ABSTRACT

THERMODYNAMIC AND KINETIC ANALYSIS ON
Cl. + RCl <--> Cl$_2$ + R. REACTIONS,
CH$_3$CjO + O$_2$ => PRODUCTS AND CjCHO + O$_2$ => PRODUCTS
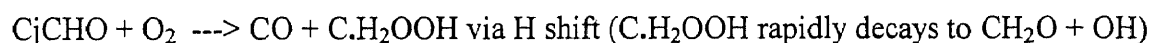
by
Jongwoo Lee

Thermodynamic Parameters, $\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$ and Cp(T) are evaluated for C$_1$ and C$_2$

chlorocarbon molecules and radicals. These thermodynamic properties are used in

evaluation and comparison of R. + Cl$_2$ => R-Cl + Cl. (defined forward direction) reaction

rate constants from the kinetics literature. Data from some 20 reactions in the literature

show linearity on a plot of Ea$_{fwd}$ vs. $\Delta H_{rxn,fwd}$, yielding a slope of (0.38 ± 0.04) and

intercept of (10.10 ± 0.77) kcal/mole. Thermodynamic properties ($\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$ and

Cp(T) from 300 to 1500 K) for reactants, adducts, transition states, and products in

reactions of CH$_3$ and C$_2$H$_5$ with Cl$_2$ are calculated using CBSQ//MP2/6-311G(d,p).

Evaluated thermodynamic property data are presented for all isomers of the stable

molecules CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$, C$_2$H$_5$Cl, C$_2$H$_4$Cl$_2$, C$_2$H$_3$Cl$_3$, C$_2$H$_2$Cl$_4$, C$_2$HCl$_5$,

C$_2$Cl$_6$, C$_2$H$_3$Cl, C$_2$H$_2$Cl$_2$, C$_2$HCl$_3$, and C$_2$Cl$_4$. Evaluated thermodynamic property data are

also presented for the alkyl radicals, (including isomers) C•H$_2$Cl, C•HCl$_2$, C•Cl$_3$,

C$_2$H$_4$Cl•, C$_2$H$_3$Cl$_2$•, C$_2$H$_2$Cl$_3$•, C$_2$HCl$_4$•, and C$_2$Cl$_5$•, for the olefin radicals (including

isomers) C$_2$H$_2$Cl•, C$_2$HCl$_2$•, and C$_2$Cl$_3$•.

Thermodynamic property and chemical kinetic analysis are performed on reactants,

intermediates, transition states and products from reactions of the two radicals resulting

via H atom abstraction from acetaldehyde: CH_3CjO and $CjCHO$ with molecular oxygen. Density functional and *ab initio* calculations are utilized to estimate thermodynamic properties: $\Delta H_f^{\circ}{}_{298}$, $S^{\circ}{}_{298}$, and $Cp^{\circ}(T)$ 300 – 1500K. Rate constants are estimated as a function of temperature and pressure using QRRK analysis for $k(E)$ and modified strong collision analysis for fall-off for application to atmospheric and combustion kinetic modeling.

The important reaction paths are determined as:

$CH_3CjO + O_2$ ---> $CH_2CO + HO_2$ via HO_2 Elimination

$CH_3CjO + O_2$ ---> $CyCOC=O + OH$ via OH Elimination

$CH_3CjO + O_2$ ---> $CCOQj$ (Stabilization)

$CjCHO + O_2$ ---> $CO + C.H_2OOH$ via H shift ($C.H_2OOH$ rapidly decays to $CH_2O + OH$)

$CjCHO + O_2$ ---> $CQjCHO$ (Stabilization)

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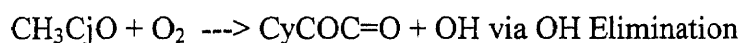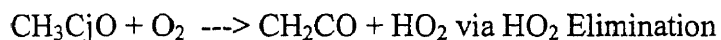
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APPROVAL PAGE

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Lee, J.; Chen, C. J.; Bozzelli, J. W., "Thermochemical and Kinetic Analysis on Acetyl Radicals Reactions with O_2 : CjCHO + O_2 => Products and CCjO + O_2 => Products", Joint Meeting of the United States Sections of the Combustion Institute, Washington D. C., March 14-17, 1999. Oral Presentation.

Bozzelli, J. W.; Lee, J.; Sawerysyn, J. P., " Thermodynamic and Kinetic Analysis on Cl Atom Abstractions of Chlorine from Halocarbons and the Reverse Alkyl Abstractions: Cl. + RCl $\leftrightarrow$ Cl_2 + R. ", Joint Meeting of the United States Sections of the Combustion Institute, Washington D. C., March 14-17, 1999. Poster.

To my beloved family

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PART I

THERMODYNAMIC AND KINETIC ANALYSIS ON Cl ATOM ABSTRACTIONS OF CHLORINE FROM HALOCARBONS AND REVERSE ALKYL ABSTRACTIONS FROM Cl_2 : Cl. + RCl <--> Cl_2 + R.

CHAPTER 1

ABSTRACT FOR PART ONE

Thermodynamic Parameters, $\Delta H^\circ_{f(298)}$, $S^\circ_{(298)}$ and $Cp(T)$ are evaluated for small, C_1 and C_2 chlorocarbon molecules and radicals. These thermodynamic properties are used in evaluation and comparison of $R. + Cl_2 => R\text{-}Cl + Cl.$ (defined forward direction) reaction rate constants from the kinetics literature. Data from some 20 reactions in the literature show linearity on a plot of Ea_{fwd} vs. $\Delta H_{rxn,fwd}$, yielding a slope of (0.38 ± 0.04) and intercept of (10.10 ± 0.77) kcal/mole. A correlation of average Arrhenius pre-exponential factor for $RCl + Cl => R. + Cl_2$ (reverse rxn) of $(4.44 \pm 1.58) \times 10^{13}$ cm^3/mol-sec on a per chlorine basis is obtained with $Ea_{Rev} = (0.64 \pm 0.04) * \Delta H_{rxn,Rev} + (9.70 \pm 0.79)$, where Ea_{Rev} is 0.0 if $\Delta H_{rxn,Rev}$ is more than 15.2 kcal/mole exothermic.

Thermodynamic properties ($\Delta H^\circ_{f(298)}$, $S^\circ_{(298)}$ and $Cp(T)$ from 300 to 1500 K) for reactants, adducts, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2 are calculated using CBSQ//MP2/6-311G(d,p). Molecular structures and vibration frequencies are determined at the MP2/6-311G(d,p), with single point calculations for energy at QCISD(T)/6-311+G(d,p), MP4(SDQ)/CbsB4 and MP2/CBSB3 levels of calculation. Vibration frequencies are scaled by 0.9748 for zero point energies. Contributions of rotational frequencies for $S^\circ_{(298)}$ and $Cp(T)$'s are calculated based on rotational barrier heights and moments of inertia using the method of Pitzer and Gwinn's[1].

CHAPTER 2

INTRODUCTION FOR PART ONE

High chlorinated solvents such as CH_2Cl_2, $CHCl_3$, CCl_4, C_2Cl_4, C_2HCl_3, $C_2H_3Cl_3$'s and

fluoro chloro-carbon solvents or chemicals are in widespread use in the chemical,

pharmaceutical and cleaning industries. The monomers are also present in a number of

valuable and versatile polymers. The combustion, incineration or high temperature

pyrolysis of these chlorocarbons includes reactions at or near surfaces and in liquids or

polymers where oxygen is not present or is low in concentration. Chlorine atom

abstraction of chlorine from the chlorocarbon is often the important chain propagation

process in these systems; yet there is limited or almost no direct experimental kinetic

information on these chlorine atom abstraction reactions. This is a due to the Cl

abstraction of Cl from R-Cl being endothermic, as the Cl-Cl bond is 57.8 kcal/mole,

while a typical R-Cl bond energy ranges from 71 kcal/mole in CCl_4 to 95 or 98 in vinyl

chloride and chlorobenzene, respectively. Most chlorocarbons also have a hydrogen

which is readily abstracted by Cl atoms, where the rate constants have high Arrhenius

pre-exponential factors ($> 10^{13}$) and little or no energies of activation. (ca 1.0 kcal/mole if

thermo neutral or exothermic) Cl abstraction of halogens is also important in designed

pyrolysis and oxidation experiments, where hydrogen is limited or not present. These

chlorocarbon oxidation or pyrolysis with no hydrogen source, are not practical for

incineration; but have value in modeling because the presence of hydrogen adds an order

of magnitude complexity to the models (number of species, and reaction product

3

permutations). Pyrolysis of trichloroethylene, for example, shows extensive molecular weight growth products such as hexachloro-benzene, pentachloro-butadiene, etc which likely result from radical processes.[2] The radical intermediates present in oxidation and pyrolysis of high chlorine to hydrogen ratio thermal processes result from Cl atom elimination, beta scission and from Cl atom abstraction of Cl reactions.

We estimate kinetic data for these $Cl + RCl \Rightarrow Cl_2 + R.$ reactions in this study by assembling and evaluating thermodynamic property data : $\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$, and $Cp(T)$ on chlorocarbon and several fluoro chlorocarbon molecules and radicals. We use the thermochemical properties with available literature data on the abstractions of Cl from Cl_2 by alkyl radicals and microscopic reversibility to evaluate trends in the forward and reverse rate constants.

Thermodynamic properties ($\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$ and $Cp(T)$ from 300 to 1500 K) for reactants, adducts, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2, are determined using CBSQ//MP2/6-311G(d,p) *ab initio* calculations and kinetic predictions compared with evaluated data.

CHAPTER 3

METHOD FOR PART ONE

3.1 Thermodynamic Properties

Evaluated thermodynamic parameters : $\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$, and Cp(300) to Cp(1500) for

species in the reaction schemes are listed in Table 1.2 along with literature references.

Some enthalpies of chlorocarbon (C_1 and C_2) radicals are from literature data and

calculations using isodesmic reactions: for example $C.H_2CH_2Cl$ is from a calculated

$\Delta Hrxn$ for $(CH_3CH_3 + C.H_2CH_2Cl \Longrightarrow CH_3CH_2Cl + C.H_2CH_3$) and the known

$\Delta H^{\circ}_{f(298)}$ for ethane, chloroethane and ethyl radical. Entropies and Cp(T) values of C_2H_3,

C_2H_5 are from use of Hydrogen Bond Increment(HBI)[3] method. 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 an H atom. The HBI

incorporates changes in radical formation, that result from loss or changes in vibrational

frequencies, internal rotations, spin degeneracy and mass.

3.2 Thermodynamic Analysis for the Reactions

Arrhenius pre exponential factors on a per chlorine basis, energies of activation and

enthalpies of reaction, A_{Rev}, $A_{Rev}/Cl\#$, Ea_{Rev} and $\Delta H^{\circ}_{rxn,fwd}$ are calculated using literature

reference data on the forward reactions Af and Eaf , the evaluated thermodynamic

properties of reactants and products, and microscopic reversibility. Forward reaction

direction is defined as R. $+ Cl_2 => R-Cl + Cl.$. C_3H_5, allyl radical and C_3H_3, propargyl

radical have resonant structures each having two radical sites with near equal population at temperature of the experimental data, 500-700K. (Ref. 4 in Table 1.1) We assess these radical reactions with Cl_2 as occurring via both radical sites, and estimate similar rates. The experimental rate constant for the forward direction is multiplied by 0.5 to obtain the forward rate constant on a per radical site basis.

3.3 *Ab initio* Calculations on CH_3 and C_2H_5 Plus Cl_2 Reaction Systems

Thermodynamic properties ($\Delta H^\circ_{f(298)}$, $S^\circ_{(298)}$ and $Cp(T)$ from 300 to 1500 K) for reactants, adduct intermediates, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2 are calculated using the established CBSQ//MP2/6-311G(d,p) composite method of Petersson's research group[4-6]. The CBSQ calculation sequence is performed on the MP2/6-311G(d,p) geometry and followed by single point calculations at the theory level of QCISD(T)/6-311+G(d,p), MP4(SDQ)/CbsB4 and MP2/CBSB3 CBSExtrap=(Nmin=10,Pop).

3.4 Determination of Enthalpies of Formation ($\Delta H^\circ_{f(298)}$)

$\Delta H^\circ_{f(298)}$ for reactants and products in reactions of CH_3 and C_2H_5 with Cl_2 are from literature data (see Table 1.2). $\Delta H^\circ_{f(298)}$ for transition states and adducts in reactions of CH_3 and C_2H_5 with Cl_2 are calculated using total energies obtained by CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p) level. Total energies are corrected by zero point vibrational energies (ZPVE) which are scaled by 0.9748 as recommended by Scott et al.[7]. Thermal correction 0 K to 298.15 K is calculated to estimate $\Delta H^\circ_{f(298)}$ at 298.15 K.[8]

3.5 Determination of Entropy ($S^{o}_{(298)}$) and Heat Capacities (Cp(T)'s, $300 \leq T/K \leq 1500$)

$S^{o}_{(298)}$ and Cp(T)'s for reactants and products in reactions of CH_3 and C_2H_5 with Cl_2 are from literature data (see Table 1.2). $S^{o}_{(298)}$ and Cp(T)'s for transition states and adducts in reactions of CH_3 and C_2H_5 with Cl_2 are calculated based on vibration frequencies and moments of inertia of the optimized MP2/6-311G(d,p) structures. Contributions of internal rotation for $S^{o}_{(298)}$ and Cp(T)'s are calculated based on rotational barrier heights, moments of inertia of the rotors, and Pitzer and Gwinn's[1] general treatment.

CHAPTER 4

RESULT AND DISCUSSION FOR PART ONE

4.1 Cl + RCl <=> Cl2 + R. Reaction

4.1.1 Overall

Data for the 20 reference reactions are listed in Table 1.1. The average A_{fwd} for reaction

R. + Cl_2 => R-Cl + Cl (defined forward direction) is

A_{fwd} = (2.35 ± 3.07) x 10^{12} cm^3/mole-sec and

Ea_{fwd} = (0.38 ± 0.04) * $\Delta H_{rxn,fwd}$ + (10.10 ± 0.77) kcal/mole.

Figure 1.1 shows the data and the correlation with several exclusions noted. A correlation

for the average Arrhenius pre-exponential factor for RCl + Cl => R. + Cl_2 (reverse rxn) of

A_{rev} = (4.44 ± 1.58) x 10^{13} cm^3/mol-sec on a per chlorine basis is obtained with

Ea_{Rev} = (0.64 ± 0.04) * $\Delta H_{rxn,Rev}$ + (9.70 ± 0.79),

where Ea_{Rev} is 0.0 if ΔH_{rxnRev} is more than 15.2 kcal/mole exothermic.

4.1.2 Hydrocarbons

Reactions involving only hydrocarbons are selected and data are listed in Table 1.1 and

shown in Figure 1.2. Data for CH_3, C_2H_5, C_3H_5 and C_3H_3 (Isopropyl, tertiary butyl and

C_2H_3 radicals are excluded.) show a slope leading to

Ea_{fwd} = (0.39 ± 0.11) * $\Delta H_{rxn,fwd}$ + (10.49 ± 2.21) kcal/mole and

Average A_{fwd} = (5.89 ± 2.48) x 10^{12} cm^3/mole-sec.

Table 1.1 Cl_2 + Radicals ------> Products + Cl

REACTIONS		A_{fwd}*	Ea_{fwd}*	A_{Rev}**	$A_{Rev}/Cl\#$	Ea_{Rev}**	$\Delta H°_{rxn,fwd}$**	P(torr)	T (K)	Reference*
\<HYDROCARBONS\>										
1. Cl_2 + CH_3	----> CH_3Cl + Cl	3.02E+12	0.53	2.99E+13	2.99E+13	26.10	-25.50	1.9-2.8	296-712	9
2. Cl_2 + C_2H_5	----> C_2H_5Cl + Cl	7.59E+12	-0.30	8.51E+13	8.51E+13	26.66	-27.18	1.7-2.2	295-498	9
3. Cl_2 + i-C_3H_7***	----> i-C_3H_7Cl + Cl	1.51E+13	-0.48	1.03E+15	1.03E+15	25.82	-26.80	1.4-1.9	295-498	9
4. Cl_2 + t-C_4H_9***	----> t-C_4H_9Cl + Cl	2.40E+13	-0.01	4.04E+15	4.04E+15	26.37	-27.11	1.4-1.8	295-498	9
5. Cl_2 + C_2H_3	----> CH_2CHCl + Cl	5.25E+12	-0.48	4.49E+13	4.49E+13	37.10	-37.72	1.4-1.7	298-435	10
6. Cl_2 + C_3H_5	----> C_3H_5Cl + Cl	4.67E+12	4.30	1.58E+13	1.58E+13	16.52	-12.29	2.0-3.6	487-693	10
7. Cl_2 + C_3H_3	----> C_3H_3Cl + Cl	8.30E+12	6.70	7.00E+13	7.00E+13	20.01	-13.49	2.6-4.1	525-693	10
(Avg.)		9.70E+12			7.59E+14	(not recommended)				
If i-C_3H_7, t-C_4H_9, C_2H_3 are excluded, (Avg.)		(5.89 +/- 2.48)E+12			(5.02 +/- 3.27)E+13					
\<C_1 CHLOROCARBONS\>										
8. Cl_2 + CH_2Cl	----> CH_2Cl_2 + Cl	9.10E+11	0.98	4.83E+13	2.42E+13	22.87	-21.90	1.7-4.3	295-719	11
9. Cl_2 + $CHCl_2$	----> $CHCl_3$ + Cl	5.18E+11	2.46	1.30E+14	4.34E+13	21.09	-18.78	1.8-4.6	357-719	11
10. Cl_2 + CCl_3	----> CCl_4 + Cl	4.08E+11	5.26	6.00E+13	1.50E+13	17.91	-13.02	3.1	690-700	12
11. Cl_2 + CF_3	----> CF_3Cl + Cl	2.69E+12	3.60	1.83E+14	1.83E+14	30.55	-27.27	2.3-2.6	487-693	12
12. Cl_2 + CF_2Cl	----> CF_2Cl_2 + Cl	7.76E+11	1.91	6.89E+13	3.44E+13	24.13	-22.56	1.8-2.9	376-626	12
13. Cl_2 + $CFCl_2$	----> $CFCl_3$ + Cl	8.32E+11	3.35	4.74E+13	1.58E+13	20.12	-17.18	1.5-2.6	435-693	12
(Avg.)		1.02E+12			5.26E+13	(not recommended)				
If CF_3 is excluded, (Avg.)		(6.89 +/- 2.15)E+11			(2.66 +/- 1.22)E+13					
\<C_2 CHLOROCARBONS\>										
14. Cl_2 + C_2Cl_5	----> C_2Cl_6 + Cl	2.00E+11	5.50	2.17E+14	3.61E+13	19.04	-13.94	50	298-423	13
15. Cl_2 + $CHCl_2CHCl$	----> $(CHCl_2)_2$ + Cl	6.31E+11	2.70	4.92E+14	1.23E+14	21.39	-18.83	50	298-423	13
16. Cl_2 + CH_2ClCCl_2	----> CH_2ClCCl_3 + Cl	6.92E+11	4.10	4.29E+14	1.07E+14	18.49	-14.66	50-300	298-321	14
17. Cl_2 + $CH_2ClCHCl$	----> $CH_2ClCHCl_2$ + Cl	2.00E+12	2.00	1.05E+15	3.49E+14	22.47	-20.61	80-280	298-328	15-(1)
18. Cl_2 + $CHCl_2CH_2$	----> $CH_2ClCHCl_2$ + Cl	6.31E+11	0.90	5.37E+13	1.79E+13	27.09	-26.19	50	298-423	13
19. Cl_2 + CCl_3CHCl	----> $CHCl_2CCl_3$ + Cl	3.16E+11	5.10	7.96E+13	1.59E+13	21.61	-16.47	50	298-423	13
20. Cl_2 + $CHCl_2CCl_2$	----> $CHCl_2CCl_3$ + Cl	3.16E+11	5.10	1.96E+14	3.91E+13	16.88	-12.01	50	298-423	13
(Avg.)		6.84E+11			9.83E+13	(not recommended)				
If $CH_2ClCHCl$ is excluded, (Avg.)		(4.64 +/- 2.10)E+11			(5.65 +/- 4.65)E+13					

TOTALS							
(TOTAL Avg.)	3.80E+12			3.03E+14	(not recommended)		
If i-C_3H_7, t-C_4H_9, C_2H_3, CF_3, $CH_2ClCHCl$ are excluded, (Avg.)	(2.35 +/- 3.07)E+12			(4.44 +/- 1.58)E+13			

UNITS :: A_{fwd} and A_{Rev} : cm^3/(mole-sec)

Ea and $\Delta H°_{rxn,fwd}$: kcal/mole

A_{fwd} = (2.35 +/- 3.07)*10^{12} cm^3/(mole-sec)

A_{Rev}(avg)/cl = (4.44 +/- 1.58)*10^{13} cm^3/(mole-sec)

(i-C_3H_7, t-C_4H_9, C_2H_3, CF_3, $CH_2ClCHCl$ are excluded in calc.of A_{fwd} and A_{Rev}(avg)/cl.)

* : references for A_{fwd} and Ea_{fwd}

** : calculated from Thermodynamic Properties of reactants and products
  - microscopic reversibility -

*** : i-C_3H_7, t-C_4H_9 Symmetries = 162 & 18 respectively

Table 1.2 Evaluated Thermodynamic Property Data

SPECIES	Hf(298)	S(298)	Cp300	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500	REF(a)
CH3	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29	JANAF(16)
TSCH3XCl2	32.10	74.11	15.86	17.27	18.43	19.42	21.06	22.41	24.82	CBSQ(in this study)
CH3Cl	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	TRC(17)
C2H5	29.30	57.42	11.89	14.57	16.95	19.09	22.76	25.66		LAY/BOZ95(3)
TSC2H5XCl2	24.20	84.10	19.94	22.96	25.60	27.84	31.46	34.25	38.82	CBSQ(in this study)
C2H5Cl	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	JANAF(16)
i-C3H7	21.02	70.39	16.58	20.27	24.03	27.49	33.13	37.52	44.37	LAY/BOZ95(3)
i-C3H7Cl	-34.70	73.41	20.85	25.88	30.48	34.34	40.33	44.92		WONG/BOZ(26)
t-C4H9	11.90	75.67	22.33	27.04	31.82	36.27	43.62	49.34	58.53	LAY/BOZ95(3)
t-C4H9Cl	-44.13	76.42	26.66	33.67	39.89	45.02	52.53	57.84		WONG/BOZ(26)
C2H3	71.64	53.79	10.10	11.93	13.57	14.97	17.22	18.95		LAY/BOZ95(3)
CH2CHCl	5.00	63.08	12.89	15.56	17.80	19.61	22.35	24.35		LI/BOZ98(22)
C3H5	40.75	62.05	14.87	18.66	21.88	24.63	28.95	32.10	36.78	LAY/BOZ95(3)
C3H5Cl	-0.46	73.31	18.14	22.12	25.51	28.40	32.94	36.28	41.45	SWS(20)
C3H3	81.58	59.57	13.76	16.10	18.10	19.80	22.48	24.43	27.31	LAY/BOZ95(3)
C3H3Cl	39.17	68.78	17.26	20.10	22.45	24.39	27.33	29.42	32.62	TRC(17)
CH2Cl	27.99	58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.30	TAY/DEL91(18)
CH2Cl2	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	JANAF(16)
CHCl2	23.50	68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	KAFAFI89(freq.)(19)
CHCl3	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		SWS(20)
CCl3	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	JANAF(16)
CCl4	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	JANAF(16)
CF3	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	JANAF(16)
CF3Cl	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	JANAF(16)
CF2Cl	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	RAYEZ94(21)
CF2Cl2	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	JANAF(16)
CFCl2	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	RAYEZ94(21)
CFCl3	-67.70	74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	TRC(17)
C2Cl5	9.06	95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	TRC(17)
C2Cl6	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11		SWS(20)
CHCl2CHCl	11.75	84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08	TRC(17)
C2H2Cl4	-36.00	84.86	23.74	27.67	30.65	32.89	35.99	38.01	40.66	TRC(17)
CH2ClCCl2	7.87	84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77	TRC(17)
CH2ClCCl3	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70	TRC(17)
CH2ClCHCl	14.73	78.56	18.33	21.15	23.40	25.19	27.82	29.73	32.70	TRC(17)
CH2ClCHCl2	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	TRC(17)
CHCl2CH2	20.31	74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	TRC(17)
CCl3CHCl	10.59	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25	TRC(17)
CHCl2CCl3	-34.80	91.18	28.30	31.96	34.52	36.34	38.64	40.17	41.99	TRC(17)
CHCl2CCl2	6.13	90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89	TRC(17)

UNITS : Hf(kcal/mol), S(cal/K*mol), Cp(cal/K*mol) (a) : reference for Cp(T) and S only

