHOO
       4.96E+ 06  2.11  -.00069   13.6   #   Ea from Dibble;  A,n, alpha from  Ing's original
   ISOMER
       CQH2O.
       6.86E8    1.   0.0  21.8
   ISOMER
      HOC.HQ
        5.90E9   1.0  0.0  37.1
   PRODUCT
      CO.H2OH+O
       7.55E14   0.0    0.0   57.5
END
WELL 2
CH2OHOO
   FREQ
     3     355.3  5.630
            403.7  1.768
           1829.3  6.602
   ISOMER
      CQ.H2OH
      3.76E7   1.0    0.0    6.3  #   Ea base on Dibble  calc higher TS; A, n from  Ing.
   PRODUCT
      CH2O+HO2
      5.87E17  -2.68  -  0.00007   7.2
END

WELL 3
CQH2O.
   FREQ
   3      279.0  4.648
           800.7  2.876
          1870.6  6.476
   ISOMER
     CQ.H2OH
     5.56E8  .84   . 00042  7.7
```

```
   PRODUCT
      CH2O+HO2
       1.40E14   0.0    0.0   5.0
END

WELL 4
HOC.HQ
   FREQ
   3       227.8  5.407
            960.1  3.501
           2149.3  4.592
   ISOMER
     CQ.H2OH
     4.19E9   .8  . 00064   31.6
   PRODUCT
     HCQ*O+H
      3.24E13   0.0    0.0   22.5
   PRODUCT
     HCO2H+OH
      3.31E13   0.0    0.0   1.0
END
TAG
comments:
```

$CH_3 + O_2$

```
# 11/15/01 Using Jeff's input parameters for CH3+O2 in     PhD dissertation
# CH3OO -> CH2O +  OH  Ea=Using Yu/Wang/ Frenklach JPC 1995 rates
chemact
dissoc
KFIT
# showshape
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
4  298.  400.  500.  600.  800.  1000.  1500.  2000.
pres
3  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER (mass),  sigma(A), e/k(K)
         28.   3.798    71.4   !keeping same as   chemdis for N2 -  jwl 7/14/00
# Rot       (external rotor included)
PARAMETERS (mass),  sigma(A), e/k(K)
47.  4.36  471.   #  Ing's original
delta (E)
   830.  0 . # (830.0 from CCOO  calc done by AMD 9/28/2001)

INT   (integration interval in kcal)
   0.5

INPUT
 6.44e10  0.53  0.0    0.0  #Jeff's original

WELL 1
CH3OO
  FREQ  # Freq uses Jeff's original
     3   603.5  4.810
        1753.8  4.961
        3772.9  1.728
   REACTANT
      CH3+O2
      3.09E15  -0.33  -  .00207  30.2  #Jeff's original


   PRODUCT
      CH2O+OH
      6.0E12  0.0   0.0  46.2  #  Ea using  Frenklach

   PRODUCT
     CH3O+O
      3.10E15  0.0   0.0  60.27 # A- factor=Jeff's original;   Ea=dHrxn CBSAPNO
END

TAG
comments:
```

$CH_3 + CH_3$

```
12/13/01  CH3+Ch3
chemact
dissoc
KFIT
# showshape
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
4  298.  400.  500.  600.  800.  1000.  1500.  2000.
pres
3  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER ( mass  ,sigma, e/k)
28.0  3.62  97.5    # same as one used for CCOO paper with cys/jwb/amd/ayc-2001
# Rot       (external rotor included)
PARAMETERS  ( mass, sigma, e/k)
30.  4.940  450.00 #base on CCOO paper with cys/jwb/amd/ayc-2001
DELTA  (E)
830.   0.  #  same as one used for CCOO paper with cys/jwb/amd/ayc-2001
# EXP (temperature exponent to alpha,    alpha= alpha (300)* (T/300)^N )
#  0.01
#BETA (do constant beta calculation if uncomment)
# .75
INT   (integration interval in kcal)
   0.5
#EHEAD integration stops at  Ehead + highest barrier,   def. 75 kcal
# 75
INPUT
  3.56E13  0.   0.   0.  # NIST 97DEA/BAU

WELL 1
C2H6
   FREQ
     3   758.4  5.279
        1420.9  6.099
        2863.3  6.122
   REACTANT
    CH3  +  CH3
    7.943E16  0.0   0.0  89.4   # AMD JPC85
   PRODUCT
    C2H5 + H
    1.2589E16  0.0   0.0  98.0  # AMD JPC85
   PRODUCT
    C2H4 + H2
    1.04E14  0.0   0.0 102.5  #  Ea Gordon et al Chem Phys Lett 86
END                          # A factor   Hidaka et al IJCK90
TAG
comments:
```

$C_2H_3 + O_2$

```
#9/13/00 REPEAT OF EARLIER JWB CALC TO TEST BERYL C2H3+   O2  8/7/99
#C2H3+O2FIXEDE.INP WITH HIGHER A IN WELL 3 CORRECTED WRONG FREQ IN
#C.*COOH

KFIT
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
4  290.  473.  700.  298.
pres
4  0.01  0.03 0.05  0.075 0.1 0.3  0.5 0.75  1.0
COLLIDER (take user's data if   collider name started with a '!')
1. 28.   3.798   71.4  # N2  Reid,Prausnitz Sherwood 3rd Ed.
chemact
dissoc
PARAMETERS  ( mass, Angstrom, K)
59.0  4.36    451.0   #  jwb/amd's value
DELTA  (E)
830.    0 .   (taken from CCOO  calc done by AMD 9/28/2001)
INT   (integration interval in kcal)
   0.5

INPUT (A,  N ,ALPHA, E KCAL   K=AT^NEXP(-ALPHA*T)EXP(-E/RT) )
1.0E13  0.  0.    0.00       #(VS. 5E13)
WELL 1
 C*COO.
  FREQ
     3  452.6  5.05
        1049.8  5.08
        2915.9  4.31
  REACTANT
    C2H3+O2
     1.61E+ 09   2.399   1.869E-03     44.2   #FIXED E  ERR=  13.01 (ORIG WAS 8.03E+09)
  ISOMER
    C.CYCOO
     3.07E+ 07   1.811   6.108E-04       23.3   #DH 1000K = 23.3ERR=   4.75 %
  PRODUCT
    CH2CHO+O
     1.16E+ 09   1.688   5.577E-04       37.7  #DELTA H 1000K =37.7         ERR=   2.80%
  PRODUCT
      C2H2+HO2     #(1)
      6.19E+ 10      0.875  0.0       42.5     #DELTA H 1000K = 42.5ERR=   3.52 %
  PRODUCT
    CH2O+HCO      #(1)
      3.34E+ 07  1.725   5.584E-04      43.6  #DELTA H 1000K  =43.6         ERR=  4.77 %
  ISOMER
    C.*COOH
      1.37E+ 10      0.966  0.0       40.1    #DELTA H 1000K = 40.1ERR=   3.22 %
  END
WELL 2
 C.*COOH
  FREQ
     3  481.5  7.31
        1191.9  4.42
        3113.3   2.27
  ISOMER
     C*COO.
      7.06E+ 05     1.838   5.752E-04       13.6    #DELTA H 1000K = 13.6      ERR=   6.81%
  PRODUCT
    HC.*CHO+OH
      8.0E14   0.0     0.0  22.55  #(MEBEL ENTHALPIES, EST A)
  PRODUCT
     C2H2+HO2       #(2)
      3.32E+ 14      0.140  -6.085E-04     26.8    #DELTA H 1000K =26.8         ERR=   5.99 %
   END
WELL 3
C.CYCOO
  FREQ
   3  250.2  1.92
      966.3  10.17
     3208.  2.27
    ISOMER
     C*COO.
```

```
     13.64E+ 05      2.206   8.807E-04      15.2    #DELTA H 1000K =15.2        ERR=   8.35 %
     ISOMER
       C.OCHO
     18.18E+ 05      2.199   8.576E-04      22.4    #DELTA H 1000K =22.4        ERR=   8.11 %
  END
WELL 4
   C.OCHO
    FREQ
      3   439.4  4.397
          419.6  1.827
         1808.6  7.202
   PRODUCT
     CH2O+HCO          #(4)
      9.66E+ 05      2.254   9.508E-04     30.1   #DELTA H 1000K =30.1        ERR=   7.63 %
   ISOMER
    C.CYCOO
     3.50E+ 05      1.879   6.135E-04      96.0    #DELTA H 1000K =96.0        ERR=   6.90 %
   END
TAG
 JWB/AMD 10/2001
COMMENTS:
 JWB/AMD 10/2001
```

Dimethyl-ether radical + O_2

```
11/24/01 Using Tak's input parameters for CH3-O-CH2+O2 in     PhD dissertation
chemact
dissoc
KFIT
# showshape
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
4  298.  400.  500.  600.  800.  1000.  1500.  2000.
pres
3  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER (mass),  sigma(A), e/k(K)
         28.   3.798    71.4   !keeping same as   chemdis for N2 -  jwl 7/14/00
# Rot       (external rotor included)
PARAMETERS (mass),  sigma(A), e/k(K)
77.  5.54  460.   #  Tak's original
delta (E)
   830.  0 . #    (830.0 from CCOO   calc done by AMD 9/28/2001)
#  1000.  0.  #jwl's value
# EXP (temperature exponent to alpha,    alpha= alpha(300)*(T/300)^N )
#  0.01
#BETA (do constant beta calculation if uncomment)
# .75
INT   (integration interval in kcal)
   0.5
#EHEAD integration stops at  Ehead + highest barrier,   def. 75 kcal
# 75
INPUT
 4.82e12  0.0  0.0   0.0

WELL 1
COCQ.
  FREQ
     3   363.6   7.347
        1221.8  10.178
        3049.6   4.975
   REACTANT
      COC .+O2
      1.58E15    0.0    0.0  33.4
   ISOMER
      C.OCQ
       1.10E7  1.21  0.0  17.13
END
WELL 2
C.OCQ
   FREQ
     3     290.1   7.028
          1102.5  11.198
          3411.5   3.774
   ISOMER
      COCQ.
      5.5604E+07    . 56845   0.0    9.9753 # MR with kfit32c
   PRODUCT
      CH2O+CH2O+OH
      1.81E12  0.38  0.0  22.19
END
TAG
comments:
```

HCO + O_2

```
rxn pathway for HCO + O2 base on   Hsu/mebel/Lin 1996 JPC publication
chemact
dissoc
KFIT
# showshape
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
5  298.  400.  500.  600.  800.  1000.  1500.  2000.
pres
4  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER (mass),  sigma(A), e/k(K)
         28.    3.798    71.4   !keeping same as   chemdis for N2 -  jwl 7/14/00
# Rot        (external rotor included)
PARAMETERS (mass),  sigma(A), e/k(K)
61.  3.62    436.3
delta (E)
   830.  0 .    (taken from CCOO  calc done by AMD 9/28/2001)
INT   (integration interval in kcal)
   0.5
#EHEAD integration stops at  Ehead + highest barrier,  def. 75 kcal
# 75
INPUT (A,  n ,alpha, E kcal      k=AT^nexp(- alpha*T) exp(-E/RT) )
5.904e9  0.932  0.0  -0.737  #  Hsu et al JPC96

#*****************************************************
# Hsu et al also report an abstraction   rxn for hco + o2 -> co + ho2
# the rate constant is as follows
#!1.5480e4  2.38  0.0  -1.526  !(Hsu96 report 2.58e-20  2.38  0.0  768.16*R)
#
# we will put this directly into   chemkin instead since no way to have
# direct to prod from reactants,   viz doesn't go through any energized adduct
#*****************************************************

WELL 1
   HCQ .*O
   FREQ
   3     386.3 3.230
        1203.6 4.713
        3298.3  .557
   #1    834.9   8.500
   REACTANT
   HCO + O2
   7.6374E18   -1.52526 0.  36.1    #Af/  Ar from Hsu and  Ea=DHrxn
   ISOMER
      ODCOOH
      1.3910E+11    . 53249   0.  42.259 # ThermKin/ SMCPS base on   Hsu value
   PRODUCT
      CO + HO2
      9.6753E+11      . 54495   0.   23.837 # ThermKin/ SMCPS base on   Hsu value
   END
WELL 2
   ODCOOH
   FREQ  #using  ING's C.Q*O vibration
   3      289.6   3.122
         1027.7   3.579
         1535.8   1.298
   #1    580.5  8.000
   ISOMER
     HCQ .*O
     2.1809E+11   . 17053    0.  32.837  # ThermKin/ SMCPS base on   Hsu value
   PRODUCT
     CO + HO2
     2.9487E+13  - .04848   0.   21.086  # ThermKin/ SMCPS base on   Hsu value
   PRODUCT
     CO2 + OH
     2.2411E+12   . 31056    0.  11.393  # ThermKin/ SMCPS base on   Hsu value
END
TAG
comments:
```

CH_3NH_2 dissociation

```
12/5/01  CH3+NH2 from AMD/JWB   gardiner book  pg 207
chemact
dissoc
KFIT
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
11  300. 400. 500 . 600.   800.  1000. 1200  . 1500.  2000.  2500.  3000.
pres
7  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER ( mass  ,sigma, e/k)
28.0  3.62  97.5    # same as one used for CCOO paper with cys/jwb/amd/ayc-2001
PARAMETERS  ( mass, sigma, e/k)
31.  3.77  364. #AMD/JWB  gardiner  pg 207
DELTA  (E)
830.   0.  #  same as one used for CCOO paper with cys/jwb/amd/ayc-2001
INT   (integration interval in kcal)
   0.5
INPUT
 2.3E13  0.0   0.0   0.0

WELL 1
CH3NH2
   FREQ  # BASE ON B3LYP/6-31G(D  ,P)
     3   724.6  3.966
        1472.4  6.318
        3039.6  4.216
   REACTANT
      CH3 + NH2
       1.2E16  0.0   0.0  84.606
   PRODUCT
      CH2NH2 + H
        2.0E15  0.0   0.0 92.33  #  Ea = dHrxn, ch2nh2=g2 isodesmic
   PRODUCT
      CH3NH + H
        1.8E15  0.0   0.0  103.38  #  Ea = avg AMD+G2/2
   PRODUCT
      H2CDNH + H2
         4.9E13  0.0   0.0  103.487
END
TAG
comments:
```

$CH_3NH + O_2$

```
12/5/01  CH3NH+O2
#thermo :  Hf base on G2 and S &  Cp base on B3LYP/6-31gdp
chemact
dissoc
KFIT
CHEB
  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
11  300. 400. 500 . 600.   800.  1000. 1200  . 1500.  2000.  2500.  3000.
pres
7  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER ( mass  ,sigma, e/k)
28.0  3.62  97.5    # same as one used for CCOO paper with cys/jwb/amd/ayc-2001
PARAMETERS  ( mass, sigma, e/k)
62.   4.940  450.00 #base on CCOO paper with cys/jwb/amd/ayc-2001
DELTA  (E)
830.   0.  #  same as one used for CCOO paper with cys/jwb/amd/ayc-2001
INT   (integration interval in kcal)
   0.5
INPUT
  2.8303E+15  -2.49952  0.0  0.  # NIST JWB/AMD 1989    jpc NH2+O2, Ea=0

WELL 1
CH3NHQJ
   FREQ  # BASE ON B3LYP/6-31G(D  ,P)
     3   436.0  5.769
        1131.7  7.715
        2893.2  3.516
   REACTANT
      CH3NH + O2       # jwb =  ok, this well is shallow, prob not   impt channel
    2.4297E+31    - 5.80644   0.0  15.058  # MR, k = 1E6 - 3E10
  PRODUCT
     H2CNHOS + OH
   4.E12  0.0  0.0  33.51  #isomer does not exist.  Use    k(isomer), which immediately form prod.
   PRODUCT #PROD RESULT FROM ISOMER H3CNJQ, IMMED DISSOC TO PROD.
      H3CNDO + OH
        8.E12   0.0     0.0  37.0 #EST.  A=4-MEM RING; EA=4-MEM RING STRAIN; JWB    est.
   PRODUCT
     CH2=NH + HO2
     8.8006E+ 05         2.24329    0.0      29.613
END

TAG
comments:
```

$CH_2NH_2 + O_2$

```
12/5/01  # thermo  :  Hf base on G2 and S &  Cp base on B3LYP/6-31gdp
chemact
dissoc
KFIT
# showshape
#CHEB
#  7 3 250 . 2500. 1.e- 3  1.e+2 50
temp
11  300. 400. 500 . 600.   800.  1000. 1200  . 1500.  2000.  2500.  3000.
pres
7  .0001 .001 .01 0.1 1.0 10.0 100.0
COLLIDER ( mass  ,sigma, e/k)
28.0  3.62  97.5    # same as one used for CCOO paper with cys/jwb/amd/ayc-2001
# Rot       (external rotor included)
PARAMETERS  ( mass, sigma, e/k)
62.  4.940  450.00 #base on CCOO paper with cys/jwb/amd/ayc-2001
DELTA  (E)
830.   0.  #  same as one used for CCOO paper with cys/jwb/amd/ayc-2001
INT   (integration interval in kcal)
   0.5
INPUT
 2.11E13  0.0  0.0    0.0  #NIST 95MAS/TSU (JPC 95, pp13126)
WELL 1
CQJNH2
   FREQ  # BASE ON B3LYP/6-31G(D  ,P)
     3   410.8  5.946
        1149.3  7.238
        3022.1  3.816
   REACTANT
      CH2NH2 + O2
     2.5505E+ 04    4.10228  0.  31.05   # MR with kfit32c
   ISOMER
      H2CQNJH
       2.E12  0.0   0.0  36.0  #EST.  Ea approx = CCOO->  CjCOOH;  cys=  adj  Ea ca 36.

    PRODUCT    #RADICAL SITE ON ADJ C WITH OOH, IMMED GO TO PROD
       NH2CHO + OH
         4.E12   0.0      0.0  46.0 #EST. CJQNH2 NOT CONVERGE,    Ea ca CCOO -> CCHO + OH

    PRODUCT
       CH2O + H2NDO   # jwb= ** ok need to further test out
        4.E12   0.0      0.0  46.3 #EST.  A=4-MEM RING; EA=4-MEM RING    STRAIN+DHrxn

   PRODUCT  #  Molec  Elim channel
      H2CDNH + HO2
      8.8006E+ 05    2.24329    0.0  31.613  #    molec elim using k fm  ccoo -> c=c + ho2;  Ea + 2 higher

END
WELL 2
H2CQNJH
   FREQ  # BASE ON B3LYP/6-31G(D  ,P)
     3   419.6  6.545
        1172.6  7.291
        3105.4  2.665
   ISOMER
      CQJNH2
     1.1679E+12  -  .16280   0.  18.300  #MR with kfit32c of above.
   PRODUCT
      H2CDNH + HO2              ** ok if beat    ascission
      1.2829E+11  . 51856  0.0  16.153  #use H-S from    CjCOOH -> C=C + HO2
END
TAG
comments:
```

APPENDIX F

THERMODYNAMIC PROPERTIES OF SPECIES

Thermodynamic properties of species used in the pressure dependent mechanism described in Chapter 8.

UNITS:KCAL

SPECIES	HF(298)	S(298)	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500	DATE	REF	ELEMENTS									
*AR	.00	36.98	4.97	4.97	4.97	4.97	4.97	4.97	4.97	7/12/93			0		0		0	AR	1	G	0
N2	.00	45.77	6.91	7.00	7.12	7.24	7.50	7.77	8.32			N	2		0		0		0	G	0
*O	59.52	38.40	5.00	5.00	5.00	5.00	5.00	5.00	5.00		120186	O	1		0		0		0	G	0
O2	.00	49.00	6.96	7.20	7.42	7.63	7.99	8.28	8.69		121386	O	2		0		0		0	G	0
*H	52.10	27.39	4.97	4.97	4.97	4.97	4.97	4.97	4.97		J 6/74	H	1		0		0		0	G	0
OH	8.96	43.88	7.14	7.09	7.06	7.07	7.15	7.31	7.88	Hf-Ruscic 2001		O	1	H	1		0		0	G	0
HO2	3.80	54.73	8.41	8.95	9.46	9.94	10.77	11.38	12.12		J 9/81	H	1	O	2		0		0	G	1
H2	.00	31.20	7.10	7.10	7.12	7.16	7.28	7.43	7.91			H	2		0		0		0	G	0
H2O	-57.80	45.07	7.97	7.94	7.93	7.96	8.09	8.31	9.16	CBS-APNO		H	2	O	1		0		0	G	1
H2O2	-32.50	55.62	10.47	11.48	12.35	13.09	14.30	15.22	16.83		120186	H	2	O	2		0		0	G	0
*C(S)	.00	21.83	4.00	4.00	4.00	4.00	4.00	4.00	4.00		J 3/61	C	1		0		0		0	S	0
*C	170.90	38.31	4.97	4.97	4.97	4.97	4.97	4.97	4.97		J 3/61	C	1		0		0		0	G	0
CO	-26.40	47.20	6.85	6.99	7.13	7.28	7.58	7.86	8.40		121286	C	1	O	1		0		0	G	0
CO2	-94.02	51.00	9.83	9.78	10.10	10.66	12.02	13.19	13.87		121286	C	1	O	2		0		0	G	0
CH	142.02	43.72	7.08	6.93	6.92	7.02	7.39	7.87	8.69		J12/67	C	1	H	1		0		0	G	0
HCO	10.90	53.42	7.55	8.04	8.56	9.10	10.15	11.09	12.71	0/12/95	ThmCa	C	1	H	1	O	1		0	G	0
HCO2.	-38.30	56.73	8.77	10.14	11.39	12.51	14.37	15.73	17.56	7/12/93		C	1	H	1	O	2		0	G	0
CYC.OO	43.93	59.09	11.74	13.35	14.66	15.70	17.18	18.06	18.98	0/12/95	ThmCa	C	1	H	1	O	2		0	G	0
HCO3	-31.30	74.10	13.30	14.74	16.03	17.17	19.04	20.44	22.43	0/12/95	ThmCa	C	1	H	1	O	3		0	G	1
HCQ.*O	-31.30	74.10	13.30	14.74	16.03	17.17	19.04	20.44	22.43	0/12/95	ThmCa	C	1	H	1	O	3		0	G	1
C.Q*O	-30.50	75.00	14.62	16.51	18.02	19.20	20.82	21.77	22.82	0/12/95	ThmCa	C	1	H	1	O	3		0	G	2
CH2	94.16	46.69	8.18	8.47	8.76	9.06	9.67	10.25	11.50	CBS-APNO		C	1	H	2		0		0	G	0
CH2S	102.48	45.21	8.05	8.22	8.46	8.77	9.47	10.19	11.60	CBS-APNO+isode		C	1	H	2		0		0	G	0
HCOHT	48.36	60.97	10.93	11.88	12.74	13.51	14.78	15.75	17.15	10/ 9/95		C	1	H	2	O	1		0	G	1
HCOH	25.82	56.99	9.73	10.33	10.94	11.55	12.72	13.74	15.55	CBS-APNO+isode		C	1	H	2	O	1		0	G	1
CH2O	-26.08	52.19	8.27	9.05	9.91	10.81	12.57	14.09	16.45	CBS-APNO		C	1	H	2	O	1		0	G	0
HCO2H	-90.22	64.27	10.91	12.89	14.59	16.05	18.34	19.97	22.20	0/12/95	ThmCa	C	1	H	2	O	2		0	G	1
O.HC.OOHT	4.86	76.54	18.66	20.22	21.57	22.75	24.62	25.96	27.77	7/01/94		C	1	H	2	O	3		0	G	2
O.HC.OOH	17.40	73.16	18.13	19.82	21.30	22.58	24.59	26.01	27.83	10/ 9/95		C	1	H	2	O	3		0	G	2
HOC.HOO.	1.54	74.84	17.01	18.12	19.21	20.28	22.26	23.93	26.56	10/ 9/95		C	1	H	2	O	3		0	G	2
HOC.HOO.T	-13.00	77.60	17.01	18.12	19.21	20.28	22.26	23.93	26.56	10/ 9/95		C	1	H	2	O	3		0	G	2
HCQ*O	-67.42	73.88	15.16	17.62	19.67	21.37	23.90	25.57	27.63	0/12/95	ThmCa	C	1	H	2	O	3		0	G	2
O.HC.OOH	17.40	75.92	18.13	19.82	21.30	22.58	24.59	26.01	27.83	0/12/95	ThmCa	C	1	H	2	O	3		0	G	2
HOCHO.O.	-31.01	72.24	14.63	16.37	18.08	19.70	22.56	24.77	27.62	0/12/95	ThmCa	C	1	H	2	O	3		0	G	1
CH3	34.96	46.85	9.61	10.18	10.77	11.37	12.58	13.71	15.91	CBS-APNO		C	1	H	3		0		0	G	0
CH3O	5.26	54.26	9.22	10.85	12.37	13.76	16.19	18.15	21.26	CBS-APNO		C	1	H	3	O	1		0	G	0
CH2OH	-3.49	58.57	10.61	11.87	13.04	14.12	16.01	17.54	20.14	CBS-APNO		C	1	H	3	O	1		0	G	1
CH3O.	3.96	55.86	9.59	11.22	12.75	14.18	16.68	18.68	21.76	0/12/95	ThmCa	C	1	H	3	O	1		0	G	0

C.H2OH	-3.60	59.05	11.67	13.24	14.57	15.69	17.46	18.77	20.97	0/12/95	ThmCa	C	1	H	3	O	1	0	G 1
CH3OO	4.50	66.56	13.05	15.20	17.08	18.72	21.36	23.32	26.32	0/12/95	ThmCa	C	1	H	3	O	2	0	G 1
CH2OOH	14.80	68.25	15.73	18.16	20.15	21.77	24.11	25.61	27.51	0/12/95	ThmCa	C	1	H	3	O	2	0	G 2
CH3OO	4.50	66.56	13.05	15.20	17.08	18.72	21.36	23.32	26.32	0/12/95	ThmCa	C	1	H	3	O	2	0	G 1
CH2O.OH	-39.07	66.12	13.01	14.78	16.44	17.97	20.64	22.78	26.10	0/12/95	ThmCa	C	1	H	3	O	2	0	G 1
CO.H2OH	-39.07	66.12	13.01	14.78	16.44	17.97	20.64	22.78	26.10	0/12/95	ThmCa	C	1	H	3	O	2	0	G 1
CH2OHOO	-30.30	81.72	19.44	21.48	23.33	24.99	27.78	29.87	32.73	rayez,lev 11/		C	1	H	3	O	3	0	G 2
CQ.H2OH	-40.36	76.82	16.65	18.40	20.10	21.73	24.68	27.14	30.98	0/12/95	ThmCa	C	1	H	3	O	3	0	G 2
CQH2O.	-24.50	75.14	17.86	20.17	22.25	24.10	27.16	29.43	32.50	0/12/95	ThmCa	C	1	H	3	O	3	0	G 2
HOC.HQ	-34.56	77.38	19.21	21.14	22.87	24.41	26.97	28.88	31.58	0/12/95	ThmCa	C	1	H	3	O	3	0	G 3
C.QOH	-32.56	80.42	18.92	20.67	22.30	23.80	26.41	28.47	31.44	0/12/95	ThmCa	C	1	H	3	O	3	0	G 3
HC(OH)2O.	-82.99	73.70	16.24	18.11	19.98	21.79	25.06	27.69	31.37	0/12/95	ThmCa	C	1	H	3	O	3	0	G 2
CH4	-17.90	44.40	8.64	9.82	11.05	12.29	14.68	16.78	20.36		J 3/61	C	1	H	4		0	0	G 0
CH3OH	-48.00	57.45	9.81	11.52	13.21	14.85	17.85	20.34	24.30	CBS-APNO		C	1	H	4	O	1	0	G 1
CH3OOH	-31.60	66.34	15.10	18.13	20.67	22.81	26.07	28.33	31.52	0/12/95	ThmCa	C	1	H	4	O	2	0	G 2
HOCH2OH	-91.05	67.58	13.94	16.07	18.05	19.89	23.09	25.66	29.73	0/12/95	ThmCa	C	1	H	4	O	2	0	G 2
HOCH2Q	-76.48	76.60	18.94	21.53	23.88	25.99	29.54	32.23	36.07	0/12/95	ThmCa	C	1	H	4	O	3	0	G 3
HC(OH)3	-134.95	75.16	17.21	19.64	21.87	23.90	27.37	30.11	34.34	0/12/95	ThmCa	C	1	H	4	O	3	0	G 3
C2H	134.48	51.51	9.62	9.98	10.35	10.70	11.36	11.92	12.80	0/12/95	ThmCa	C	2	H	1		0	0	G 0
HCCO	41.36	60.51	12.27	13.69	14.79	15.63	16.75	17.41	18.39	0/12/95	ThmCa	C	2	H	1	O	1	0	G 0
CYC.*CO	81.01	54.84	13.88	15.00	15.90	16.60	17.59	18.21	19.00	0/12/95	ThmCa	C	2	H	1	O	1	0	G 0
C#COO	85.15	69.85	15.93	17.45	18.68	19.67	21.10	22.03	23.29	0/12/95	ThmCa	C	2	H	1	O	2	0	G 1
C.#COOH	129.65	71.74	17.44	19.04	20.24	21.12	22.19	22.71	23.31	0/12/95	ThmCa	C	2	H	1	O	2	0	G 2
C.*OCHO	-17.10	63.01	12.82	15.13	16.99	18.49	20.61	21.91	23.38	0/12/95	ThmCa	C	2	H	1	O	2	0	G 1
CJ*OCHO	-23.31	69.67	13.57	14.99	16.23	17.31	19.08	20.38	22.29		cys 4/98	C	2	H	1	O	2	0	G 1
CQ.*C*O	5.47	77.35	19.04	21.42	23.18	24.45	26.00	26.83	28.25	0/12/95	ThmCa	C	2	H	1	O	3	0	G 1
C.Q*C*O	23.77	78.99	21.13	23.50	25.21	26.41	27.77	28.36	29.11	0/12/95	ThmCa	C	2	H	1	O	3	0	G 2
CHOCO2	-60.76	75.92	15.74	18.73	21.15	23.08	25.77	27.38	29.12	0/12/95	ThmCa	C	2	H	1	O	3	0	G 1
C.*OCO2H	-70.42	73.85	16.50	19.62	22.01	23.80	26.08	27.27	28.58	0/12/95	ThmCa	C	2	H	1	O	3	0	G 2
C2H2	54.19	47.65	10.12	11.50	12.60	13.48	14.77	15.72	17.57		cys 4/98	C	2	H	2		0	0	G 0
H2C*CJJ	97.20	52.34	9.97	10.80	11.53	12.19	13.29	14.17	15.76	4/8/99 CYS		C	2	H	2		0	0	G 0
HC#COH	20.43	58.73	13.18	14.82	16.23	17.46	19.39	20.76	22.59	0/12/95	ThmCa	C	2	H	2	O	1	0	G 1
C*C*O	-11.74	57.84	12.71	14.77	16.43	17.76	19.70	20.98	22.94	0/12/95	ThmCa	C	2	H	2	O	1	0	G 0
CH2CO	-11.80	57.58	12.29	14.08	15.59	16.86	18.84	20.29	22.59	JWL	7/98CBSQ	C	2	H	2	O	1	0	G 0
C*C*O	-11.80	57.58	12.29	14.08	15.59	16.86	18.84	20.29	22.59	JWL	7/98CBSQ	C	2	H	2	O	1	0	G 0
CYC*CO	24.09	51.63	14.04	16.33	18.10	19.45	21.23	22.28	23.80	0/12/95	ThmCa	C	2	H	2	O	1	0	G 0
HCJJCHOT	61.46	63.28	13.08	14.75	16.16	17.35	19.21	20.56	22.72	JWB 3/01		C	2	H	2	O	1	0	G 0
C#COOH	49.03	69.63	18.04	20.42	22.31	23.80	25.83	27.03	28.42	0/12/95	ThmCa	C	2	H	2	O	2	0	G 2
O*CC*O	-50.60	65.44	14.90	17.53	19.70	21.49	24.14	25.87	28.10	0/12/95	ThmCa	C	2	H	2	O	2	0	G 1
CO.C.*O	15.36	73.25	15.67	17.29	18.81	20.21	22.62	24.51	27.30	0/12/95	ThmCa	C	2	H	2	O	2	0	G 1
OCYCO	-43.92	62.30	11.96	14.71	17.05	19.03	22.09	24.25	27.39	JWL CBSQ		C	2	H	2	O	2	0	G 0
CJJYCOO	93.39	67.75	14.98	17.49	19.52	21.14	23.50	25.06	27.40		cys 4/98	C	2	H	2	O	2	0	G 1
HCJOJ*CHO	-2.43	70.16	14.52	16.74	18.64	20.25	22.78	24.58	27.20		cys 4/98	C	2	H	2	O	2	0	G 1
HCJ*COOJ	79.00	69.61	15.42	17.88	19.84	21.40	23.63	25.09	27.36		cys 4/98	C	2	H	2	O	2	0	G 1