$Cl_2 + R. \longrightarrow RCl + Cl$

	R.	$\Delta H^\circ_{rxn,fwd}$	Ea_{fwd}	Reference
1	CH_3	-25.50	0.53	JANAF(16)
2	C_2H_5	-27.18	-0.30	CIO/LIU97(23)
3	$i-C_3H_7$	-26.80	-0.48	LAY/BOZ95(3)
4	$t-C_4H_9$	-27.11	-0.01	LAY/BOZ95(3)
5	C_2H_3	-37.32	-0.48	LAY/BOZ95(3)
6	C_3H_5	-12.29	4.30	LAY/BOZ95(3)
7	C_3H_3	-13.49	6.70	LAY/BOZ95(3)
8	CH_2Cl	-21.90	0.98	Seet98(24)
9	$CHCl_2$	-18.78	2.46	ROUX/PAD87(25)
10	CCl_3	-13.02	5.26	JANAF(16)
11	CF_3	-27.27	3.60	JANAF(16)
12	CF_2Cl	-22.56	1.91	RAYEZ94(21)
13	$CFCl_2$	-17.18	3.35	RAYEZ94(21)
14	C_2Cl_5	-13.94	5.50	CIO/LIU97(23)
15	$CHCl_2CHCl$	-18.83	2.70	CIO/LIU97(23)
16	CH_2ClCCl_2	-14.66	4.10	CIO/LIU97(23)
17	$CH_2ClCHCl$	-20.61	2.00	CIO/LIU97(23)
18	$CHCl_2CH_2$	-26.19	0.90	CIO/LIU97(23)
19	CCl_3CHCl	-16.47	5.10	CIO/LIU97(23)
20	$CHCl_2CCl_2$	-12.01	5.10	CIO/LIU97(23)

$Ea_{fwd}(R.+ Cl_2 \rightarrow RCl + Cl.) = (0.38 +/- 0.04) \Delta H^\circ_{rxn,fwd} + (10.10 +/- 0.77)$

$Ea_{Rev}(RCl + Cl. \rightarrow R. + Cl_2) = (0.64 +/- 0.04) \Delta H^\circ_{rxn,Rev} + (9.70 +/- 0.79)$

  if $\Delta H^\circ_{rxn,Rev} <= -15.16$ $Ea_{Rev} = 0.0$

(* : $i-C_3H_7$, $t-C_4H_9$, C_2H_3, CF_3, $CH_2ClCHCl$ are excluded.)
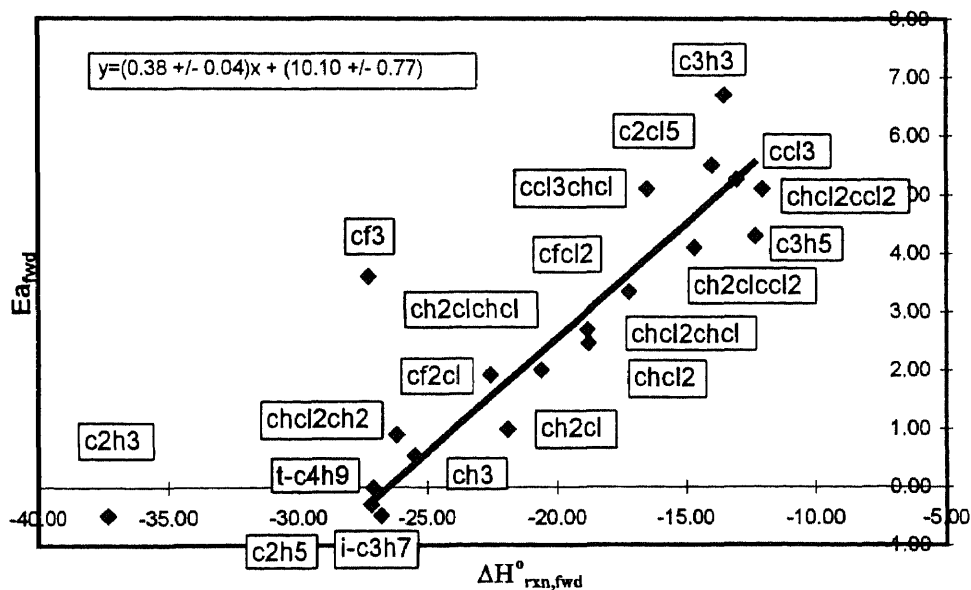
Figure 1.1 Ea_{fwd} vs $\Delta H^\circ_{rxn,fwd}$

R.	$\Delta H^{\circ}_{rxn,fwd}$	Ea_{fwd}
1 CH3	-25.50	0.53
2 C2H5	-27.18	-0.30
3 i-C3H7	-26.80	-0.48
4 t-C4H9	-27.11	-0.01
5 C2H3	-37.32	-0.48
6 C3H5	-12.29	4.30
7 C3H3	-13.49	6.70

$$Cl_2 + R. \ \text{--------} > RCl + Cl$$
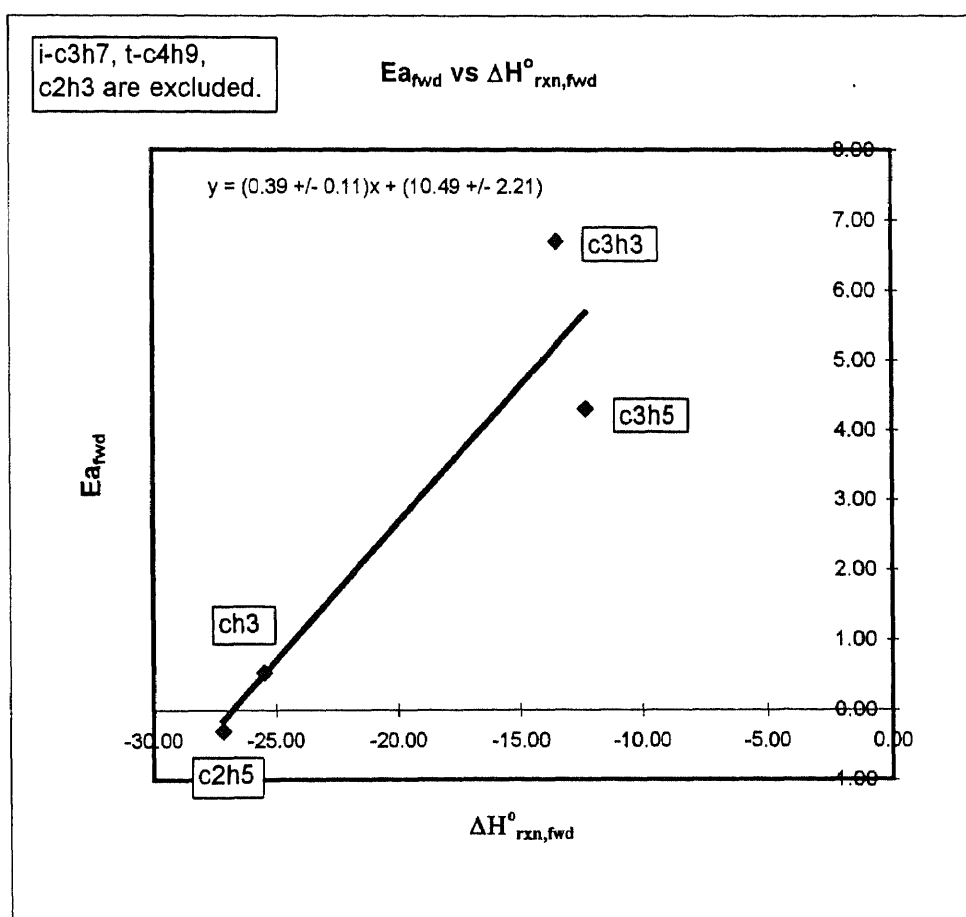
Figure 1.2 Hydrocarbons

Tertiary butyl, isopropyl and ethyl radicals show slightly negative Ea's for the forward

reactions. This may suggest adduct formation occurs before further reaction to $RCl + Cl$

products. The tertiary butyl and isopropyl radical reactions with Cl_2 are unusual. The

literature values of Arrhenius pre-exponential factor show values of 1.5 and 2.4 x 10^{13}

cm^3/mol-sec respectively. Thermodynamic analysis of the reaction systems lead to

calculated pre-exponential factors for reverse reaction of 1 x 10^{15} and 4 x 10^{15} cm^3/mol-

sec respectively; Approximately 2.5 to 10 times higher than the estimated collision rate at

300K. We have re-evaluated the thermodynamic properties of species in these reactions

and do not find errors in entropy terms that can account for the unreasonably large

reverse rate constants that are calculated. We choose to omit these reactions from our

analysis.

4.1.3 C_1 Chlorocarbons

Data for C_1 chlorocarbons are shown in Table 1.1 and Figure 1.3. Data for CH_2Cl,

$CHCl_2$, CCl_3, CF_2Cl and $CFCl_2$ yield a slope leading to

$Ea_{fwd} = (0.40 \pm 0.07) * \Delta H_{rxn,fwd} + (10.32 \pm 1.31)$ kcal/mole and

Average $A_{fwd} = (6.89 \pm 2.15)$ x 10^{11} cm^3/mole-sec.

The CF_3 value is considered on outlier and is excluded.

4.1.4 C_2 Chlorocarbons

Data for C_2 chlorocarbons are shown in Table 1.1 and Figure 1.4. Data for C_2Cl_5,

$CHCl_2CHCl$, CH_2ClCCl_2, $CHCl_2CH_2$, CCl_3CHCl and $CHCl_2CCl_2$ show a slope resulting

in $Ea_{fwd} = (0.33 \pm 0.07) * \Delta H_{rxn,fwd} + (9.46 \pm 1.17)$ kcal/mole and

R.	$\Delta H^\circ_{rxn,fwd}$	Ea_{fwd}
8 CH2Cl	-21.90	0.98
9 CHCl2	-18.78	2.46
10 CCl3	-13.02	5.26
11 CF3	-27.27	3.58
12 CF2Cl	-22.56	1.91
13 CFCl2	-17.18	3.35

$$Cl_2 + R. \ \text{--------} \!\!> RCl + Cl$$
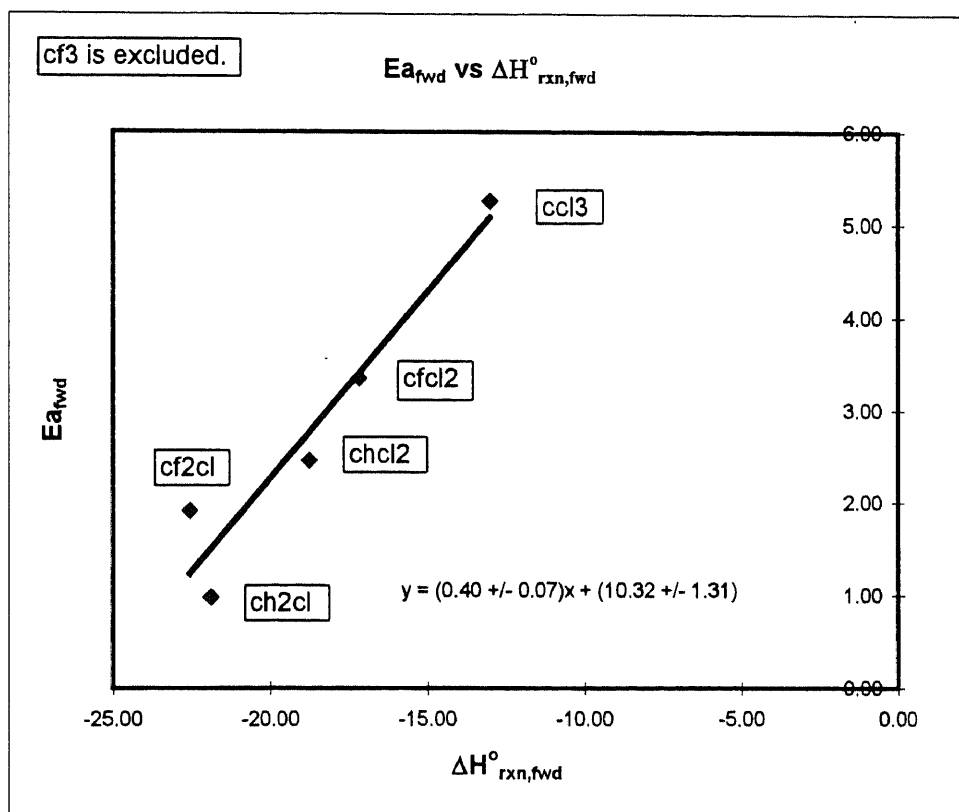
Figure 1.3 C_1 Chlorocarbons

R.	$\Delta H^{\circ}_{rxn,fwd}$	Ea_{fwd}
14 C2Cl5	-13.94	5.50
15 CHCl2CHCl	-18.83	2.70
16 CH2ClCCl2	-14.66	4.10
17 CH2ClCHCl	-20.61	2.00
18 CHCl2CH2	-26.19	0.90
19 CCl3CHCl	-16.47	5.10
20 CHCl2CCl2	-12.01	5.10

$$Cl_2 + R. \ \text{--------}> RCl + Cl$$

ch2clchcl is excluded.

Ea_{fwd} vs $\Delta H^{\circ}_{rxn,fwd}$

$y = (0.33 +/- 0.07)x + (9.46 +/- 1.17)$
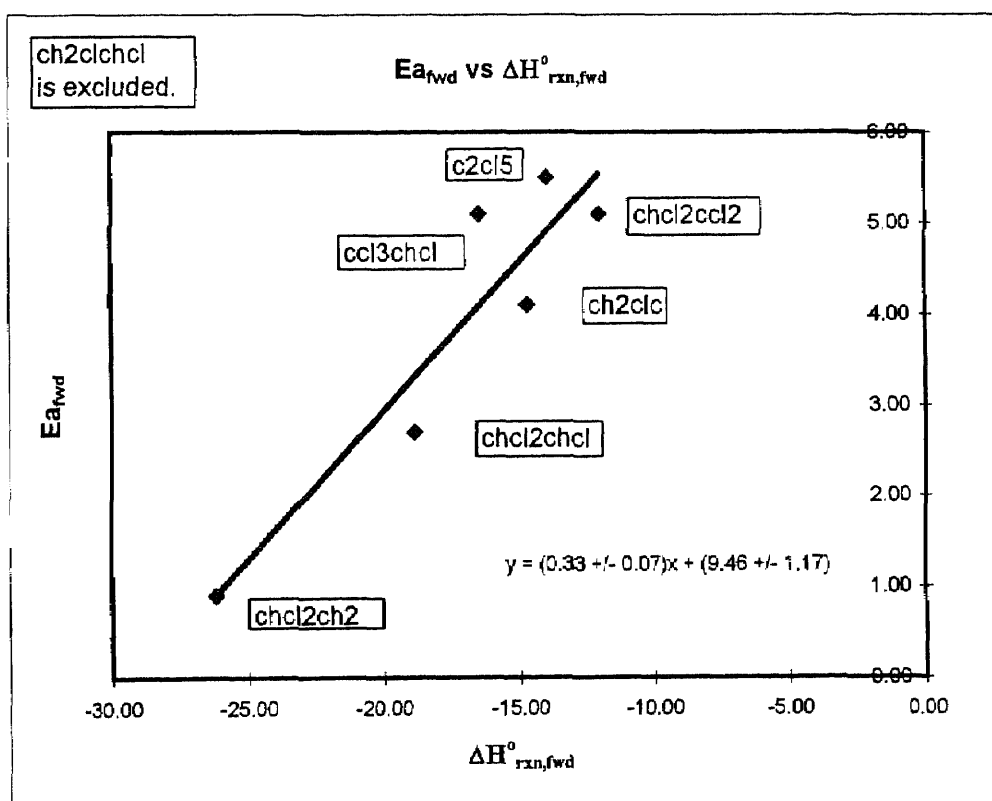
Figure 1.4 C_2 Chlorocarbons

Average A_{fwd} = (4.64 ± 2.10) x 10^{11} cm^3/mole-sec.

The $CH_2ClCHCl$ value is considered on outlier and is excluded.

Ea's for these reactions are determined by thermochemical analysis of experimental and theoretical data in the literature references (see Table 1.2).

4.1.5 Kinetic Trends

The more exothermic R + Cl_2 reactions (ΔH_{fwd}^{298} < -20 kcal/mole) are those which involve hydrocarbon free radicals; these are shown to have small activation energies (less than 1 kcal/mole) in Table 1.1. The calculated transition states in CH_3 and C_2H_5 reaction with Cl_2 in Table 1.1, have enthalpy values which are –2.7 and –5.1 kcal/mole relative to the reactants (at the CBSQ composite level), respectively, in these exothermic R + Cl_2 reactions. (Figure 1.5)

Timonen et al.[10] studied the kinetics of the reactions of unsaturated hydrocarbon free radicals (vinyl, allyl, and propargyl) with molecular chlorine. They report the reactivities of C_3H_3 and C_3H_5 are significantly reduced below that of the vinyl radical in these Cl atom transfer reactions, and suggest the reduction is due entirely to the presence of energy barriers in reactions C_3H_3 and C_3H_5. The Arrhenius preexponential factors of reactions C_2H_3, C_3H_3 and C_3H_5 are all similar. They indicate that the relatively low exothermicities of reactions C_3H_3 and C_3H_5 (ΔH_{fwd}^{298} = -13.5 and -12.3 kcal/mole, respectively) could account for the existence of the observed 4.3 - 6.7 kcal/mole activation energies.

Seetula[27] shows a linear correlation in a plot of the rate constants for R + Cl_2 reactions at 500K vs. Δelectronegativity of the radical species R. He suggests this results from a

a) $Cl_2 + CH_3 \longleftrightarrow CH_3Cl + Cl$

34.82 $Cl_2 + CH_3$

$TSCH_3XCl_2$ CBSQ (32.09)

MP2 **(37.22)**

3.94
(MP2)

2.73
(CBSQ)

CH_3-ClCl

CBSQ(33.37)

MP2 **(33.28)**

25.59
(CBSQ)

CH_3Cl-Cl $CH_3Cl + Cl$ CBSQ(8.83)

CBSQ(6.50)

2.33
(CBSQ)

b) $Cl_2 + C_2H_5 \longleftrightarrow C_2H_5Cl + Cl$

29.30 $Cl_2 + C_2H_5$

$TSC_2H_5XCl_2$ CBSQ (24.23)

MP2 **(27.57)**

1.75(MP2)

5.10
(CBSQ)

CC-ClCl

CBSQ(26.8)

24.78
(CBSQ)

MP2 **(26.42)**

CCCl-Cl $C_2H_5Cl + Cl$ CBSQ(1.77)

CBSQ(-0.55)

2.31
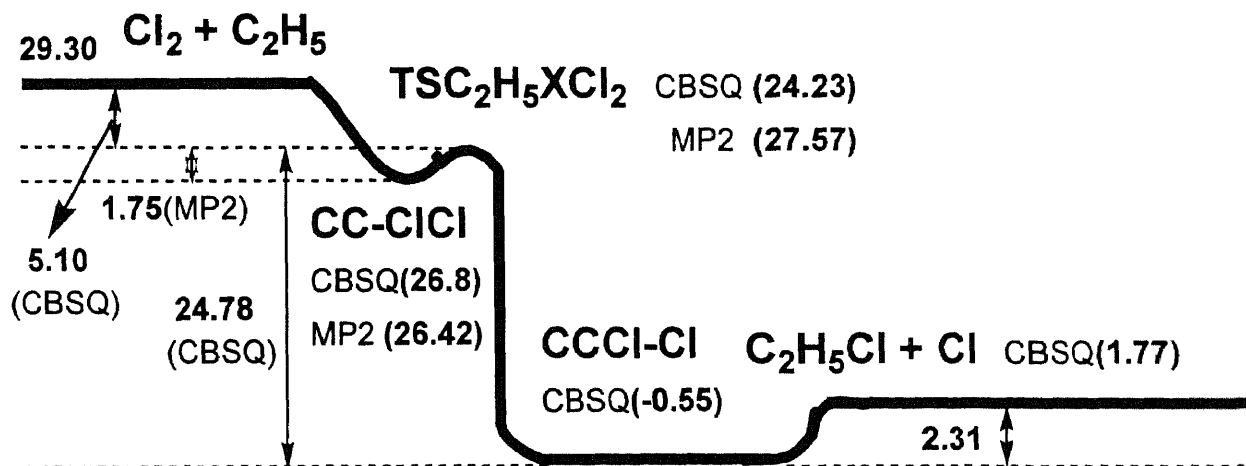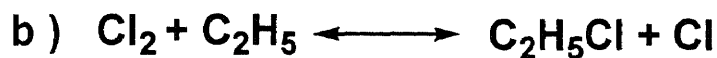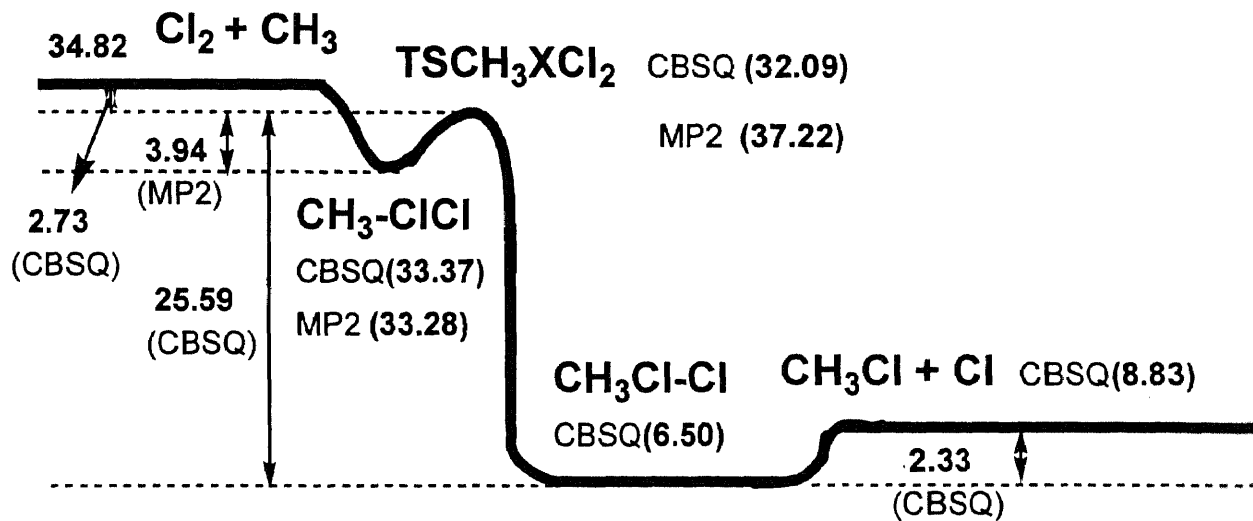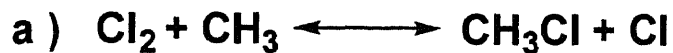
Figure1.5 Reaction path diagrams in CH_3 with Cl_2 and
C_2H_5 with Cl2

polar transition state, which involves intramolecular electronic repulsion or attraction

forces in R. and that these forces determine properties such as stability. They are driving

forces behind reactivity of the radical. He suggests that an electronegative substituent at

the radical site improves thermal stability of the radical and makes it less reactive by

inductive effects.[28,29] He also suggests that similar intramolecular electron delocalization

forces act at the transition state of this radical reaction. Seetula concludes the trend in

reactivity among R + Cl_2 reactions is due primarily to changes in the activation energies

(which are related to the free energies of activation) for these reactions. This Ea_{fwd} vs

$\Delta H_{rxn,fwd}$ trend is illustrated by our data in Figures 1.1 to 1.4. Table 1.3 shows the

presence of Cl on the carbon of the radical site reduces bond energy of new R-Cl bonds

being formed.

Table 1.3 Cl_2 + Radicals ------> Products + Cl (C-Cl bond energy)

REACTIONS	ΔHf^{298}	C--Cl bond energy
1. $Cl_2 + CH_3$ -----> $CH_3Cl + Cl$	-25.50	83.34
8. $Cl_2 + CH_2Cl$ -----> $CH_2Cl_2 + Cl$	-21.90	79.74
9. $Cl_2 + CHCl_2$ -----> $CHCl_3 + Cl$	-18.78	76.62
10. $Cl_2 + CCl_3$ -----> $CCl_4 + Cl$	-13.02	70.86
11. $Cl_2 + CF_3$ -----> $CF_3Cl + Cl$	-27.27	85.11
12. $Cl_2 + CF_2Cl$ -----> $CF_2Cl_2 + Cl$	-22.56	80.40
13. $Cl_2 + CFCl_2$ -----> $CFCl_3 + Cl$	-17.18	75.02

UNITS :: ΔHf^{298} and bond energy : kcal/mole

4.2 *Ab initio* Calculations in Reactions of CH$_3$ and C$_2$H$_5$ with Cl$_2$

4.2.1 Results from *Ab initio* Calculations of Thermodynamic Properties in Reactions of CH$_3$ and C$_2$H$_5$ with Cl$_2$

CH$_3$ + Cl$_2$ ---> CH$_3$Cl + Cl   Reaction
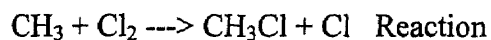
CH$_3$ + Cl$_2$ forms an initial CH$_3$-ClCl adduct which has a shallow well 1.45 kcal/mole

below that of the reactants (CBSQ//MP2/6-311G(d,p) level) with C-Cl bond length of

3.10Å and Cl-Cl bond length of 2.04Å. The Cl-Cl bond in this adduct is 0.01Å longer

than calculated for Cl$_2$. This CH$_3$-ClCl adduct reacts to the Transition State (TS) which is

4 kcal/mole above the adduct at the MP2/6-311G(d,p) level, but not higher in energy at

the CBSQ level of calculation. The C-Cl bond length is 0.77Å shorter and the Cl-Cl bond

is 0.06Å longer in the TS than in the CH$_3$-ClCl adduct. The carbon-Cl bond is forming

and the Cl-Cl bond is breaking. The TS has a 9.12 cal/mol-K lower S°$_{(298)}$ than the CH$_3$-

ClCl adduct. The TS then goes to a CH$_3$Cl-Cl adduct which has a 25.59 kcal/mole well

(CBSQ) with the C-Cl bond length 0.55Å shorter and the Cl-Cl bond length 1.20Å longer

than in the TS. The CH$_3$Cl-Cl has a 6.34 cal/mol-K higher S°$_{(298)}$ than the TS structure.