```
C.CO2.        -9.08    67.08    14.41    17.27    19.62    21.56    24.49    26.58    30.08   0/12/95   ThmCa    C   2 H   2 O   3        0 G 1
CQ*C*O       -30.63    77.13    20.81    23.93    26.32    28.11    30.42    31.70    33.38   0/12/95   ThmCa    C   2 H   2 O   3        0 G 2
CHOCO2H     -112.72    77.38    17.37    20.50    23.09    25.20    28.32    30.35    32.94   0/12/95   ThmCa    C   2 H   2 O   3        0 G 2
C2H3          71.63    56.62    10.09    11.98    13.61    15.02    17.30    19.03    21.82    JWB 4/30/98       C   2 H   3     0        0 G 0
CC.*O         -2.67    64.28    12.25    14.39    16.32    18.04    20.92    23.12    26.41   JWL    2/00CBSQ   C   2 H   3 O   1        0 G 1
C.CHO          3.12    60.42    12.96    15.37    17.46    19.26    22.11    24.17    27.15   0/12/95   ThmCa    C   2 H   3 O   1        0 G 1
CH2*C.OH      24.79    64.79    14.18    16.53    18.45    20.00    22.30    23.89    26.46   0/12/95   ThmCa    C   2 H   3 O   1        0 G 1
C.*COH        29.49    64.32    14.02    16.51    18.51    20.11    22.42    23.99    26.53   10/12/95           C   2 H   3 O   1        0 G 1
CYC.CO        29.32    60.69    11.57    14.50    16.94    18.97    22.05    24.20    27.37   0/12/95   ThmCa    C   2 H   3 O   1        0 G 0
C*CO.         13.79    61.82    12.85    15.36    17.49    19.30    22.12    24.15    27.27   10/12/95           C   2 H   3 O   1        0 G 0
CYCOCO.       -6.42    65.28    14.82    18.72    21.87    24.40    28.03    30.35    33.48   0/12/95   ThmCa    C   2 H   3 O   2        0 G 0
CYCOOC.       41.61    67.35    14.10    17.92    21.16    23.88    28.03    30.81    34.19   0/12/95   ThmCa    C   2 H   3 O   2        0 G 0
C*COO.        29.73    73.37    16.61    19.40    21.69    23.57    26.42    28.45    31.76   0/12/95   ThmCa    C   2 H   3 O   2        0 G 1
O*CCO.       -21.54    72.13    16.47    18.75    20.81    22.67    25.80    28.23    31.89   0/12/95   ThmCa    C   2 H   3 O   2        0 G 1
CCO2         -51.38    68.43    14.77    17.75    20.29    22.44    25.80    28.21    31.77   0/12/95   ThmCa    C   2 H   3 O   2        0 G 1
C.CYCOO       37.56    69.29    16.38    20.23    23.37    25.91    29.55    31.78    34.29   0/12/95   ThmCa    C   2 H   3 O   2        0 G 1
CC*OOJ       -41.41    68.43    13.79    16.54    18.96    21.09    24.56    27.17    31.12    CBSQ              C   2 H   3 O   2        0 G 1
C.*COOH       52.73    74.54    18.47    21.49    23.87    25.73    28.30    29.92    32.30   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
C*C.OOH       50.53    74.96    18.27    21.12    23.41    25.24    27.87    29.58    32.07   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
C.CO2H       -61.00    64.91    15.83    19.08    21.73    23.88    27.03    29.12    32.05   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
C.CO2H       -60.99    60.05    15.87    19.11    21.75    23.89    27.01    29.08    32.06   JWB  4/30/98      C   2 H   3 O   2        0 G 2
COHC.*O      -36.60    74.71    16.57    18.59    20.45    22.14    25.03    27.31    30.85   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
C.OHCHO      -33.70    71.22    16.14    18.55    20.68    22.55    25.62    27.92    31.31   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
C.OCHO       -39.99    75.07    17.50    19.88    22.02    23.92    27.05    29.37    32.48   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
COC.*O       -47.49    72.67    16.13    18.66    20.94    22.97    26.34    28.85    32.21   0/12/95   ThmCa    C   2 H   3 O   2        0 G 2
HC*OCOO.     -22.83    82.83    20.30    22.59    24.70    26.66    30.07    32.85    37.37   0/12/95   ThmCa    C   2 H   3 O   3        0 G 0
C.*OCOOH     -22.03    83.73    21.48    24.07    26.35    28.34    31.63    34.14    38.10   0/12/95   ThmCa    C   2 H   3 O   3        0 G 0
O*COO.C      -44.38    77.47    18.45    21.48    24.09    26.32    29.86    32.46    36.40   0/12/95   ThmCa    C   2 H   3 O   3        0 G 2
CCOQJ        -38.87    75.57    19.48    23.22    26.28    28.78    32.43    34.83    38.00   JWL    9/00CBSQ   C   2 H   3 O   3        0 G 2
CJCOQ        -32.45    79.26    21.80    25.45    28.29    30.46    33.39    35.13    37.54   JWL    7/98CBSQ   C   2 H   3 O   3        0 G 3
HC*OC.OOH    -19.13    80.24    20.96    24.03    26.64    28.84    32.23    34.55    37.52   0/12/95   ThmCa    C   2 H   3 O   3        0 G 3
CCO3         -44.38    77.47    18.45    21.47    24.07    26.31    29.86    32.44    36.13   0/12/95   ThmCa    C   2 H   3 O   3        0 G 3
C.CO3H       -38.18    75.90    20.28    23.96    26.91    29.27    32.57    34.61    37.11   0/12/95   ThmCa    C   2 H   3 O   3        0 G 4
C2H4          12.52    52.47    10.33    12.82    15.02    16.94    20.12    22.54    26.33   0/12/95   ThmCa    C   2 H   4     0        0 G 0
CH3CHO       -39.18    63.15    13.17    15.84    18.26    20.46    24.16    27.02    31.25   0/12/95   ThmCa    C   2 H   4 O   1        0 G 1
C*COH        -29.61    62.93    14.23    17.36    19.94    22.06    25.26    27.51    31.05   0/12/95   ThmCa    C   2 H   4 O   1        0 G 1
CYCCO        -12.57    59.36    11.35    14.87    17.90    20.48    24.55    27.48    31.78   12/19/96 THERM    C   2 H   4 O   1        0 G 0
CYCCO        -12.58    58.16    11.72    15.24    18.24    20.78    24.76    27.61    31.85   0/12/95   ThmCa    C   2 H   4 O   1        0 G 0
CYC2O2        -2.29    60.78    14.13    18.89    22.89    26.23    31.29    34.69    39.01   0/12/95   ThmCa    C   2 H   4 O   2        0 G 0
CCYCOO       -11.44    64.50    17.10    21.33    24.89    27.86    32.33    35.29    38.92   0/12/95   ThmCa    C   2 H   4 O   2        0 G 1
CYCOCOH      -58.38    66.74    16.16    20.12    23.40    26.10    30.15    32.90    36.88   0/12/95   ThmCa    C   2 H   4 O   2        0 G 1
C*COOH        -6.37    73.15    18.58    22.26    25.24    27.63    31.11    33.41    36.83   0/12/95   ThmCa    C   2 H   4 O   2        0 G 2
CCO2H       -103.30    67.64    16.11    19.60    22.58    25.12    29.09    31.94    36.12   0/12/95   ThmCa    C   2 H   4 O   2        0 G 2
O*CCOH       -73.52    73.59    17.40    20.03    22.41    24.57    28.23    31.08    35.42   0/12/95   ThmCa    C   2 H   4 O   2        0 G 2
```

COCHO	-84.41	71.55	16.97	20.07	22.88	25.39	29.55	32.67	36.90	0/12/95	ThmCa	C	2	H	4	O	2	0	G	2
O*COOHC	-80.50	77.25	20.56	24.41	27.65	30.36	34.52	37.41	41.50	0/12/95	ThmCa	C	2	H	4	O	3	0	G	3
O*CCQ	-58.93	82.61	21.33	24.49	27.32	29.84	34.00	37.11	41.50	0/12/95	ThmCa	C	2	H	4	O	3	0	G	3
CCO3H	-80.50	77.25	20.47	24.37	27.65	30.40	34.56	37.41	41.25	0/12/95	ThmCa	C	2	H	4	O	3	0	G	4
C2H5	28.60	60.61	12.16	14.70	17.00	19.08	22.62	25.42	29.92	CBS-Q//B3LYP		C	2	H	5		0	0	G	1
CCO.	-4.24	65.66	14.48	17.95	20.97	23.59	27.82	30.97	35.79	0/12/95	ThmCa	C	2	H	5	O	1	0	G	1
CC.OH	-14.30	67.90	15.87	18.89	21.53	23.83	27.57	30.42	34.98	0/12/95	ThmCa	C	2	H	5	O	1	0	G	2
C.COH	-7.20	70.53	14.67	17.85	20.63	23.06	27.02	30.02	34.70	0/12/95	ThmCa	C	2	H	5	O	1	0	G	2
COC.	1.00	67.30	16.30	19.15	21.72	24.03	27.90	30.92	35.57	0/12/95	ThmCa	C	2	H	5	O	1	0	G	2
COC.	.10	67.68	14.79	17.96	20.75	23.18	27.14	30.13	34.82	Tak PhD	CBS-q	C	2	H	5	O	1	0	G	2
CCOO	-5.53	76.36	18.28	21.78	24.88	27.60	32.07	35.48	40.71	0/12/95	ThmCa	C	2	H	5	O	2	0	G	2
CCOO	-6.72	73.83	16.15	19.97	23.34	26.28	31.07	34.64	40.02	CBS-Q/B3&isode		C	2	H	5	O	2	0	G	2
CCO.OH	-50.04	72.86	18.89	22.86	26.21	29.03	33.39	36.49	41.06	0/12/95	ThmCa	C	2	H	5	O	2	0	G	2
COCO.	-34.47	73.96	18.30	21.66	24.70	27.43	32.00	35.52	40.79	0/12/95	ThmCa	C	2	H	5	O	2	0	G	2
C.COOH	6.87	79.55	19.53	23.29	26.52	29.27	33.61	36.72	41.17	10/12/95		C	2	H	5	O	2	0	G	3
C.COOH	11.22	81.91	20.28	23.56	26.33	28.68	32.38	35.12	39.65	CBS-Q//B3LYP		C	2	H	5	O	2	0	G	3
CC.OOH	2.27	79.96	20.40	23.81	26.79	29.38	33.56	36.64	41.11	0/12/95	ThmCa	C	2	H	5	O	2	0	G	3
C.C(OH)2	-54.50	79.11	19.21	22.87	25.95	28.54	32.55	35.43	39.87	10/12/95		C	2	H	5	O	2	0	G	3
CC.(OH)2	-62.82	78.79	19.29	22.17	24.82	27.24	31.39	34.67	39.71	10/12/95		C	2	H	5	O	2	0	G	3
COC.OH	-44.53	76.20	19.63	22.59	25.27	27.69	31.78	34.97	39.88	10/12/95		C	2	H	5	O	2	0	G	3
C.OCOH	-42.03	77.56	19.79	22.76	25.45	27.86	31.93	35.09	39.91	0/12/95	ThmCa	C	2	H	5	O	2	0	G	3
COHCQ.	-41.33	87.00	21.42	25.25	28.57	31.45	36.13	39.69	45.41	0/12/95	ThmCa	C	2	H	5	O	3	0	G	2
CO.CQ	-25.47	85.32	22.45	26.84	30.54	33.65	38.45	41.87	46.94	0/12/95	ThmCa	C	2	H	5	O	3	0	G	2
C.OHCQ	-35.53	87.56	23.81	27.76	31.07	33.86	38.17	41.28	46.07	0/12/95	ThmCa	C	2	H	5	O	3	0	G	3
COHC.OOH	-33.53	90.60	23.51	27.26	30.47	33.23	37.63	40.88	45.86	0/12/95	ThmCa	C	2	H	5	O	3	0	G	3
CCQO.	-35.47	81.88	23.89	28.44	32.21	35.33	39.99	43.13	47.42	0/12/95	ThmCa	C	2	H	5	O	3	0	G	3
CCQ.OH	-51.33	83.56	23.15	26.90	30.15	32.96	37.47	40.82	45.88	0/12/95	ThmCa	C	2	H	5	O	3	0	G	3
COCQ.	-33.90	83.11	21.37	25.65	29.27	32.31	37.02	40.39	45.48	Tak PhD	CBS-q	C	2	H	5	O	3	0	G	3
C.CQOH	-38.43	88.13	24.01	28.19	31.68	34.57	38.95	41.96	46.21	0/12/95	ThmCa	C	2	H	5	O	3	0	G	4
CC.QOH	-46.73	89.99	24.05	27.69	30.85	33.58	37.95	41.15	45.77	0/12/95	ThmCa	C	2	H	5	O	3	0	G	4
C.OCQ	-26.50	88.03	23.11	27.67	31.33	34.25	38.46	41.21	45.37	Tak PhD	CBS-q	C	2	H	5	O	3	0	G	4
HOOCCOO.	-26.76	93.27	26.13	30.66	34.50	37.74	42.77	46.34	51.42	0/12/95	ThmCa	C	2	H	5	O	4	0	G	4
HOOCC.OOH	-18.96	98.24	28.13	32.65	36.44	39.59	44.36	47.60	51.87	0/12/95	ThmCa	C	2	H	5	O	4	0	G	5
C2H6	-20.40	55.10	12.44	15.81	18.83	21.53	26.06	29.58	35.06	0/12/95	ThmCa	C	2	H	6		0	0	G	1
CCOH	-56.20	67.12	15.44	19.23	22.54	25.44	30.17	33.75	39.32	0/12/95	ThmCa	C	2	H	6	O	1	0	G	2
COC	-43.40	63.78	15.72	19.33	22.58	25.50	30.39	34.16	39.88	0/12/95	ThmCa	C	2	H	6	O	1	0	G	2
CCOOH	-41.63	76.14	20.33	24.69	28.44	31.66	36.77	40.48	45.86	0/12/95	ThmCa	C	2	H	6	O	2	0	G	3
CC(OH)2	-102.02	74.32	19.89	24.18	27.82	30.91	35.74	39.23	44.59	0/12/95	ThmCa	C	2	H	6	O	2	0	G	3
COCOH	-86.45	75.42	19.24	22.96	26.32	29.34	34.40	38.32	44.33	0/12/95	ThmCa	C	2	H	6	O	2	0	G	3
COHCOOH	-77.45	86.78	23.41	28.14	32.15	35.55	40.85	44.69	50.55	0/12/95	ThmCa	C	2	H	6	O	3	0	G	3
CCQOH	-87.45	83.34	24.88	29.71	33.76	37.14	42.29	45.88	50.98	0/12/95	ThmCa	C	2	H	6	O	3	0	G	4
HOOCCOOH	-62.88	94.42	27.49	32.73	37.15	40.87	46.60	50.60	56.10	0/12/95	ThmCa	C	2	H	6	O	4	0	G	5
C#CCBR	50.43	71.37	17.70	20.63	23.04	25.00	27.90	29.87	32.78	0/12/95	ThmCa	C	3	H	3	BR	1	0	G	1
C#CC.	81.60	59.59	13.77	16.09	18.08	19.78	22.48	24.43	27.27	0/12/95	ThmCa	C	3	H	3		0	0	G	1

C*C*C.	81.64	62.53	13.64	16.08	18.14	19.88	22.57	24.51	27.48	0/12/95	ThmCa	C	3	H	3		0	0	G 0
CYC.C*C	103.15	60.71	11.97	14.85	17.24	19.22	22.21	24.28	27.37	0/12/95	ThmCa	C	3	H	3		0	0	G 0
C#CCCL	39.17	68.80	17.26	20.08	22.43	24.39	27.39	29.49	32.62	0/12/95	ThmCa	C	3	H	3	CL	1	0	G 1
C*C.CHOA	36.58	69.22	16.69	19.63	22.08	24.13	27.24	29.42	32.61	0/12/95	ThmCa	C	3	H	3	O	1	0	G 1
C*CC.*O	21.58	68.56	16.97	20.10	22.65	24.73	27.78	29.83	32.83	0/12/95	ThmCa	C	3	H	3	O	1	0	G 1
C*C.CHOB	16.98	66.90	16.25	19.66	22.42	24.66	27.90	30.02	32.99	0/12/95	ThmCa	C	3	H	3	O	1	0	G 1
C*C*CO.	40.49	67.82	16.68	19.70	22.21	24.29	27.44	29.64	32.95	0/12/95	ThmCa	C	3	H	3	O	1	0	G 0
C*C.C*O	38.99	70.23	16.49	19.46	21.97	24.08	27.35	29.63	32.84	0/12/95	ThmCa	C	3	H	3	O	1	0	G 1
C#CCO.	61.80	68.48	16.80	19.43	21.74	23.77	27.05	29.46	32.81	0/12/95	ThmCa	C	3	H	3	O	1	0	G 1
C#CC.OH	44.72	69.49	17.21	19.67	21.77	23.58	26.43	28.49	31.55	0/12/95	ThmCa	C	3	H	3	O	1	0	G 2
C#CCOO	61.51	78.83	19.77	22.47	24.87	26.99	30.47	33.10	36.95	0/12/95	ThmCa	C	3	H	3	O	2	0	G 2
C.#CCOOH	106.01	80.72	22.00	24.76	27.15	29.19	32.40	34.64	37.56	0/12/95	ThmCa	C	3	H	3	O	2	0	G 3
C#CC.OOH	58.91	74.80	20.04	23.09	25.74	28.03	31.65	34.20	37.43	0/12/95	ThmCa	C	3	H	3	O	2	0	G 3
C*C*COO	63.95	79.37	20.46	23.74	26.40	28.56	31.73	33.90	37.34	0/12/95	ThmCa	C	3	H	3	O	2	0	G 1
C.*C*COOH	61.52	79.80	21.86	25.34	28.15	30.41	33.64	35.69	38.41	0/12/95	ThmCa	C	3	H	3	O	2	0	G 2
C.#COOC	129.82	80.68	21.42	24.60	27.29	29.54	32.96	35.22	37.93	0/12/95	ThmCa	C	3	H	3	O	2	0	G 3
C#COOC.	93.62	80.71	23.49	26.88	29.60	31.74	34.74	36.54	38.66	0/12/95	ThmCa	C	3	H	3	O	2	0	G 3
C*CO.CHO	-5.45	74.07	20.17	23.64	26.52	28.88	32.41	34.78	38.07	0/12/95	ThmCa	C	3	H	3	O	2	0	G 1
C.C*OCHO	-23.01	76.83	19.59	22.75	25.46	27.78	31.42	33.99	37.51	0/12/95	ThmCa	C	3	H	3	O	2	0	G 2
C.C*OC*O	-22.18	74.90	18.78	22.49	25.59	28.16	32.01	34.59	37.96	0/12/95	ThmCa	C	3	H	3	O	2	0	G 2
CC*OC.*O	-24.68	73.88	17.69	21.52	24.75	27.45	31.54	34.31	37.84	0/12/95	ThmCa	C	3	H	3	O	2	0	G 2
CYC*C.COO	61.09	71.28	16.35	20.56	24.15	27.19	31.86	35.07	39.20	0/12/95	ThmCa	C	3	H	3	O	2	0	G 0
C.CYC*COO	63.51	67.47	19.27	24.05	27.82	30.74	34.71	37.04	39.82	0/12/95	ThmCa	C	3	H	3	O	2	0	G 1
CCYC*C.OO	81.81	71.09	19.81	23.88	27.17	29.82	33.62	36.04	39.19	0/12/95	ThmCa	C	3	H	3	O	2	0	G 1
CYC*CC.OO	37.67	65.66	15.17	20.08	24.17	27.54	32.54	35.78	39.67	0/12/95	ThmCa	C	3	H	3	O	2	0	G 0
CYC.*CCOO	58.59	71.33	16.74	21.01	24.62	27.65	32.26	35.39	39.38	0/12/95	ThmCa	C	3	H	3	O	2	0	G 0
C.*CYCCOO	83.23	73.37	17.32	21.63	25.22	28.19	32.66	35.64	39.48	0/12/95	ThmCa	C	3	H	3	O	2	0	G 0
C*CYCC.OO	57.63	68.17	15.70	20.38	24.32	27.62	32.59	35.85	39.72	0/12/95	ThmCa	C	3	H	3	O	2	0	G 0
C*C*C	45.90	58.32	14.21	17.25	19.83	22.02	25.42	27.88	31.63		API53	C	3	H	4		0	0	G 0
C#CC	44.28	59.30	13.98	16.66	19.11	21.32	25.03	27.87	31.89	0/12/95	ThmCa	C	3	H	4		0	0	G 1
C*C*C	46.72	58.49	14.12	17.14	19.73	21.95	25.47	28.05	32.01	0/12/95	ThmCa	C	3	H	4		0	0	G 0
CYCC*C	66.25	58.21	12.82	16.30	19.21	21.63	25.36	28.00	31.99	0/12/95	ThmCa	C	3	H	4		0	0	G 0
C*CCHO	-20.32	67.41	17.05	20.86	24.03	26.66	30.63	33.38	37.39	0/12/95	ThmCa	C	3	H	4	O	1	0	G 1
C*C*COH	4.59	68.93	18.07	21.69	24.64	27.04	30.58	33.01	36.75	0/12/95	ThmCa	C	3	H	4	O	1	0	G 1
C#CCOH	9.82	69.94	17.96	20.66	23.14	25.39	29.20	32.15	36.45	0/12/95	ThmCa	C	3	H	4	O	1	0	G 2
C#CCOOH	25.39	78.61	22.95	26.46	29.44	31.96	35.86	38.59	42.34	0/12/95	ThmCa	C	3	H	4	O	2	0	G 3
C*C*COOH	27.83	79.15	22.49	26.64	29.97	32.63	36.42	38.87	42.42	0/12/95	ThmCa	C	3	H	4	O	2	0	G 2
C#COOC	48.20	78.92	23.10	26.75	29.87	32.53	36.67	39.51	43.07	0/12/95	ThmCa	C	3	H	4	O	2	0	G 3
C*COHCHO	-57.41	75.53	21.13	25.00	28.21	30.85	34.82	37.53	41.53	0/12/95	ThmCa	C	3	H	4	O	2	0	G 2
CC*OC*O	-64.50	76.25	19.04	22.99	26.42	29.38	34.10	37.49	42.16	0/12/95	ThmCa	C	3	H	4	O	2	0	G 2
CC*OC*O	-64.50	76.25	19.04	22.99	26.42	29.38	34.10	37.49	42.16	0/12/95	ThmCa	C	3	H	4	O	2	0	G 2
CYC*CCOO	4.17	69.47	16.78	21.81	26.07	29.67	35.19	38.99	44.00	0/12/95	ThmCa	C	3	H	4	O	2	0	G 0
CCYC*COO	27.39	69.23	19.89	24.67	28.58	31.78	36.48	39.58	43.76	0/12/95	ThmCa	C	3	H	4	O	2	0	G 1
C*CYCCOO	24.11	71.98	17.46	22.40	26.58	30.09	35.43	39.06	43.69	0/12/95	ThmCa	C	3	H	4	O	2	0	G 1

C*CCBR	10.80	75.90	18.63	22.69	26.11	29.00	33.48	36.69	41.58	0/12/95	ThmCa	C	3	H	5	BR	1	0	G 1
C.*CC	63.77	65.22	15.24	18.50	21.36	23.86	27.93	31.00	35.78	0/12/95	ThmCa	C	3	H	5		0	0	G 1
C*C.C	61.57	65.64	15.06	18.10	20.83	23.27	27.38	30.58	35.57	0/12/95	ThmCa	C	3	H	5		0	0	G 1
C*CC.	40.75	62.07	14.91	18.66	21.87	24.62	28.97	32.12	36.74	0/12/95	ThmCa	C	3	H	5		0	0	G 1
CC*C.	63.77	65.22	15.24	18.50	21.36	23.86	27.93	31.00	35.78	0/12/95	ThmCa	C	3	H	5		0	0	G 1
CC.*C	61.57	65.64	15.06	18.10	20.83	23.27	27.38	30.58	35.57	0/12/95	ThmCa	C	3	H	5		0	0	G 1
C.C*C	40.75	62.07	14.91	18.66	21.87	24.62	28.97	32.12	36.74	0/12/95	ThmCa	C	3	H	5		0	0	G 1
C*CCCL	-.46	73.33	18.13	22.11	25.51	28.40	32.96	36.29	41.41	0/12/95	ThmCa	C	3	H	5	CL	1	0	G 1
CCC.*O	-7.60	73.87	18.49	21.95	25.01	27.70	32.11	35.46	40.55	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
CC.CHO	-4.70	70.38	18.07	21.89	25.20	28.07	32.66	36.05	41.05	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C.CCHO	4.50	76.16	18.53	21.97	25.02	27.70	32.10	35.43	40.47	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C2.C*O	-9.26	71.13	18.28	22.29	25.77	28.76	33.51	36.94	41.76	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C*CCO.	22.15	73.01	17.55	21.55	25.00	27.96	32.66	36.07	41.10	0/12/95	ThmCa	C	3	H	5	O	1	0	G 1
C*CC.OH	3.69	70.66	17.10	21.05	24.48	27.46	32.23	35.73	40.81	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C.*CCOH	29.29	75.86	18.24	22.01	25.28	28.09	32.56	35.81	40.59	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C*C.COH	24.59	76.33	18.41	22.02	25.17	27.91	32.33	35.59	40.40	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C*CO.C	13.15	71.18	18.08	21.98	25.38	28.32	33.03	36.48	41.50	0/12/95	ThmCa	C	3	H	5	O	1	0	G 1
C*COHC.	-2.71	70.88	18.55	22.58	25.97	28.80	33.15	36.23	40.84	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C.*COHC	20.29	74.03	18.80	22.48	25.65	28.37	32.69	35.85	40.56	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
CC*C.OH	16.92	73.38	19.39	23.09	26.21	28.84	32.91	35.85	40.45	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
CC.*COH	19.42	73.33	19.02	22.64	25.72	28.34	32.48	35.51	40.27	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C.C*COH	-1.38	69.76	18.83	23.21	26.80	29.73	34.08	37.05	41.49	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C.*CCOH	29.29	75.86	18.24	22.01	25.28	28.09	32.56	35.81	40.59	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
C.CYC2O	27.12	70.38	16.89	21.51	25.35	28.54	33.38	36.74	41.67	0/12/95	ThmCa	C	3	H	5	O	1	0	G 1
CCYC.CO	20.02	68.12	17.54	22.13	25.92	29.05	33.75	36.99	41.80	0/12/95	ThmCa	C	3	H	5	O	1	0	G 1
CYCC.CO	27.99	69.00	13.74	18.68	22.91	26.49	32.06	35.96	41.47	0/12/95	ThmCa	C	3	H	5	O	1	0	G 0
CYC.CCO	23.54	65.71	15.17	20.17	24.34	27.82	33.10	36.77	42.15	0/12/95	ThmCa	C	3	H	5	O	1	0	G 0
C*COC.	18.86	73.90	20.57	24.75	28.18	31.01	35.22	38.09	42.28	0/12/95	ThmCa	C	3	H	5	O	1	0	G 2
CO.CCHO	-28.34	81.93	21.46	25.54	29.08	32.13	37.00	40.56	45.77	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
C*CCOO.	20.86	83.71	21.46	25.39	28.84	31.88	36.85	40.60	46.26	0/12/95	ThmCa	C	3	H	5	O	2	0	G 2
C*CC.OOH	18.26	79.68	21.94	26.45	30.31	33.60	38.75	42.41	47.51	0/12/95	ThmCa	C	3	H	5	O	2	0	G 2
C.*CCOOH	43.17	85.32	23.97	28.04	31.47	34.35	38.78	41.90	46.48	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
C*COOC.	40.20	84.00	24.11	28.67	32.46	35.60	40.32	43.56	48.11	0/12/95	ThmCa	C	3	H	5	O	2	0	G 2
C*C.COOH	41.66	85.30	23.21	27.11	30.51	33.45	38.17	41.62	46.56	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
C.*COOHC	43.53	84.25	23.31	27.32	30.71	33.57	38.00	41.14	45.74	0/12/95	ThmCa	C	3	H	5	O	2	0	G 4
C*COOHC.	20.53	81.10	22.96	27.50	31.26	34.36	39.01	42.19	46.77	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
C*COO.C	20.53	85.26	21.50	25.25	28.54	31.42	36.13	39.69	45.18	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
CC*C.OOH	40.16	83.60	23.86	28.05	31.53	34.41	38.76	41.75	46.06	0/12/95	ThmCa	C	3	H	5	O	2	0	G 4
CC.*COOH	42.66	83.55	23.51	27.64	31.09	33.96	38.34	41.43	46.07	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
C.C*COOH	21.86	79.98	23.25	28.16	32.12	35.30	39.89	42.89	47.13	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
CC*COO.	21.86	81.96	21.74	25.91	29.43	32.38	37.00	40.37	45.72	0/12/95	ThmCa	C	3	H	5	O	2	0	G 2
CCO.C*O	-31.24	79.66	21.07	25.78	29.73	33.03	38.09	41.63	46.78	0/12/95	ThmCa	C	3	H	5	O	2	0	G 2
C.COHC*O	-34.20	85.91	21.29	25.72	29.44	32.55	37.33	40.71	45.74	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3
CCOHC.*O	-46.30	82.24	21.22	25.67	29.41	32.53	37.33	40.72	45.74	0/12/95	ThmCa	C	3	H	5	O	2	0	G 3

C.C*OCOH	-43.58	80.58	21.94	25.85	29.25	32.18	36.88	40.37	45.60	0/12/95	ThmCa	C	3	H	5	O	2	0	G	3
CC*OC.OH	-46.08	79.56	20.89	24.85	28.34	31.39	36.35	40.06	45.53	0/12/95	ThmCa	C	3	H	5	O	2	0	G	3
C.*CCOOH	44.86	84.53	23.30	27.48	31.03	34.03	38.72	42.13	47.36	0/12/95	ThmCa	C	3	H	5	O	2	0	G	1
CYC.CCOO	16.71	74.38	19.56	25.32	30.14	34.14	40.16	44.20	49.50	0/12/95	ThmCa	C	3	H	5	O	2	0	G	0
CYCC.COO	19.16	75.00	17.96	23.87	28.87	33.05	39.41	43.70	49.19	0/12/95	ThmCa	C	3	H	5	O	2	0	G	0
C.CYCCOO	37.41	75.75	19.31	25.14	29.98	33.96	39.87	43.80	48.90	0/12/95	ThmCa	C	3	H	5	O	2	0	G	1
CCYC.COO	29.91	78.32	20.20	25.20	29.49	33.14	38.86	42.88	48.32	0/12/95	ThmCa	C	3	H	5	O	2	0	G	1
CCYCC.OO	32.31	76.16	20.19	25.65	30.23	34.04	39.81	43.71	48.83	0/12/95	ThmCa	C	3	H	5	O	2	0	G	1
CC.QC*O	-25.73	90.54	26.71	31.77	35.92	39.31	44.31	47.63	52.18	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CC*OCQ.	-35.21	91.17	25.10	28.92	32.39	35.52	40.81	44.90	50.98	0/12/95	ThmCa	C	3	H	5	O	3	0	G	3
C.C*OCQ	-29.01	89.60	26.77	31.29	35.15	38.42	43.50	47.07	51.96	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CC*OC.OOH	-34.01	90.44	25.43	29.73	33.50	36.79	42.09	45.96	51.32	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CCQ.C*O	-31.53	89.61	24.82	29.62	33.68	37.10	42.39	46.14	51.63	0/12/95	ThmCa	C	3	H	5	O	3	0	G	3
C.CQC*O	-18.63	94.18	25.99	31.10	35.32	38.78	43.93	47.38	52.07	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CCQC.*O	-30.73	90.51	25.90	31.04	35.27	38.75	43.92	47.38	52.08	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CQC.C*O	-25.93	90.04	25.99	30.78	34.81	38.19	43.37	46.94	51.85	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CQCC.*O	-28.83	93.53	26.67	30.97	34.66	37.81	42.79	46.37	51.46	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
C.QCC*O	-19.33	93.52	27.92	32.29	35.99	39.12	43.96	47.36	52.07	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
CQ.CC*O	-29.63	92.63	24.20	28.29	31.92	35.14	40.45	44.46	50.34	0/12/95	ThmCa	C	3	H	5	O	3	0	G	4
C*OCQCO.	-52.67	98.67	29.62	34.89	39.28	42.92	48.40	52.15	57.34	0/12/95	ThmCa	C	3	H	5	O	4	0	G	4
C*OCQ.COH	-68.55	100.35	28.47	33.21	37.26	40.70	46.12	50.04	55.90	0/12/95	ThmCa	C	3	H	5	O	4	0	G	4
C.*OCQCOH	-67.75	101.25	29.44	34.47	38.67	42.18	47.51	51.23	56.59	0/12/95	ThmCa	C	3	H	5	O	4	0	G	4
CYCC.OOCQ	-7.89	93.07	27.90	34.94	40.61	45.15	51.56	55.54	60.43	0/12/95	ThmCa	C	3	H	5	O	4	0	G	2
CYCCOOCQ.	-15.69	89.47	25.84	32.89	38.65	43.30	50.06	54.42	60.10	0/12/95	ThmCa	C	3	H	5	O	4	0	G	1
CYC.COOCQ	-5.44	92.32	27.15	34.27	40.03	44.65	51.21	55.29	60.31	0/12/95	ThmCa	C	3	H	5	O	4	0	G	2
C*CC	4.65	63.83	15.45	19.34	22.77	25.79	30.74	34.50	40.33	0/12/95	ThmCa	C	3	H	6		0	0	G	1
CC*C	4.65	63.83	15.45	19.34	22.77	25.79	30.74	34.50	40.33	0/12/95	ThmCa	C	3	H	6		0	0	G	1
CCCHO	-44.50	72.75	19.32	23.36	26.93	30.08	35.25	39.18	45.16	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C2C*O	-51.56	70.11	17.90	22.15	25.95	29.33	34.92	39.16	45.43	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C.CO.C	35.46	76.50	19.73	24.23	28.05	31.30	36.39	40.09	45.74	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
CC.O.C	28.36	73.86	20.87	25.22	28.90	32.02	36.88	40.42	45.90	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
CC.CO.	37.18	79.52	18.28	22.60	26.40	29.72	35.11	39.10	44.95	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C2.CHO.	35.46	75.69	19.75	24.19	28.00	31.27	36.43	40.18	45.64	0/12/95	ThmCa	C	3	H	6	O	1	0	G	3
CCCHO	-44.50	72.75	19.32	23.36	26.93	30.08	35.25	39.18	45.16	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C*CCOH	-29.81	74.47	18.54	22.86	26.62	29.88	35.10	38.96	44.76	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C*COHC	-38.81	72.64	18.99	23.33	27.10	30.37	35.60	39.44	45.17	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
CC*COH	-37.48	71.52	19.40	23.87	27.65	30.84	35.82	39.43	45.03	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C*COC	-24.54	53.24	18.87	22.95	26.45	29.46	34.30	37.98	44.10	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
C*COHC	-38.81	72.64	18.99	23.33	27.10	30.37	35.60	39.44	45.17	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
CCYC2O	-21.88	66.97	17.65	22.88	27.26	30.92	36.53	40.48	46.32	0/12/95	ThmCa	C	3	H	6	O	1	0	G	1
CYCCCO	-18.36	64.56	15.31	20.93	25.69	29.69	35.89	40.26	46.64	0/12/95	ThmCa	C	3	H	6	O	1	0	G	0
C*COC	-25.54	71.76	20.03	24.92	29.02	32.45	37.69	41.37	46.72	0/12/95	ThmCa	C	3	H	6	O	1	0	G	2
COHCCHO	-80.32	83.39	22.38	26.81	30.66	34.00	39.37	43.37	49.47	0/12/95	ThmCa	C	3	H	6	O	2	0	G	3
C*CCOOH	-15.24	83.49	23.48	28.29	32.42	35.96	41.54	45.56	51.35	0/12/95	ThmCa	C	3	H	6	O	2	0	G	3

C*COOC	-7.20	82.44	23.49	28.64	32.99	36.65	42.30	46.30	52.15	0/12/95	ThmCa	C	3	H	6	O	2	0	G	2
C*COOHC	-15.57	82.86	23.52	28.15	32.11	35.49	40.80	44.64	50.25	0/12/95	ThmCa	C	3	H	6	O	2	0	G	4
CC*COOH	-14.24	81.74	23.85	28.82	32.97	36.42	41.68	45.33	50.63	0/12/95	ThmCa	C	3	H	6	O	2	0	G	4
CCOHC*O	-83.22	81.12	22.07	27.10	31.36	34.93	40.48	44.44	50.38	0/12/95	ThmCa	C	3	H	6	O	2	0	G	3
C*CMOOH	-15.57	82.86	23.48	28.14	32.11	35.49	40.81	44.64	50.37	0/12/95	ThmCa	C	3	H	6	O	2	0	G	3
CC*OCO.	-33.92	80.47	21.13	25.14	28.72	31.90	37.21	41.34	48.05	0/12/95	ThmCa	C	3	H	6	O	2	0	G	2
C(OH)CCHO	-80.32	83.39	22.38	26.81	30.66	34.00	39.37	43.37	49.47	0/12/95	ThmCa	C	3	H	6	O	2	0	G	3
CYC3O2	-27.19	70.56	19.50	26.20	31.79	36.41	43.36	48.02	54.19	0/12/95	ThmCa	C	3	H	6	O	2	0	G	0
CCYCCOO	-11.59	72.34	20.12	26.54	31.90	36.35	43.04	47.56	53.58	0/12/95	ThmCa	C	3	H	6	O	2	0	G	1
CC*OCQ	-71.33	90.95	27.11	31.83	36.00	39.64	45.55	49.92	56.12	0/12/95	ThmCa	C	3	H	6	O	3	0	G	4
CCQC*O	-67.65	89.39	26.83	32.53	37.26	41.19	47.10	51.14	56.75	0/12/95	ThmCa	C	3	H	6	O	3	0	G	4
CQCC*O	-65.48	92.23	26.60	31.75	36.17	39.96	45.94	50.23	56.26	0/12/95	ThmCa	C	3	H	6	O	3	0	G	4
C*OCQCOH	-104.65	100.13	30.35	36.08	40.88	44.90	51.05	55.34	61.51	0/12/95	ThmCa	C	3	H	6	O	4	0	G	4
CYCCOOCQ	-52.16	89.65	26.79	34.60	41.01	46.23	53.84	58.75	64.91	0/12/95	ThmCa	C	3	H	6	O	4	0	G	2
CCC.	23.67	69.31	17.09	21.37	25.15	28.48	33.97	38.15	44.58	0/12/95	ThmCa	C	3	H	7		0	0	G	2
CC.C	21.02	68.96	16.22	20.42	24.19	27.56	33.19	37.53	44.14	0/12/95	ThmCa	C	3	H	7		0	0	G	2
CCCO.	-9.17	75.08	19.96	24.90	29.18	32.89	38.85	43.27	49.98	0/12/95	ThmCa	C	3	H	7	O	1	0	G	2
C2.COH	-16.50	77.96	20.73	25.55	29.66	33.18	38.77	42.89	49.33	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
C2C.OH	-23.60	73.95	21.88	26.54	30.51	33.89	39.25	43.22	49.49	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
C2CO.	-13.54	73.08	20.56	25.62	29.95	33.66	39.52	43.82	50.37	0/12/95	ThmCa	C	3	H	7	O	1	0	G	2
C.CCOH	-12.13	79.95	20.15	24.82	28.87	32.39	38.07	42.33	48.92	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
CC.COH	-14.78	80.98	19.28	23.92	28.03	31.64	37.56	41.99	48.63	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
CCC.OH	-19.23	77.32	21.26	25.82	29.76	33.15	38.61	42.70	49.14	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
C.OCC	-7.20	77.10	21.24	25.95	30.00	33.50	39.09	43.25	49.67	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
COCC.	-2.60	78.37	19.94	24.74	28.93	32.55	38.41	42.79	49.47	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
COC.C	-9.70	76.10	20.59	25.37	29.50	33.07	38.79	43.04	49.59	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
CCOHC.	-16.50	77.96	20.73	25.55	29.66	33.18	38.77	42.89	49.33	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
CC.OHC	-23.60	73.95	21.88	26.54	30.51	33.89	39.25	43.22	49.49	0/12/95	ThmCa	C	3	H	7	O	1	0	G	3
CCO.C	-13.54	73.08	20.56	25.62	29.95	33.66	39.52	43.82	50.37	0/12/95	ThmCa	C	3	H	7	O	1	0	G	2
CC.COOH	-.21	90.00	24.13	29.31	33.81	37.69	43.87	48.35	54.77	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
CCC.OOH	-2.66	89.38	25.94	30.83	35.08	38.75	44.66	49.01	55.40	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
CCCOO	-10.46	85.78	23.78	28.76	33.13	36.94	43.17	47.86	55.01	0/12/95	ThmCa	C	3	H	7	O	2	0	G	3
C.CCOOH	2.44	88.97	25.04	30.28	34.78	38.62	44.67	49.05	55.43	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
C2COO	-13.83	83.03	24.31	29.47	33.90	37.72	43.81	48.31	55.21	0/12/95	ThmCa	C	3	H	7	O	2	0	G	3
C2C.OOH	-8.43	88.79	26.46	31.13	35.21	38.77	44.55	48.90	55.54	0/12/95	ThmCa	C	3	H	7	O	2	0	G	3
C2.COOH	-.93	87.61	25.53	30.98	35.56	39.41	45.35	49.59	55.95	0/12/95	ThmCa	C	3	H	7	O	2	0	G	3
CCOOC.	3.94	88.72	26.11	31.20	35.67	39.57	45.83	50.37	56.53	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
C.COOC	6.54	90.22	24.24	29.46	34.07	38.11	44.65	49.44	56.00	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
CC.OOC	3.44	87.74	25.44	30.22	34.52	38.34	44.65	49.36	55.91	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
C.COOHC	-.93	87.61	25.54	30.98	35.57	39.42	45.36	49.56	55.67	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
CC.OOHC	-8.43	88.79	26.49	31.11	35.16	38.69	44.43	48.72	55.16	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
COCOC.	-37.43	85.40	25.06	29.67	33.76	37.37	43.34	47.87	54.67	0/12/95	ThmCa	C	3	H	7	O	2	0	G	4
COC.OC	-39.93	83.03	24.50	29.09	33.21	36.87	42.97	47.65	54.63	10/12/95		C	3	H	7	O	2	0	G	4
C.CQCOH	-36.73	98.25	28.64	34.45	39.29	43.33	49.49	53.81	60.17	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5

CCQCO.	-33.77	92.00	28.40	34.51	39.60	43.83	50.26	54.74	61.21	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
CCQ.COH	-49.63	93.68	27.40	32.93	37.64	41.64	47.95	52.56	59.70	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
CCQC.OH	-43.83	94.24	29.94	35.58	40.28	44.17	50.09	54.22	60.37	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
CC.QCOH	-44.23	99.44	29.66	34.55	38.79	42.47	48.41	52.88	59.83	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
C.COHCQ	-37.73	99.00	28.64	34.45	39.29	43.33	49.49	53.81	60.17	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
CCO.CQ	-34.77	92.75	28.40	34.51	39.60	43.83	50.26	54.74	61.21	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
CCOHCQ.	-50.63	94.43	27.40	32.93	37.64	41.64	47.95	52.56	59.70	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
CCOHC.Q	-42.83	98.03	29.76	35.17	39.74	43.60	49.59	53.87	60.21	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
CQCCO.	-30.40	94.74	27.94	33.81	38.80	43.01	49.55	54.20	60.94	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
CQ.CCOH	-46.26	96.42	26.93	32.22	36.81	40.79	47.21	52.02	59.44	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
C.QCCOH	-38.46	100.02	29.01	34.24	38.73	42.59	48.72	53.20	59.86	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
CQC.COH	-36.01	100.64	27.21	32.76	37.53	41.61	48.02	52.62	59.21	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
CQCC.OH	-40.46	96.98	29.27	34.72	39.33	43.22	49.27	53.60	60.06	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
COCOCOH	-124.88	93.52	27.79	33.49	38.53	42.95	50.09	55.23	61.80	0/12/95	ThmCa	C	3	H	7	O	3	0	G	5
COCOCO.	-72.92	92.06	27.19	32.16	36.65	40.66	47.37	52.50	60.03	0/12/95	ThmCa	C	3	H	7	O	3	0	G	4
CCQ.CQ	-34.06	102.75	32.17	38.32	43.50	47.84	54.50	59.19	65.97	0/12/95	ThmCa	C	3	H	7	O	4	0	G	5
CCQCQ.	-34.06	102.75	32.17	38.32	43.50	47.84	54.50	59.19	65.97	0/12/95	ThmCa	C	3	H	7	O	4	0	G	5
C.CQCQ	-21.16	107.32	33.39	39.81	45.11	49.48	56.00	60.39	66.40	0/12/95	ThmCa	C	3	H	7	O	4	0	G	6
CC.QCQ	-28.66	108.51	34.42	39.98	44.72	48.75	55.04	59.52	65.85	0/12/95	ThmCa	C	3	H	7	O	4	0	G	6
CCQC.Q	-26.26	106.35	33.14	39.06	44.07	48.29	54.79	59.36	65.77	0/12/95	ThmCa	C	3	H	7	O	4	0	G	6
QCC.CQ	-21.44	109.66	32.18	38.23	43.39	47.76	54.55	59.32	65.86	0/12/95	ThmCa	C	3	H	7	O	4	0	G	6
Q.CCCQ	-31.69	105.44	31.69	37.65	42.74	47.06	53.84	58.70	65.74	0/12/95	ThmCa	C	3	H	7	O	4	0	G	5
CQCCQ.	-31.69	105.44	31.69	37.65	42.74	47.06	53.84	58.70	65.74	0/12/95	ThmCa	C	3	H	7	O	4	0	G	5
QCCC.Q	-21.89	108.34	32.79	38.50	43.41	47.61	54.21	58.94	65.57	0/12/95	ThmCa	C	3	H	7	O	4	0	G	6
CCC	-25.33	64.52	17.87	22.76	27.08	30.88	37.14	41.90	49.24	0/12/95	ThmCa	C	3	H	8		0	0	G	2
C2COH	-65.52	74.54	21.54	26.92	31.56	35.54	41.89	46.61	53.96	0/12/95	ThmCa	C	3	H	8	O	1	0	G	3
CCCOH	-61.15	76.54	20.93	26.20	30.78	34.77	41.22	46.06	53.54	0/12/95	ThmCa	C	3	H	8	O	1	0	G	3
COCC	-51.60	74.95	20.75	26.12	30.82	34.90	41.53	46.50	54.08	0/12/95	ThmCa	C	3	H	8	O	1	0	G	3
CCOHC	-65.52	74.54	21.54	26.92	31.56	35.54	41.89	46.61	53.96	0/12/95	ThmCa	C	3	H	8	O	1	0	G	3
CCOC	-51.60	74.95	20.75	26.12	30.82	34.90	41.53	46.50	54.08	0/12/95	ThmCa	C	3	H	8	O	1	0	G	3
CCCOOH	-46.56	85.56	25.79	31.66	36.70	41.02	47.85	52.81	60.11	0/12/95	ThmCa	C	3	H	8	O	2	0	G	4
C2COOH	-49.93	82.81	26.30	32.36	37.49	41.81	48.52	53.31	60.34	0/12/95	ThmCa	C	3	H	8	O	2	0	G	4
CCOOC	-42.46	85.42	25.22	31.14	36.31	40.81	48.03	53.30	60.71	0/12/95	ThmCa	C	3	H	8	O	2	0	G	4
CCOOHC	-49.93	82.81	26.30	32.36	37.49	41.81	48.52	53.31	60.34	0/12/95	ThmCa	C	3	H	8	O	2	0	G	4
COCOC	-81.85	81.88	24.55	29.84	34.58	38.79	45.77	51.08	59.00	0/12/95	ThmCa	C	3	H	8	O	2	0	G	4
CCQCOH	-85.75	93.46	29.36	35.81	41.22	45.74	52.67	57.58	64.84	0/12/95	ThmCa	C	3	H	8	O	3	0	G	5
CCOHCQ	-86.75	94.21	29.36	35.81	41.22	45.74	52.67	57.58	64.84	0/12/95	ThmCa	C	3	H	8	O	3	0	G	5
CQCCOH	-82.38	96.20	28.89	35.12	40.41	44.91	51.94	57.02	64.56	0/12/95	ThmCa	C	3	H	8	O	3	0	G	5
CCQCQ	-70.18	102.53	34.15	41.20	47.06	51.90	59.19	64.17	71.09	0/12/95	ThmCa	C	3	H	8	O	4	0	G	6
QCCCQ	-65.81	104.52	33.73	40.56	46.31	51.13	58.53	63.67	70.85	0/12/95	ThmCa	C	3	H	8	O	4	0	G	6
C#CC#C.	185.70	63.29	16.58	17.96	19.11	20.05	21.44	22.36	23.55	0/12/95	ThmCa	C	4	H	1		0	0	G	1
C#CC#C	105.08	59.80	17.64	19.83	21.61	23.04	25.13	26.50	28.46	0/12/95	ThmCa	C	4	H	2		0	0	G	1
C#CC*C.	127.29	68.18	17.25	20.59	23.28	25.44	28.53	30.52	33.28	0/12/95	ThmCa	C	4	H	3		0	0	G	1
C#CC.*C	117.59	67.50	18.28	21.05	23.42	25.44	28.58	30.76	33.61	0/12/95	ThmCa	C	4	H	3		0	0	G	1

C#CC*C	68.19	66.79	17.49	21.46	24.72	27.40	31.37	34.05	37.82	0/12/95	ThmCa	C	4	H	4		0	0	G	1
C.*CC*C.	144.30	69.40	18.87	22.59	25.57	27.96	31.43	33.76	37.42	0/12/95	ThmCa	C	4	H	4		0	0	G	1
C*C.C*C.	142.10	71.20	18.72	22.20	25.05	27.39	30.90	33.35	37.20	0/12/95	ThmCa	C	4	H	4		0	0	G	1
C*C*C*C	80.94	64.49	17.97	21.50	24.47	26.97	30.82	33.57	37.72	0/12/95	ThmCa	C	4	H	4		0	0	G	0
C#CC*C	68.19	66.79	17.49	21.46	24.72	27.40	31.37	34.05	37.82	0/12/95	ThmCa	C	4	H	4		0	0	G	1
C*CC.*C	75.50	68.71	19.34	23.41	26.87	29.79	34.37	37.65	42.49	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C*C*CC.	74.97	68.07	18.81	23.02	26.60	29.62	34.31	37.64	42.49	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C#CCC.	88.57	73.01	18.65	22.05	25.17	28.00	32.80	36.47	41.64	0/12/95	ThmCa	C	4	H	5		0	0	G	2
C#CC.C	74.47	69.15	18.91	22.66	25.89	28.66	33.09	36.36	41.42	0/12/95	ThmCa	C	4	H	5		0	0	G	1
CC#CC.	72.02	69.47	17.84	21.46	24.74	27.68	32.63	36.41	41.92	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C*C*CCJ	74.97	66.70	18.81	23.02	26.60	29.62	34.31	37.64	42.49	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C*C.C*C	75.50	68.71	19.34	23.41	26.87	29.79	34.37	37.65	42.49	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C.*C*CC	73.77	71.12	18.83	22.59	25.83	28.63	33.10	36.40	41.43	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C*C*C.C	73.77	71.12	18.83	22.59	25.83	28.63	33.10	36.40	41.43	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C*CC*C.	85.20	69.39	19.09	23.42	26.97	29.88	34.23	37.26	41.95	0/12/95	ThmCa	C	4	H	5		0	0	G	1
C*CC.*C	75.50	68.71	19.34	23.41	26.87	29.79	34.37	37.65	42.49	0/12/95	ThmCa	C	4	H	5		0	0	G	1
CC*CC.*O	2.71	74.61	22.08	26.47	30.15	33.23	37.99	41.42	46.79	0/12/95	ThmCa	C	4	H	5	O	1	0	G	1
C.C*CCHO	7.91	74.24	21.69	26.74	30.90	34.31	39.41	42.89	47.95	0/12/95	ThmCa	C	4	H	5	O	1	0	G	1
C*C*CC	38.85	69.83	19.29	23.66	27.46	30.75	36.05	39.99	45.99	0/12/95	ThmCa	C	4	H	6		0	0	G	1
C*CC*C	26.08	66.62	19.26	24.23	28.36	31.79	37.03	40.74	46.47	0/12/95	ThmCa	C	4	H	6		0	0	G	1
C#CCC	39.55	69.60	19.60	23.59	27.21	30.47	35.94	40.13	46.21	0/12/95	ThmCa	C	4	H	6		0	0	G	2
CC#CC	34.70	67.80	18.49	22.55	26.29	29.69	35.49	39.99	46.44	0/12/95	ThmCa	C	4	H	6		0	0	G	2
C*C*CC	38.85	69.83	19.29	23.66	27.46	30.75	36.05	39.99	45.99	0/12/95	ThmCa	C	4	H	6		0	0	G	1
C*C*CC	38.85	69.83	19.29	23.66	27.46	30.75	36.05	39.99	45.99	0/12/95	ThmCa	C	4	H	6		0	0	G	1
C*CC*C	26.08	66.62	19.26	24.23	28.36	31.79	37.03	40.74	46.47	0/12/95	ThmCa	C	4	H	6		0	0	G	1
CC*CCHO	-28.19	76.00	22.28	27.42	31.76	35.44	41.17	45.30	51.58	0/12/95	ThmCa	C	4	H	6	O	1	0	G	1
C*CCCHO	-18.54	80.70	21.00	26.13	30.53	34.29	40.23	44.55	50.92	0/12/95	ThmCa	C	4	H	6	O	1	0	G	2
C*CC2*O	-27.34	74.66	23.19	28.32	32.63	36.22	41.74	45.64	51.47	0/12/95	ThmCa	C	4	H	6	O	1	0	G	2
C2C*C*O	-28.06	73.99	24.28	28.96	32.92	36.27	41.51	45.31	51.19	0/12/95	ThmCa	C	4	H	6	O	1	0	G	2
C2C*C*O	-28.06	73.99	24.28	28.96	32.92	36.27	41.51	45.31	51.19	0/12/95	ThmCa	C	4	H	6	O	1	0	G	2
C*CICC*O	-27.34	74.66	23.19	28.32	32.63	36.22	41.74	45.64	51.47	0/12/95	ThmCa	C	4	H	6	O	1	0	G	2
C*CC*OC	-30.40	76.84	21.23	26.38	30.81	34.59	40.57	44.90	51.26	0/12/95	ThmCa	C	4	H	6	O	1	0	G	2
C*CC2.	32.30	69.63	21.01	26.08	30.44	34.18	40.14	44.50	51.02	0/12/95	ThmCa	C	4	H	7		0	0	G	2
C2.C*C	32.30	69.63	21.01	26.08	30.44	34.18	40.14	44.50	51.02	0/12/95	ThmCa	C	4	H	7		0	0	G	2
C*CC.C	33.39	69.82	19.05	24.39	28.99	32.94	39.23	43.85	50.82	0/12/95	ThmCa	C	4	H	7		0	0	G	1
CC*CC.	32.88	70.66	20.05	25.19	29.64	33.47	39.59	44.09	50.77	0/12/95	ThmCa	C	4	H	7		0	0	G	2
CC.*CC	53.68	74.22	20.24	24.61	28.54	32.06	37.95	42.51	49.53	0/12/95	ThmCa	C	4	H	7		0	0	G	2
C*C.CC	56.81	75.44	20.20	24.95	29.11	32.73	38.63	43.07	49.88	0/12/95	ThmCa	C	4	H	7		0	0	G	2
C*CCC.	48.89	77.04	19.80	24.80	29.12	32.85	38.82	43.24	49.98	0/12/95	ThmCa	C	4	H	7		0	0	G	2
CC.*CC	53.68	74.22	20.24	24.61	28.54	32.06	37.95	42.51	49.53	0/12/95	ThmCa	C	4	H	7		0	0	G	2
C.*CCC	59.01	75.02	20.38	25.37	29.65	33.33	39.18	43.49	50.11	0/12/95	ThmCa	C	4	H	7		0	0	G	2
C2C*C.	55.30	72.77	21.36	25.93	29.92	33.41	39.10	43.40	50.07	0/12/95	ThmCa	C	4	H	7		0	0	G	2
CC.*CC	53.68	74.22	20.24	24.61	28.54	32.06	37.95	42.51	49.53	0/12/95	ThmCa	C	4	H	7		0	0	G	2
CC*CCO.	14.28	81.60	22.78	28.07	32.69	36.71	43.18	47.96	55.05	0/12/95	ThmCa	C	4	H	7	O	1	0	G	2

C*CCCO.	16.05	82.81	22.64	28.31	33.15	37.26	43.70	48.36	55.36	0/12/95	ThmCa	C	4 H	7 O	1	0 G 2
C*CCO.C	12.71	80.34	23.16	29.51	34.83	39.26	45.97	50.53	56.76	0/12/95	ThmCa	C	4 H	7 O	1	0 G 2
C*CC2O.	13.70	80.57	23.69	28.94	33.50	37.44	43.74	48.38	55.32	0/12/95	ThmCa	C	4 H	7 O	1	0 G 2
C2CC.*O	-14.30	80.79	22.68	28.19	32.94	37.02	43.49	48.23	55.31	0/12/95	ThmCa	C	4 H	7 O	1	0 G 2
C2C.C*O	-13.50	77.96	24.09	29.28	33.77	37.63	43.84	48.48	55.83	0/12/95	ThmCa	C	4 H	7 O	1	0 G 0
C2C*CO.	6.03	77.61	24.53	29.98	34.60	38.51	44.62	49.02	55.73	0/12/95	ThmCa	C	4 H	7 O	1	0 G 2
C*CC2O.	13.70	80.57	23.69	28.94	33.50	37.44	43.74	48.38	55.32	0/12/95	ThmCa	C	4 H	7 O	1	0 G 2
C*C(C.)OC	1.36	79.71	24.38	30.14	35.03	39.17	45.61	50.17	56.66	0/12/95	ThmCa	C	4 H	7 O	1	0 G 3
C*C(C)OC.	9.66	83.61	25.56	30.66	35.07	38.87	44.94	49.42	56.06	0/12/95	ThmCa	C	4 H	7 O	1	0 G 3
C*CCOOC.	35.97	95.25	28.78	34.78	39.83	44.06	50.48	54.84	60.78	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
C*CCCOO	14.76	93.51	26.52	32.18	37.07	41.27	47.98	52.93	60.46	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C.*CCCOOH	37.76	94.68	28.36	34.28	39.26	43.44	49.88	54.42	61.03	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
C*CC.COOH	12.16	89.48	26.97	33.27	38.59	43.06	49.94	54.79	61.74	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CCC.OOH	22.56	97.11	28.63	34.23	39.02	43.10	49.50	54.12	60.88	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
C*CC2OO.	11.72	91.71	28.18	33.31	37.75	41.61	47.84	52.55	59.98	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CIC.CQ	11.72	89.73	29.68	35.57	40.46	44.53	50.72	55.06	61.57	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CICC.Q	9.12	87.68	28.67	34.37	39.23	43.35	49.81	54.45	61.29	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C.*CC2OOH	34.72	92.88	30.08	35.51	40.12	44.02	50.09	54.45	60.87	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
CC*CC.Q	9.70	88.71	27.79	33.47	38.34	42.50	49.09	53.88	60.97	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
CC*CCOO.	12.30	92.74	27.26	32.39	36.88	40.80	47.20	52.07	59.72	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CCOO.C	12.42	90.29	27.12	33.09	38.13	42.38	48.96	53.69	60.87	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CCQC.	25.32	93.48	28.35	34.61	39.79	44.07	50.50	54.93	61.32	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
C.*CCQC	35.42	91.46	28.97	35.19	40.32	44.54	50.86	55.18	61.45	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
C*CC.QC	7.62	86.38	27.29	33.68	39.03	43.51	50.35	55.12	61.93	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C.C*CCQ	12.30	90.76	28.77	34.64	39.57	43.70	50.07	54.58	61.31	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
CC*CCOO	12.30	92.74	27.26	32.39	36.88	40.80	47.20	52.07	59.72	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
CC.*CCQ	33.10	94.33	28.93	34.11	38.63	42.55	48.86	53.53	60.43	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
CC*C.CQ	33.10	94.33	28.93	34.11	38.63	42.55	48.86	53.53	60.43	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
CC*OCCO.	-40.72	90.27	26.21	31.83	36.71	40.94	47.72	52.74	60.27	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
CC*OC.COH	-52.88	89.36	25.91	31.66	36.60	40.84	47.54	52.43	59.72	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
C.C*OCCOH	-50.38	89.00	26.96	32.65	37.50	41.61	48.05	52.72	59.79	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
CC*OCC.OH	-50.78	92.51	27.52	32.75	37.27	41.18	47.46	52.14	59.36	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
O*CCC2O.	-35.04	88.86	25.67	31.80	37.02	41.46	48.39	53.35	60.60	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
O*CCM.COH	-38.00	93.73	25.86	31.71	36.70	40.95	47.61	52.41	59.52	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
O*C.CC2OH	-50.10	91.44	25.80	31.66	36.66	40.92	47.60	52.41	59.53	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
CCO.CCHO	-37.64	89.36	27.43	33.20	38.09	42.24	48.72	53.40	60.43	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
CCOHCC.*O	-52.70	91.94	27.57	33.06	37.74	41.71	47.94	52.46	59.36	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
O*C.CCOHC	-52.70	91.94	27.57	33.06	37.74	41.71	47.94	52.46	59.36	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
O*CC.COHC	-49.80	88.45	27.19	33.04	37.97	42.12	48.55	53.15	60.04	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
O*CCCO.C	-37.64	89.36	27.43	33.20	38.09	42.24	48.72	53.40	60.43	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
O*CCCOHC.	-40.60	94.23	27.62	33.11	37.78	41.74	47.95	52.45	59.33	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4
CCICO.C*O	-35.04	88.86	25.67	31.80	37.02	41.46	48.39	53.35	60.60	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CICOOC.	30.00	95.44	29.07	34.57	39.33	43.45	50.03	54.85	61.86	0/12/95	ThmCa	C	4 H	7 O	2	0 G 3
C*CC2.OOH	9.12	88.48	28.66	34.36	39.22	43.35	49.79	54.38	61.00	0/12/95	ThmCa	C	4 H	7 O	2	0 G 4

C*CC2.Q	9.12	87.68	28.72	34.41	39.25	43.37	49.82	54.49	61.57	0/12/95	ThmCa	C	4	H	7	O	2	0 G 2
C*CCOO.C	12.42	90.29	27.09	33.08	38.14	42.39	48.97	53.66	60.58	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
C.*CCQC	35.42	91.46	28.97	35.19	40.32	44.54	50.86	55.18	61.45	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
C*CC.QC	7.62	86.38	27.26	33.63	39.00	43.48	50.34	55.09	61.66	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
CC*OCCO.	-40.72	90.27	26.21	31.83	36.71	40.94	47.72	52.74	60.27	0/12/95	ThmCa	C	4	H	7	O	2	0 G 3
CC*OCC.OH	-48.28	92.66	28.54	33.90	38.44	42.30	48.36	52.80	59.71	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
C.*CCCOOH	38.76	94.33	28.36	34.28	39.26	43.44	49.88	54.42	61.03	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
C.*CC2OOH	36.41	92.09	29.52	34.95	39.60	43.57	49.87	54.51	61.64	0/12/95	ThmCa	C	4	H	7	O	2	0 G 2
C.*CCQC	35.42	91.86	28.90	35.18	40.35	44.59	50.89	55.15	61.15	0/12/95	ThmCa	C	4	H	7	O	2	0 G 5
CC.*CCQ	34.79	93.54	28.43	33.65	38.25	42.26	48.79	53.63	60.67	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
CC*C.CQ	34.79	93.54	28.43	33.65	38.25	42.26	48.79	53.63	60.67	0/12/95	ThmCa	C	4	H	7	O	2	0 G 4
CYCC.CCOO	8.43	79.39	22.17	29.97	36.57	42.11	50.58	56.37	64.07	0/12/95	ThmCa	C	4	H	7	O	2	0 G 0
CYCCCC.OO	5.98	78.77	23.74	31.39	37.82	43.19	51.34	56.90	64.41	0/12/95	ThmCa	C	4	H	7	O	2	0 G 0
C.CYCCOOC	14.64	82.08	23.94	31.71	38.17	43.49	51.45	56.77	63.89	0/12/95	ThmCa	C	4	H	7	O	2	0 G 1
CCYCC.OOC	7.14	84.65	24.80	31.77	37.71	42.73	50.50	55.93	63.35	0/12/95	ThmCa	C	4	H	7	O	2	0 G 1
CCYC.COOC	10.04	83.91	23.74	30.67	36.65	41.76	49.79	55.47	63.16	0/12/95	ThmCa	C	4	H	7	O	2	0 G 1
CCYCC.COO	9.86	83.80	23.94	31.54	37.90	43.18	51.14	56.51	63.69	0/12/95	ThmCa	C	4	H	7	O	2	0 G 1
CCYCCC.OO	7.41	83.18	25.53	33.01	39.22	44.35	52.03	57.20	64.17	0/12/95	ThmCa	C	4	H	7	O	2	0 G 1
CCYC.CCOO	5.01	85.34	25.49	32.51	38.43	43.41	51.06	56.36	63.65	0/12/95	ThmCa	C	4	H	7	O	2	0 G 1
C2CQ.C*O.	-39.73	93.51	30.42	36.83	42.28	46.90	54.09	59.18	66.40	0/12/95	ThmCa	C	4	H	7	O	3	0 G 4
C2CQC.*O	-38.93	94.41	31.68	38.34	43.93	48.61	55.72	60.60	67.29	0/12/95	ThmCa	C	4	H	7	O	3	0 G 4
C2C.OOC*O	-43.23	105.62	31.57	37.34	42.36	46.72	53.73	58.87	66.30	0/12/95	ThmCa	C	4	H	7	O	3	0 G 4
C2.CQC*O	-26.43	98.94	31.96	38.52	44.03	48.63	55.62	60.40	66.86	0/12/95	ThmCa	C	4	H	7	O	3	0 G 5
C*CICCO.Q	-17.87	96.04	33.08	39.27	44.48	48.86	55.58	60.27	66.95	0/12/95	ThmCa	C	4	H	7	O	3	0 G 4
CCYQCOOC	-25.66	92.78	30.51	38.99	46.04	51.86	60.58	66.45	74.33	0/12/95	ThmCa	C	4	H	7	O	4	0 G 2
C.CYQCOOC	-12.76	95.98	31.65	40.49	47.72	53.60	62.16	67.69	74.74	0/12/95	ThmCa	C	4	H	7	O	4	0 G 3
CCYQC.OOC	-19.86	95.09	32.40	41.16	48.32	54.11	62.52	67.94	74.86	0/12/95	ThmCa	C	4	H	7	O	4	0 G 3
C*CC2	-3.80	70.01	21.54	26.73	31.31	35.33	41.91	46.90	54.58	0/12/95	ThmCa	C	4	H	8		0	0 G 2
C2C*C	-3.80	70.01	21.54	26.73	31.31	35.33	41.91	46.90	54.58	0/12/95	ThmCa	C	4	H	8		0	0 G 2
C*CCC	-.11	73.63	20.57	26.18	31.04	35.24	41.99	46.99	54.63	0/12/95	ThmCa	C	4	H	8		0	0 G 2
CC*CC	-3.22	71.04	20.61	25.83	30.46	34.55	41.30	46.43	54.27	0/12/95	ThmCa	C	4	H	8		0	0 G 2
C*CCC	-.11	73.63	20.57	26.18	31.04	35.24	41.99	46.99	54.63	0/12/95	ThmCa	C	4	H	8		0	0 G 2
CC*CC	-3.22	71.04	20.61	25.83	30.46	34.55	41.30	46.43	54.27	0/12/95	ThmCa	C	4	H	8		0	0 G 2
C2C*C	-3.80	70.01	21.54	26.73	31.31	35.33	41.91	46.90	54.58	0/12/95	ThmCa	C	4	H	8		0	0 G 2
C*CMOC	-34.74	81.46	25.01	30.82	35.88	40.29	47.40	52.69	60.50	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
CC*CCOH	-37.68	83.06	23.72	29.35	34.29	38.61	45.60	50.82	58.65	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C*CCCOH	-35.91	84.27	23.62	29.64	34.78	39.17	46.11	51.18	58.96	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C*CCOHC	-39.25	81.80	24.09	30.79	36.43	41.16	48.37	53.34	60.32	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C*CC2OH	-38.26	82.03	24.64	30.22	35.09	39.30	46.11	51.16	58.86	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C2CC*O	-51.20	79.67	23.54	29.66	34.94	39.48	46.69	51.95	59.76	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C2C*COH	-45.93	79.07	25.50	31.28	36.21	40.40	47.00	51.82	59.31	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C2CYC2O	-31.48	72.63	23.39	30.21	35.92	40.69	47.98	53.10	60.73	0/12/95	ThmCa	C	4	H	8	O	1	0 G 2
C*C(C)OC	-34.74	81.46	25.01	30.82	35.88	40.29	47.40	52.69	60.50	0/12/95	ThmCa	C	4	H	8	O	1	0 G 3
C*CCOOC	-20.13	111.47	35.80	43.27	49.34	54.23	61.22	65.54	70.53	0/12/95	ThmCa	C	4	H	8	O	2	0 G 4

C*CCCOOH	-21.34	93.29	28.51	35.08	40.66	45.37	52.70	57.93	65.58	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CCOHCCHO	-89.62	90.82	28.40	34.49	39.69	44.12	51.10	56.20	64.02	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
O*CCCOHC	-89.62	90.82	28.40	34.49	39.69	44.12	51.10	56.20	64.02	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
O*CCC2OH	-87.02	90.32	26.63	33.09	38.62	43.34	50.76	56.14	64.17	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CC*CCQ	-23.80	92.52	29.36	35.31	40.44	44.85	51.87	57.04	64.82	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CC*OCCOH	-92.70	91.73	27.17	33.12	38.31	42.82	50.10	55.54	63.84	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
C*CC2OOH	-24.38	91.49	30.26	36.24	41.35	45.72	52.60	57.61	65.15	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
C*CCQC	-23.68	90.07	29.11	35.98	41.71	46.46	53.66	58.68	65.99	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CC*OCCOH	-92.70	91.73	27.17	33.12	38.31	42.82	50.10	55.54	63.84	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CCICOCOH	-87.02	90.32	26.63	33.09	38.62	43.34	50.76	56.14	64.17	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CCICOC*O	-87.02	90.32	26.63	33.09	38.62	43.34	50.76	56.14	64.17	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
C*CICOOC	-16.40	92.14	28.43	34.52	39.85	44.49	52.00	57.56	65.59	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
C2C*CQ	-23.92	88.65	29.81	36.05	41.37	45.90	53.00	58.10	65.57	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CC*OCCOH	-92.70	91.73	27.17	33.12	38.31	42.82	50.10	55.54	63.84	0/12/95	ThmCa	C	4	H	8	O	2	0	G	4
CYCCCCOO	-37.92	73.57	23.72	32.30	39.49	45.48	54.54	60.71	69.09	0/12/95	ThmCa	C	4	H	8	O	2	0	G	0
CCYCCOOC	-34.36	78.67	24.72	33.09	40.08	45.88	54.61	60.52	68.54	0/12/95	ThmCa	C	4	H	8	O	2	0	G	1
CCYCCCOO	-36.49	79.36	25.30	33.78	40.79	46.57	55.18	60.95	68.78	0/12/95	ThmCa	C	4	H	8	O	2	0	G	1
C2CQC*O	-75.45	93.99	32.54	39.75	45.83	50.92	58.70	64.07	71.48	0/12/95	ThmCa	C	4	H	8	O	3	0	G	5
C2COOC*O	-84.75	100.04	31.10	38.46	44.68	49.91	57.94	63.54	71.27	0/12/95	ThmCa	C	4	H	8	O	3	0	G	5
C*CICCOHQ	-69.85	97.50	34.06	40.57	46.08	50.73	57.95	63.08	70.56	0/12/95	ThmCa	C	4	H	8	O	3	0	G	5
CCYQCCOOC	-61.76	92.56	32.55	41.90	49.62	55.94	65.28	71.43	79.44	0/12/95	ThmCa	C	4	H	8	O	4	0	G	3
C3C.	11.90	74.31	22.24	27.27	31.92	36.18	43.55	49.38	58.34	0/12/95	ThmCa	C	4	H	9		0	0	G	3
C3.CH	16.50	77.42	22.38	28.27	33.43	37.93	45.23	50.71	59.04	0/12/95	ThmCa	C	4	H	9		0	0	G	3
C2CC.	16.50	77.42	22.38	28.27	33.43	37.93	45.23	50.71	59.04	0/12/95	ThmCa	C	4	H	9		0	0	G	3
CCCC.	18.74	78.73	22.56	28.34	33.41	37.84	45.06	50.49	58.79	0/12/95	ThmCa	C	4	H	9		0	0	G	3
CC.CC	16.09	79.75	21.71	27.37	32.42	36.89	44.27	49.86	58.23	0/12/95	ThmCa	C	4	H	9		0	0	G	3
CCC.C	16.09	79.75	21.71	27.37	32.42	36.89	44.27	49.86	58.23	0/12/95	ThmCa	C	4	H	9		0	0	G	3
C3.COH	-26.10	85.00	26.45	32.85	38.29	42.91	50.17	55.47	63.64	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
CCCCO	-14.10	84.50	25.45	31.87	37.43	42.22	49.91	55.60	64.22	0/12/95	ThmCa	C	4	H	9	O	1	0	G	3
CCO.CC	-18.47	82.50	26.07	32.62	38.22	43.00	50.58	56.13	64.57	0/12/95	ThmCa	C	4	H	9	O	1	0	G	3
C2CCO	-16.34	81.81	25.15	31.79	37.49	42.38	50.12	55.77	64.29	0/12/95	ThmCa	C	4	H	9	O	1	0	G	3
C3CO	-23.14	76.57	26.25	32.93	38.60	43.42	50.95	56.41	64.70	0/12/95	ThmCa	C	4	H	9	O	1	0	G	3
C2CCO.	-16.34	81.81	25.15	31.79	37.49	42.38	50.12	55.77	64.29	0/12/95	ThmCa	C	4	H	9	O	1	0	G	3
C3.COH	-26.10	85.00	26.45	32.85	38.29	42.91	50.17	55.47	63.64	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
C2C.COH	-23.90	88.51	25.23	30.71	35.67	40.14	47.67	53.51	62.49	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
C3.COH	-26.10	83.63	26.45	32.85	38.29	42.91	50.17	55.47	63.64	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
C3CO.	-23.14	76.57	26.25	32.93	38.60	43.42	50.95	56.41	64.70	0/12/95	ThmCa	C	4	H	9	O	1	0	G	3
C2C.OC	-16.50	83.72	27.26	33.62	39.03	43.62	50.83	56.09	64.20	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
C2COC.	-16.50	84.53	27.26	33.62	39.03	43.62	50.83	56.09	64.20	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
C2.COC	-11.90	85.80	25.99	32.43	37.94	42.66	50.14	55.63	64.00	0/12/95	ThmCa	C	4	H	9	O	1	0	G	4
C3.COOH	-10.93	92.57	31.26	38.28	44.19	49.15	56.80	62.25	70.43	0/12/95	ThmCa	C	4	H	9	O	2	0	G	4
C.COOCC	3.12	100.07	28.71	35.79	41.85	47.00	55.04	60.70	68.69	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C3COO	-23.83	85.82	30.08	36.78	42.52	47.43	55.22	60.95	69.68	0/12/95	ThmCa	C	4	H	9	O	2	0	G	4
CCCCOO	-15.39	95.20	29.28	35.73	41.36	46.26	54.21	60.16	69.25	0/12/95	ThmCa	C	4	H	9	O	2	0	G	4

CCCC.OOH	-7.59	98.80	31.39	37.80	43.35	48.14	55.78	61.40	69.71	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
CCC.COOH	-5.14	99.42	29.59	36.27	42.05	47.03	54.95	60.71	69.04	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
CC.CCOOH	-5.14	99.42	29.59	36.27	42.05	47.03	54.95	60.71	69.04	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C.CCCOOH	-2.49	99.77	30.47	37.26	43.07	48.02	55.81	61.44	69.73	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C2CCOO	-17.63	92.51	29.03	35.68	41.43	46.40	54.39	60.32	69.33	0/12/95	ThmCa	C	4	H	9	O	2	0	G	4
C2CC.OOH	-9.83	96.11	31.16	37.74	43.39	48.24	55.92	61.52	69.76	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C2.CCOOH	-4.73	97.09	30.27	37.22	43.13	48.14	55.98	61.59	69.81	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C2C.COOH	-9.33	97.53	30.16	36.23	41.63	46.42	54.33	60.31	69.11	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
CCOO.CC	-18.76	92.45	29.79	36.44	42.16	47.07	54.89	60.67	69.48	0/12/95	ThmCa	C	4	H	9	O	2	0	G	4
CCOOHCC.	-5.86	97.03	31.06	37.97	43.83	48.77	56.44	61.91	69.94	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
CCOOHC.C	-8.51	96.67	30.27	37.06	42.87	47.83	55.64	61.28	69.52	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
CC.OOHCC	-13.36	98.21	31.95	38.09	43.44	48.09	55.61	61.19	69.51	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C.COOHCC	-5.86	97.03	31.06	37.97	43.83	48.77	56.44	61.91	69.94	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C2C.CQ	-9.53	96.88	30.47	36.53	41.92	46.68	54.52	60.44	69.17	0/12/95	ThmCa	C	4	H	9	O	2	0	G	5
C2CC.Q	-10.93	91.74	31.63	38.37	44.09	48.92	56.46	61.91	70.19	0/12/95	ThmCa	C	4	H	9	O	2	0	G	4
C2CO.CQ	-44.37	98.41	34.24	41.85	48.22	53.54	61.66	67.34	75.63	0/12/95	ThmCa	C	4	H	9	O	3	0	G	5
C2CQ.COH	-59.23	99.34	33.19	40.24	46.24	51.33	59.33	65.17	74.14	0/12/95	ThmCa	C	4	H	9	O	3	0	G	5
C2CQCO.	-43.37	97.66	34.24	41.85	48.22	53.54	61.66	67.34	75.63	0/12/95	ThmCa	C	4	H	9	O	3	0	G	5
C2CO.CQ	-44.37	98.41	34.24	41.85	48.22	53.54	61.66	67.34	75.63	0/12/95	ThmCa	C	4	H	9	O	3	0	G	5
C2COHCQ.	-60.23	100.09	33.19	40.24	46.24	51.33	59.33	65.17	74.14	0/12/95	ThmCa	C	4	H	9	O	3	0	G	5
C3CH	-32.50	70.45	23.15	29.65	35.34	40.31	48.39	54.45	63.69	0/12/95	ThmCa	C	4	H	10		0	0	G	3
C3C	-32.50	70.45	23.15	29.65	35.34	40.31	48.39	54.45	63.69	0/12/95	ThmCa	C	4	H	10		0	0	G	3
CCCC	-30.26	73.94	23.32	29.72	35.33	40.24	48.22	54.24	63.44	0/12/95	ThmCa	C	4	H	10		0	0	G	3
C2COC	-60.90	82.38	26.78	33.81	39.86	45.04	53.28	59.36	68.63	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
CCCCOH	-66.08	85.96	26.42	33.17	39.03	44.10	52.29	58.40	67.79	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
CCOHCC	-70.45	83.96	27.05	33.92	39.82	44.89	52.96	58.93	68.15	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
C3COH	-75.12	78.03	27.22	34.23	40.21	45.30	53.33	59.20	68.27	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
C2CCOH	-68.32	83.27	26.14	33.10	39.10	44.26	52.50	58.57	67.85	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
C3COH	-75.12	78.03	27.22	34.23	40.21	45.30	53.33	59.20	68.27	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
C2COC	-60.90	82.38	26.78	33.81	39.86	45.04	53.28	59.36	68.63	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
C3COOH	-59.93	85.60	32.07	39.67	46.10	51.53	59.94	65.94	74.80	0/12/95	ThmCa	C	4	H	10	O	1	0	G	4
CCOOCC	-45.88	95.27	29.37	37.17	43.82	49.45	58.22	64.41	73.25	0/12/95	ThmCa	C	4	H	10	O	2	0	G	5
CCCCOOH	-51.49	94.98	31.23	38.62	44.96	50.38	58.95	65.18	74.37	0/12/95	ThmCa	C	4	H	10	O	2	0	G	5
CCOOHCC	-54.86	93.60	31.83	39.33	45.71	51.12	59.57	65.64	74.59	0/12/95	ThmCa	C	4	H	10	O	2	0	G	5
C2CCOOH	-53.73	92.29	31.08	38.57	44.99	50.46	59.07	65.29	74.43	0/12/95	ThmCa	C	4	H	10	O	2	0	G	5
C2CCQ	-53.73	92.29	31.08	38.57	44.99	50.46	59.07	65.29	74.43	0/12/95	ThmCa	C	4	H	10	O	2	0	G	5
C2CQCOH	-95.35	99.12	35.22	43.17	49.85	55.44	64.05	70.16	79.24	0/12/95	ThmCa	C	4	H	10	O	3	0	G	6
C2COHCQ	-96.35	99.87	35.22	43.17	49.85	55.44	64.05	70.16	79.24	0/12/95	ThmCa	C	4	H	10	O	3	0	G	6
C#CC.C#C	123.08	69.25	21.26	22.93	25.07	27.46	32.25	36.16	41.01	0/12/95	ThmCa	C	5	H	3		0	0	G	1
C#CC#CC	95.50	71.06	21.65	25.22	28.34	31.05	35.38	38.51	42.78	0/12/95	ThmCa	C	5	H	4		0	0	G	2
C#CC*C*C	102.39	72.79	21.34	25.77	29.38	32.32	36.63	39.48	43.46	0/12/95	ThmCa	C	5	H	4		0	0	G	1
C#CC#C	99.18	71.92	21.27	24.89	28.06	30.83	35.28	38.49	42.80	0/12/95	ThmCa	C	5	H	4		0	0	G	2
C#CC.C*C	88.99	73.30	20.09	25.27	29.65	33.34	38.98	42.85	47.95	0/12/95	ThmCa	C	5	H	5		0	0	G	2
C#CCC.*C	121.52	78.76	22.57	26.05	29.26	32.19	37.19	41.07	46.73	0/12/95	ThmCa	C	5	H	5		0	0	G	2

C#CCC*C.	123.72	78.34	22.95	26.50	29.74	32.66	37.58	41.36	46.87	0/12/95	ThmCa	C	5	H	5		0	0	G 2
CY13PD5	57.18	63.59	18.63	24.65	29.51	33.42	39.06	42.76	48.12	0/12/95	ThmCa	C	5	H	5		0	0	G 0
C#CC*CC	60.32	75.38	22.66	27.95	32.41	36.14	41.88	45.92	51.77	0/12/95	ThmCa	C	5	H	6		0	0	G 2
C#CC*C	65.09	77.35	22.49	27.28	31.45	35.07	40.91	45.24	51.61	0/12/95	ThmCa	C	5	H	6		0	0	G 2
C#CCC*C	64.62	76.95	22.90	27.41	31.40	34.92	40.71	45.08	51.53	0/12/95	ThmCa	C	5	H	6		0	0	G 2
CY13PD	31.26	65.51	18.31	24.79	30.15	34.59	41.25	45.83	52.47	0/12/95	ThmCa	C	5	H	6		0	0	G 0
C*CCJC*C	49.31	75.95	21.20	27.64	33.07	37.63	44.64	49.55	56.57	0/12/95	ThmCa	C	5	H	7		0	0	G 2
C*CCC*C.	84.53	82.77	23.05	28.80	33.65	37.72	44.01	48.52	55.41	0/12/95	ThmCa	C	5	H	7		0	0	G 2
C*CCC.*C	82.33	83.19	22.83	28.35	33.08	37.11	43.46	48.10	55.17	0/12/95	ThmCa	C	5	H	7		0	0	G 2
C*CC.C*C	49.31	75.95	21.20	27.64	33.07	37.63	44.64	49.55	56.57	0/12/95	ThmCa	C	5	H	7		0	0	G 2
C*CCC*C	25.41	78.63	23.20	29.60	35.03	39.63	46.82	52.02	59.92	0/12/95	ThmCa	C	5	H	8		0	0	G 2
C*CCC*C	25.41	80.00	23.20	29.60	35.03	39.63	46.82	52.02	59.92	0/12/95	ThmCa	C	5	H	8		0	0	G 2
C5DE23	30.98	77.04	24.40	30.19	35.23	39.60	46.66	51.92	60.00	0/12/95	ThmCa	C	5	H	8		0	0	G 1
CYC5E	7.82	69.26	19.63	26.97	33.21	38.49	46.71	52.57	61.19	0/12/95	ThmCa	C	5	H	8		0	0	G 0
C5DE14	25.41	80.00	23.20	29.60	35.03	39.63	46.82	52.02	59.92	0/12/95	ThmCa	C	5	H	8		0	0	G 2
C*CC.CC	28.46	79.24	24.55	31.33	37.20	42.25	50.30	56.20	64.92	0/12/95	ThmCa	C	5	H	9		0	0	G 3
C*CCCC.	43.96	86.46	25.25	31.76	37.37	42.19	49.89	55.56	64.16	0/12/95	ThmCa	C	5	H	9		0	0	G 3
C*CCC.C	41.31	87.49	24.39	30.80	36.41	41.28	49.15	54.97	63.63	0/12/95	ThmCa	C	5	H	9		0	0	G 3
C*CC.CC	28.46	79.24	24.48	31.32	37.20	42.25	50.29	56.16	64.97	0/12/95	ThmCa	C	5	H	9		0	0	G 2
C*C.CCC	54.06	84.44	25.84	32.34	37.91	42.68	50.26	55.81	64.29	0/12/95	ThmCa	C	5	H	9		0	0	G 3
C.*CCCC	54.06	84.44	25.84	32.34	37.91	42.68	50.26	55.81	64.29	0/12/95	ThmCa	C	5	H	9		0	0	G 3
C*C.CCC	51.86	84.86	25.57	31.91	37.39	42.13	49.73	55.37	64.09	0/12/95	ThmCa	C	5	H	9		0	0	G 2
C.*CCCC	54.06	84.44	25.78	32.33	37.92	42.70	50.25	55.78	64.31	0/12/95	ThmCa	C	5	H	9		0	0	G 2
C*CCCCQ.	9.83	102.93	31.98	39.15	45.33	50.63	59.07	65.29	74.72	0/12/95	ThmCa	C	5	H	9	O	2	0	G 4
C*CCCC.Q	17.63	106.53	34.16	41.23	47.28	52.44	60.58	66.47	75.14	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C*CCC.CQ	20.08	107.15	32.30	39.69	46.01	51.38	59.80	65.82	74.50	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C*CC.CCQ	7.23	98.90	32.50	40.25	46.82	52.37	60.99	67.12	75.98	0/12/95	ThmCa	C	5	H	9	O	2	0	G 4
C.*CCCCQ	32.83	104.10	33.89	41.28	47.53	52.80	60.96	66.77	75.30	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C*C.CCCQ	30.63	104.52	33.69	40.86	46.99	52.21	60.42	66.35	75.07	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C*CCQ.CC	7.49	99.71	32.62	40.07	46.37	51.71	60.03	66.04	75.14	0/12/95	ThmCa	C	5	H	9	O	2	0	G 4
C*CCQCC.	20.39	102.90	33.84	41.58	48.04	53.41	61.58	67.28	75.60	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C*CCQC.C	17.74	103.93	33.01	40.63	47.06	52.46	60.78	66.65	75.15	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C.*CCQCC	30.49	100.88	34.44	42.15	48.57	53.88	61.94	67.53	75.72	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C.*CCCCQ	33.83	103.75	33.89	41.29	47.52	52.77	60.93	66.83	76.02	0/12/95	ThmCa	C	5	H	9	O	2	0	G 2
C*C.CCCQ	30.63	104.52	33.69	40.86	46.99	52.21	60.42	66.35	75.07	0/12/95	ThmCa	C	5	H	9	O	2	0	G 5
C.*CCQCC	30.49	101.28	34.45	42.20	48.62	53.93	61.99	67.64	76.29	0/12/95	ThmCa	C	5	H	9	O	2	0	G 3
2ME1BUTE	-8.56	81.18	26.68	33.60	39.60	44.80	53.16	59.39	68.91	0/12/95	ThmCa	C	5	H	10		0	0	G 3
2ME2BUTE	-11.67	79.97	26.72	33.26	39.03	44.12	52.47	58.82	68.56	0/12/95	ThmCa	C	5	H	10		0	0	G 3
3ME1BUTE	-7.03	80.36	25.82	33.11	39.37	44.74	53.27	59.53	69.04	0/12/95	ThmCa	C	5	H	10		0	0	G 3
C*CCCC	-5.04	83.05	26.03	33.14	39.28	44.58	53.05	59.30	68.81	0/12/95	ThmCa	C	5	H	10		0	0	G 3
C*CCCC	-5.04	83.05	26.03	33.14	39.28	44.58	53.05	59.30	68.81	0/12/95	ThmCa	C	5	H	10		0	0	G 3
C*CCCCQ	-26.27	102.71	34.04	42.06	48.88	54.68	63.74	70.25	79.81	0/12/95	ThmCa	C	5	H	10	O	2	0	G 5
C*CCQCC	-28.61	98.47	34.53	42.96	49.99	55.85	64.80	71.15	80.83	0/12/95	ThmCa	C	5	H	10	O	2	0	G 3
C3CC.	8.70	79.06	28.32	36.27	43.04	48.77	57.72	64.14	73.68	0/12/95	ThmCa	C	5	H	11		0	0	G 4

CCCCC.	13.81	88.15	28.04	35.31	41.65	47.17	56.11	62.79	72.96	0/12/95	ThmCa	C	5	H	11		0	0	G	4
CCCC.C	11.16	89.17	27.16	34.33	40.66	46.23	55.33	62.16	72.37	0/12/95	ThmCa	C	5	H	11		0	0	G	4
C.CCCC	13.81	88.15	28.04	35.31	41.65	47.17	56.11	62.79	72.96	0/12/95	ThmCa	C	5	H	11		0	0	G	4
CC.CCC	11.16	89.17	27.16	34.33	40.66	46.23	55.33	62.16	72.37	0/12/95	ThmCa	C	5	H	11		0	0	G	4
CCC.CC	11.16	87.80	27.16	34.33	40.66	46.23	55.33	62.16	72.37	0/12/95	ThmCa	C	5	H	11		0	0	G	4
C2.CCC	11.57	85.47	27.82	35.24	41.69	47.29	56.31	63.03	73.23	0/12/95	ThmCa	C	5	H	11		0	0	G	4
C2C.CC	6.97	85.91	27.64	34.24	40.23	45.62	54.72	61.80	72.60	0/12/95	ThmCa	C	5	H	11		0	0	G	4
C2CC.C	8.92	86.49	26.95	34.26	40.69	46.33	55.51	62.39	72.71	0/12/95	ThmCa	C	5	H	11		0	0	G	4
C2CCC.	11.57	85.47	27.82	35.24	41.69	47.29	56.31	63.03	73.23	0/12/95	ThmCa	C	5	H	11		0	0	G	4
CC4.	8.70	79.06	28.32	36.27	43.04	48.77	57.72	64.14	73.68	0/12/95	ThmCa	C	5	H	11		0	0	G	4
C3CCO.	-24.14	84.83	31.16	39.79	47.07	53.18	62.59	69.25	79.09	0/12/95	ThmCa	C	5	H	11	O	1	0	G	4
C3.CCOH	-27.10	93.26	31.38	39.72	46.76	52.68	61.82	68.32	78.03	0/12/95	ThmCa	C	5	H	11	O	1	0	G	5
C3.COC	-21.50	91.46	31.61	39.70	46.58	52.42	61.57	68.19	78.15	0/12/95	ThmCa	C	5	H	11	O	1	0	G	5
C3COC.	-26.10	88.01	32.94	40.92	47.68	53.39	62.29	68.69	78.42	0/12/95	ThmCa	C	5	H	11	O	1	0	G	5
C3.COOH	-12.53	100.91	36.33	45.20	52.65	58.87	68.41	75.07	84.68	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C3CCOO	-25.43	95.53	35.08	43.69	51.00	57.19	66.86	73.83	84.22	0/12/95	ThmCa	C	5	H	11	O	2	0	G	5
C2Q.CCC	-22.56	101.93	34.45	42.64	49.71	55.80	65.52	72.71	83.63	0/12/95	ThmCa	C	5	H	11	O	2	0	G	5
CQCIC.CC	-9.66	105.13	35.76	44.15	51.32	57.42	67.00	73.90	84.04	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2QC.CC	-14.26	106.95	35.65	43.20	49.89	55.78	65.44	72.69	83.40	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2QCC.C	-12.31	106.15	34.77	43.17	50.38	56.54	66.25	73.22	83.28	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2QCCC.	-9.66	105.13	35.76	44.15	51.32	57.42	67.00	73.90	84.04	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CQ.CC	-28.36	98.12	35.50	43.75	50.80	56.83	66.36	73.34	83.97	0/12/95	ThmCa	C	5	H	11	O	2	0	G	5
C2.CQCC	-15.46	101.32	36.80	45.28	52.45	58.49	67.87	74.56	84.41	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CQC.C	-18.11	102.34	35.95	44.33	51.48	57.55	67.06	73.89	83.90	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CQCC.	-15.46	101.32	36.80	45.28	52.45	58.49	67.87	74.56	84.41	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CCQ.C	-25.93	99.19	34.91	43.35	50.54	56.66	66.28	73.29	83.91	0/12/95	ThmCa	C	5	H	11	O	2	0	G	5
C2.CCQC	-13.03	102.39	36.22	44.87	52.18	58.32	67.81	74.54	84.37	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2C.CQC	-17.63	104.21	36.27	44.02	50.80	56.70	66.23	73.29	83.69	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CCQC.	-13.03	102.39	36.22	44.87	52.18	58.32	67.81	74.54	84.37	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CCCQ.	-22.56	101.93	34.45	42.64	49.71	55.80	65.52	72.71	83.63	0/12/95	ThmCa	C	5	H	11	O	2	0	G	5
C2.CCCQ	-9.66	105.13	35.76	44.15	51.32	57.42	67.00	73.90	84.04	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2C.CCQ	-14.26	106.95	35.65	43.20	49.89	55.78	65.44	72.69	83.40	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C2CC.CQ	-12.31	106.15	34.77	43.17	50.38	56.54	66.25	73.22	83.28	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
CC4Q.	-25.43	95.53	35.08	43.69	51.00	57.19	66.86	73.83	84.22	0/12/95	ThmCa	C	5	H	11	O	2	0	G	5
CC4.Q	-12.53	100.91	36.33	45.20	52.65	58.87	68.41	75.07	84.68	0/12/95	ThmCa	C	5	H	11	O	2	0	G	6
C4C	-40.30	72.89	29.09	37.65	44.95	51.16	60.89	67.90	78.34	0/12/95	ThmCa	C	5	H	12		0	0	G	4
CCCCC	-35.19	83.36	28.81	36.68	43.57	49.56	59.27	66.54	77.61	0/12/95	ThmCa	C	5	H	12		0	0	G	4
CCICCC	-35.83	82.05	28.59	36.64	43.63	49.69	59.44	66.70	77.73	0/12/95	ThmCa	C	5	H	12		0	0	G	4
C2CCC	-37.43	82.05	28.61	36.62	43.61	49.67	59.47	66.77	77.87	0/12/95	ThmCa	C	5	H	12		0	0	G	4
CC4	-40.30	72.89	29.09	37.65	44.95	51.16	60.89	67.90	78.34	0/12/95	ThmCa	C	5	H	12		0	0	G	4
C3CCOH	-76.12	86.29	32.15	41.10	48.67	55.06	64.97	72.05	82.66	0/12/95	ThmCa	C	5	H	12	O	1	0	G	5
C3COC	-70.52	85.86	32.40	41.09	48.50	54.81	64.73	71.95	82.87	0/12/95	ThmCa	C	5	H	12	O	1	0	G	5
C3CCOOH	-61.53	95.31	37.12	46.59	54.57	61.26	71.56	78.81	89.32	0/12/95	ThmCa	C	5	H	12	O	2	0	G	6
C2QCCC	-58.66	101.71	36.58	45.55	53.23	59.80	70.14	77.64	88.68	0/12/95	ThmCa	C	5	H	12	O	2	0	G	6

C2CQCC	-65.48	98.65	37.53	46.64	54.36	60.88	71.04	78.31	89.07	0/12/95	ThmCa	C	5	H	12	O	2		0	G	6
C2CCQC	-62.03	98.97	36.95	46.24	54.09	60.71	70.99	78.30	89.05	0/12/95	ThmCa	C	5	H	12	O	2		0	G	6
C2CCCQ	-58.66	101.71	36.58	45.55	53.23	59.80	70.14	77.64	88.68	0/12/95	ThmCa	C	5	H	12	O	2		0	G	6
CC4Q	-61.53	95.31	37.12	46.59	54.57	61.26	71.56	78.81	89.32	0/12/95	ThmCa	C	5	H	12	O	2		0	G	6
C#CC#CC#C	156.28	71.56	24.78	27.92	30.44	32.43	35.24	36.98	39.23	0/12/95	ThmCa	C	6	H	2		0		0	G	2
C#CC#CC*C	119.39	78.55	24.25	29.18	33.22	36.51	41.34	44.51	48.76	0/12/95	ThmCa	C	6	H	4		0		0	G	2
ORTACLO.	4.69	84.89	26.84	33.71	39.28	43.78	50.28	54.49	60.24	0/12/95	ThmCa	C	6	H	4	O	1	CL	1	G	0
C#CC.CC#C	134.42	82.27	26.09	30.64	34.56	37.93	43.24	47.06	52.36	0/12/95	ThmCa	C	6	H	5		0		0	G	3
LINC6H5P.	140.85	80.94	25.89	31.70	36.34	40.02	45.23	48.54	53.10	0/12/95	ThmCa	C	6	H	5		0		0	G	3
C6H5.	80.72	69.30	19.16	25.44	30.68	35.02	41.61	46.19	52.86	0/12/95	ThmCa	C	6	H	5		0		0	G	0
C6H5CL	12.39	74.84	23.46	30.56	36.39	41.14	48.14	52.79	59.21	0/12/95	ThmCa	C	6	H	5	CL	1		0	G	0
PHENOXY	12.10	76.49	22.96	29.83	35.55	40.29	47.44	52.32	59.11	0/12/95	ThmCa	C	6	H	5	O	1		0	G	0
CYC6.CLO.	51.61	86.22	28.43	36.57	43.01	48.06	55.07	59.39	65.35	0/12/95	ThmCa	C	6	H	5	O	1	CL	1	G	0
CL.CYC6O.	53.74	87.95	26.46	34.24	40.69	46.00	53.89	59.12	65.94	0/12/95	ThmCa	C	6	H	5	O	1	CL	1	G	0
ORTACLOH	-29.71	83.59	28.41	35.87	41.87	46.67	53.52	57.92	64.04	0/12/95	ThmCa	C	6	H	5	O	1	CL	1	G	1
FULVENE	42.79	63.24	24.14	31.70	37.68	42.37	48.93	53.07	59.12	0/12/95	ThmCa	C	6	H	6		0		0	G	0
FULVENE	42.79	63.24	24.14	31.70	37.68	42.37	48.93	53.07	59.12	0/12/95	ThmCa	C	6	H	6		0		0	G	0
C#CCCC#C	99.52	81.34	26.70	31.79	36.24	40.11	46.32	50.84	57.15	0/12/95	ThmCa	C	6	H	6		0		0	G	3
C*C*CC*C*	98.12	81.80	26.17	31.52	36.09	39.97	46.04	50.41	56.91	0/12/95	ThmCa	C	6	H	6		0		0	G	1
C#CC#CCC	90.77	81.36	26.55	31.72	36.21	40.08	46.26	50.74	57.05	0/12/95	ThmCa	C	6	H	6		0		0	G	3
C#CC*C*CC	94.52	81.38	26.51	32.29	37.11	41.13	47.22	51.42	57.44	0/12/95	ThmCa	C	6	H	6		0		0	G	2
C#CC*CC*C	81.75	79.55	26.46	32.81	37.98	42.15	48.23	52.23	57.79	0/12/95	ThmCa	C	6	H	6		0		0	G	3
CYC6H6	19.80	64.26	19.61	26.71	32.67	37.66	45.29	50.61	58.12	0/12/95	ThmCa	C	6	H	6		0		0	G	0
C6H5OH	-22.30	75.19	24.55	32.03	38.17	43.21	50.69	55.73	62.93	0/12/95	ThmCa	C	6	H	6	O	1		0	G	1
PHENOL	-22.30	75.19	24.55	32.03	38.17	43.21	50.69	55.73	62.93	0/12/95	ThmCa	C	6	H	6	O	1		0	G	1
CYHXE.O.	62.77	79.92	24.86	33.30	40.18	45.74	53.75	58.82	65.21	0/12/95	ThmCa	C	6	H	6	O	1		0	G	0
CYC6.CLOH	-.35	87.68	29.40	37.87	44.61	49.94	57.44	62.18	68.93	0/12/95	ThmCa	C	6	H	6	O	1	CL	1	G	1
CYC6CL.OH	1.78	89.41	29.17	36.82	43.21	48.52	56.54	62.03	69.57	0/12/95	ThmCa	C	6	H	6	O	1	CL	1	G	1
C#CC.CC*C	94.76	86.30	27.19	33.09	38.11	42.37	49.03	53.82	60.95	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCC.C*C	93.36	82.94	26.80	32.54	37.60	42.01	49.15	54.40	61.77	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCCC.*C	116.76	88.56	27.33	32.91	37.76	41.96	48.74	53.75	61.16	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCC.C*C	93.36	82.94	26.80	32.54	37.60	42.01	49.15	54.40	61.77	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCCC*C.	118.96	88.14	27.68	33.42	38.35	42.58	49.29	54.19	61.40	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCC.*CC	114.12	87.75	27.02	32.46	37.23	41.42	48.23	53.34	60.92	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCC*C.C	114.12	87.75	27.02	32.46	37.23	41.42	48.23	53.34	60.92	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CCC*CC.	93.32	84.18	27.84	33.39	38.27	42.53	49.43	54.53	61.78	0/12/95	ThmCa	C	6	H	7		0		0	G	3
C#CC.C*CC	86.12	82.39	26.32	32.07	37.08	41.44	48.51	53.77	61.59	0/12/95	ThmCa	C	6	H	7		0		0	G	2
CYHEXE.OH	10.79	81.38	25.33	34.36	41.64	47.48	55.83	61.14	68.31	0/12/95	ThmCa	C	6	H	7	O	1		0	G	1
CYC6CLOH1	-24.87	88.36	30.16	39.16	46.42	52.24	60.59	66.02	73.72	0/12/95	ThmCa	C	6	H	7	O	1	CL	1	G	1
CYC6CLOH2	-22.74	90.09	29.25	37.66	44.73	50.66	59.72	65.97	74.51	0/12/95	ThmCa	C	6	H	7	O	1	CL	1	G	1
C#CCCC*C	59.86	86.75	27.69	34.18	39.76	44.56	52.17	57.74	65.97	0/12/95	ThmCa	C	6	H	8		0		0	G	3
C.*CC*CC.	106.07	83.97	27.79	35.00	40.97	45.89	53.32	58.50	66.45	0/12/95	ThmCa	C	6	H	8		0		0	G	1
C#CCCC*C	59.86	86.75	27.69	34.18	39.76	44.56	52.17	57.74	65.97	0/12/95	ThmCa	C	6	H	8		0		0	G	3
C#CCC*CC	57.22	85.94	27.35	33.72	39.25	44.02	51.68	57.33	65.74	0/12/95	ThmCa	C	6	H	8		0		0	G	3

CY13HD	25.41	73.88	22.79	30.93	37.78	43.52	52.32	58.48	67.38	0/12/95	ThmCa	C	6	H	8		0	0	G 0
CYC6H7OH	-13.73	82.06	26.45	35.66	43.24	49.42	58.52	64.50	72.67	0/12/95	ThmCa	C	6	H	8	O	1	0	G 1
C*CC*CC.C	41.35	84.84	27.78	35.75	42.43	48.03	56.62	62.68	71.61	0/12/95	ThmCa	C	6	H	9		0	0	G 2
C*CCCC*C.	79.30	92.17	28.54	35.77	41.90	47.07	55.13	60.92	69.68	0/12/95	ThmCa	C	6	H	9		0	0	G 3
C*CCCC.*C	77.10	92.59	28.29	35.32	41.34	46.48	54.59	60.50	69.45	0/12/95	ThmCa	C	6	H	9		0	0	G 3
C*CCC.C*C	53.68	86.97	27.23	34.76	41.17	46.62	55.16	61.30	70.30	0/12/95	ThmCa	C	6	H	9		0	0	G 3
C*CC*CCC	13.45	86.39	29.62	37.65	44.41	50.08	58.87	65.17	74.78	0/12/95	ThmCa	C	6	H	10		0	0	G 3
CC*CC*CC	10.34	85.17	29.64	37.30	43.84	49.41	58.19	64.61	74.44	0/12/95	ThmCa	C	6	H	10		0	0	G 3
C*CC*CCC	13.45	86.39	29.62	37.65	44.41	50.08	58.87	65.17	74.78	0/12/95	ThmCa	C	6	H	10		0	0	G 3
C*CCCC*C	20.18	89.40	28.66	36.54	43.26	48.97	57.93	64.41	74.19	0/12/95	ThmCa	C	6	H	10		0	0	G 3
C*CCC.CC	36.38	96.91	29.87	37.75	44.62	50.58	60.19	67.28	77.73	0/12/95	ThmCa	C	6	H	11		0	0	G 5
C*CC.CCC	23.53	88.66	30.03	38.33	45.48	51.63	61.40	68.55	79.15	0/12/95	ThmCa	C	6	H	11		0	0	G 4
C*CCCCC.	39.03	95.88	30.79	38.76	45.65	51.58	61.03	67.96	78.32	0/12/95	ThmCa	C	6	H	11		0	0	G 5
C.C*CCCC	23.19	89.88	30.75	39.09	46.22	52.31	61.91	68.88	79.28	0/12/95	ThmCa	C	6	H	11		0	0	G 4
CC*CCCC.	36.09	95.05	30.42	38.28	45.10	51.00	60.48	67.50	78.15	0/12/95	ThmCa	C	6	H	11		0	0	G 4
CC*CC.CC	20.59	87.82	29.64	37.83	44.93	51.06	60.87	68.10	78.95	0/12/95	ThmCa	C	6	H	11		0	0	G 3
CC*CCC.C	33.44	96.07	29.57	37.31	44.12	50.06	59.71	66.89	77.58	0/12/95	ThmCa	C	6	H	11		0	0	G 4
C*CCQ.CCC	2.56	106.94	38.08	47.03	54.63	61.07	71.13	78.36	89.13	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
C*CCQC.CC	12.81	111.16	38.50	47.60	55.31	61.80	71.85	78.98	89.39	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
C*CCQCC.C	12.81	111.16	38.50	47.60	55.31	61.80	71.85	78.98	89.39	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
C*CCQCCC.	15.46	110.14	39.37	48.56	56.27	62.73	72.64	79.62	89.84	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
C.*CCQCCC	25.56	110.30	39.97	49.14	56.81	63.21	73.00	79.88	89.97	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
C*C.CQCCC	23.36	110.72	39.76	48.75	56.33	62.70	72.54	79.53	89.80	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
C*CC.QCCC	-2.24	105.22	38.30	47.62	55.51	62.16	72.48	79.81	90.45	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
C*CCQCCC.	15.46	112.32	39.37	48.56	56.27	62.73	72.64	79.62	89.84	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
Q.CC*CCCC	2.61	111.96	37.96	46.25	53.41	59.59	69.51	76.90	88.30	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
QC.C*CCCC	.01	107.93	38.42	47.29	54.86	61.30	71.41	78.71	89.53	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
QCC.*CCCC	32.00	121.52	44.08	53.64	61.74	68.55	78.91	85.86	94.38	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
QCC*CC.CC	.01	107.93	38.42	47.29	54.86	61.30	71.41	78.71	89.53	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
QCC*CCC.C	12.86	116.18	38.20	46.75	54.08	60.35	70.24	77.39	87.87	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
QCC*CCCC.	15.51	116.53	39.19	47.73	55.02	61.24	71.02	78.12	88.74	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CC*CCQ.CC	-.38	108.29	37.83	46.61	54.11	60.51	70.62	78.00	89.20	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
C.C*CCQCC	-.38	107.70	39.31	48.86	56.83	63.45	73.52	80.53	90.79	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
CC.*CCQCC	20.42	109.88	39.48	48.31	55.80	62.15	72.04	79.13	89.60	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CC*C.CQCC	20.42	109.88	39.48	48.31	55.80	62.15	72.04	79.13	89.60	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CC*CC.QCC	-5.18	104.38	37.99	47.24	55.10	61.75	72.10	79.49	90.30	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
CC*CCQC.C	9.87	112.51	38.22	47.18	54.80	61.26	71.36	78.59	89.16	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CC*CCQCC.	12.52	112.87	39.05	48.17	55.84	62.29	72.24	79.30	89.69	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CCQ.C*CCC	-.21	108.67	37.49	46.50	54.15	60.63	70.79	78.14	89.27	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
C.CQC*CCC	12.69	113.25	38.77	48.05	55.83	62.34	72.34	79.39	89.73	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CCQC*CCC.	12.69	113.25	38.77	48.05	55.83	62.34	72.34	79.39	89.73	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CC.QC*CCC	-5.01	104.76	37.69	47.08	55.03	61.74	72.16	79.56	90.32	0/12/95	ThmCa	C	6	H	11	O	2	0	G 5
CCQC.*CCC	20.59	110.26	39.18	48.20	55.81	62.22	72.15	79.21	89.62	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6
CCQC*C.CC	20.59	110.26	39.18	48.20	55.81	62.22	72.15	79.21	89.62	0/12/95	ThmCa	C	6	H	11	O	2	0	G 6

CCQC*CC.C	-2.81	104.64	38.01	47.62	55.68	62.42	72.75	79.99	90.55	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
C*C.CQCCC	23.36	110.72	39.74	48.73	56.30	62.68	72.54	79.58	90.08	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
QCC*C.CCC	24.10	113.11	38.99	47.43	54.72	61.01	71.05	78.45	89.48	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
QCC.*CCCC	24.10	113.11	38.99	47.43	54.72	61.01	71.05	78.45	89.48	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
CC.*CCQCC	20.42	109.88	39.46	48.32	55.82	62.15	72.03	79.14	89.84	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
CC*C.CQCC	20.42	109.88	39.46	48.32	55.82	62.15	72.03	79.14	89.84	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
CCQC.*CCC	20.59	110.26	39.12	48.22	55.87	62.29	72.22	79.30	89.93	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
CCQC*C.CC	20.59	110.26	39.12	48.22	55.87	62.29	72.22	79.30	89.93	0/12/95	ThmCa	C	6	H	11	O	2	0	G	5
C*CCCCC	-9.97	92.47	31.48	40.10	47.53	53.93	64.13	71.63	82.99	0/12/95	ThmCa	C	6	H	12		0	0	G	4
CC*CCCC	-12.91	91.63	31.19	39.66	47.01	53.38	63.63	71.24	82.78	0/12/95	ThmCa	C	6	H	12		0	0	G	4
C*CCQCCC	-33.54	106.72	40.14	49.94	58.19	65.11	75.80	83.37	94.50	0/12/95	ThmCa	C	6	H	12	O	2	0	G	6
QCC*CCCC	-33.49	111.74	39.98	49.12	56.94	63.62	74.17	81.85	93.37	0/12/95	ThmCa	C	6	H	12	O	2	0	G	6
CC*CCQCC	-36.48	108.07	39.80	49.52	57.74	64.66	75.39	83.04	94.34	0/12/95	ThmCa	C	6	H	12	O	2	0	G	6
CCQC*CCC	-36.31	108.45	39.52	49.40	57.71	64.70	75.48	83.12	94.36	0/12/95	ThmCa	C	6	H	12	O	2	0	G	6
CYC6H5C.	48.71	75.65	25.93	33.76	40.35	45.88	54.37	60.27	68.50	0/12/95	ThmCa	C	7	H	7		0	0	G	1
C6H5CH3	11.81	76.83	25.18	33.37	40.36	46.32	55.66	62.35	71.98	0/12/95	ThmCa	C	7	H	8		0	0	G	1
CYC6H5C	11.81	76.83	25.18	33.37	40.36	46.32	55.66	62.35	71.98	0/12/95	ThmCa	C	7	H	8		0	0	G	1
LINC7H9.	90.89	90.74	33.36	41.41	48.04	53.49	61.67	67.36	76.10	0/12/95	ThmCa	C	7	H	9		0	0	G	3
LINC7H9VS	88.69	91.16	33.15	40.99	47.49	52.89	61.12	66.93	75.87	0/12/95	ThmCa	C	7	H	9		0	0	G	3
LINC7H10	31.77	89.35	33.52	42.21	49.43	55.40	64.47	70.85	80.62	0/12/95	ThmCa	C	7	H	10		0	0	G	3
C*CC2CC*C	11.73	96.96	34.78	43.98	51.83	58.54	69.11	76.81	88.48	0/12/95	ThmCa	C	7	H	12		0	0	G	4
C*CCICCC*	13.26	96.14	34.02	43.53	51.61	58.46	69.20	76.96	88.66	0/12/95	ThmCa	C	7	H	12		0	0	G	4
C*CC2CC*C	11.73	98.34	34.92	44.02	51.84	58.53	69.13	76.87	88.45	0/12/95	ThmCa	C	7	H	12		0	0	G	5
C*CCCCCC.	34.10	105.30	36.17	45.69	53.88	60.90	72.05	80.21	92.51	0/12/95	ThmCa	C	7	H	13		0	0	G	5
C*CCCCC.C	31.45	106.33	35.29	44.71	52.88	59.95	71.27	79.58	91.93	0/12/95	ThmCa	C	7	H	13		0	0	G	5
C*CC.CCCC	18.60	98.08	35.52	45.30	53.72	60.96	72.45	80.85	93.31	0/12/95	ThmCa	C	7	H	13		0	0	G	5
C*CCCCCC	-14.90	101.89	36.91	47.05	55.78	63.28	75.21	83.96	97.17	0/12/95	ThmCa	C	7	H	14		0	0	G	5
C3CCIC*C	-22.52	90.93	37.85	48.49	57.50	65.11	76.93	85.36	97.92	0/12/95	ThmCa	C	7	H	14		0	0	G	5
C*CYHEPE.	51.65	85.70	32.49	43.59	52.87	60.59	72.34	80.53	92.55	0/12/95	ThmCa	C	8	H	11		0	0	G	0
C*CYHEPE	19.92	85.64	32.85	44.45	54.24	62.48	75.21	84.21	97.37	0/12/95	ThmCa	C	8	H	12		0	0	G	0
DIC2.C*C	3.28	105.89	40.92	51.40	60.40	68.09	80.28	89.21	102.78	0/12/95	ThmCa	C	8	H	14		0	0	G	5
C3.CCC3	-4.80	101.22	45.10	58.20	69.20	78.40	92.53	102.48	117.26	0/12/95	ThmCa	C	8	H	17		0	0	G	6
C3.CCC3	-4.80	101.22	45.10	58.20	69.20	78.40	92.53	102.48	117.26	0/12/95	ThmCa	C	8	H	17		0	0	G	6
C2C.COCC3	-46.40	115.70	47.18	59.35	69.86	78.90	93.36	104.03	120.34	0/12/95	ThmCa	C	8	H	17	O	1	0	G	7
C3CCC3Q.	-45.33	116.88	51.89	65.61	77.14	86.81	101.68	112.19	127.69	0/12/95	ThmCa	C	8	H	17	O	2	0	G	8
C2C.COOTB	-35.26	125.47	51.78	64.38	75.31	84.75	99.88	111.03	127.56	0/12/95	ThmCa	C	8	H	17	O	2	0	G	8
C3.COOCC3	-37.46	121.94	53.02	66.48	77.85	87.44	102.32	112.93	128.59	0/12/95	ThmCa	C	8	H	17	O	2	0	G	8
C3CCC3	-53.80	95.62	45.88	59.58	71.11	80.79	95.70	106.22	121.72	0/12/95	ThmCa	C	8	H	18		0	0	G	7
C3CCC3	-53.80	95.62	45.94	59.60	71.12	80.81	95.72	106.21	121.38	0/12/95	ThmCa	C	8	H	18		0	0	G	9
C3CCCICC	-54.13	101.22	45.33	58.52	69.77	79.32	94.28	105.06	121.14	0/12/95	ThmCa	C	8	H	18		0	0	G	7
C2CCOCC3	-90.82	111.82	48.10	61.76	73.31	83.05	98.20	109.10	125.71	0/12/95	ThmCa	C	8	H	18	O	1	0	G	7
C2CCOOCC3	-79.68	121.59	52.80	66.78	78.68	88.79	104.63	116.04	132.90	0/12/95	ThmCa	C	8	H	18	O	2	0	G	8
C3COOCC3	-86.48	114.97	53.84	67.87	79.77	89.82	105.47	116.68	133.25	0/12/95	ThmCa	C	8	H	18	O	2	0	G	8
INDENE.	71.57	82.83	28.22	38.22	46.45	53.19	63.15	69.79	78.93	0/12/95	ThmCa	C	9	H	7		0	0	G	0

INDENE	39.82	82.77	29.11	39.16	47.61	54.70	65.52	72.98	83.34	0/12/95 ThmCa	C	9	H	8		0		0	G	0
INDANEAL.	46.39	84.58	30.40	41.86	51.31	59.07	70.55	78.16	88.53	0/12/95 ThmCa	C	9	H	9		0		0	G	0
CC7H913V.	88.48	51.40	38.38	49.99	59.59	67.46	78.94	86.16	94.28	0/12/95 ThmCa		9		9		0		0	G	1
INDANE	14.66	83.14	30.75	42.63	52.53	60.72	73.03	81.35	92.84	0/12/95 ThmCa	C	9	H	10		0		0	G	0
CC7H1013V	31.56	89.54	38.50	51.11	61.56	70.11	82.61	90.49	99.41	0/12/95 ThmCa	C	9	H	10		0		0	G	1
PHPH.	103.84	98.14	38.92	51.70	62.16	70.70	83.29	91.74	103.83	0/12/95 ThmCa	C	12	H	9		0		0	G	1
CLBIPHENY	35.51	103.68	43.13	56.78	67.87	76.84	89.87	98.40	110.24	0/12/95 ThmCa	C	12	H	9	CL	1		0	G	1
BIPHENYL	42.92	93.91	39.29	52.94	64.17	73.38	87.02	96.19	109.08	0/12/95 ThmCa	C	12	H	10		0		0	G	1
C.*C*O	41.36	60.50	12.23	13.70	14.81	15.64	16.72	17.36	18.37	10/25/96	C	2	H	1	O	1		0	G	0
*N	112.97	36.61	4.97	4.97	4.97	4.97	4.97	4.97	4.97	J 3/61	N	1		0		0		0	G	0
NH	85.76	43.29	6.92	6.96	7.01	7.08	7.26	7.46	8.00	melius/91	N	1	H	1		0		0	G	0
NH1	120.89	41.67	6.87	7.03	7.18	7.33	7.62	7.88	8.41	RADICALC/92	N	1	H	1		0		0	G	0
NO	21.58	50.34	7.00	7.20	7.37	7.54	7.83	8.08	8.53	J 6/63	N	1	O	1		0		0	G	0
CN	104.01	48.41	6.87	7.05	7.23	7.39	7.70	7.97	8.48	J 6/69	C	1	N	1		0		0	G	0
NH2	45.49	46.51	8.07	8.25	8.51	8.81	9.49	10.18	11.53	L 9/81	N	1	H	2		0		0	G	0
HNO	25.40	52.73	8.27	8.81	9.33	9.82	10.70	11.42	12.51	WA/93	H	1	N	1	O	1		0	G	0
HON	61.04	51.24	8.27	8.81	9.33	9.82	10.70	11.42	12.51	HF MELIUS93	H	1	N	1	O	1		0	G	0
HONT	50.00	54.01	8.27	8.81	9.33	9.82	10.70	11.42	12.51	HF MELIUS93	H	1	N	1	O	1		0	G	0
NO2	7.91	57.35	8.84	9.65	10.35	10.95	11.87	12.48	13.18	J 9/64	N	1	O	2		0		0	G	0
NNH	59.58	53.63	8.46	8.93	9.41	9.89	10.79	11.54	12.60	Melius93	N	2	H	1		0		0	G	0
N2O	19.61	52.55	9.27	10.18	10.93	11.55	12.48	13.10	13.93	J12/64	N	2	O	1		0		0	G	0
HCN	32.30	48.20	8.60	9.32	9.94	10.47	11.34	12.02	13.18	L12/69	H	1	C	1	N	1		0	G	0
HNC	45.20	49.20	8.60	9.32	9.94	10.47	11.34	12.02	13.18	MEL/LIN92	H	1	C	1	N	1		0	G	0
NCO	31.60	55.49	9.59	10.48	11.22	11.83	12.74	13.34	14.09	HFEASTJ12/70	N	1	C	1	O	1		0	G	0
NCN	107.01	56.47	10.16	10.81	11.35	11.79	12.47	12.95	13.74	MELIUS/93		0	C	1	N	2		0	G	0
CLNO	12.35	62.51	10.71	11.24	11.69	12.07	12.64	13.01	13.46	NOCL	N	1		0	CL	1	O	1	G	0
NH3	-10.97	46.03	8.56	9.32	10.08	10.83	12.25	13.50	15.78	J 9/65	N	1	H	3		0		0	G	0
HNOH	21.60	57.81	10.29	11.26	12.14	12.92	14.25	15.28	16.84	JWB/94	N	1	H	2	O	1		0	G	1
NH2O	15.90	55.71	9.30	10.39	11.36	12.22	13.68	14.84	16.78	M/JB86	N	1	H	2	O	1		0	G	0
HNO2	-14.15	56.75	9.07	10.43	11.64	12.71	14.46	15.75	17.57	SANDIA90	N	1	H	1	O	2		0	G	0
HNOO	56.30	59.71	10.55	11.92	13.15	14.24	16.01	17.26	18.59	MELIUS88	N	1	H	1	O	2		0	G	1
HONO	-18.60	60.71	10.56	11.80	12.85	13.73	15.10	16.06	17.38	NBS	N	1	H	1	O	2		0	G	1
N2H2	50.00	52.22	8.62	9.87	10.97	11.93	13.53	14.76	16.85	J12/65	N	2	H	2		0		0	G	0
H2NN	68.91	53.27	8.58	9.51	10.41	11.27	12.84	14.16	16.40	M93/JBPM3 96	N	2	H	2		0		0	G	0
HNNO	55.39	60.56	10.73	12.13	13.29	14.25	15.72	16.72	18.14	MELIUS	N	2	H	1	O	1		0	G	0
H2CN	59.12	53.60	9.17	10.41	11.55	12.58	14.29	15.57	17.33	MELIUS 88	H	2	C	1	N	1		0	G	0
HCNH	66.12	55.92	9.13	10.37	11.49	12.48	14.14	15.40	17.28	MELIUS 88	H	2	C	1	N	1		0	G	0
HCNO	42.13	58.01	11.21	12.59	13.72	14.66	16.08	17.04	18.37	LAY/BOZ94	H	1	N	1	C	1	O	1	G	0
HNCO	-24.30	57.54	11.07	12.27	13.28	14.11	15.39	16.28	17.60	SAND90	H	1	N	1	C	1	O	1	G	0
HOCN	-2.28	57.87	11.08	12.04	12.90	13.66	14.92	15.87	17.25	SAND/LAY	H	1	N	1	C	1	O	1	G	1
HCNN	109.01	59.36	10.66	12.10	13.33	14.39	16.01	17.10	18.41	CHEMACT91	C	1	H	1	N	2		0	G	0
NCCN	73.91	57.71	13.61	14.69	15.59	16.33	17.46	18.24	19.41	BENSON/76		0	C	2	N	2		0	G	0
NH2OH	-10.50	56.19	10.46	12.18	13.63	14.85	16.78	18.21	20.65	JWB/SAND88	N	1	H	3	O	1		0	G	1
HONHO	4.70	62.51	11.87	14.49	16.60	18.28	20.62	21.99	23.44	M/JB86	N	1	H	2	O	2		0	G	1

N2H3	48.10	54.63	10.50	12.29	13.84	15.18	17.35	18.98	21.51	J12/65	N	2	H	3		0		0	G	1
NH2NO	17.90	60.31	12.03	14.32	16.27	17.91	20.40	22.07	24.00	M/JB189	N	2	H	2	O	1		0	G	1
HNNOHC	21.48	62.05	11.74	14.16	16.19	17.88	20.40	22.05	23.96	M/88 AVG	N	2	H	2	O	1		0	G	1
HNNOHT	19.30	61.71	11.77	14.63	16.88	18.61	20.93	22.21	23.57	M/88 AVG	N	2	H	2	O	1		0	G	1
HNNHO	26.30	58.70	10.53	12.88	14.89	16.59	19.24	21.09	23.46	M/B686	N	2	H	2	O	1		0	G	1
H2C*NH	21.85	55.95	9.47	10.94	12.42	13.86	16.48	18.62	21.72	MELIUS 88	H	3	C	1	N	1		0	G	0
CH2NO	41.43	61.03	11.77	13.86	15.59	17.03	19.19	20.70	22.93	MELIUS 88	H	2	N	1	C	1	O	1	G	0
N*CHOH	13.85	62.91	12.44	14.57	16.23	17.50	19.25	20.39	22.40	MELIUS 88	H	2	N	1	C	1	O	1	G	0
CH2NN	68.46	57.97	11.77	13.86	15.59	17.03	19.19	20.70	22.93	MELIUS 88	H	2	N	2	C	1		0	G	0
N2H4	22.79	57.04	12.26	14.72	16.77	18.49	21.14	23.08	26.23	J12/65	N	2	H	4		0		0	G	1
H2NNHO	33.96	64.41	13.65	15.70	17.45	18.94	21.30	23.07	26.01	m93/jwb96pm3	N	2	H	3	O	1		0	G	1
HNNNH2	54.08	60.68	12.58	14.84	16.81	18.51	21.26	23.32	26.51	MOPAC/JWB	N	3	H	3		0		0	G	1
CH3N.H	43.26	59.68	11.15	13.24	15.08	16.70	19.40	21.52	25.10	THERM92	H	4	C	1	N	1		0	G	1
C.H2NH2	36.26	57.93	12.98	14.98	16.72	18.24	20.75	22.69	25.93	THERM92	H	4	C	1	N	1		0	G	1
CH3NO	18.50	63.49	12.06	14.21	16.14	17.86	20.75	22.97	26.36	MELIUS93	H	3	N	1	C	1	O	1	G	1
CH3NH2	-5.50	57.99	12.01	14.49	16.77	18.84	22.41	25.26	29.85	SWS	H	5	C	1	N	1		0	G	1
NH2CH2O	2.16	65.56	13.06	15.80	18.21	20.32	23.78	26.40	30.51	6/ 3/94	C	1	H	4	O	1	N	1	G	1
CH2*NNH2	45.46	63.11	13.82	16.69	19.27	21.58	25.42	28.31	32.34	THERM/92	H	4	N	2	C	1		0	G	1
CH3N*NH	42.77	61.39	13.66	16.28	18.65	20.79	24.39	27.16	31.30	THERM/92	H	4	N	2	C	1		0	G	1
HNO3	-32.10	63.67	12.84	15.11	16.93	18.36	20.37	21.63	23.37	J 6/63	H	1	N	1	O	3		0	G	0

APPENDIX G

PRESSURE-DEPENDENT MECHANISM

Detailed pressure and temperature dependent elementary reaction mechanism for C1-C2 hydrocarbon with nitrogen chemistry.