The CH$_3$Cl-Cl adduct dissociates to CH$_3$Cl + Cl with a low barrier of 2.33 kcal/mole.

C$_2$H$_5$ + Cl$_2$ ---> C$_2$H$_5$Cl + Cl   Reaction
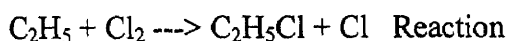
C$_2$H$_5$ + Cl$_2$ forms an initial adduct CC-ClCl which also has a shallow well, about 2.5

kcal/mole below that of the reactants at the CBSQ//MP2/6-311G(d,p) level, with C-Cl

bond length of 2.85Å and Cl-Cl bond length of 2.04Å. The Cl-Cl bond in this adduct is

0.01Å longer than calculated for Cl$_2$. This CC-ClCl adduct reacts to the TS which is 1.15

kcal/mole higher in energy at the MP2/6-311G(d,p) level, but not higher in energy at the

CBSQ level of calculation. (see Figure 1.6) The C-Cl bond length is 0.45Å shorter and

the Cl-Cl bond is 0.04Å longer in the TS than in the CC-ClCl adduct. The TS has a 3.37

cal/mol-K lower $S^o_{(298)}$ than the CH_3-ClCl adduct. The TS goes to the CCCl-Cl which has a well of 24.78 kcal/mole at the CBSQ level where the C-Cl bond length is 0.61Å shorter and the Cl-Cl bond is 1.17Å longer than in the TS. The CCCl-Cl adduct has a 2.06 cal/mol-K higher $S^o_{(298)}$ than the TS structure. The CCCl-Cl adduct dissociates to products of C_2H_5Cl + Cl with low barrier of 2.31 kcal/mole.

4.2.2 Geometries of Transition States

Structures of the adducts and transition states in CH_3 and C_2H_5 with Cl_2 are shown in Figure 1.6. The bond lengths of CH_3---Cl_2 and C_2H_5 ---Cl_2 in the transition state structures are 2.330 and 2.402, respectively. The bond length of C_2H_5 ---Cl_2 is 0.17Å longer than that of CH_3---Cl_2. The C-Cl bond lengths of 2.33 and 2.40 are calculated to be longer than the Cl-Cl bond lengths of 2.10 and 2.08 in $TSCH_3XCl_2$ and $TSC_2H_5XCl_2$, respectively. The C-Cl-Cl angles in $TSCH_3XCl_2$ and $TSC_2H_5XCl_2$ are 180.0 and 177.3, respectively. Figures 1.8a shows changes in bond lengths from CH_3 + Cl_2 to CH_3Cl + Cl via CH_3-ClCl, $TSCH_3XCl_2$ and CH_3Cl-Cl. Table 1.4 lists vibrational frequencies of adducts and transition states in MP2/6-311G(d,p).

The two transition states each have one imaginary frequency. Table 1.5 lists moments of inertia of adducts and transition states from MP2/6-311G(d,p) level calculations.

	Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0797040				
C1-H3	1.0797040	H3-C1-H2	119.859270		
C1-H4	1.0797040	H4-C1-H2	119.859270	H4-C1-H2-H3	-172.533729
C1-Cl5	3.0975079	Cl5-C1-H2	93.733141	Cl5-C1-H2-H3	92.158888
Cl5-Cl6	2.0349651	Cl6-Cl5-C1	179.999899	Cl6-Cl5-C1-H2	-179.459202
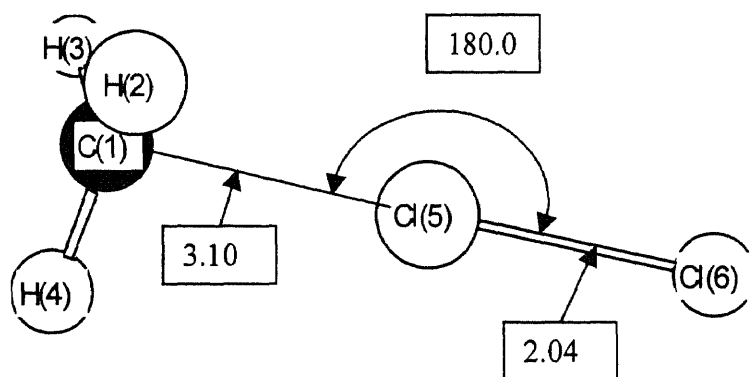
(a) CH₃-ClCl

Figure 1.6a Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CH₃-ClCl)

	Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0817521				
C1-H3	1.0817521	H3-C1-H2	118.024009		
C1-H4	1.0817521	H4-C1-H2	118.024003	H4-C1-H2-H3	-152.403027
C1-Cl5	2.3301785	Cl5-C1-H2	98.151660	Cl5-C1-H2-H3	103.798497
Cl5-Cl6	2.0978717	Cl6-Cl5-C1	179.999742	Cl6-Cl5-C1-H2	-179.009882
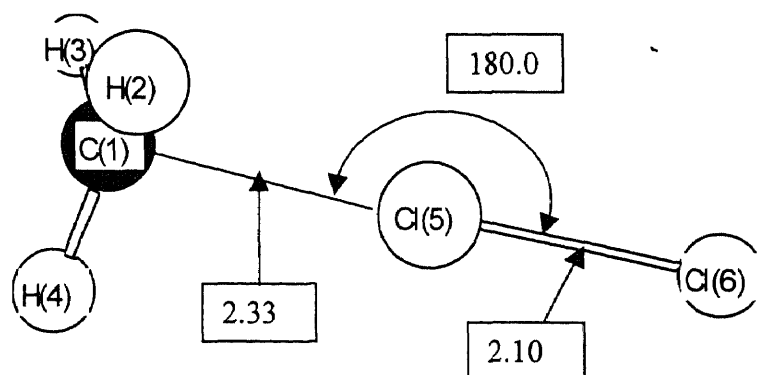
(b) TSCH₃XCl₂

Figure 1.6b Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory.(TSCH₃XCl₂)

	Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0878704				
C1-H3	1.0878704	H3-C1-H2	110.205132		
C1-H4	1.0878704	H4-C1-H2	110.205141	H4-C1-H2-H3	-121.641201
C1-Cl5	1.7786100	Cl5-C1-H2	108.678680	Cl5-C1-H2-H3	119.179376
Cl5-Cl6	3.3008227	Cl6-Cl5-C1	89.068799	Cl6-Cl5-C1-H2	179.951884
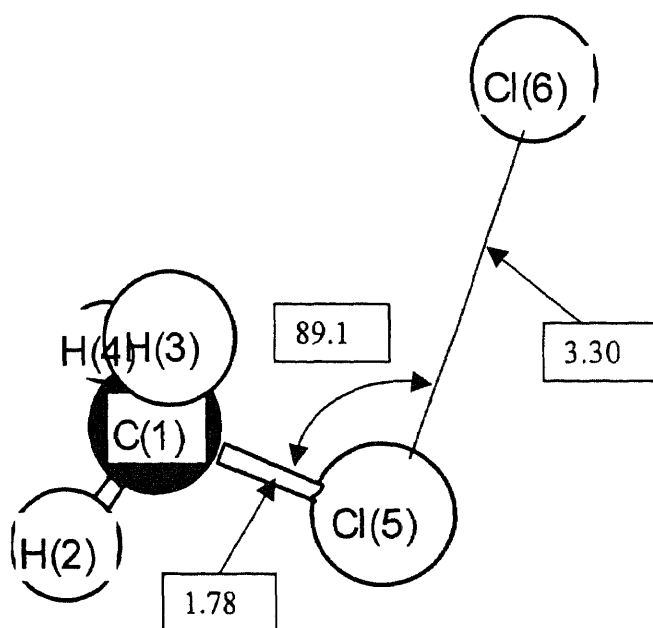
(c) CH₃Cl-Cl

Figure 1.6c Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CH₃Cl-Cl)

	Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0832597				
C1-H3	1.0832618	H3-C1-H2	117.295260		
C1-C4	1.4918126	C4-C1-H2	120.192555	C4-C1-H2-H3	-162.731790
C1-Cl5	2.8512380	Cl5-C1-H2	94.185453	Cl5-C1-H2-H3	96.911657
Cl5-Cl6	2.0416507	Cl6-Cl5-C1	176.273561	Cl6-Cl5-C1-H2	121.199932
C4-H7	1.0928203	H7-C4-C1	111.366252	H7-C4-C1-H2	-159.402229
C4-H8	1.0928105	H8-C4-C1	111.367406	H8-C4-C1-H2	-38.279669
C4-H9	1.0999090	H9-C4-C1	111.055344	H9-C4-C1-H2	81.161692
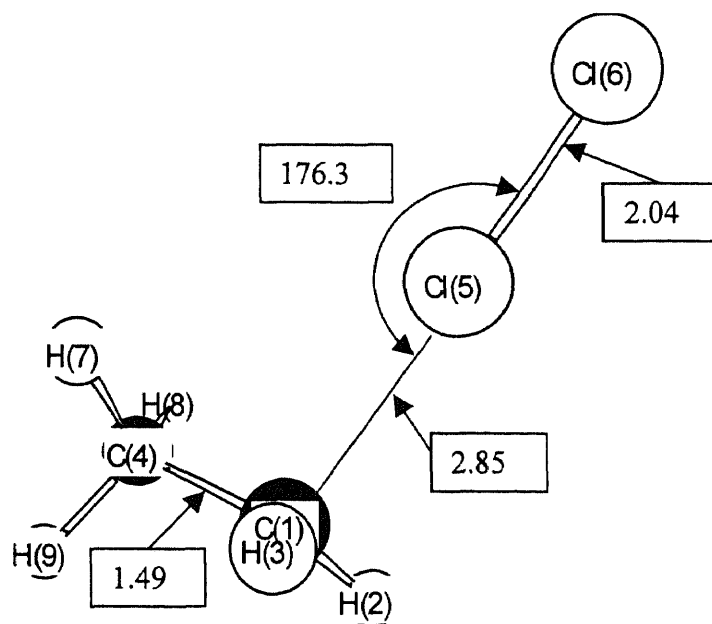
(d) CC-ClCl

Figure 1.6d Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CC-ClCl)

	Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0845277				
C1-H3	1.0845213	H3-C1-H2	116.330713		
C1-C4	1.4894599	C4-C1-H2	-119.133298	C4-C1-H2-H3	-153.918681
C1-Cl5	2.4021188	Cl5-C1-H2	95.431259	Cl5-C1-H2-H3	98.798312
Cl5-Cl6	2.0835974	Cl6-Cl5-C1	177.346547	Cl6-Cl5-C1-H2	119.768136
C4-H7	1.0916716	H7-C4-C1	111.368261	H7-C4-C1-H2	-164.638694
C4-H8	1.0917337	H8-C4-C1	111.356443	H8-C4-C1-H2	-42.914304
C4-H9	1.0999643	H9-C4-C1	109.714949	H9-C4-C1-H2	76.199249
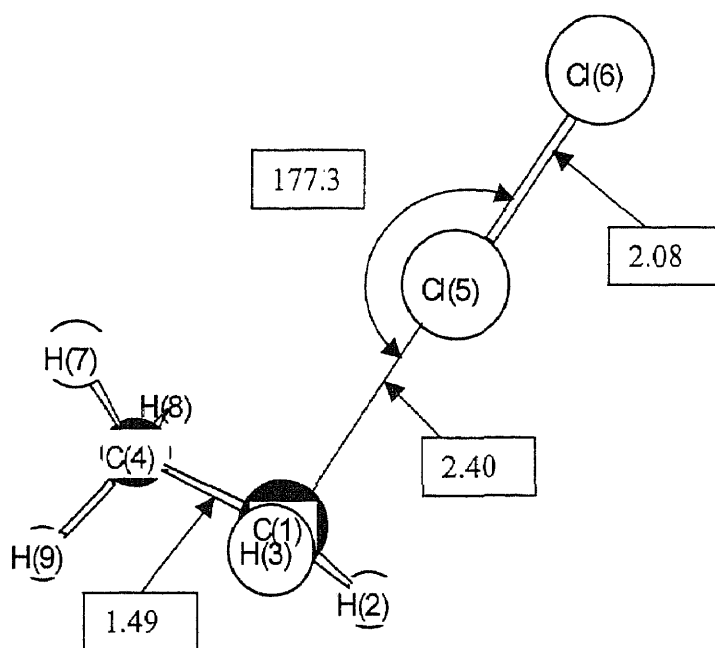
(e) TSC$_2$H$_5$XCl$_2$

Figure 1.6e Structures for the adducts and transition states involved in the reactions (1) and (2).Geometry optimizations at the MP2/6-311G(d,p) level of theory. (TSC$_2$H$_5$XCl$_2$)

	Bond Length (A)		Bond Angle (deg)		Dihedral Angle (deg)
C1-H2	1.0899852				
C1-H3	1.0900362	H3-C1-H2	109.175033		
C1-C4	1.5163650	C4-C1-H2	111.610294	C4-C1-H2-H3	-123.711020
C1-Cl5	1.7906557	Cl5-C1-H2	106.602062	Cl5-C1-H2-H3	115.017378
Cl5-Cl6	3.2529477	Cl6-Cl5-C1	89.594795	Cl6-Cl5-C1-H2	-158.991415
C4-H7	1.0915756	H7-C4-C1	110.744746	H7-C4-C1-H2	-179.287169
C4-H8	1.0918485	H8-C4-C1	110.773085	H8-C4-C1-H2	-58.815927
C4-H9	1.0944691	H9-C4-C1	109.448585	H9-C4-C1-H2	60.992411
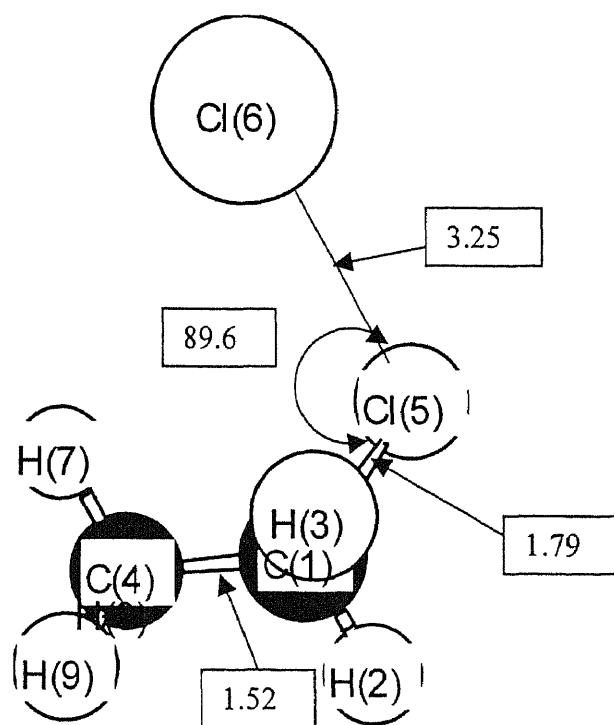
(f) CCCl-Cl

Figure 1.6f Structures for the adducts and transition states involved in the reactions (1) and (2). Geometry optimizations at the MP2/6-311G(d,p) level of theory. (CCCl-Cl)

Table 1.4 Vibrational Frequencies[a] (v cm^{-1}) MP2/6-311G(d,p) level of calculation

Species	Vibrational Frequencies										
ch3-clcl	47	47	82	146	146	525	545	1447	1447	3170	
	3364	3364									
tsch3xcl2[b]	-495[d]	65	65	394	530	530	976	1446	1446	3158	
	3345	3345									
ch3cl-cl	42	43	61	779	1066	1067	1441	1494	1494	3121	
	3231	3232									
cc-clcl	48	63	87	120	131	271	579	607	822	1008	
	1092	1224	1420	1494	1504	1511	3040	3130	3176	3202	3314
tsc2h5xcl2[c]	-348[d]	72	87	170	196	433	517	814	825	1044	
	1102	1234	1414	1492	1493	1510	3045	3144	3192	3193	3305
cccl-cl	44	54	63	293	343	718	805	1014	1116	1120	
	1305	1369	1437	1504	1505	1518	3086	3134	3176	3185	3207

[a] non-scaled. [b,c] Transition State Structure described in Figure 5.

[d] Transition State, one imaginary frequency.

Table 1.5 Moments of Inertia (amu-Bohr^2) MP2/6-311G(d,p) level of calculation

Species	I_A	I_B	I_C
ch3-clcl	12.57	1015.66	1015.66
tsch3xcl2	12.38	794.63	794.63
ch3cl-cl	131.82	833.62	953.99
cc-clcl	93.92	1461.85	1532.15
tsc2h5xcl2	89.57	1282.56	1348.56
cccl-cl	339.96	979.25	1230.03

4.2.3 Estimation of Entropy ($S^o_{(298)}$) and Heat Capacity (Cp(T)'s, 300 - 1500K) for Transition States and Adducts

$S^o_{(298)}$ and Cp(T)'s are calculated based on vibration frequencies and moments of inertia of the optimized MP2/6-311G(d,p) structures. The calculation results using MP2/6-311G(d,p) determined geometries and frequencies are summarized in Table 1.6. TVR represents the sum of the contributions from translations, vibrations and external rotations for $S^o_{(298)}$ and Cp(T)'s. Symmetry is incorporated in estimation of $S^o_{(298)}$ as described in Table 1.6. Contributions of internal rotation for $S^o_{(298)}$ and Cp(T)'s are calculated based on rotational barrier heights, moments of inertia of the rotors using the method of Pitzer and Gwinn's[1].

4.2.4 Calculated Enthalpies of Formation ($\Delta H^o_{f(298)}$)

$\Delta H^o_{f(298)}$ for reactants, adducts, transition states, and products in reactions of CH_3 and C_2H_5 with Cl_2 are calculated using CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p). The calculation results are summarized in Table 1.7. The activation energies of $TSCH_3XCl_2$ are estimated by taking the difference of total energy between reactants and $TSCH_3XCl_2$ resulting in −2.73 and 2.4 kcal/mole for CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p), and $\Delta H^o_{f(298)}$ of the CH_3-ClCl intermediate adduct is calculated as 33.37 and 33.28 kcal/mole, respectively. Activation energies of $TSC_2H_5XCl_2$ are estimated by taking the difference of total energy between reactants and $TSC_2H_5XCl_2$ resulting in -5.07 and -1.73 kcal/mole for CBSQ//MP2/6-311G(d,p) and MP2/6-311G(d,p). $\Delta H^o_{f(298)}$ of CC-ClCl is calculated as 26.80 and 26.42 kcal/mole, respectively.

The overall energy diagram is illustrated in Figure 1.5.

Table 1.6 Ideal Gas Phase Thermodynamic Properties[a] :

$\Delta H_f^{\circ}{}_{298}$: CBSQ//MP2/6-311G(d,p), $S^{\circ}{}_{298}$ and Cp(T) : MP2/6-311G(d,p)

Species and Symmetry #		$\Delta Hf^{\circ}{}_{298}$	$S^{\circ}{}_{298}{}^{b}$	$Cp_{300}{}^{b}$	Cp_{400}	Cp_{500}	Cp_{600}	Cp_{800}	Cp_{1000}	Cp_{1500}
ch3-clcl	TVR[c]		83.23	20.23	21.32	22.23	23.03	24.43	25.64	27.91
(3)	Total[f]	33.37	83.23[e]	20.23	21.32	22.23	23.03	24.43	25.64	27.91
tsch3xcl2	TVR		68.68	14.39	15.96	17.22	18.27	19.97	21.36	23.80
(3)	Internal Rotor 1[d]		5.42	1.48	1.31	1.21	1.15	1.08	1.05	1.02
	Total[f]	32.10	74.11[e]	15.86	17.27	18.43	19.42	21.06	22.41	24.82
ch3cl-cl	TVR		74.70	13.48	15.15	16.79	18.25	20.62	22.44	25.40
(3)	Internal Rotor 1		5.75	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	Total[f]	6.23	80.45[e]	14.47	16.14	17.79	19.24	21.61	23.43	26.39
cc-clcl	TVR		83.09	21.39	24.37	27.05	29.35	33.06	35.92	40.63
(3)	Internal Rotor 1		4.38	1.63	1.76	1.76	1.70	1.58	1.47	1.27
	Total[f]	26.8	87.47[e]	23.02	26.13	28.81	31.05	34.64	37.39	41.90
tsc2h5xcl2	TVR		72.22	16.70	19.84	22.65	25.05	28.87	31.80	36.58
(3)	Internal Rotor 1,2		11.89	3.24	3.11	2.95	2.79	2.59	2.44	2.24
	Total[f]	24.2	84.10[e]	19.94	22.96	25.60	27.84	31.46	34.25	38.82
cccl-cl	TVR		74.31	16.16	19.48	22.62	25.35	29.72	33.00	38.20
(3)	Internal Rotor 1,2		11.85	3.46	3.33	3.16	2.99	2.76	2.58	2.32
	Total[f]	-1.19	86.16[e]	19.62	22.81	25.78	28.35	32.47	35.58	40.52

[a] Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiometer at 1 atm. [b] In cal/mol-K. [c] The sum of contributions from translations, external rotations, and vibrations. [d] Contribution from internal rotation.

[e] Symmetry number is taken into account (-R * ln(number of symmetry))

[f] Spin degeneracy contribution for entropy = 1.987 * ln(2) (cal/mol-K) is taken into account.

Table 1.7 Total Energy, ZPVE, Thermal Correction, and $\Delta H_f^{\circ}{}_{298}$ in CBSQ and MP2/6-311G(d,p) Calculation[a]

Species	Total Energy at 298K[b] MP2/6-311G(d,p)	Total Energy at 298K[b] CBSQ	ZPVE[c]	Thermal Correction[d]	$\Delta H_f^{\circ}{}_{298}$ (MP2)	$\Delta H_f^{\circ}{}_{298}$ (CBSQ)
cl2	-919.2357806	-919.45662	0.0011961	0.0035010	0.00	0.00
ch3	-39.7072381	-39.7406173	0.0293571	0.0040820	34.82[e]	34.82[e]
ch3-clcl	-958.9454736	-959.1995455	0.0318214	0.0079400	33.28	33.37
tsch3xcl2	-958.9391929	-959.2015846	0.0339796	0.0061560	37.22	32.09
ch3cl-cl	-959.0137142	-959.2423618	0.0379109	0.0064490	-9.54	6.50
ch3cl	-499.4262791	-449.5581297	0.0372296	0.0039680	-	-
cl	-459.5851374	-459.6805237	0.0000000	0.0023600	-	-
c2h5	-78.9029613	-78.9664974	0.0589530	0.0048250	29.30[e]	29.30[e]
cc-clcl	-998.1433280	-998.4270989	0.0618296	0.0085130	26.42	26.80
tsc2h5xcl2	-998.1414941	-998.4311891	0.0628073	0.0072330	27.57	24.23
cccl-cl	-998.2137368	-998.4706799	0.0666130	0.0073610	-17.76	-0.55
c2h5cl	-538.6258002	-538.7864702	0.0660780	0.0048980	-	-

[a] Unit in Hartree 1 HF=627.51 kcal/mol. [b] Scaled ZPVE are included. Scaling factor is recommended as 0.9748 by Scott et al.[24] for MP2/6-311G(d,p). [c] Scaled by 0.9748 [d] Non-scaled.

[e] $\Delta H_f^{\circ}{}_{298}$ CH$_3$ and C$_2$H$_5$ are set to literature values in Table 2 for isodesmic reaction.

4.2.5 Thermodynamic Analysis for reactions of CH$_3$ and C$_2$H$_5$ with Cl$_2$

ΔH_{rxn}, ΔU_{rxn} and the Arrhenius pre-exponential factor are calculated using

thermodynamic properties of the transition state structures for temperature from 300K to

2000K and results are shown in Table 1.8. The experimental A_{fwd} of 3.02 * 10^{12} for Cl$_2$ +

CH$_3$ => CH$_3$Cl + Cl reaction in Table 1.1, corresponds to the calculated A_{fwd} value near

700K in Table 1.8 (a). The experimental A_{Rev} of 2.99 * 10^{13} in CH$_3$Cl + Cl => Cl$_2$ + CH$_3$

reaction in Table 1.1, corresponds to the calculated A_{Rev} near 500K in Table 1.8 (b).