```
!Master Eqn for Cheby with dates after 01/01/2001  all cheby prior are by chemdis-cheby
!
!**** Nov 6, 2001 Entry********
! The following subsystems were calc at 300-1500K 0.001-100atm  7x3 Cheby  - CYS 11/02/01
!       CH3OH  (current work 11/2001)
!       HCCH to vinylidene  (IJCK/2000/CS/JWB) (Chem phys lett laskin/wang)
!       C2H2 + O2   (IJCK/2000/CS/JWB)
!       CH3+CO    (NIST 2001- jwl/jwb)
!       CH3C.O+O2  (NIST 2001- jwl/jwb)
!       C.CHO+O2  (NIST 2001- jwl/jwb)
!       CC.+O2    (submit jpc 2001 cs/jwb/amd/ayc)
!       C2H3+O2   (zeit phys. 2000  ayc/amd/jwb)
!Unified the species to be consistent with meohcys2.lst
!removed redundant specie nomeclature.
!*****End Nov 6,2001 entry*** CYS ****
!
!**** Nov 19, 2001 Entry********
!Recalculated the CH2OH+O2 system using Jeff's rate constants from his
!PhD dissertation using Cheby Master Equation with following conditions
!       7x3 Cheby, 250-2500K, 0.001-100 atm at 50x50 grid.
!**** End Nov 19, 2001 Entry**** CYS ****
!
!**** Nov 20, 2001 Entry********
!Add in reactions to form HCO2H.  The 3 rxns of Held/Dryer are included in this
!mec file, but are commented out.  Instead will use the series of reactions base
!on estimation from JWB.
!**** End Nov 20, 2001 Entry*** CYS *****
!
!**** Dec 14, 2001 Entry********
! The following subsystems were calc at 250-2500K 0.001-100atm  7x3 Cheby
!   using a 50x50 matrix for Master Eqn.  The following reaction sets supersedes any
!   previously calculated reaction systems  - CYS 12/13/01
!       CH3+CO    (NIST 2001- jwl/jwb)
!       CH3C.O+O2  (NIST 2001- jwl/jwb)
!       C.CHO+O2  (NIST 2001- jwl/jwb)
!       C2H3+O2   (zeit phys. 2000  ayc/amd/jwb)
!       CH3+O2    k(inf) using jeff's phd dissertation input.
!                 Ea of CH2O+OH from Yu/Wang/Frenklach JPC 1995
!       CH2OH+O2  k(inf) using Jeff's phd dissertation input.  Ea for CQ.H2OH => CH2OH+O2
!                 and CQ.H2OH => CH2OHOO using Theodore Dibble (Chem Phys Lett submit
2001) value.
!       HCO+O2    BASE ON RECENT CALCULATIONS BY Hsu/mebel/Lin 1996 JPC publication
!                 USING AB INITIO AND VTST CALCULATIONS.       -  CYS 12/14/2001
!       CH3+CH3   rate constants from AMD JPC(86).  Ea for molec elim to c2h4+h2 from
!                 Gordon/Truong/Popel Chem Phys Lett 86 A-factor Hidaka et al IJCK90
!       COC.+O2   k(inf) from Tak Yamada's PhD dissertation.
!       C.CHO+O2  (NIST 2001- jwl/jwb) using Master Eqn w/ 50x50 matrix.
!       CH3+CO    (NIST 2001- jwl/jwb) using Master Eqn with 50x50 matrix.
!       CC.*O+O2  (NIST 2001- jwl/jwb) using Master Eqn w/ 50x50 matrix.
!Unified the species to be consistent with meohcys2.lst
!removed redundant specie nomeclature.
!*****End Dec 14,2001 entry*** CYS ****
!
!*****Dec 21, 2001 Entry*******************************
!  Add in the nitrogen mechanism of Dean/Bozzelli.  Refer to Gardiner (Editor)
!  book "Gas-phase Combustion Chemistry" for details.
!  "Gas Phase Combustion Chemistry", Verlag-Springer 2000
!
!  The nitrogen system is at the end of this hydrocarbon mechanism.
!
!  In the nitrogen system, AMD/JWB used "CH3O." while in the C1-C2 system
!  "CH3O" is used.  The "CH3O." specie in nitrogen system is changed to
!  "CH3O".
!  Other species changed in nitrogen system.
!  C.H2OH    =>  CH2OH
!
!                                                     - CYS 12/21/2001
!*****End Dec 21, 2001 Entry********************************
```

```
!*****Dec 24, 2001 Entry********************************
!  After running INFERNO, found out some radical specie concentrations are too
!  high b/c of lack of destruction for these species.
!  Destruction of these species are estimated from DHT method mention in
!  Gas-Phase Combustion book, Editor = W.C. Gardiner, Chapter by AMD/JWB.
!
!  Destruction of species are O*CCOH, HCJJCHOT, CYC.CO, HCO2H, O*CC*O and CYCCO.
!
!                                         - CYS 12/24/2001
!*****End Dec 24, 2001 Entry**********************************

ELEMENTS
H C O N AR
END
SPECIES
CH4               CH3OH             CO                CO2               CH2O
C2H4              C2H6              COC               COCOC             C2H2
C3COC             C2C*C             C*CC              H2O               O2
H2                HO2               H2O2              AR                N2
OH                O                 H                 CH2OH             CH3O
CH3               CH2               CH2S              CH                HCO
HCOH              C                 COC.              COCOC.            COCOH
COCO.             C.OCOH            CQ.H2OH           CO.H2OH           CH2OHOO
CQH2O.            C.QOH
C2H5              C2H               C2H3
HCQ*O             HOC.HOO.T         HCO2H             O.HC.OOHT         HOCHO.O.
HCCO              C.COH             CCO.              CCO2              CCO3
CC.OH             CH3OO             CCOO              CH3OOH            C*COOH
CCOH              CCOOH             C.COOH            CH3CHO            HCQ.*O
HCO2.             CCC.              CCC               C*C*O             CC.*O
CCQO.             COHCQ.            C.OHCQ            CO.CQ             CCQ.OH
C*COH             CCO3H             CYC.CO            C.CHO             CYCCO
COC.OC            COC.OH            CH2OOH            C.Q*O
C*COO.            C.*COOH           CYCOOC.           O*CCO.
O*CC*O            C.*CC             C#CC              C*CC.             C*C*C
C.*COH            HC#COH            C*CO.             C.OCQ
CC.OOH            COCQ.             COHC.OOH          O*CCOH            C.CQOH
CC.QOH            O*COOHC           CCO2H             CC.C              O*CCQ
C3C               C3C.              C2CC.
C*C(C)OC          C2.C*C            CC*C.             C#CC.
C2C*O             C2COC.            C2.COC            C2C.OC
C3COC.            C3.COC            C3COO             C3CO.             C3.COOH
HC*OCOO.          C.*OCOOH          H2C*CJJ           CJJYCOO           CJ*OCHO
HCJOJ*CHO         HCJ*COOJ          HOC.HQ            CJCOQ             CC*OOJ
OCYCO             C.CYCOO           C.OCHO            CCOQJ             HCJJCHOT
NH3 NO N2O NO2
N   HNO2 NH NH2 NNH N2H4 N2H3 N2H2  H2NN HNOH
HNO HON  HNOO  HONO HNNO NH2O
NH2NO   NH2OH HNNNH2 H2NNHO HONHO HNNHO
HCN CN HCNO NCO HNCO HOCN
CH3NO H2CN HCNH CH2NN HCNN HNC CH2NO N*CHOH  NCN  NCCN
CH3NH2 CH3N.H  C.H2NH2 H2C*NH CH2*NNH2 CH3N*NH
C.*C*O
END
REACTIONS
O + O + M             <=> O2 + M                1.88E+13    0.0     -1788. !86 TSANG
      AR/1.0/
H + O + M             <=> OH + M                4.71E+18   -1.0         0. !86 TSANG
H + O2                <=> O + OH                1.99E+14    0.0     16802. !92 BAULCH
H + O2 + M            <=> HO2 + M               6.16E+17   -0.8         0. !92 BAULCH
      AR/1.0/ H2/3.41/ N2/2.29/ H2O/2.53/
H + H + M             <=> H2 + M                6.52E+17   -1.0         0. !92 BAULCH
      AR/1.0/ N2/1.53/
H2 + O                <=> H + OH                5.12E+04    2.67     6285. !92 BAULCH
OH + H + M            <=> H2O + M               8.34E+21   -2.0         0. !92 BAULCH
      AR/1.0/ N2/2.65/ H2O/16.96/
OH + OH               <=> H2O + O               1.51E+09    1.14       99. !92 BAULCH
OH + H2               <=> H + H2O               1.02E+08    1.60     3298. !92 BAULCH
HO2 + O               <=> OH + O2               3.25E+13    0.0         0. !92 BAULCH
HO2 + H               <=> OH + OH               1.69E+14    0.0       874. !92 BAULCH
HO2 + H               <=> H2 + O2               4.28E+13    0.0      1411. !92 BAULCH
```

```
HO2 + H              <=> H2O + O              3.01E+13     0.0       1721. !92 BAULCH
HO2 + OH             <=> H2O + O2             2.89E+13     0.0       -497. !92 BAULCH
HO2 + HO2            <=> H2O2 + O2            1.87E+12     0.0       1540. !92BAULCH/500-
1250K
H2O2 + M             <=> OH + OH + M          1.21E+17     0.0      45507. !92 BAULCH
H2O2 + H             <=> H2O + OH             1.02E+13     0.0       3577. !92 BAULCH
H2O2 + H             <=> H2 + HO2             1.69E+12     0.0       3756. !92 BAULCH
H2O2 + O             <=> OH + HO2             9.63E+06     2.0       3974. !92 BAULCH
H2O2 + OH            <=> H2O + HO2            7.83E+12     0.0       1311. !92 BAULCH
C + O2               <=> O + CO               5.80E+13     .000       576.
C + OH               <=> H + CO               5.00E+13     .000         0.
C + CH2              <=> H + C2H              5.00E+13     .000         0.
C + CH3              <=> H + C2H2             5.00E+13     .000         0.
CO + O + M           <=> CO2 + M              6.17E+14     0.0       3001. !86 TSANG
       H2/2.0/ O2/6.0/ H2O/6.0/ CH4/2.0/ CO/1.5/ CO2/3.5/ C2H6/3.0/ AR/0.5/
CO + OH              <=> CO2 + H              6.32E+06     1.50      -497. !92 BAULCH
CO + O2              <=> CO2 + O              2.53E+12     0.00     47693. !86 TSANG
CO + HO2             <=> CO2 + OH             1.51E+14     0.00     23648. !86 TSANG
CH + O               <=> H + CO               5.70E+13     .000         0.
CH + O2              <=> CO + OH              3.31E+13     0.0          0. !92 BAULCH
CH + O2              <=> HCO + O              3.31E+13     0.0          0. !92 BAULCH
CH + H               <=> C + H2               1.10E+14     .000         0.
CH + OH              <=> H + HCO              3.00E+13     .000         0.
CH + H2              <=> CH3                  1.45E+14     0.00      3497. !92 BAULCH
CH + H2O             <=> H + CH2O             1.71E+13     .000      -755.
CH + CH2             <=> H + C2H2             4.00E+13     .000         0.
CH + CH3             <=> H + C2H3             3.00E+13     .000         0.
CH + CH4             <=> H + C2H4             6.00E+13     .000         0.
CH + CO (+M)         <=> HCCO (+M)            5.00E+13     .000         0.
     LOW  /  2.690E+28   -3.740   1936.00/
     TROE/   .5757  237.00  1652.00  5069.00 /
     H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
CH + CO2             <=> HCO + CO             3.40E+12     .000       690.
CH + CH2O            <=> H + C*C*O            9.46E+13     .000      -515.
CH + HCCO            <=> CO + C2H2            5.00E+13     .000         0.
!HCO + M               <=> CO + H + M           1.87E+17    -1.00     17000. !87TIMONEN
HCO + M  <=>   CO + H + M                     4.62e13      0.0       15544.9 ! Krasnoperov
2000 16th Gas Kin. conf.
    H2/2.0/ H2O/6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6/3.0/ AR/0.7/ N2/1.0/
HCO + O              <=> CO + OH              3.01E+13     0.00         0.
!92BAULCH/86TSANG
HCO + O              <=> H + CO2              3.00E+13     0.00         0. !SRI2
HCO + H              <=> CO + H2              9.04E+13     0.00         0. !92 BAULCH
HCO + OH             <=> CO + H2O             3.00E+13     0.00         0. !92 BAULCH
HCO + HO2            <=> CO2 + OH + H         3.00E+13     0.00         0. !92 BAULCH
HCO + CH3            <=> CH4 + CO             1.21E+14     0.00         0. !86 TSANG
!*****************************************************************************************
**
!************HCO + O2 MODIFIED BASE ON RECENT CALCULATIONS BY Hsu/mebel/Lin 1996 JPC
publication
!************USING AB INITIO AND VTST CALCULATIONS.       -  CYS 12/14/2001
!************BEGIN HCO + O2
BLOCK**********************************************************
HCO + O2 (+M)        <=> HCO2. + O (+M)       1.00E+00     .000         0. ! ING341   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.1338E+00 -4.2012E-02 -3.0570E-02  3.6623E+00/
    CHEB/  5.3923E-02  3.8997E-02  3.0405E-02 -8.6167E-03 -5.8740E-03/
    CHEB/ -5.2534E-02 -4.4954E-03 -3.4104E-03  4.9426E-03  4.4950E-04/
    CHEB/  2.8644E-04  2.2599E-02  1.0334E-03  7.6782E-04 -1.1284E-02/
    CHEB/ -3.1293E-04 -2.1614E-04/
HCO + O2 (+M)        <=> HCQ.*O (+M)          1.00E+00    0.000         0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.8081E+00  5.4660E+00  7.3867E-01 -2.8830E+00/
    CHEB/ -5.9109E-01  3.5536E-01 -1.0156E+00 -3.1307E-01 -9.7823E-02/
    CHEB/ -3.9917E-01 -1.0764E-01 -5.5494E-02 -1.5645E-01 -3.2124E-02/
    CHEB/ -1.8572E-02 -6.3296E-02 -9.0699E-03 -5.3399E-03 -2.7179E-02/
    CHEB/ -2.7236E-03 -1.4804E-03/
HCO + O2 (+M)        <=> CO + HO2 (+M)        1.00E+00    0.000         0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2643E+01 -3.5599E-02 -3.0043E-02  1.5111E-01/
    CHEB/  5.3487E-02  4.4706E-02  9.3923E-02 -1.9666E-02 -1.5710E-02/
```

```
    CHEB/  3.9383E-02 -1.3515E-04 -6.6401E-04  1.7704E-02  1.9995E-03/
    CHEB/  1.7208E-03  7.3735E-03  2.3821E-04  2.7734E-04  2.9269E-03/
    CHEB/ -2.5499E-04 -2.1476E-04/
    DUPLICATE
HCO + O2 (+M)        <=> C.Q*O (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -7.4932E+00  5.0667E+00  1.3506E+00 -3.6821E-01/
    CHEB/ -1.3991E+00 -5.7553E-01 -8.2875E-01 -2.9497E-01 -1.8116E-01/
    CHEB/ -2.6843E-01 -1.0819E-01 -5.9417E-02 -6.9978E-02 -6.1531E-02/
    CHEB/ -3.0576E-02 -4.3259E-03 -4.1300E-02 -2.0242E-02  1.3129E-02/
    CHEB/ -2.8295E-02 -1.4521E-02/
HCO + O2 (+M)        <=> CO + HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.1614E+00 -2.1529E-02 -1.6442E-02  3.3235E+00/
    CHEB/  2.8801E-02  2.2047E-02  3.8404E-01 -6.3964E-03 -4.9733E-03/
    CHEB/  1.2295E-01 -1.4413E-03 -1.0635E-03  3.6009E-02  3.6434E-04/
    CHEB/  2.8441E-04  1.2032E-02  1.9842E-04  1.4693E-04  5.4637E-03/
    CHEB/  1.2912E-05  8.3816E-06/
    DUPLICATE
HCO + O2 (+M)        <=> CO2 + OH (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.0717E+00 -1.9109E-02 -1.4614E-02  3.1484E+00/
    CHEB/  2.5031E-02  1.9196E-02  2.9392E-01 -4.8041E-03 -3.7673E-03/
    CHEB/  9.6442E-02 -1.5631E-03 -1.1578E-03  3.0204E-02  2.3542E-04/
    CHEB/  1.8745E-04  1.0572E-02  1.8697E-04  1.3872E-04  4.9436E-03/
    CHEB/  2.9762E-05  2.1029E-05/
HCQ.*O (+M)          <=> CO + HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       2.3335E-01  1.6219E+00 -2.8450E-01  7.7851E+00/
    CHEB/  7.5823E-01  1.9395E-01 -6.8054E-01  9.1936E-02  7.4730E-02/
    CHEB/ -2.5427E-01 -2.2404E-02 -7.6694E-04 -6.8666E-02 -1.3846E-02/
    CHEB/ -8.9286E-03 -5.2961E-03  1.1259E-03 -2.2974E-03  8.1666E-03/
    CHEB/  5.9882E-03  1.2628E-03/
HCQ.*O (+M)          <=> C.Q*O (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.8574E+01  6.4106E+00  1.2897E+00  1.3731E+01/
    CHEB/ -1.1773E+00  7.6801E-02 -9.5577E-01 -3.8635E-01 -1.6246E-01/
    CHEB/ -2.9666E-01 -1.0587E-01 -6.1515E-02 -7.3826E-02 -2.4746E-02/
    CHEB/ -1.6830E-02 -7.5823E-03 -2.5875E-03 -3.6927E-03  6.2919E-03/
    CHEB/  3.0016E-03 -1.8289E-04/
C.Q*O (+M)          <=> CO + HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.5741E+00  3.0400E+00  3.1610E-01  6.2587E+00/
    CHEB/ -2.8018E-01 -1.2107E-01 -6.4397E-01 -6.4999E-02 -5.2653E-02/
    CHEB/ -1.8970E-01 -8.9357E-03 -8.5182E-03 -3.9217E-02 -1.3547E-03/
    CHEB/ -1.2944E-03 -2.3552E-04 -6.3330E-04 -5.3507E-04  3.5917E-03/
    CHEB/ -3.6448E-04 -3.0317E-04/
C.Q*O (+M)          <=> CO2 + OH (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       3.7397E+00  2.3375E+00 -1.0733E-01  4.7946E+00/
    CHEB/  1.4461E-01  9.1610E-02 -5.9656E-01 -4.5867E-03 -7.4435E-04/
    CHEB/ -1.7706E-01 -2.6437E-03 -1.8911E-03 -3.3807E-02 -3.5037E-05/
    CHEB/ -4.1036E-05  2.3883E-03  2.1969E-04  1.7761E-04  4.8285E-03/
    CHEB/  1.1618E-04  9.4329E-05/
!***********END HCO + O2 BLOCK ***************************************************

CH2S + O             <=> H2 + CO              1.50E+13    .000        0.
CH2S + O             <=> H + HCO              1.50E+13    .000        0.
CH2S + H             <=> CH + H2              3.00E+13    .000        0.
CH2S + O2            <=> CO + H2O             1.20E+13    .000        0.
CH2S + OH            <=> CH2O + H             3.00E+13    .000        0.
CH2S + H2            <=> CH3 + H              7.23E+13    .000        0.
CH2S + H2O           <=> CH2 + H2O            3.00E+13    .000        0.
CH2S + CH3           <=> H + C2H4             1.20E+13    .000     -570.
CH2S + CO            <=> CH2 + CO             9.00E+12    .000        0.
CH2S + CO2           <=> CH2 + CO2            7.00E+12    .000        0.
CH2S + CO2           <=> CO + CH2O            1.40E+13    .000        0.
CH2S + M             <=> CH2 + M              1.00E+13    0.0         0. !MILLER
CH2S + CH4           <=> 2CH3                 4.00E+13    0.0         0. !MILLER
CH2S + C2H6          <=> CH3 + C2H5           1.20E+14    0.0         0. !MILLER
CH2S + O2            <=> CO + OH + H          3.00E+13    0.0         0. !MILLER
```

```
CH2S + H              <=> CH2 + H              2.00E+14    0.0          0. !MILLER
CH2 + H (+M)          <=> CH3 (+M)             2.50E+16    -.80         0.
     LOW  /  3.200E+27   -3.140   1230.00/
     TROE/   .6800   78.00  1995.00  5590.00 /
     H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
CH2 + H2              <=> H + CH3              5.00E+05    2.00      7230.
2CH2                  <=> H2 + C2H2            3.200E+13   .000         0.
CH2 + CH3             <=> H + C2H4             4.000E+13   .000         0.
CH2 + CH4             <=> 2CH3                 2.460E+06   2.00      8270.
CH2 + CO (+M)         <=> C*C*O (+M)           8.100E+11    .50      4510.
     LOW  /  2.690E+33   -5.110   7095.00/
     TROE/   .5907  275.00  1226.00  5185.00 /
     H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
CH2 + HCCO            <=> C2H3 + CO            3.00E+13    .000        0.
CH2 + O               <=> CO + H + H           5.00E+13    0.00         0. !MILLER
CH2 + O2              <=> CO2 + H + H          1.60E+12    0.00      1000. !MILLER
CH2 + O2              <=> CH2O + O             5.00E+13    0.00      9011. !MILLER
CH2 + O2              <=> CO2 + H2             6.90E+11    0.00       502. !MILLER
CH2 + O2              <=> CO + OH + H          8.60E+10    0.00      -502. !MILLER
CH2 + O2              <=> HCO + OH             4.30E+10    0.00      -502. !MILLER
CH2 + H               <=> CH + H2              4.00E+13    0.0          0. !MILLER
CH2 + OH              <=> CH + H2O             1.13E+07    2.0       3011. !MILLER
CH2 + OH              <=> CH2O + H             2.50E+13    0.0          0. !MILLER
HCOH (+M)             <=> CH2O (+M)            1.00E+00    .000         0. ! ING111    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.1562E+00  2.0857E+00 -2.0733E-01  1.8817E+00/
    CHEB/  4.3977E-01  2.0117E-01 -3.5772E-01 -7.3874E-03  1.4671E-02/
    CHEB/ -5.0220E-02 -2.7614E-02 -1.3531E-02  8.7047E-03 -6.1176E-03/
    CHEB/ -4.9343E-03  6.9705E-03  1.3861E-03  1.6764E-04  9.3469E-04/
    CHEB/  1.1733E-03  6.7250E-04/
HCOH + O2 (+M)         <=> HOC.HOO.T (+M)      1.00E+00     .000        0. ! ING121    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.8754E+00  2.4000E+00 -6.9109E-02 -1.3323E+00/
    CHEB/  1.2612E-01  8.5682E-02 -3.9071E-01 -2.0950E-02 -1.2240E-02/
    CHEB/ -7.1692E-02 -8.4939E-03 -6.5982E-03  5.6278E-03  4.6319E-04/
    CHEB/  9.7938E-05  7.1146E-03  1.3651E-03  1.0155E-03 -1.4034E-03/
    CHEB/  4.1476E-04  3.4317E-04/
HCOH + O2 (+M)         <=> HCO2H + O (+M)      1.00E+00     .000        0. ! ING121    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2574E+01 -9.4583E-02 -6.5484E-02 -1.3858E-01/
    CHEB/  1.2220E-01  8.3300E-02 -1.2444E-01 -2.2717E-02 -1.3643E-02/
    CHEB/ -5.6074E-02 -7.9480E-03 -6.2684E-03 -2.0959E-02  9.0130E-04/
    CHEB/  4.3887E-04 -7.1897E-03  1.3559E-03  1.0246E-03 -2.3980E-03/
    CHEB/  3.0783E-04  2.6385E-04/
HCOH + O2 (+M)         <=> O.HC.OOHT (+M)      1.00E+00     .000        0. ! ING121    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.3550E+00  2.3607E+00 -9.7302E-02 -4.0759E-01/
    CHEB/  1.8126E-01  1.2489E-01 -5.8387E-02 -4.1168E-02 -2.6111E-02/
    CHEB/ -4.8702E-03 -6.6320E-03 -5.6742E-03 -1.7010E-02  2.1535E-03/
    CHEB/  1.3989E-03 -1.6592E-02  1.2474E-03  9.7091E-04 -8.8423E-03/
    CHEB/  1.8141E-04  1.6455E-04/
HCOH + O2 (+M)         <=> HCO + HO2 (+M)      1.00E+00     .000        0. ! ING121    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.7604E+00 -1.0537E-01 -7.4657E-02  9.4673E-01/
    CHEB/  1.4115E-01  9.8933E-02  6.6641E-02 -3.6850E-02 -2.4383E-02/
    CHEB/ -2.1516E-03 -3.5706E-03 -3.3300E-03 -6.1249E-03  2.1393E-03/
    CHEB/  1.5085E-03 -4.1403E-03  8.8101E-04  7.0049E-04 -2.0348E-03/
    CHEB/  1.7186E-05  2.8953E-05/
HCOH + O2 (+M)         <=> HOCHO.O. (+M)       1.00E+00     .000        0. ! ING121    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.5693E+00  2.4055E+00 -6.5473E-02 -4.6626E-01/
    CHEB/  1.2204E-01  8.3276E-02 -9.1759E-02 -2.3037E-02 -1.3900E-02/
    CHEB/ -3.7390E-02 -7.8243E-03 -6.1866E-03 -2.3282E-02  9.6387E-04/
    CHEB/  4.8882E-04 -1.3562E-02  1.3487E-03  1.0215E-03 -6.7901E-03/
    CHEB/  2.9458E-04  2.5380E-04/
HCOH + O2 (+M)         <=> HCO2. + OH (+M)     1.00E+00     .000        0. ! ING121    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2463E+01 -9.4112E-02 -6.5226E-02 -6.5963E-02/
    CHEB/  1.2179E-01  8.3120E-02 -1.0078E-01 -2.3167E-02 -1.4001E-02/
    CHEB/ -4.8667E-02 -7.7882E-03 -6.1650E-03 -1.8865E-02  9.9518E-04/
    CHEB/  5.1314E-04 -6.7783E-03  1.3486E-03  1.0226E-03 -2.4298E-03/
```

```
    CHEB/  2.8742E-04  2.4861E-04/
HCOH + O2 (+M)       <=> CO2 + H2O (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0967E+01 -9.3770E-02 -6.4995E-02 -3.2750E-02/
    CHEB/  1.2155E-01  8.2975E-02 -8.5631E-02 -2.3291E-02 -1.4099E-02/
    CHEB/ -4.2054E-02 -7.7562E-03 -6.1459E-03 -1.6095E-02  1.0262E-03/
    CHEB/  5.3718E-04 -5.6744E-03  1.3493E-03  1.0240E-03 -2.0120E-03/
    CHEB/  2.8023E-04  2.4296E-04/
CH2O (+M)            <=> HCO + H (+M)         1.00E+00     .000       0. ! ING431   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.4865E+01  2.4983E+00 -1.2744E-03  2.7176E+01/
    CHEB/  2.0398E-03  1.5344E-03 -4.0470E-01 -3.1637E-04 -2.3747E-04/
    CHEB/ -1.7801E-01 -4.0163E-05 -3.0210E-05 -7.3725E-02 -7.1875E-06/
    CHEB/ -5.4854E-06 -2.9768E-02 -1.2684E-06 -9.4980E-07 -1.2275E-02/
    CHEB/ -1.7169E-07 -3.1177E-07/
CH2O (+M)            <=> CO + H2 (+M)         1.00E+00     .000       0. ! ING431   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.6268E+01  2.4663E+00 -2.4732E-02  2.1289E+01/
    CHEB/  3.9566E-02  2.8837E-02 -4.6831E-01 -4.8873E-03 -3.3334E-03/
    CHEB/ -2.1142E-01 -1.2857E-03 -1.0002E-03 -9.2226E-02 -1.7399E-04/
    CHEB/ -1.4019E-04 -3.9322E-02 -1.6145E-06 -1.8082E-06 -1.6707E-02/
    CHEB/  1.0825E-05  8.5672E-06/
CH2O + O             <=> HCO + OH             3.50E+13    0.0      3513. !HUN 94
CH2O + H             <=> HCO + H2             2.19E+08    1.77     3000. !86 TSANG
CH2O + OH            <=> HCO + H2O            3.44E+09    1.18     -447. !92 BAULCH/86
TSANG
CH2O + HO2           <=> HCO + H2O2           3.01E+12    0.0     13076. !92 BAULCH
CH2O + CH3           <=> HCO + CH4            5.54E+03    2.81     5862. !86 TSANG
HOC.HOO.T (+M)       <=> HCO + HO2 (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.1521E+00  2.3515E+00 -1.0373E-01  6.7230E+00/
    CHEB/  1.8812E-01  1.2943E-01 -3.7538E-01 -3.8917E-02 -2.4401E-02/
    CHEB/ -6.6129E-02 -7.7131E-03 -6.3515E-03  6.2980E-03  1.9514E-03/
    CHEB/  1.2115E-03  6.4857E-03  1.3587E-03  1.0405E-03 -1.8611E-03/
    CHEB/  2.7897E-04  2.3868E-04/
HOC.HOO.T (+M)       <=> CO2 + H2O (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       2.7856E+00  2.0202E+00 -2.2705E-01  3.4407E+00/
    CHEB/  5.2878E-01  2.2434E-01 -4.9591E-01 -1.0532E-02  2.3468E-02/
    CHEB/ -1.1532E-01 -4.2092E-02 -2.0364E-02 -8.3447E-03 -1.1935E-02/
    CHEB/ -9.6433E-03  4.5276E-03  2.2807E-03 -4.5572E-05 -1.5180E-03/
    CHEB/  3.2669E-03  1.8814E-03/
O.HC.OOHT (+M)       <=> HCO + HO2 (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.0115E+00  2.4367E+00 -4.4686E-02  1.8625E+00/
    CHEB/  8.1362E-02  5.6689E-02 -1.5311E-01 -2.0381E-02 -1.3303E-02/
    CHEB/ -5.1438E-03 -8.8841E-04 -1.0796E-03 -6.7028E-03  1.5635E-03/
    CHEB/  1.1257E-03 -9.1339E-03  1.0021E-04  1.1286E-04 -5.0691E-03/
    CHEB/ -1.6477E-04 -1.2066E-04/
O.HC.OOHT (+M)       <=> CO2 + H2O (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.9603E+00  2.3986E+00 -6.0571E-02  8.3622E-01/
    CHEB/  8.3202E-02  4.1942E-02 -1.6474E-01  3.9956E-02  3.3133E-02/
    CHEB/ -5.4621E-02 -2.1324E-02 -1.2735E-02 -3.3022E-02 -9.8959E-03/
    CHEB/ -8.7100E-03 -1.5086E-02  4.1572E-03  2.6470E-03 -6.4273E-03/
    CHEB/  2.6020E-03  2.2528E-03/
HOCHO.O. (+M)        <=> HCO + HO2 (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.2500E+01  2.3612E+00 -9.7133E-02  1.4780E+01/
    CHEB/  1.8024E-01  1.2441E-01 -8.8125E-02 -4.0654E-02 -2.5884E-02/
    CHEB/ -5.0792E-02 -6.8133E-03 -5.7570E-03 -2.8858E-02  2.1948E-03/
    CHEB/  1.4212E-03 -1.5079E-02  1.2623E-03  9.8156E-04 -7.0613E-03/
    CHEB/  1.8265E-04  1.6573E-04/
HOCHO.O. (+M)        <=> CO2 + H2O (+M)       1.00E+00     .000       0. ! ING121   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.4464E+00  2.4974E+00 -1.9593E-03  1.4572E+00/
    CHEB/  2.8658E-03  2.1535E-03 -8.1607E-02 -5.9869E-04 -4.4854E-04/
    CHEB/ -8.2366E-03  3.1303E-05  2.3178E-05 -5.2053E-03  1.8335E-05/
    CHEB/  1.3961E-05 -4.8180E-03  2.7942E-06  2.1542E-06 -3.1329E-03/
    CHEB/  5.6376E-07  4.9922E-07/
CH3 + O              <=> CH2O + H             1.34E+14   -0.08       79. !CHEM221
```

```
CH3 + O              <=> CH2OH                6.57E+12    0.04      -24. !CHEM221
CH3 + HO2            <=> CH3O + OH            1.81E+13    0.0         0. !92 BAULCH



!*************************************************************************
!************CH3+O2 subsystem uses Jeff's k(inf) and Frenklach's Ea for CH2O+OH.
!************calc using Master Eqn.    - CYS 12/14/2001
!************Begin CH3+O2 block********************************************
CH3+O2 (+M)          <=> CH3OO (+M)           1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.5044E+00  2.0206E+00 -2.3113E-01 -2.1946E+00/
    CHEB/  4.8217E-01  2.1200E-01 -1.1756E+00  2.5496E-02  3.1094E-02/
    CHEB/ -5.7909E-01 -2.4366E-02 -1.0247E-02 -2.7440E-01 -1.0356E-02/
    CHEB/ -6.3297E-03 -1.2946E-01 -1.2905E-03 -9.7158E-04 -6.2000E-02/
    CHEB/  4.8672E-04  3.3257E-04/
CH3+O2 (+M)          <=> CH2O+OH (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       2.0672E+00 -2.0956E-04 -1.9427E-04  5.9442E+00/
    CHEB/  3.5704E-04  3.3076E-04 -2.8324E-01 -2.1614E-04 -1.9985E-04/
    CHEB/ -1.6462E-01  8.6020E-05  7.9091E-05 -9.0188E-02 -1.6485E-05/
    CHEB/ -1.4877E-05 -4.8351E-02 -2.0332E-06 -2.0545E-06 -2.5683E-02/
    CHEB/  1.5274E-06  1.3972E-06/
CH3+O2 (+M)          <=> CH3O+O (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.9750E+00  3.4923E-07  2.4493E-07  1.1464E+01/
    CHEB/ -3.5742E-07 -2.5968E-07 -2.8127E-01  1.4637E-07  8.7686E-08/
    CHEB/ -1.6510E-01  6.4187E-08  5.5563E-08 -9.1196E-02  6.7522E-08/
    CHEB/  5.5937E-08 -4.9340E-02  3.6703E-08  1.4986E-08 -2.6506E-02/
    CHEB/ -1.9401E-08 -1.5932E-08/

!*************************************************************************
!************Modified CH3OH subsystem base on CBS-APNO for thermo and CTST
!************and VTST for hp kinetic.    - CYS 11/2001
!************Begin CH3OH block********************************************
CH3 + OH (+M)       <=> CH3OH (+M)            1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.1555E+01  1.7001E+00 -5.4287E-01 -1.1926E+00/
    CHEB/  1.1049E+00 -6.8443E-02 -4.0119E-01  2.1047E-01  5.9666E-02/
    CHEB/ -1.6227E-01  1.0455E-02  1.8481E-02 -5.6551E-02 -1.2394E-02/
    CHEB/ -1.7001E-04 -1.7310E-02 -5.7620E-03 -1.8340E-03 -4.8958E-03/
    CHEB/ -9.4940E-04 -3.8047E-04/
CH3 + OH (+M)       <=> CH2O + H2 (+M)        1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.7349E+00 -8.9596E-01 -2.6375E-01  6.0189E-01/
    CHEB/  9.3224E-01  2.0259E-01  6.3523E-02  4.4087E-02  8.6689E-02/
    CHEB/ -3.1875E-02 -7.2611E-02 -1.6255E-02 -8.6601E-03 -2.6554E-02/
    CHEB/ -1.7470E-02  3.2989E-03  2.5110E-04 -3.1876E-03  2.6929E-03/
    CHEB/  2.9614E-03  1.0370E-03/
CH3 + OH (+M)       <=> CH3O + H (+M)         1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.0822E+00 -2.4590E-01 -1.6150E-01  3.2960E+00/
    CHEB/  3.2046E-01  2.0064E-01  1.1781E-01 -5.4873E-02 -1.9862E-02/
    CHEB/  2.1332E-02 -2.4977E-02 -2.1573E-02  1.0085E-02  7.8817E-04/
    CHEB/ -1.5147E-03  5.2366E-03  3.8265E-03  2.9030E-03  1.8056E-03/
    CHEB/  1.1992E-03  1.2219E-03/
CH3 + OH (+M)        <=> CH2OH + H (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.8123E+00 -7.7455E-01 -2.7255E-01  1.3375E+00/
    CHEB/  8.3647E-01  2.3621E-01  1.4004E-01  1.5334E-02  7.0755E-02/
    CHEB/ -7.4970E-04 -6.7888E-02 -2.3240E-02  1.5411E-03 -2.2505E-02/
    CHEB/ -1.6954E-02  5.6774E-03  1.1975E-03 -2.1341E-03  3.1651E-03/
    CHEB/  3.1628E-03  1.4578E-03/
CH3 + OH (+M)        <=> CH2S + H2O (+M)      1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
```

```
    CHEB/  7   3       1.1227E+01 -6.5284E-01 -2.7599E-01  1.2994E+00/
    CHEB/  7.2771E-01  2.6032E-01  7.0072E-02 -9.1374E-03  5.2472E-02/
    CHEB/ -1.7657E-02 -5.9098E-02 -2.6947E-02 -2.9554E-03 -1.6500E-02/
    CHEB/ -1.4829E-02  3.9496E-03  1.9330E-03 -1.0531E-03  2.6063E-03/
    CHEB/  2.7147E-03  1.5761E-03/
CH3 + OH (+M)        <=> HCOH + H2 (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0696E+01 -9.2547E-01 -2.9874E-01  3.5976E-01/
    CHEB/  9.0940E-01  1.9159E-01 -6.8519E-03  7.2461E-02  1.0564E-01/
    CHEB/ -5.1443E-02 -5.4452E-02 -2.6759E-03 -1.7167E-02 -2.6764E-02/
    CHEB/ -1.5670E-02  1.2696E-04 -3.3706E-03 -5.0721E-03  2.3685E-03/
    CHEB/  1.6871E-03  4.5613E-05/
!************End CH3OH block  -CYS 11/2001*******************************************


!**************************************************************************
!************Modified CH3+CH3 system base on AMD estimates (JPC 86) and also from
!************Gordon/Truong/Pople for Ea of molec elim and Afactor from Hidaka IJCK90.
!************     - CYS 11/2001
!************Begin CH3+CH3 block*******************************************
CH3 +  CH3 (+M)      <=> C2H6 (+M)            1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2812E+01  6.1030E-01 -1.2037E-01 -1.2080E+00/
    CHEB/  8.4880E-01 -6.8703E-02 -8.0773E-01  4.0524E-01  4.5733E-02/
    CHEB/ -4.7927E-01  1.3469E-01  5.4921E-02 -2.6050E-01  1.9629E-02/
    CHEB/  2.6644E-02 -1.2994E-01 -1.2832E-02  4.3658E-03 -5.8494E-02/
    CHEB/ -1.3783E-02 -4.0510E-03/
CH3 +  CH3 (+M)      <=> C2H5 + H (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.9776E+00 -9.5623E-01 -3.0430E-01  3.9988E+00/
    CHEB/  9.0997E-01  2.1975E-01  9.6699E-02  1.8289E-01  1.2466E-01/
    CHEB/ -4.5716E-02 -5.0635E-02  8.6833E-03 -4.6767E-02 -6.8091E-02/
    CHEB/ -2.9140E-02 -1.9349E-02 -2.9803E-02 -2.1178E-02 -2.1257E-03/
    CHEB/ -1.9196E-03 -5.6993E-03/
CH3 +  CH3 (+M)      <=> C2H4 + H2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       3.9443E+00 -6.9600E-01 -3.0486E-01  5.5662E+00/
    CHEB/  6.9483E-01  2.6278E-01  4.9979E-02  1.0588E-01  9.0336E-02/
    CHEB/ -4.0140E-02 -4.9690E-02 -1.0392E-02 -3.4912E-02 -4.9025E-02/
    CHEB/ -2.8180E-02 -1.4060E-02 -1.7297E-02 -1.4501E-02 -2.4057E-03/
    CHEB/  1.5507E-03 -1.5874E-03/
C2H6 (+M)            <=> C2H5 + H (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.3198E+01  2.7431E+00 -9.8574E-01  3.6456E+01/
    CHEB/  1.4196E+00  6.6237E-02 -9.9158E-01  3.9904E-01  1.6180E-01/
    CHEB/ -5.3354E-01  9.2982E-02  7.3714E-02 -2.7457E-01  4.3014E-03/
    CHEB/  1.9808E-02 -1.3086E-01 -1.1619E-02  5.0296E-04 -5.6413E-02/
    CHEB/ -8.1261E-03 -2.8483E-03/
C2H6 (+M)            <=> C2H4 + H2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.8711E+01  4.3106E+00 -1.3129E+00  3.7901E+01/
    CHEB/  1.4129E+00  3.4142E-01 -1.0836E+00  3.1620E-01  2.1522E-01/
    CHEB/ -5.6427E-01  5.4066E-02  7.2552E-02 -2.8286E-01 -7.5146E-03/
    CHEB/  1.5262E-02 -1.3178E-01 -1.2576E-02 -1.7361E-04 -5.5863E-02/
    CHEB/ -6.6333E-03 -1.6851E-03/
!************END CH3+CH3 block*********************************************

CH3O + O2            <=> CH2O+HO2             3.61E+10    0.00     2126. !92 BAULCH
CH3O + O             <=> CH2O + OH            6.02E+12    0.00        0. !NORTON
CH3O + H             <=> CH2O + H2            1.99E+13    0.00        0. !NORTON
CH3O + OH            <=> CH2O + H2O           1.81E+13    0.00        0. !NORTON
CH3O + HO2           <=> CH2O + H2O2          3.01E+11    0.00        0. !NORTON
CH3O + CO            <=> CH3 + CO2            1.57E+13    0.00    11797. !NORTON
CH3O + CH2O          <=> CH3OH + HCO          1.02E+11    0.00     2981. !86 TSANG
CH3O + C2H6          <=> C2H5 + CH3OH         2.41E+11    0.00     7094. !86 TSANG
CH3O + CH3           <=> CH2O + CH4           2.41E+13    0.00        0. !86 TSANG
CH3O + CH3 (+M)      <=> COC (+M)             1.00E+00     .000       0. ! ING131    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2114E+01  6.9341E-01 -1.0286E-01 -1.6652E+00/
    CHEB/  1.0564E+00 -8.2152E-02 -1.1477E+00  5.2850E-01  4.1011E-02/
```

```
    CHEB/ -6.7729E-01  1.6105E-01  6.2820E-02 -3.5610E-01  2.4959E-03/
    CHEB/  3.2070E-02 -1.6871E-01 -3.3499E-02  4.5106E-03 -7.0487E-02/
    CHEB/ -2.5548E-02 -5.2867E-03/
CH3O + CH3 (+M)       <=> COC. + H (+M)        1.00E+00     .000        0. ! ING131   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3         4.4340E+00 -7.7128E-01 -2.8202E-01  4.9374E+00/
    CHEB/  8.2139E-01  2.5007E-01 -2.0666E-01  8.1549E-02  8.9885E-02/
    CHEB/ -1.7759E-01 -8.5995E-02 -2.1477E-02 -8.9828E-02 -5.5854E-02/
    CHEB/ -3.4125E-02 -3.1076E-02 -8.6274E-03 -1.2427E-02 -7.4614E-03/
    CHEB/  9.4737E-03  2.6644E-03/
CH3O + CH3 (+M)       <=> CH2S + CH3OH (+M)    1.00E+00     .000        0. ! ING131   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3         5.5054E+00 -7.7401E-01 -2.8258E-01  4.9065E+00/
    CHEB/  8.2208E-01  2.4960E-01 -2.1453E-01  8.3935E-02  9.0785E-02/
    CHEB/ -1.7833E-01 -8.5071E-02 -2.0849E-02 -8.9554E-02 -5.6577E-02/
    CHEB/ -3.4248E-02 -3.1159E-02 -9.3621E-03 -1.2772E-02 -7.5350E-03/
    CHEB/  9.3834E-03  2.5130E-03/
CH3O + CH2O (+M)      <=> COCO. (+M)           1.00E+00     .000        0. ! ING171   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3         4.8507E+00  2.4880E+00 -8.9090E-03  1.0885E+00/
    CHEB/  8.4556E-03  6.3254E-03 -3.8968E-01  4.2288E-03  3.1392E-03/
    CHEB/ -4.9090E-03 -4.9612E-04 -3.7005E-04  8.4576E-02 -8.9232E-04/
    CHEB/ -6.6124E-04  6.0023E-02 -1.4535E-04 -1.0935E-04  2.1901E-02/
    CHEB/  1.8052E-04  1.3041E-04/
CH3O + CH2O (+M)      <=> COC. + O (+M)        1.00E+00     .000        0. ! ING171   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        -2.4111E+01 -9.9228E-06 -7.6427E-06  2.9025E+01/
    CHEB/ -6.2432E-06 -4.3240E-06  2.9663E-01 -4.6701E-06 -3.5965E-06/
    CHEB/  9.0999E-02 -4.5005E-06 -3.0985E-06  3.1464E-02 -3.6235E-06/
    CHEB/ -2.7602E-06  1.1995E-02 -2.1099E-06 -1.6468E-06  4.8342E-03/
    CHEB/ -1.1241E-06 -8.9420E-07/
CH3O + CH2O (+M)      <=> C.OCOH (+M)          1.00E+00     .000        0. ! ING171   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3         3.7598E+00  1.3138E+00 -2.8299E-01  2.3923E+00/
    CHEB/  1.0212E+00  1.2356E-01 -2.0388E-01  2.3200E-01  1.2998E-01/
    CHEB/ -5.2722E-02 -3.2222E-02  3.3932E-02  3.5542E-02 -6.0108E-02/
    CHEB/ -1.3784E-02  4.5057E-02 -2.6695E-02 -1.7156E-02  2.4618E-02/
    CHEB/ -5.3400E-04 -6.4646E-03/
CH2OH (+M)            <=> CH2O + H (+M)        1.00E+00     .000        0. ! ING092   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        -2.7083E+00  1.8020E+00 -3.0931E-01  9.9291E+00/
    CHEB/  5.9467E-01  2.1337E-01 -6.2201E-01  1.0554E-01  7.9454E-02/
    CHEB/ -2.7808E-01 -3.9170E-03  1.0325E-02 -1.1301E-01 -1.6324E-02/
    CHEB/ -6.6713E-03 -3.9890E-02 -9.5562E-03 -5.9374E-03 -1.0784E-02/
    CHEB/ -3.5702E-03 -2.7335E-03/
CH2OH (+M)            <=> CH3O (+M)            1.00E+00     .000        0. ! ING092   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        -5.2526E+00  2.1026E+00 -2.2272E-01  1.1233E+01/
    CHEB/  3.9362E-01  2.0200E-01 -5.8249E-01  3.3501E-02  3.6550E-02/
    CHEB/ -2.4821E-01 -1.7730E-02 -7.0233E-03 -9.4377E-02 -1.3182E-02/
    CHEB/ -8.9032E-03 -3.0028E-02 -4.8613E-03 -3.9840E-03 -6.3238E-03/
    CHEB/ -7.8881E-04 -9.0552E-04/
CH2OH + H             <=> CH2O + H2            6.03E+12    0.0          0. !87 TSANG
CH2OH + O             <=> CH2O + OH            4.22E+13    0.0          0. !87 TSANG
CH2OH + OH            <=> CH2O + H2O           2.41E+13    0.0          0. !87 TSANG
CH2OH + CH2O          <=> CH3OH + HCO          5.49E+03    2.8       5872. !87 TSANG
CH2OH + CH3O          <=> CH3OH + CH2O         2.41E+13    0.0          0. !87 TSANG
CH2OH + CH2OH         <=> CH3OH + CH2O         4.82E+12    0.0          0. !87 TSANG
CH2OH + CH3OH         <=> CH3OH + CH3O         7.83E+09    0.0      12062. !87 TSANG
CH2OH + CH3           <=> CH2O + CH4           2.41E+12    0.00         0. !87 TSANG
CH2OH + CH3           <=> CCOH                 1.21E+13    0.0          0. !87 TSANG

!***************************************************************************
!************Modified CH2OH+O2 using Jeff's (PhD) input with except to two Ea.  See
!************notation at beginning for references.  - CYS 12/14/2001
!************Begin CH2OH+O2 block********************************************
!CH2OH + O2            = CH2O + HO2            2.41E+14    0.0       5000. !NORTON
CH2OH+O2 (+M)         <=> CQ.H2OH (+M)         1.00E+00    0.000        0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3         6.5159E+00  6.6291E+00 -1.0657E+00 -1.5692E+00/
    CHEB/  2.5066E-01 -4.9372E-02 -1.0401E+00 -3.5094E-02  7.5189E-02/
```

```
    CHEB/ -6.8247E-01 -1.6275E-01  4.7213E-02 -3.3797E-01 -1.6483E-01/
    CHEB/ -2.9514E-02 -1.3761E-01 -8.9426E-02 -3.0612E-02 -4.4245E-02/
    CHEB/ -2.9660E-02 -1.9429E-02/
CH2OH+O2 (+M)        <=> CO.H2OH+O (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.9894E+00 -3.7791E-02 -2.8921E-02  9.2142E+00/
    CHEB/ -1.6975E-02 -1.1981E-02  1.6451E-01  2.0371E-02  1.4964E-02/
    CHEB/  4.6049E-02  2.7453E-02  2.0533E-02 -2.3720E-03  1.2253E-02/
    CHEB/  9.4430E-03 -1.4277E-02 -5.0824E-04 -1.2278E-04 -1.2381E-02/
    CHEB/ -4.2202E-03 -3.1450E-03/
CH2OH+O2 (+M)        <=> CH2OHOO (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.8810E+00  7.0222E+00 -9.9401E-01 -1.0119E+00/
    CHEB/ -1.2196E-01 -5.0533E-02 -7.4535E-01 -1.8798E-01 -6.3899E-02/
    CHEB/ -4.7967E-01 -8.1853E-02  7.0953E-02 -2.5390E-01 -1.0519E-01/
    CHEB/  1.6904E-02 -1.2111E-01 -9.0999E-02 -2.6360E-02 -4.1178E-02/
    CHEB/ -4.4421E-02 -2.9809E-02/
CH2OH+O2 (+M)        <=> CH2O+HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2140E+01 -4.0040E-01 -2.7758E-01  5.4824E-02/
    CHEB/  3.8577E-01  2.6187E-01 -7.2838E-02  6.1294E-02  4.3000E-02/
    CHEB/ -4.5505E-02  2.0377E-02  1.4637E-02 -3.5462E-02 -1.5968E-02/
    CHEB/ -6.4225E-03 -2.6294E-02 -2.9620E-02 -1.8845E-02 -1.3844E-02/
    CHEB/ -2.0697E-02 -1.5456E-02/
    DUPLICATE
CH2OH+O2 (+M)        <=> CQH2O. (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -8.5302E-01  5.9600E+00 -3.9786E-01 -1.5515E+00/
    CHEB/  5.1348E-01 -3.5048E-01 -7.2870E-01  7.1739E-02 -2.6924E-02/
    CHEB/ -4.6316E-01 -1.0513E-01  2.2181E-02 -2.7130E-01 -1.4707E-01/
    CHEB/ -3.9769E-02 -1.3860E-01 -9.2116E-02 -3.2691E-02 -5.3544E-02/
    CHEB/ -3.0333E-02 -1.3580E-02/
CH2OH+O2 (+M)        <=> CH2O+HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0941E+01 -2.6409E-01 -1.6930E-01  6.3915E-01/
    CHEB/  2.1539E-01  1.3366E-01  1.8930E-01  5.1616E-02  3.3914E-02/
    CHEB/  2.0367E-02  5.2306E-02  3.4838E-02 -2.5916E-02 -2.8901E-03/
    CHEB/  3.1899E-03 -2.8202E-02 -2.9192E-02 -1.8051E-02 -1.7487E-02/
    CHEB/ -2.3014E-02 -1.6931E-02/
    DUPLICATE
CH2OH+O2 (+M)        <=> HOC.HQ (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.1600E+01  2.1959E+00 -1.7504E-01  2.0845E+00/
    CHEB/  2.2063E-01  1.2218E-01  3.9902E-01  2.9663E-02  1.7529E-02/
    CHEB/  8.0082E-02  5.8337E-02  3.3284E-02  8.3114E-04  1.4709E-02/
    CHEB/  1.5617E-02 -6.7340E-02 -1.0708E-02 -4.6772E-03 -1.2216E-02/
    CHEB/ -1.3917E-02 -1.0905E-02/
CH2OH+O2 (+M)        <=> HCQ*O+H (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.7931E+00 -2.8632E-01 -1.6909E-01  3.2456E+00/
    CHEB/  2.3318E-01  1.3144E-01  8.0451E-01  8.6707E-03  5.6280E-03/
    CHEB/  2.0964E-01  4.5834E-02  2.8199E-02  3.0097E-02  1.4214E-02/
    CHEB/  1.4627E-02 -8.2022E-03 -9.7595E-03 -4.5530E-03 -9.8945E-03/
    CHEB/ -1.0873E-02 -8.2265E-03/
CH2OH+O2 (+M)        <=> HCO2H+OH (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.4981E+00 -3.1337E-01 -1.8090E-01  2.3380E+00/
    CHEB/  2.3756E-01  1.3282E-01  4.8516E-01  2.4031E-02  1.3213E-02/
    CHEB/  1.1716E-01  5.5672E-02  3.2873E-02  5.8136E-03  1.6895E-02/
    CHEB/  1.6467E-02 -1.6154E-02 -1.2093E-02 -5.5124E-03 -1.3287E-02/
    CHEB/ -1.4771E-02 -1.0713E-02/
CQ.H2OH (+M)         <=> CO.H2OH+O (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.4786E+01  1.0755E+01  2.3602E+00  1.4955E+01/
    CHEB/ -5.7890E+00 -4.4319E-01 -1.9270E+00 -1.9559E+00 -1.3077E+00/
    CHEB/ -2.5688E-01 -1.3508E-01 -3.2942E-01  5.3855E-02  1.7528E-01/
    CHEB/  5.9633E-02  2.5098E-02  8.7536E-02  6.2540E-02 -1.3799E-02/
    CHEB/  6.6578E-03  1.0127E-02/
CQ.H2OH (+M)         <=> CH2OHOO (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.3071E+00  1.4550E+00 -2.0928E-01  4.1963E+00/
```

```
    CHEB/  1.0982E+00  1.4190E-01 -5.8785E-01  5.2153E-02  1.0683E-01/
    CHEB/ -1.6336E-01 -9.8396E-02 -1.8957E-02 -1.8509E-02 -4.0650E-02/
    CHEB/ -3.1281E-02  2.9593E-03 -7.7174E-03 -1.2237E-02 -4.7036E-03/
    CHEB/ -6.9583E-03 -5.6122E-03/
CQ.H2OH (+M)          <=> CQH2O. (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.3888E+00  4.1841E+00 -1.6133E-01  5.0954E+00/
    CHEB/ -2.5410E-03  9.5819E-01 -1.1992E+00 -7.1132E-01 -9.1188E-02/
    CHEB/ -3.6406E-01 -3.2564E-01 -2.2404E-01 -8.5437E-02 -8.8366E-02/
    CHEB/ -1.0554E-01 -2.3886E-02 -1.7269E-02 -3.3912E-02 -1.8133E-02/
    CHEB/ -1.1118E-02 -1.4362E-02/
CQ.H2OH (+M)          <=> HOC.HQ (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.7615E+01  7.6096E+00  8.2532E-01  9.0745E+00/
    CHEB/ -2.7345E+00  7.8295E-01 -1.5467E+00 -1.5155E+00 -8.1603E-01/
    CHEB/ -3.3184E-01 -3.3552E-01 -3.8071E-01 -1.9638E-02  2.0840E-02/
    CHEB/ -5.7358E-02  9.8189E-03  4.6562E-02  1.6905E-02 -6.6219E-03/
    CHEB/  1.2402E-02  9.0908E-03/
CH2OHOO (+M)          <=> CH2O+HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       3.9951E+00  2.0415E+00 -2.2189E-01  1.8418E+00/
    CHEB/  5.2577E-01  2.6431E-01 -9.6479E-01  1.1180E-01  9.3824E-02/
    CHEB/ -2.2851E-01  2.7880E-02  3.4678E-02 -3.3366E-02  3.5637E-02/
    CHEB/  2.8791E-02  4.9554E-03  3.8169E-02  2.8470E-02  7.8619E-03/
    CHEB/  3.1739E-02  2.3377E-02/
CQH2O. (+M)           <=> CH2O+HO2 (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.1070E+00  2.4955E+00 -3.3879E-03  3.7784E+00/
    CHEB/  4.3280E-03  3.2422E-03 -6.3808E-01 -4.2442E-04 -3.1527E-04/
    CHEB/ -1.4659E-01 -2.2255E-05 -1.7183E-05 -1.0036E-02  1.5257E-06/
    CHEB/  1.1815E-06  9.8117E-03  1.3847E-06  1.0233E-06  3.6710E-03/
    CHEB/  1.0962E-06  8.3946E-07/
HOC.HQ (+M)           <=> HCQ*O+H (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.1446E+01  2.5908E+00  6.8004E-02  7.4770E+00/
    CHEB/ -7.5135E-02 -5.6055E-02 -1.5618E-01  3.4370E-03  2.4539E-03/
    CHEB/ -6.7442E-03 -1.8552E-05 -7.9988E-06 -2.7624E-03 -7.7570E-05/
    CHEB/ -5.8392E-05 -3.9824E-03 -4.0890E-05 -3.0355E-05 -2.1512E-03/
    CHEB/ -3.2908E-05 -2.4663E-05/
HOC.HQ (+M)           <=> HCO2H+OH (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.9314E+00  2.4968E+00 -2.4196E-03  8.5104E-01/
    CHEB/  3.3141E-03  2.4857E-03 -2.4213E-01 -3.9716E-04 -2.9603E-04/
    CHEB/ -2.0998E-02 -2.4273E-05 -1.8475E-05 -4.8441E-03 -6.5957E-07/
    CHEB/ -5.1488E-07 -4.3042E-03  2.7305E-07  1.5470E-07 -2.2011E-03/
    CHEB/  5.9364E-07  4.1286E-07/
!************END CH2OH+O2 BLOCK*****************************************************


!************Reactions for HCO2H ***************************************************
!CH2OH + HO2 <=> HCO2H + OH + H          2.0E13     0.      0.     ! HELD/DRYER  1999
!HCO2H  +M <=> CO + H2O + M              2.09E14   0.     40400   ! HELD/DRYER 1999
!HCO2H +M  <=> CO2 + H2 + M              1.35E15    0.     60600  ! HELD/DRYER 1999
!HCO2H + OH <=> H2O + CO2 + H                3.00E11    0.0    0.0     ! HELD/DRYER 1999

CH2O + OH <=> CO.H2OH                        2.3E12  0.0  3500  ! JWB ESTIMATE 11/2001
CO.H2OH <=> HCO2H + H                        1.0E13  0.0  6960  ! JWB EST.  EA=DHRXN +
6  11/2001
HCO + HO2 <=> HCO2. + OH                     1.0E11   0.0  1500 ! JWB ESTIMATE 11/2001
HCO + CH3OO <=> HCO2. + CH3O                 1.0E11  0.0   1500 ! JWB ESTIMATE 11/2001
HCO2. + CH3OH <=> CH3O + HCO2H               1.0E12  0.0  8000 ! JWB ESTIMATE 11/2001
HCO2. + CH3OH <=> CH2OH + HCO2H              1.0E12  0.0  7000 ! JWB ESTIMATE 11/2001
HCO2. + CH4 <=> CH3 + HCO2H                  1.0E12  0.0  10000 ! JWB ESTIMATE 11/2001
!**********************************************************************************

CH2OH + CH3O (+M)     <=> COCOH (+M)          1.00E+00     .000       0. ! ING151   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2765E+01  3.1585E-01 -5.3598E-02 -5.8913E-01/
    CHEB/  5.7115E-01 -8.6727E-02 -4.7133E-01  4.2284E-01 -4.1197E-02/
    CHEB/ -3.2940E-01  2.5509E-01  2.4025E-04 -2.0398E-01  1.2181E-01/
    CHEB/  2.0563E-02 -1.1346E-01  4.0965E-02  2.1313E-02 -5.7199E-02/
```

```
    CHEB/  3.5239E-03  1.3004E-02/
CH2OH + CH3O (+M)    <=> COC. + OH (+M)      1.00E+00     .000       0. ! ING151   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.4362E+00 -1.8074E+00 -9.7130E-02  4.1392E+00/
    CHEB/  1.1160E+00 -1.0038E-01  5.1088E-01  5.9278E-01  3.7423E-02/
    CHEB/ -2.9236E-02  1.7853E-01  8.6223E-02 -9.0916E-02 -1.4344E-02/
    CHEB/  5.7277E-02 -5.9203E-02 -5.5903E-02  1.4795E-02 -2.6655E-02/
    CHEB/ -4.0148E-02 -7.7983E-03/
CH2OH + CH3O (+M)    <=> COCO. + H (+M)      1.00E+00     .000       0. ! ING151   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.0405E+00 -1.6906E+00 -1.3637E-01  5.9746E+00/
    CHEB/  1.1660E+00 -7.9029E-02  3.6138E-01  5.1796E-01  8.7344E-02/
    CHEB/  8.1062E-03  1.1445E-01  9.7251E-02 -7.5612E-02 -3.5707E-02/
    CHEB/  4.2447E-02 -5.0719E-02 -5.5418E-02  6.1221E-04 -1.8706E-02/
    CHEB/ -3.4559E-02 -1.3994E-02/
CH2OH + CH3O (+M)    <=> COC.OH + H (+M)     1.00E+00     .000       0. ! ING151   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.1247E+00 -1.8315E+00 -9.0990E-02  3.7136E+00/
    CHEB/  1.0962E+00 -1.0180E-01  5.3473E-01  6.0448E-01  2.7028E-02/
    CHEB/ -3.6833E-02  1.9585E-01  8.0984E-02 -9.6025E-02 -5.3785E-03/
    CHEB/  5.8977E-02 -6.2474E-02 -5.4119E-02  1.8236E-02 -2.8035E-02/
    CHEB/ -4.1083E-02 -5.7476E-03/
CH2OH + CH2O (+M)    <=> C.OCOH (+M)         1.00E+00     .000       0. ! ING181   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.8994E+00  1.1028E+00 -2.0010E-01  9.1185E-01/
    CHEB/  1.1577E+00  2.3886E-02 -6.6539E-01  3.1431E-01  1.2276E-01/
    CHEB/ -2.0079E-01 -1.7867E-02  5.2954E-02 -9.5693E-03 -6.9152E-02/
    CHEB/ -4.4478E-03  3.5394E-02 -3.6961E-02 -1.7204E-02  2.5521E-02/
    CHEB/ -5.9296E-03 -9.3026E-03/
CH2OH + CH2O (+M)    <=> COCO. (+M)          1.00E+00     .000       0. ! ING181   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.7013E-01  1.3674E+00 -2.8718E-01  2.7185E+00/
    CHEB/  1.0031E+00  1.4815E-01 -3.9961E-01  2.2583E-01  1.3106E-01/
    CHEB/ -9.7280E-02 -3.8185E-02  2.8726E-02  1.7643E-02 -6.5749E-02/
    CHEB/ -1.8485E-02  3.3334E-02 -2.9647E-02 -1.9569E-02  1.7779E-02/
    CHEB/ -1.2999E-03 -7.0409E-03/
CH2OH + CH2O (+M)    <=> CH3O + CH2O (+M)    1.00E+00     .000       0. ! ING181   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.2929E+00 -9.7875E-01 -2.7206E-01  3.6774E+00/
    CHEB/  1.0033E+00  1.8913E-01 -1.4265E-01  1.0708E-01  1.1757E-01/
    CHEB/ -1.4623E-01 -9.4929E-02 -4.5817E-03 -7.0153E-02 -6.1151E-02/
    CHEB/ -3.3393E-02 -1.9392E-02 -9.5076E-03 -1.5869E-02 -8.9030E-04/
    CHEB/  1.0714E-02  1.0726E-03/
CH2OH + CH2O (+M)    <=> COC. + O (+M)       1.00E+00     .000       0. ! ING181   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.7707E+01 -7.1296E-02 -5.0802E-02  2.9566E+01/
    CHEB/  8.7206E-02  6.1354E-02  4.1510E-02 -1.2480E-02 -7.7945E-03/
    CHEB/ -4.1169E-03 -6.7633E-03 -5.1554E-03 -6.5663E-03 -7.3466E-04/
    CHEB/ -6.6434E-04 -2.3978E-03  8.2975E-04  6.0861E-04  3.0678E-04/
    CHEB/  5.5392E-04  4.2834E-04/


!*************************************************************************
!************CH3+O2 subsystem uses Jeff's k(inf) and Frenklach's Ea for CH2O+OH.
!************calc using Master Eqn.    - CYS 12/14/2001
!************Begin CH3O2 dissoc block*******************************************
!  Leave in CH2OOH => CH2+OH.  Although recent studies show this goes immediately
!  to CH2O + OH, some other reaction steps in this mech also generate CH2OOH.
!  By leaving this rxn step in, CH2OOH will not become a "sink" but rather go to
!  products.    -  CYS  12/14/2001
CH2OOH (+M)          <=> CH2O + OH (+M)      1.00E+00     .000       0. ! ING061   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.6405E+00  2.4963E+00 -2.8001E-03  1.1638E-01/
    CHEB/  3.5304E-03  2.6505E-03 -1.0409E-01 -3.2234E-04 -2.4017E-04/
    CHEB/ -2.1004E-02 -1.2670E-05 -9.6422E-06 -7.8210E-03 -1.7268E-05/
    CHEB/ -1.2727E-05 -3.3591E-03 -6.0558E-06 -4.4509E-06 -9.3367E-04/
    CHEB/  4.2036E-07  3.8397E-07/
CH3OO (+M)           <=> CH2O+OH (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.0973E+01  4.7100E+00  1.0524E+00  1.4619E+01/
```

```
    CHEB/ -1.4867E+00 -5.5101E-01 -1.3719E+00 -4.5792E-01 -2.7794E-01/
    CHEB/ -5.4886E-01 -1.2530E-01 -9.6912E-02 -2.0873E-01 -2.1530E-02/
    CHEB/ -2.6941E-02 -7.2607E-02  6.1157E-03 -3.2101E-03 -2.1882E-02/
    CHEB/  9.7531E-03  3.1115E-03/
CH3OO (+M)          <=> CH3O+O (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.2754E+01  5.1799E+00  1.3879E+00  1.9862E+01/
    CHEB/ -1.9903E+00 -9.0542E-01 -1.3640E+00 -4.5350E-01 -2.8067E-01/
    CHEB/ -5.3702E-01 -1.0567E-01 -8.2791E-02 -2.0345E-01 -1.2270E-02/
    CHEB/ -1.9896E-02 -7.0789E-02  9.3782E-03 -6.5754E-04 -2.1461E-02/
    CHEB/  1.0521E-02  3.7365E-03/
!************END CH3O2 dissoc block*********************************************


CH3OO + CH2O         <=> CH3OOH + HCO         5.60E+12    0.00     13600.
CH3OO + C2H6         <=> C2H5 + CH3OOH        1.70E+13    0.00     20460.
CH3OO + CH3OH        <=> CH2OH + CH3OOH       6.30E+12    0.00     21360.
CH3OO + CH3          <=> CH3O + CH3O          3.80E+12    0.00     -1200.
CH3OO + C2H5         <=> CH3O + CCO.          3.80E+12    0.00     -1200.
CH3OO + CH3OO        <=> CH2O + CH3OH + O2    3.00E+10    0.00      -830.
CH3OO + CH3OO        <=> CH3O + CH3O + O2     3.00E+10    0.00      -830.
CH3OO + C2H4         <=> CYCCO + CH3O         2.82E+11    0.00     17110.
CH4 (+M)             <=> CH3 + H (+M)         1.00E+00     .000        0. ! ING221   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.8596E+01  1.9137E+00 -2.9631E-01  3.2580E+01/
    CHEB/  4.5476E-01  1.9218E-01 -5.0368E-01  9.2796E-02  6.6035E-02/
    CHEB/ -2.5914E-01  8.6217E-03  1.2947E-02 -1.2334E-01 -6.4856E-03/
    CHEB/ -1.6143E-03 -5.5482E-02 -5.1440E-03 -2.9219E-03 -2.4031E-02/
    CHEB/ -2.3138E-03 -1.6043E-03/
CH4 + H              <=> CH3 + H2             1.33E+04    3.00      8038. !92 BAULCH
CH4 + OH             <=> CH3 + H2O            2.36E+07    1.83      2782. !1.5*92 BAULCH
CH4 + O              <=> CH3 + OH             2.13E+06    2.21      6480. !83 MICHAEL
CH4 + HO2            = CH3 + H2O2             9.04E+12    0.00     24641. !92 BAULCH

!*************************************************************************
!************Modified CH3OH subsystem base on CBS-APNO for thermo and CTST
!************and VTST for hp kinetic.    - CYS 11/2001
!************Begin CH3OH block*******************************************
CH3OH (+M)          <=> CH2O + H2 (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.8248E+01  1.7114E+00 -5.3989E-01  2.5267E+01/
    CHEB/  1.1189E+00 -6.3093E-02 -4.4413E-01  2.1649E-01  6.2749E-02/
    CHEB/ -1.6758E-01  1.3125E-02  1.9962E-02 -5.7309E-02 -1.1238E-02/
    CHEB/  5.2575E-04 -1.8085E-02 -5.4851E-03 -1.6016E-03 -5.5519E-03/
    CHEB/ -1.0640E-03 -4.0470E-04/
CH3OH (+M)          <=> CH3O + H (+M)        1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.5024E+01  5.0615E+00 -2.8694E-01  2.7336E+01/
    CHEB/  5.1256E-01  7.6804E-01 -5.8198E-01 -1.4375E-01  3.5558E-02/
    CHEB/ -1.9429E-01 -7.8292E-02 -3.9970E-02 -5.8153E-02 -2.6370E-02/
    CHEB/ -1.6138E-02 -1.6707E-02 -6.7320E-03 -3.9991E-03 -5.3191E-03/
    CHEB/ -1.6412E-03 -9.6349E-04/
CH3OH (+M)          <=> CH2OH + H (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.7654E+01  2.1347E+00 -5.8784E-01  2.5953E+01/
    CHEB/  1.1089E+00  6.8664E-02 -3.9630E-01  1.7287E-01  8.2284E-02/
    CHEB/ -1.5395E-01  7.9939E-04  1.5622E-02 -5.2327E-02 -1.3269E-02/
    CHEB/ -1.4010E-03 -1.6215E-02 -5.4212E-03 -1.6900E-03 -4.9387E-03/
    CHEB/ -9.5318E-04 -2.5656E-04/
CH3OH (+M)          <=> CH2S + H2O (+M)      1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.6700E+01  2.5834E+00 -6.2092E-01  2.5828E+01/
    CHEB/  1.0863E+00  2.1008E-01 -4.7774E-01  1.3085E-01  9.8571E-02/
    CHEB/ -1.7575E-01 -1.2480E-02  1.0717E-02 -5.7789E-02 -1.5919E-02/
    CHEB/ -3.4366E-03 -1.7503E-02 -5.5260E-03 -1.8720E-03 -5.3389E-03/
    CHEB/ -9.2979E-04 -2.0655E-04/
```

```
CH3OH (+M)           <=> HCOH + H2 (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.4350E+01  3.4585E-01 -8.9926E-02  2.4827E+01/
    CHEB/  4.3575E-01 -6.5712E-02 -2.5423E-01  1.5754E-01  3.1912E-03/
    CHEB/ -1.2214E-01  2.6528E-02  7.4035E-03 -4.7900E-02 -6.0235E-03/
    CHEB/ -1.0862E-03 -1.6761E-02 -5.8966E-03 -3.2911E-03 -5.4388E-03/
    CHEB/ -1.9255E-03 -1.8303E-03/
!************End CH3OH block   - CYS 11/2001*******************************************

CH3OH + O            <=> CH2OH + OH           2.91E+05    2.50      3080. !86 TSANG
CH3OH + O            <=> CH3O + OH            9.70E+04    2.50      3080. !86 TSANG
CH3OH + H            <=> CH2OH + H2           3.20E+13    0.0       6095. !84 WARANTZ
CH3OH + H            <=> CH3O + H2            8.00E+12    0.0       6095. !84 WARANTZ
CH3OH + OH           <=> CH2OH + H2O          9.96E+04    2.5       -960. !86TSANG
CH3OH + OH           <=> CH3O + H2O           1.32E+05    2.5       -960. !86TSANG
CH3OH + HO2          <=> CH2OH + H2O2         9.64E+10    0.0      12579. !86 TSANG
CH3OH + CH3          <=> CH2OH + CH4          3.19E+01    3.20      7170. !86 TSANG
CH3OH + CH3          <=> CH3O + CH4           1.44E+01    3.10      6935. !86 TSANG
CH3OOH               <=> CH3O + OH            6.46E+14    0.00     43000.
CH3OOH + O2          <=> CH3OO + HO2          3.00E+12    0.00     39000.
C2H + O2             <=> HCO + CO             9.00E+11    0.0          0. !JWB NCA
C2H + O2             <=> HCCO + O             9.00E+11    0.0          0. !JWB NCA
C2H + O              <=> CH + CO              5.00E+13    .000         0.
C2H + OH             <=> H + HCCO             2.00E+13    .000         0.
HCCO + O             <=> HCO + CO             3.40E+13    0.00       500.
HCCO + O             <=> H + 2CO              1.00E+14    .000         0.
HCCO + O2            <=> HCO + CO2            3.00E+12    0.0          0.
HCCO + H             <=> CH2S + CO            9.00E+13    0.0          0.
C2H2 + O             <=> OH + C2H             4.60E+19   -1.41     28950.