The experimental A_{fwd} of 7.59 * 10^{12} for Cl$_2$ + C$_2$H$_5$ => C$_2$H$_5$Cl + Cl reaction in

Table 1.1, corresponds to the calculated A_{fwd} near 1100K in Table 1.8 (c). The

experimental A_{Rev} of 8.51 * 10^{13} for C$_2$H$_5$Cl + Cl => Cl$_2$ + C$_2$H$_5$ reaction in Table 1.1,

corresponds to the calculated A_{Rev} near 1200K in Table 1.8 (d).

4.2.6 Atomic Charges in Reactants, Adducts, Transition States, and Products

CH$_3$ + Cl$_2$ ---> CH$_3$Cl + Cl and C$_2$H$_5$ + Cl$_2$ ---> C$_2$H$_5$Cl + Cl Reactions

Table 1.9 illustrates Mulliken Atomic Charges on the H, C, and Cl atoms in the CH$_3$ +

Cl$_2$ and C$_2$H$_5$ + Cl$_2$ reaction systems. Calculated charges on the H atoms remain positive

throughout the reaction process at ca. 0.1. Charges on the carbon bonding to Cl are

negative 0.34 in CH$_3$ with a progressive increase to – 0.26 in CH$_3$Cl. The corresponding

carbon in the C$_2$H$_5$ reaction experiences a decrease from – 0.25 to – 0.31 when C$_2$H$_5$ +

Cl$_2$ react to the TSC$_2$H$_5$XCl$_2$ and then increases to – 0.21 in C$_2$H$_5$Cl. The Cl atom

bonding to the carbon has no charge in Cl$_2$, positive 0.01 and 0.02 charges in the

TSCH$_3$XCl$_2$ and the TSC$_2$H$_5$XCl$_2$, respectively, then decreases to – 0.16 in the Cl atom of

the products (both CH$_3$Cl and C$_2$H$_5$Cl). The leaving Cl has no charge in Cl$_2$, negative

0.13 charge in both the TSCH$_3$XCl$_2$ and the TSC$_2$H$_5$XCl$_2$, then increases near zero (- 0.

01) in both the CH$_3$Cl-Cl adduct and the CCCl-Cl adduct.

Figure 1.7 and the description of charges show that H atoms donate e$^-$ to the carbon

radical center and to chlorine in R-Cl. Replacement of the H's with electronegative

halogens or other electronegative species must reduce the available e$^-$ density to/at the

carbon site. This likely reduces bond energy of additional R-Cl bonds being formed.

Repulsive effects may also be important in the reduced bond energies.

Table 1.8 Thermodynamic and Kinetic analysis for reactions of CH_3 and C_2H_5
with Cl_2 comparing with experiment data* (Timonen/Gutman1986)

(a) $Cl_2 + CH_3$ ----> $TSCH_3XCl_2$

T(K)	ΔH^arxn	ΔU^arxn	Af^a
300	-2.723	-2.127	1.08E+12
400	-2.862	-2.068	1.57E+12
500	-2.975	-1.982	2.15E+12
600	-3.068	-1.876	2.85E+12
800	-3.218	-1.628	4.54E+12
1000	-3.344	-1.357	6.61E+12
1200	-3.464	-1.080	9.00E+12
1500	-3.639	-0.659	1.32E+13
2000	-3.868	0.106	2.19E+13

P(torr)	T(K)		
1.9 - 2.8	296-712	Expt.*	3.02E+12

(b) $CH_3Cl + Cl$ ----> $TSCH_3XCl_2$

T(K)	ΔHrxn	ΔUrxn	Af
300	22.78	23.38	9.04E+12
400	22.84	23.63	1.74E+13
500	22.84	23.84	2.75E+13
600	22.80	24.00	3.82E+13
800	22.61	24.20	5.93E+13
1000	22.30	24.29	7.78E+13
1200	21.91	24.29	9.37E+13
1500	21.25	24.23	1.14E+14
2000	20.11	24.08	1.46E+14

P(torr)	T(K)		
1.9 - 2.8	296-712	Expt.*	2.99E+13

(c) $Cl_2 + C_2H_5$ ----> $TSC_2H_5XCl_2$

T(K)	ΔHrxn	ΔUrxn	Af
300	-5.1	-4.504	6.39E+11
400	-5.11	-4.315	1.12E+12
500	-5.108	-4.114	1.75E+12
600	-5.103	-3.911	2.54E+12
800	-5.112	-3.523	4.48E+12
1000	-5.165	-3.178	6.80E+12
1200	-5.259	-2.875	9.38E+12
1500	-5.439	-2.458	1.37E+13
2000	-5.7	-1.726	2.26E+13

P(torr)	T(K)		
1.7 - 2.2	295-498	Expt.*	7.59E+12

(d) $C_2H_5Cl + Cl$ ----> $TSC_2H_5XCl_2$

T(K)	ΔHrxn	ΔUrxn	Af
300	22.08	22.68	9.98E+12
400	22.07	22.87	1.75E+13
500	22.03	23.02	2.60E+13
600	21.95	23.14	3.49E+13
800	21.71	23.30	5.25E+13
1000	21.40	23.38	6.87E+13
1200	21.03	23.41	8.36E+13
1500	20.43	23.41	1.05E+14
2000	19.43	23.40	1.39E+14

P(torr)	T(K)		
1.7 - 2.2	295-498	Expt.*	8.51E+13

^{a}Units ; ΔH and ΔU : kcal/mole, Af : cm^3/mole-sec

Table 1.9 Calculated atomic charges, bond lengths(A) and bond angles(deg)
MP2/6-311G(d,p)

(a) $CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$ **Expt. Ea = 0.53 kcal/mole**

	CH_3	Cl_1-Cl_2	CH_3-Cl_1Cl_2	$TSCH_3XCl_2$	CH_3Cl-Cl	CH_3Cl
Charges						
H	0.11		0.12	0.16	0.145	0.14
C	-0.34		-0.36	-0.35	-0.264	-0.26
Cl_1		0	0.02	0.01	-0.161	-0.159
Cl_2		0	-0.04	-0.13	-0.011	
Bond Length						
C-Cl			3.10	2.33	1.78	1.78
Cl-Cl		2.03	2.04	2.10	3.30	
Bond Angle						
C-Cl-Cl			180.0	180.0	89.1	

(b) $C_2H_5 + Cl_2 \longrightarrow C_2H_5Cl + Cl$ **Expt. Ea = -0.30 kcal/mole**

	C_2H_5	Cl_5-Cl_6	C_3C_4-Cl_5Cl_6	$TSC_2H_5XCl_2$	$CCCl$-Cl	C_2H_5Cl
Charges						
H_1	0.095		0.105	0.12	0.11	0.1
H_2	0.11		0.13	0.153	0.147	0.11
C_3	-0.25		-0.24	-0.23	-0.234	-0.24
C_4	-0.25		-0.29	-0.31	-0.22	-0.21
Cl_5		0	0.03	0.02	-0.161	-0.16
Cl_6		0	-0.06	-0.13	-0.01	
Bond Length						
C-Cl			2.85	2.40	1.79	1.79
Cl-Cl		2.03	2.04	2.08	3.25	
Bond Angle						
C-Cl-Cl			176.3	177.3	89.6	

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

$CH_3 + Cl_2$

H
 \
H—C·   +   Cl—Cl
 /
H (1.08)   (2.03)

CH_3-ClCl

H (1.08)
 \
H—C—Cl—Cl
 / (3.10) (2.04)
H

TSCH$_3$XCl$_2$

H (1.08)
 \
H—C—Cl—Cl
 / (2.33) (2.10)
H

CH_3Cl-Cl

H (1.09)
 \
H—C—Cl—Cl
 / (1.78) (3.30)
H

CH_3Cl + Cl

H (1.09)
 \
H—C—Cl   +   Cl
 / (1.78)
H
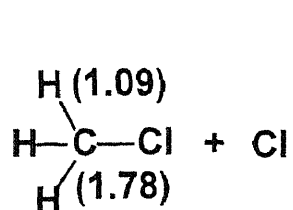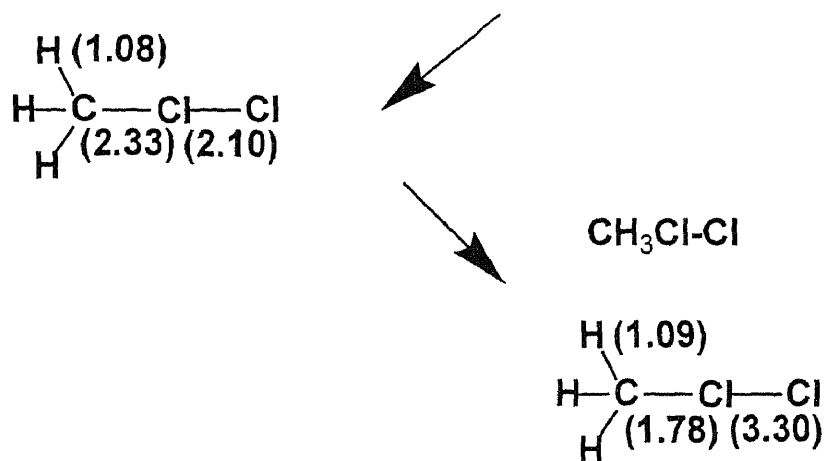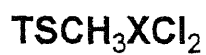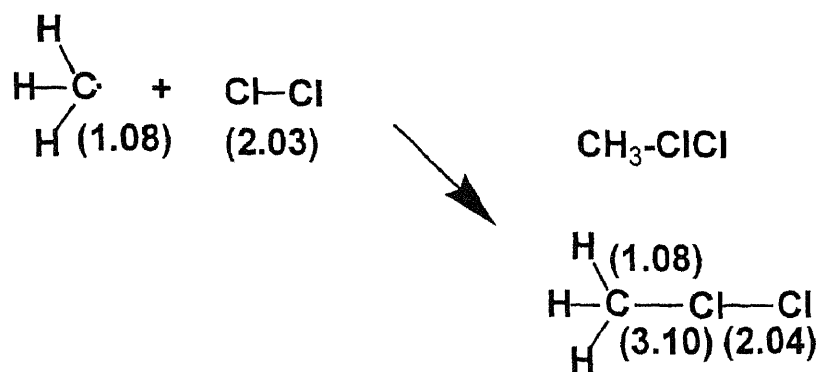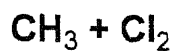
Figure 1.7a Bond lengths MP2/6-311G(d,p)
CH3 + Cl2 ----> CH3Cl + Cl

$$C_2H_5 + Cl_2 \longrightarrow C_2H_5Cl + Cl$$

$C_2H_5 + Cl_2$

CC-ClCl

$TSC_2H_5XCl_2$

CCCl-Cl
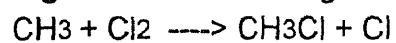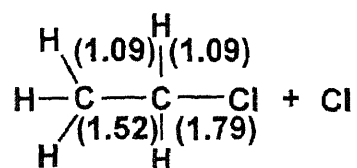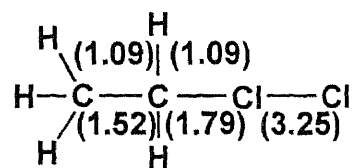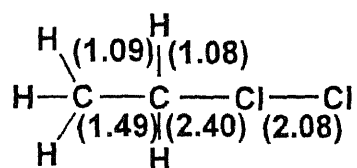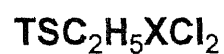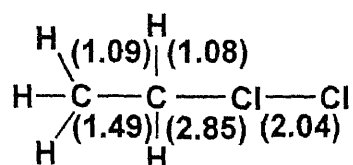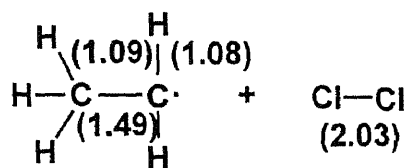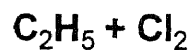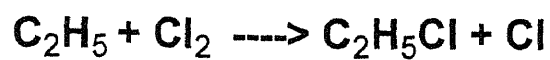
$C_2H_5Cl + Cl$

Figure 1.7b Bond lengths MP2/6-311G(d,p)
C2H5 + Cl2 ----> C2H5Cl + Cl

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

CH₃ + Cl₂

H
|
H—C·   +   Cl—Cl
/H (-0.34) (0) (0)
(0.11)

CH₃-ClCl

H\   (0.02)
H—C——Cl—Cl
/H (-0.36) (-0.04)
(0.12)

TSCH₃XCl₂

H\   (0.01)
H—C——Cl—Cl
/H (-0.35) (-0.13)
(0.16)

CH₃Cl-Cl

H\   (-0.161)
H—C——Cl—Cl
/H(-0.264) (-0.011)
(0.145)

CH₃Cl + Cl

H\ (-0.159)
H—C—Cl   +   Cl
/H (-0.260)   (0)
(0.140)
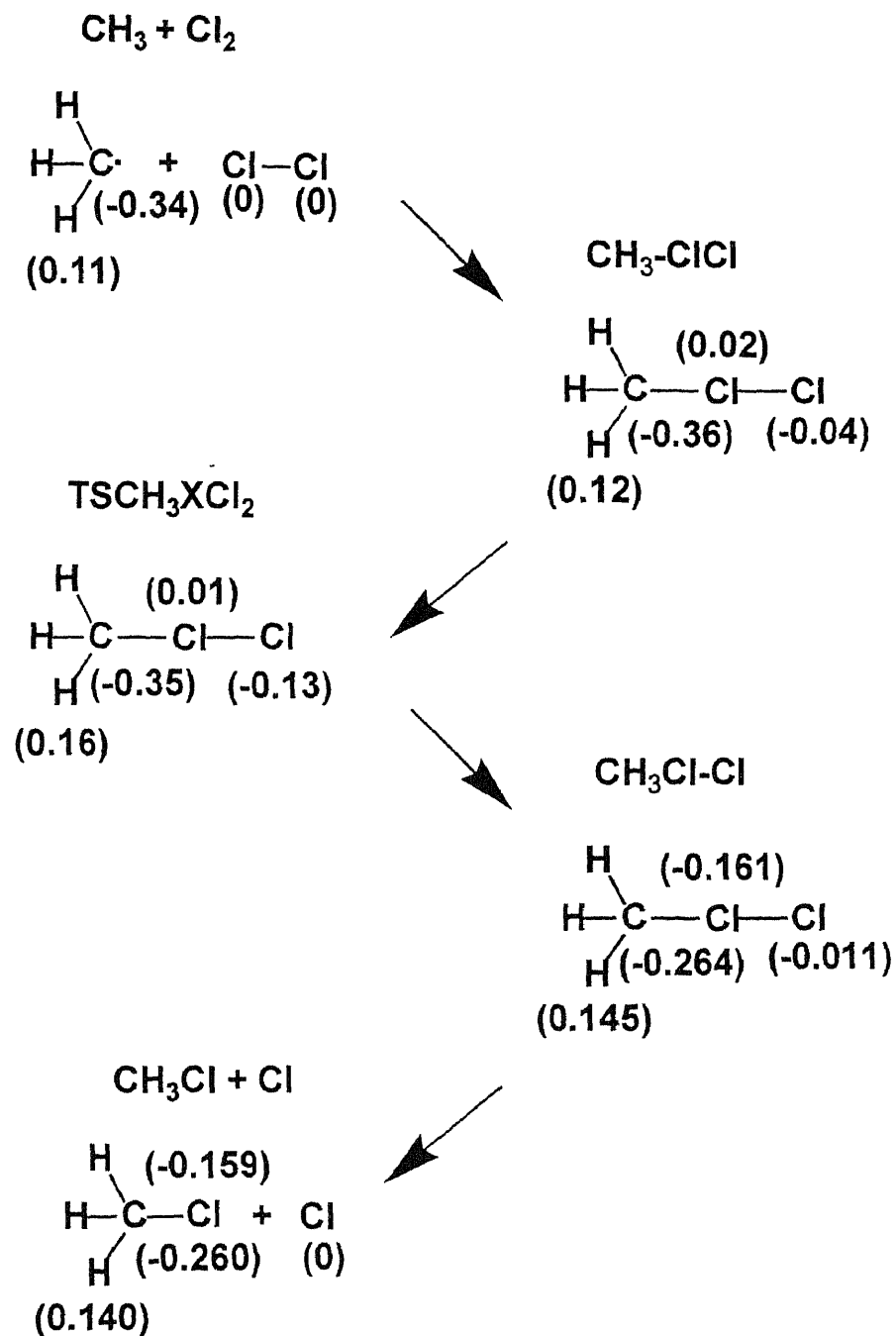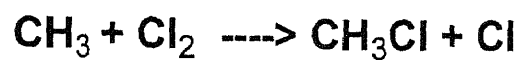
Figure 1.8a Calculated atomic charges MP2/6-311G(d,p)
CH₃ + Cl₂ ----> CH₃Cl + Cl

$$C_2H_5 + Cl_2 \longrightarrow C_2H_5Cl + Cl$$

$C_2H_5 + Cl_2$

CC-ClCl

$TSC_2H_5XCl_2$

CCCl-Cl

$C_2H_5Cl + Cl$
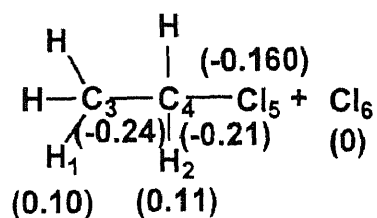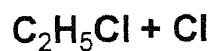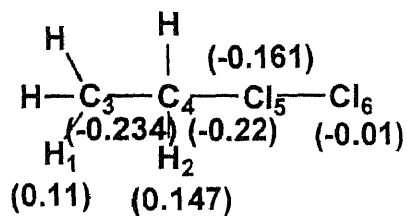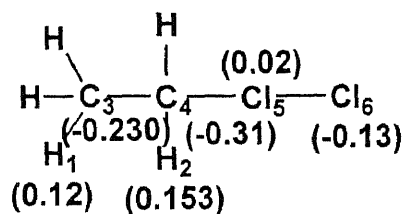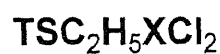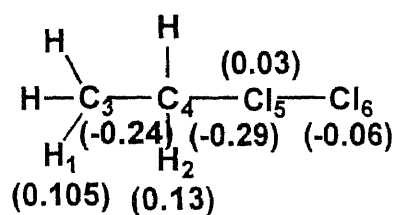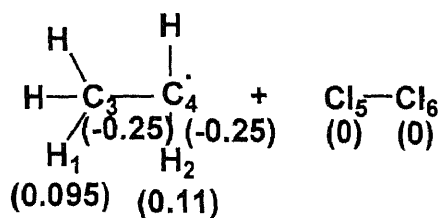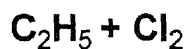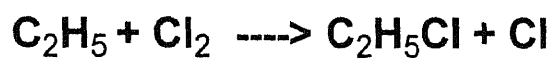
Figure 1.8b Calculated atomic charges MP2/6-311G(d,p)
$C_2H_5 + Cl_2 \longrightarrow C_2H_5Cl + Cl$
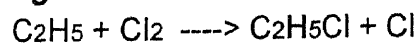
CHAPTER 5

SUMMARY FOR PART ONE

Thermodynamic Parameters, $\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$ and Cp(T) are evaluated for reactants and products in R. + Cl_2 <=> R-Cl + Cl reactions. The forward rate constants are evaluated from the literature. The reverse rate constants are calculated from thermodynamic properties of reactants and products and microscopic reversibility. The trends of Ea_{fwd} vs $\Delta H_{rxn,fwd}$ and Arrhenius pre-exponential factor for overall, hydrocarbons, C_1 chlorocarbons, and C_2 chlorocarbons are evaluated.

We recommend rate expression of average A_{fwd} = (2.35 ± 3.07) x 10^{12} cm^3/mole-sec and Ea_{fwd} = (0.38 ± 0.04) * $\Delta H_{rxn,fwd}$ + (10.10 ± 0.77) kcal/mole for overall, average A_{fwd} = (5.89 ± 2.48) x 10^{12} cm^3/mole-sec and Ea_{fwd} = (0.39 ± 0.11) * $\Delta H_{rxn,fwd}$ + (10.49 ± 2.21) kcal/mole for hydrocarbons, average A_{fwd} of (6.89 ± 2.15) x 10^{11} cm^3/mole-sec and Ea_{fwd} = (0.40 ± 0.07) * $\Delta H_{rxn,fwd}$ + (10.32 ± 1.31) kcal/mole for C_1 chlorocarbons, and average A_{fwd} of (4.64 ± 2.10) x 10^{11} cm^3/mole-sec and Ea_{fwd} = (0.33 ± 0.07) * $\Delta H_{rxn,fwd}$ + (9.46 ± 1.17) kcal/mole for C_2 chlorocarbons.

We have performed *ab initio* calculation on CH_3 + Cl_2 <=> CH_3Cl + Cl and C_2H_5 + Cl_2 <=> C_2H_5Cl + Cl reaction. We show canonical transition state calculations agree well with experimental data for these two, low Ea_{fwd}, reaction systems. The carbon atom which undergoes bonding to the Cl has a slightly increasing negative charge in the transition state then the charge increases, becomes less negative.

APPENDIX 1.1

THERMODYNAMIC ANALYSIS FOR Cl_2 + R. <-> RCl + Cl.

THERMODYNAMIC ANALYSIS for REACTION

Rx	CL2	+ CH3	= CH3CL	+ CL
Hf {Kcal/mol}	.000	34.820	-19.600	28.920
S {cal/mol K}	53.290	46.380	56.000	39.460

dHr {kcal/mol} (298K) =   -25.50   dHr avg (298., 1000. K) =   -25.57
dU (dE) {kcal/mol} (") =   -25.50   dUr avg (298., 1000. K) =   -25.57
dSr {cal/mol K} (") =   -4.21   dSr avg (298., 1000. K) =   -4.56
dGr {kcal/mol} (") =   -24.24   dGr avg (298., 1000. K) =   -22.62
       Af/Ar (") = 1.202E-01   Af/Ar avg (298., 1000. K) = 1.010E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.550E+01	-2.550E+01	-4.225E+00	1.193E-01	-2.424E+01
400.00	-2.570E+01	-2.570E+01	-4.789E+00	8.982E-02	-2.378E+01
500.00	-2.582E+01	-2.582E+01	-5.057E+00	7.848E-02	-2.329E+01
600.00	-2.587E+01	-2.587E+01	-5.158E+00	7.456E-02	-2.278E+01
800.00	-2.583E+01	-2.583E+01	-5.105E+00	7.662E-02	-2.175E+01
1000.00	-2.565E+01	-2.565E+01	-4.900E+00	8.490E-02	-2.075E+01
1200.00	-2.537E+01	-2.537E+01	-4.654E+00	9.610E-02	-1.979E+01
1500.00	-2.489E+01	-2.489E+01	-4.294E+00	1.152E-01	-1.845E+01
2000.00	-2.397E+01	-2.397E+01	-3.769E+00	1.500E-01	-1.644E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CL2	+ C2H5	= C2H5CL	+ CL
Hf {Kcal/mol}	.000	29.300	-26.800	28.920
S {cal/mol K}	53.290	57.420	66.010	39.460

dHr {kcal/mol} (298K) =   -27.18   dHr avg (298., 1000. K) =   -26.96
dU (dE) {kcal/mol} (") =   -27.18   dUr avg (298., 1000. K) =   -26.96
dSr {cal/mol K} (") =   -5.24   dSr avg (298., 1000. K) =   -4.80
dGr {kcal/mol} (") =   -25.62   dGr avg (298., 1000. K) =   -23.85
       Af/Ar (") = 7.157E-02   Af/Ar avg (298., 1000. K) = 8.918E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.718E+01	-2.718E+01	-5.239E+00	7.162E-02	-2.561E+01
400.00	-2.712E+01	-2.712E+01	-5.069E+00	7.800E-02	-2.509E+01
500.00	-2.700E+01	-2.700E+01	-4.803E+00	8.917E-02	-2.460E+01
600.00	-2.684E+01	-2.684E+01	-4.510E+00	1.034E-01	-2.413E+01
800.00	-2.644E+01	-2.644E+01	-3.946E+00	1.372E-01	-2.329E+01
1000.00	-2.602E+01	-2.602E+01	-3.468E+00	1.745E-01	-2.255E+01
1200.00	-2.559E+01	-2.559E+01	-3.078E+00	2.125E-01	-2.189E+01
1500.00	-2.496E+01	-2.496E+01	-2.611E+00	2.688E-01	-2.104E+01
2000.00	-2.393E+01	-2.393E+01	-2.019E+00	3.619E-01	-1.989E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CC.C   = CCCLC   + CL
Hf {Kcal/mol}   .000   21.020   -34.700   28.920
S {cal/mol K}   53.290   69.010   73.410   39.460

dHr {kcal/mol}   (298K) =   -26.80   dHr avg (298., 1000. K) =   -26.30
dU (dE) {kcal/mol} (") =   -26.80   dUr avg (298., 1000. K) =   -26.30
dSr {cal/mol K}   (") =   -9.43   dSr avg (298., 1000. K) =   -8.38
dGr {kcal/mol}   (") =   -23.99   dGr avg (298., 1000. K) =   -20.86
        Af/Ar (") = 8.688E-03   Af/Ar avg (298., 1000. K) = 1.473E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.680E+01	-2.680E+01	-9.421E+00	8.728E-03	-2.397E+01
400.00	-2.660E+01	-2.660E+01	-8.847E+00	1.165E-02	-2.306E+01
500.00	-2.631E+01	-2.631E+01	-8.220E+00	1.597E-02	-2.220E+01
600.00	-2.598E+01	-2.598E+01	-7.614E+00	2.167E-02	-2.141E+01
800.00	-2.524E+01	-2.524E+01	-6.554E+00	3.693E-02	-2.000E+01
1000.00	-2.449E+01	-2.449E+01	-5.716E+00	5.632E-02	-1.878E+01
1200.00	-2.377E+01	-2.377E+01	-5.055E+00	7.853E-02	-1.770E+01
1500.00	-2.274E+01	-2.274E+01	-4.287E+00	1.156E-01	-1.630E+01
2000.00	-2.117E+01	-2.117E+01	-3.382E+00	1.823E-01	-1.440E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + C3C.   = C3CCL   + CL
Hf {Kcal/mol}   .000   11.900   -44.130   28.920
S {cal/mol K}   53.290   74.290   76.420   39.460

dHr {kcal/mol}   (298K) =   -27.11   dHr avg (298., 1000. K) =   -26.38
dU (dE) {kcal/mol} (") =   -27.11   dUr avg (298., 1000. K) =   -26.38
dSr {cal/mol K}   (") =   -11.70   dSr avg (298., 1000. K) =   -10.18
dGr {kcal/mol}   (") =   -23.62   dGr avg (298., 1000. K) =   -19.77
        Af/Ar (") = 2.772E-03   Af/Ar avg (298., 1000. K) = 5.942E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.711E+01	-2.711E+01	-1.169E+01	2.785E-03	-2.360E+01
400.00	-2.685E+01	-2.685E+01	-1.095E+01	4.034E-03	-2.246E+01
500.00	-2.643E+01	-2.643E+01	-1.002E+01	6.444E-03	-2.142E+01
600.00	-2.592E+01	-2.592E+01	-9.096E+00	1.028E-02	-2.046E+01
800.00	-2.482E+01	-2.482E+01	-7.516E+00	2.277E-02	-1.881E+01
1000.00	-2.379E+01	-2.379E+01	-6.364E+00	4.065E-02	-1.742E+01
1200.00	-2.290E+01	-2.290E+01	-5.549E+00	6.125E-02	-1.624E+01
1500.00	-2.175E+01	-2.175E+01	-4.696E+00	9.409E-02	-1.471E+01
2000.00	-2.015E+01	-2.015E+01	-3.769E+00	1.500E-01	-1.261E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + C2H3   = CH2CHCL   + CL
Hf {Kcal/mol}   .000   71.640   5.000   28.920
S {cal/mol K}   53.290   53.790   63.080   39.460

dHr {kcal/mol} (298K) =   -37.72   dHr avg (298., 1000. K) =   -37.58
dU (dE) {kcal/mol} (") =   -37.72   dUr avg (298., 1000. K) =   -37.58
dSr {cal/mol K} (") =   -4.54   dSr avg (298., 1000. K) =   -4.27
dGr {kcal/mol} (") =   -36.37   dGr avg (298., 1000. K) =   -34.81
        Af/Ar (") = 1.018E-01   Af/Ar avg (298., 1000. K) = 1.169E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.772E+01	-3.772E+01	-4.540E+00	1.018E-01	-3.636E+01
400.00	-3.770E+01	-3.770E+01	-4.474E+00	1.052E-01	-3.591E+01
500.00	-3.762E+01	-3.762E+01	-4.305E+00	1.146E-01	-3.547E+01
600.00	-3.750E+01	-3.750E+01	-4.097E+00	1.272E-01	-3.505E+01
800.00	-3.720E+01	-3.720E+01	-3.667E+00	1.579E-01	-3.427E+01
1000.00	-3.685E+01	-3.685E+01	-3.277E+00	1.922E-01	-3.358E+01
1200.00	-3.648E+01	-3.648E+01	-2.938E+00	2.280E-01	-3.296E+01
1500.00	-3.590E+01	-3.590E+01	-2.504E+00	2.836E-01	-3.214E+01
2000.00	-3.489E+01	-3.489E+01	-1.924E+00	3.797E-01	-3.104E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + C3H5   = C3H5CL   + CL
Hf {Kcal/mol}   .000   40.750   -.460   28.920
S {cal/mol K}   53.290   62.050   73.310   39.460

dHr {kcal/mol} (298K) =   -12.29   dHr avg (298., 1000. K) =   -12.22
dU (dE) {kcal/mol} (") =   -12.29   dUr avg (298., 1000. K) =   -12.22
dSr {cal/mol K} (") =   -2.57   dSr avg (298., 1000. K) =   -2.42
dGr {kcal/mol} (") =   -11.52   dGr avg (298., 1000. K) =   -10.65
        Af/Ar (") = 2.743E-01   Af/Ar avg (298., 1000. K) = 2.958E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.229E+01	-1.229E+01	-2.568E+00	2.746E-01	-1.152E+01
400.00	-1.226E+01	-1.226E+01	-2.471E+00	2.883E-01	-1.127E+01
500.00	-1.222E+01	-1.222E+01	-2.384E+00	3.012E-01	-1.102E+01
600.00	-1.217E+01	-1.217E+01	-2.306E+00	3.133E-01	-1.079E+01
800.00	-1.208E+01	-1.208E+01	-2.172E+00	3.352E-01	-1.034E+01
1000.00	-1.197E+01	-1.197E+01	-2.055E+00	3.555E-01	-9.920E+00
1200.00	-1.185E+01	-1.185E+01	-1.942E+00	3.763E-01	-9.520E+00
1500.00	-1.161E+01	-1.161E+01	-1.765E+00	4.114E-01	-8.964E+00
2000.00	-1.106E+01	-1.106E+01	-1.452E+00	4.817E-01	-8.160E+00

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + C3H3   = C3H3CL   + CL
Hf {Kcal/mol}   .000   81.580   39.170   28.920
S {cal/mol K}   53.290   59.570   68.780   39.460

dHr {kcal/mol} (298K) =   -13.49   dHr avg (298., 1000. K) =   -13.31
dU (dE) {kcal/mol} (") =   -13.49   dUr avg (298., 1000. K) =   -13.31
dSr {cal/mol K} (") =   -4.62   dSr avg (298., 1000. K) =   -4.24
dGr {kcal/mol} (") =   -12.11   dGr avg (298., 1000. K) =   -10.56
          Af/Ar (") = 9.777E-02   Af/Ar avg (298., 1000. K) = 1.185E-01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.349E+01	-1.349E+01	-4.616E+00	9.796E-02	-1.210E+01
400.00	-1.341E+01	-1.341E+01	-4.396E+00	1.094E-01	-1.165E+01
500.00	-1.331E+01	-1.331E+01	-4.170E+00	1.226E-01	-1.122E+01
600.00	-1.319E+01	-1.319E+01	-3.955E+00	1.366E-01	-1.082E+01
800.00	-1.293E+01	-1.293E+01	-3.577E+00	1.652E-01	-1.007E+01
1000.00	-1.265E+01	-1.265E+01	-3.266E+00	1.933E-01	-9.383E+00
1200.00	-1.236E+01	-1.236E+01	-3.003E+00	2.207E-01	-8.757E+00
1500.00	-1.190E+01	-1.190E+01	-2.661E+00	2.620E-01	-7.909E+00
2000.00	-1.106E+01	-1.106E+01	-2.181E+00	3.336E-01	-6.702E+00

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CH2CL   = CH2CL2   + CL
Hf {Kcal/mol}   .000   27.990   -22.830   28.920
S {cal/mol K}   53.290   58.610   64.570   39.460

dHr {kcal/mol} (298K) =   -21.90   dHr avg (298., 1000. K) =   -21.89
dU (dE) {kcal/mol} (") =   -21.90   dUr avg (298., 1000. K) =   -21.89
dSr {cal/mol K} (") =   -7.87   dSr avg (298., 1000. K) =   -7.89
dGr {kcal/mol} (") =   -19.55   dGr avg (298., 1000. K) =   -16.77
          Af/Ar (") = 1.905E-02   Af/Ar avg (298., 1000. K) = 1.884E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.190E+01	-2.190E+01	-7.875E+00	1.900E-02	-1.954E+01
400.00	-2.195E+01	-2.195E+01	-8.025E+00	1.762E-02	-1.874E+01
500.00	-2.196E+01	-2.196E+01	-8.034E+00	1.754E-02	-1.794E+01
600.00	-2.192E+01	-2.192E+01	-7.965E+00	1.816E-02	-1.714E+01
800.00	-2.174E+01	-2.174E+01	-7.716E+00	2.059E-02	-1.557E+01
1000.00	-2.147E+01	-2.147E+01	-7.414E+00	2.396E-02	-1.406E+01
1200.00	-2.114E+01	-2.114E+01	-7.114E+00	2.787E-02	-1.260E+01
1500.00	-2.059E+01	-2.059E+01	-6.708E+00	3.418E-02	-1.053E+01
2000.00	-1.962E+01	-1.962E+01	-6.148E+00	4.531E-02	-7.322E+00

THERMODYNAMIC ANALYSIS for REACTION
```
Rx         CL2     + CHCL2    = CHCL3    + CL
Hf {Kcal/mol}   .000    23.500    -24.200    28.920
S {cal/mol K}  53.290    68.100    70.660    39.460
```

```
dHr {kcal/mol}  (298K) =    -18.78    dHr avg (298., 1000. K) =    -18.63
dU (dE) {kcal/mol} (") =    -18.78    dUr avg (298., 1000. K) =    -18.63
dSr {cal/mol K}  ( " ) =    -11.27    dSr avg (298., 1000. K) =    -10.98
dGr {kcal/mol}   ( " ) =    -15.42    dGr avg (298., 1000. K) =    -11.51
         Af/Ar  ( " ) = 3.441E-03   Af/Ar avg (298., 1000. K) = 3.975E-03
```

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.878E+01	-1.878E+01	-1.127E+01	3.441E-03	-1.540E+01
400.00	-1.875E+01	-1.875E+01	-1.119E+01	3.586E-03	-1.427E+01
500.00	-1.867E+01	-1.867E+01	-1.101E+01	3.917E-03	-1.316E+01
600.00	-1.856E+01	-1.856E+01	-1.080E+01	4.352E-03	-1.207E+01
800.00	-1.826E+01	-1.826E+01	-1.038E+01	5.396E-03	-9.956E+00
1000.00	-1.791E+01	-1.791E+01	-9.990E+00	6.554E-03	-7.920E+00
1200.00	-1.754E+01	-1.754E+01	-9.654E+00	7.763E-03	-5.956E+00
1500.00	-1.696E+01	-1.696E+01	-9.222E+00	9.644E-03	-3.127E+00
2000.00	-1.596E+01	-1.596E+01	-8.645E+00	1.290E-02	1.334E+00

THERMODYNAMIC ANALYSIS for REACTION
```
Rx         CL2     + CCL3     = CCL4     + CL
Hf {Kcal/mol}   .000    19.000    -22.940    28.920
S {cal/mol K}  53.290    70.920    74.020    39.460
```

```
dHr {kcal/mol}  (298K) =    -13.02    dHr avg (298., 1000. K) =    -12.65
dU (dE) {kcal/mol} (") =    -13.02    dUr avg (298., 1000. K) =    -12.65
dSr {cal/mol K}  ( " ) =    -10.73    dSr avg (298., 1000. K) =    -9.92
dGr {kcal/mol}   ( " ) =    -9.82    dGr avg (298., 1000. K) =    -6.21
         Af/Ar  ( " ) = 4.516E-03   Af/Ar avg (298., 1000. K) = 6.803E-03
```

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.302E+01	-1.302E+01	-1.072E+01	4.541E-03	-9.801E+00
400.00	-1.282E+01	-1.282E+01	-1.017E+01	5.993E-03	-8.757E+00
500.00	-1.261E+01	-1.261E+01	-9.692E+00	7.614E-03	-7.765E+00
600.00	-1.239E+01	-1.239E+01	-9.282E+00	9.359E-03	-6.817E+00
800.00	-1.193E+01	-1.193E+01	-8.621E+00	1.305E-02	-5.030E+00
1000.00	-1.147E+01	-1.147E+01	-8.116E+00	1.683E-02	-3.358E+00
1200.00	-1.103E+01	-1.103E+01	-7.714E+00	2.061E-02	-1.776E+00
1500.00	-1.038E+01	-1.038E+01	-7.227E+00	2.633E-02	4.619E-01
2000.00	-9.296E+00	-9.296E+00	-6.604E+00	3.602E-02	3.912E+00

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + C2CL5   = C2CL6   + CL
Hf {Kcal/mol}   .000   9.060   -33.800   28.920
S {cal/mol K}   53.290   95.680   94.770   39.460

dHr {kcal/mol} (298K) =   -13.94   dHr avg (298., 1000. K) =   -13.54
dU (dE) {kcal/mol} (") =   -13.94   dUr avg (298., 1000. K) =   -13.54
dSr {cal/mol K} (") =   -14.74   dSr avg (298., 1000. K) =   -13.88
dGr {kcal/mol} (") =   -9.55   dGr avg (298., 1000. K) =   -4.53
        Af/Ar (") = 6.002E-04   Af/Ar avg (298., 1000. K) = 9.233E-04

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.394E+01	-1.394E+01	-1.473E+01	6.028E-04	-9.518E+00
400.00	-1.376E+01	-1.376E+01	-1.423E+01	7.766E-04	-8.070E+00
500.00	-1.353E+01	-1.353E+01	-1.371E+01	1.007E-03	-6.673E+00
600.00	-1.327E+01	-1.327E+01	-1.324E+01	1.277E-03	-5.326E+00
800.00	-1.273E+01	-1.273E+01	-1.247E+01	1.882E-03	-2.759E+00
1000.00	-1.223E+01	-1.223E+01	-1.191E+01	2.499E-03	-3.240E-01
1200.00	-1.176E+01	-1.176E+01	-1.148E+01	3.097E-03	2.013E+00
1500.00	-1.108E+01	-1.108E+01	-1.097E+01	4.004E-03	5.377E+00
2000.00	-9.957E+00	-9.957E+00	-1.032E+01	5.539E-03	1.069E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CF3   = CF3CL   + CL
Hf {Kcal/mol}   .000   -113.010   -169.200   28.920
S {cal/mol K}   53.290   63.420   68.170   39.460

dHr {kcal/mol} (298K) =   -27.27   dHr avg (298., 1000. K) =   -26.95
dU (dE) {kcal/mol} (") =   -27.27   dUr avg (298., 1000. K) =   -26.95
dSr {cal/mol K} (") =   -9.08   dSr avg (298., 1000. K) =   -8.38
dGr {kcal/mol} (") =   -24.56   dGr avg (298., 1000. K) =   -21.50
        Af/Ar (") = 1.036E-02   Af/Ar avg (298., 1000. K) = 1.471E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.727E+01	-2.727E+01	-9.072E+00	1.040E-02	-2.455E+01
400.00	-2.712E+01	-2.712E+01	-8.648E+00	1.288E-02	-2.366E+01
500.00	-2.693E+01	-2.693E+01	-8.236E+00	1.585E-02	-2.282E+01
600.00	-2.673E+01	-2.673E+01	-7.858E+00	1.916E-02	-2.201E+01
800.00	-2.629E+01	-2.629E+01	-7.227E+00	2.633E-02	-2.051E+01
1000.00	-2.585E+01	-2.585E+01	-6.738E+00	3.368E-02	-1.911E+01
1200.00	-2.542E+01	-2.542E+01	-6.348E+00	4.099E-02	-1.780E+01
1500.00	-2.478E+01	-2.478E+01	-5.872E+00	5.208E-02	-1.597E+01
2000.00	-2.372E+01	-2.372E+01	-5.259E+00	7.090E-02	-1.320E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CL2	+ CF2CL	= CF2CL2	+ CL
Hf {Kcal/mol}	.000	-66.020	-117.500	28.920
S {cal/mol K}	53.290	67.720	71.910	39.460

dHr {kcal/mol} (298K) = -22.56   dHr avg (298., 1000. K) = -22.22
dU (dE) {kcal/mol} (") = -22.56   dUr avg (298., 1000. K) = -22.22
dSr {cal/mol K} (") = -9.64   dSr avg (298., 1000. K) = -8.91
dGr {kcal/mol} (") = -19.69   dGr avg (298., 1000. K) = -16.44
        Af/Ar (") = 7.816E-03   Af/Ar avg (298., 1000. K) = 1.127E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.256E+01	-2.256E+01	-9.632E+00	7.848E-03	-1.967E+01
400.00	-2.240E+01	-2.240E+01	-9.186E+00	9.825E-03	-1.873E+01
500.00	-2.221E+01	-2.221E+01	-8.754E+00	1.221E-02	-1.783E+01
600.00	-2.199E+01	-2.199E+01	-8.362E+00	1.487E-02	-1.697E+01
800.00	-2.154E+01	-2.154E+01	-7.713E+00	2.062E-02	-1.537E+01
1000.00	-2.110E+01	-2.110E+01	-7.217E+00	2.646E-02	-1.388E+01
1200.00	-2.067E+01	-2.067E+01	-6.825E+00	3.222E-02	-1.248E+01
1500.00	-2.003E+01	-2.003E+01	-6.348E+00	4.097E-02	-1.050E+01
2000.00	-1.896E+01	-1.896E+01	-5.733E+00	5.583E-02	-7.490E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx	CL2	+ CFCL2	= CFCL3	+ CL
Hf {Kcal/mol}	.000	-21.600	-67.700	28.920
S {cal/mol K}	53.290	69.170	74.070	39.460

dHr {kcal/mol} (298K) = -17.18   dHr avg (298., 1000. K) = -16.77
dU (dE) {kcal/mol} (") = -17.18   dUr avg (298., 1000. K) = -16.77
dSr {cal/mol K} (") = -8.93   dSr avg (298., 1000. K) = -8.03
dGr {kcal/mol} (") = -14.52   dGr avg (298., 1000. K) = -11.55
        Af/Ar (") = 1.117E-02   Af/Ar avg (298., 1000. K) = 1.757E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.718E+01	-1.718E+01	-8.919E+00	1.124E-02	-1.450E+01
400.00	-1.697E+01	-1.697E+01	-8.327E+00	1.513E-02	-1.364E+01
500.00	-1.673E+01	-1.673E+01	-7.796E+00	1.977E-02	-1.283E+01
600.00	-1.648E+01	-1.648E+01	-7.334E+00	2.495E-02	-1.208E+01
800.00	-1.597E+01	-1.597E+01	-6.598E+00	3.613E-02	-1.069E+01
1000.00	-1.548E+01	-1.548E+01	-6.058E+00	4.742E-02	-9.425E+00
1200.00	-1.503E+01	-1.503E+01	-5.642E+00	5.846E-02	-8.257E+00
1500.00	-1.436E+01	-1.436E+01	-5.143E+00	7.515E-02	-6.642E+00
2000.00	-1.326E+01	-1.326E+01	-4.510E+00	1.033E-01	-4.237E+00

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CHCL2CHCL = C2H2CL4   + CL
Hf {Kcal/mol}   .000   11.750   -36.000   28.920
S {cal/mol K}   53.290   84.510   84.860   39.460

dHr {kcal/mol} (298K) =   -18.83   dHr avg (298., 1000. K) =   -18.69
dU (dE) {kcal/mol} (") =   -18.83   dUr avg (298., 1000. K) =   -18.69
dSr {cal/mol K} (") =   -13.48   dSr avg (298., 1000. K) =   -13.23
dGr {kcal/mol} (") =   -14.81   dGr avg (298., 1000. K) =   -10.11
        Af/Ar (") = 1.132E-03   Af/Ar avg (298., 1000. K) = 1.283E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.883E+01	-1.883E+01	-1.348E+01	1.130E-03	-1.479E+01
400.00	-1.883E+01	-1.883E+01	-1.348E+01	1.133E-03	-1.344E+01
500.00	-1.876E+01	-1.876E+01	-1.333E+01	1.222E-03	-1.210E+01
600.00	-1.864E+01	-1.864E+01	-1.310E+01	1.367E-03	-1.077E+01
800.00	-1.827E+01	-1.827E+01	-1.258E+01	1.782E-03	-8.204E+00
1000.00	-1.779E+01	-1.779E+01	-1.205E+01	2.328E-03	-5.742E+00
1200.00	-1.726E+01	-1.726E+01	-1.157E+01	2.966E-03	-3.382E+00
1500.00	-1.645E+01	-1.645E+01	-1.096E+01	4.014E-03	-6.244E-03
2000.00	-1.515E+01	-1.515E+01	-1.021E+01	5.856E-03	5.278E+00

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CH2CLCCL2 = CH2CLCCL3   + CL
Hf {Kcal/mol}   .000   7.870   -35.710   28.920
S {cal/mol K}   53.290   84.560   85.070   39.460

dHr {kcal/mol} (298K) =   -14.66   dHr avg (298., 1000. K) =   -14.39
dU (dE) {kcal/mol} (") =   -14.66   dUr avg (298., 1000. K) =   -14.39
dSr {cal/mol K} (") =   -13.32   dSr avg (298., 1000. K) =   -12.77
dGr {kcal/mol} (") =   -10.69   dGr avg (298., 1000. K) =   -6.10
        Af/Ar (") = 1.227E-03   Af/Ar avg (298., 1000. K) = 1.614E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.466E+01	-1.466E+01	-1.332E+01	1.228E-03	-1.066E+01
400.00	-1.458E+01	-1.458E+01	-1.310E+01	1.367E-03	-9.341E+00
500.00	-1.444E+01	-1.444E+01	-1.278E+01	1.610E-03	-8.047E+00
600.00	-1.423E+01	-1.423E+01	-1.241E+01	1.936E-03	-6.787E+00
800.00	-1.372E+01	-1.372E+01	-1.167E+01	2.807E-03	-4.379E+00
1000.00	-1.312E+01	-1.312E+01	-1.101E+01	3.925E-03	-2.112E+00
1200.00	-1.250E+01	-1.250E+01	-1.044E+01	5.222E-03	3.149E-02
1500.00	-1.158E+01	-1.158E+01	-9.760E+00	7.358E-03	3.057E+00
2000.00	-1.016E+01	-1.016E+01	-8.938E+00	1.113E-02	7.719E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx   CL2   + CH2CLCHCL = CH2CLCHCL2 + CL

Hf {Kcal/mol} .000   14.730   -34.800   28.920

S {cal/mol K} 53.290   78.560   79.710   39.460

dHr {kcal/mol} (298K) =   -20.61   dHr avg (298., 1000. K) =   -20.47

dU (dE) {kcal/mol} (") =   -20.61   dUr avg (298., 1000. K) =   -20.47

dSr {cal/mol K} (") =   -12.68   dSr avg (298., 1000. K) =   -12.44

dGr {kcal/mol} (") =   -16.83   dGr avg (298., 1000. K) =   -12.39

Af/Ar (") = 1.693E-03 Af/Ar avg (298., 1000. K) = 1.909E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.061E+01	-2.061E+01	-1.269E+01	1.688E-03	-1.681E+01
400.00	-2.064E+01	-2.064E+01	-1.277E+01	1.621E-03	-1.553E+01
500.00	-2.057E+01	-2.057E+01	-1.261E+01	1.753E-03	-1.426E+01
600.00	-2.042E+01	-2.042E+01	-1.235E+01	1.999E-03	-1.301E+01
800.00	-1.999E+01	-1.999E+01	-1.173E+01	2.732E-03	-1.060E+01
1000.00	-1.945E+01	-1.945E+01	-1.113E+01	3.697E-03	-8.319E+00
1200.00	-1.887E+01	-1.887E+01	-1.060E+01	4.815E-03	-6.147E+00
1500.00	-1.801E+01	-1.801E+01	-9.962E+00	6.648E-03	-3.067E+00
2000.00	-1.664E+01	-1.664E+01	-9.173E+00	9.886E-03	1.706E+00