!*******Added acetylene + O2.  Computation of thermo at CBS-Q//B3LYP/6-31G(d,p)*******
!*******and hp kinetic from IJCK (2000) C.Sheng and J.W. Bozzelli.  - CYS 11/2001*****
!*******Begin C2H2 + O2 block*********************************************************
C2H2 + O2            <=> C*C*O + O            4.00E+12    0.0      28000. !JWB
C2H2+O2 (+M)         <=> HCJ*COOJ (+M)         1.00E+00     .000        0. ! ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -9.0556E+00  2.4964E+00 -2.6861E-03  9.4478E+00/
    CHEB/  4.7854E-03  3.5714E-03 -4.5449E-01 -1.4529E-03 -1.0801E-03/
    CHEB/ -1.4712E-01  1.4925E-04  1.0896E-04 -4.8505E-02  1.5673E-05/
    CHEB/  1.2277E-05 -1.5648E-02 -2.6962E-06 -2.0229E-06 -4.7854E-03/
    CHEB/ -3.0013E-07 -2.2227E-07/
C2H2+O2 (+M)         <=> CJJYCOO (+M)         1.00E+00    0.000       0. ! ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.6369E+01  1.5405E+00 -2.9036E-01  1.6894E+01/
    CHEB/  7.2855E-01  1.5325E-01 -4.3188E-01  8.8368E-02  6.6230E-02/
    CHEB/ -1.6965E-01 -1.6601E-02  2.2774E-03 -5.7892E-02 -1.3163E-02/
    CHEB/ -6.5213E-03 -1.7498E-02 -3.4460E-03 -2.7044E-03 -4.7002E-03/
    CHEB/ -2.1757E-05 -3.0155E-04/
C2H2+O2 (+M)         <=> HCJOJ*CHO (+M)        1.00E+00    0.000       0. ! ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.8978E+01  2.3819E+00 -8.7637E-02  2.1107E+01/
    CHEB/  1.5347E-01  1.1145E-01  5.2397E-02 -2.6140E-02 -1.5434E-02/
    CHEB/  2.6181E-02 -1.3201E-02 -1.0941E-02  1.5187E-02  2.3232E-03/
    CHEB/  1.0617E-03 -1.0432E-01  9.3151E-04  9.8377E-04  2.9681E-02/
    CHEB/  7.0386E-04  3.5220E-04/
C2H2+O2 (+M)         <=> CJ*OCHO + H (+M)     1.00E+00    0.000       0. ! ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.0076E+01 -1.1888E-01 -8.7923E-02  2.1299E+01/
    CHEB/  1.5703E-01  1.1362E-01  1.1213E-01 -3.1105E-02 -1.8723E-02/
    CHEB/  2.0026E-02 -1.0381E-02 -9.2716E-03  1.5752E-03  1.4414E-03/
    CHEB/  6.2292E-04 -7.1821E-04  1.6899E-03  1.4119E-03 -1.6322E-05/
    CHEB/  3.1313E-04  3.3970E-04/
C2H2+O2 (+M)         <=> HCO + HCO (+M)       1.00E+00    0.000       0. !ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.9228E+01 -1.1942E-01 -8.8309E-02  2.1271E+01/
```

```
    CHEB/  1.5737E-01  1.1383E-01  1.0034E-01 -3.0786E-02 -1.8454E-02/
    CHEB/  1.5850E-02 -1.0429E-02 -9.2918E-03  2.0695E-04  1.3485E-03/
    CHEB/  5.4620E-04 -1.2084E-03  1.6696E-03  1.3899E-03 -2.3254E-04/
    CHEB/  3.2692E-04  3.4962E-04/
HCJ*COOJ (+M)          <=> CJJYCOO (+M)         1.00E+00    0.000       0. !ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.1225E+01  2.4985E+00 -1.1219E-03  2.2571E+01/
    CHEB/  1.4560E-03  1.0949E-03 -5.1391E-01 -1.9823E-04 -1.4859E-04/
    CHEB/ -1.6999E-01  9.6416E-08 -2.8910E-08 -5.5679E-02  1.7363E-07/
    CHEB/  1.3384E-07 -1.7813E-02  8.4631E-08  1.3200E-07 -5.4687E-03/
    CHEB/  1.5967E-07  8.3345E-08/
CJJYCOO (+M)          <=> HCJOJ*CHO (+M)        1.00E+00    0.000       0. !ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.8027E+01  2.4839E+00 -1.1937E-02  2.8772E+01/
    CHEB/  1.4532E-02  1.0745E-02 -5.0167E-01 -1.5177E-03 -1.0885E-03/
    CHEB/ -1.6366E-01 -6.4412E-05 -5.5717E-05 -5.0781E-02  1.4776E-06/
    CHEB/  1.0049E-06 -1.5409E-02  4.9888E-06  4.4639E-06 -4.9985E-03/
    CHEB/  2.0294E-06  2.0143E-06/
HCJOJ*CHO (+M)         <=> CJ*OCHO + H (+M)     1.00E+00    0.000       0. !ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -6.7011E+00  4.8325E+00  1.0101E+00  5.8505E+00/
    CHEB/ -4.4893E-01 -2.8291E-02 -4.0303E-01 -1.1637E-01 -5.7042E-02/
    CHEB/ -6.9939E-02 -2.4580E-02 -1.3746E-02 -1.4558E-03 -1.8882E-03/
    CHEB/ -8.8406E-04  4.1708E-03  2.0387E-03  1.4614E-03  1.4282E-03/
    CHEB/  1.5542E-03  1.1516E-03/
HCJOJ*CHO (+M)         <=> HCO + HCO (+M)       1.00E+00    0.000       0. !ME 7x3 300-
1500K, 1e-3-100atm  10/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.7190E+00  2.0301E+00 -2.2493E-01  2.9964E+00/
    CHEB/  3.7150E-01  1.6458E-01 -3.5135E-01 -4.7996E-04  1.0140E-02/
    CHEB/ -6.7630E-02 -1.5780E-02 -7.9456E-03 -1.8398E-03 -2.0735E-03/
    CHEB/ -1.5266E-03  4.2001E-03  2.0658E-03  1.1992E-03  1.4574E-03/
    CHEB/  1.5670E-03  1.0497E-03/
!*******End C2H2 + O2 block**********************************************************


!*******Added acetylene -> vinylidene isomerization.  Computation of thermo at *******
!*******B3LYP/6-31G(d,p) and hp kinetic from canonical TST.  See IJCK (2000)
Sheng/Bozzelli
!******* and Chem. Phys. Letter (1999) Laskin/Wang.  - CYS 11/2001*****
!*******Begin C2H2 -> vinylidene
block**********************************************************
C2H2 (+M)            <=> H2C*CJJ (+M)           1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -6.1870E+00  2.0016E+00 -2.6010E-01  1.1439E+01/
    CHEB/  3.3020E-01  1.5209E-01 -3.1626E-01  2.5293E-02  2.2639E-02/
    CHEB/ -1.0140E-01 -5.2252E-03 -1.8417E-03 -3.1191E-02 -2.7127E-03/
    CHEB/ -1.7839E-03 -9.6508E-03 -4.8381E-04 -3.9209E-04 -3.1404E-03/
    CHEB/  1.9512E-05 -6.5332E-06/
!*******END C2H2 -> vinylidene
block**********************************************************



C2H2 + H (+M)        <=> C2H3 (+M)             1.00E+00     .000       0. ! ING371   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.9505E+00  1.8486E+00 -3.0648E-01 -4.0050E-01/
    CHEB/  5.3507E-01  2.0668E-01 -5.6379E-01  1.0741E-01  7.7576E-02/
    CHEB/ -2.7037E-01  5.1829E-03  1.4241E-02 -1.2008E-01 -1.2664E-02/
    CHEB/ -4.2738E-03 -4.7119E-02 -9.5902E-03 -5.7234E-03 -1.4750E-02/
    CHEB/ -4.5560E-03 -3.3187E-03/
C2H2 + H             <=> C2H + H2              6.03E+13    0.0     27821. !92 BAULCH
C2H2 + OH            <=> C2H + H2O             1.45E+04    2.68    12042. !92 JPCRD
C2H2 + O (+M)        <=> HCCO + H (+M)         1.00E+00     .000       0. ! ING321   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.1729E+01 -1.3629E-02 -1.0150E-02  4.8017E-01/
    CHEB/  1.7020E-02  1.2643E-02  7.9983E-02 -2.8096E-03 -2.0439E-03/
```

```
      CHEB/  3.3869E-02 -7.5738E-04 -5.8019E-04  1.1376E-02 -8.9164E-05/
      CHEB/ -6.9103E-05  2.7879E-03  5.1650E-05  3.8866E-05  2.4160E-04/
      CHEB/  4.4238E-05  3.3464E-05/
  C2H2 + O (+M)        <=> CO + CH2 (+M)        1.00E+00     .000       0. ! ING321   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       1.2321E+01 -2.1016E-02 -1.5683E-02  2.8691E-01/
      CHEB/  2.6106E-02  1.9440E-02 -3.3189E-02 -4.3143E-03 -3.1579E-03/
      CHEB/ -1.7547E-02 -1.0922E-03 -8.3533E-04 -8.5775E-03 -1.3660E-04/
      CHEB/ -1.0512E-04 -3.9687E-03  6.8281E-05  5.1428E-05 -1.7689E-03/
      CHEB/  6.2862E-05  4.7500E-05/
  C2H2 + OH (+M)       <=> C.*COH (+M)          1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       1.0769E+01  1.4089E+00 -3.0836E-01 -9.5854E-01/
      CHEB/  8.5442E-01  1.4350E-01 -6.9047E-01  2.0855E-01  1.1050E-01/
      CHEB/ -3.0913E-01  1.3552E-02  3.1719E-02 -1.2104E-01 -2.3855E-02/
      CHEB/ -2.1790E-03 -3.7769E-02 -1.8197E-02 -7.8642E-03 -6.0314E-03/
      CHEB/ -8.1163E-03 -4.9381E-03/
  C2H2 + OH (+M)       <=> HC#COH + H (+M)      1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       7.3601E+00 -2.9843E-01 -1.7784E-01  4.5508E+00/
      CHEB/  3.3417E-01  1.8859E-01 -5.3322E-02 -1.6445E-03  1.2210E-02/
      CHEB/ -3.7782E-02 -2.8518E-02 -1.7008E-02  1.3173E-02 -6.3116E-03/
      CHEB/ -6.3874E-03 -2.4911E-02 -4.0262E-03 -2.6980E-03  3.2831E-03/
      CHEB/  1.5509E-03  7.9542E-04/
  C2H2 + OH (+M)       <=> C*CO. (+M)           1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       8.3465E+00  9.2655E-01 -6.0198E-01  3.1015E-01/
      CHEB/  1.2276E+00  3.2281E-01 -1.8191E-01  2.0386E-01  1.4378E-01/
      CHEB/ -1.2738E-01 -2.2458E-02  1.9651E-02 -6.5066E-02 -3.2062E-02/
      CHEB/ -1.0805E-02 -2.7209E-02 -1.1231E-02 -7.5906E-03 -1.0685E-02/
      CHEB/ -4.5671E-04 -1.8044E-03/
  C2H2 + OH (+M)       <=> C*C*O + H (+M)       1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       1.0254E+01 -1.4778E+00 -5.7317E-01  1.1621E+00/
      CHEB/  1.2639E+00  3.5716E-01  1.3562E-02  1.6820E-01  1.4050E-01/
      CHEB/ -5.8777E-02 -4.6609E-02  8.1247E-03 -2.9256E-02 -3.5625E-02/
      CHEB/ -1.5692E-02 -7.3221E-03 -7.8038E-03 -7.4423E-03 -5.0567E-04/
      CHEB/  2.1340E-03 -6.5550E-04/
  C2H2 + OH (+M)       <=> C.CHO (+M)           1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       9.1348E+00  9.3140E-01 -6.0049E-01  4.4515E-01/
      CHEB/  1.2299E+00  3.2467E-01 -2.2607E-01  2.0237E-01  1.4378E-01/
      CHEB/ -1.5782E-01 -2.3630E-02  1.9146E-02 -7.4680E-02 -3.2287E-02/
      CHEB/ -1.1043E-02 -2.8543E-02 -1.1072E-02 -7.5848E-03 -9.8603E-03/
      CHEB/ -3.0388E-04 -1.7386E-03/
  C2H2 + OH (+M)       <=> CC.*O (+M)           1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       5.5444E+00  9.8454E-01 -5.8843E-01  1.2663E-01/
      CHEB/  1.2666E+00  3.5619E-01 -2.6994E-01  1.7794E-01  1.4033E-01/
      CHEB/ -1.1000E-01 -4.0190E-02  1.1262E-02 -1.5717E-02 -3.5276E-02/
      CHEB/ -1.4449E-02  1.2742E-02 -9.0783E-03 -7.6100E-03  1.1320E-02/
      CHEB/  1.3920E-03 -1.0274E-03/
  C2H2 + OH (+M)       <=> CH3 + CO (+M)        1.00E+00     .000       0. ! ING331   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       9.5811E+00 -1.4917E+00 -5.8112E-01  1.1463E+00/
      CHEB/  1.2749E+00  3.6436E-01  3.2797E-03  1.6788E-01  1.3895E-01/
      CHEB/ -6.3254E-02 -4.6408E-02  8.2158E-03 -3.1512E-02 -3.5754E-02/
      CHEB/ -1.5537E-02 -8.4663E-03 -7.9215E-03 -7.4338E-03 -1.0756E-03/
      CHEB/  2.0876E-03 -6.9570E-04/
  C2H2 + CH3 (+M)      <=> C.*CC (+M)           1.00E+00     .000       0. ! ING381   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       7.8331E+00  8.0212E-01 -1.5489E-01  1.2244E+00/
      CHEB/  1.0506E+00 -6.3760E-02 -7.1519E-01  4.4017E-01  7.0714E-02/
      CHEB/ -3.2748E-01  9.7211E-02  6.5628E-02 -1.1286E-01 -2.3987E-02/
      CHEB/  2.3138E-02 -1.8345E-02 -3.8411E-02 -3.2425E-03  1.1818E-02/
      CHEB/ -2.1644E-02 -9.4895E-03/
  C2H2 + CH3 (+M)      <=> C#CC + H (+M)        1.00E+00     .000       0. ! ING381   10/95
      LOW / 1.0 0.0 0.0 /
      CHEB/  7   3       4.6770E+00 -1.2763E+00 -2.3222E-01  4.3939E+00/
      CHEB/  1.1169E+00  7.9203E-02  1.1364E-01  2.4353E-01  1.3215E-01/
      CHEB/ -6.1288E-02 -4.8022E-02  3.4731E-02 -4.6289E-02 -6.2486E-02/
```

```
    CHEB/ -2.0100E-02 -1.4005E-02 -2.3670E-02 -2.1416E-02  2.6562E-04/
    CHEB/ -1.1415E-03 -6.9376E-03/
C2H2 + CH3 (+M)      <=> C*CC. (+M)            1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3          6.1521E+00 -8.8276E-01 -3.0666E-01  3.6983E+00/
    CHEB/  1.8080E+00 -3.3626E-02 -3.9387E-01  7.0984E-01  9.2474E-02/
    CHEB/ -3.7732E-01  1.9166E-01  4.9412E-02 -2.1653E-01  2.5609E-02/
    CHEB/  1.0274E-02 -9.3963E-02 -8.6513E-03  2.0048E-04 -3.1994E-02/
    CHEB/ -1.0110E-02  1.2116E-03/
C2H2 + CH3 (+M)      <=> C*C*C + H (+M)        1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3          3.1288E+00 -2.7516E+00 -3.7241E-01  6.9018E+00/
    CHEB/  2.1018E+00  7.6160E-02  3.5488E-01  6.3039E-01  1.5012E-01/
    CHEB/ -1.0455E-01  7.4399E-02  7.2302E-02 -8.9364E-02 -5.9148E-02/
    CHEB/  2.5112E-02 -3.7566E-02 -5.4525E-02  4.6445E-03 -1.2001E-02/
    CHEB/ -2.8410E-02 -3.8103E-03/

C*C*O + H            <=> CH3 + CO              5.60E+12    0.00      3400. !JWB NCA

C*C*O + H            <=> HCCO + H2             7.50E+13    0.00     13000.
C*C*O + O            <=> HCO + HCO             7.80E+12    0.00      2400.
C*C*O + O            <=> HCCO + OH             1.10E+12    0.0       8000. !MILLER
C*C*O + O            <=> CH2 + CO2             1.74E+12    0.0       1350. !MILLER
C*C*O + OH           <=> HCCO + H2O            7.50E+12    0.00      4000.
C*C*O + OH           <=> CH2O + HCO            5.70E+12    0.0        250.
C2H3 + O             <=> H + C*C*O             3.00E+13    .000         0.
C2H3 + H             <=> C2H2 + H2             1.21E+13    0.0          0. !92 BAULCH
C2H3 + OH            <=> H2O + C2H2            5.00E+12    .000         0.
C2H3 + H (+M)        <=> C2H4 (+M)             6.08E+12    .270       280. !GRI 2.0
     LOW  /  1.400E+30   -3.860   3320.00/
     TROE/   .7820  207.50  2663.00  6095.00 /
     H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

!************************************************************************
!************C2H3 + O2 subsystem base on hp k in recent AYC/AMD/JWB publication in
!************ Zeit. Phys. 2000.    - CYS 12/14/2001
!************Begin C2H3+O2 Chemical Activation block*******************************
C2H3+O2 (+M)          <=> C*COO. (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3          1.1392E+01  1.7409E+00 -5.4351E-01 -2.3418E+00/
    CHEB/  2.2010E+00 -4.8929E-01 -1.3414E+00  9.1727E-01 -1.5227E-02/
    CHEB/ -6.7353E-01  2.3927E-01  1.0195E-01 -3.2054E-01  8.8833E-03/
    CHEB/  6.3923E-02 -1.4708E-01 -3.8925E-02  2.1069E-02 -6.3810E-02/
    CHEB/ -3.5040E-02  1.6964E-03/
C2H3+O2 (+M)          <=> C.CHO+O (+M)        1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3          1.1158E+01 -1.3809E+00 -1.8020E-01  1.1179E+00/
    CHEB/  1.2271E+00  1.4933E-02  6.4374E-02  3.2187E-01  1.4726E-01/
    CHEB/ -6.1207E-02 -4.1942E-02  6.9029E-02 -3.2665E-02 -8.3104E-02/
    CHEB/ -1.0312E-02 -2.1670E-03 -4.2812E-02 -2.6873E-02  1.0365E-02/
    CHEB/ -1.0652E-02 -1.4795E-02/
!   The following rxn is chem act to prod via 1st well
C2H3+O2 (+M)          <=> C2H2+HO2   (+M)     1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3          9.7170E+00 -1.3393E+00 -1.8074E-01  1.4892E+00/
    CHEB/  1.2398E+00  2.8379E-02  1.8150E-01  2.8149E-01  1.5021E-01/
    CHEB/ -7.2143E-03 -6.7399E-02  5.7113E-02 -1.0131E-03 -8.6196E-02/
    CHEB/ -1.9399E-02  1.3895E-02 -3.6831E-02 -2.7929E-02  1.7573E-02/
    CHEB/ -4.6677E-03 -1.2169E-02/
    DUPLICATE
!   The following rxn is chem act to prod via 1st well
C2H3+O2 (+M)          <=> CH2O+HCO   (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3          8.2977E+00 -1.3211E+00 -1.8411E-01  1.8565E+00/
    CHEB/  1.2377E+00  3.4882E-02  1.9515E-01  2.6598E-01  1.5216E-01/
    CHEB/ -1.9709E-02 -7.2599E-02  5.2878E-02 -1.1716E-02 -8.5067E-02/
    CHEB/ -2.1984E-02  6.2791E-03 -3.4822E-02 -2.7790E-02  1.2706E-02/
    CHEB/ -3.3838E-03 -1.1255E-02/
    DUPLICATE
C2H3+O2 (+M)          <=> C.CYCOO (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
```

```
    CHEB/  7   3        1.0240E+01  8.9666E-01 -8.9310E-01 -1.9357E+00/
    CHEB/  3.1427E+00 -2.6889E-01 -1.3863E+00  9.9618E-01  1.2623E-01/
    CHEB/ -7.4020E-01  1.4411E-01  1.0506E-01 -3.5775E-01 -7.3042E-02/
    CHEB/  2.4073E-02 -1.5906E-01 -7.7339E-02 -1.1623E-02 -6.2544E-02/
    CHEB/ -4.2980E-02 -1.2775E-02/
C2H3+O2 (+M)          <=> C.*COOH (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        8.8334E+00 -6.9260E-01 -3.4587E-01 -5.9872E-01/
    CHEB/  2.2518E+00 -1.9751E-01 -1.0444E+00  7.8240E-01  8.3213E-02/
    CHEB/ -6.5676E-01  7.3153E-02  7.2624E-02 -3.1011E-01 -8.6125E-02/
    CHEB/  6.6676E-03 -1.2062E-01 -6.0497E-02 -1.5070E-02 -3.7571E-02/
    CHEB/ -1.9219E-02 -1.0510E-02/
C2H3+O2 (+M)          <=> HCJJCHOT+OH (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        8.4336E+00 -2.2465E+00 -4.2203E-01  2.8314E+00/
    CHEB/  2.2343E+00  2.2595E-01 -1.9631E-01  2.9666E-01  2.3726E-01/
    CHEB/ -1.8510E-01 -1.5326E-01  2.9571E-02 -6.7874E-02 -1.0891E-01/
    CHEB/ -3.8650E-02 -8.4517E-03 -3.2741E-02 -2.6691E-02  8.0292E-03/
    CHEB/ -1.8112E-03 -8.7706E-03/
!   The following rxn is chem act to prod via 2nd well
C2H3+O2 (+M)          <=> C2H2+HO2       (+M)  1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        6.6516E+00 -1.6011E+00 -5.4311E-01  4.4822E+00/
    CHEB/  1.6947E+00  4.4963E-01  9.0871E-03  1.2303E-01  1.8027E-01/
    CHEB/ -6.7534E-02 -1.3891E-01 -2.5051E-02 -1.5604E-02 -7.5828E-02/
    CHEB/ -4.6605E-02  1.3713E-02 -1.5434E-02 -1.9077E-02  1.7088E-02/
    CHEB/  4.0683E-03 -1.9874E-03/
    DUPLICATE
C2H3+O2 (+M)          <=> C.OCHO (+M)           1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        2.5729E+00  7.1721E+00 -2.1614E+00 -2.1712E+00/
    CHEB/  3.0357E+00  3.8617E+00 -9.2950E-01 -3.7397E-01  1.2754E+00/
    CHEB/ -4.9699E-01 -4.8939E-01  8.7614E-02 -2.1597E-01 -3.4975E-01/
    CHEB/ -1.0965E-01 -8.4212E-02 -1.7217E-01 -1.1071E-01 -2.1359E-02/
    CHEB/ -7.6863E-02 -5.8079E-02/
!   The following rxn is chem act to prod via 4th well
C2H3+O2 (+M)          <=> CH2O+HCO     (+M)     1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0115E+01 -3.0440E+00 -7.9172E-01  1.8706E+00/
    CHEB/  2.8591E+00  4.5779E-01 -5.3230E-02  5.2267E-01  3.7442E-01/
    CHEB/ -1.8951E-01 -1.0203E-01  8.4428E-02 -1.0421E-01 -1.4820E-01/
    CHEB/ -4.6251E-02 -3.1676E-02 -7.6749E-02 -5.3682E-02  2.0545E-03/
    CHEB/ -2.2554E-02 -2.5901E-02/
    DUPLICATE
C2H3 + O2 (+M)        <=> CYCOOC. (+M)          1.00E+00     .000       0. ! ING271    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.5192E+00  2.0539E+00 -2.3242E-01 -6.4332E-01/
    CHEB/  4.8290E-01  2.3025E-01 -2.5023E-01  1.7970E-02  3.4012E-02/
    CHEB/ -1.3014E-01 -4.3085E-02 -2.0885E-02 -6.3527E-02 -2.0821E-02/
    CHEB/ -1.5346E-02 -2.4922E-02 -1.6768E-03 -3.0324E-03 -7.3249E-03/
    CHEB/  3.9287E-03  2.1018E-03/
C2H3 + O2 (+M)        <=> O*CCO. (+M)           1.00E+00     .000       0. ! ING271    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.3080E+00  2.0554E+00 -2.3219E-01 -9.9024E-01/
    CHEB/  4.8331E-01  2.3135E-01 -3.6212E-01  1.5940E-02  3.2820E-02/
    CHEB/ -9.4300E-02 -4.3374E-02 -2.1267E-02 -7.5129E-03 -2.0566E-02/
    CHEB/ -1.5258E-02  5.0164E-03 -1.4821E-03 -2.8830E-03  3.7334E-04/
    CHEB/  3.9949E-03  2.1733E-03/
!   The following rxn is from ING's original, via a 4 member ring.
C2H3 + O2 (+M)        <=> CH2O + HCO (+M)       1.00E+00     .000       0. ! ING271    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.2134E+01 -4.4216E-01 -2.3095E-01 -1.4641E-01/
    CHEB/  4.8344E-01  2.3182E-01 -2.4621E-01  1.4188E-02  3.1877E-02/
    CHEB/ -1.4138E-01 -4.4168E-02 -2.1909E-02 -5.6157E-02 -2.0436E-02/
    CHEB/ -1.5275E-02 -1.4680E-02 -1.1636E-03 -2.6773E-03 -9.0923E-04/
    CHEB/  4.1452E-03  2.3018E-03/
    DUPLICATE
C2H3 + O2 (+M)        <=> O*CC*O + H (+M)       1.00E+00     .000       0. ! ING271    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0813E+01 -4.3764E-01 -2.2867E-01 -2.9839E-02/
    CHEB/  4.8351E-01  2.3258E-01 -1.8651E-01  1.0836E-02  3.0051E-02/
```

```
    CHEB/ -1.1166E-01 -4.5631E-02 -2.3100E-02 -4.1386E-02 -2.0143E-02/
    CHEB/ -1.5271E-02 -7.7431E-03 -5.4426E-04 -2.2714E-03  2.0231E-03/
    CHEB/  4.4232E-03  2.5410E-03/
!************END C2H3+O2 Chemical Activation block********************************


C2H3 + CH3           <=> CH4 + C2H2           3.92E+11    0.0          0. !86 TSANG
C2H3 + CH3OOH        <=> C2H4 + CH3OO         7.00E+11    0.0       1000. !CH3
C2H3 + CCOOH         <=> C2H4 + CCOO          7.00E+11    0.0       1000. !CH3
C2H3 + HO2           <=> C.CHO + OH           1.00E+13    0.0          0. !JWB
C2H3 + HO2           <=> C2H4 + O2            1.00E+12    0.0          0. !JWB
C2H3 + H2O2          <=> C2H4 + HO2           1.00E+12    0.0          1. !JWB EST
CCO2                 <=> CH3+CO2              4.40E+15    0.00     10500.
CCO3                 <=> CC.*O + O2           5.00E+14    0.0      37300.
CCO3 + CH3OO         <=> CCO2 + CH3O + O2     6.00E+10    0.00      -830.
CCO3H + O2           <=> CCO3 + HO2           3.00E+12    0.00     39000.
CCO3H + CH3          <=> CH4 + CCO3           7.43E+11    0.00      5500.
CCO3H + HO2          <=> H2O2 + CCO3          2.40E+12    0.00     10000.
CCO3H + C2H5         <=> C2H6 + CCO3          5.00E+11    0.00      6500.
CCO3H + HCO          <=> CH2O + CCO3          8.00E+11    0.00     10000.
C.*COH (+M)          <=> HC#COH + H (+M)      1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -7.9146E+00  2.1749E+00 -1.9181E-01  1.3972E+01/
    CHEB/  3.4423E-01  1.9094E-01 -5.3430E-01  2.0319E-02  2.5205E-02/
    CHEB/ -3.0422E-01 -3.2819E-02 -1.7541E-02 -8.5108E-02 -1.2511E-02/
    CHEB/ -9.6799E-03  1.6470E-02  3.6870E-03  7.5736E-04 -1.0588E-02/
    CHEB/ -3.4751E-04 -2.2562E-07/
C.*COH (+M)          <=> C*CO. (+M)           1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.7219E+00  2.6975E+00 -5.6963E-01  9.1649E+00/
    CHEB/  1.1580E+00  9.4938E-02 -7.6868E-01  3.3404E-01  9.7358E-02/
    CHEB/ -3.4177E-01  6.7734E-02  3.9860E-02 -1.4754E-01 -2.2196E-03/
    CHEB/  7.7757E-03 -5.6648E-02 -1.0663E-02 -1.1466E-03 -1.7374E-02/
    CHEB/ -6.0379E-03 -1.2578E-03/
C.*COH (+M)          <=> CC.*O (+M)           1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -7.7299E+00  2.7840E+00 -5.5582E-01  8.8080E+00/
    CHEB/  1.2701E+00  1.4523E-01 -9.4070E-01  3.5550E-01  1.1482E-01/
    CHEB/ -3.6432E-01  6.5013E-02  4.2613E-02 -1.1610E-01 -6.1056E-03/
    CHEB/  6.2882E-03 -2.2910E-02 -1.1109E-02 -2.0246E-03  3.7734E-03/
    CHEB/ -4.7421E-03 -1.1360E-03/
C.*COH (+M)          <=> CH3 + CO (+M)        1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.7673E+00  3.1985E-01 -5.4776E-01  9.7610E+00/
    CHEB/  1.3074E+00  1.6010E-01 -6.9853E-01  3.6374E-01  1.2120E-01/
    CHEB/ -3.3122E-01  6.3372E-02  4.3196E-02 -1.3726E-01 -8.0578E-03/
    CHEB/  5.4854E-03 -4.5387E-02 -1.1566E-02 -2.4154E-03 -8.2895E-03/
    CHEB/ -4.4782E-03 -1.1075E-03/
C*CO. (+M)           <=> C*C*O + H (+M)       1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.4170E+00  7.7079E-01 -2.5699E-01  1.2223E+01/
    CHEB/  7.0490E-01 -7.0541E-02 -2.9767E-01  2.8512E-01  3.2272E-02/
    CHEB/ -1.2468E-01  1.0506E-01  3.1831E-02 -5.8994E-02  3.3910E-02/
    CHEB/  1.7226E-02 -2.8162E-02  8.9070E-03  7.3469E-03 -1.3128E-02/
    CHEB/  1.5255E-03  2.6492E-03/
C*CO. (+M)           <=> C.CHO (+M)           1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.6978E+00  2.5138E+00  1.2768E-04  5.0303E-01/
    CHEB/  2.6748E-02  3.0752E-04 -1.6340E-01  2.4387E-02  4.4031E-04/
    CHEB/ -4.4588E-02  2.0883E-02  6.1514E-04 -1.9840E-02  1.6759E-02/
    CHEB/  7.7708E-04 -1.3857E-02  1.2565E-02  8.7937E-04 -1.0277E-02/
    CHEB/  8.7556E-03  8.9623E-04/
C*CO. (+M)           <=> CH3 + CO (+M)        1.00E+00     .000        0. ! ING331   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.7337E+00  6.0390E-01 -1.9304E-01  1.1945E+01/
    CHEB/  7.5576E-01 -8.8225E-02 -3.0497E-01  3.1121E-01  8.2559E-03/
    CHEB/ -1.3119E-01  1.1547E-01  2.5402E-02 -6.2522E-02  3.7684E-02/
    CHEB/  1.6176E-02 -2.9725E-02  1.0474E-02  7.3674E-03 -1.3731E-02/
    CHEB/  2.2256E-03  2.7562E-03/
```

```
!***************************************************************************
!************CH3 + CO subsystem base on hp k from Jong Woo Lee
!************ Ref NIST 2001 conference.    - CYS 12/14/2001
!************Begin CH3+CO block*********************************************
CH3+CO (+M)          <=> CC.*O (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.2861E+00  2.0889E+00 -2.1469E-01 -2.1398E+00/
    CHEB/  4.2374E-01  2.0394E-01 -1.0007E+00 -2.8681E-03  1.5938E-02/
    CHEB/ -4.5410E-01 -2.4943E-02 -1.4134E-02 -1.9748E-01 -6.9299E-03/
    CHEB/ -5.5065E-03 -8.4253E-02  5.5312E-04  1.2006E-05 -3.6193E-02/
    CHEB/  1.0697E-03  7.3141E-04/
CH3+CO (+M)          <=> C*C*O+H (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.3784E+00 -5.6350E-06 -5.3305E-06  1.0995E+01/
    CHEB/  1.0299E-05  9.8612E-06  1.4798E-01 -7.6629E-06 -7.3678E-06/
    CHEB/  4.9005E-02  5.0249E-06  4.6388E-06  1.7159E-02 -2.2308E-06/
    CHEB/ -2.1586E-06  5.8604E-03  9.4601E-07  9.0993E-07  1.7626E-03/
    CHEB/ -2.6693E-07 -2.4545E-07/
CH3+CO (+M)          <=> C.CHO (+M)           1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.6574E+00  5.3054E-01 -9.7447E-02  1.0101E+01/
    CHEB/  7.4162E-01 -6.4605E-02 -6.5273E-01  3.0786E-01  3.6534E-02/
    CHEB/ -3.9159E-01  6.0268E-02  3.7334E-02 -2.0300E-01 -1.9367E-02/
    CHEB/  7.7976E-03 -9.5206E-02 -2.4402E-02 -7.7439E-03 -4.0688E-02/
    CHEB/ -1.2226E-02 -8.1926E-03/
CH3+CO (+M)          <=> C*C*O+H (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.8761E+00 -1.2109E+00 -2.2329E-01  1.3473E+01/
    CHEB/  1.1808E+00  1.0044E-01  8.1632E-02  1.9969E-01  1.4964E-01/
    CHEB/ -7.5011E-02 -8.1465E-02  2.4369E-02 -4.5663E-02 -7.5251E-02/
    CHEB/ -2.9139E-02 -9.3537E-03 -2.5709E-02 -2.2497E-02  4.6109E-03/
    CHEB/  4.6922E-04 -6.1240E-03/

CC.*O (+M)          <=> C*C*O+H (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.3915E+01  5.9228E+00  1.8000E+00  1.4673E+01/
    CHEB/ -2.0590E+00 -8.3343E-01 -5.9834E-01 -3.1269E-01 -2.4165E-01/
    CHEB/ -1.4141E-01 -3.7176E-02 -3.5520E-02 -1.3934E-02 -3.3421E-03/
    CHEB/ -4.1366E-03  1.1298E-02 -6.5597E-04 -6.5922E-04  7.6158E-03/
    CHEB/ -1.9585E-03 -1.1925E-03/
CC.*O (+M)          <=> C.CHO (+M)           1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.5981E+01  5.9786E+00  1.8387E+00  1.4960E+01/
    CHEB/ -2.1127E+00 -8.6951E-01 -6.1573E-01 -3.1067E-01 -2.4134E-01/
    CHEB/ -1.4724E-01 -3.5965E-02 -3.4575E-02 -1.6403E-02 -3.1977E-03/
    CHEB/ -4.0054E-03  1.0232E-02 -6.6472E-04 -6.6453E-04  7.1448E-03/
    CHEB/ -1.9781E-03 -1.2078E-03/
C.CHO (+M)           <=> C*C*O+H (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -6.9301E+00  9.4878E-01 -2.1000E-01  1.4994E+01/
    CHEB/  9.3935E-01  4.2605E-03 -6.7392E-01  2.6297E-01  9.5281E-02/
    CHEB/ -3.5350E-01  2.0283E-02  3.6840E-02 -1.6157E-01 -2.7588E-02/
    CHEB/ -3.5932E-03 -6.3740E-02 -2.0025E-02 -1.1035E-02 -1.9897E-02/
    CHEB/ -7.2971E-03 -6.1930E-03/
!************END CH3+CO block*********************************************

!***************************************************************************
!************CH3C.O+O2 subsystem base on hp k from Jong Woo Lee
!************ Ref NIST 2001 conference.    - CYS 12/14/2001
!************Begin CH3C.O+O2 block*********************************************
CC.*O+O2 (+M)        <=> CCOQJ (+M)           1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.9683E+00  2.1150E+00 -5.2284E-01 -3.3364E+00/
    CHEB/  2.0298E+00 -4.4407E-02 -1.7635E+00  4.4882E-01  2.2584E-01/
    CHEB/ -8.3747E-01 -6.6004E-02  1.0426E-01 -3.7067E-01 -1.1996E-01/
    CHEB/  5.4152E-03 -1.5327E-01 -6.6783E-02 -1.9052E-02 -5.8608E-02/
    CHEB/ -2.1464E-02 -1.3180E-02/
CC.*O+O2 (+M)        <=> C*C*O+HO2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.1393E+01 -1.0292E+00 -2.2751E-01  7.9587E-01/
    CHEB/  1.1500E+00  1.6055E-01 -7.5248E-02  5.1135E-02  1.3205E-01/
```

```
    CHEB/ -9.2453E-02 -1.3476E-01 -2.0341E-02 -2.1345E-02 -5.8509E-02/
    CHEB/ -4.3436E-02  8.5902E-03 -1.2355E-04 -1.4060E-02  1.0065E-02/
    CHEB/  1.2957E-02  4.1535E-03/
    DUPLICATE
CC.*O+O2 (+M)        <=> CC*OOJ+O (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       2.7504E+00 -1.1723E-01 -8.7063E-02  8.1096E+00/
    CHEB/  1.6022E-01  1.1684E-01 -5.6123E-02 -3.5218E-02 -2.2041E-02/
    CHEB/ -3.2257E-02 -1.3768E-02 -1.2170E-02 -1.6982E-02  3.2501E-03/
    CHEB/  1.9081E-03 -1.3535E-02  3.3151E-03  2.8484E-03 -1.1894E-02/
    CHEB/  2.8427E-04  4.1166E-04/
CC.*O+O2 (+M)        <=> CJCOQ (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.3253E+00  1.0144E+00 -7.4197E-01 -1.8926E+00/
    CHEB/  2.7729E+00  1.1553E-01 -1.5734E+00  5.4582E-01  2.5449E-01/
    CHEB/ -8.4675E-01 -1.0576E-01  6.6640E-02 -3.8216E-01 -1.4302E-01/
    CHEB/ -2.3933E-02 -1.5215E-01 -6.7045E-02 -2.8244E-02 -5.4201E-02/
    CHEB/ -1.4814E-02 -1.2788E-02/
CC.*O+O2 (+M)        <=> C*C*O+HO2 (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.7120E+00 -1.1977E+00 -4.9970E-01  3.9596E+00/
    CHEB/  1.4126E+00  5.1607E-01  1.7783E-01 -4.2715E-02  8.5715E-02/
    CHEB/ -3.4599E-02 -1.5508E-01 -7.1116E-02 -1.1011E-02 -4.3461E-02/
    CHEB/ -4.1478E-02  2.6313E-03  8.4126E-03 -3.0023E-03  1.2117E-03/
    CHEB/  1.2544E-02  7.5196E-03/
    DUPLICATE
CC.*O+O2 (+M)        <=> OCYCO+OH (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0032E+01 -1.7940E+00 -4.8872E-01  1.3453E+00/
    CHEB/  1.9844E+00  3.9442E-01 -1.5086E-01  8.6315E-02  2.0448E-01/
    CHEB/ -1.7262E-01 -2.0307E-01 -3.7979E-02 -5.6768E-02 -9.2479E-02/
    CHEB/ -6.3405E-02 -6.4976E-03 -1.0108E-02 -2.2867E-02  3.4651E-03/
    CHEB/  1.2363E-02  1.1989E-03/
CCOQJ (+M)           <=> C*C*O+HO2 (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.3370E+00  9.9724E-01 -1.8827E-01  9.5482E+00/
    CHEB/  1.4305E+00 -1.7349E-01 -9.4123E-01  5.6646E-01  3.0198E-02/
    CHEB/ -4.2777E-01  7.7167E-02  5.6269E-02 -1.4246E-01 -5.0956E-02/
    CHEB/  1.9750E-02 -3.5389E-02 -3.4900E-02  4.9653E-03 -9.6764E-03/
    CHEB/ -3.5505E-03  1.0683E-02/
CCOQJ (+M)           <=> CC*OOJ+O (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.0605E+01  8.7293E+00 -1.9275E-01  1.6321E+01/
    CHEB/  8.3981E-01  1.1127E+00 -1.8353E+00 -2.5381E-01  2.5383E-01/
    CHEB/ -6.5302E-01 -2.5851E-01  3.5204E-02 -1.9657E-01 -1.3718E-01/
    CHEB/  4.8984E-03 -5.1860E-02 -5.2491E-02  1.1641E-02 -1.9424E-02/
    CHEB/ -1.1626E-02  1.8375E-02/
CCOQJ (+M)           <=> CJCOQ (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -9.9968E-01  6.2301E-01 -7.8661E-02  9.1661E+00/
    CHEB/  9.7667E-01 -8.4723E-02 -6.3765E-01  4.5304E-01  2.2055E-02/
    CHEB/ -3.2919E-01  7.7455E-02  5.1562E-02 -1.1199E-01 -4.9915E-02/
    CHEB/  2.7540E-02 -2.4153E-02 -4.1497E-02  8.4007E-03 -4.4488E-03/
    CHEB/ -8.8204E-03  8.4155E-03/
CJCOQ (+M)           <=> C*C*O+HO2 (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -6.0595E+00  4.5257E+00 -9.7709E-01  1.0261E+01/
    CHEB/  1.2833E+00  5.4538E-01 -9.1843E-01  1.7249E-01  2.0396E-01/
    CHEB/ -3.1216E-01 -6.3117E-02  2.5298E-02 -7.4658E-02 -6.1508E-02/
    CHEB/ -1.1044E-02 -1.0771E-02 -2.4551E-02  1.6731E-03 -6.8651E-03/
    CHEB/ -4.5732E-03  1.5973E-02/
CJCOQ (+M)           <=> OCYCO+OH (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.8910E+00  9.4075E-01 -1.6038E-01  6.5571E+00/
    CHEB/  1.1263E+00 -4.2811E-02 -7.5719E-01  3.5669E-01  6.4626E-02/
    CHEB/ -2.7944E-01  2.1414E-02  2.6351E-02 -7.2684E-02 -4.3437E-02/
    CHEB/ -7.7840E-03 -1.1530E-02 -2.5305E-02 -7.2380E-03 -5.0654E-03/
    CHEB/ -5.6383E-03  5.1869E-03/
!***********Begin CH3C.O+O2 block*******************************************
```

```
!***************************************************************************
!************C2H3 + O2 subsystem base on hp k in recent AYC/AMD/JWB publication in
!************ Zeit. Phys. 2000.    - CYS 12/14/2001
!************Begin C2H3+O2 Dissociation block*******************************
C*COO. (+M)          <=> C.CHO+O (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.2273E+01  2.0439E+00 -2.4598E-01  3.1133E+01/
    CHEB/  3.9884E-01  1.8409E-01 -9.8824E-01 -1.7549E-02  1.1082E-02/
    CHEB/ -4.2826E-01 -2.2035E-02 -1.3214E-02 -1.8474E-01 -6.5300E-03/
    CHEB/ -5.2936E-03 -7.9547E-02 -1.2832E-03 -1.0017E-03 -3.3750E-02/
    CHEB/ -4.9251E-04 -2.2205E-04/
!   The following rxn is chem act to prod via 1st well
C*COO. (+M)          <=> C2H2+HO2    (+M)     1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.3025E+01  2.0455E+00 -2.4507E-01  3.0967E+01/
    CHEB/  3.9977E-01  1.8491E-01 -9.7988E-01 -1.7580E-02  1.1140E-02/
    CHEB/ -4.0750E-01 -2.2055E-02 -1.3250E-02 -1.6964E-01 -6.4502E-03/
    CHEB/ -5.2582E-03 -7.0346E-02 -1.1964E-03 -9.4523E-04 -2.8504E-02/
    CHEB/ -4.3837E-04 -1.8347E-04/
!   The following rxn is chem act to prod via 1st well
C*COO. (+M)          <=> CH2O+HCO      (+M)     1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.4241E+01  2.0461E+00 -2.4480E-01  3.1152E+01/
    CHEB/  3.9993E-01  1.8512E-01 -9.8367E-01 -1.7599E-02  1.1145E-02/
    CHEB/ -4.2674E-01 -2.2056E-02 -1.3259E-02 -1.8410E-01 -6.4284E-03/
    CHEB/ -5.2486E-03 -7.9253E-02 -1.1739E-03 -9.3046E-04 -3.3614E-02/
    CHEB/ -4.2437E-04 -1.7366E-04/
C*COO. (+M)          <=> C.CYCOO (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.2414E+01  2.0404E+00 -2.4792E-01  3.1166E+01/
    CHEB/  3.9698E-01  1.8238E-01 -9.8426E-01 -1.7487E-02  1.0967E-02/
    CHEB/ -4.2852E-01 -2.1996E-02 -1.3140E-02 -1.8559E-01 -6.6971E-03/
    CHEB/ -5.3677E-03 -8.0233E-02 -1.4656E-03 -1.1198E-03 -3.4184E-02/
    CHEB/ -6.0568E-04 -3.0298E-04/
C*COO. (+M)          <=> C.*COOH (+M)         1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.3212E+01  2.0447E+00 -2.4556E-01  3.1007E+01/
    CHEB/  3.9929E-01  1.8448E-01 -9.6937E-01 -1.7561E-02  1.1112E-02/
    CHEB/ -4.0384E-01 -2.2045E-02 -1.3230E-02 -1.6823E-01 -6.4928E-03/
    CHEB/ -5.2769E-03 -6.9777E-02 -1.2423E-03 -9.7504E-04 -2.8262E-02/
    CHEB/ -4.6691E-04 -2.0390E-04/
C*COO. (+M)          <=> CYCOOC. (+M)         1.00E+00     .000       0. ! ING271   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.9899E+00  3.5681E+00 -2.5171E-01  6.1143E+00/
    CHEB/  9.9138E-01  1.5488E-02 -7.8844E-01  2.8337E-01  9.9654E-02/
    CHEB/ -2.9406E-01  1.9392E-02  4.6947E-02 -1.0220E-01 -3.7615E-02/
    CHEB/  4.0462E-03 -2.8976E-02 -2.8104E-02 -8.8939E-03 -5.5588E-03/
    CHEB/ -9.7591E-03 -6.8532E-03/
C.CYCOO (+M)         <=> C.OCHO (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.1670E+01  1.5880E+00 -3.4413E-01  3.1150E+01/
    CHEB/  6.8285E-01  1.5916E-01 -1.1695E+00  7.8788E-02  7.8239E-02/
    CHEB/ -5.3885E-01 -1.2215E-02  6.7486E-03 -2.2912E-01 -1.3888E-02/
    CHEB/ -7.0998E-03 -9.4295E-02 -5.7939E-03 -4.4085E-03 -4.0090E-02/
    CHEB/ -1.1719E-03 -1.1007E-03/
C.*COOH (+M)         <=> HCJJCHOT+OH (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.7804E+01  2.4691E+00 -2.2838E-02  3.6851E+01/
    CHEB/  2.5362E-02  1.8575E-02 -1.2833E+00  1.1680E-03  9.6640E-04/
    CHEB/ -5.5813E-01  3.1276E-04  2.4089E-04 -2.4489E-01  1.0608E-04/
    CHEB/  8.0767E-05 -1.1024E-01  2.9718E-05  2.2831E-05 -5.0515E-02/
    CHEB/  3.7780E-06  3.0276E-06/
!   The following rxn is chem act to prod via 2ND well
C.*COOH (+M)         <=> C2H2+HO2       (+M)  1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.7848E+01  2.4691E+00 -2.2829E-02  3.7131E+01/
    CHEB/  2.5350E-02  1.8567E-02 -1.1541E+00  1.1663E-03  9.6518E-04/
    CHEB/ -4.9386E-01  3.1314E-04  2.4112E-04 -2.1224E-01  1.0643E-04/
    CHEB/  8.0963E-05 -9.3512E-02  2.9672E-05  2.2763E-05 -4.1903E-02/
    CHEB/  3.8538E-06  3.2585E-06/
```

```
!   The following rxn is chem act to prod via 4TH well
C.OCHO (+M)          <=> CH2O+HCO      (+M)   1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.8972E+00  3.7597E-01 -8.4317E-02  1.1939E+01/
    CHEB/  6.5728E-01 -1.3187E-01 -3.1511E-01  4.3377E-01 -5.2368E-02/
    CHEB/ -2.3013E-01  2.0134E-01  1.4363E-02 -1.0997E-01  4.3954E-02/
    CHEB/  3.9564E-02 -3.4807E-02 -2.5051E-02  3.1538E-02 -3.0467E-03/
    CHEB/ -3.5975E-02  1.2916E-02/
CYCOOC. (+M)         <=> CH2O + HCO (+M)      1.00E+00     .000       0. ! ING271   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.9392E+00  2.4879E+00 -7.8189E-03  3.9358E-01/
    CHEB/  5.8142E-03  5.6855E-03 -2.0594E-01 -2.6030E-03 -2.6423E-03/
    CHEB/ -3.2166E-02  2.7535E-03  5.6156E-04 -1.0019E-02  3.0554E-03/
    CHEB/  1.4152E-03 -9.9434E-03  1.5429E-03  1.1941E-03 -7.9529E-03/
    CHEB/  6.2838E-05  4.9228E-04/
CYCOOC. (+M)         <=> O*CC*O + H (+M)      1.00E+00     .000       0. ! ING271   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.3647E+00  2.4880E+00 -7.6974E-03  5.9802E-01/
    CHEB/  6.0032E-03  5.7841E-03 -9.0019E-02 -1.9401E-03 -2.4034E-03/
    CHEB/  2.1153E-02  3.4456E-03  8.9793E-04  9.7857E-03  3.2858E-03/
    CHEB/  1.6512E-03 -4.1060E-03  1.2814E-03  1.1949E-03 -6.4318E-03/
    CHEB/ -3.8045E-04  3.0177E-04/
O*CCO. (+M)          <=> C.CHO + O (+M)       1.00E+00     .000       0. ! ING271   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.7031E+01  1.9527E+00 -2.6242E-01  2.7671E+01/
    CHEB/  5.7206E-01  2.4385E-01 -3.6789E-01  4.1134E-02  5.2198E-02/
    CHEB/ -1.0277E-01 -4.7711E-02 -1.8415E-02 -1.5151E-02 -2.8217E-02/
    CHEB/ -1.9003E-02  1.5813E-03 -4.5347E-03 -5.5961E-03 -4.9989E-04/
    CHEB/  4.1441E-03  1.6363E-03/
O*CCO. (+M)          <=> CH2O + HCO (+M)      1.00E+00     .000       0. ! ING271   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.9535E+00  2.2546E+00 -1.4641E-01  2.2157E+00/
    CHEB/  2.9404E-01  1.6859E-01 -5.2622E-01 -2.5102E-02 -5.6939E-03/
    CHEB/ -7.1956E-02 -2.5103E-02 -1.6307E-02  3.1340E-02 -3.3056E-03/
    CHEB/ -3.3721E-03  2.6654E-02  2.6803E-03  1.4415E-03  8.4614E-03/
    CHEB/  1.5293E-03  1.1104E-03/
O*CCO. (+M)          <=> O*CC*O + H (+M)      1.00E+00     .000       0. ! ING271   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.5361E+00  2.4889E+00 -8.2849E-03  8.2726E+00/
    CHEB/  1.4693E-02  1.0944E-02 -2.4782E-01 -3.5813E-03 -2.6391E-03/
    CHEB/  3.6022E-03 -4.7377E-04 -3.6951E-04  3.6328E-02  1.5435E-04/
    CHEB/  1.1550E-04  1.7397E-02  1.0292E-04  7.8185E-05  1.2943E-03/
    CHEB/  1.4470E-05  1.1090E-05/
!************END C2H3+O2 Dissociation block*******************************


C2H4                 <=> C2H2 + H2            9.33E+13    0.0     77200. !NDISSOC HPL
C2H4 + H (+M)        <=> C2H5 (+M)            1.00E+00     .000       0. ! ING361   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.1661E+01  1.0359E+00 -2.6912E-01 -3.7752E-01/
    CHEB/  9.4025E-01  2.0266E-02 -6.8299E-01  3.5172E-01  1.0581E-01/
    CHEB/ -3.4527E-01  8.8351E-02  6.4621E-02 -1.5108E-01 -5.2684E-03/
    CHEB/  2.0222E-02 -5.2057E-02 -2.4334E-02 -1.6496E-03 -9.0972E-03/
    CHEB/ -1.8380E-02 -6.8157E-03/
    H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4 + H             <=> C2H3 + H2            5.42E+14    0.0     14904. !92 BAULCH
C2H4 + CH3           <=> C2H3 + CH4           4.16E+12    0.0     11128. !92 BAULCH
C2H4 + OH            <=> C2H3 + H2O           2.05E+13    0.0      5942. !92 BAULCH
C2H4 + CO            <=> C2H3 + HCO           1.51E+14    0.0     90561. !86 TSANG
C2H4 + O (+M)        <=> C.CHO+ H (+M)        1.00E+00     .000       0. ! ING301   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2123E+01 -5.5629E-03 -4.1734E-03  4.7606E-01/
    CHEB/  6.4949E-03  4.8663E-03 -3.0064E-02 -1.4580E-03 -1.0861E-03/
    CHEB/ -1.8526E-02 -4.7484E-05 -3.8379E-05 -1.0411E-02  6.5035E-05/
    CHEB/  4.9246E-05 -5.3067E-03  2.1670E-05  1.6592E-05 -2.4514E-03/
    CHEB/  5.4526E-06  4.2551E-06/
C2H4 + O (+M)        <=> CH2O + CH2 (+M)      1.00E+00     .000       0. ! ING301   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0185E+01 -5.4288E-03 -4.0726E-03  1.3237E+00/
    CHEB/  6.5347E-03  4.8965E-03  3.4442E-01 -1.5248E-03 -1.1365E-03/
```

```
    CHEB/  8.4879E-02 -8.7966E-05 -6.8893E-05  4.7002E-04  6.5149E-05/
    CHEB/  4.9201E-05 -1.0173E-02  2.7381E-05  2.0709E-05 -4.8293E-03/
    CHEB/  6.0790E-06  4.7285E-06/
C2H4 + O (+M)         <=> CH3CHO (+M)           1.00E+00     .000       0. ! ING301
10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.4090E+00  2.2536E+00 -1.6416E-01 -6.2953E-01/
    CHEB/  2.7976E-01  1.8152E-01 -5.8322E-01 -1.3800E-02 -3.4383E-03/
    CHEB/ -2.9128E-01 -1.9412E-02 -1.3279E-02 -1.3435E-01 -6.2285E-03/
    CHEB/ -4.9381E-03 -5.7490E-02 -1.2264E-04 -3.4308E-04 -2.2987E-02/
    CHEB/  9.7642E-04  6.6584E-04/
C2H4 + O (+M)         <=> CC.*O + H (+M)        1.00E+00     .000       0. ! ING301    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0149E+01 -2.3605E-01 -1.5735E-01  1.0651E+00/
    CHEB/  2.7994E-01  1.8238E-01  1.4277E-01 -2.1840E-02 -8.9609E-03/
    CHEB/  2.3446E-02 -2.3306E-02 -1.6290E-02 -6.6407E-03 -5.5669E-03/
    CHEB/ -4.6163E-03 -8.7191E-03  1.5801E-03  8.7975E-04 -5.0566E-03/
    CHEB/  1.8518E-03  1.3441E-03/
C2H4 + O (+M)         <=> HCO + CH3 (+M)        1.00E+00     .000       0. ! ING301    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.4689E+00 -2.3627E-01 -1.5741E-01  1.0919E+00/
    CHEB/  2.8078E-01  1.8284E-01  1.6253E-01 -2.2322E-02 -9.2605E-03/
    CHEB/  3.0087E-02 -2.3644E-02 -1.6518E-02 -5.1033E-03 -5.4560E-03/
    CHEB/ -4.5536E-03 -8.3850E-03  1.7168E-03  9.7377E-04 -4.9885E-03/
    CHEB/  1.8761E-03  1.3657E-03/
C2H4 + OH (+M)        <=> C.COH (+M)            1.00E+00     .000       0. ! ING311    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.1404E+01  1.2697E+00 -2.6561E-01 -1.5697E+00/
    CHEB/  9.9945E-01  1.0505E-01 -7.7960E-01  2.5859E-01  1.2033E-01/
    CHEB/ -3.2208E-01  2.8545E-03  3.8799E-02 -9.8984E-02 -4.2643E-02/
    CHEB/ -4.5785E-03 -8.5909E-03 -2.8262E-02 -1.2254E-02  1.6777E-02/
    CHEB/ -9.8758E-03 -7.1983E-03/
C2H4 + OH (+M)        <=> C*COH + H (+M)        1.00E+00     .000       0. ! ING311    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0602E+01 -8.1901E-01 -2.7411E-01  1.2797E+00/
    CHEB/  8.6331E-01  2.2662E-01  1.5478E-02  6.9200E-02  9.1985E-02/
    CHEB/ -5.4971E-02 -7.3546E-02 -1.2791E-02 -2.6334E-02 -4.4509E-02/
    CHEB/ -2.7166E-02 -4.4020E-03 -1.0157E-02 -1.1927E-02  3.1007E-03/
    CHEB/  4.0671E-03 -2.2874E-04/
C2H4 + OH (+M)        <=> CCO. (+M)             1.00E+00     .000       0. ! ING311    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        3.3398E+00  1.9388E+00 -3.0608E-01  2.0686E+00/
    CHEB/  6.0856E-01  3.1033E-01 -4.8489E-01  1.8517E-02  3.3886E-02/
    CHEB/ -1.4075E-01 -4.6626E-02 -2.2520E-02 -2.2978E-03 -2.4657E-02/
    CHEB/ -1.7092E-02  2.9409E-02 -4.9817E-03 -5.2428E-03  2.1908E-02/
    CHEB/  2.4699E-03  8.0522E-04/
C2H4 + OH (+M)        <=> CH2O + CH3 (+M)       1.00E+00     .000       0. ! ING311    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        6.4834E+00 -5.3567E-01 -2.9302E-01  3.5421E+00/
    CHEB/  6.0454E-01  3.1124E-01 -2.0973E-02 -5.2460E-04  2.3426E-02/
    CHEB/ -3.6225E-02 -5.3640E-02 -2.8138E-02 -1.3059E-02 -2.2729E-02/
    CHEB/ -1.6861E-02 -4.8853E-04 -1.5579E-03 -3.1417E-03  2.4722E-03/
    CHEB/  4.2520E-03  2.2396E-03/
C2H4 + CH3 (+M)       <=> CCC. (+M)             1.00E+00     .000       0. ! ING421    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.6536E+00  6.9501E-01 -1.0737E-01  1.2850E+00/
    CHEB/  1.0743E+00 -9.7044E-02 -7.3591E-01  5.3974E-01  3.5666E-02/
    CHEB/ -3.4943E-01  1.5104E-01  6.9360E-02 -1.1826E-01 -1.8284E-02/
    CHEB/  3.9591E-02 -1.4986E-02 -5.0436E-02  6.1893E-03  1.6305E-02/
    CHEB/ -3.3050E-02 -8.2393E-03/
C2H4 + CH3 (+M)       <=> C*CC + H (+M)         1.00E+00     .000       0. ! ING421    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        4.9510E+00 -1.3614E+00 -2.1076E-01  5.4115E+00/
    CHEB/  1.1994E+00  3.5293E-02  9.2586E-02  3.0861E-01  1.4847E-01/
    CHEB/ -8.9644E-02 -4.3377E-02  6.4266E-02 -6.4249E-02 -8.5662E-02/
    CHEB/ -1.1626E-02 -2.3171E-02 -4.5264E-02 -2.8972E-02 -2.6382E-03/
    CHEB/ -1.0376E-02 -1.6650E-02/
CH3CHO (+M)           <=> C.CHO+ H (+M)         1.00E+00     .000       0. ! ING301
10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -2.5810E+01  2.5000E+00 -1.0595E-06  2.9261E+01/
```

```
    CHEB/ -2.7703E-06 -1.9038E-06 -1.1587E+00 -2.1712E-06 -1.2926E-06/
    CHEB/ -5.4980E-01 -1.3412E-06 -1.3306E-06 -2.3917E-01 -7.7882E-07/
    CHEB/ -4.0902E-07 -1.0007E-01 -7.5240E-07 -4.3823E-07 -4.1122E-02/
    CHEB/ -1.8862E-07 -3.6643E-07/
CH3CHO (+M)           <=> CH2O + CH2 (+M)      1.00E+00     .000       0. ! ING301
10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.6506E+01  2.2408E+00 -1.7159E-01  3.5053E+01/
    CHEB/  2.9239E-01  1.8839E-01 -6.6883E-01 -1.1775E-02 -1.7446E-03/
    CHEB/ -3.1046E-01 -2.0652E-02 -1.3886E-02 -1.2949E-01 -7.1171E-03/
    CHEB/ -5.5581E-03 -5.2263E-02 -2.2121E-04 -4.6364E-04 -2.1186E-02/
    CHEB/  1.1093E-03  7.3966E-04/
CH3CHO (+M)           <=> CC.*O + H (+M)       1.00E+00     .000       0. ! ING301
10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.8649E+01  8.2564E-01 -2.1561E-01  2.5739E+01/
    CHEB/  9.1367E-01 -4.7264E-02 -8.4020E-01  3.9495E-01  7.0267E-02/
    CHEB/ -4.4606E-01  1.2649E-01  5.9189E-02 -2.1280E-01  1.7696E-02/
    CHEB/  2.5494E-02 -9.6639E-02 -1.1894E-02  4.3898E-03 -4.1793E-02/
    CHEB/ -1.2231E-02 -2.6921E-03/
CH3CHO (+M)           <=> HCO + CH3 (+M)       1.00E+00     .000       0. ! ING301
10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.1871E+01  9.3743E-01 -2.5009E-01  2.6135E+01/
    CHEB/  9.1711E-01 -9.7020E-03 -8.4463E-01  3.6995E-01  8.8784E-02/
    CHEB/ -4.4827E-01  1.0890E-01  6.0959E-02 -2.1132E-01  9.4819E-03/
    CHEB/  2.2748E-02 -9.4581E-02 -1.4411E-02  2.2105E-03 -4.0172E-02/
    CHEB/ -1.2423E-02 -3.5873E-03/

!*******The following system is from JWL - NIST 2001 conf.********
!*******Begin block Jong Woo's C.CHO + O2 system ************
C.CHO+O2 (+M)         <=> HC*OCOO. (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.3613E+00  1.5229E+00 -4.2448E-01 -3.6512E-01/
    CHEB/  1.7556E+00 -2.2723E-01 -1.4129E+00  5.5981E-01  7.9678E-02/
    CHEB/ -7.5970E-01  3.8807E-02  6.7954E-02 -3.5917E-01 -7.8145E-02/
    CHEB/  5.5823E-03 -1.5230E-01 -5.6456E-02 -1.7864E-02 -5.7259E-02/
    CHEB/ -1.8781E-02 -1.3436E-02/
C.CHO+O2 (+M)         <=> C*C*O+HO2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.9849E-01 -2.8778E-01 -1.8189E-01  1.0709E+01/
    CHEB/  3.6461E-01  2.1947E-01  2.6700E-01 -3.9911E-02 -6.9142E-03/
    CHEB/  6.3082E-02 -4.2198E-02 -3.1406E-02  2.0090E-02 -5.6899E-03/
    CHEB/ -7.6882E-03  6.0676E-03  7.5821E-03  4.9240E-03 -1.7764E-03/
    CHEB/  4.9070E-03  4.3280E-03/
    DUPLICATE
C.CHO+O2 (+M)         <=> C.*OCOOH (+M)           1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.8769E+00  1.6103E+00 -3.2631E-01 -9.5279E-01/
    CHEB/  1.5589E+00 -3.0149E-01 -1.5014E+00  5.7069E-01  1.2892E-01/
    CHEB/ -7.8060E-01  2.0231E-02  8.3360E-02 -3.6324E-01 -9.0400E-02/
    CHEB/  1.2204E-02 -1.5389E-01 -6.2423E-02 -1.4375E-02 -5.8288E-02/
    CHEB/ -2.1492E-02 -1.1817E-02/
C.CHO+O2 (+M)         <=> C*C*O+HO2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.8005E-01 -1.1238E+00 -1.9637E-01  3.6361E+00/
    CHEB/  1.2444E+00  1.1255E-01  2.3211E-01  7.7826E-02  1.4529E-01/
    CHEB/ -4.8790E-02 -1.5521E-01 -9.2102E-03 -2.3244E-02 -6.9693E-02/
    CHEB/ -4.8812E-02  4.5750E-03  3.6555E-04 -1.8608E-02  7.6724E-03/
    CHEB/  1.6475E-02  4.6439E-03/
    DUPLICATE
C.CHO+O2 (+M)         <=> CO+CH2O+OH (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.3433E+00 -1.2686E+00 -1.9173E-01  2.9124E+00/
    CHEB/  1.2641E+00  7.1667E-02 -3.3691E-03  2.2382E-01  1.5522E-01/
    CHEB/ -1.0850E-01 -1.1377E-01  2.9051E-02 -4.1367E-02 -1.0196E-01/
    CHEB/ -3.8175E-02  5.8265E-03 -3.1185E-02 -3.1020E-02  1.6814E-02/
    CHEB/  6.2999E-03 -7.5890E-03/
HC*OCOO. (+M)           <=> C*C*O+HO2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.6254E+01  7.7523E+00 -8.7393E-01  1.4879E+01/
```

```
    CHEB/  1.2636E+00  1.1919E+00 -1.3920E+00 -1.5663E-01  2.8072E-01/
    CHEB/ -5.0536E-01 -2.2811E-01  3.0998E-02 -1.4222E-01 -1.2146E-01/
    CHEB/  4.7512E-03 -2.9382E-02 -3.4004E-02  1.6603E-02 -1.0004E-02/
    CHEB/  4.5684E-03  2.3767E-02/
HC*OCOO. (+M)          <=> C.*OCOOH (+M)          1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        5.3136E-01  5.2320E-01 -9.7369E-02  7.3686E+00/
    CHEB/  8.1113E-01 -1.1209E-01 -5.5549E-01  3.7255E-01  6.3624E-03/
    CHEB/ -2.8262E-01  6.0886E-02  4.8809E-02 -9.8761E-02 -4.4799E-02/
    CHEB/  3.2909E-02 -2.4624E-02 -3.5188E-02  1.3257E-02 -7.3515E-03/
    CHEB/ -4.7547E-03  9.1217E-03/
C.*OCOOH (+M)           <=> C*C*O+HO2 (+M)       1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -1.3539E+01  2.6248E+00  8.7248E-02  6.5453E+00/
    CHEB/ -1.7019E-01 -1.1744E-01 -5.2234E-01  4.6557E-02  2.9955E-02/
    CHEB/ -8.4322E-02  1.0175E-03  1.9482E-03 -1.3885E-02 -1.4712E-03/
    CHEB/ -1.0815E-03 -1.0844E-02 -3.7614E-04 -3.3544E-04 -7.3896E-03/
    CHEB/ -1.0302E-05 -1.4355E-05/
C.*OCOOH (+M)           <=> CO+CH2O+OH (+M)      1.00E+00    0.000       0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        6.7309E+00  2.4657E+00 -2.3993E-02  1.9829E+00/
    CHEB/  5.0695E-02  3.5175E-02 -4.4397E-01 -1.9491E-02 -1.3052E-02/
    CHEB/ -3.6270E-02  2.7080E-03  1.5095E-03  7.3852E-03  5.0610E-04/
    CHEB/  4.4969E-04 -1.8354E-03 -1.6290E-04 -1.0928E-04 -3.4323E-03/
    CHEB/ -3.4529E-05 -3.0280E-05/
!*******End block Jong Woo's C.CHO + O2 system ************

C*COH + OH            <=> H2O + C.CHO          1.00E+13    0.0       440.
C*COH + H             <=> H2 + C.CHO             4.00E+13    0.0      3200.
C*COH + O             <=> C.CHO + OH             1.50E+13    0.0      1790.
C*COH + CH3           <=> CH4 + C.CHO          5.00E+11    0.0      6600.
C*COH + HO2           <=> H2O2 + C.CHO         4.00E+11    0.0      9178.
CH3CHO + O2             <=> CC.*O + HO2          2.00E+13    0.50     42200.
CH3CHO + OH             <=> CC.*O + H2O          1.00E+13    0.00         0.
CH3CHO + H              <=> CC.*O + H2           4.00E+13    0.00      4200.
CH3CHO + O              <=> CC.*O + OH           5.00E+12    0.00      1790.
CH3CHO + HO2            <=> CC.*O + H2O2         1.70E+12    0.00     10700.
CH3CHO + CH3            <=> CH4 + C.CHO          5.00E+11    0.00      8000.
CH3CHO + CH3OO          <=> CH3OOH + CC.*O       2.80E+12    0.00     13600.
CH3CHO + CCO3           <=> CC.*O + CCO3H        2.80E+12    0.00     13600.
CYCCO + OH            <=> CYC.CO + H2O         4.80E+13    0.00      5955.
CYCCO + H             <=> CYC.CO + H2          7.90E+13    0.00      9800.
CYCCO + CH3OO         <=> CYC.CO + CH3OOH      2.83E+12    0.00     24000.
CYCCO + CCOO          <=> CYC.CO + CCOOH       2.83E+12    0.00     24000.
CYCCO + CH3           <=> CYC.CO + CH4         1.07E+12    0.00     11830.
C2H5 + O              <=> CH3CHO + H             8.02E+13    0.0           0. !86 TSANG
C2H5 + O              <=> CH2O + CH3           1.61E+13    0.0           0. !86 TSANG
C2H5 + H              <=> H2 + C2H4            2.00E+12    .00           0. ! GRI 2.0
C2H5 + OH             <=> C2H4 + H2O           2.41E+13    0.0           0. !86TSANG
C2H5 + OH             <=> CCOH                 3.70E+13    0.0           0.
C2H5 + HO2            <=> CCO. + OH            3.00E+13    0.00          0. !90 BOZZELLI


!*******The following system is from Sheng/Bozzelli/Dean/Chang.  Process of
!*******publication to JPC.  Thermo at CBS-Q//B3LYP/6-31G(d,p).  Kinetic base
!*******canonical and variational TST for hi-p rate constant.  - CYS 2001*******
!*******Begin block CC. + O2 system ************
C2H5 + O2 (+M)        <=> CCOO (+M)            1.00E+00    0.000         0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0648E+01  1.6914E+00 -4.5021E-01 -1.7983E+00/
    CHEB/  1.2539E+00 -1.0471E-01 -7.9081E-01  3.9266E-01  2.4699E-03/
    CHEB/ -3.1899E-01  8.2473E-02  1.5849E-02 -1.1892E-01  4.4983E-03/
    CHEB/  9.8409E-03 -4.0961E-02 -5.4887E-03  3.7478E-03 -1.2984E-02/
    CHEB/ -3.1869E-03  8.8170E-04/
C2H5 + O2 (+M)        <=> CH3CHO + OH (+M)       1.00E+00    0.000         0. !   ME 7x3
300-1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        6.7762E+00 -2.5984E-01 -1.6348E-01  2.6710E+00/
    CHEB/  2.8925E-01  1.7489E-01  1.1152E-01 -6.1846E-04  7.8591E-03/
    CHEB/  1.5400E-02 -2.3332E-02 -1.4351E-02  3.8958E-03 -7.6938E-03/
```

```
    CHEB/ -6.0593E-03  2.1391E-03 -4.2456E-04 -7.5550E-04  1.1303E-03/
    CHEB/  9.1744E-04  5.4377E-04/
C2H5 + O2 (+M)       <=> C2H4 + HO2 (+M)        1.00E+00    0.000       0. !   ME 7x3
300-1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.0105E+01 -8.6141E-01 -2.4194E-01  7.9372E-01/
    CHEB/  8.6151E-01  1.7920E-01  3.4629E-02  7.7542E-02  7.4398E-02/
    CHEB/ -1.8220E-02 -5.3277E-02  4.1458E-04 -6.4999E-03 -2.9468E-02/
    CHEB/ -1.1751E-02  7.3956E-04 -6.8387E-03 -6.1751E-03  2.2167E-03/
    CHEB/  3.3892E-04 -1.6213E-03/
    DUPLICATE
C2H5 + O2 (+M)       <=> CCO.  +  O (+M)      1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        5.2169E-01 -2.9427E-04 -2.7338E-04  7.8527E+00/
    CHEB/  4.0318E-04  3.7551E-04  2.2772E-02 -1.1322E-04 -1.0496E-04/
    CHEB/  5.3466E-03 -7.1231E-06 -7.0518E-06  1.0738E-03  6.2517E-06/
    CHEB/  5.7344E-06  5.6882E-05  2.0154E-06  1.8813E-06 -1.4474E-04/
    CHEB/  9.3592E-08  1.2041E-07/
C2H5 + O2 (+M)       <=> C.COOH (+M)          1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        6.0998E+00  1.1509E+00 -6.4659E-01 -5.0817E-01/
    CHEB/  1.7891E+00  2.9649E-01 -6.8250E-01  1.9036E-01  1.3165E-01/
    CHEB/ -3.1389E-01 -4.9527E-02 -2.2499E-03 -1.1649E-01 -3.2707E-02/
    CHEB/ -1.8396E-02 -3.7037E-02 -7.5047E-03 -7.4647E-03 -9.7406E-03/
    CHEB/  1.3532E-03 -5.2525E-04/
C2H5 + O2 (+M)       <=> C2H4 + HO2 (+M)      1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.3406E+00 -1.2046E+00 -4.3450E-01  1.9373E+00/
    CHEB/  1.3714E+00  4.1593E-01  7.4320E-02 -4.6235E-02  8.0173E-02/
    CHEB/ -2.7475E-02 -1.0104E-01 -3.9862E-02 -5.5053E-03 -3.0101E-02/
    CHEB/ -2.4092E-02  3.2855E-03 -5.3892E-04 -4.3211E-03  3.1951E-03/
    CHEB/  4.0331E-03  1.4030E-03/
    DUPLICATE
C2H5 + O2 (+M)       <=> CYCCO + OH (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.1356E+00 -1.2418E+00 -4.3897E-01  1.9028E+00/
    CHEB/  1.4013E+00  4.1394E-01  6.7487E-02 -3.5542E-02  8.5737E-02/
    CHEB/ -2.9368E-02 -1.0207E-01 -3.7957E-02 -5.5591E-03 -3.2149E-02/
    CHEB/ -2.4652E-02  3.7193E-03 -1.5371E-03 -4.9716E-03  3.5298E-03/
    CHEB/  3.8057E-03  1.1490E-03/
!*******END block CC. + O2 system ************


C2H5 + CH3           <=> CH4 + C2H4           1.15E+12    0.0         0. !92 BAULCH
C2H5 + C2H3          <=> C2H6 + C2H2          4.80E+11   0.0        0.
C2H5 + C2H3          <=> C2H4 + C2H4          3.00E+12    0.00        0.
C2H5 + C2H4          <=> C2H6 + C2H3          6.30E+02   3.13   18000.
C2H5 + C2H5          <=> C2H6 + C2H4          1.45E+12    0.00        0. !92 BAULCH
C.COH (+M)           <=> C*COH + H (+M)       1.00E+00     .000       0. ! ING311   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -1.3887E+00  1.5309E+00 -3.0481E-01  8.5035E+00/
    CHEB/  8.6007E-01  1.8919E-01 -7.7478E-01  1.7494E-01  1.1404E-01/
    CHEB/ -3.0536E-01 -2.2552E-02  1.9230E-02 -8.2165E-02 -4.3352E-02/
    CHEB/ -1.4449E-02  1.9017E-03 -2.2968E-02 -1.4139E-02  2.1014E-02/
    CHEB/ -5.6401E-03 -6.0400E-03/
C.COH (+M)           <=> CYCCO + H (+M)       1.00E+00     .000       0. ! ING311   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -1.3383E+01  2.3396E+00 -1.0671E-01  1.6304E+01/
    CHEB/  1.8705E-01  1.2109E-01 -5.9180E-01 -9.5067E-03 -1.6816E-03/
    CHEB/ -1.8071E-01 -1.5593E-02 -1.0953E-02 -1.8391E-02 -4.7812E-03/
    CHEB/ -3.9625E-03  2.6193E-02  4.0910E-04  9.8834E-05  2.5789E-02/
    CHEB/  1.1796E-03  8.7039E-04/
C.COH (+M)           <=> CCO. (+M)            1.00E+00     .000       0. ! ING311   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -9.3918E+00  4.4043E+00 -3.2439E-01  9.8496E+00/
    CHEB/  6.0577E-01  3.0442E-01 -1.1077E+00  4.0813E-02  4.5415E-02/
    CHEB/ -3.4256E-01 -3.5273E-02 -1.4264E-02 -4.0912E-02 -2.4591E-02/
```

```
    CHEB/ -1.5660E-02  4.0654E-02 -8.2982E-03 -6.9560E-03  3.9084E-02/
    CHEB/  7.3998E-05 -9.4111E-04/
C.COH (+M)           <=> CH2O + CH3 (+M)       1.00E+00     .000        0. ! ING311   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -6.3702E+00  1.9268E+00 -3.1238E-01  1.1174E+01/
    CHEB/  6.0857E-01  3.0896E-01 -7.0323E-01  2.7524E-02  3.8671E-02/
    CHEB/ -2.5330E-01 -4.2642E-02 -1.9558E-02 -4.9829E-02 -2.5137E-02/
    CHEB/ -1.6877E-02  1.7238E-02 -6.4291E-03 -6.0523E-03  2.5584E-02/
    CHEB/  1.6127E-03  1.4811E-04/
C.COH + O2 (+M)      <=> COHCQ. (+M)           1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.1412E+01  1.5416E+00 -3.3510E-01 -1.0332E+00/
    CHEB/  6.8866E-01  1.6106E-01 -4.4033E-01  1.8314E-01  8.3713E-02/
    CHEB/ -1.2852E-01 -9.1913E-04  2.1335E-02 -9.6156E-03 -2.9432E-02/
    CHEB/ -4.1089E-03  1.8045E-02 -1.6107E-02 -7.1547E-03  1.3601E-02/
    CHEB/ -2.7650E-03 -3.3295E-03/
C.COH + O2 (+M)      <=> CO.CQ (+M)            1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        9.6558E+00  1.4590E+00 -4.1393E-01 -6.1839E-02/
    CHEB/  8.3471E-01  2.5749E-01 -7.1019E-02  1.5396E-01  7.9926E-02/
    CHEB/ -5.9520E-02 -2.3979E-02  1.1657E-02 -4.1507E-02 -3.6181E-02/
    CHEB/ -9.2331E-03 -2.3296E-02 -1.5320E-02 -8.3475E-03 -1.1219E-02/
    CHEB/ -7.0540E-04 -2.7336E-03/
C.COH + O2 (+M)      <=> CH2O + CH2OOH (+M)    1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        8.5117E+00 -4.6701E-01 -2.8641E-01  3.3414E+00/
    CHEB/  4.0373E-01  2.3219E-01  2.1527E-01  4.0399E-02  3.0755E-02/
    CHEB/  2.0888E-02 -2.1832E-02 -9.6609E-03 -1.5460E-02 -1.5267E-02/
    CHEB/ -9.1665E-03 -1.4532E-02 -3.1590E-03 -2.6963E-03 -8.8686E-03/
    CHEB/  2.0963E-03  8.9136E-04/
C.COH + O2 (+M)      <=> C.OHCQ (+M)           1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        9.0225E+00  1.3167E+00 -4.7776E-01 -6.9030E-01/
    CHEB/  9.9446E-01  3.4078E-01 -3.4887E-01  1.5543E-01  8.0193E-02/
    CHEB/ -9.0633E-02 -3.5821E-02 -2.2110E-04  5.6248E-03 -3.6592E-02/
    CHEB/ -1.0463E-02  1.8774E-02 -1.2910E-02 -5.7132E-03  8.4763E-03/
    CHEB/ -1.4992E-04 -1.5453E-03/
C.COH + O2 (+M)      <=> C*COH + HO2 (+M)      1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        1.1380E+01 -1.0861E+00 -4.4409E-01  7.6186E-01/
    CHEB/  1.0216E+00  3.6334E-01  5.9485E-02  1.0676E-01  6.9498E-02/
    CHEB/ -2.3437E-02 -6.4116E-02 -1.2052E-02 -1.5816E-02 -4.0520E-02/
    CHEB/ -1.5394E-02 -6.1300E-03 -9.5225E-03 -6.4829E-03 -2.3969E-03/
    CHEB/  2.5544E-03 -8.8904E-04/
C.COH + O2 (+M)      <=> O*CCQ + H (+M)        1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.8663E+00 -5.3843E-01 -3.1642E-01  3.0472E+00/
    CHEB/  5.2917E-01  2.9665E-01  2.3249E-01  2.8707E-02  2.5600E-02/
    CHEB/  4.0234E-02 -3.7902E-02 -1.9791E-02  1.2767E-03 -1.9076E-02/
    CHEB/ -1.1648E-02 -4.6689E-03 -2.7238E-03 -2.3662E-03 -4.4155E-03/
    CHEB/  2.6524E-03  1.1871E-03/
C.COH + O2 (+M)      <=> COHC.OOH (+M)         1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        3.3476E+00  2.2289E+00 -1.6978E-01  3.8630E+00/
    CHEB/  2.2955E-01  1.3636E-01  1.7244E-01  4.1064E-02  2.8961E-02/
    CHEB/  2.1655E-02 -1.4764E-02 -7.1785E-03 -9.1671E-03 -1.3552E-02/
    CHEB/ -8.5571E-03 -8.1048E-03 -3.6260E-03 -2.8437E-03 -3.6983E-03/
    CHEB/  1.3684E-03  5.7962E-04/
C.COH + O2 (+M)      <=> C*COOH + OH (+M)      1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        4.2097E+00 -2.1094E-01 -1.3509E-01  5.6538E+00/
    CHEB/  2.1382E-01  1.3141E-01  7.2095E-01  8.1548E-03  9.6245E-03/
    CHEB/  1.8902E-01 -1.9722E-02 -1.1842E-02  3.9771E-02 -8.0107E-03/
    CHEB/ -5.9094E-03  2.0745E-03  3.6759E-05 -4.1024E-04 -4.4217E-03/
    CHEB/  1.8998E-03  1.2112E-03/
C.COH + O2 (+M)      <=> O*CCOH + OH (+M)      1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        7.6481E+00 -2.7025E-01 -1.6926E-01  4.1161E+00/
    CHEB/  2.2967E-01  1.3651E-01  2.3611E-01  4.0742E-02  2.8790E-02/
    CHEB/  5.8229E-02 -1.4936E-02 -7.2993E-03  6.9529E-03 -1.3561E-02/
    CHEB/ -8.5765E-03 -4.3192E-03 -3.5829E-03 -2.8203E-03 -4.8663E-03/
```

```
    CHEB/  1.3935E-03  5.9787E-04/
CCO. (+M)            <=> CH2O + CH3 (+M)      1.00E+00     .000       0. ! ING311   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       3.1172E+00  1.8138E+00 -2.7940E-01  5.1622E+00/
    CHEB/  6.8206E-01  2.3732E-01 -7.9423E-01  7.4240E-02  6.8497E-02/
    CHEB/ -2.5175E-01 -4.4433E-02 -1.0020E-02 -3.0779E-02 -3.1397E-02/
    CHEB/ -1.6975E-02  2.8067E-02 -8.1226E-03 -6.8498E-03  2.6254E-02/
    CHEB/  1.9133E-03 -2.3185E-04/
CC.OH                <=> C*COH + H            5.00E+13    0.0     36490.
CC.OH                <=> CH3CHO + H            5.00E+13    0.0     26620.
CC.OH + O2 (+M)      <=> CCQ.OH (+M)          1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0960E+01  2.2831E+00 -1.2574E-01 -7.9955E-01/
    CHEB/  1.6878E-01  9.9060E-02 -2.2655E-01  1.9352E-02  9.6396E-03/
    CHEB/ -3.3475E-03 -1.0809E-02 -7.5008E-03  2.7343E-02 -2.1210E-03/
    CHEB/ -1.8811E-03  1.4738E-02  9.4142E-04  6.8641E-04  2.4064E-03/
    CHEB/  5.5310E-04  5.8570E-04/
CC.OH + O2 (+M)      <=> CH3CHO + HO2 (+M)    1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2844E+01 -7.3026E-01 -4.2201E-01  2.6246E-01/
    CHEB/  3.5738E-01  1.8327E-01 -2.8422E-02  6.0139E-02  3.3250E-02/
    CHEB/ -1.6230E-03  5.8290E-03  2.1688E-03  4.4587E-03  3.5696E-03/
    CHEB/  1.8566E-03  3.7992E-03  2.4208E-03  1.9184E-03  1.3977E-03/
    CHEB/  8.6794E-04  9.4938E-04/
CC.OH + O2 (+M)      <=> CCQO. (+M)           1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.2339E+00  2.2851E+00 -1.2792E-01 -7.1793E-03/
    CHEB/  1.9358E-01  1.1659E-01  1.4285E-01  7.3304E-03  2.3760E-03/
    CHEB/  1.2422E-01 -1.5885E-02 -1.0126E-02  5.4836E-02 -3.0065E-03/
    CHEB/ -2.0873E-03  1.5471E-02  1.3996E-03  1.0097E-03  1.0981E-03/
    CHEB/  9.6869E-04  7.4723E-04/
CC.OH + O2 (+M)      <=> C.CQOH (+M)          1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.6862E+00  1.2113E+00 -4.1903E-01 -3.8382E-01/
    CHEB/  1.1008E+00  2.4923E-01 -2.8194E-01  2.1613E-01  1.2776E-01/
    CHEB/ -9.0346E-02 -4.5406E-02  1.8285E-02 -7.9751E-03 -5.6499E-02/
    CHEB/ -1.6910E-02  1.2990E-02 -2.2387E-02 -1.5328E-02  8.4285E-03/
    CHEB/ -5.5649E-04 -5.2476E-03/
CC.OH + O2 (+M)      <=> C*COH + HO2 (+M)     1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0130E+01 -1.1285E+00 -3.8030E-01  1.7124E+00/
    CHEB/  1.1010E+00  2.7576E-01  2.7543E-01  1.1393E-01  1.1160E-01/
    CHEB/ -2.6195E-02 -9.1766E-02 -6.3693E-03 -4.7302E-02 -5.3490E-02/
    CHEB/ -2.7571E-02 -1.9932E-02 -7.4068E-03 -1.3016E-02 -4.1776E-03/
    CHEB/  7.9968E-03 -2.4303E-05/
CC.OH + O2 (+M)      <=> C*COOH + OH (+M)     1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       5.5258E+00 -4.7434E-01 -2.5442E-01  6.5225E+00/
    CHEB/  4.6463E-01  2.2313E-01  9.5994E-02  3.4180E-02  4.3102E-02/
    CHEB/ -2.9810E-02 -3.7624E-02 -1.6993E-02 -1.3687E-02 -2.1484E-02/
    CHEB/ -1.6041E-02 -2.1993E-02 -5.0848E-03 -4.9489E-03  5.3770E-03/
    CHEB/  4.9945E-03  2.2940E-03/
CC.OH + O2 (+M)      <=> CC.QOH (+M)          1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       6.2724E+00  1.7816E+00 -3.4495E-01  2.4379E+00/
    CHEB/  6.1940E-01  2.4715E-01 -7.8884E-02  1.1520E-01  8.9055E-02/
    CHEB/  1.7588E-02 -3.1529E-02 -3.6145E-03  4.8187E-02 -3.9154E-02/
    CHEB/ -2.1067E-02  3.7530E-02 -1.4759E-02 -1.1613E-02  1.9435E-02/
    CHEB/  1.1237E-03 -1.7277E-03/
CC.OH + O2 (+M)      <=> O*COOHC + H (+M)     1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.2739E+00 -6.9836E-01 -3.3501E-01  3.8738E+00/
    CHEB/  6.2910E-01  2.5418E-01  3.5671E-01  1.0277E-01  8.4041E-02/
    CHEB/  8.5875E-02 -4.1837E-02 -9.3801E-03  1.0568E-02 -4.0450E-02/
    CHEB/ -2.2758E-02 -2.2783E-03 -1.1881E-02 -1.0595E-02  5.6472E-04/
    CHEB/  3.2846E-03 -4.5732E-04/
CC.OH + O2 (+M)      <=> CCO2H + OH (+M)      1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.2086E+00 -6.9836E-01 -3.3501E-01  3.8738E+00/
    CHEB/  6.2910E-01  2.5418E-01  3.5671E-01  1.0277E-01  8.4041E-02/
    CHEB/  8.5875E-02 -4.1837E-02 -9.3800E-03  1.0568E-02 -4.0450E-02/
```

```
     CHEB/ -2.2758E-02 -2.2783E-03 -1.1881E-02 -1.0595E-02  5.6471E-04/
     CHEB/  3.2848E-03 -4.5745E-04/
COC. (+M)             <=> CH2O + CH3 (+M)      1.00E+00     .000       0. ! ING141   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        5.6217E+00  2.3436E+00 -1.0276E-01  2.5723E+00/
     CHEB/  1.8156E-01  1.1681E-01 -5.9802E-01 -3.9483E-03  5.5797E-04/
     CHEB/ -9.0487E-02 -1.9868E-02 -1.3021E-02  3.8220E-02 -4.9527E-03/
     CHEB/ -3.9400E-03  3.6463E-02  1.8520E-03  9.9320E-04  1.3357E-02/
     CHEB/  1.7255E-03  1.2137E-03/
COC. + OH (+M)        <=> COCOH (+M)           1.00E+00     .000       0. ! ING161   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        1.2748E+01  5.1691E-01 -8.4377E-02 -1.0361E+00/
     CHEB/  8.8176E-01 -1.1165E-01 -7.7259E-01  5.6363E-01 -1.5227E-02/
     CHEB/ -4.9472E-01  2.6746E-01  4.2135E-02 -2.8041E-01  8.2316E-02/
     CHEB/  4.7168E-02 -1.4327E-01 -2.0255E-04  2.7274E-02 -6.5698E-02/
     CHEB/ -2.2763E-02  7.9314E-03/
COC. + OH (+M)        <=> COC.OH + H (+M)      1.00E+00     .000       0. ! ING161   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        8.9509E+00 -1.6877E+00 -1.0227E-01  2.4751E+00/
     CHEB/  1.2391E+00 -7.4799E-02  3.1361E-01  5.5452E-01  8.0757E-02/
     CHEB/ -1.2061E-01  8.4084E-02  9.9640E-02 -1.1358E-01 -8.2410E-02/
     CHEB/  3.9507E-02 -5.9087E-02 -8.1385E-02 -9.3348E-03 -2.0857E-02/
     CHEB/ -3.8883E-02 -2.2298E-02/
COC. + OH (+M)        <=> COCO. + H (+M)       1.00E+00     .000       0. ! ING161   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        6.2299E+00 -1.5339E+00 -1.5449E-01  4.2818E+00/
     CHEB/  1.2500E+00 -2.7234E-02  2.8417E-01  4.3902E-01  1.2889E-01/
     CHEB/ -7.3747E-02  1.2599E-02  9.1248E-02 -9.0472E-02 -9.1724E-02/
     CHEB/  1.1989E-02 -4.8677E-02 -6.6805E-02 -2.4354E-02 -1.6821E-02/
     CHEB/ -2.5240E-02 -2.2942E-02/
COC. + CH2O (+M)      <=> COCOC. (+M)          1.00E+00     .000       0. ! ING191   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        7.3386E+00  8.6775E-01 -2.2009E-01  1.5616E+00/
     CHEB/  9.5215E-01 -1.0416E-01 -2.9533E-01  2.9759E-01  2.2133E-02/
     CHEB/ -1.1099E-02 -1.5171E-02  2.9623E-02  6.4234E-02 -7.2026E-02/
     CHEB/  4.0996E-03  4.5366E-02 -3.8675E-02 -7.3243E-03  1.1590E-02/
     CHEB/ -3.9312E-03 -5.3316E-03/
COC. + CH3O (+M)      <=> COCOC (+M)           1.00E+00     .000       0. ! ING211   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        1.2648E+01  4.0346E-01 -6.0306E-02 -8.1025E-01/
     CHEB/  7.3487E-01 -9.8816E-02 -6.5604E-01  5.5155E-01 -4.7451E-02/
     CHEB/ -4.6081E-01  3.3227E-01  3.6642E-03 -2.7911E-01  1.4773E-01/
     CHEB/  3.1825E-02 -1.4292E-01  3.1734E-02  3.3713E-02 -5.7960E-02/
     CHEB/ -1.9918E-02  2.0580E-02/
COC. + CH3O (+M)      <=> COC.OC + H (+M)      1.00E+00     .000       0. ! ING211   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        6.0208E+00 -1.7874E+00 -8.0731E-02  5.3378E+00/
     CHEB/  1.1798E+00 -8.8244E-02  5.3667E-01  6.4696E-01  4.0590E-02/
     CHEB/ -1.1412E-01  1.7741E-01  9.7258E-02 -1.2197E-01 -5.8598E-02/
     CHEB/  6.5374E-02 -6.1992E-02 -1.0384E-01  8.8590E-03 -2.8131E-02/
     CHEB/ -6.8168E-02 -2.2488E-02/
COC. + CH3O (+M)      <=> COCOC. + H (+M)      1.00E+00     .000       0. ! ING211   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        5.8984E+00 -1.7638E+00 -8.6208E-02  6.0078E+00/
     CHEB/  1.2004E+00 -8.7622E-02  5.0081E-01  6.3043E-01  5.1752E-02/
     CHEB/ -9.8726E-02  1.5268E-01  1.0310E-01 -1.1366E-01 -7.0093E-02/
     CHEB/  6.1446E-02 -5.8604E-02 -1.0269E-01  2.2482E-03 -2.6258E-02/
     CHEB/ -6.2988E-02 -2.5858E-02/
COCO. (+M)            <=> COC. + O (+M)        1.00E+00     .000       0. ! ING171   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3       -3.0198E+01  2.5000E+00 -7.6998E-06  3.0958E+01/
     CHEB/ -6.6850E-06 -4.7538E-06  1.0275E-01 -4.7111E-06 -3.6149E-06/
     CHEB/  1.3585E-01 -4.9079E-06 -3.2995E-06  9.7239E-02 -3.4142E-06/
     CHEB/ -2.8630E-06  4.4402E-02 -2.5507E-06 -1.7947E-06  9.3218E-03/
     CHEB/ -1.1669E-06 -1.1312E-06/
COCO. (+M)            <=> C.OCOH (+M)          1.00E+00     .000       0. ! ING171   10/95
     LOW / 1.0 0.0 0.0 /
     CHEB/  7   3        4.9125E-01  3.6034E+00 -3.2472E-01  3.4644E+00/
     CHEB/  8.4682E-01  4.0020E-02 -7.8596E-01  2.5990E-01  1.0368E-01/
     CHEB/ -1.8359E-01  3.6673E-02  5.3176E-02  1.2318E-02 -1.7229E-02/
     CHEB/  1.3405E-02  3.0816E-02 -1.0815E-02 -1.4726E-03  7.2021E-03/
```

```
    CHEB/  3.3084E-03 -2.3345E-03/
COCO. + CH3 (+M)      <=> COCOC (+M)           1.00E+00     .000       0. ! ING201   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.2711E+01  3.4528E-01 -4.9612E-02 -6.9842E-01/
    CHEB/  6.3741E-01 -8.4275E-02 -5.7995E-01  4.9858E-01 -4.7593E-02/
    CHEB/ -4.2400E-01  3.2389E-01 -7.7641E-03 -2.7084E-01  1.6534E-01/
    CHEB/  1.8677E-02 -1.4843E-01  5.4438E-02  2.6077E-02 -6.6480E-02/
    CHEB/ -4.0021E-03  1.9502E-02/
COCO. + CH3 (+M)      <=> COC. + CH3O (+M)     1.00E+00     .000       0. ! ING201   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       7.1556E+00 -1.8570E+00 -6.8789E-02  5.1014E+00/
    CHEB/  1.1037E+00 -8.8101E-02  5.5471E-01  6.7790E-01  1.1342E-02/
    CHEB/ -1.4857E-01  2.5257E-01  7.4811E-02 -1.5527E-01 -8.4290E-03/
    CHEB/  6.9849E-02 -8.1635E-02 -9.4088E-02  2.7707E-02 -3.5942E-02/
    CHEB/ -7.9701E-02 -8.2069E-03/
COCO. + CH3 (+M)      <=> COC.OC + H (+M)      1.00E+00     .000       0. ! ING201   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.9261E+00 -1.8124E+00 -7.7339E-02  6.5074E+00/
    CHEB/  1.1529E+00 -8.9539E-02  4.6527E-01  6.5865E-01  3.0080E-02/
    CHEB/ -1.2181E-01  2.0410E-01  9.0727E-02 -1.3657E-01 -4.1190E-02/
    CHEB/  6.8663E-02 -7.1111E-02 -1.0022E-01  1.6183E-02 -3.0373E-02/
    CHEB/ -7.1712E-02 -1.7784E-02/
COCO. + CH3 (+M)      <=> COCOC. + H (+M)      1.00E+00     .000       0. ! ING201   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       4.7396E+00 -1.7873E+00 -8.3099E-02  7.2407E+00/
    CHEB/  1.1765E+00 -8.9634E-02  4.2512E-01  6.4310E-01  4.1690E-02/
    CHEB/ -1.1238E-01  1.7736E-01  9.8216E-02 -1.2694E-01 -5.5280E-02/
    CHEB/  6.5814E-02 -6.6615E-02 -1.0017E-01  9.2684E-03 -2.8348E-02/
    CHEB/ -6.6318E-02 -2.2071E-02/


!*******The following system is from Sheng/Bozzelli/Dean/Chang.  Process of
!*******publication to JPC.  Thermo at CBS-Q//B3LYP/6-31G(d,p).  Kinetic base
!*******canonical and variational TST for hi-p rate constant.  - CYS 2001********
!*******Begin block CC. + O2 system ***********
CCOO (+M)             <=> CH3CHO + OH (+M)       1.00E+00    0.000       0. !   ME 7x3
300-1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -9.2770E+00  4.3930E+00 -6.5901E-01  1.0860E+01/
    CHEB/  9.4478E-01  6.4293E-02 -6.1227E-01  2.7359E-01  8.5069E-03/
    CHEB/ -2.2444E-01  4.5858E-02  1.1279E-02 -6.3801E-02 -6.9457E-03/
    CHEB/  8.1815E-03 -9.7439E-03 -9.7451E-03  2.3566E-03  3.7546E-03/
    CHEB/ -4.6741E-03 -8.1974E-04/
CCOO (+M)             <=> C2H4 + HO2 (+M) 1.00E+00    0.000       0. !   ME 7x3 300-1500K,
1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.3921E+00  5.2595E-01 -8.9234E-02  8.4310E+00/
    CHEB/  7.8077E-01 -1.0272E-01 -3.7393E-01  3.4396E-01 -1.2494E-02/
    CHEB/ -1.7771E-01  8.3359E-02  1.2781E-02 -5.4974E-02 -6.9400E-04/
    CHEB/  5.1889E-03 -7.9246E-03 -1.0863E-02 -2.1021E-03  4.2515E-03/
    CHEB/ -5.6555E-03 -3.4113E-03/
CCOO (+M)             <=> CCO.  +  O (+M)      1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.4971E+01  9.1651E+00  1.3460E+00  1.5917E+01/
    CHEB/  4.0054E-01 -1.4954E-01 -7.4489E-01  1.6692E-01 -4.9065E-02/
    CHEB/ -2.5033E-01  2.6143E-02  3.4851E-03 -6.9821E-02 -1.2215E-02/
    CHEB/  8.7046E-03 -1.1756E-02 -1.2455E-02  3.0477E-03  2.8862E-03/
    CHEB/ -6.2282E-03 -5.2609E-04/
CCOO (+M)             <=> C.COOH (+M)          1.00E+00    0.000       0. !   ME 7x3 300-
1500K, 1e-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -5.5238E+00  1.9079E+00 -5.2514E-01  9.4393E+00/
    CHEB/  1.2366E+00 -8.9895E-02 -5.5358E-01  3.8255E-01 -5.9976E-03/
    CHEB/ -2.1648E-01  7.6911E-02  6.5892E-03 -6.3823E-02  5.8792E-04/
    CHEB/  3.4135E-03 -1.0009E-02 -8.0750E-03 -5.1849E-04  3.8399E-03/
    CHEB/ -4.3138E-03 -1.9689E-03/!*******End block CC. + O2 system ***********


CCOO + CH2O           <=> CCOOH + HCO          5.60E+12    0.00    13600.
CCOO + CCOO           <=> CCO. + CCO.+ O2      6.00E+10    0.00     -830.
```

```
CCOO + CH3OO        <=> CCO.+ CH3O + O2      6.00E+10    0.00     -830.
CCOO + CH4          <=> CH3 + CCOOH          1.12E+13    0.00    24640.
CCOO + CH3OH        <=> CH2OH + CCOOH        6.30E+12    0.00    21336.
CCOO + C2H6         <=> C2H5 + CCOOH          1.70E+13    0.00    20460.
CCOO + C2H4         <=> CYCCO + CCO.         2.82E+11    0.00    17110.

!*******The following system is from Sheng/Bozzelli/Dean/Chang.  Process of
!*******publication to JPC.  Thermo at CBS-Q//B3LYP/6-31G(d,p).  Kinetic base
!*******canonical and variational TST for hi-p rate constant.  - CYS 2001********
!*******Begin block CC. + O2 system ************
C.COOH (+M)         <=> C2H4 + HO2 (+M)      1.00E+00    0.000       0. !   ME 7x3 300-
1500K, le-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.7314E+00  1.8486E+00 -3.0861E-01  6.4534E+00/
    CHEB/  3.9748E-01  1.5237E-01 -6.5959E-01  3.2046E-02  2.9637E-02/
    CHEB/ -1.8813E-01 -8.0455E-03 -3.0292E-03 -3.9649E-02 -5.5178E-03/
    CHEB/ -3.9752E-03 -9.8039E-04 -1.3389E-03 -1.2047E-03  4.6799E-03/
    CHEB/  2.4774E-04  9.4133E-05/
C.COOH (+M)         <=> CYCCO + OH (+M)       1.00E+00    0.000       0. !   ME 7x3 300-
1500K, le-3-100atm  11/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.4643E+00  1.8436E+00 -3.1087E-01  6.5155E+00/
    CHEB/  3.9400E-01  1.4989E-01 -6.4750E-01  3.1619E-02  2.9083E-02/
    CHEB/ -1.8485E-01 -7.8365E-03 -2.9630E-03 -3.8662E-02 -5.3765E-03/
    CHEB/ -3.8807E-03 -6.8394E-04 -1.3042E-03 -1.1761E-03  4.7675E-03/
    CHEB/  2.4586E-04  9.3101E-05/
!*******End block CC. + O2 system ************

CC.OOH (+M)         <=> C2H4 + HO2 (+M)      1.00E+00     .000       0. ! ING261   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.0291E+00  2.5000E+00 -1.1789E-06  5.9712E+00/
    CHEB/ -3.1806E-06 -2.2507E-06 -1.0437E+00 -3.0625E-06 -2.1848E-06/
    CHEB/ -5.5543E-01 -2.7486E-06 -1.8966E-06 -2.4544E-01 -2.6460E-06/
    CHEB/ -1.8578E-06 -9.4126E-02 -2.2843E-06 -1.6418E-06 -3.7081E-02/
    CHEB/ -1.9329E-06 -1.4241E-06/
CC.OOH (+M)         <=> CH3CHO + OH (+M)     1.00E+00     .000       0. ! ING261   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.9743E+00  2.4994E+00 -4.8604E-04 -8.3599E-02/
    CHEB/  5.5019E-04  4.1436E-04 -9.4675E-02 -1.3017E-05 -9.6315E-06/
    CHEB/ -3.5251E-02 -2.5226E-06 -1.7224E-06 -1.0080E-02 -6.5690E-06/
    CHEB/ -4.8828E-06  1.4553E-03 -4.1501E-06 -3.1103E-06  1.8006E-03/
    CHEB/  1.8420E-08  7.4184E-08/
CCQ.OH (+M)         <=> CCQO. (+M)           1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -6.1473E+00  4.6653E+00 -1.8392E-01  7.2275E+00/
    CHEB/  2.8590E-01  1.5600E-01 -4.7499E-01  7.0204E-04  1.5236E-03/
    CHEB/ -2.6669E-02 -8.7963E-03 -7.6434E-03  4.2220E-02  2.2395E-06/
    CHEB/ -1.1044E-03  2.1099E-02  1.8819E-03  1.2117E-03  1.3202E-03/
    CHEB/  7.8811E-04  7.9499E-04/
CCQ.OH (+M)         <=> C.CQOH (+M)          1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.8677E+00  2.9860E+00 -3.9415E-01  6.7157E+00/
    CHEB/  1.1684E+00  7.6935E-02 -7.3691E-01  3.4817E-01  8.1669E-02/
    CHEB/ -2.3264E-01  6.7598E-02  5.2348E-02 -5.8515E-02 -5.7668E-03/
    CHEB/  1.9558E-02 -1.4775E-02 -1.0793E-02  1.0633E-03 -7.7461E-03/
    CHEB/ -2.7157E-03 -3.9438E-03/
CCQ.OH (+M)         <=> CC.QOH (+M)          1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -7.7259E+00  4.2140E+00 -3.7470E-01  1.0968E+01/
    CHEB/  6.1228E-01  2.3275E-01 -5.8505E-01  1.3372E-01  9.5741E-02/
    CHEB/ -9.5276E-02 -1.3551E-02  6.6927E-03  3.6022E-02 -3.1647E-02/
    CHEB/ -1.5140E-02  3.6747E-02 -1.5660E-02 -1.0934E-02  1.5483E-02/
    CHEB/ -2.2122E-03 -3.4309E-03/
CCQO. (+M)          <=> CH3CHO + HO2 (+M)    1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       2.7816E+00  2.2420E+00 -1.3573E-01  2.2120E+00/
    CHEB/ -2.5314E-01 -1.5954E-01 -1.6543E-02  6.4972E-02  6.4546E-03/
    CHEB/  1.7321E-02  1.0625E-01  5.7263E-02  2.1160E-02  3.0192E-02/
    CHEB/  2.7220E-02  1.1181E-02 -8.1000E-03 -1.2265E-03 -1.3243E-03/
    CHEB/ -8.1937E-03 -6.6888E-03/
CCQO. (+M)          <=> C.CQOH (+M)          1.00E+00     .000       0. ! ING041   10/95
```

```
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.0946E+00  3.4420E+00 -3.2398E-01  2.6480E+00/
    CHEB/  1.0836E+00  2.9159E-02 -4.3124E-01  4.4910E-01  2.1540E-01/
    CHEB/ -1.3888E-01 -4.7502E-02  5.5323E-03  9.4823E-03 -4.3470E-02/
    CHEB/  4.4200E-04  2.1451E-02 -2.3076E-02 -3.6125E-03  5.3579E-03/
    CHEB/ -1.2400E-02 -1.0904E-02/
CCQO. (+M)            <=> CC.QOH (+M)           1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.4535E+00  4.8656E+00 -7.5698E-02  3.1020E+00/
    CHEB/ -1.2725E-01 -7.8846E-02  7.8938E-01  1.0932E-01  4.9128E-02/
    CHEB/  1.6894E-01  1.5329E-01  8.6804E-02 -1.0601E-01  1.1187E-02/
    CHEB/  2.0136E-02 -1.9583E-02 -8.7996E-02 -4.2856E-02  6.7268E-02/
    CHEB/ -4.3720E-02 -3.2982E-02/
CCQO. (+M)            <=> O*COOHC + H (+M)      1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.2190E+00  2.3212E+00 -9.5990E-02  5.4085E+00/
    CHEB/ -1.1202E-01 -7.2702E-02  1.1962E+00  2.1641E-01  1.0173E-01/
    CHEB/  3.0487E-03  1.4649E-01  9.1602E-02 -1.2696E-01 -8.9038E-02/
    CHEB/ -2.9000E-02  5.2943E-02 -9.5467E-02 -5.8487E-02  4.5274E-02/
    CHEB/  3.1170E-02  2.4633E-03/
C.CQOH (+M)           <=> C*COH + HO2 (+M)  1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       2.7982E+00  1.3797E+00 -3.4735E-01  5.0358E+00/
    CHEB/  7.8723E-01  1.0700E-01 -7.0072E-01  1.6434E-01  8.9395E-02/
    CHEB/ -2.9710E-01 -2.5942E-02  1.7318E-02 -1.1695E-01 -4.6693E-02/
    CHEB/ -1.3240E-02 -4.7049E-02 -2.3010E-02 -1.3497E-02 -2.2123E-02/
    CHEB/ -3.6109E-03 -5.4408E-03/
C.CQOH (+M)           <=> C*COOH + OH (+M)      1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -3.6836E+00  1.9947E+00 -2.7717E-01  9.2143E+00/
    CHEB/  3.8264E-01  1.7111E-01 -1.0617E+00  2.9637E-02  3.1738E-02/
    CHEB/ -3.9822E-01 -2.8269E-02 -1.1460E-02 -1.3343E-01 -2.1947E-02/
    CHEB/ -1.3697E-02 -4.5556E-02 -7.9984E-03 -6.3942E-03 -2.0415E-02/
    CHEB/ -4.5830E-04 -1.0774E-03/
CC.QOH (+M)           <=> O*COOHC + H (+M)      1.00E+00     .000       0. ! ING041   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       3.0229E+00  1.1356E+00 -2.8337E-01  4.7052E+00/
    CHEB/  9.7188E-01  4.4777E-02 -5.1815E-01  3.0990E-01  1.1753E-01/
    CHEB/ -1.7488E-01  3.9046E-02  5.8938E-02 -3.2370E-02 -3.4175E-02/
    CHEB/  9.0321E-03  1.0401E-02 -3.1184E-02 -9.6394E-03  1.4319E-02/
    CHEB/ -1.3020E-02 -9.4219E-03/
COHCQ. (+M)           <=> CO.CQ (+M)            1.00E+00     .000       0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0872E+00  2.5995E+00 -1.9314E-01  4.8601E+00/
    CHEB/  8.8281E-01  1.4184E-01 -6.7909E-01  3.7006E-01  4.0873E-02/
    CHEB/ -2.9548E-01  1.5573E-01  2.5039E-02 -1.1831E-01  5.8499E-02/
    CHEB/  8.0597E-03 -4.2506E-02  2.1910E-02 -5.1895E-03 -1.3329E-02/
    CHEB/  1.0449E-02 -8.5620E-03/
COHCQ. (+M)           <=> C.OHCQ (+M)           1.00E+00     .000       0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.2652E-02  2.3430E+00 -4.5253E-01  5.0471E+00/
    CHEB/  1.3726E+00  1.0691E-01 -1.0222E+00  3.7612E-01  7.3779E-02/
    CHEB/ -3.4752E-01  4.9755E-02  2.7752E-02 -7.1517E-02 -1.4588E-02/
    CHEB/  1.1949E-02  4.6983E-03 -8.3623E-03  7.1938E-03  8.8224E-03/
    CHEB/  2.7131E-03  3.8305E-03/
COHCQ. (+M)           <=> COHC.OOH (+M)         1.00E+00     .000       0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -9.6519E+00  4.6896E+00 -1.9253E-01  1.1698E+01/
    CHEB/  2.1774E-01  1.2581E-01 -4.2576E-01  4.9859E-02  3.3255E-02/
    CHEB/ -1.2843E-01 -6.9469E-03 -1.9836E-03 -7.1501E-03 -1.1907E-02/
    CHEB/ -6.9677E-03  2.0474E-02 -4.7035E-03 -3.2844E-03  1.3947E-02/
    CHEB/  5.5744E-04  2.9934E-05/
CO.CQ (+M)            <=> CH2O + CH2OOH (+M)    1.00E+00     .000       0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.8767E+00  2.3509E+00 -9.8923E-02  6.2854E+00/
    CHEB/  9.0346E-02  5.7855E-02 -1.5003E-01  2.1112E-03  4.3560E-04/
    CHEB/ -5.5151E-02  5.0870E-03  3.2074E-03 -2.9015E-02  2.7539E-03/
    CHEB/  2.5028E-03 -1.7688E-02  7.7005E-04  9.2543E-04 -1.0790E-02/
    CHEB/  3.1843E-04  2.6247E-04/
CO.CQ (+M)            <=> C.OHCQ (+M)           1.00E+00     .000       0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
```

```
    CHEB/  7   3        4.2362E+00  2.3604E+00 -5.4579E-01  7.4906E-01/
    CHEB/  1.7446E+00  2.5148E-01 -6.9911E-01  4.1267E-01  7.7250E-02/
    CHEB/ -2.8285E-01  5.2046E-02  2.1463E-02 -8.5690E-02 -1.3114E-02/
    CHEB/  8.4837E-03 -1.6996E-02 -9.8104E-03  3.8108E-03 -1.5134E-03/
    CHEB/ -1.4494E-03  4.4388E-04/
CO.CQ (+M)           <=> C*COH + HO2 (+M)     1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        5.7257E+00  2.7306E-01 -5.0176E-01  2.4741E+00/
    CHEB/  1.8703E+00  2.8199E-01 -2.5958E-01  2.9411E-01  8.7092E-02/
    CHEB/ -1.7435E-01 -3.5892E-02  2.1504E-02 -6.4060E-02 -5.8279E-02/
    CHEB/  1.1409E-03 -1.4977E-02 -3.0373E-02 -3.6397E-03 -8.4530E-04/
    CHEB/ -8.7732E-03 -3.4003E-03/
CO.CQ (+M)           <=> O*CCQ + H (+M)       1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        3.5024E-01  1.7784E+00 -4.3300E-01  6.3189E+00/
    CHEB/  6.3027E-01  3.5850E-01 -9.8002E-02  4.4731E-02  3.3311E-02/
    CHEB/ -7.7528E-02 -2.9861E-02 -1.4681E-02 -4.3598E-02 -1.8552E-02/
    CHEB/ -1.0198E-02 -2.2248E-02 -4.1700E-03 -2.7142E-03 -1.1752E-02/
    CHEB/  1.9266E-03  7.5475E-04/
CO.CQ (+M)           <=> COHC.OOH (+M)        1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -4.3995E+00  4.5880E+00 -2.6529E-01  7.2584E+00/
    CHEB/  3.1616E-01  1.9292E-01 -1.2848E-01  4.0739E-02  2.9027E-02/
    CHEB/ -9.2391E-02 -1.0238E-02 -4.2805E-03 -5.3331E-02 -1.1544E-02/
    CHEB/ -6.8591E-03 -2.5817E-02 -3.7781E-03 -2.7066E-03 -1.1412E-02/
    CHEB/  1.1176E-03  4.3297E-04/
C.OHCQ (+M)          <=> CH2O + CH2OOH (+M)   1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -4.8150E+00  1.7422E+00 -4.7352E-01  8.6559E+00/
    CHEB/  3.5708E-01  2.1170E-01 -8.1222E-01 -2.8103E-02 -1.3111E-02/
    CHEB/ -3.2579E-01 -4.6055E-02 -2.5975E-02 -1.1057E-01 -3.0548E-02/
    CHEB/ -1.6483E-02 -4.1046E-02 -1.5101E-02 -7.7691E-03 -2.1918E-02/
    CHEB/ -4.7337E-03 -2.2374E-03/
C.OHCQ (+M)          <=> C*COH + HO2 (+M)     1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        4.6062E+00  1.8000E+00 -2.8515E-01  3.3128E+00/
    CHEB/  6.7716E-01  2.2913E-01 -8.2419E-01  5.7514E-02  6.2000E-02/
    CHEB/ -3.0478E-01 -5.4994E-02 -1.5867E-02 -9.4035E-02 -3.3303E-02/
    CHEB/ -1.9335E-02 -3.0069E-02 -5.8810E-03 -6.2762E-03 -1.6936E-02/
    CHEB/  3.9463E-03  1.0589E-03/
C.OHCQ (+M)          <=> O*CCQ + H (+M)       1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -1.8606E+00  2.3330E+00 -1.1073E-01  7.0660E+00/
    CHEB/  1.8418E-01  1.1829E-01 -1.0357E+00 -1.9587E-02 -7.8722E-03/
    CHEB/ -3.9385E-01 -1.6750E-02 -1.1798E-02 -1.2161E-01 -3.9605E-03/
    CHEB/ -3.2410E-03 -3.6854E-02  4.0532E-04  2.9840E-04 -1.8251E-02/
    CHEB/  6.8410E-04  6.3322E-04/
C.OHCQ (+M)          <=> COHC.OOH (+M)        1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -4.8374E+00  4.9544E+00 -2.5952E-02  2.7779E+00/
    CHEB/ -8.6086E-02 -4.9019E-02 -7.6505E-01 -7.2236E-02 -4.1182E-02/
    CHEB/ -1.9621E-01 -5.3407E-02 -3.0498E-02 -2.0107E-02 -3.4107E-02/
    CHEB/ -1.9505E-02  7.8927E-03 -1.7965E-02 -1.0268E-02 -1.8760E-03/
    CHEB/ -6.7975E-03 -3.8419E-03/
COHC.OOH (+M)        <=> O*CCOH + OH (+M)     1.00E+00     .000        0. ! ING051   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        8.9204E+00  2.4959E+00 -3.0588E-03 -2.0269E-01/
    CHEB/  2.8911E-03  2.1697E-03 -3.2281E-01  1.7127E-04  1.3009E-04/
    CHEB/ -1.8814E-01 -5.0728E-06 -3.5129E-06 -1.1306E-01 -2.4196E-05/
    CHEB/ -1.8003E-05 -6.7641E-02 -1.7972E-05 -1.3486E-05 -3.8263E-02/
    CHEB/ -1.2124E-05 -9.0576E-06/
C2H6 + O2            <=> C2H5 + HO2           6.03E+13    0.00     51866. !92 BAULCH
C2H6 + HO2           <=> C2H5 + H2O2          1.70E+13    0.00     20460. !86 BALDWIN
C2H6 + CH3           <=> C2H5 + CH4           1.51E-07    6.00      6047. !92 BAULCH
C2H6 + H             <=> C2H5 + H2            1.44E+09    1.50      7412. !92 BAULCH
C2H6 + OH            <=> C2H5 + H2O           7.22E+06    2.00       864. !92 BAULCH
C2H6 + O             <=> C2H5 + OH            9.99E+08    1.50      5803. !92 BAULCH
CCOH + O2            <=> C.COH +HO2           2.00E+13    0.0      53800.
CCOH + O2            <=> CC.OH+HO2            1.33E+13    0.0      48400.
CCOH + OH            <=> C.COH + H2O          7.55E+09    0.97      1586.
CCOH + OH            <=> CC.OH + H2O          6.78E+07    1.61        35.
```

```
CCOH + OH           <=> CCO. + H2O          5.00E+09    0.97      2586.
CCOH + H            <=> C.COH + H2          9.60E+06    2.0       7700.
CCOH + H            <=> CC.OH + H2          2.52E+14    0.0       7300.
CCOH + H            <=> CCO. + H2           6.40E+06    0.0      10700.
CCOH + O            <=> C.COH + OH          2.25E+13    0.0       7700.
CCOH + O            <=> CC.OH + OH          3.07E+13    0.0       5200.
CCOH + CH3          <=> C.COH + CH4         3.19E+01    3.17      7172.
CCOH + CH3          <=> CC.OH + CH4         1.74E+00    3.46      5480.
CCOH + C2H5         <=> C.COH + C2H6        5.00E+10    0.0      13400.
CCOH + C2H5         <=> CC.OH + C2H6        3.30E+10    0.0      10400.
CCOH + HO2          <=> C.COH + H2O2        8.40E+12    0.0      20430.
CCOH + HO2          <=> CC.OH + H2O2        5.60E+12    0.0      17700.
CCOH + C2H3         <=> C.COH + C2H4        5.00E+11    0.0      10400.
CCOH + C2H3         <=> CC.OH + C2H4        3.30E+11    0.0       5200.
COC (+M)            <=> COC. + H (+M)       1.00E+00     .000        0. ! ING131    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.6507E+01  1.6551E+00 -3.0699E-01  2.9143E+01/
    CHEB/  8.0116E-01  2.2723E-01 -1.2081E+00  1.4867E-01  1.1258E-01/
    CHEB/ -6.0669E-01 -3.5496E-02  9.3434E-03 -2.8167E-01 -4.9669E-02/
    CHEB/ -2.2572E-02 -1.1780E-01 -2.4160E-02 -1.7769E-02 -4.2397E-02/
    CHEB/ -4.6646E-03 -6.4519E-03/
COC (+M)            <=> CH2S + CH3OH (+M)   1.00E+00     .000        0. ! ING131    10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.5427E+01  1.6525E+00 -3.0760E-01  2.9118E+01/
    CHEB/  8.0116E-01  2.2643E-01 -1.2159E+00  1.5036E-01  1.1317E-01/
    CHEB/ -6.0918E-01 -3.4008E-02  1.0202E-02 -2.8231E-01 -4.9312E-02/
    CHEB/ -2.2196E-02 -1.1812E-01 -2.4555E-02 -1.7855E-02 -4.2648E-02/
    CHEB/ -5.0827E-03 -6.6719E-03/
COC + O             <=> COC. + OH           3.24E+12    0.0       2623. !90 LIU
COC + H             <=> COC. + H2           1.90E+13    0.0       5167. !79 FAUBEL
COC + OH            <=> COC. + H2O          6.27E+12    0.0        739. !87 TULLY
COC + CH3           <=> COC. + CH4          3.55E+12    0.0      11800. !82 BATT

!*************************************************************************************
**
!************COC. + O2 from Tak's PhD.  Using Master Eqn-cheby.       -  CYS 12/14/2001
!************BEGIN COC. + O2
BLOCK**********************************************************
COC.+O2 (+M)        <=> COCQ. (+M)          1.00E+00    0.000        0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0425E+01  1.5768E+00 -3.0602E-01 -3.4664E+00/
    CHEB/  1.8283E+00 -8.8564E-02 -2.1150E+00  6.0085E-01  1.1276E-01/
    CHEB/ -1.1259E+00  5.2278E-02  6.5958E-02 -5.2412E-01 -9.0347E-02/
    CHEB/  5.6493E-03 -1.9729E-01 -8.4634E-02 -1.4201E-02 -4.4588E-02/
    CHEB/ -4.3969E-02 -1.3484E-02/
COC.+O2 (+M)        <=> C.OCQ (+M)          1.00E+00    0.000        0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       8.9499E+00  1.3987E-01 -6.1846E-01 -2.9380E+00/
    CHEB/  2.5685E+00 -8.3265E-02 -2.2622E+00  5.7152E-01  1.9659E-01/
    CHEB/ -1.2480E+00 -1.3206E-01  6.4607E-02 -5.4839E-01 -1.9533E-01/
    CHEB/ -3.5889E-02 -1.6742E-01 -9.0372E-02 -4.6539E-02 -4.7372E-03/
    CHEB/ -4.9830E-04 -2.0562E-02/
COC.+O2 (+M)        <=> CH2O+CH2O+OH (+M)   1.00E+00    0.000        0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       9.9375E+00 -2.2172E+00 -4.0337E-01  1.0947E+00/
    CHEB/  2.3569E+00  2.4586E-01 -4.5489E-01  2.3360E-01  2.5357E-01/
    CHEB/ -3.2234E-01 -2.2858E-01  1.3947E-03 -1.0208E-01 -1.4771E-01/
    CHEB/ -6.7809E-02  2.3343E-03 -4.3588E-02 -4.0232E-02  3.3100E-02/
    CHEB/  4.3872E-03 -1.0497E-02/
COCQ. (+M)          <=> C.OCQ (+M)          1.00E+00    0.000        0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.6001E+00  4.8852E-01 -1.1951E-01  6.3403E+00/
    CHEB/  7.8827E-01 -1.6194E-01 -4.6902E-01  4.0343E-01 -2.4988E-02/
    CHEB/ -2.6272E-01  1.0452E-01  4.6651E-02 -1.0675E-01 -1.1297E-02/
    CHEB/  4.0136E-02 -3.5682E-02 -1.5064E-02  1.2673E-02 -9.4396E-03/
    CHEB/  2.0568E-03  2.8989E-03/
C.OCQ (+M)          <=> CH2O+CH2O+OH (+M)   1.00E+00    0.000        0. !  12/01
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.0431E+00  1.7027E+00 -6.0616E-01  6.8285E+00/
    CHEB/  1.6989E+00 -2.8815E-01 -8.8143E-01  3.6379E-01  1.3486E-01/
    CHEB/ -3.1538E-01 -6.1198E-02  1.0793E-01 -9.4367E-02 -6.2664E-02/
```

```
    CHEB/  2.2723E-02 -2.5768E-02 -1.1942E-03 -2.7200E-03 -3.4235E-03/
    CHEB/  1.6901E-02  3.4479E-03/
!************END COC. + O2
BLOCK**********************************************************

CCOOH                   <=> CCO. + OH              6.46E+14    0.00    43000.
CCOOH + O2              <=> CCOO + HO2             3.00E+12    0.00    39000.
COCOH (+M)              <=> COCO. + H (+M)         1.00E+00     .000       0. ! ING151   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -2.6877E+01  5.8798E-01 -1.3647E-01  3.1295E+01/
    CHEB/  8.7664E-01 -1.1799E-01 -6.6639E-01  4.9848E-01  8.5840E-03/
    CHEB/ -3.8359E-01  2.1884E-01  5.4383E-02 -2.0767E-01  6.7834E-02/
    CHEB/  4.5988E-02 -1.0438E-01  4.4182E-03  2.3454E-02 -4.8968E-02/
    CHEB/ -1.4331E-02  6.6350E-03/
COCOH (+M)              <=> COC.OH + H (+M)        1.00E+00     .000       0. ! ING151   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       -2.2596E+01  3.6088E-01 -6.4998E-02  2.8374E+01/
    CHEB/  6.4162E-01 -1.0043E-01 -5.4112E-01  4.5606E-01 -4.0522E-02/
    CHEB/ -3.4782E-01  2.5983E-01  7.7360E-03 -2.0505E-01  1.1514E-01/
    CHEB/  2.6526E-02 -1.0973E-01  3.3948E-02  2.3184E-02 -5.4873E-02/
    CHEB/ -5.7950E-04  1.2342E-02/

!*****************************************************************************************
*****
!*****Begin section of destruction of species (see above notes dated
12/24/2001**************
O*CCOH + H              <=> COHC.*O + H2           9.6E8       1.5       -440.
O*CCOH + OH             <=> COHC.*O + H2O          4.8E6       2.       -1192.2
O*CCOH + O              <=> COHC.*O + OH           6.8E8       1.5      -1192.2
O*CCOH + CH3            <=> COHC.*O + CH4          3.24E6      1.87      2650.
COHC.*O                 <=> CO + CH2OH             1.E13  0.    7500.