THERMODYNAMIC ANALYSIS for REACTION

Rx   CL2   + CHCL2CH2 = CH2CLCHCL2 + CL

Hf {Kcal/mol} .000   20.310   -34.800   28.920

S {cal/mol K} 53.290   74.640   79.710   39.460

dHr {kcal/mol} (298K) =   -26.19   dHr avg (298., 1000. K) =   -26.19

dU (dE) {kcal/mol} (") =   -26.19   dUr avg (298., 1000. K) =   -26.19

dSr {cal/mol K} (") =   -8.76   dSr avg (298., 1000. K) =   -8.83

dGr {kcal/mol} (") =   -23.58   dGr avg (298., 1000. K) =   -20.46

Af/Ar (") = 1.217E-02 Af/Ar avg (298., 1000. K) = 1.176E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.619E+01	-2.619E+01	-8.769E+00	1.212E-02	-2.356E+01
400.00	-2.629E+01	-2.629E+01	-9.050E+00	1.052E-02	-2.267E+01
500.00	-2.630E+01	-2.630E+01	-9.079E+00	1.036E-02	-2.176E+01
600.00	-2.624E+01	-2.624E+01	-8.976E+00	1.092E-02	-2.086E+01
800.00	-2.597E+01	-2.597E+01	-8.590E+00	1.326E-02	-1.910E+01
1000.00	-2.556E+01	-2.556E+01	-8.135E+00	1.667E-02	-1.743E+01
1200.00	-2.508E+01	-2.508E+01	-7.699E+00	2.076E-02	-1.584E+01
1500.00	-2.433E+01	-2.433E+01	-7.140E+00	2.751E-02	-1.362E+01
2000.00	-2.308E+01	-2.308E+01	-6.421E+00	3.950E-02	-1.024E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CCL3CHCL   = CHCL2CCL3   + CL
Hf {Kcal/mol}   .000   10.590   -34.800   28.920
S {cal/mol K}   53.290   88.260   91.180   39.460

dHr {kcal/mol} (298K) =   -16.47   dHr avg (298., 1000. K) =   -16.51
dU (dE) {kcal/mol} (") =   -16.47   dUr avg (298., 1000. K) =   -16.51
dSr {cal/mol K} (") =   -10.91   dSr avg (298., 1000. K) =   -10.99
dGr {kcal/mol}   (") =   -13.22   dGr avg (298., 1000. K) =   -9.38
        Af/Ar (") = 4.125E-03   Af/Ar avg (298., 1000. K) = 3.972E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.647E+01	-1.647E+01	-1.091E+01	4.130E-03	-1.320E+01
400.00	-1.647E+01	-1.647E+01	-1.089E+01	4.161E-03	-1.211E+01
500.00	-1.650E+01	-1.650E+01	-1.097E+01	4.001E-03	-1.102E+01
600.00	-1.654E+01	-1.654E+01	-1.104E+01	3.862E-03	-9.915E+00
800.00	-1.654E+01	-1.654E+01	-1.105E+01	3.850E-03	-7.703E+00
1000.00	-1.639E+01	-1.639E+01	-1.089E+01	4.176E-03	-5.507E+00
1200.00	-1.612E+01	-1.612E+01	-1.064E+01	4.722E-03	-3.354E+00
1500.00	-1.563E+01	-1.563E+01	-1.028E+01	5.673E-03	-2.175E-01
2000.00	-1.472E+01	-1.472E+01	-9.751E+00	7.392E-03	4.786E+00

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CHCL2CCL2   = CHCL2CCL3   + CL
Hf {Kcal/mol}   .000   6.130   -34.800   28.920
S {cal/mol K}   53.290   90.650   91.180   39.460

dHr {kcal/mol} (298K) =   -12.01   dHr avg (298., 1000. K) =   -11.78
dU (dE) {kcal/mol} (") =   -12.01   dUr avg (298., 1000. K) =   -11.78
dSr {cal/mol K} (") =   -13.30   dSr avg (298., 1000. K) =   -12.77
dGr {kcal/mol}   (") =   -8.04   dGr avg (298., 1000. K) =   -3.49
        Af/Ar (") = 1.239E-03   Af/Ar avg (298., 1000. K) = 1.615E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-1.201E+01	-1.201E+01	-1.329E+01	1.247E-03	-8.020E+00
400.00	-1.184E+01	-1.184E+01	-1.281E+01	1.584E-03	-6.718E+00
500.00	-1.172E+01	-1.172E+01	-1.253E+01	1.821E-03	-5.451E+00
600.00	-1.161E+01	-1.161E+01	-1.233E+01	2.014E-03	-4.208E+00
800.00	-1.136E+01	-1.136E+01	-1.198E+01	2.405E-03	-1.777E+00
1000.00	-1.104E+01	-1.104E+01	-1.162E+01	2.883E-03	5.839E-01
1200.00	-1.064E+01	-1.064E+01	-1.126E+01	3.452E-03	2.872E+00
1500.00	-1.002E+01	-1.002E+01	-1.080E+01	4.365E-03	6.179E+00
2000.00	-8.949E+00	-8.949E+00	-1.018E+01	5.947E-03	1.142E+01

KINETIC ANALYSIS

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + CH3   = TSCXCL2
Hf {Kcal/mol}   .000   34.820   32.100
S {cal/mol K}   53.290   46.380   74.110

dHr {kcal/mol} (298K) =   -2.72   dHr avg (298., 1500. K) =   -3.18
dU (dE) {kcal/mol} (") =   -2.13   dUr avg (298., 1500. K) =   -1.39
dSr {cal/mol K} (") =   -25.56   dSr avg (298., 1500. K) =   -26.28
dGr {kcal/mol} (") =   4.90   dGr avg (298., 1500. K) =   20.45
            Af/Ar (") = 1.723E-01   Af/Ar avg (298., 1500. K) = 3.622E-01
Fit Af/Ar   : A = 2.154E-02 n = .34 alpha =-2.993E-04 avg error   1.71 %
Fit Af/Ar w/ddU: A = 2.740E-03 n = .71 alpha =-2.359E-04 avg error   2.47 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.723E+00	-2.127E+00	-2.557E+01	1.725E-01	4.948E+00
400.00	-2.862E+00	-2.068E+00	-2.597E+01	1.877E-01	7.527E+00
500.00	-2.975E+00	-1.982E+00	-2.623E+01	2.067E-01	1.014E+01
600.00	-3.068E+00	-1.876E+00	-2.640E+01	2.277E-01	1.277E+01
800.00	-3.218E+00	-1.628E+00	-2.661E+01	2.722E-01	1.807E+01
1000.00	-3.344E+00	-1.357E+00	-2.675E+01	3.169E-01	2.341E+01
1200.00	-3.464E+00	-1.080E+00	-2.686E+01	3.599E-01	2.877E+01
1500.00	-3.639E+00	-6.588E-01	-2.699E+01	4.213E-01	3.685E+01
2000.00	-3.868E+00	1.057E-01	-2.713E+01	5.253E-01	5.038E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = Aprime * T^n * exp(-Ea/RT)$
    Aprime = 5.2703E+07   n = 1.61232   Ea = -2.5676E+03

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.079E+12	9.861E+03	3.824E+13	3.859E+13
400.00	1.565E+12	1.568E+04	2.111E+13	2.090E+13
500.00	2.154E+12	2.247E+04	1.583E+13	1.570E+13
600.00	2.848E+12	3.015E+04	1.374E+13	1.369E+13
800.00	4.541E+12	4.794E+04	1.264E+13	1.271E+13
1000.00	6.607E+12	6.870E+04	1.308E+13	1.318E+13
1200.00	9.004E+12	9.218E+04	1.416E+13	1.426E+13
1500.00	1.318E+13	1.321E+05	1.643E+13	1.648E+13
2000.00	2.190E+13	2.101E+05	2.133E+13	2.112E+13

THERMODYNAMIC ANALYSIS for REACTION
Rx   CH3CL-CL = TSCXCL2
Hf {Kcal/mol}   6.230   32.100
S {cal/mol K} 80.450   74.110

dHr {kcal/mol} (298K) =   25.87   dHr avg (298., 1500. K) =   25.54
dU (dE) {kcal/mol} (") =   25.87   dUr avg (298., 1500. K) =   25.54
dSr {cal/mol K} (") =   -6.34   dSr avg (298., 1500. K) =   -6.44
dGr {kcal/mol} (") =   27.76   dGr avg (298., 1500. K) =   31.33
        Af/Ar (") = 4.114E-02   Af/Ar avg (298., 1500. K) = 3.919E-02
Fit Af/Ar   : A = 8.306E-04 n = .75 alpha = 1.098E-03 avg error   3.91 %
Fit Af/Ar w/ddU: A = 1.142E-04 n = 1.15 alpha = 1.847E-03 avg error   9.19 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.587E+01	2.587E+01	-6.331E+00	4.133E-02	2.777E+01
400.00	2.599E+01	2.599E+01	-5.979E+00	4.935E-02	2.839E+01
500.00	2.607E+01	2.607E+01	-5.808E+00	5.376E-02	2.897E+01
600.00	2.610E+01	2.610E+01	-5.747E+00	5.544E-02	2.955E+01
800.00	2.606E+01	2.606E+01	-5.807E+00	5.379E-02	3.070E+01
1000.00	2.590E+01	2.590E+01	-5.986E+00	4.916E-02	3.188E+01
1200.00	2.565E+01	2.565E+01	-6.205E+00	4.403E-02	3.310E+01
1500.00	2.521E+01	2.521E+01	-6.533E+00	3.734E-02	3.501E+01
2000.00	2.440E+01	2.440E+01	-6.997E+00	2.956E-02	3.840E+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 = 4.9360E+09   n = .79197   Ea = 2.6226E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.583E+11	9.158E+01	3.651E-08	3.533E-08
400.00	4.113E+11	1.150E+02	2.573E-03	2.654E-03
500.00	5.601E+11	1.372E+02	2.251E+00	2.326E+00
600.00	6.932E+11	1.586E+02	2.149E+02	2.188E+02
800.00	8.967E+11	1.991E+02	6.815E+04	6.720E+04
1000.00	1.024E+12	2.376E+02	2.242E+06	2.174E+06
1200.00	1.101E+12	2.745E+02	2.340E+07	2.266E+07
1500.00	1.167E+12	3.276E+02	2.473E+08	2.440E+08
2000.00	1.232E+12	4.114E+02	2.651E+09	2.765E+09

THERMODYNAMIC ANALYSIS for REACTION
Rx   CH3CL   + CL   = TSCXCL2
Hf {Kcal/mol} -19.600   28.920   32.100
S {cal/mol K} 56.000   39.460   74.110

dHr {kcal/mol} (298K) =   22.78   dHr avg (298., 1500. K) =   22.01
dU (dE) {kcal/mol} (") =   23.37   dUr avg (298., 1500. K) =   23.80
dSr {cal/mol K} (") =   -21.35   dSr avg (298., 1500. K) =   -22.02
dGr {kcal/mol} (") =   29.15   dGr avg (298., 1500. K) =   41.82
        Af/Ar (") = 1.433E+00   Af/Ar avg (298., 1500. K) = 3.078E+00
Fit Af/Ar   : A = 7.364E-04 n = 1.40 alpha = 1.106E-03 avg error   4.25 %
Fit Af/Ar w/ddU: A = 5.664E-06 n = 2.33 alpha = 2.153E-03 avg error   11.46 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.278E+01	2.338E+01	-2.135E+01	1.446E+00	2.918E+01
400.00	2.284E+01	2.363E+01	-2.118E+01	2.090E+00	3.131E+01
500.00	2.284E+01	2.384E+01	-2.117E+01	2.633E+00	3.343E+01
600.00	2.280E+01	2.400E+01	-2.124E+01	3.053E+00	3.555E+01
800.00	2.261E+01	2.420E+01	-2.151E+01	3.553E+00	3.982E+01
1000.00	2.230E+01	2.429E+01	-2.185E+01	3.733E+00	4.415E+01
1200.00	2.191E+01	2.429E+01	-2.221E+01	3.745E+00	4.856E+01
1500.00	2.125E+01	2.423E+01	-2.270E+01	3.657E+00	5.530E+01
2000.00	2.011E+01	2.408E+01	-2.336E+01	3.501E+00	6.682E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = Aprime * T^n * exp(-Ea/RT)$
        Aprime = 2.4686E+09   n = 1.42724   Ea = 2.3358E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	9.044E+12	3.431E+03	8.402E-05	8.125E-05
400.00	1.743E+13	5.173E+03	2.133E+00	2.201E+00
500.00	2.745E+13	7.113E+03	1.045E+03	1.081E+03
600.00	3.820E+13	9.227E+03	6.928E+04	7.055E+04
800.00	5.927E+13	1.391E+04	1.447E+07	1.426E+07
1000.00	7.782E+13	1.913E+04	3.823E+08	3.705E+08
1200.00	9.369E+13	2.482E+04	3.521E+09	3.409E+09
1500.00	1.144E+14	3.412E+04	3.370E+10	3.326E+10
2000.00	1.460E+14	5.145E+04	3.410E+11	3.557E+11

THERMODYNAMIC ANALYSIS for REACTION
Rx   CH3CL   + CL   = CH3CL-CL
Hf {Kcal/mol} -19.600   28.920   6.230
S {cal/mol K}   56.000   39.460   80.450

dHr {kcal/mol} (298K) =   -3.09   dHr avg (298., 1500. K) =   -3.53
dU (dE) {kcal/mol} (") =   -2.50   dUr avg (298., 1500. K) =   -1.74
dSr {cal/mol K} (") =   -15.01   dSr avg (298., 1500. K) =   -15.59
dGr {kcal/mol} (") =   1.39   dGr avg (298., 1500. K) =   10.49
          Af/Ar (") = 3.484E+01   Af/Ar avg (298., 1500. K) = 7.854E+01
Fit Af/Ar   : A = 8.866E-01 n = .65 alpha = 8.294E-06 avg error   .33 %
Fit Af/Ar w/ddU: A = 4.958E-02 n = 1.17 alpha = 3.057E-04 avg error   2.05 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.091E+00	-2.495E+00	-1.501E+01	3.499E+01	1.413E+00
400.00	-3.158E+00	-2.363E+00	-1.521E+01	4.235E+01	2.924E+00
500.00	-3.227E+00	-2.234E+00	-1.536E+01	4.898E+01	4.453E+00
600.00	-3.298E+00	-2.106E+00	-1.549E+01	5.507E+01	5.996E+00
800.00	-3.445E+00	-1.855E+00	-1.570E+01	6.605E+01	9.116E+00
1000.00	-3.594E+00	-1.607E+00	-1.587E+01	7.592E+01	1.227E+01
1200.00	-3.744E+00	-1.359E+00	-1.600E+01	8.506E+01	1.546E+01
1500.00	-3.963E+00	-9.824E-01	-1.617E+01	9.794E+01	2.029E+01
2000.00	-4.298E+00	-3.244E-01	-1.636E+01	1.185E+02	2.842E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = Aprime * T^n * exp(-Ea/RT)$
      Aprime = 1.0421E+10   n = 1.63527   Ea = -2.8673E+03

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.188E+14	1.124E+04	1.439E+16	1.438E+16
400.00	3.532E+14	1.799E+04	6.908E+15	6.914E+15
500.00	5.106E+14	2.591E+04	4.837E+15	4.840E+15
600.00	6.889E+14	3.492E+04	4.031E+15	4.031E+15
800.00	1.102E+15	5.589E+04	3.539E+15	3.537E+15
1000.00	1.583E+15	8.050E+04	3.554E+15	3.551E+15
1200.00	2.128E+15	1.085E+05	3.763E+15	3.762E+15
1500.00	3.063E+15	1.562E+05	4.259E+15	4.260E+15
2000.00	4.940E+15	2.501E+05	5.360E+15	5.362E+15

THERMODYNAMIC ANALYSIS for REACTION
Rx   CL2   + C2H5   = TSCCXCL2
Hf {Kcal/mol}   .000   29.300   24.200
S {cal/mol K}   53.290   57.420   84.100

dHr {kcal/mol} (298K) =   -5.10   dHr avg (298., 1500. K) =   -5.27
dU (dE) {kcal/mol} (") =   -4.51   dUr avg (298., 1500. K) =   -3.48
dSr {cal/mol K} (") =   -26.61   dSr avg (298., 1500. K) =   -26.76
dGr {kcal/mol} (") =   2.83   dGr avg (298., 1500. K) =   18.79
        Af/Ar (") =   1.016E-01   Af/Ar avg (298., 1500. K) = 2.836E-01
Fit Af/Ar   : A = 1.867E-04 n = 1.12 alpha = 2.635E-04 avg error   .86 %
Fit Af/Ar w/ddU: A = 1.389E-06 n = 2.02 alpha = 8.979E-04 avg error   2.54 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-5.100E+00	-4.504E+00	-2.661E+01	1.021E-01	2.883E+00
400.00	-5.110E+00	-4.315E+00	-2.664E+01	1.342E-01	5.546E+00
500.00	-5.108E+00	-4.114E+00	-2.663E+01	1.682E-01	8.210E+00
600.00	-5.103E+00	-3.911E+00	-2.663E+01	2.027E-01	1.087E+01
800.00	-5.112E+00	-3.523E+00	-2.664E+01	2.686E-01	1.620E+01
1000.00	-5.165E+00	-3.178E+00	-2.670E+01	3.262E-01	2.153E+01
1200.00	-5.259E+00	-2.875E+00	-2.678E+01	3.749E-01	2.688E+01
1500.00	-5.439E+00	-2.458E+00	-2.692E+01	4.382E-01	3.493E+01
2000.00	-5.700E+00	-1.726E+00	-2.707E+01	5.414E-01	4.843E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = Aprime * T^n * exp(-Ea/RT)$
        Aprime = 5.4494E+06   n = 1.89769   Ea = -5.0051E+03

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	6.388E+11	5.021E+04	1.222E+15	1.212E+15
400.00	1.119E+12	8.668E+04	2.552E+14	2.565E+14
500.00	1.753E+12	1.324E+05	1.102E+14	1.112E+14
600.00	2.535E+12	1.871E+05	6.740E+13	6.787E+13
800.00	4.480E+12	3.230E+05	4.109E+13	4.102E+13
1000.00	6.800E+12	4.933E+05	3.366E+13	3.337E+13
1200.00	9.380E+12	6.972E+05	3.132E+13	3.100E+13
1500.00	1.370E+13	1.065E+06	3.126E+13	3.111E+13
2000.00	2.257E+13	1.838E+06	3.485E+13	3.529E+13

THERMODYNAMIC ANALYSIS for REACTION
Rx   CCCL-CL = TSCCXCL2
Hf {Kcal/mol} -1.190   24.200
S {cal/mol K} 86.160   84.100

dHr {kcal/mol} (298K) =   25.39   dHr avg (298., 1500. K) =   24.79
dU (dE) {kcal/mol} (") =   25.39   dUr avg (298., 1500. K) =   24.79
dSr {cal/mol K} (") =   -2.06   dSr avg (298., 1500. K) =   -2.62
dGr {kcal/mol} (") =   26.00   dGr avg (298., 1500. K) =   27.15
       Af/Ar (") = 3.546E-01   Af/Ar avg (298., 1500. K) = 2.672E-01
Fit Af/Ar   : A = 1.312E-01 n = .22 alpha = 7.671E-04 avg error   2.66 %
Fit Af/Ar w/ddU: A = 1.292E-01 n = .25 alpha = 1.150E-03 avg error   5.57 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.539E+01	2.539E+01	-2.058E+00	3.550E-01	2.601E+01
400.00	2.541E+01	2.541E+01	-1.999E+00	3.658E-01	2.621E+01
500.00	2.540E+01	2.540E+01	-2.013E+00	3.630E-01	2.641E+01
600.00	2.537E+01	2.537E+01	-2.076E+00	3.518E-01	2.661E+01
800.00	2.522E+01	2.522E+01	-2.285E+00	3.166E-01	2.705E+01
1000.00	2.499E+01	2.499E+01	-2.547E+00	2.776E-01	2.753E+01
1200.00	2.469E+01	2.469E+01	-2.816E+00	2.424E-01	2.807E+01
1500.00	2.419E+01	2.419E+01	-3.185E+00	2.013E-01	2.897E+01
2000.00	2.334E+01	2.334E+01	-3.675E+00	1.573E-01	3.069E+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 = 1.9116E+11   n = .55094   Ea =   2.5816E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.219E+12	2.316E+01	7.040E-07	6.878E-07
400.00	3.048E+12	2.714E+01	3.974E-02	4.060E-02
500.00	3.782E+12	3.069E+01	2.971E+01	3.042E+01
600.00	4.398E+12	3.393E+01	2.523E+03	2.557E+03
800.00	5.277E+12	3.976E+01	6.790E+05	6.723E+05
1000.00	5.784E+12	4.496E+01	2.001E+07	1.957E+07
1200.00	6.062E+12	4.971E+01	1.931E+08	1.887E+08
1500.00	6.293E+12	5.621E+01	1.878E+09	1.860E+09
2000.00	6.554E+12	6.587E+01	1.844E+10	1.900E+10

THERMODYNAMIC ANALYSIS for REACTION
Rx   C2H5CL   + CL   = TSCCXCL2
Hf {Kcal/mol} -26.800   28.920   24.200
S {cal/mol K} 65.790   39.460   84.100

dHr {kcal/mol} (298K) =   22.08   dHr avg (298., 1500. K) =   21.26
dU (dE) {kcal/mol} (") =   22.67   dUr avg (298., 1500. K) =   23.04
dSr {cal/mol K} (") =   -21.15   dSr avg (298., 1500. K) =   -22.01
dGr {kcal/mol} (") =   28.39   dGr avg (298., 1500. K) =   41.05
        Af/Ar (") =   1.585E+00   Af/Ar avg (298., 1500. K) = 3.094E+00
Fit Af/Ar   : A = 6.529E-03 n = 1.01 alpha = 7.453E-04 avg error   3.13 %
Fit Af/Ar w/ddU: A = 1.869E-04 n = 1.69 alpha = 1.477E-03 avg error   8.31 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.208E+01	2.268E+01	-2.115E+01	1.596E+00	2.842E+01
400.00	2.207E+01	2.287E+01	-2.118E+01	2.100E+00	3.054E+01
500.00	2.203E+01	2.302E+01	-2.127E+01	2.497E+00	3.266E+01
600.00	2.195E+01	2.314E+01	-2.141E+01	2.793E+00	3.480E+01
800.00	2.171E+01	2.330E+01	-2.175E+01	3.146E+00	3.911E+01
1000.00	2.140E+01	2.338E+01	-2.210E+01	3.294E+00	4.350E+01
1200.00	2.103E+01	2.341E+01	-2.244E+01	3.340E+00	4.795E+01
1500.00	2.043E+01	2.341E+01	-2.288E+01	3.342E+00	5.475E+01
2000.00	1.943E+01	2.340E+01	-2.346E+01	3.328E+00	6.634E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = Aprime * T^n * exp(-Ea/RT)$
        Aprime = 3.9790E+09   n = 1.35426   Ea =   2.2629E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	9.980E+12	2.263E+03	3.007E-04	2.939E-04
400.00	1.751E+13	3.341E+03	5.616E+00	5.740E+00
500.00	2.603E+13	4.520E+03	2.255E+03	2.307E+03
600.00	3.493E+13	5.786E+03	1.299E+05	1.315E+05
800.00	5.247E+13	8.542E+03	2.257E+07	2.233E+07
1000.00	6.867E+13	1.156E+04	5.321E+08	5.208E+08
1200.00	8.355E+13	1.479E+04	4.546E+09	4.449E+09
1500.00	1.045E+14	2.001E+04	4.050E+10	4.016E+10
2000.00	1.388E+14	2.954E+04	3.846E+11	3.956E+11

THERMODYNAMIC ANALYSIS for REACTION
Rx   C2H5CL   + CL   = CCCL-CL
Hf {Kcal/mol} -26.800   28.920   -1.190
S {cal/mol K}   65.790   39.460   86.160

dHr {kcal/mol} (298K) =   -3.31   dHr avg (298., 1500. K) =   -3.53
dU (dE) {kcal/mol} (") =   -2.72   dUr avg (298., 1500. K) =   -1.75
dSr {cal/mol K} (") =   -19.09   dSr avg (298., 1500. K) =   -19.39
dGr {kcal/mol} (") =   2.38   dGr avg (298., 1500. K) =   13.90
        Af/Ar (") =   4.470E+00   Af/Ar avg (298., 1500. K) = 1.158E+01
Fit Af/Ar   : A = 4.975E-02 n = .79 alpha =-2.173E-05 avg error   .50 %
Fit Af/Ar w/ddU: A = 1.447E-03 n = 1.44 alpha = 3.272E-04 avg error   2.65 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.310E+00	-2.714E+00	-1.909E+01	4.495E+00	2.417E+00
400.00	-3.340E+00	-2.545E+00	-1.918E+01	5.742E+00	4.330E+00
500.00	-3.378E+00	-2.385E+00	-1.926E+01	6.878E+00	6.252E+00
600.00	-3.421E+00	-2.229E+00	-1.934E+01	7.939E+00	8.182E+00
800.00	-3.508E+00	-1.918E+00	-1.946E+01	9.937E+00	1.206E+01
1000.00	-3.589E+00	-1.602E+00	-1.955E+01	1.187E+01	1.597E+01
1200.00	-3.661E+00	-1.277E+00	-1.962E+01	1.377E+01	1.988E+01
1500.00	-3.759E+00	-7.789E-01	-1.969E+01	1.660E+01	2.578E+01
2000.00	-3.914E+00	5.984E-02	-1.978E+01	2.116E+01	3.565E+01

The model fitted is for bi-molecular reaction.

The 3 parameters for the model equation of $A(T) = Aprime * T^n * exp(-Ea/RT)$
        Aprime = 4.3372E+08   n = 1.80332   Ea = -3.1876E+03

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.811E+13	2.931E+04	2.670E+15	2.671E+15
400.00	4.788E+13	4.924E+04	1.178E+15	1.178E+15
500.00	7.170E+13	7.364E+04	7.907E+14	7.902E+14
600.00	9.931E+13	1.023E+05	6.439E+14	6.431E+14
800.00	1.657E+14	1.719E+05	5.540E+14	5.537E+14
1000.00	2.474E+14	2.570E+05	5.541E+14	5.545E+14
1200.00	3.446E+14	3.571E+05	5.888E+14	5.896E+14
1500.00	5.191E+14	5.340E+05	6.741E+14	6.748E+14
2000.00	8.823E+14	8.971E+05	8.691E+14	8.677E+14

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PART II

EVALUATED THERMODYNAMIC PROPERTY DATA OF C_1 AND C_2 CHLOROCARBON MOLECULES AND RADICALS

.