HCJJCHOT                <=> C.*C*O + H             1.5E13  0.   36010.
C.*C*O                  <=> CO + HCO2.             1.E13  0.0  5000.

O*CC*O + H              <=> CJ*OCHO + H2           4.8E8      1.5      -1192.2
O*CC*O + OH             <=> CJ*OCHO + H2O          2.4E6      2.       -1192.2
O*CC*O + O              <=> CJ*OCHO + OH           3.4E8      1.5      -1192.2
O*CC*O + CH3            <=> CJ*OCHO + CH4          1.62E6     1.87     -1192.2
CJ*OCHO                 <=> CO + HCO               3.4E13      0.      12810.   ! EA = DHRXN +
5.

CYCCO  + H              <=> CYC.CO     + H2        9.6E8   1.5  4740.
CYCCO  + OH             <=> CYC.CO     + H2O       4.8E6   2.   -870.
CYCCO  + O              <=> CYC.CO     + OH        6.8E8  1.5  2390.
CYCCO  + CH3            <=> CYC.CO     + CH4       3.24E6   1.87   7840.

CYC.CO                  <=> C.CHO + H              1.8E13   0.    31900.  ! EA=DHRX + 6

HCO2H   + H              <=>  HCO2.    + H2        4.8E8  1.5  9310.
HCO2H   + OH             <=>  HCO2.    + H2O       2.4E6   2.0  2640.
HCO2H   + O              <=>  HCO2.    + OH        3.4E8   1.5   7650.
HCO2H   + CH3            <=>  HCO2.    + CH4       1.62E6   1.87  12400.
HCO2.                    <=>  CO2 + H              1.E13  0.0   1390.
!*****END section of destruction of species (see above notes dated
12/24/2001**************
!*****************************************************************************************
*****



C#CC + H                <=> C#CC. + H2             5.00E+13   0.0      5000.
C#CC + H                <=> CC*C.                  2.59E+34  -6.587  12401.
C#CC + CH3              <=> C#CC. + CH4            3.80E+11   0.0      9000.
C*C*C + H               <=> CC*C.                  6.38E+25  -4.047  14693.
C*C*C + H               <=> C#CC. + H2             5.00E+13   0.0      5000.
C*C*C + CH3             <=> C2.C*C                 6.60E+10   0.0      7990.
C*C*C + CH3             <=> C#CC. + CH4            3.80E+11   0.0      9000.
C*C*C + H (+M)          <=> C#CC + H (+M)          1.00E+00     .000       0. ! ING391   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3        6.0892E+00 -2.6850E+00 -3.7644E-01  3.9672E+00/
```

```
    CHEB/  2.1188E+00  8.8175E-02  3.9106E-01  5.9831E-01  1.5674E-01/
    CHEB/ -9.3986E-02  4.5723E-02  7.5101E-02 -8.9163E-02 -6.8816E-02/
    CHEB/  2.5153E-02 -3.7449E-02 -5.2734E-02  1.3932E-03 -1.0298E-02/
    CHEB/ -2.6410E-02 -7.2624E-03/
C*CC. + H            <=> C*C*C + H2          3.60E+12   0.0        0.
C*CC. + CH3          <=> C*C*C + CH4         8.92E+11   0.0    -1571.
C*CC. + CH3O         <=> C*C*C + CH3OH       1.00E+13   0.0        0.
C*CC. + C2H5         <=> C*C*C + C2H6        2.40E+12   0.0        0.
C*CC. + C2H5         <=> C*CC + C2H4         1.20E+12   0.0        0.
C*CC. + C*CC.        <=> C*CC + C*C*C        1.00E+12   0.0        0.
C.*CC (+M)           <=> C#CC + H (+M)       1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -4.5209E+00  1.0416E+00 -2.4309E-01  1.0338E+01/
    CHEB/  1.0137E+00  2.3092E-02 -6.9760E-01  3.4655E-01  1.1362E-01/
    CHEB/ -2.8827E-01  4.8651E-02  6.0548E-02 -9.1424E-02 -3.7335E-02/
    CHEB/  7.7984E-03 -9.6363E-03 -3.6696E-02 -1.2765E-02  1.5280E-02/
    CHEB/ -1.6660E-02 -1.2175E-02/
C.*CC (+M)           <=> C*CC. (+M)          1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.8051E+00  1.1978E+00 -2.8334E-01  1.0063E+01/
    CHEB/  1.2971E+00 -4.3697E-02 -9.0963E-01  5.5930E-01  7.6091E-02/
    CHEB/ -4.3400E-01  1.8084E-01  5.0334E-02 -1.8209E-01  3.0332E-02/
    CHEB/  1.3010E-02 -6.0826E-02 -9.5896E-03 -3.3478E-03 -1.0956E-02/
    CHEB/ -1.0159E-02 -4.6454E-03/
C.*CC (+M)           <=> C*C*C + H (+M)      1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -6.6715E+00 -5.4142E-01 -3.6237E-01  1.2971E+01/
    CHEB/  1.9400E+00  2.6823E-02 -2.4068E-01  7.0789E-01  1.1400E-01/
    CHEB/ -2.4635E-01  1.7081E-01  5.6233E-02 -1.1411E-01 -7.9385E-04/
    CHEB/  1.9063E-02 -2.8871E-02 -3.1066E-02  7.5524E-03  3.2105E-03/
    CHEB/ -2.2730E-02  4.0548E-03/
C*CC. (+M)           <=> C#CC + H (+M)       1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.4761E+01 -7.5547E-01 -3.2468E-01  1.9626E+01/
    CHEB/  1.8941E+00 -2.5941E-02 -3.9897E-01  7.0383E-01  1.0431E-01/
    CHEB/ -3.8665E-01  1.8770E-01  4.9141E-02 -2.1272E-01  1.9231E-02/
    CHEB/  1.1641E-02 -9.1182E-02 -1.7357E-02  3.6735E-03 -2.8652E-02/
    CHEB/ -1.5285E-02  3.4793E-03/
C*CC. (+M)           <=> C*C*C + H (+M)      1.00E+00     .000       0. ! ING381   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -1.2521E+01  4.5196E-01 -9.2834E-02  1.8954E+01/
    CHEB/  7.7481E-01 -1.3182E-01 -5.3330E-01  5.0514E-01 -3.7759E-02/
    CHEB/ -3.2329E-01  2.5226E-01  2.4120E-02 -1.6529E-01  8.9490E-02/
    CHEB/  3.8772E-02 -7.3952E-02  1.1641E-02  2.7438E-02 -2.8424E-02/
    CHEB/ -1.4114E-02  1.1927E-02/
C*CC + CH3O          <=> C*CC. + CH3OH       1.00E+13   0.0     8000.
C*CC + CH2OH         <=> C*CC. + CH3OH       1.00E+11   0.0     9000.
C*CC + H             <=> C*CC. + H2          5.00E+13   0.0     5000.
C*CC + CH3           <=> C*CC. + CH4         3.80E+11   0.0     9000.
C*CC + C2H5          <=> C*CC. + C2H6        3.80E+11   0.0     9000.
C*CC + H (+M)        <=> CC.C (+M)           1.00E+00     .000       0. ! ING411   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3       1.1711E+01  6.6497E-01 -1.0609E-01 -7.9259E-01/
    CHEB/  1.0395E+00 -9.8903E-02 -7.6574E-01  5.4787E-01  3.0518E-02/
    CHEB/ -3.9857E-01  1.7991E-01  6.7713E-02 -1.6231E-01  4.4191E-03/
    CHEB/  4.2964E-02 -4.1519E-02 -4.3125E-02  1.0836E-02  6.6360E-03/
    CHEB/ -3.6299E-02 -5.7006E-03/
CCC.                 <=> C*CC + H            1.20E+13   0.0    38500.
CCC. + CH3O          <=> C*CC + CH3OH        5.00E+12   0.0        0.
CC.C + CH3           <=> C3C                 1.03E+15  -0.645     -83.
CCC + H              <=> CC.C + H2           1.30E+06   2.40     4470.
CCC + H              <=> CCC. + H2           1.30E+06   2.54     6760.
CCC + CH3            <=> CC.C + CH4          9.00E-02   4.00     6285.
CCC + CH3            <=> CCC. + CH4          2.70E-01   4.00     8285.
COCOC (+M)           <=> COC.OC + H (+M)     1.00E+00     .000       0. ! ING201   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3      -2.3533E+01  4.8162E-01 -7.4361E-02  2.9241E+01/
    CHEB/  8.5635E-01 -1.1302E-01 -7.5928E-01  5.9877E-01 -3.6074E-02/
    CHEB/ -4.8983E-01  3.1714E-01  2.8559E-02 -2.7568E-01  1.0828E-01/
    CHEB/  5.1681E-02 -1.2534E-01 -1.6503E-03  4.0270E-02 -4.1010E-02/
    CHEB/ -3.7194E-02  1.7336E-02/
```

```
COCOC (+M)          <=> COCOC. + H (+M)      1.00E+00     .000       0. ! ING201   10/95
    LOW / 1.0 0.0 0.0 /
    CHEB/  7   3     -2.4053E+01  5.2176E-01 -8.1832E-02  3.0173E+01/
    CHEB/  9.1282E-01 -1.1757E-01 -7.8858E-01  6.1075E-01 -2.5095E-02/
    CHEB/ -4.9860E-01  2.9892E-01  4.3968E-02 -2.7124E-01  8.4611E-02/
    CHEB/  6.0297E-02 -1.1800E-01 -1.6735E-02  4.0269E-02 -3.5791E-02/
    CHEB/ -4.2592E-02  1.3226E-02/
C2.C*C + C*CC.      <=> C2C*C + C*C*C        2.40E+12   0.0        0.
C2C*C + CH3O        <=> C2.C*C + CH3OH       2.00E+13   0.0     8000.
C2C*C + CH2OH       <=> C2.C*C + CH3OH       2.00E+11   0.0     9000.
C2C*C               <=> C2.C*C + H           3.98E+15   0.0    80160.
C2C*C + H           <=> C2.C*C + H2          1.30E+14   0.0     5000.
C2CC.               <=> C*CC + CH3           4.00E+13   0.0    30240.
C2CC.               <=> C2C*C + H            6.00E+12   0.0    33800.
C2CC. + H           <=> C2C*C + H2           1.81E+12   0.0        0.
C2CC. + OH          <=> C2C*C + H2O          2.41E+13   0.0        0.
C2CC. + HO2         <=> C2C*C + H2O2         3.01E+11   0.0        0.
C2CC. + CH3         <=> C2C*C + CH4          1.13E+12   0.50       0.
C2CC. + CH3O        <=> C2C*C + CH3OH        2.40E+12   0.50       0.
C2CC. + CH2OH       <=> C2C*C + CH3OH        2.40E+11   0.0        0.
C3C.                <=> C2CC.                1.37E+13   0.0    40700.
C3C.                <=> C2C*C + H            2.35E+13   0.0    37000.
C3C. + H            <=> C2C*C + H2           5.43E+12   0.0        0.
C3C. + OH           <=> C2C*C + H2O          7.23E+13   0.0        0.
C3C. + HO2          <=> C2C*C + H2O2         9.03E+11   0.0        0.
C3C. + CH3          <=> C2C*C + CH4          3.39E+12   0.50       0.
C3C. + CH3O         <=> C2C*C + CH3OH        7.20E+12   0.50       0.
C3C. + CH2OH        <=> C2C*C + CH3OH        7.21E+11   0.0        0.
C3C. + O2           <=> C3COO                4.46E+07   0.0   -15700.
C3C. + O2           <=> C3CO. + O            9.84E+10   0.0    25600.
C3C. + O2           <=> C3.COOH              3.69E+03   0.0   -12700.
C3C. + O2           <=> C2C*C + HO2          1.77E+09   0.0    -4520.
C2COC.              <=> C2C.OC               7.17E+07   0.0     1990.
C2COC.              <=> C2.COC               1.64E+07   0.0     6720.
C2C.OC              <=> C2C*O + CH3          8.18E+08   0.0     -869.
C2C.OC              <=> C*C(C)OC + H         1.32E+09   0.0    32100.
C2.COC              <=> C*CC + CH3O          1.42E+11   0.0    24500.
C2.COC              <=> C*C(C)OC + H         1.91E+11   0.0    22300.
C2.COC              <=> C2C.OC               6.44E+10   0.0    30700.
C3COC.              <=> C3C. + CH2O          3.02E+10   0.0     7830.
C3COC.              <=> C3.COC               2.84E+08   0.0    10800.
C3.COC              <=> C2C*C + CH3O         1.09E+12   0.0    17900.
C3.COC              <=> C*C(C)OC + CH3       8.66E+10   0.0    17900.
C3COC               <=> C2C*C + CH3OH        7.94E+13   0.0    59000.
C3COC               <=> C3C. + CH3O          9.84E+17   0.0    81300.
C3COC               <=> C3CO. + CH3          3.96E+16   0.0    83000.
C3COC               <=> C2C.OC + CH3         2.26E+17   0.0    83700.
C3COC               <=> C3.COC + H           1.72E+16   0.0    99700.
C3COC               <=> C3COC. + H           6.13E+14   0.0    93400.
C3COC + O           <=> C3.COC + OH          4.53E+13   0.0     5800.
C3COC + O           <=> C3COC. + OH          1.86E+13   0.0     3306.
C3COC + H           <=> C3.COC + H2          1.89E+13   0.0     8700.
C3COC + H           <=> C3COC. + H2          8.00E+12   0.0     5951.
C3COC + O2          <=> C3.COC + HO2         6.06E+13   0.0    50867.
C3COC + O2          <=> C3COC. + HO2         1.05E+13   0.0    44900.
C3COC + OH          <=> C3.COC + H2O         1.53E+13   0.0     2216.
C3COC + OH          <=> C3COC. + H2O         7.76E+12   0.0      769.
C3COC + HO2         <=> C3.COC + H2O2        2.52E+11   0.0    12000.
C3COC + HO2         <=> C3COC. + H2O2        8.50E+10   0.0    13000.
C3COC + CH3         <=> C3.COC + CH4         1.19E+11   0.0    11600.
C3COC + CH3         <=> C3COC. + CH4         2.46E+12   0.0    12073.
C3COC + CH3O        <=> C3.COC + CH3OH       3.62E+11   0.0     7094.
C3COC + CH3O        <=> C3COC. + CH3OH       1.20E+11   0.0     3500.
C3COC + CH2OH       <=> C3.COC + CH3OH       3.62E+11   0.0     7094.
C3COC + CH2OH       <=> C3COC. + CH3OH       1.20E+11   0.0     3500.
C3COC + HCO         <=> C3.COC + CH2O        7.04E+04   2.72    18233.
C3COC + HCO         <=> C3COC. + CH2O        2.68E+04   2.72    18233.
C3COC + C2H5        <=> C3.COC + C2H6        4.74E+11   0.0    12300.
C3COC + C2H5        <=> C3COC. + C2H6        1.58E+11   0.0    12300.
C3COC + C3C.        <=> C3.COC + C3C         1.50E+11   0.0    12900.
C3COC + C3C.        <=> C3COC. + C3C         5.01E+10   0.0    12900.
```

```
C3COC + CC.C        <=> C3.COC + CCC          1.50E+11   0.0    12900.
C3COC + CC.C        <=> C3COC. + CCC          5.01E+10   0.0    12900.

!**********************************************************************
!
!  Nitrogen mechanism of Dean/Bozzelli, refer to Gardiner (Editor)
!  "Gas Phase Combustion Chemistry", Verlag-Springer 2000
!
!
!**********************************************************************
!
!   5/7/01  updated o+n2o rxns:  Meagher/Anderson (2000)
!   5/10/00  updated some rxns after detailed comparison to GRImech3.0
!  updates:
!  NH2+H=NH+H2  7.20E+05        2.32    1590   !  Linder et al (1995)  500-3000K
!  NH+O2=NO+OH         4.50E+08        0.79    1194.   !96ROM/WAG 298-2200 K
!  NO+C.*C*O=HCNO+CO                            1.17E+11        0.65    0       ! Miller
et al., 27 symp. 235-243 T=300-2000
!  NO+C.*C*O=HCN+CO2                            1.45E+16        -0.968  648     ! Miller
et al., 27 symp. 235-243 T=300-2000
!  HNCO+H=NCO+H2   1.05E+05     2.5     13300  !  Miller-Melius IJCK 1992 (now written in
reverse)
!  HNCO+O=NCO+OH  2.20E+06      2.11    11400  ! 92HE/LIN2  24th Symp, 711-717 (1992)
(now written in reverse)
!  HNCO+O=HNO+CO                        1.50E+08        1.57    44000  ! 92HE/LIN2  24th
Symp, 711-717 (1992)
!  HNCO+O=NH+CO2                        9.80E+07        1.41    8500  ! 92HE/LIN2  24th
Symp, 711-717 (1992)
!   3/22/00  updated nh2+no branching ratio to Stanford values
!   8/22/98  updated ch3+NO
!   7/13/98  assuming rapid dissociation of hco2.
!   6/24/98  version of mbbd062498.mec
!***************************************************************************************
*****!
!
!
!           A MECHANISM FOR THE COMBUSTION CHEMISTRY OF NITROGEN
!           DEVELOPED BY
!           ANTHONY M. DEAN AND JOSEPH W. BOZZELLI
!           CORPORATE RESEARCH LABS
!           EXXON RESEARCH AND ENGINEERING CO.
!           ANNANDALE, NJ 08801 USA
!
!           (PERMANENT ADDRESS OF JWB IS:
!           DEPT. OF CHEMICAL ENGINEERING AND CHEMISTRY
!           NEW JERSEY INSTITUTE OF TECHNOLOGY
!           NEWARK, NJ 07039)
!
!           THIS MECHANISM IS DESCRIBED IN THE CHAPTER
!           "COMBUSTION CHEMISTRY OF NITROGEN"
!                           BY
!           ANTHONY M. DEAN AND JOSEPH W. BOZZELLI
!
!           THIS CHAPTER IS PUBLISHED IN GAS-PHASE COMBUSTION
!           W. C. GARDINER, JR., EDITOR
!           SPRINGER (2000)
!
!
!           AS DISCUSSED IN THE CHAPTER, THIS MECHANISM WAS DEVELOPED
!           ON THE BASIS OF ANALYSIS OF INDIVIDUAL REACTIONS RATHER THAN BY ATTEMPTING
!           TO FIT ANY SPECIFIC SET OF EXPERIMENTS.  THE RATE CONSTANTS LISTED ARE
!           BASED ON AN ANALYSIS OF ELEMENTARY REACTION DATA AND/OR THERMOCHEMICAL
KINETIC
!           PRINCIPLES.  ALTHOUGH WE SHOW IN THE CHAPTER THAT THIS MECHANISM
!           PROVIDES A REASONABLE DESCRIPTION OF SOME ASPECTS OF HIGH-TEMPERATURE
NITROGEN
!           CHEMISTRY, WE HAVE NOT ATTEMPTED A COMPREHENSIVE COMPARISON. WE ENCOURAGE
USERS
!           TO APPLY THIS MECHANISM TO OTHER SYSTEMS.  IN THOSE INSTANCES  WHERE THIS
!           MECHANISM IS NOT SATISFACTORY, WE HOPE THAT THE DISCREPANCIES WILL SUGGEST
!           THOSE ADDITIONAL ASPECTS OF C-H-O-N CHEMISTRY THAT NEED TO BE STUDIED IN
```

```
!           MORE DETAIL.
!
!
!
!           THE MECHANISM WAS LAST REVISED AUGUST 22, 1998
!           THE RATE CONSTANTS ARE TABULATED IN A MODIFIED ARRHENIUS FORM,
!           K = A T^N EXP(-E/RT),
!           WITH A (CM^3/MOLE-SEC), N AND E (CAL/MOLE) GIVEN.
!
!           AS LISTED, THE MECHANISM IS CONSISTENT WITH THE CHEMKIN-II FORMAT
!           (CF. SANDIA REPORT SAND89-8009 BY R. J. KEE, F. M. RUPLEY, AND J. A. MILLER)
!           THE USER SHOULD BE WARNED THAT THERE ARE SOME VERSIONS OF CHEMKIN-II WHICH DO
!           NOT PROPERLY HANDLE "." AS PART OF THE SPECIES NAME.  A SIMPLE FIX TO THIS IS
!           TO REPLACE ALL "." IN THE SPECIES NAMES WITH SOME OTHER SYMBOL, E.G. "Q".
!           OF COURSE, A SIMILAR CHANGE MUST BE MADE TO THE SPECIES NAME IN THE THERMO
FILE.
!
!
!          FOR SOME REACTIONS WITH A PRESSURE DEPENDENCE, RATE CONSTANT VALUES
!          ARE LISTED AT SEVERAL PRESSURES, AND THE USER MUST CHOOSE THE DESIRED
PRESSURE.
!
!
!          FOR EXAMPLE, CONSIDER THE ADDITION OF H TO N2O TO FORM HNNO.
!          THE FOLLOWING VALUES ARE LISTED:
!        N2O+H=HNNO      1.16E+24         -4.46   10700    ! 0.1 ATM N2
!        N2O+H=HNNO      1.34E+25         -4.48   10770    ! 1 ATM N2
!        N2O+H=HNNO      3.22E+26         -4.58   11227    ! 10. ATM N2
!        N2O+H+M=HNNO+M          1.10E+27         -3.48   10770    ! M= N2, OK IF P=10,
T>1000 OR P=1, T>300
!                  AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
!
!         THE USER SHOULD REMOVE THE "!" IN COLUMN 1 FOR THE DESIRED PRESSURE.
!         (IN THIS INSTANCE, A "LOW PRESSURE" VALUE IS ALSO LISTED THAT IS APPLICABLE
!         OVER A RANGE OF PRESSURES.  IF THIS OPTION IS USED, THE "!" IN COLUMN 1
!         FOR THE COLLISON EFFICIENCIES SHOULD ALSO BE REMOVED.)
!
!         THE DEFAULT CHOICE FOR THE PRESSURE IS 1 ATM.
!
!
!         THE THERMODYNAMIC PARAMETERS WE RECOMMEND ARE LISTED IN THE CHAPTER.
!         A POLYNOMIAL FIT TO THESE VALUES (NASA FORMAT COMPATIBLE WITH CHEMKIN)
!         IS AVAILABLE FROM THE AUTHORS.
!
!
!         WE HAVE INCLUDED THE UNDERLYING C-H-O CHEMISTRY OF MILLER AND BOWMAN IN THIS
MECHANISM.
!         THE USER MIGHT WANT TO REPLACE THAT WITH A MORE RECENT HYDROCARBON MECHANISM.
!
!
!
!********************************************************************************************
*****!
!ELEMENTS
!H O N C CL AR
!END
!SPECIES
!NH3 NO N2O NO2
!N   HNO2 NH NH2 NNH N2H4 N2H3 N2H2  H2NN HNOH
!HNO HON  HNOO  HONO HNNO NH2O
!H H2 O OH O2 HO2 H2O H2O2 N2 NH2NO   NH2OH HNNNH2 H2NNHO HONHO HNNHO
!HCN CN HCNO NCO HNCO HOCN
!CH3NO H2CN HCNH CH2NN HCNN HNC CH2NO N*CHOH  NCN  NCCN
!CH3NH2 CH3N.H  C.H2NH2 H2C*NH CH2*NNH2 CH3N*NH
!C CO CO2 HCO CH CH2 CH3 CH2S CH2O CH3O. C2H C.*C*O C2H3 C2H5
!CH4 C2H2 C2H4 C2H6 CH3OH C.H2OH  HCOH
!AR
!END
!REACTIONS
! Beginning of nitrogen chapter mechanism
        O+N2=N+NO        1.95E+14         0.00    76817
```

```
        NO+M=N+O+M      9.60E+14        0.00    148429  ! M=AR
                  N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
        N2O+M=N2+O+M    4.00E+14        0.00    56093   ! M=AR
                  N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
!       N2O+O=N2+O2     1.40E+12        0.00    10809
        N2O+O=N2+O2     3.69E+12        0.00    15936   ! Meagher/Anderson (2000)
!       N2O+O=2NO       2.90E+13        0.00    23149
        N2O+O=2NO       9.15E+13        0.00    27679   ! Meagher/Anderson (2000)
        NH3+M=NH2+H+M   2.50E+16        0.00    93786   ! M=AR
                  N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
        NH3+H=NH2+H2    5.40E+05        2.40    9915
        NH3+OH=NH2+H2O  5.00E+07        1.60    954
        NH3+O=NH2+OH    9.40E+06        1.94    6458
!       NH2+H=NH+H2     4.80E+08        1.50    7938    ! 1/15/96 UPDATE
  NH2+H=NH+H2  7.20E+05 2.32    1590   !  Linder et al (1995)  500-3000K  5/10/00 update
        HO2+NO=NO2+OH   2.20E+12        0.00    -477
!        N2O+H=HNNO     1.16E+24        -4.46   10700   ! 0.1 ATM N2
!        N2O+H=HNNO     1.34E+25        -4.48   10770   ! 1 ATM N2
!        N2O+H=HNNO     3.22E+26        -4.58   11227   ! 10. ATM N2
        N2O+H+M=HNNO+M  1.10E+27        -3.48   10770   ! M= N2, OK IF P=10, T=1000 OR
P=1, T=300
                   AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
        N2O+H=N2+OH     2.20E+14        0.00    16750   !  T=1000-2000K
        H+N2O=NH+NO     8.50E+20        -1.62   35369
        H+N2O=NNH+O     2.40E+19        -1.26   47092
        NH+NO=N2+OH     1.40E+17        -1.49   1311
!        NH+NO=N2O+H    3.00E+18        -1.65   1431    !REV. OF 11C
        NH+NO=NNH+O     1.70E+14        -0.20   12200
!        NH+O2=HNOO     3.52E+23        -5.00   2275    ! 0.1 ATM N2
!        NH+O2=HNOO     3.69E+24        -5.00   2295    ! 1 ATM N2
!        NH+O2=HNOO     5.43E+25        -5.05   2454    ! 10. ATM N2
        NH+O2+M=HNOO+M          3.03E+26        -4.00   2295    ! M=N2, SLIGHT FALLOFF
T=300, P=10
                   AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
!       NH+O2=NO+OH     7.60E+10        0.00    1530
  NH+O2=NO+OH           4.50E+08        0.79    1194.   !96ROM/WAG 298-2200 K     5/10/00
update
        NH+O2=H+NO2     2.30E+10        0.00    2484
        NH+O2=HNO+O     4.60E+05        2.00    6497
        NH2+O2=NH2O+O   2.50E+11        0.48    29586   !1/24/96 UPDATE
        NH2+O2=HNO+OH   6.20E+07        1.23    35100   !1/24/96 UPDATE
        NH2+HO2=NH2O+OH 2.50E+13        0.00    0
        NH2+HO2=NH3+O2  9.20E+05        1.94    -1152   !1/15/96 UPDATE
        NH2+O=HNO+H     4.60E+13        0.00    0
        NH2+O=NH+OH     7.00E+12        0.00    0       ! ADDITION
        DUPLICATE
        NH2+O=NH+OH     3.33E+08        1.50    5077    !1/15/96 UPDATE (ABSTRACTION)
        DUPLICATE
!       NH2+OH=NH2OH    1.80E+32        -6.91   4113    !0.1 ATM
        NH2+OH=NH2OH    3.90E+33        -7.00   4441    !1.0 ATM  1/15/96
!       NH2+OH=NH2OH    5.60E+34        -7.02   5365    !10. ATM
        NH2+OH=NH+H2O   2.40E+06        2.00    50      !  1/15/96 UPDATE
!         NH2+NH2=N2H4  2.00E+46        -10.93  9995    !  1/26/96 0.1 ATM N2 (600-2500K)
        NH2+NH2=N2H4    5.60E+48        -11.30  11882   ! 1/26/96 1 ATM N2 M(600-2500K)
!         NH2+NH2=N2H4  3.20E+49        -11.18  13988   ! 1/26/96 10. ATM N2 (600-2500K)
!         NH2+NH2=H2NN+H2       2.40E+20        -2.91   2136    !  1/26/96 0.1 ATM N2
         NH2+NH2=H2NN+H2        1.20E+21        -3.08   3368    ! 1/26/96 1 ATM N2
!         NH2+NH2=H2NN+H2       2.30E+19        -2.54   4183    ! 1/26/96 10. ATM N2
!        NH2+NH2=N2H3+H 9.20E+11        -0.01   10014   !  1/26/96 0.1 ATM N2
        NH2+NH2=N2H3+H  1.20E+12        -0.03   10084   ! 1/26/96 1 ATM N2
!        NH2+NH2=N2H3+H 4.70E+12        -0.20   10621   ! 1/26/96 10. ATM N2
        NH2+NH2=NH3+NH  5.00E+13        0.00    9935
!       NH2+NH2=NH3+NH  1.84E+06        1.94    5146    ! H ABSTRACTION EST.
        NH2+NO=N2+H2O   3.53e11   0.   -2900    !  UPDATED 3/22/00
        NH2+NO=NNH+OH   1.40e12   0.    1780     !  UPDATED 3/22/00
!       NH2+NO=N2+H2O   4.70E+12        -0.25   -1204   !  UPDATED 9/25/96
!       NH2+NO=NNH+OH   3.50E+10        0.34    -765    !  UPDATED 9/25/96
!        NH2+NO=NH2NO   1.92E+30        -6.67   3499    ! 0.1 ATM N2 ADDED 10/31/97
        NH2+NO=NH2NO    3.53E+31        -6.75   3725    ! 1.0 ATM N2 ADDED 10/31/97
!        NH2+NO=NH2NO   1.72E+33        -6.92   4611    ! 10 ATM N2 ADDED 10/31/97
!       CH3+NO (+M) =CH3NO (+M)         1.00E+13        0.00    0       ! KINF
```

```
!       LOW  /  1.30E+18        0.00    0        /  !  M=AR
!       SRI/    2.99E-02        -790.00 1       /      !12/16/95 UPDATE
!                 N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
!       CH3 + NO = CH3NO                  3.61E+35        -8.25     4810. !8/22/98 update
0.1 atm,  300-2500 K,  11% err,  N2
        CH3 + NO = CH3NO                  1.02E+37        -8.38     5228. !8/22/98 update
1.0 atm,  300-2500 K,  11% err,  N2
!       CH3 + NO = CH3NO                  4.62E+41        -9.39     8260. !8/22/98 update
10. atm,  450-2500 K,   7% err,  N2
        CH3 + NO = H2CN+OH    2.15E+09    0.75    11724. ! 8/22/98 update
        CH3 + NO = HCN+H2O    4.87E+08    0.46    12392. !8/22/98 update
        CH3+N=H2CN+H    6.10E+14        -0.31   288
        CH3+N=HCN+H2    3.70E+12        0.15    -89
        CH3+N=HCNH+H    1.20E+11        0.52    -368
!
!****************Begin CH3 + NH2 association block**********************************
!        CH3+NH2=CH3NH2 1.30E+54        -12.72  15608   !0.1 ATM N2 (600-2500K)
        CH3+NH2=CH3NH2  5.10E+52        -11.99  16790   !1.0 ATM N2(600-2500K)
!        CH3+NH2=CH3NH2 1.60E+47        -10.15  15687   !10. ATM N2 (600-2500K)
!        CH3+NH2=C.H2NH2+H      1.10E+13        -0.13   9905    ! 0.1 ATM N2
        CH3+NH2=C.H2NH2+H       1.40E+14        -0.43   11107   ! 1.0ATM N2
!        CH3+NH2=C.H2NH2+H      7.40E+12        0.00    12071   ! 10. ATM N2
!        CH3+NH2=CH3N.H+H       1.20E+13        -0.15   16144   ! 0.1 ATM N2
        CH3+NH2=CH3N.H+H        4.40E+13        -0.31   16641   ! 1.0ATM N2
!        CH3+NH2=CH3N.H+H       1.40E+14        -0.42   17863   ! 10. ATM N2
!       CH3+NH2=H2C*NH+H2       2.10E+11        -0.10   19095   ! 0.1 ATM N2
        CH3+NH2=H2C*NH+H2       4.80E+11        -0.20   19403   ! 1.0 ATM N2
!        CH3+NH2=H2C*NH+H2      2.90E+12        -0.40   20506   ! 10. ATM N2
        CH3+NH2=CH4+NH  2.80E+06        1.94    9210    ! 1/15/96 UPDATE
        CH3+NH2=CH2+NH3 1.60E+06        1.87    7570    ! 1/15/96 UPDATE
!****************End CH3 + NH2 association block*********************************
!
!       CH2+N2=CH2NN    9.30E+30        -7.01   19741   ! 0.1 ATM N2
        CH2+N2=CH2NN    1.60E+32        -7.07   19969   ! 1 ATM N2
!        CH2+N2=CH2NN   4.30E+33        -7.18   20864   ! 10. ATM N2
        CH2+N2=HCN+NH   1.00E+13        0.00    73996
!        1CH2+N2=PRODUCTS                               NOT IMPORTANT
!       CH2+NO=PRODUCTS 1.00E+13        0.00    -378
        CH2+NO=HCNO+H   3.80E+13        -0.36   576
        CH2+NO=HCN+OH   2.90E+14        -0.69   755
        CH2+NO=HNCO+H   3.10E+17        -1.38   1272
        CH2+NO=NH2+CO   2.30E+16        -1.43   1331
        CH2+NO=H2CN+O   8.10E+07        1.42    4113
!        CH+N2=HCNN     2.30E+27        -5.78   2444    ! 0.1 ATM N2
        CH+N2=HCNN      3.60E+28        -5.84   2623    ! 1 ATM N2
!        CH+N2=HCNN     1.80E+30        -6.02   3447    ! 10. ATM N2
        CH+N2=HCN+N     4.40E+12        0.00    21976
        CH+NO=HCN+O     5.30E+13        0.00    0
        CH+NO=H+NCO     2.00E+13        0.00    0
        CH+NO=N+HCO     2.90E+13        0.00    0       !12/16/95 UPDATE
        CH+NO=NH+CO     5.50E+12        0.00    0       !12/16/95 UPDATE
        CH+NO=OH+CN     3.30E+12        0.00    0       !12/16/95 UPDATE
        N+O2=NO+O       9.00E+09        1.00    6497
!        N+OH=NH+O      6.40E+12        0.10    21261   ! REV. OF 27E2
        N+OH=NO+H       1.10E+14        0.00    1123    ! UPDATE 8/13/94
        CH+N=CN+H       1.67E+14        -0.09   0       !BROWNSWORD ET AL (1966) ADDED
7/1/97
        CH2+N=HCN+H     5.00E+13        0.00    0
        NH+N=N2+H       1.50E+13        0.00    0       ! UPDATE 8/13/94
        NH2+N=N2+2H     7.10E+13        0.00    0
        CN+N=C+N2       2.40E+13        0.00    -556    !UPDATE 8/5/97
        2NH=N2+2H       5.10E+13        0.00    0
        NH2+NH=N2H2+H   1.50E+15        -0.50   0
        NH2+NH=NH3+N    9.20E+05        1.94    2444    ! ABSTRACTION  1/15/96
        NH+OH=HNO+H     2.00E+13        0.00    0
        NH+OH=N+H2O     1.20E+06        2.00    -487    !ABSTRACTION  1/15/96
        NH+H=N+H2       3.50E+13        0.00    1728    ! 8/5/97 UPDATE
        NH+O=NO+H       6.00E+13        0.00    0       ! UPDATE 1/29/96
        NH+O=N+OH       1.70E+08        1.50    3368    !ABSTRACTION  1/15/96
!
!************Begin CH3 + NH block***************************************************
```

```
        NH+CH3=H2C*NH+H 4.00E+13        0.00    0
        NH+CH3=N+CH4    8.20E+05        1.87    5852    ! ABSTRACTION  1/29/96
!************End CH3 + NH block**************************************************
!
        NNH=N2+H        3.00E+08        0.00    0       !PRESSURE INDEPENDENT
        DUPLICATE
        NNH+M=N2+H+M    1.00E+13        0.50    3060    !PRESSURE DEPENDENT
        DUPLICATE
                   AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
        NNH+O2=N2+HO2   1.20E+12        -0.34   149
        NNH+O2=N2O+OH   2.90E+11        -0.34   149
        NNH+H=N2+H2     2.40E+08        1.50    -894    !ABSTRACTION  1/15/96
        NNH+OH=N2+H2O   2.40E+22        -2.88   2454    !ADDITION
        DUPLICATE
        NNH+OH=N2+H2O   1.20E+06        2.00    -1192   !ABSTRACTION  1/15/96
        DUPLICATE
        NNH+O=N2+OH     1.70E+16        -1.23   497     !RECOMBINATION
        DUPLICATE
        NNH+O=N2+OH     1.70E+08        1.50    -894    !ABSTRACTION  1/15/96
        DUPLICATE
        NNH+NH2=N2+NH3  9.20E+05        1.94    -1152   !ABSTRACTION  1/15/96
        NNH+HO2=N2+H2O2 1.40E+04        2.69    -1600   !ABSTRACTION 2/3/96
        NNH+HO2=HNNO+OH 2.40E+13        0.00    1699    !RECOMB 2/3/96
        NNH+NO=HNO+N2   1.20E+06        2.00    -1192   !ABSTRACTION EST 2/12/96
!       N2H2 = H+NNH                    5.56E+36        -7.75   70250   ! 2/10/98
H+NNH5.INP 1.00E-01 ATM,  600-2500 K,   1% ERR, 1.00 X N2
        N2H2 = H+NNH                    1.79E+40        -8.41   73391   !1.00E+00 ATM,
600-2500 K,   1% ERR, 1.00 X N2
!       N2H2 = H+NNH                    3.14E+41        -8.42   76043   !1.00E+01 ATM,
600-2500 K,   4% ERR, 1.00 X N2
        DUPLICATE
!       N2H2 = NNH+H                    1.64E+37        -7.94   70751   ! 2/10/98
H+NNH5.INP  1.00E-01 ATM,  600-2500 K,   2% ERR, 1.00 X N2
        N2H2 = NNH+H                    2.60E+40        -8.53   72925   !1.00E+00 ATM,
600-2500 K,   1% ERR, 1.00 X N2
!       N2H2 = NNH+H                    1.26E+44        -9.22   77080   !1.00E+01 ATM,
600-2500 K,   3% ERR, 1.00 X N2
        DUPLICATE
!       N2H2 = H2NN                     9.21E+38        -9.01   67724   !2/10/98
H+NNH5.INP  1.00E-01 ATM,  600-2500 K,   2% ERR, 1.00 X N2
        N2H2 = H2NN                     1.98E+41        -9.38   68453   !1.00E+00 ATM,
600-2500 K,   1% ERR, 1.00 X N2
!       N2H2 = H2NN                     1.25E+45        -10.13  70749   !1.00E+01 ATM,
600-2500 K,   2% ERR, 1.00 X N2
        N2H2+H=NNH+H2   4.80E+08        1.50    1580    ! HTRAN EST.  12/22/95
        N2H2+O=NNH+OH   3.30E+08        1.50    497     ! HTRAN EST.  12/22/95
        N2H2+OH=NNH+H2O 2.40E+06        2.00    -1192   ! HTRAN EST.  12/22/95
        N2H2+NH2=NH3+NNH        1.80E+06        1.94    -1152   ! HTRAN EST.  12/22/95
        N2H2+CH3=NNH+CH4        1.60E+06        1.87    2971    ! HTRAN EST.  12/22/95
        N2H2+NH=NNH+NH2 2.40E+06        2.00    -1192   !SAME AS OH
        N2H2+NO=N2O+NH2 4.00E+12        0.00    11922
!       H2NN  = H+NNH                   5.87E+32        -6.99   51789   ! 2/10/98
H+NNH5.INP 1.00E-01 ATM,  600-2500 K,   1% ERR, 1.00 X N2
        H2NN  = H+NNH                   9.60E+35        -7.57   54838   !1.00E+00 ATM,
600-2500 K,   2% ERR, 1.00 X N2
!       H2NN  = H+NNH                   4.97E+36        -7.43   57295   !1.00E+01 ATM,
600-2500 K,   3% ERR, 1.00 X N2
        DUPLICATE
!       H2NN  = NNH+H                   7.16E+28        -5.77   50760   ! 2/10/98
H+NNH5.INP 1.00E-01 ATM,  600-2500 K,   2% ERR, 1.00 X N2
        H2NN  = NNH+H                   3.19E+31        -6.22   52321   !1.00E+00 ATM,
600-2500 K,   1% ERR, 1.00 X N2
!       H2NN  = NNH+H                   5.10E+33        -6.52   54215   !1.00E+01 ATM,
600-2500 K,   3% ERR, 1.00 X N2
        DUPLICATE
        H2NN+O2=NH2+NO2 1.50E+12        0.00    5961    !ADDUCT FORMATION
        H2NN+H=NNH+H2   4.80E+08        1.50    -894    !ABSTRACTION
        H2NN+H=N2H2+H   1.83E+10        0.97    4471    ! 2/2/98 TST CALC.
        H2NN+O=NNH+OH   3.30E+08        1.50    -894    !ABSTRACTION
        H2NN+O=NH2+NO   3.18E+09        1.03    2695    ! 2/2/98 TST CALC.
        H2NN+OH=NNH+H2O 2.40E+06        2.00    -1192   !ABSTRACTION
```

```
        H2NN+OH=NH2NO+H 2.00E+12        0.00    0       !9/16/96 UPDATE RECOMBINATION
        H2NN+CH3=CH2*NNH2+H     8.30E+05        1.93    6506    ! 2/7/98 TST/2
        H2NN+CH3=CH3N*NH+H      8.30E+05        1.93    6506    ! 2/7/98 TST/2
        H2NN+CH3=CH4+NNH        1.60E+06        1.87    129     !ABSTRACTION
        H2NN+NH2=HNNNH2+H       7.88E+06        1.90    -1333   !  2/7/98  TST CALC.
        H2NN+NH2=NNH+NH3        1.80E+06        1.94    -1152   !ABSTRACTION
        H2NN+HO2=NH2NO+OH       6.56E+05        1.94    7053    !  2/7/98  TST CALC.
        H2NN+HO2=NNH+H2O2       2.90E+04        2.69    -1600   !ABSTRACTION
!        N2H3=N2H2+H    2.30E+43        -9.55   64468   ! 0.1 ATM N2 (600-2500K)
        N2H3=N2H2+H     3.60E+47        -10.38  69009   ! 1 ATM N2 600-2500K)
!        N2H3=N2H2+H    1.80E+45        -9.39   70141   ! 10. ATM N2 (600-2500K)
        N2H3+H=N2H2+H2  2.40E+08        1.50    -10     !ABSTRACTION  1/15/96
        N2H3+O=NH2+HNO  3.00E+13        0.00    0
        N2H3+O=NH2NO+H  3.00E+13        0.00    0
        N2H3+O=N2H2+OH  1.70E+08        1.50    -646    !ABSTRACTION  1/15/96
        N2H3+OH=N2H2+H2O        1.20E+06        2.00    -1192   !ABSTRACTION  1/15/96
        N2H3+OH=H2NN+H2O        3.00E+13        0.00    0       ! 2/15/96 SAME AS ADDUCT
FORMATION
        N2H3+CH3=N2H2+CH4       8.20E+05        1.87    1818    !ABSTRACTION  1/15/96
        N2H3+CH3=H2NN+CH4       3.00E+13        0.00    0       !RECOMB.SAME AS NH2
        N2H3+NH2=N2H2+NH3       9.20E+05        1.94    -1152   !ABSTRACTION  1/15/96
        N2H3+NH2=H2NN+NH3       3.00E+13        0.00    0        !SAME AS ADDUCT FORM.
(2/20/96)
        N2H3+HO2=H2NNHO+OH      3.00E+13        0.00    0       !RECOMBINATION(-5KCAL)
        N2H3+HO2=N2H2+H2O2      2.90E+04        2.69    -1600   ! UPDATE  10/18/97
        N2H3+HO2=N2H4+O2        9.20E+05        1.94    2126    !NH2 WITH ADJUSTED THERMO
!        N2H4=H2NN+H2   4.02E+44        -9.85   71357    !1.00E-01 ATM, 600-2500 K, ADDED
12/3/97
        N2H4=H2NN+H2    5.27E+39        -8.35   69303   !1.00E+00 ATM,  600-2500 K,
ADDED 12/3/97
!        N2H4=H2NN+H2   2.52E+39        -8.19   69665    !1.00E+01 ATM,  600-2500 K,
ADDED 12/3/97
        N2H4+H=N2H3+H2  9.60E+08        1.50    4838    ! HTRAN EST.  12/22/95
        N2H4+O=N2H3+OH  6.70E+08        1.50    2851    ! HTRAN EST.  12/22/95
        N2H4+OH=N2H3+H2O        4.80E+06        2.00    -646    ! HTRAN EST.  12/22/95
        N2H4+CH3=N2H3+CH4       3.30E+06        1.87    5325    ! HTRAN EST.  12/22/95
        N2H4+NH2=N2H3+NH3       3.70E+06        1.94    1629    ! HTRAN EST.  12/22/95
        NO+C=CO+N       1.70E+13        0.00    0
        NO+C=CN+O       1.10E+13        0.00    0
!       NO+C.*C*O=HCNO+CO       4.60E+13        0.00    695     ! ADDED 10/2/96
!       NO+C.*C*O=HCN+CO2       1.40E+13        0.00    695     ! ADDED 10/2/96
  NO+C.*C*O=HCNO+CO             1.17E+11        0.65    0       ! Miller et al., 27
symp. 235-243 T=300-2000  5/10/00 update
  NO+C.*C*O=HCN+CO2             1.45E+16        -0.968  648     ! Miller et al., 27
symp. 235-243 T=300-2000  5/10/00 update
!       NO+C2H=PRODUCTS 6.02E+13        0.00    570     !ADDED 6/26/97 PEETERS ET AL JPC
1996 (295-440K
        NO2+H=NO+OH     1.30E+14        0.00    358
        NO2+O=NO+O2     3.90E+12        0.00    -238
        NO2+M=NO+O+M    4.00E+15        0.00    59988   ! RORHIG ET AL 1997 M=AR
                N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
        NO2+NH2=N2O+H2O 1.54E+16        -1.44   268     ! PARK-LIN (ADDED 7/2/97
        NO2+NH2=NH2O+NO 6.56E+16        -1.44   268     ! PARK-LIN (ADDED 7/2/97
        NO2+CH3=CH3O+NO 1.40E+13        0.00    0       ! ADDED 9/27/96
        N2O+OH=N2+HO2   1.29E-02        4.72    36561   ! MEBEL ET AL (1996) 1000-5000
!        N2O+OH=NO+HNO  1.18E-04        4.33    25086   !(REV. USED) MEBEL ET AL (1996)
1000-5000
        HNO+M=H+NO+M    1.80E+16        0.00    48682   ! M=AR
                N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
        2HNO=N2O+H2O    8.50E+08        0.00    3080    !  1 ATM
        HNO+OH=NO+H2O   1.30E+07        1.88    -954    !SOTO/PAGE
        HNO+H=H2+NO     4.50E+11        0.72    656
!        HNO+H=O+NH2    3.50E+15        -0.30   29269   !REV. OF 15C
        HNO+O=OH+NO     4.50E+11        0.72    656     ! SAME AS H
        HNO+NH2=NH3+NO  9.20E+05        1.94    -1152   ! HTRAN EST.  12/22/95
        HNO+NO=N2O+OH   8.50E+12        0.00    29586   !DIAU ET AL 1995
        HNO+O2=NO+HO2   2.00E+13        0.00    15896
        HNO+CH3=NO+CH4  8.20E+05        1.87    954     ! HTRAN EST.  12/22/95
!        NH2O=H+HNO     3.30E+21        -3.82   64915   ! 0.1 ATM N2
!        NH2O=H+HNO     3.40E+22        -3.83   64915   ! 1.0 ATM N2
!        NH2O=H+HNO     3.80E+23        -3.84   64975   ! 10. ATM N2
```

```
        NH2O+M=HNO+H+M  2.79E+24        -2.83   64915   !  M=N2
                 AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
!        NH2O=HNOH      8.20E+25        -4.94   43784   ! 0.1 ATM N2
!        NH2O=HNOH      1.30E+27        -4.99   43982   ! 1.0 ATM N2
!        NH2O=HNOH      2.60E+28        -5.06   44767   !10. ATM N2
        NH2O+M=HNOH+M   1.07E+29        -3.99   43982   ! M=N2, OK T>1000
                 AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
        NH2O+H=NH2+OH   4.00E+13        0.00    0       !RECOMBINATION
        NH2O+H=HNO+H2   4.80E+08        1.50    1560    !ABSTRACTION
        NH2O+O=HNO+OH   3.30E+08        1.50    487     !ABSTRACTION
        NH2O+OH=HNO+H2O 2.40E+06        2.00    -1192   !ABSTRACTION
        NH2O+CH3=CH3O+NH2       2.00E+13        0.00    0       !RECOMBINATION
        NH2O+CH3=HNO+CH4        1.60E+06        1.87    2961    !ABSTRACTION
        NH2O+NH2=HNO+NH3        1.80E+06        1.94    -1152   !ABSTRACTION
        NH2O+HO2=HNO+H2O2       2.90E+04        2.69    -1600   !ABSTRACTION
        NH2O+HO2=NH2OH+O2       2.90E+04        2.69    -1600   !SAME AS 37H1
!        HNOH=H+HNO     2.30E+21        -3.84   58915   !  0.1 ATM N2
!        HNOH=H+HNO     2.40E+22        -3.84   58934   !  1.0 ATM N2
!        HNOH=H+HNO     3.30E+23        -3.88   59083   !  10. ATM N2
        HNOH+M=H+HNO+M  1.97E+24        -2.84   58934   !  M=N2
                 AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
        HNOH+H=NH2+OH   4.00E+13        0.00    0       !RECOMBINATION
        HNOH+H=HNO+H2   4.80E+08        1.50    378     !ABSTRACTION
        HNOH+O=HNO+OH   7.00E+13        0.00    0       !RECOMBINATION
        DUPLICATE
        HNOH+O=HNO+OH   3.30E+08        1.50    -358    !ABSTRACTION
        DUPLICATE
        HNOH+OH=HNO+H2O 2.40E+06        2.00    -1192   !ABSTRACTION
        HNOH+CH3=CH3N.H+OH      2.00E+13        0.00    0       !RECOMBINATION
        HNOH+CH3=HNO+CH4        1.60E+06        1.87    2096    !ABSTRACTION
        HNOH+NH2=HNO+NH3        1.80E+06        1.94    -1152   !ABSTRACTION
        HNOH + NH2 = N2H3 + OH                  6.72E+06        1.82    715     !(+15)
1.00E+00 ATM,  300-2400 K,  17% ERR, 1.00 X N2
        HNOH + NH2 = H2NN + H2O                 4.57E+19        -1.94   1927    ! (+15)
1.00E+00 ATM,  300-2400 K,  13% ERR, 1.00 X N2
        HNOH+HO2=HONHO+OH       4.00E+13        0.00    0       !RECOMBINATION (-11 KCAL)
        HNOH+HO2=HNO+H2O2       2.90E+04        2.69    -1600   !ABSTRACTION
        HNOH+HO2=NH2OH+O2       2.90E+04        2.69    -1600   !SAME AS 38G2
        HNOO + M = OH + NO + M                  1.52E+36        -6.18   31131   ! m=n2
                 AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
!        HONO=OH+NO     2.30E+28        -5.55   51145   ! 0.1 ATM N2
!        HONO=OH+NO     2.50E+29        -5.56   51175   ! 1 ATM N2 (LINEAR IN P)
!        HONO=OH+NO     4.90E+30        -5.65   51384   ! 10. ATM N2
        HONO+M=OH+NO+M  2.05E+31        -4.56   51175   ! M=N2
                 AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
        HONO+H=H2+NO2   2.00E+08        1.55    6614    !HSU ET AL ('97) ADDED 7/2/97
        HONO+H=HNO+OH   5.63E+10        0.86    4969    !HSU ET AL ('97) ADDED 7/2/97
        HONO+H=H2O+NO   8.13E+06        1.89    3846    !HSU ET AL ('97) ADDED 7/2/97
        HONO+O=OH+NO2   1.70E+08        1.50    3030    ! HTRAN EST.  12/22/95
        HONO+OH=H2O+NO2 1.20E+06        2.00    -596    ! HTRAN EST.  12/22/95
        HONO+CH3=NO2+CH4        8.10E+05        1.87    5504    ! HTRAN EST.  12/22/95
        HONO+NH2=NO2+NH3        9.20E+05        1.94    1917    ! HTRAN EST.  12/22/95
!        HNO2=HONO      7.10E+27        -5.40   52536   ! 0.1 ATM N2
        HNO2=HONO       1.30E+29        -5.47   52814   ! 1 ATM N2
!        HNO2=HONO      2.00E+30        -5.50   53689   ! 10. ATM N2
        HNO2+H=H2+NO2   2.40E+08        1.50    4163    ! HTRAN EST.  12/22/95
        HNO2+O=OH+NO2   1.70E+08        1.50    2365    ! HTRAN EST.  12/22/95
        HNO2+OH=H2O+NO2 1.20E+06        2.00    -795    ! HTRAN EST.  12/22/95
        HNO2+CH3=NO2+CH4        8.10E+05        1.87    4838    ! HTRAN EST.  12/22/95
        HNO2+NH2=NO2+NH3        9.20E+05        1.94    874     ! HTRAN EST.  12/22/95
!        HCN=HNC        1.50E+23        -4.20   49456   ! 0.1 ATM N2
!        HCN=HNC        1.90E+24        -4.23   49576   !1.0 ATM N2
!        HCN=HNC        5.30E+25        -4.34   50192   ! 10 ATM N2
        HCN+M=HNC+M     1.56E+26        -3.23   49576   !  M=N2 (T>1000K)
                 AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
        HCN+OH=CN+H2O   3.90E+06        1.83    10293   ! 11/95 UPDATE
        OH+HCN=HNCO+H   4.40E+03        2.26    6398    !MILLER/MELIUS
        OH+HCN=HOCN+H   1.10E+06        2.03    13373   !MILLER/MELIUS
        OH+HCN=NH2+CO   1.60E+02        2.56    9001    !MILLER/MELIUS
!        OH+HCN=N*CHOH  1.70E+29        -6.31   5126    ! 0.1 ATM N2
        OH+HCN=N*CHOH   2.80E+30        -6.37   5345    ! 1 ATM N2
```

```
!         OH+HCN=N*CHOH  1.10E+32         -6.53    6239    ! 10. ATM N2
         HCN+O=NH+CO     5.40E+08         1.21     7491    ! PERRY-MELIUS
         HCN+O=NCO+H     2.00E+08         1.47     7590    ! PERRY-MELIUS
         HCN+O=CN+OH     4.20E+10         0.40     20675   !CHEMACT
         O+HNC=NH+CO     4.60E+12         0.00     2186
         OH+HNC=HNCO+H   2.80E+13         0.00     3696
         HNC+O2=HNCO+O   1.50E+12         0.01     4113
         HNC+O2=NH+CO2   1.60E+19         -2.25    1778
         CN+H2=HCN+H     3.60E+08         1.55     3000
!         CN+H2O=HCN+OH  7.80E+12         0.00     7451    ! REV. OF 41A
         CN+O=CO+N       7.70E+13         0.00     0
         CN+O2=NCO+O     1.00E+13         0.00     0       ! 8/5/97 UPDATE
         CN+OH=NCO+H     4.00E+13         0.00     0
         CN+HCN=NCCN+H   1.50E+07         1.71     1530
         CN+N2O=NCN+NO   4.20E+11         0.00     7173    ! UPDATE WILLIAMS 1995
         CN+NO2=NCO+NO   6.20E+15         -0.75    348     ! UPDATE 8/13/94
         CN+CH4=HCN+CH3  1.20E+05         2.64     -159
         CN+NH3=HCN+NH2  9.20E+12         0.00     -358
!          H2CN=HCN+H    1.30E+29         -6.03    29894   ! 0.1 ATM N2
         H2CN=HCN+H      6.00E+31         -6.46    32110   ! 1 ATM N2
!          H2CN=HCN+H    3.50E+29         -5.46    32547   ! 10. ATM N2
         H2CN+HO2=CH2NO+OH        3.00E+13         0.00     0
         H2CN+HO2=HCN+H2O2        1.45E+04         2.69     -1604    ! EST SP2
         H2CN+HO2=H2C*NH+O2       1.45E+04         2.69     -1604    !SAME AS OTHER CHANNEL
         H2CN+O2=CH2O+NO 3.00E+12         0.00     5961
         H2CN+CH3=HCN+CH4         8.10E+05         1.87     -1113    !ABSTRACTION
!          H2CN+OH=HCN+H2O        2.10E+17         -1.68    318      ! 0.1 ATM N2
         H2CN+OH=HCN+H2O 1.50E+19         -2.18    2166    ! 1 ATM N2
!          H2CN+OH=HCN+H2O        9.50E+21         -2.91    5633     ! 10 ATM N2
         DUPLICATE
         H2CN+OH=HCN+H2O 1.20E+06         2.00     -1192   !ABSTRACTION
         DUPLICATE
         H2CN+N=N2+CH2   6.00E+13         0.00     397
         H2CN+H=HCN+H2   2.40E+08         1.50     -894    !ABSTRACTION
         H2CN+NH2=HCN+NH3         9.20E+05         1.94     -1152    !ABSTRACTION
         H2CN+O=HCN+OH   1.70E+08         1.50     -894    !ABSTRACTION
         H2CN+O=HNCO+H   6.00E+13         0.00     0       !EST.  12/30/97
         H2CN+O=HCNO+H   2.00E+13         0.00     0       !EST.  12/30/97
!          HCNH=HCN+H    7.70E+25         -5.20    21986   ! 0.1 ATM N2
         HCNH=HCN+H      6.10E+28         -5.69    24271   ! 1 ATM N2
!          HCNH=HCN+H    6.20E+26         -4.77    24818   ! 10. ATM N2
         HCNH+H=H2CN+H   2.00E+13         0.00     0       !RECOMBINATION
         HCNH+H=HCN+H2   2.40E+08         1.50     -894    !ABSTRACTION
         HCNH+O=HNCO+H   7.00E+13         0.00     0       !RECOMBINATION
         HCNH+O=HCN+OH   1.70E+08         1.50     -894    !ABSTRACTION
         HCNH+OH=HCN+H2O 1.20E+06         2.00     -1192   !ABSTRACTION
         HCNH+CH3=HCN+CH4         8.20E+05         1.87     -1113    !ABSTRACTION
         HCNN+O2=H+CO2+N2         4.00E+12         0.00     0        !   assuming rapid
dissociation of hco2.
         HCNN+O2=HCO+N2O 4.00E+12         0.00     0
         H2C*NH+H=H2CN+H2         2.40E+08         1.50     7322     ! HTRAN EST. 12/22/95
         H2C*NH+O=H2CN+OH         1.70E+08         1.50     4630     ! HTRAN EST. 12/22/95
         H2C*NH+OH=H2CN+H2O       1.20E+06         2.00     -89      ! HTRAN EST. 12/22/95
         H2C*NH+CH3=H2CN+CH4      8.20E+05         1.87     7123     ! HTRAN EST. 12/22/95
         H2C*NH+NH2=H2CN+NH3      9.20E+05         1.94     4441     ! HTRAN EST. 12/22/95
         H2C*NH+H=HCNH+H2         3.00E+08         1.50     6130     ! EST (RESON.) 12/22/95
         H2C*NH+O=HCNH+OH         2.20E+08         1.50     5404     ! EST (RESON.)  12/22/95
         H2C*NH+OH=HCNH+H2O       2.40E+06         2.00     457      ! EST (RESON.) 12/22/95
         H2C*NH+CH3=HCNH+CH4      5.30E+05         1.87     9687     ! EST RESON.  12/22/95
         H2C*NH+NH2=HCNH+NH3      1.80E+06         1.94     6090     ! EST SP3 12/22/95
         H2C*NH+O=CH2O+NH         1.70E+06         2.08     0
!          CH3N.H=H2C*NH+H        1.60E+36         -7.92    36342    ! 0.1 ATM N2 (600-2500K)
         CH3N.H=H2C*NH+H          1.30E+42         -9.24    41340    ! 1 ATM N2 (600-2500K)
!          CH3N.H=H2C*NH+H        2.30E+44         -9.51    45244    ! 10. ATM N2 (600-2500K)
         CH3N.H+H=H2C*NH+H2       7.20E+08         1.50     -894     !ABSTRACTION
         CH3N.H+O=H2C*NH+OH       5.00E+08         1.50     -894     !ABSTRACTION
         CH3N.H+OH=H2C*NH+H2O     3.60E+06         2.00     -1192    !ABSTRACTION
         CH3N.H+CH3=H2C*NH+CH4    2.40E+06         1.87     -1113    !ABSTRACTION
!          C.H2NH2=H2C*NH + H     1.10E+45         -10.24   47817    ! 0.1 ATM N2 (600-2500K)
         C.H2NH2=H2C*NH + H       2.40E+48         -10.82   52040    ! 1 ATM N2 (600-2500K)
!          C.H2NH2=H2C*NH + H     3.20E+46         -9.95    53530    ! 10. ATM N2 (600-2500K)
```

```
        C.H2NH2+O2=NH2+CH2O+O   6.00E+18        -1.59   30192   ! assume fast dissoc of
nh2ch2o to nh2+ch2o
        C.H2NH2+O2=H2C*NH+HO2   1.00E+22        -3.09   6756
        C.H2NH2+H=H2C*NH+H2     4.80E+08        1.50    -894    !ABSTRACTION
        C.H2NH2+O=CH2O+NH2      7.00E+13        0.00    0
        C.H2NH2+O=H2C*NH+OH     3.33E+08        1.50    -894    !ABSTRACTION
        C.H2NH2+OH=CH2OH+NH2    4.00E+13        0.00    0
        C.H2NH2+OH=H2C*NH+H2O   2.40E+06        2.00    -1192   !ABSTRACTION
        C.H2NH2+CH3=C2H5+NH2    2.00E+13        0.00    2702
        C.H2NH2+CH3=H2C*NH+CH4  1.60E+06        1.87    -626    !ABSTRACTION
        CH3NH2+H=C.H2NH2+H2     5.60E+08        1.50    5464    ! EST PARTIAL RESON.
9/16/96
        CH3NH2+O=C.H2NH2+OH     4.00E+08        1.50    5196    ! EST PARTIAL RESON.
9/16/96
        CH3NH2+OH=C.H2NH2+H2O   3.60E+06        2.00    238     ! EST PARTIAL RESON.
9/16/96
        CH3NH2+CH3=C.H2NH2+CH4  1.50E+06        1.87    9170    ! EST PARTIAL RESON.
9/16/96
        CH3NH2+NH2=C.H2NH2+NH3  2.80E+06        1.94    5494    ! EST SP3  12/22/95
        CH3NH2+H=CH3N.H+H2      4.80E+08        1.50    9706    ! N EST. 12/22/95
        CH3NH2+O=CH3N.H+OH      3.30E+08        1.50    6348    ! N EST.  12/22/95
        CH3NH2+OH=CH3N.H+H2O    2.40E+06        2.00    447     ! N EST. 12/22/95
        CH3NH2+CH3=CH3N.H+CH4   1.60E+06        1.87    8842    ! N EST. 12/22/95
        CH3NH2+NH2=CH3N.H+NH3   1.80E+06        1.94    7143    ! EST SP3 12/22/95
        NCCN+M=CN+CN+M  1.10E+34        -4.32   130079  ! M=AR
                  N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
!        H+NCCN=HCN+CN  1.40E+14        0.00    7948    ! REV. OF 43F
        NCCN+O=NCO+CN   4.60E+12        0.00    8882
        NCCN+OH=HOCN+CN 2.00E+12        0.00    19000   ! ADDED 12/30/97
!        NCO+NO =PRODUCTS        1.40E+18        -1.73   763
        NCO+NO=CO2+N2   7.84E+17        -1.73   763     ! UPDATE 8/13/94
        NCO+NO=N2O+CO   6.16E+17        -1.73   763     ! UPDATE 8/13/94
        NCO+M=N+CO+M    2.20E+14        0.00    54046   !MERTENS 26 SYMP (2370-3050K)
ADDED 8/12/97
                  N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
!       NCO+H2=HNCO+H   7.60E+02        3.00    3974
  HNCO+H=NCO+H2   1.05E+05      2.5     13300  !  Miller-Melius IJCK 1992 (now written in
reverse) 5/10/00 update
        NCO+O=NO+CO     4.20E+13        0.00    0
        NCO+O=N+CO2     8.00E+12        0.00    2500    !ADDED 12/30/97
        NCO+H=NH+CO     5.20E+13        0.00    0
        NCO+N=N2+CO     3.31E+13        0.00    0       ! BROWNSWORD ET AL 1997
!       NCO+OH=HNCO+O   7.80E+04        2.27    -984    !TSANG
   HNCO+O=NCO+OH  2.20E+06      2.11    11400  ! 92HE/LIN2  24th Symp, 711-717 (1992)
(now written in reverse)  5/10/00 update
        NCO+OH=HON+CO   5.30E+12        -0.07   5126
        NCO+OH=H+CO+NO  8.30E+12        -0.05   18042
        NCO+NO2=CO2+N2O 2.30E+12        0.00    -874
        NCO+NO2=CO+2NO  2.10E+11        0.00    -874
        NCO+CH4=HNCO+CH3        9.80E+12        0.00    8127    ! UPDATE 8/13/94
        NCO+NH3=HNCO+NH2        2.77E+04        2.48    981     ! BECKER ET AL (997)
ADDED 7/2/97
!        HCNO=HCN+O     2.00E+30        -6.03   60733   ! P=0.1 ATM N2
        HCNO=HCN+O      4.20E+31        -6.12   61210   ! P=1.0 ATM N2
!        HCNO=HCN+O     5.90E+31        -5.85   61935   ! P=10. ATM N2
        HCNO+H=HNCO+H   2.10E+15        -0.69   2851
        HCNO+H=HCN+OH   2.70E+11        0.18    2116
        HCNO+H=NH2+CO   1.70E+14        -0.75   2891
        HCNO+H=HOCN+H   1.40E+11        -0.19   2484
        HCNO+O=HCO+NO   7.00E+13        0.00    0
        HCNO+OH=HCOH+NO 4.00E+13        0.00    0
!        H+HOCN=HCN+OH  2.00E+13        -0.04   2136    ! REV. OF 41B2
        HOCN+H=HNCO+H   3.10E+08        0.84    1917
        H+HOCN=NH2+CO   1.20E+08        0.61    2076
        HOCN+H=H2+NCO   2.40E+08        1.50    6617    ! HTRAN EST. 12/22/95
        HOCN+O=OH+NCO   1.70E+08        1.50    4133    ! HTRAN EST. 12/22/95
        HOCN+OH=H2O+NCO 1.20E+06        2.00    -248    ! HTRAN EST. 12/22/95
        HOCN+CH3=CH4+NCO        8.20E+05        1.87    6617    ! HTRAN EST. 12/22/95
        HOCN+NH2=NCO+NH3        9.20E+05        1.94    3646    ! HTRAN EST. 12/22/95
        HNCO+M = NH+CO+M        8.40E+15        0.00    84368   ! ADDED 9/27/96
                  N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
```

```
        HNCO+H=NH2+CO   3.60E+04        2.49    2345    ! UPDATE  9/27/96
!       HNCO+O=HNO+CO   1.70E+06        2.08    0
!       HNCO+O=NH+CO2   1.70E+06        2.08    0
   HNCO+O=HNO+CO                        1.50E+08        1.57    44000  ! 92HE/LIN2  24th
Symp, 711-717 (1992) 5/10/00 update
   HNCO+O=NH+CO2                        9.80E+07        1.41    8500   ! 92HE/LIN2  24th
Symp, 711-717 (1992) 5/10/00 update
        HNCO+OH=NH2+CO2 6.30E+10        -0.06   11644
        HNCO+OH=NCO+H2O 5.20E+10        -0.03   17565
        DUPLICATE
!        HNCO+H=NCO+H2  1.80E+05        2.40    9915    ! REV USED (52C)
!        HNCO+O=NCO+OH  3.13E+06        1.94    6458    ! REV USED (52G)
        HNCO+OH=NCO+H2O 3.60E+07        1.50    3594    ! 8/5/97 UPDATE
        DUPLICATE
!        HNCO+CH3=NCO+CH4       1.00E+12        0.00    9935    ! REV USED (52I)
!        HNCO+NH2=NCO+NH3       1.00E+12        0.00    8942    ! REV USED (52J)
!        CH2NO=HNCO+H   6.90E+41        -9.30   51702   ! 0.1 ATM N2 (600-2500K)
        CH2NO=HNCO+H    2.30E+42        -9.11   53838   ! 1 ATM N2 (600-2500K)
!        CH2NO=HNCO+H   1.70E+38        -7.64   53579   ! 10. ATM N2 (600-2500K)
        CH2NO+O2=CH2O+NO2       1.20E+15        -1.01   20128   ! 12/3/97 UPDATE 1000-
2500K (ALLYL+O2)
!        CH2NO+O2=CH2O+NO2      2.88E+12        -0.31   17707   ! 12/3/97 UPDATE 300-
1000K (ALLYL+O2)
        CH2NO+H=CH3+NO  4.00E+13        0.00    0
        CH2NO+H=HCNO+H2 4.80E+08        1.50    -894    !ABSTRACTION
        CH2NO+O=CH2O+NO 7.00E+13        0.00    0
        CH2NO+O=HCNO+OH 3.30E+08        1.50    -894    !ABSTRACTION
        CH2NO+OH=CH2OH+NO       4.00E+13        0.00    0
        CH2NO+OH=HCNO+H2O       2.40E+06        2.00    -1192   !ABSTRACTION
        CH2NO+CH3=C2H5+NO       3.00E+13        0.00    0
        CH2NO+CH3=HCNO+CH4      1.60E+06        1.87    -1113   !ABSTRACTION
        CH2NO+NH2=C.H2NH2+NO    3.00E+13        0.00    0
        CH2NO+NH2=HCNO+NH3      1.80E+06        1.94    -1152   !ABSTRACTION
        CH3NO+H=CH2NO+H2        4.40E+08        1.50    378     ! EST (RESON.) 12/22/95
        CH3NO+O=CH2NO+OH        3.30E+08        1.50    3616    ! EST (RESON.) 12/22/95
        CH3NO+OH=CH2NO+H2O      3.60E+06        2.00    -1192   ! EST (RESON.) 12/22/95
        CH3NO+CH3=CH2NO+CH4     7.90E+05        1.87    5415    ! EST RESON. 12/22/95
        CH3NO+NH2=CH2NO+NH3     2.80E+06        1.94    1073    ! EST SP3 12/22/95
        CH3NO+H=CH3+HNO 1.80E+13        0.00    2782
        CH3NO+O=CH3+NO2 1.70E+06        2.08    0
        CH3NO+OH=CH3+HONO       2.50E+12        0.00    994
!        HON=NO+H       6.20E+16        -2.73   16045   !0.1 ATM N2
!        HON=NO+H       6.20E+17        -2.73   16045   !1.0 ATM N2
!        HON=NO+H       6.20E+18        -2.73   16045   !10. ATM N2
        HON+M=NO+H+M    5.09E+19        -1.73   16045   !M=N2
                   AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/
!       HON=HNO 3.16E+14        -2.68   21420   ! 0.1 ATM N2
!       HON=HNO 3.16E+15        -2.68   21420   ! 1.0 ATM N2
!       HON=HNO 3.16E+16        -2.68   21420   ! 10.ATM N2
!       HON+M=HNO+M     2.59E+17        -1.68   21420   !M=N2
        HON+H=HNO+H     2.00E+13        0.00    0
        HON+H=OH+NH     2.00E+13        0.00    0
        HON+O=OH+NO     7.00E+13        0.00    0
        HON+OH=HONO+H   4.00E+13        0.00    0
        HON+O2=HONO+O   1.00E+12        0.00    4968    ! 2/4/98
!        HCOH=CH2O      3.50E+17        -2.86   8882    !10 KCAL BARRIER, 0.1 ATM
        HCOH=CH2O       2.10E+19        -3.07   9538    !10 KCAL BARRIER, 1.0 ATM
!        HCOH=CH2O      1.80E+21        -3.32   10859   !10 KCAL BARRIER, 10 ATM
!        NH2OH=NH2+OH   1.60E+34        -6.91   69356    !1.00E-01 ATM  2/6/96
!        NH2OH=NH2+OH   1.50E+35        -6.90   69356    !1.00E+00 ATM
!        NH2OH=NH2+OH   7.00E+35        -6.80   69386   !1.00E+01 ATM
!        NH2OH+M=NH2+OH+M       1.23E+37        -5.90   69356   !  OK EVERYWHERE
!                  AR/0.7/  H2O/7.0/  CO2/2.0/  CH4/2.0/    (REVERSE OF 16A
        NH2OH+H=HNOH+H2 4.80E+08        1.50    6249    !HTRANS 2/6/96
        NH2OH+H=NH2O+H2 2.40E+08        1.50    5067    !HTRANS 2/6/96
        NH2OH+O=HNOH+OH 3.30E+08        1.50    3865    !HTRANS 2/6/96
        NH2OH+O=NH2O+OH 1.70E+08        1.50    3010    !HTRANS 2/6/96
        NH2OH+OH=HNOH+H2O       2.40E+06        2.00    -328    !HTRANS 2/6/96
        NH2OH+OH=NH2O+H2O       1.20E+06        2.00    -596    !HTRANS 2/6/96
        NH2OH+CH3=HNOH+CH4      1.60E+06        1.87    6348    !HTRANS 2/6/96
        NH2OH+CH3=NH2O+CH4      8.20E+05        1.87    5494    !HTRANS 2/6/96
```

```
        NH2OH+NH2=HNOH+NH3       1.80E+06         1.94    3229    !HTRANS 2/6/96
        NH2OH+NH2=NH2O+NH3       9.20E+05         1.94    1888    !HTRANS 2/6/96
        NH2OH+HO2=HNOH+H2O2      2.90E+04         2.69    9557    !HTRANS 2/6/96
        NH2OH+HO2=NH2O+H2O2      1.40E+04         2.69    6418    !HTRANS 2/6/96
!        NH2NO=N2+H2O    4.10E+33         -7.18   35170   !DISSOC (TOT.)  0.1 ATM
        NH2NO=N2+H2O    3.10E+34         -7.11   36283   !DISSOC (TOT.) 1.0 ATM
!        NH2NO=N2+H2O    2.90E+31         -5.91   36173   !DISSOC (TOT.)  10. ATM
        NH2NO+H=HNNO+H2 4.80E+08         1.50    7412    !HTRANS 2/6/96
        NH2NO+O=HNNO+OH 3.30E+08         1.50    4699    !HTRANS 2/6/96
        NH2NO+OH=HNNO+H2O        2.40E+06         2.00    -70     !HTRANS 2/6/96
        NH2NO+CH3=HNNO+CH4       1.60E+06         1.87    7183    !HTRANS 2/6/96
        NH2NO+NH2=HNNO+NH3       1.80E+06         1.94    4540    !HTRANS 2/6/96
        NH2NO+HO2=HNNO+H2O2      2.90E+04         2.69    12627   !HTRANS 2/6/96
!        H2NNHO=NH2+HNO 2.70E+39         -8.74   41618   ! 0.1 ATM DISSOC 2/6/96
        H2NNHO=NH2+HNO  2.40E+40         -8.73   41608   !1.00E+00 ATM
!        H2NNHO=NH2+HNO 1.20E+41         -8.64   41578    !1.00E+01 ATM
        H2NNHO+H=HNNHO+H2        4.80E+08         1.50    -894    !HTRANS 2/6/96
        H2NNHO+O=HNNHO+OH        3.30E+08         1.50    -894    !HTRANS 2/6/96
        H2NNHO+OH=HNNHO+H2O      2.40E+06         2.00    -1192   !HTRANS 2/6/96
        H2NNHO+CH3=HNNHO+CH4     1.60E+06         1.87    378     !HTRANS 2/6/96
        H2NNHO+NH2=HNNHO+NH3     1.80E+06         1.94    -1152   !HTRANS 2/6/96
        H2NNHO+HO2=HNNHO+H2O2    2.90E+04         2.69    -1600   !HTRANS 2/6/96
!       CLNO+M=NO+CL+M  1.30E+15         0.00    31991   ! M=AR
!                 N2/1.5/  O2/1.5/  H2/1.5/  H2O/10./   CO2/3.0/  CH4/3.0/
!       O+CLNO=CLO+NO   5.00E+12         0.00    3020
!       OH+CLNO=HOCL+NO 5.40E+12         0.00    2245
!       OH+CLNO=HONO+CL 5.50E+10         0.00    -477
!       CL+CLNO=CL2+NO  4.00E+13         0.00    -258
!       H+CLNO=HCL+NO   4.60E+13         0.00    904
END
```

REFERENCES

(1) Niessen, W. *Combustion and Incineration Processes, Applications in Environmental Engineering*; Marcel Dekker Publishers: New York, NY, 1995.

(2) USEPA “Characterization of Municipal Solid Waste in the United States,”EPA 350 - R - 97 - 015, USEPA, 1996.

(3) Wallis, M.; Watson, A. "MSW Incineration: A Critical Assessment", *Energy World* **1994**, *12*, 14.

(4) Brunner, C. R. *Handbook of Hazardous Waste Incineration*; Tab Books: Blue Ridge Summit, PA, 1989.

(5) Soud, H.; Fukasawa, K. *Developments in NOx Abatement and Control*; International Energy Agency: Paris, France, 1996.

(6) Hunt, T.; Muzio, L.; Smith, R.; Hanley, T. J. "Integrating Low-NOx Burners, Overfire Air, and Selective Non-Catalytic Reduction on a Utility Coal-Fired Boiler", *Environmental Progress* **1995**, *14*, 115-120.

(7) Han, J.-H. "A Hot-flow Model Analysis of the MSW Incinerator", *Fuel and Energy* **1997**, *38*, 337.

(8) Piao, G.; Aono, S.; Mori, S.; Deguchi, S.; Fujima, Y.; Kondoh, M.; Yamaguchi, M. "Combustion of Refuse Derived Fuel in a Fluidized Bed", *Waste Management* **1998**, *18*, 509-512.

(9) Wu, C.-H.; Chang, C.-Y.; Lin, J.-P.; Liang, Y. "Effects of Hydrogen Chloride on the Pyrolysis of Polyethylene: Pyrolysis Kinetics", *J. of Haz. Mat.* **1998**, *59*, 195-205.

(10) Brouwer, J.; Sacchi, G.; Longwell, J. P.; Sarofim, A. F. "Mixing of Chemical Kinetic Constraints on PIC production during Chlorocarbon Combustion", *Combust. and Flame* **1994**, *99*, 231-239.

(11) Bette, M.; Kirschner, H.; Schuetzenduebel, W. G. “The Achievement of 'Good Combustion' by Improvement of Secondary Air Injection at the Montgomery County Waste to Energy Facility”; ASME 16th Biennial National Waste Processing Conference Proceedings, 1994.

(12) Ravichandran, M.; Gouldin, F. C. "Numerical Simulation of Incinerator Overfiring Mixing", *Combust. Sci. and Tech.* **1992**, *85*, 165-185.

(13) Ryu, C. K.; Choi, S. "Design Consideration for Cross Jet Air Mixing in Municipal Solid Waste Incinerators", *Fuel and Energy* **1997**, *38*, 270.

(14) Phillips, J. B.; Price, G.; Fry, S.; Arcziscewski, T.; DeMonsabert, S.; Menawat, A. S. "An Object-oriented Approach to Numerical Methods: The Regula Falsi Method for Solving Equations with Tight Tolerances for Environmental Applications", *J. of Haz. Mat.* **1998**, *63*, 145-162.

(15) Tuttle, K. L. "Combustion generated particulate emissions", *Fuel and Energy* **1998**, *39*, 218.

(16) Kuo, J. T.; Hsu, W.-S.; Yo, T.-C. "Effect of Air Distribution on Solid Fuel Bed Combustion", *Transactions of the ASME* **1997**, *119*, 120-128.

(17) Benson, S. W. "Oxygen Initiated Combustion: Thermochemistry and Kinetics of Unsaturated Hydrocarbons", *Int. J. of Chem. Kinet.* **1996**, *28*, 665-672.

(18) Berkowitz, J.; Ellison, G. B.; Gutman, D. "Enthalpy of CH3O and C2H5O", *J. Phys. Chem.* **1994**, *98*, 2744.

(19) Bozzelli, J. W.; Dean, A. M. "Hydrocarbon Radical Reactions with O2: Comparison of Allyl, Formyl, and Vinyl to Ether", *J. Phys. Chem.* **1993**, *97*, 4427-4441.

(20) Cobos, C. J.; Hippler, H.; Luther, K.; Ravishankara, A. R.; Troe, J. "High Pressure Limit Parameters for CH3 + O2 -> CH3OO", *J. Phys. Chem.* **1985**, *89*, 4332.

(21) Curtiss, L. A.; Lucas, D. J.; Pople, J. A. "Energies of C2H5O and C2H5O+ Isomers", *J. Chem. Phys.* **1995**, *102*, 3292.

(22) Evleth, E. M.; Melius, C. F.; Rayez, M. T. "Theoretical Characterization of the Reactions of HO2 with Formaldehyde", *J. Phys. Chem.* **1993**, *97*, 5040-5045.

(23) Fagerstrom, K.; Lund, A.; Mahmoud, G.; Jodkowski, J. T.; Ratajczak, E. "Kinetics of the Gas-Phase Reaction between Ethyl and Hydroxyl Radicals", *Chem. Phys. Lett.* **1993**, *208*, 321-327.

(24) Held, T. J.; Dryer, F. L. "A Comprehensive Mechanism for Methanol Oxidation", *Int. J. of Chem. Kinet.* **1998**, *30*, 805-830.

(25) Ignatyev, I. S.; Xie, Y.; Allen, W. D.; Schaefer, H. F. "Mechanism of the C2H5 + O2 Reaction", *J. Chem. Phys.* **1997**, *107*, 141-155.

(26) Jachimowski, C. J. "On HCCH oxidation", *Combust. Flame* **1977**, *29*, 55.

(27) Procaccini, C.; Kraft, M.; Fey, H.; Bockhorn, H.; Longwell, J. P.; Sarofim, A. F.; Smith, K. A. “PIC Formation During the Combustion of Simple Hydrocarbons in Inhomogeneous Incineration Systems”; 27th International Symposium on Combustion, 1998, Boulder, CO.

(28) Quelch, G. E.; Gallo, M. M.; Shen, M.; Xie, Y.; Schaefer III, H. F.; Moncrieff, D. "Aspects of the Reaction Mechanism of Enthane Combustion. Nature of the Intramolecular Hydrogen Transfer", *J. Am. Chem. Soc.* **1994**, *116*, 4953.

(29) Wagner, A. F.; Slagle, I. R.; Sarzynski, D.; Gutman, D. "Experimental and Theoritical Studies of the C2H5 + O2 Reaction Kinetics", *J. Phys. Chem.* **1990**, *94*, 1853-1868.

(30) Walch, S. P. "Theoretical characterization of the reaction CH3+OH -> CH3OH -> products: The 1CH2+H2O, H2+HCOH, and H2+H2CO channels", *J. of Chem. Phys.* **1993**, *98*, 3163-3167.

(31) Baulch, L. D.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. "Evaluated Kinetic Data for Combustion Modeling", *J. Phys. Chem. Ref. Data* **1992**, *21*, 411-429.

(32) Hidaka, Y.; Hattori, K.; Okuno, T.; Inami, K.; Abe, T.; Koike, T. "On HCCH Oxidation", *Combust. Flame* **1996**, *107*, 401.

(33) Norton, T. S.; Dryer, F. L. *Combust. Sci. and Tech.* **1989**, *63*.

(34) Norton, T. S.; Dryer, F. L. *Int. J. Chem. Kinet.* **1990**, *22*.

(35) Bozzelli, J. W., Discussion on H2C.NHOOH rapid dissociation to H2C=NHO + OH from B3LYP/6-31G(d,p) calculations.

(36) Dean, A. M.; Bozzelli, J. W. Combustion Chemistry of Nitrogen. In *Gas-Phase Combustion Chemistry*; Gardiner, J., W.C., Ed.; Verlag-Springer: New York, 2000.

(37) Mao, F.; Barat, R. B. "Minimization of NO During Staged Combustion of CH3NH2", *Combust. and Flame* **1996**, *105*, 557-568.

(38) Atkinson, R.; Carter, W. P. L.; Daranall, K. R.; Winer, A. M.; Pitts, J. N., Jr. "A Smog Chamber and Modeling Study of the Gas Phase NOx-Air Photooxidation of Toluene and the Cresols", *Int. J. Chem. Kinet.* **1980**, *12*, 779-836.

(39) Atkinson, R.; Carter, W. P. L.; Winer, A. M. "Effects of Pressure on Product Yields in the NOx Photooxidations of Selected Aromatic Hydrocarbons", *J. Phys. Chem.* **1983**, *87*, 1605.

(40) Atkinson, R.; Lloyd, A. C. "Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog", *J. Phys. Chem. Ref. Data* **1984**, *13*, 315-440.

(41) Kantak, M. K.; De Manrique, K. S.; Aglave, R. H.; Hesketh, R. P. "Methylamine Oxidation in a Flow Reactor: Mechanism and Modeling", *Combust. and Flame* **1997**, *108*, 235-265.

(42) Jursic, B. S. "The Evaluation of Nitrogen Containing Bond Dissociation Energies Using the Ab Initio and Density Functional Methods", *Theochem* **1996**, *366*, 103-108.

(43) Lifshitz, A.; Bidani, M.; Carroll, H. F.; Hwang, S. M.; Fu, P. Y.; Shin, K. S.; Gardiner, J., W.C. "Ignition of Monomethylamine", *Combust. Flame* **1991**, *86*, 229-236.

(44) Melius, C.; Unpublished data at website http://z.ca.sandia.gov/~melius/; Sandia National Laboratory: Livermore, CA, 1997.

(45) Wayner, D. D. M.; Clark, K. B.; Rauk, A.; Yu, D.; Armstrong, D. A. "C-H Bond Dissociation Energies of Alkyl Amines: Radical Structures and Stabilization Energies", *J. Am. Chem. Soc.* **1997**, *119*, 8925-8932.

(46) Sheng, C.; Thipse, S.; Sun, H.-Y.; Bozzelli, J. W.; Booty, M. R.; Magee, R. S.; Hoecke, D. “A Pilot-scale Incinerator for Evaluating the Combustion of Co-fired Plastics”; Proc. Int. Conf. Incineration Therm. Treat. Technol., 1999.

(47) Thipse, S. S.; Sheng, C.; Booty, M. R.; Magee, R. S.; Bozzelli, J. W. "Chemical makeup and physical characterization of a synthetic fuel and methods of heat content evaluation for studies on MSW incineration", *Fuel* **2002**, *81*, 211-217.

(48) Dagaut, P.; Ristori, A.; El Bakali, A.; Cathonnet, M. "Experimental and kinetic Modeling Study of the Oxidation of n-Propylbenzene", *Fuel* **2001**, *81*, 173-18.

(49) Bass, J., C.; INFERNO2; 2.0 ed. Newark, NJ, 2001.

(50) Bass, J., C., Personal communication on use of INFERNO computer code.

(51) McQuigg, K. "Starved Air Gasification Tests on Five Biomass Feedstocks", *Bioenergy ' 98* **1998**.

(52) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; John Wiley & Sons, Inc.: New York, 1960.

(53) Ritter, E.; Bozzelli, J. W. "THERM program", *Int. J. Chem. Kinet.* **1991**, *23*, 767.

(54) *MOPAC: A General Molecular Orbital Package (QCPE445)*; OCPE Bull: , 1983.

(55) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gromperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Eds. *Gaussian 94 computer program, Revision C.2*; Gaussian Inc.: Pittsburgh, 1995.

(56) Ing, W.-C. Reaction Kinetics of Methanol and MTBE Oxidation and Pyrolysis. Ph. D. Dissertation, New Jersey Institute of Technology, 1996.

(57) Yamada, T. Oxidation of Dimethyl-ether and Ethylene in the Atmosphere and Combustion Environment and Thermodynamic Studies on Hydrofluorocarbons Using Ab Initio Calculation Methods. Ph. D. Dissertation, New Jersey Institute of Technology, 1999.

(58) Becke, A. D. "Density-functional Thermochemistry. III. The Role of Exact Exchange.", *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(59) Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. "A Complete Basis Set Model Chemistry. IV. An Improved Atomic Pair Natural Orbital Method.", *J. Chem. Phys.* **1994**, *101*, 5900.

(60) Chang, A. Y.; Bozzelli, J. W.; Dean, A. M. "On Using Multi-Frequency QRRK analysis", *Zeit. Phys. Ch.* **2000**, 1533-1568.

(61) Mao, F. Combustion of Methyl Chloride, Monomethyl Amine and Their Mixtures in a Two Stage Turbulent Flow Reactor. Ph. D. Dissertation, New Jersey Institute of Technology, 1995.

(62) Scott, A. P.; Radom, L. "Harmonic Vibrational Frequencies: An Evalution of HF, MP, QCI, DFT, and Semiempirical Scale Factors", *J. Phys. Chem.* **1996**, *100*, 16502-16513.

(63) Zhong, X.; Bozzelli, J. W. *J. Phys. Chem. A* **1998**, *102*, 3537.

(64) Sheng, C.; Bozzelli, J. W.; Dean, A. M.; Chang, A. Y. "Detailed Kinetics and Thermochemistry of C2H5 + O2:
Reaction Kinetics of the Chemically-Activated and Stabilized C2H5OO Adduct", *Submitted to J. Phys. Chem. A* **2001**.

(65) Bozzelli, J. W.; Dean, A. M.; Chang, A. "Density of Energy", *Int. J. Chem. Kinet.* **1997**, *29*, 161-170.

(66) Jungkamp, T. P. W.; Seinfeld, J. H. "The enthalpy of formation of trioxy radicals ROOO (R=H, CH3, C2H5). An ab initio study.", *Chem. Phys. Letters* **1996**, *257*, 15-22.

(67) Karni, M.; Oref, I.; Burcat, A. "Ab initio calculation and Ideal Gas Thermodynamic Functions of Cyclopentadiene and Cyclopentadiene Derivatives", *J. Phys. Chem. Ref. Data* **1991**, *20*, 665.

(68) Lay, T. H.; Krasnoperov, L. N.; Venanzi, C. A.; Bozzelli, J. W.; Shokhirev, N. V. "Ab Initio Study of α-Chlorinated Enthyl Hydroperoxides CH3CH2OOH, CH3CHClOOH, and CH3CCl2OOH: Conformational Analysis, Internal Rotation Barriers, Vibrational Frequencies, and Thermodynamic Properties", *J. Phys. Chem.* **1996**, *100*, 8240-8249.

(69) Melius, C. F. *BAC-MP4 Heats of Formation and Free Energies*, 1993.

(70) Mebel, A. M.; Diau, E. W. G.; Lin, M. C.; Morokuma, K. "Ab Initio and RRKM Calculations for Multichannel Rate Constants of the C2H3 + O2 Reaction", *J. Am. Chem. Soc.* **1996**, *118*, 9759-9771.

(71) Chen, C.-J.; Bozzelli, J. W. "Kinetic Analysis for HO2 addition to ethylene, propene and isobutene and thermochemical parameters of alkyl hydroperoxides and hydroperoxide alkyl radicals", *J. Phys. Chem. A* **2000**, *104*, 4997-5012.

(72) Laskin, A.; Wang, H. "On initiation reactions of acetylene oxidation in shock tubes. A quantum mechanical and kinetic modeling study", *Chemical Physics Letters* **1999**, *303*, 43-49.

(73) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. "Assessment of G-2 and DFT for enthalpies of formation", *J. Chem. Phys.* **1997**, *106*, 1063-1079.

(74) Levine, I. N. *Quantum Chemistry*, 5th ed.; Prentice Hall: Upper Saddle River, NJ, 2000.

(75) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(76) Dupuis, M.; Spangler, D.; Wendoloski, J. J.; General Atomic and Molecular Electronic Structure System (GAMESS); Program QG01 ed.; National Resource for Computations in Chemistry: Berkley, CA, 1980.

(77) Werner, H.-J.; Knowles, P. J.; MOLPRO; University of Birmingham: Birmingham, UK.

(78) Spartan; Wavefunction, Inc.: Irvine, CA, 1995-98.

(79) Amos, R. D.; CADPAC, The Cambridge Analytic Derivatives Package; Issue 6 ed.; University of Cambridge: Cambridge, UK, 1995.

(80) Schrodinger, I.; Jaguar; Schrodinger, Inc.: Portland, OR, 2001.

(81) NWChem; High Performance Computational Chemistry Group, W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory: Richland, WA, 2001.

(82) Q-Chem, I.; Q-Chem; Q-Chem, Inc.: Export, PA, 2001.

(83) Hypercube.; HyperChem; HyperCube, Inc.: Gainsville, FL.

(84) McBride, B. J.; Gordon, S. "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications II. User's Manual and Program Description,"NASA RP-1311-P2, NASA, 1996.

(85) Eriksson, G.; Hack, K. "ChemSage - A Computer Program for the Calculation of Complex Chemical Equilibria", *Metallurgical Transactions B* **1990**, *21B*, 1013.

(86) Reynolds, W. C.; STANJAN Chemical Equilibrium Solver; 3.70s ed. Stanford, CA, 1987.

(87) Kee, R. J.; Miller, J. A.; Jefferson, T. H.; CHEMKIN: Fortran Chemical Kinetics Code Package, 1980.

(88) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(89) Metz, C. R. *Theory and Problems of Physical Chemistry*; McGraw-Hill Book Company: New York, 1976.

(90) Pitzer, K. S.; Gwinn, W. D. "internal rotor, the major paper of Pitzer and Gwinn", *J. Chem. Phys.* **1942**, *10*, 428.

(91) Lay, T. S.; VIBIR - a code applying Pitzer-Gwinn's method 1 for internal rotor.

(92) McClurg, R. B.; Flagan, R. C.; Goddard III, W. A. "Hinder Rotor paper", *J. Chem. Phys.* **1997**, *106*, 6675.

(93) McClurg, R. B. "The hindered rotor density of states interpolation function", *J. Chem. Phys.* **1999**, *111*, 7165.

(94) Knyazev, V. D. "Hinder rotor paper", *J. Chem. Phys.* **1999**, *111*, 7161.

(95) Ritter, E.; Bozzelli, J. W. *Int. J. Chem. Kinet.* **1991**, *23*, 767.

(96) Roothan, C. C. J. "New Developments in Molecular Orbital Theory", *Rev. Mod. Phys.* **1951**, *23*, 69.

(97) Pople, J. A.; Nesbet, R. K. "Self-Consistent Orbitals for Radicals", *J. Chem. Phys.* **1959**, *22*, 571-574.

(98) McWeeny, R.; Dierksen, G. *J. Chem. Phys.* **1968**, *49*, 4852.

(99) NIST Standard Reference Database; Number 69 ed.; http://webbook.nist.gov/chemistry/:, February 2000.

(100) TRC.; Thermodynamic Properties of the Substances in Ideal Gas State; 1.0M ed.; Thermodynamic Research Center of the Texas Engineering Experiment Station: Texas A&M University, 1994.

(101) Atkinson, R. "Kinetics and Mechanisms of the Gas-Phase Reactions of the NO3 Radical with Organic Compounds", *J. Phys. Chem. Ref. Data* **1991**, *20*, 459.

(102) Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution*; John Wiley & Sons: New York, 1986.

(103) Kline, L. E. "Plasma studies with kinetic model", *IEEE Trans. Plasma Sci.* **1986**, *PS-14*, 145.

(104) Lutz, A. E.; Kee, R. J.; Miller, J. A. "SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis,"Sandia Report, SAND87-8248.UC-4, Sandia National Laboratories, 1988.

(105) Manka, M.; REACT; Alchemy Software: Wesley Chapel, FL, 2000.

(106) Glasstone, S.; Laidler, K.; Eyring, H. *The Theory of Rate Processes*, First ed.; McGraw-Hill Book Co., Inc.: New York, 1941.

(107) Eyring, H. "Description of "activated complex"", *J. Chem. Phys.* **1935**, *3*, 107.

(108) Sheng, C.; Bozzelli, J. W. "SMCPS", *Process of submission to journal* **2001**.

(109) Kee, R. J.; Rupley, F. M.; Miller, J. A. "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics,"SAND89-8009B, Sandia National Laboratories, 1991.

(110) Gordon, S.; McBride, B. J. "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performances, Incident and Reflected Shocks and Chapman-Jouguet Detonations,", 1971.

(111) Burcat, A.; Zeleznik, F. J.; McBride, B. J. "NASA Technical Memorandum # 83800 on NASA polynomial format,"NASA Technical Memorandum # 83800, NASA, 1985.

(112) Sheng, C.; Bozzelli, J. W. "ab initio molecular orbital and density functional analysis of acetylene + o2 reactions with chemkin evaluation", *Int. J. Chem. Kinet.* **2000**, *32*, 623-641.

(113) Yamada, T.; El-Sinawi, A.; Siraj, M.; Taylor, P. H.; Peng, J.; Hu, X.; Marshall, P. "Rate Coefficients and Mechanistic Analysis for the Reaction of Hydroxyl Radicals wtih 1,1-Dichloroethylene and trans-1,2-dichrloroethylene over an extended temperature range", *J. Phys. Chem. A* **2001**, *105*, 7588-7597.

(114) Zhu, R.; Lin, M. C. "The CH3 + HO2 Reaction: First-Principles Prediction of Its Rate Constant and Product Branching Probabilities", *J. Phys. Chem. A* **2001**, *105*, 6243-6248.

(115) Holbrook, K. A.; Pilling, M. J. *Unimolecular Reactions*; Wiley: New York, 1996.

(116) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, 1990.

(117) Klippenstein, S. J.; Yand, D. L.; Yu, T.; Kistyan, S.; Lin, M. C. "RRKM - variflex used", *J. Phys. Chem. A* **1998**, *102*, 6973.

(118) Klippenstein, S. J.; Wagner, A. F.; Dunbar, R. C.; Wardlaw, D. M.; Robertson, S. H.; VARIFLEX; version 1.00 ed., 1999.

(119) Miller, J. A.; Klippenstein, S. J.; Robertson, S. H. "RRKM - with master eqn", *J. Phys. Chem. A* **2000**, *104*, 7525.

(120) Tan, Y.; Dagaut, P.; Cathonnet, M.; Boether, J. C. *Combust. Sci. and Tech.* **1995**, *102*.

(121) Miller, J. A.; Mitchell, R. E.; Smooke, M. D.; Kee, R. J. "Toward a Comprehensive Chemical Kinetic Mechanism for the Oxidation of Acetylene: Comparison of Model Predictions With Results From Flame and Shock Tube Experiments"; 19th Symposium (International) on Combustion, 1982.

(122) Gardiner Jr., W. C.; Walker, B. F. "Ref on HCCH oxidation", *J. Chem. Phys.* **1968**, *48*, 5279.

(123) Marinov, N. M.; Pitz, W. J.; Westbrook, C. K.; Vincitore, A. M.; Castaldi, M. J.; Senkan, S. M.; Melius, C. F. "Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Laminar Premixed n-Butane Flame", *Combust. and Flame* **1998**, *114*, 192-213.

(124) Laskin, A.; Wang, H. “On Initiation Reactions of Acetylene Oxidation in Shock Tubes. A Kinetic Modeling and Quantum Mechanical Study.”; First Joint Meeting of the U.S. Sections of the Combustion Institute: Western States, Central States, Eastern States, 1999, Washington, DC.

(125) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. "CBS-4 and CBS-q (3rd paper)", *J. Chem. Phys.* **1996**, *104*, 2598.

(126) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. "CBS-4 and CBS-q (2nd paper)", *J. Am. Chem. Soc.* **1995**, *117*, 11299.

(127) Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. "CBS-4 and CBS-q (1st paper)", *J. Chem. Phys.* **1994**, *101*, 5900.

(128) NASA “Chemical Kinetics and Photochemical Data for Use in Stratoshperic Modeling,”11, Jet Propulsion Laboratory, Pasedena, CA, 1994.

(129) Lee, C.; Yang, W.; Parr, R. G. "LYP density functional theory method", *Phys. Rev. B* **1988**, *37*, 785.

(130) Lay, T. H.; Bozzelli, J. W.; Dean, A. M.; Ritter, E. R. "Hydrogen atom Bond Increments for Thermodynamic properties of Hydrocarbon Radical Species", *J. Phys. Chem.* **1995**, *99*, 14514-14527.

(131) Stewart, J. J. P. "PM3 paper 2", *J. Comput. Chem.* **1989**, *10*, 221.

(132) Stewart, J. J. P. "PM3 paper 1", *J. Comput. Chem.* **1989**, *10*, 209.

(133) Stewart, J. J. P. *MOPAC 6.0*; Frank J. Seiler Research Lab., US Air Force Academy: Colorado, 1990.

(134) Frisch, M. J.; Frisch, Æ.; Foresman, J. B. *Gaussian 94 User's Reference*; Gaussian Inc.: Pittsburgh, PA, 1995.

(135) Durant, J. L. “Evaluation of Transition State Properties by Density Functional Theory”; Fourth International Conference on Chemical Kinetics, 1997, Gaithersburg, MD.

(136) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(137) Gilbert, R. G.; Luther, K.; Troe, J. "Strong Collisison", *J. Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 169-175.

(138) Carpenter, B. K. *J. Phys. Chem.* **1995**, *99*, 9801.

(139) Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 9806.

(140) Bencsura, A.; Knyazev, V. D.; Slagle, I. R.; Gutman, D.; Tsang, W. *Ber. Bunsenges Phys. Chem.* **1992**, *96*, 1338-1347.

(141) Lias, S. G.; Karpas, Z.; Liebman, J. F. *Am. Chem. Soc.* **1985**, *107*, 6089.

(142) Taylor, P. H.; Rahman, M. S.; Arif, M.; Dellinger, B.; Marshall, P. "Kinetic and mechanistic studies of the reaction of hydroxyl radicals with acetaldehyde over an extended temperature range"; Twenty-sixth Symposium (International) on Combustion, 1996, Napoli, Italy.

(143) Wong, M. W.; Radom, L. "Radical Addition to Alkenes: An Assessment of Theoretical Procedures", *J. Phys. Chem* **1995**, *99*, 8582-8588.

(144) Chen, W.; Schlegel, H. B. "Evaluation of S2 for Correlated Wave Functions and Spin Projection of Unrestricted Moller-Plesset Perturbation Theory", *J. Phys. Chem* **1994**, *101*, 5957-5968.

(145) Kee, R. J.; Rupley, F. M.; Miller, J. A. "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics,"SAND89-8009B, Sandia National Laboratories, 1989.

(146) Maranzana, A.; Ghigo, G.; Tonachini, G. "Diradical and Peroxirane Pathways in the [pi2+pi2] Cycloaddition Reactions of 1Dg Dioxygen with Ethene, Methyl Vinyl Ether, and Butadiene: A Density Functional and Multireference Perturbation Theory Study", *J. Am. Chem. Soc.* **2000**, *122*, 1414-1423.

(147) Kaiser, E. W. "Temperature and Pressure Dependence of the C2H4 Yield from the Reaction C2H5 + O2", *J. Phys. Chem.* **1995**, *99*, 707-711.

(148) Clifford, E. P.; Farrell, J. T.; DeSain, J. D.; Taatjes, C. A. "Infrared Frequency-Modulation Probing of Product Formation in Alkyl + O2 Reactions: I. The Reaction of C2H5 with O2 between 295 and 698K", *J. Phys. Chem A* **2000**, *104*, 11549-11560.

(149) Slagle, I. R.; Feng, Q.; Gutman, D. *J. Phys. Chem.* **1984**, *88*, 3648.

(150) Slagle, I. R.; Ratajczak, E.; Gutman, D. *J. Phys. Chem.* **1986**, *90*, 402.

(151) McAdam, G. K.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 1509.

(152) Plumb, I. C.; Ryan, K. R. *Int. J. Chem. Kinet.* **1981**, *13*, 1011-1028.

(153) Gutman, D. *J. Chem. Phys.* **1987**, *84*, 409-414.

(154) Kaiser, E. W.; Rimai, L.; Wallington, T. J. *J. Phys. Chem.* **1989**, *93*, 4094-4098.

(155) Bozzelli, J. W.; Dean, A. M. "Chemical Activation Analysis of the Reaction of C2H5 with O2", *J. Phys. Chem.* **1990**, *94*, 3313-3317.

(156) Green, W. H. "DFT for CH3OO and C2H5OO", *Int. J. Quan. Chem.* **1994**, *52*, 837.

(157) Quelch, G. E.; Gallo, M. M.; Schaefer III, H. F. "C2H5OO pathway, geom, freq", *J. Am. Chem. Soc.* **1992**, *114*, 8239.

(158) Atkinson, D. B.; Hudgens, J. W. "Chemical Kinetic Studies Using Ultraviolet Cavity Ring-Down Spectroscopic Detection: Self-Reaction of Ethyl and Ethylperoxy Radicals and the Reaction O2 + C2H5 -> C2H5OO", *J. Phys. Chem. A* **1997**, *101*, 3901-3909.

(159) Shen, D.; Moise, A.; Pritchard, H. O. "Oxirane formation competes w/ C2H4 formation", *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1425.

(160) Skancke, A.; Skancke, P. N. "CCOO -> CjCOOH barrier calculation", *J. Molec. Struct. (THEOCHEM)* **1990**, *207*, 201.

(161) Rienstra-Kiracofe, J. C.; Allen, W. D.; Schaefer III, H. F. "The C2H5 + O2 Reaction Mechanism: High-Level ab Initio Characterizations", *J. Phys. Chem. A* **2000**, *104*, 9823-9840.

(162) Miller, J. A.; Klippenstein, S. J.; Robertson, S. H. "A Theoretical Analysis of the Reaction Between Ethyl and Molecular Oxygen"; 28th Symposium (International) on Combustion, 2000, Edinburgh, England.

(163) Venkatesh, P. K.; Dean, A. M.; Cohen, M. H.; Carr, R. W. "Chebyshev Expansions and Sensitivity Analysis for Approximating the Temperature- and Pressure-Dependence of Chemically-Activated Reactions", *Reviews in Chemical Engineering* **1997**, *13*.

(164) Venkatesh, P. K.; Chang, A. Y.; Dean, A. M.; Cohen, M. H.; Carr, R. W. "Parameterization of Pressure- and Temperature- Dependent Kinetics in Multiple Well Reactions", *AIChE Journal* **1997**, *43*, 1331-1339.

(165) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. "CBS-4, CBS-q and CBS-Q(3rd paper)", *J. Chem. Phys.* **1996**, *104*, 2598.

(166) Becke, A. D. "B3 density functional theory method", *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(167) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. "Gaussian-2 theory for molecular energies of first- and second-row compounds", *J. Chem. Phys.* **1991**, *94*, 7221.

(168) Sheng, C.; Bozzelli, J. W. "SMCPS", *Process of Submitting to Journal* **2001**.

(169) Gilbert, R. G.; Luther, K.; Troe, J. "Strong Collisison", *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 169-177.

(170) Ritter, E. R. *Int. J. Chem. Kinet.* **1997**, *29*, 161.

(171) Ritter, E. R. *J. Chem. Info. Comput. Sci.* **1991**, *31*, 400.

(172) Dobis, O.; Benson, S. W. "Temperature Coefficients of Rates of Ethyl Radical Reactions with HBr and Br in the 228-368 K Temperature Range at millitorr pressures", *J. Phys. Chem. A* **1997**, *101*, 6030-6042.

(173) Marshall, P. "Thermochemistry of the Ethyl Radical and the C-H Bond Strength in Ethane", *J. Phys. Chem. A* **1999**, *103*, 4560-4563.

(174) Quelch, G. E.; Gallo, M. M.; Shen, M.; Xie, Y.; Schaefer III, H. F.; Moncrieff, D. "Aspects of the Reaction Mechanism of Ethane Combustion. Nature of the Intramolecular Hydrogen Transfer", *J. Am. Chem. Soc.* **1994**, *116*, 4953-4962.

(175) Walker, R. W.; Morley, C. Basic Chemistry of Combustion. In *Low-Temperature Combustion and Autoignition*; Pilling, M. J., Ed.; Elsevier: Amsterdam; New York, 1997; pp 1-124.

(176) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. "Gaussian-3 theory using reduced Møller-Plesset order", *J. Chem. Phys.* **1999**, *110*, 4703.

(177) Sheng, C.; Bozzelli, J. W.; Dean, A. M. “Thermochemical Parameters, Reaction paths and a Detailed Kinetic Model for the C2H5 + O2 Reaction System”; Second Joint Meeting of the U.S. Sections of the Combustion Institute: Western States, Central States, Eastern States, 2001, Oakland, CA.

(178) Reints, W.; Pratt, D. A.; Korth, H.-G.; Mulder, P. "O-O Bond Dissociation Enthalpy in Di(trifluoromethyl) Peroxide (CF3OOCH3) as Determined by Very Low Pressure Pyrolysis. Density Functional Theory Computations on O-O and O-H Bonds in (Fluorinated) Derivates", *J. Phys. Chem. A* **2000**, *104*, 10713-10720.

(179) Westmoreland, P. R.; Howard, J. B.; Longwell, J. P.; Dean, A. M. AIChE Annual Meeting, 1986.

(180) Westmoreland, P. R. *Combust. Sci. and Tech.* **1992**, *82*, 1515.

(181) Dean, A. M.; Westmoreland, P. R. *Int. J. Chem. Kinet.* **1987**, *19*, 207.

(182) Gilbert, R. G.; Smith, S. C.; Jordan, M. J. T.; UNIMOL program suite (calculation of falloff curves for unimolecular and recombination reactions) Sydney, Australia, 1993.

(183) Gilbert, R. G.; Luther, K.; Troe, J. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 164.

(184) Bozzelli, J. W.; Jung, D. "Theoretical Investigation on Stability of the C.H2OCl Radical", *J. Phys. Chem. A* **2001**, *105*, 3941-3946.

(185) Stull, D. R.; Westrum, J., E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Robert E. Krieger Publishing Company: Malabar, FL, 1987.

(186) Sebbar, N.; Bockhorn, H.; Bozzelli, J. W. "Thermodynamic Properties and Reactions of vinyl hydroperoxides, peroxy radicals and phenyl hydroperoxide"; The Seventh International Congress on Toxic Combustion-by-products: Origins, Fate and Health Effects, 2001, Research Triangle Park, NC.

(187) Bach, R. D.; Ayala, P. Y.; Schlegel, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 12578-12765.

(188) Sebbar, N.; Bockhorn, H.; Bozzelli, J. W. *Submitted to Phys. Chem. Chem. Phys.* **2001**.

(189) Seiser, R.; Pitsch, H.; Seshadri, K.; Pitz, W. J.; Curran, H. J. "Extinction and Autoignition of n-Heptane in Counterflow Configuration"; 28th Symposium (International) on Combustion, 2000, University of Edinburgh, Scotland.

(190) Ribaucour, M.; Minetti, R.; Sochet, L. R.; Curran, H. J.; Pitz, W. J.; Westbrook, C. K. "Ignition of Isomers of Pentane: An Experimental and Kinetic Modeling Study"; 28th Symposium (International) on Combustion, 2000, University of Edinburgh, Scotland.

(191) Chen, C.-J.; Bozzelli, J. W. "Thermochemical Property, Pathway and Kinetic Analysis on the Reactions of Allylic Isobutenyl Radical with O2: an Elementary Reaction Mechanism for Isobutene Oxidation", *J. Phys. Chem. A.* **2000**, *104*, 9715-9732.

(192) Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F.; Frizzell, D. H.; NIST Chemical Kinetics Database; Version 2Q98 ed.; NIST Standard Reference Data: Gaithersburg, MD, 1998.

(193) De Avillez Pereira, R.; Baulch, D. L.; Pilling, M. J.; Robertson, S. H.; Zeng, G. "Temperature and Pressure Dependence of the Multichannel Rate Coefficents for the CH3+OH System", *J. Phys. Chem. A* **1997**, *101*, 9681-9693.

(194) Smith, S. R.; Gordon, A. S. *J. Phys. Chem.* **1956**, *60*.

(195) Fletcher, J. C. *Proc. Roy. Soc. (London)* **1934**, *A147*.

(196) Someno, F. *Bull. Ins. Phys. Chem. Research (Tokyo)* **1942**, *21*.

(197) Cooke, D. F.; Dodson, M. G.; Williams, A. *Combust. and Flame* **1971**, *16*.

(198) Bowman, C. T. *Combustion and Flame* **1975**, *25*.

(199) Aronowitz, D.; Santoro, R. J.; Dryer, F. L.; Glassman, I. 17th Symposium (International) on Combustion, 1978.

(200) Westbrook, C. K.; Creighton, J.; Lund, C.; Dryer, F. L. *J. Phys. Chem.* **1977**, *81*.

(201) Westbrook, C. K.; Dryer, F. L. *Combust. Sci. and Tech.* **1979**, *20*.

(202) Vandooren, J.; Van Tiggelen, P. J. 18th Symposium (International) on Combustion, 1981.

(203) Norton, T. S.; Dryer, F. L. 23rd Symposium (International) on Combustion, 1990.

(204) Grotheer, H.; Riekert, G.; Walter, D.; Just, T. 22nd Symposium (International) on Combustion, 1988.

(205) Yetter, R. A.; Dryer, F. L.; Rabitz, H. *Combust. Sci. and Tech.* **1991**, *79*.

(206) Hochgreb, S.; Dryer, F. L. *Combust. Flame* **1992**, *91*.

(207) Ing, W.-C. Reaction Kinetics on Methanol and MTBE Oxidation and Pyrolysis. Ph. D. Dissertation, New Jersey Institute of Technology, 1996.

(208) Lay, T. H. Thermodynamic Properties of Hydrocarbon Radicals, Peroxy Hydrocarbon and Peroxy Chlorohydrocarbon Molecules and Radicals. Ph. D. Dissertation, New Jersey Institute of Technology, 1994.

(209) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. "A complete basis set model chemistry. IV. An improved atomic pair natural orbital method. (CBS-APNO)", *J. Chem. Phys.* **1994**, *101*, 5900-5909.

(210) Sheng, C.; Bozzelli, J. W. "SMCPS - submitted", *J. Chem. Ed.* **2001**, *Submitted to J. Chem. Ed.*

(211) Ritter, E. R. "CPFIT", *J. Chem. Info. Comput. Sci.* **1991**, *31*, 400.

(212) Carter, W. P.; Tardy, D. C. *J. Phys. Chem.* **1974**, *78*, 1579-1582.

(213) Fox, L.; Parker, I. B. *Chebyshev Polynomials in Numerical Analysis*; Oxford University Press: London, 1968.

(214) Rivlin, T. J. *Chebyshev Polynomials From Approximation Theory to Algebra and Number Theory*, Second ed.; Wiley-Interscience: New York, 1990.

(215) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. "QCISD method", *J. Chem. Phys.* **1987**, *87*, 5968.

(216) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of organic compounds*; Robert E. Krieger Pub. Co.: Malabar, Florida, 1987.

(217) Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394-3401.

(218) Warnatz, J. . In *Combustion Chemistry*; Gardiner, J., W. C., Ed.; Springer-Verlag: New York, 1984.

(219) Krasnoperov, L. N.; Chesnokov, E. N. "Reaction of unimolecular dissociation of formyl radical, HCO->H+CO, studied over 1-100 bar buffer gas pressure range.", *Chem. Phys. Processes Combust.* **1999**, 293-295.

(220) Cobos, C. J.; Hippler, H.; Luther, K.; Ravishankara, A. R.; Troe, J. "high pressure limit param for CH3 + O2 -> CH3OO", *J. Phys. Chem.* **1985**, *89*, 4332.

(221) Semmes, D. H.; Ravishankara, A. R.; Gump-Perkins, C. A.; Wine, P. H. *Int. J. Chem. Kinet.* **1985**, *17*, 303.

(222) Dean, A. M.; Westmoreland, P. R. "QRRK agreement", *Int. J. Chem. Kinet.* **1987**, *19*.

(223) Lee, J. W.; Bozzelli, J. W. "CH3CjO and CjCHO Oxidation"; Fifth International Conference on Chemical Kinetics, 2001, Gaithersburg, MD.

(224) Yamada, C.; Endo, Y.; Hirota, E. "HO2 expt. Vibrations", *J. Chem. Phys.* **1983**, *78*, 4379.

(225) Hwang, S. M.; Higashihara, T.; Gardiner, J., W.C.; Shin, K. S. "Shock Tube and Modeling Study of Monomethylamine Oxidation", *J. Phys. Chem.* **1990**, *94*, 2883-2889.

(226) Jolley, L. J. *J. Chem. Soc.* **1934**, 1957.

(227) Cullis, C. F.; Issac, I. *Trans. Faraday Soc.* **1952**, *48*, 1023.

(228) Cullis, C. F.; Smith, L. S. *Trans. Faraday Soc.* **1950**, *46*, 42.

(229) Cullis, C. F.; Willsher, J. P. *Proc. Royal Soc. London A* **1951**, *209-218*, 218.

(230) Basevich, V. Y. *Prog. Energy Combust. Sci.* **1987**, *13*, 199.

(231) Higashihara, T.; Gardiner, J., W.C.; Hwang, S. M. *J. Phys. Chem.* **1987**, *91*, 1900.

(232) Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. "Bond Dissociation Energies and Radical Stabilization Energies Associated with Substituted Methyl Radicals", *J. Phys. Chem. A* **2001**, *105*, 6750-6756.

(233) Brinck, T.; Lee, H. N.; Jonsson, M. "Quantum Chemical Studies on the Thermochemistry of Alkyl and Peroxyl Radicals", *J. Phys. Chem. A* **1999**, *103*, 7094-7104.

(234) *CRC Handbook of Chemistry and Physics*, 63rd Edition ed.; CRC Press, Inc.: , 1974.

(235) Froese, R. D. J.; Humbel, S.; Svensson, M.; Morokuma, K. "IMOMO(G2MS): A New High-Level G2-Like Method for Large Molecules and its Applications to Diels-Alder Reactions", *J. Phys. Chem. A* **1997**, *101*, 227-233.

(236) Gordon, M. S.; Truong, T. N.; Pople, J. A. *Chem. Phys. Lett.* **1986**, 245.

(237) Du, J.; Hessler, J.; Ogren, P. J. "Recombination of Methyl Radicals. 1. New Data between 1175 and 1750 K in the Falloff Region", *J. Phys. Chem.* **1996**, *100*, 974-983.

(238) ASTM “Annaul Book of ASTM Standards, Sections 5 and 11,” American Society for Testing and Materials, 1996.

(239) Thipse, S. S.; Sheng, C.; Booty, M. R.; Magee, R. S.; Bozzelli, J. W. "Chemical Makeup and Physical Characterization of a Synthetic Fuel and Methods of Heat Content Evaluation for Studies on MSW incineration", *Fuel* **2002**, *81*, 211-217.