CHAPTER 1

ABSTRACT FOR PART TWO

Ideal gas thermodynamic parameters, $\Delta H^{\circ}_{f(298)}$, $S^{\circ}_{(298)}$ and $Cp(T)$ are evaluated for C_1 and

C_2 chlorocarbon molecules and radicals from literature data. Enthalpies of some

chlorocarbon radicals are from a combination of literature data and *ab initio* or density

functional calculations along with isodesmic reactions: for example $C\bullet H_2CH_2Cl$ is from a
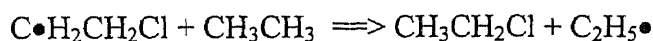
calculated ΔH_{rxn} for

$$C\bullet H_2CH_2Cl + CH_3CH_3 \Longrightarrow CH_3CH_2Cl + C_2H_5\bullet$$

and the known $\Delta H^{\circ}_{f(298)}$ for ethane, chloroethane and ethyl radical. Entropies and $Cp(T)$

values of C_2H_5 are from evaluated literature.

Evaluated thermodynamic property data are presented for all isomers of the stable

molecules CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5,

C_2Cl_6, C_2H_3Cl, $C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4.

Evaluated thermodynamic property data are also presented for the alkyl radicals,

(including isomers when they exist) $C\bullet H_2Cl$, $C\bullet HCl_2$, $C\bullet Cl_3$, $C_2H_4Cl\bullet$, $C_2H_3Cl_2\bullet$,

$C_2H_2Cl_3\bullet$, $C_2HCl_4\bullet$, and $C_2Cl_5\bullet$, for the olefin radicals (including isomers) $C_2H_2Cl\bullet$,

$C_2HCl_2\bullet$, and $C_2Cl_3\bullet$.

CHAPTER 2

INTRODUCTION FOR PART TWO

Chlorocarbons are widely used chemicals or solvents in synthesis and in chemical

industry, as cleaning agents and starting materials in synthesis of polymers, pesticides,

and other products. Many chlorocarbons are present in the atmosphere and chlorinated

organic species are present in both municipal and hazardous wastes as polyvinyl chloride

and other halogenated polymers and products. Thermodynamic properties of

chlorocarbons are important to industries utilizing them, in analysis of environmental

effects and in evaluation of kinetics or thermodynamic equilibrium for both destruction

and synthesis processes. These properties are also needed as input in kinetic modeling

and in equilibrium codes. The presence of chlorocarbon is known to slow the overall

oxidation rate of hydrocarbons through studies of flame velocity, temperature, and flame

stability.[73] Reports of studies under varied condition sets indicate that both acceleration

and inhibition effects can be observed in hydrocarbon reaction systems with a chlorinated

hydrocarbon present.[74-76] It would be of significant value to have knowledge of their

fundamental thermodynamic properties for equilibrium calculations and for an accurate

and fundamental understanding of the reaction pathways relating to chlorocarbon

formation, destruction, and interactions in synthesis, combustion, and other

environmental degradation/transformation processes.

CHAPTER 3

CALCULATION OF C_2 CHLOROCARBON RADICAL ΔH_f^{298}
FROM *AB INITIO* DATA FOR PART TWO

ΔH_{rxn} is calculated for reactions involving a number of C_2 chlorocarbon radicals when *ab initio* data are available by the G2 composite calculation method from the study of Cioslowski et al.[12]. The calculations use equations which are illustrated in the example below. $\Delta H^\circ_{f(298)}$ of evaluated experimental or accepted *ab initio* data are taken for the stable molecule species : ethane (-20.20 kcal/mole[3]), chloroethane (-26.80[3]) and for the ethyl radical (29.30[this study]). The known $\Delta H^\circ_{f(298)}$ of the three species and the calculated ΔH_{rxn} allows calculation of $\Delta H^\circ_{f(298)}$ for the target radical, $C \bullet H_2CH_2Cl$, in the example equation.

$$C \bullet H_2CH_2Cl + CH_3CH_3 \Longrightarrow CH_3CH_2Cl + C_2H_5 \bullet$$
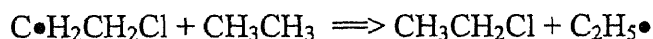
Table II.1 below is a listing of the isodesmic reactions used for the C_2 chlorocarbon radicals with G2 *ab initio* energies determined from atomization analysis reported by Cioslowski et al.[12].

This same method, isodesmic reactions for $\Delta H^\circ_{f(298)}$, is also utilized to determine $\Delta H^\circ_{f(298)}$ for C_2 chlorocarbon radicals using the density functional calculations B3LYP/6-311G** values of Cioslowski et al.[12]. We find the B3LYP/6-311G** values from isodesmic reactions yield slightly lower values than those obtained from the G2 isodesmic reactions.

We also compare these B3LYP-isodesmic reaction values and G2-isodesmic reaction

values to the direct(atomization) B3LYP values of Cioslowski et al.[12] and to our

evaluated literature data. We find a near constant bias of 2.7 kcal/mole from comparison

with the values from G2 isodesmic reaction in this work, values for Seetula's[9] or other

experimental values[29,48].

A third estimation method is the use of this constant applied to B3LYP/6-311G**

calculations of chlorocarbons. Data are listed in Table II.2.

Table 2.1 Isodesmic Reactions

$\underline{CH_3CHCl\bullet}^a + CH_3CH_3 \Longrightarrow CH_3CH_2Cl + C\bullet H_2CH_3$

$\underline{CH_2ClCH_2\bullet} + CH_3CH_3 \Longrightarrow CH_3CH_2Cl + C\bullet H_2CH_3$

$\underline{CH_3CCl_2\bullet} + CH_3CH_3 \Longrightarrow CH_3CHCl_2 + C\bullet H_2CH_3$

$\underline{CHCl_2CH_2\bullet} + CH_3CH_3 \Longrightarrow CH_3CHCl_2 + C\bullet H_2CH_3$

$\underline{CH_2ClCHCl\bullet} + CH_3CH_3 \Longrightarrow CH_2ClCH_2Cl + C\bullet H_2CH_3$

$\underline{CCl_3CH_2\bullet} + CH_3CH_3 \Longrightarrow CH_3CCl_3 + C\bullet H_2CH_3$

$\underline{CH_2ClCCl_2\bullet} + CH_3CH_3 \Longrightarrow CH_2ClCHCl_2 + C\bullet H_2CH_3$

$\underline{CHCl_2CHCl\bullet} + CH_3CH_3 \Longrightarrow CH_2ClCHCl_2 + C\bullet H_2CH_3$

$\underline{CCl_3CHCl\bullet} + CH_3CH_3 \Longrightarrow CCl_3CH_2Cl + C\bullet H_2CH_3$

$\underline{CHCl_2CCl_2\bullet} + CH_3CH_3 \Longrightarrow CHCl_2CHCl_2 + C\bullet H_2CH_3$

$\underline{C_2Cl_5\bullet} + CH_3CH_3 \Longrightarrow CCl_3CHCl_2 + C\bullet H_2CH_3$

---

[a] underlined species are the target radicals in the equations.

Table 2.2 Thermodynamic Property Data[a]

[a]UNITS : $H_f^o{}_{298}$(kcal/mol), $S^o{}_{298}$(cal/K * mol)

SPECIES	REFERENCE []	$Hf^o{}_{298}$	$S^o{}_{298}$	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
*CL	Benson[1]	28.90	39.50	5.32	5.32	5.32	5.32	5.32	5.32	5.32	0		0	CL	1	0	G	0	
	JANAF[3]	28.92	39.46	5.22	5.37	5.44	5.45	5.39	5.31	5.18	0		0	CL	1	0	G	0	
	TRC[2]	28.99	39.48	5.22	5.37	5.43	5.44	5.39	5.31	5.17	0		0	CL	1	0	G	0	
	MELIUS93[7]	29.00									0		0	CL	1	0	G	0	
	Seet98[9]	28.99									0		0	CL	1	0	G	0	
	89COX/WAG[44]	28.992+-0.002									0		0	CL	1	0	G	0	
	NJIT99	28.92	39.46	5.22	5.37	5.44	5.45	5.39	5.31	5.18	0		0	CL	1	0	G	0	
CL2	Benson[1]	0.00	53.30	8.16	8.39	8.57	8.71	8.89	8.99	9.11	0		0	CL	2	0	G	0	
	JANAF[3]	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07	0		0	CL	2	0	G	0	
	TRC[2]	0.00	53.32	8.12	8.44	8.62	8.74	8.87	8.95	9.07	0		0	CL	2	0	G	0	
	NJIT99	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07	0		0	CL	2	0	G	0	
CCL	ROD/HOP96[14]	104.30									C	1	CL	1		0	0	G	0
	85LIAS[52]	104.00									C	1	CL	1		0	0	G	0
	85CHASE[51]	120.00									C	1	CL	1		0	0	G	0
1CCL2	ROD/HOP96[14]	54.50									C	1	CL	2		0	0	G	0
	91PAULINO[41]	52.40									C	1	CL	2		0	0	G	0
	93KOHN[37]	51.00									C	1	CL	2		0	0	G	0
CCL3	BSN,RADI[1,72]	19.00	72.01	15.89	17.00	17.81	18.37	19.00	19.26	19.59	C	1	CL	3		0	0	G	0
	JANAF[3]	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	C	1	CL	3		0	0	G	0
	MELIUS93[7]	16.60									C	1	CL	3		0	0	G	0
	73MEN/GOL[63]	19.00									C	1	CL	3		0	0	G	0
	88HOL/LOS[48]	18.0 +- 2.0									C	1	CL	3		0	0	G	0
	91HUD/SEET[39]	17.0 +- 0.6									C	1	CL	3		0	0	G	0

SPECIES	REFERENCE [ ]	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS									
	ROD/HOP96[14]	18.00									C	1	CL	3			0	0	G	0
	NJIT99	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	C	1	CL	3			0	0	G	0
CCL4	SWS[4]	-22.90	74.21	19.92	21.55	22.72	23.55	24.48	24.88	25.38	C	1	CL	4			0	0	G	0
	JANAF[3]	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	C	1	CL	4			0	0	G	0
	TRC[2]	-22.90	74.09	19.98	21.92	23.09	23.82	24.64	25.05	25.50	C	1	CL	4			0	0	G	0
	MELIUS93[7]	-20.20									C	1	CL	4			0	0	G	0
	74ROD/CHAO[62]	-22.90									C	1	CL	4			0	0	G	0
	NJIT99	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	C	1	CL	4			0	0	G	0
CF3	JANAF[3]	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	C	1	F	3			0	0	G	0
	MELIUS93[7]	-112.79	65.43	12.00		15.12		17.48	18.23	19.09	C	1	F	3			0	0	G	0
	TRC[2]	-111.71	63.22	11.90	13.70	15.11	16.16	17.49	18.25	19.10	C	1	F	3			0	0	G	0
	86TSA[50]	-110.00									C	1	F	3			0	0	G	0
	ROUX/PAD87[26]	-112.00									C	1	F	3			0	0	G	0
	NJIT99	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	C	1	F	3			0	0	G	0
CF2CL	RAYEZ94[17]	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	C	1	CL	1	F	2	0	G	0
	MELIUS93[7]	-66.20									C	1	CL	1	F	2	0	G	0
	NJIT99	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	C	1	CL	1	F	2	0	G	0
CF3CL	PED&JANAF[3,27]	-168.82	68.32	16.10	18.42	20.19	21.50	23.17	24.03	24.97	C	1	CL	1	F	3	0	G	0
	JANAF[3]	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0
	TRC[2]	-168.30	68.21	16.04	18.52	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0
	MELIUS93[7]	-169.80									C	1	CL	1	F	3	0	G	0
	NJIT99	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0
CFCL2	RAYEZ94[17]	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	C	1	CL	2	F	1	0	G	0
	MELIUS93[7]	-22.80									C	1	CL	2	F	1	0	G	0
	NJIT99	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	C	1	CL	2	F	1	0	G	0

Table 2.2 (Continued)

Table 2.2 (Continued)																					
SPECIES	REFERENCE [ ]	Hf^{o}_{298}	S^{o}_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS										
CF2CL2	PED&JANAF[3,27]	-114.12	72.02	17.39	19.52	21.11	22.27	23.68	24.37	25.14	C	1	CL	2	F	2	0	G	0		
	JANAF[3]	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	C	1	CL	2	F	2	0	G	0		
	TRC[2]	-117.30	71.84	17.33	19.67	21.27	22.37	23.68	24.38	25.17	C	1	CL	2	F	2	0	G	0		
	MELIUS93[7]	-117.70									C	1	CL	2	F	2	0	G	0		
	NJIT99	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	C	1	CL	2	F	2	0	G	0		
CFCL3	PED&JANAF[3,27]	-64.12	74.12	18.78	20.66	22.04	23.03	24.20	24.73	25.32	C	1	CL	3	F	1	0	G	0		
	JANAF[3]	-69.00	74.00	18.70	20.83	22.21	23.12	24.18	24.73	25.32	C	1	CL	3	F	1	0	G	0		
	TRC[2]	-67.80	74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	C	1	CL	3	F	1	0	G	0		
	MELIUS93[7]	-67.70									C	1	CL	3	F	1	0	G	0		
	NJIT99	-67.70	74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	C	1	CL	3	F	1	0	G	0		
CH	ROD/HOP96[14]	142.40									C	1	H	1			0	G	0		
	91GREV/JAN[40]	142.50									C	1	H	1			0	G	0		
	69HERZ/JONES[70]	142.30									C	1	H	1			0	G	0		
¹CH2	ROD/HOP96[14]	102.70									C	1	H	2			0	G	0		
	78LENGEL[59]	101.70									C	1	H	2			0	G	0		
	78LENGEL[59]	102.60									C	1	H	2			0	G	0		
³CH2	ROD/HOP96[14]	93.80									C	1	H	2			0	G	0		
	78LENGEL[59]	93.60									C	1	H	2			0	G	0		
	65DIBELER[71]	93.90									C	1	H	2			0	G	0		
	78LENGEL[59]	94.10									C	1	H	2			0	G	0		
	85LEOPOLD[53]	92.80									C	1	H	2			0	G	0		
¹CHCL	ROD/HOP96[14]	76.80									C	1	H	1	CL	1	0	G	0		
	94BORN[35]	76.00									C	1	H	1	CL	1	0	G	0		
	85LIAS[52]	71.00									C	1	H	1	CL	1	0	G	0		
	85CHASE[51]	80.00									C	1	H	1	CL	1	0	G	0		

Table 2.2 (Continued)																			
SPECIES	REFERENCE []	Hf°$_{298}$	S°$_{298}$	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
^{3}CHCL	ROD/HOP96[14]	83.30									C	1	H	1	CL	1	0	G	0
	94BORN[35]	82.40									C	1	H	1	CL	1	0	G	0
	85LIAS[52]	73.00									C	1	H	1	CL	1	0	G	0
CHCL2	ROUX,RADI[26,72]	23.50	66.71	12.35	13.73	14.79	15.59	16.67	17.34	18.46	C	1	H	1	CL	2	0	G	0
	89TSC/CHE[46]	23.50	67.40	13.11		14.68		16.83	17.98	19.80	C	1	H	1	CL	2	0	G	0
	TAY/DEL91[21]	23.50	67.30	11.75		14.36		16.44	17.23	18.39	C	1	H	1	CL	2	0	G	0
	MOPAC[5]	11.04	66.78	12.41	13.91	14.97	15.72	16.74	17.42	18.45	C	1	H	1	CL	2	0	G	0
	KAFAFI89[24]		68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	C	1	H	1	CL	2	0	G	0
	MELIUS93[7]	19.50									C	1	H	1	CL	2	0	G	0
	Seet98[9]	21.27									C	1	H	1	CL	2	0	G	0
	SEET96[10]	21.27	66.92								C	1	H	1	CL	2	0	G	0
	ROUX/PAD87[26]	23.50									C	1	H	1	CL	2	0	G	0
	83WEI/BEN[54]	25.70									C	1	H	1	CL	2	0	G	0
	88HOL/LOS[48]	22.3+-2.0									C	1	H	1	CL	2	0	G	0
	ROD/HOP96[14]	22.40									C	1	H	1	CL	2	0	G	0
	NJIT99	23.50	68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	C	1	H	1	CL	2	0	G	0
CHCL3	SWS[4]	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		C	1	H	1	CL	3	0	G	0
	RAYEZ94[17]	-23.30	69.83	15.37	17.29	18.80	19.99	21.63	22.64	24.06	C	1	H	1	CL	3	0	G	0
	TRC[2]	-24.59	70.65	15.67	17.75	19.26	20.38	21.87	22.83	24.16	C	1	H	1	CL	3	0	G	0
	JANAF[3]	-24.66	70.63	15.67	17.75	19.27	20.38	21.87	22.83	24.16	C	1	H	1	CL	3	0	G	0
	MELIUS93[7]	-23.30									C	1	H	1	CL	3	0	G	0
	74ROD/CHAO[62]	-24.60									C	1	H	1	CL	3	0	G	0
	ROD/HOP96[14]	-25.40									C	1	H	1	CL	3	0	G	0
	88LIAS[47]	-25.00									C	1	H	1	CL	3	0	G	0
	NJIT99	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		C	1	H	1	CL	3	0	G	0
CH2CL	ROUX,RADI[26,72]	29.10	58.51	9.97	11.42	12.60	13.55	14.94	15.88	17.31	C	1	H	2	CL	1	0	G	0
	MOPAC[5]		58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.30	C	1	H	2	CL	1	0	G	0
	89TSC/CHE[46]	29.10	59.60	9.32		11.14		14.10	15.83	18.31	C	1	H	2	CL	1	0	G	0
	TAY/DEL91[21]	29.10	58.17	9.56		12.03		14.49	15.59	17.36	C	1	H	2	CL	1	0	G	0

Table 2.2 (Continued)

SPECIES	REFERENCE [ ]	Hf^o_{298}	S^o_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
	MELIUS93[7]	27.10									C	1	H	2	CL	1	0	G	0
	Seet98[9]	28.04									C	1	H	2	CL	1	0	G	0
	SEET96[10]	28.04	64.77								C	1	H	2	CL	1	0	G	0
	ROUX/PAD87[26]	29.10									C	1	H	2	CL	1	0	G	0
	83WEI/BEN[54]	31.10									C	1	H	2	CL	1	0	G	0
	88HOL/LOS[48]	27.7 +- 2.0									C	1	H	2	CL	1	0	G	0
	ROD/HOP96[14]	28.20									C	1	H	2	CL	1	0	G	0
	NJIT99	27.99	58.51	9.97	11.42	12.60	13.55	14.94	15.88	17.31	C	1	H	2	CL	1	0	G	0
CH2CL2	SWS[4]	-22.80	64.61	12.24	14.19	15.83	17.20	19.32	20.82	23.01	C	1	H	2	CL	2	0	G	0
	JANAF[3]	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	C	1	H	2	CL	2	0	G	0
	TRC[2]	-22.80	64.64	12.20	14.24	15.93	17.30	19.32	20.76	22.90	C	1	H	2	CL	2	0	G	0
	85CHASE[51]	-22.83	64.60								C	1	H	2	CL	2	0	G	0
	MELIUS93[7]	-22.60									C	1	H	2	CL	2	0	G	0
	74ROD/CHAO[62]	-22.80									C	1	H	2	CL	2	0	G	0
	ROD/HOP96[14]	-23.20									C	1	H	2	CL	2	0	G	0
	88LIAS[47]	-22.90									C	1	H	2	CL	2	0	G	0
	NJIT99	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	C	1	H	2	CL	2	0	G	0
CH3	JANAF[3]	34.82	46.38	9.26	10.05	10.82	11.54	12.69	14.09	16.29	C	1	H	3		0	0	G	0
	TRC[2]	35.11	46.46	9.20	9.99	10.76	11.49	12.86	14.07	16.29	C	1	H	3		0	0	G	0
	MELIUS93[7]	34.90									C	1	H	3		0	0	G	0
	Seet98[9]	34.89									C	1	H	3		0	0	G	0
	NICOVICH91[22]	35.30									C	1	H	3		0	0	G	0
	RUSS/SEET88[25]	35.37	50.91								C	1	H	3		0	0	G	0
	81HEN/KNO[56]	35.10									C	1	H	3		0	0	G	0
	NJIT99	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29	C	1	H	3		0	0	G	0
CH3CL	74ROD/CHAO[62]	-19.59	56.01	9.76	11.57	13.18	14.61	16.99	18.84	21.76	C	1	H	3	CL	1	0	G	0
	TRC[2]	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	C	1	H	3	CL	1	0	G	0
	JANAF[3]	-20.66	55.99	9.76	11.50	13.17	14.64	17.03	18.86	21.75	C	1	H	3	CL	1	0	G	0
	85CHASE[51]	-20.00	56.01								C	1	H	3	CL	1	0	G	0

Table 2.2 (Continued)

SPECIES	REFERENCE [ ]	Hf^{o}_{298}	S^{o}_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS							
	MELIUS93[7]	-20.10									C	1	H	3	CL	1	0	G	0
	74ROD/CHAO[62]	-19.60									C	1	H	3	CL	1	0	G	0
	ROD/HOP96[14]	-20.10									C	1	H	3	CL	1	0	G	0
	88LIAS[47]	-19.60									C	1	H	3	CL	1	0	G	0
	NJIT99	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	C	1	H	3	CL	1	0	G	0
C2CL3	RADICALC[72]	53.00	79.11	19.25	20.20	21.23	22.25	24.03	25.24	25.80	C	2	CL	3		0	0	G	0
	TAY/DEL91[21]	48.00	78.12	18.66		21.82		23.81	24.54	25.86	C	2	CL	3		0	0	G	0
	MELIUS93[7]	54.40									C	2	CL	3		0	0	G	0
	NJIT99	54.40	79.11	19.25	20.20	21.23	22.25	24.03	25.24	25.80	C	2	CL	3		0	0	G	0
C2CL4	SWS[4]	-3.40	81.41	22.43	24.86	26.66	27.95	29.40	29.95	30.78	C	2	CL	4		0	0	G	0
	JANAF[3]	-2.97	82.05	22.89	25.19	26.78	27.91	29.30	30.09	30.98	C	2	CL	4		0	0	G	0
	TRC[2]	-2.89	81.49	22.74	25.10	26.72	27.86	29.28	30.07	30.97	C	2	CL	4		0	0	G	0
	MOPAC[5]	(-8.081)	82.70	23.06	25.38	26.91	27.98	29.31	30.08	30.96	C	2	CL	4		0	0	G	0
	MELIUS93[7]	-5.70									C	2	CL	4		0	0	G	0
	93BEN/COH[36]	-3.40	81.45								C	2	CL	4		0	0	G	0
	CHEN/BOZ98[8]	-3.15	81.47	22.73	25.10	26.72	27.86	29.28	30.07	30.97	C	2	CL	4		0	0	G	0
	NJIT99	-3.40	81.41	22.43	24.86	26.66	27.95	29.40	29.95	30.78	C	2	CL	4		0	0	G	0
C2CL5	OLK84[28]	7.50	92.21	27.61	30.17	32.10	33.53	35.28	36.14	37.01	C	2	CL	5		0	0	G	1
	TRC[2]	8.60	95.82	27.15	30.07	31.93	33.17	34.58	35.32	36.09	C	2	CL	5		0	0	G	1
	TAY/DEL91[21]	7.70	96.37	32.04		36.34		38.04	38.43	38.63	C	2	CL	5		0	0	G	1
	MOPAC[5]	-10.50	95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	C	2	CL	5		0	0	G	1
	80WEI/BSN[57]	7.7+- 1									C	2	CL	5		0	0	G	1
	MC/GOL82[29]	8.4+- 1.9									C	2	CL	5		0	0	G	1
	CIO/LIU97[12]	9.06 G2(isodesmic)									C	2	CL	5		0	0	G	1
	CIO/LIU97[12]	7.44 B3LYP(isodesmic)									C	2	CL	5		0	0	G	1
	CIO/LIU97[12]	7.63 B3LYP(adjusted)									C	2	CL	5		0	0	G	1
	MELIUS93[7]	7.40									C	2	CL	5		0	0	G	1
	NJIT99	9.06	95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	C	2	CL	5		0	0	G	1

Table 2.2 (Continued)

SPECIES	REFERENCE [ ]	Hf^o_{298}	S^o_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
C2CL6	SWS[4]	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11		C	2	CL	6		0	0	G	1
	JANAF[3]	-32.08	95.07	33.29	36.68	38.78	40.14	41.71	42.55	43.37	C	2	CL	6		0	0	G	1
	TRC[2]	-33.20	95.33	32.76	36.21	38.40	39.82	41.48	42.38	43.31	C	2	CL	6		0	0	G	1
	CHAO74[31]	-33.20	95.30	32.76	36.21	38.40	39.82	41.48	42.38	43.34	C	2	CL	6		0	0	G	1
	83KOL/PAP[55]	-32.9, -34.7, -33.0, -36.1									C	2	CL	6		0	0	G	1
	80WEI/BSN[57]	-33.70									C	2	CL	6		0	0	G	1
	MELIUS93[7]	-32.40									C	2	CL	6		0	0	G	1
	NJIT99	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11		C	2	CL	6		0	0	G	1
CHCLCCL	RADICALC[72]	55.30	70.51	15.78	17.56	18.99	20.13	21.73	22.72	24.02	C	2	H	1	CL	2	0	G	0
	TAY/DEL91[21]	55.99	71.91	15.39		18.78		21.49	22.60	25.04	C	2	H	1	CL	2	0	G	0
	MOPAC[5]	47.72	73.62	15.53	17.35	18.72	19.78	21.31	22.37	23.89	C	2	H	1	CL	2	0	G	0
	MELIUS93[7]	56.00									C	2	H	1	CL	2	0	G	0
	NJIT99	56.00	73.62	15.53	17.35	18.72	19.78	21.31	22.37	23.89	C	2	H	1	CL	2	0	G	0
CCL2CH	RADICALC[72]	58.21	69.51	15.70	17.63	19.12	20.26	21.77	22.61	23.72	C	2	H	1	CL	2	0	G	0
	TAY/DEL91[21]	62.30	71.47	15.30		19.04		21.71	22.76	24.85	C	2	H	1	CL	2	0	G	0
	HO/BAR92[19]	58.20	68.88	17.52		22.16		25.74	26.90	28.60	C	2	H	1	CL	2	0	G	0
	MOPAC[5]	54.86	71.28	16.75	18.60	19.82	20.70	21.91	22.75	24.02	C	2	H	1	CL	2	0	G	0
	MELIUS93[7]	62.30									C	2	H	1	CL	2	0	G	0
	NJIT99	62.30	71.28	16.75	18.60	19.82	20.70	21.91	22.75	24.02	C	2	H	1	CL	2	0	G	0
C2HCL3	TRC[2]	-2.29	77.72	19.23	21.80	23.68	25.07	26.95	28.16	29.79	C	2	H	1	CL	3	0	G	0
	69STU/WES[69]	-1.40	77.63	19.22		23.75		26.80	27.60	28.98	C	2	H	1	CL	3	0	G	0
	MELIUS93[7]	-3.90									C	2	H	1	CL	3	0	G	0
	93BEN/COH[36]	-1.10	77.50								C	2	H	1	CL	3	0	G	0
	PEDLEY86[27]	-2.30									C	2	H	1	CL	3	0	G	0
	CHEN/BOZ98[8]	-1.88	77.67	19.26	21.80	23.67	25.06	26.94	28.15	29.79	C	2	H	1	CL	3	0	G	0
	NJIT99	-2.29	77.72	19.23	21.80	23.68	25.07	26.95	28.16	29.79	C	2	H	1	CL	3	0	G	0
CHCL2CCL2	RADICALC[72]	5.80	87.81	24.19	26.58	28.44	29.88	31.83	32.98	34.53	C	2	H	1	CL	4	0	G	1
(1,1,2,2)	TRC[2]	5.21	90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89	C	2	H	1	CL	4	0	G	1

Table 2.2 (Continued)																		
SPECIES	REFERENCE []	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS							
	HO/BAR92[19]	5.80	87.90	23.50		28.76		32.52	33.68	35.70	C	2	H	1	CL	4	0	G	1
	TAY/DEL91[21]	4.90	89.63	23.50		28.86		32.71	33.95	36.65	C	2	H	1	CL	4	0	G	1
	MELIUS93[7]	8.50									C	2	H	1	CL	4	0	G	1
	CIO/LIU97[12]	6.55 G2(isodesmic)									C	2	H	1	CL	4	0	G	1
	CIO/LIU97[12]	4.80 B3LYP(isodesmic)									C	2	H	1	CL	4	0	G	1
	CIO/LIU97[12]	4.99 B3LYP(adjusted)									C	2	H	1	CL	4	0	G	1
	NJIT99	6.55	90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89	C	2	H	1	CL	4	0	G	1
CCL3CHCL	THERM[6]	9.34	86.47	25.20	28.00	30.17	31.37	33.31	34.15	0.00	C	2	H	1	CL	4	0	G	1
(1,2,2,2)	TRC[2]	12.19	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25	C	2	H	1	CL	4	0	G	1
	MELIUS93[7]	11.10									C	2	H	1	CL	4	0	G	1
	CIO/LIU97[12]	11.28 G2(isodesmic)									C	2	H	1	CL	4	0	G	1
	CIO/LIU97[12]	9.59 B3LYP(isodesmic)									C	2	H	1	CL	4	0	G	1
	CIO/LIU97[12]	9.78 B3LYP(adjusted)									C	2	H	1	CL	4	0	G	1
	NJIT99	11.28	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25	C	2	H	1	CL	4	0	G	1
CHCL2CCL3	SWS[4]	-34.00	91.01	27.11	30.78	33.56	35.62	38.20	39.56	41.19	C	2	H	1	CL	5	0	G	1
	TRC[2]	-34.80	91.18	28.30	31.96	34.52	36.34	38.64	40.17	41.99	C	2	H	1	CL	5	0	G	1
	69STU/WES[69]	-38.00	90.70	28.40		34.50		38.50	39.70		C	2	H	1	CL	5	0	G	1
	CHAO74[31]	-34.80	91.16	28.30	31.96	34.52	36.35	38.71	40.17	42.04	C	2	H	1	CL	5	0	G	1
	83KOL/PAP[55]	-33.0, -34.2, -34.8									C	2	H	1	CL	5	0	G	1
	72CHAO/ROD[65]	-34.80									C	2	H	1	CL	5	0	G	1
	MELIUS93[7]	-35.20									C	2	H	1	CL	5	0	G	1
	NJIT99	-34.80	91.18	28.30	31.96	34.52	36.34	38.64	40.17	41.99	C	2	H	1	CL	5	0	G	1
CH2CCL	RADICALC[72]	60.41	63.01	11.93	14.18	15.98	17.40	19.41	20.68	22.59	C	2	H	2	CL	1	0	G	0
	HO/BAR92[19]	60.40	64.46	11.39		16.35		21.23	23.38	26.87	C	2	H	2	CL	1	0	G	0
	TAY/DEL91[21]	61.43	64.30	12.29		15.93		19.22	20.71	23.60	C	2	H	2	CL	1	0	G	0
	MOPAC[5]	52.39	62.77	13.00	14.82	16.27	17.44	19.26	20.61	22.76	C	2	H	2	CL	1	0	G	0
	MELIUS93[7]	61.40									C	2	H	2	CL	1	0	G	0
	NJIT99	61.40	62.77	13.00	14.82	16.27	17.44	19.26	20.61	22.76	C	2	H	2	CL	1	0	G	0

Table 2.2 (Continued)																			
SPECIES	REFERENCE []	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}				ELEMENTS				
CHCHCL	RADICALC[72]	63.31	62.31	12.14	14.54	16.40	17.82	19.73	20.88	22.67	C	2	H	2	CL	1	0	G	0
	TAY/DEL91[21]	64.00	64.21	12.11		15.98		19.35	20.82	23.66	C	2	H	2	CL	1	0	G	0
	MOPAC[5]	59.79	65.60	13.72	15.55	16.94	18.03	19.67	20.90	22.88	C	2	H	2	CL	1	0	G	0
	MELIUS93[7]	64.60									C	2	H	2	CL	1	0	G	0
	NJIT99	64.80	65.60	13.72	15.55	16.94	18.03	19.67	20.90	22.88	C	2	H	2	CL	1	0	G	0
CH2CCL2	TRC[2]	0.57	68.83	16.06	18.77	20.83	22.41	24.69	26.28	28.63	C	2	H	2	CL	2	0	G	0
	69STU/WES[69]	0.62	69.25	15.81		20.56		24.68	26.19	28.21	C	2	H	2	CL	2	0	G	0
	71MAN/SUN[66]	0.60									C	2	H	2	CL	2	0	G	0
	MELIUS93[7]	0.70									C	2	H	2	CL	2	0	G	0
	PEDLEY86[27]	0.62									C	2	H	2	CL	2	0	G	0
	CHEN/BOZ98[8]	0.50	67.00	16.07	18.78	20.84	22.42	24.70	26.28	28.63	C	2	H	2	CL	2	0	G	0
	93BEN/COH[36]	4.56	69.71								C	2	H	2	CL	2	0	G	0
	NJIT99	0.57	68.83	16.06	18.77	20.83	22.41	24.69	26.28	28.63	C	2	H	2	CL	2	0	G	0
CHCLCHCL	SWS[4]	1.00	69.29	15.99	18.58	20.65	22.26	24.62	26.24		C	2	H	2	CL	2	0	G	0
(trans)	TRC[2]	-0.10	69.30	15.96	18.55	20.63	22.26	24.61	26.22	28.61	C	2	H	2	CL	2	0	G	0
	69STU/WES[69]	-0.64									C	2	H	2	CL	2	0	G	0
	MELIUS93[7]	-0.60									C	2	H	2	CL	2	0	G	0
	93BEN/COH[36]	2.20	69.42								C	2	H	2	CL	2	0	G	0
	PEDLEY86[27]	1.20									C	2	H	2	CL	2	0	G	0
	CHEN/BOZ98[8]	0.70	69.29	15.96	18.55	20.63	22.25	24.58	26.22	28.63	C	2	H	2	CL	2	0	G	0
	NJIT99	-0.45	69.29	15.99	18.58	20.65	22.28	24.62	26.24		C	2	H	2	CL	2	0	G	0
Z_CHCLCHCL	SWS[4]	0.45	69.21	15.69	18.37	20.52	22.23	24.68	26.29	28.66	C	2	H	2	CL	2	0	G	0
(cis)	TRC[2]	-0.67	69.24	15.59	18.38	20.54	22.21	24.59	26.22	28.61	C	2	H	2	CL	2	0	G	0
	69STU/WES[69]	0.75	69.25	15.81		20.56		24.68	26.19	28.21	C	2	H	2	CL	2	0	G	0
	MELIUS93[7]	-1.10									C	2	H	2	CL	2	0	G	0
	93BEN/COH[36]	1.20	69.42								C	2	H	2	CL	2	0	G	0
	PEDLEY86[27]	1.10									C	2	H	2	CL	2	0	G	0
	CHEN/BOZ98[8]	0.30	69.21	15.66	18.34	20.49	22.20	24.65	26.26	28.65	C	2	H	2	CL	2	0	G	0
	NJIT99	-0.67	69.24	15.59	18.38	20.54	22.21	24.59	26.22	28.61	C	2	H	2	CL	2	0	G	0

SPECIES	REFERENCE [ ]	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}							ELEMENTS		
Table 2.2 (Continued)																			
CHCL2CHCL	RADICALC[72]	9.80	82.11	20.91	23.54	25.63	27.28	29.66	31.25	33.72	C	2	H	2	CL	3	0	G	1
(1,2,2)	TRC[2]	11.09	84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08	C	2	H	2	CL	3	0	G	1
	HO/BAR92[19]	8.50	83.10	20.21		25.68		30.14	31.77	34.50	C	2	H	2	CL	3	0	G	1
	TAY/DEL91[21]	9.80	82.23	20.94		26.42		30.20	31.59	35.02	C	2	H	2	CL	3	0	G	1
	MELIUS93[7]	10.30									C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	11.53	G2(isodesmic)								C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	9.93	B3LYP(isodesmic)								C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	10.12	B3LYP(adjusted)								C	2	H	2	CL	3	0	G	1
	NJIT99	11.53	84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08	C	2	H	2	CL	3	0	G	1
CH2CLCCL2	RADICALC[72]	7.00	81.31	20.82	23.31	25.33	26.98	29.41	31.08	33.61	C	2	H	2	CL	3	0	G	1
(1,1,2)	TRC[2]	6.31	84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77	C	2	H	2	CL	3	0	G	1
	HO/BAR92[19]	7.05	83.20	20.21		25.68		30.14	31.77	34.50	C	2	H	2	CL	3	0	G	1
	TAY/DEL91[21]	8.20	82.15	20.69		25.99		29.86	31.33	34.89	C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	7.65	G2(isodesmic)								C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	6.30	B3LYP(isodesmic)								C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	6.49	B3LYP(adjusted)								C	2	H	2	CL	3	0	G	1
	MELIUS93[7]	6.00									C	2	H	2	CL	3	0	G	1
	NJIT99	7.65	84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77	C	2	H	2	CL	3	0	G	1
CCL3CH2	RADICALC[72]	14.80	81.41	22.04	24.60	26.63	28.22	30.46	31.91	34.07	C	2	H	2	CL	3	0	G	1
(2,2,2)	TRC[2]	17.21	80.50	22.01	24.86	26.86	28.35	30.40	31.83	33.94	C	2	H	2	CL	3	0	G	1
	89ATK/BAU[45]	10.70									C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	18.39	G2(isodesmic)								C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	16.72	B3LYP(isodesmic)								C	2	H	2	CL	3	0	G	1
	CIO/LIU97[12]	16.91	B3LYP(adjusted)								C	2	H	2	CL	3	0	G	1
	MELIUS93[7]	18.80									C	2	H	2	CL	3	0	G	1
	NJIT99	18.39	80.50	22.01	24.86	26.86	28.35	30.40	31.83	33.94	C	2	H	2	CL	3	0	G	1
CH2CLCCL3	THERM[6]	-35.16	84.46	24.62	28.29	31.07	33.17	36.11	37.68		C	2	H	2	CL	4	0	G	1
(1,1,1,2)	TRC[2]	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70	C	2	H	2	CL	4	0	G	1
	SWS[4]	-37.20	86.01	27.17	30.13	32.52	34.42	37.08	38.71	40.67	C	2	H	2	CL	4	0	G	1

Table 2.2 (Continued)																			
SPECIES	REFERENCE [ ]	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
	83KOL/PAP[55]	-36.00	85.90	25.00		31.20		35.80	37.50		C	2	H	2	CL	4	0	G	1
	CHAO74[31]	-35.70	85.05	24.67	28.36	31.16	33.28	36.24	38.17	40.69	C	2	H	2	CL	4	0	G	1
	93BEN/COH[36]	-34.70	86.02								C	2	H	2	CL	4	0	G	1
	CHEN/BOZ98[8]	-35.54	84.53	24.62	28.29	31.07	33.17	36.11	38.11	40.61	C	2	H	2	CL	4	0	G	1
	MELIUS93[7]	-35.30									C	2	H	2	CL	4	0	G	1
	NJIT99	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70	C	2	H	2	CL	4	0	G	1
C2H2CL4	THERM[6]	-36.46	86.37	24.47	27.74	30.34	32.41	35.32	37.15	39.67	C	2	H	2	CL	4	0	G	1
(CHCL2CHCL2)	SWS[4]	-37.20	86.01	27.17	30.13	32.52	34.42	37.08	38.71	40.67	C	2	H	2	CL	4	0	G	1
(1,1,2,2)	TRC[2]	-35.61	84.86	23.74	27.67	30.65	32.89	35.99	38.01	40.66	C	2	H	2	CL	4	0	G	1
	MELIUS93[7]	-36.00									C	2	H	2	CL	4	0	G	1
	83KOL/PAP[55]	-37.60 +- 0.72									C	2	H	2	CL	4	0	G	1
	94Lide[33]	-35.66									C	2	H	2	CL	4	0	G	1
	93BEN/COH[36]	-35.80	86.02								C	2	H	2	CL	4	0	G	1
	PEDLEY86[27]	-35.66									C	2	H	2	CL	4	0	G	1
	CHEN/BOZ98[8]	-36.98	86.29	24.03	27.85	30.80	33.00	36.08	38.03	39.59	C	2	H	2	CL	4	0	G	1
	NJIT99	-36.00	84.86	23.74	27.67	30.65	32.89	35.99	38.01	40.66	C	2	H	2	CL	4	0	G	1
C2H3	THERM[6]	71.62	56.61	10.09	11.98	13.61	15.02	17.30	19.03	21.82	C	2	H	3		0	0	G	0
	LAY/BOZ95[16]	71.64	53.79	10.10	11.93	13.57	14.97	17.22	18.95		C	2	H	3		0	0	G	0
	MOPAC[5]	62.98	54.79	11.11	12.91	14.37	15.58	17.53	19.08	21.72	C	2	H	3		0	0	G	0
	MELIUS93[7]	71.00									C	2	H	3		0	0	G	0
	DEFREES80[30]	71.50									C	2	H	3		0	0	G	0
	70BENSON[68]	69.00									C	2	H	3		0	0	G	0
	79ROSS/GOL[58]	64.00									C	2	H	3		0	0	G	0
	NJIT99	71.64	53.79	10.10	11.93	13.57	14.97	17.22	18.95		C	2	H	3		0	0	G	0
CH2CHCL	TRC[2]	6.81	63.12	12.86	15.54	17.77	19.58	22.33	24.33	27.43	C	2	H	3	CL	1	0	G	0
	69STU/WES[69]	5.00	63.09	12.33		17.73		22.47	24.26	26.88	C	2	H	3	CL	1	0	G	0
	SWS[4]	8.40	63.08	12.89	15.56	17.80	19.61	22.35	24.35		C	2	H	3	CL	1	0	G	0
	Gluk97(G2)	5.21									C	2	H	3	CL	1	0	G	0
	COL/THOM97[11]	5.00									C	2	H	3	CL	1	0	G	0

Table 2.2 (Continued)

SPECIES	REFERENCE []	Hf°$_{298}$	S°$_{298}$	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
	88LIAS[47]	5.5 +- 0.478									C	2	H	3	CL	1	0	G	0
	MELIUS93[7]	4.70									C	2	H	3	CL	1	0	G	0
	NJIT99	5.00	63.08	12.89	15.56	17.80	19.61	22.35	24.35		C	2	H	3	CL	1	0	G	0
CH2CLCHCL	RADICALC[72]	11.40	75.71	17.67	20.11	22.27	24.16	27.26	29.57	32.89	C	2	H	3	CL	2	0	G	1
(1,2) a,b	TRC[2]	15.61	78.56	18.33	21.15	23.40	25.19	27.82	29.73	32.70	C	2	H	3	CL	2	0	G	1
	HO/BAR92[19]	11.49	75.80	16.81		22.56		27.67	29.75	33.21	C	2	H	3	CL	2	0	G	1
	TAY/DEL91[21]	13.30	77.00	18.39		23.37		27.97	29.94	34.78	C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	14.65	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	13.43	B3LYP(isodesmic)								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	13.62	B3LYP(adjusted)								C	2	H	3	CL	2	0	G	1
	MELIUS93[7]	13.10									C	2	H	3	CL	2	0	G	1
	NJIT99	14.65	78.56	18.33	21.15	23.40	25.19	27.82	29.73	32.70	C	2	H	3	CL	2	0	G	1
CH3CCL2	RADICALC[72]	11.30	73.61	17.16	20.31	22.97	25.20	28.59	30.88	33.73	C	2	H	3	CL	2	0	G	1
(1,1) a,a	TRC[2]	10.21	76.12	18.02	20.63	22.80	24.62	27.37	29.40	32.50	C	2	H	3	CL	2	0	G	1
	HO/BAR92[19]	10.50	73.60	17.28		22.86		28.09	30.18	33.09	C	2	H	3	CL	2	0	G	1
	CHEN/ROUX92[18]	11.75	75.18	18.17	20.75	22.91	24.70	27.48	29.51	32.60	C	2	H	3	CL	2	0	G	1
	Seet98[9]	10.16									C	2	H	3	CL	2	0	G	1
	SEET96[10]	10.16	68.83								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	12.43	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	12.40	B3LYP(isodesmic)								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	12.59	B3LYP(adjusted)								C	2	H	3	CL	2	0	G	1
	MELIUS93[7]	10.30									C	2	H	3	CL	2	0	G	1
	NJIT99	12.43	75.18	18.17	20.75	22.91	24.70	27.48	29.51	32.60	C	2	H	3	CL	2	0	G	1
CHCL2CH2	RADICALC[72]	16.00	77.31	17.92	20.85	23.23	25.17	28.04	30.01	32.97	C	2	H	3	CL	2	0	G	1
(2,2) b,b	TRC[2]	19.31	74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	C	2	H	3	CL	2	0	G	1
	HO/BAR92[19]	16.40	74.30	17.35		22.95		28.03	30.29	33.07	C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	20.31	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	18.86	B3LYP(isodesmic)								C	2	H	3	CL	2	0	G	1
	CIO/LIU97[12]	19.05	B3LYP(adjusted)								C	2	H	3	CL	2	0	G	1

Table 2.2 (Continued)																		
SPECIES	REFERENCE [ ]	Hf^o_{298}	S^o_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS							
	MELIUS93[7]	20.20									C	2	H	3	CL	2	0	G	1
	NJIT99	20.31	74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	C	2	H	3	CL	2	0	G	1
CH2CLCHCL2	TRC[2]	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	C	2	H	3	CL	3	0	G	1
(1,1,2)	69STU/WES[69]	-33.10	80.57	21.34		27.92		33.28	35.42	38.91	C	2	H	3	CL	3	0	G	1
	83KOL/PAP[55]	-34.58 +- 0.45									C	2	H	3	CL	3	0	G	1
	94Lide[33]	-36.14									C	2	H	3	CL	3	0	G	1
	MELIUS93[7]	-33.90									C	2	H	3	CL	3	0	G	1
	93BEN/COH[36]	-34.60	81.50								C	2	H	3	CL	3	0	G	1
	PEDLEY86[27]	-34.80									C	2	H	3	CL	3	0	G	1
	CHEN/BOZ98[8]	-33.99	81.22	21.31	24.85	27.65	29.81	33.00	35.03	38.09	C	2	H	3	CL	3	0	G	1
	NJIT99	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	C	2	H	3	CL	3	0	G	1
CH3CCL3	TRC[2]	-34.01	76.51	22.14	25.72	28.52	30.68	33.75	35.81	38.80	C	2	H	3	CL	3	0	G	1
(1,1,1)	PEDLEY86[27]	-30.90	78.60	22.52		28.45		33.70	35.73	38.91	C	2	H	3	CL	3	0	G	1
	CHAO74[31]	-34.01	76.49	22.07							C	2	H	3	CL	3	0	G	1
	83KOL/PAP[55]	-34.56+- 0.19									C	2	H	3	CL	3	0	G	1
	MELIUS93[7]	-33.60									C	2	H	3	CL	3	0	G	1
	NJIT99	-34.01	76.51	22.14	25.72	28.52	30.68	33.75	35.81	38.80	C	2	H	3	CL	3	0	G	1
C2H4	JANAF[3]	12.54	52.40	10.29	12.68	14.93	16.89	20.04	22.44	26.29	C	2	H	4		0	0	G	0
	SWS[4]	12.50	52.45	10.45	12.90	15.16	17.10	20.20	22.57		C	2	H	4		0	0	G	0
	MELIUS93[7]	12.30									C	2	H	4		0	0	G	0
	NJIT99	12.54	52.40	10.29	12.68	14.93	16.89	20.04	22.44	26.29	C	2	H	4		0	0	G	0
CH3CHCL	TRC[2]	18.50	68.69	14.65	17.28	19.67	21.70	24.93	27.37	31.24	C	2	H	4	CL	1	0	G	1
a	89TSC/CHE[46]	17.51	67.31	14.10		19.79		25.42	27.99	32.50	C	2	H	4	CL	1	0	G	1
	CHEN/ROUX92[18]	18.26	68.86	14.84	17.57	20.00	22.05	25.29	27.72	31.51	C	2	H	4	CL	1	0	G	1
	Seet98[9]	18.28									C	2	H	4	CL	1	0	G	1
	SEET96[10]	18.28	66.68								C	2	H	4	CL	1	0	G	1
	88HOL/LOS[48]	19.3+-2.0									C	2	H	4	CL	1	0	G	1
	CIO/LIU97[12]	19.18 G2(isodesmic)									C	2	H	4	CL	1	0	G	1

												ELEMENTS								
Table 2.2 (Continued)																				
SPECIES	REFERENCE [ ]	Hf$^{o}_{298}$	S$^{o}_{298}$	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}										
	CIO/LIU97[12]	19.09	B3LYP(isodesmic)								C	2	H	4	CL	1	0	G	1	
	CIO/LIU97[12]	19.25	B3LYP(adjusted)								C	2	H	4	CL	1	0	G	1	
	MELIUS93[7]	18.20									C	2	H	4	CL	1	0	G	1	
	MIYO/ROUX90[23]	17.60									C	2	H	4	CL	1	0	G	1	
	NJIT99	19.18	68.86	14.84	17.57	20.00	22.05	25.29	27.72	31.51	C	2	H	4	CL	1	0	G	1	
CH2CLCH2	TRC[2]	22.39	68.00	15.65	18.55	20.96	22.92	25.88	28.08	31.57	C	2	H	4	CL	1	0	G	1	
b	HO/BAR92[19]	20.78	68.50	14.01		20.09		25.88	28.98	33.44	C	2	H	4	CL	1	0	G	1	
	CHEN/ROUX92[18]	22.44	69.07	15.51	18.09	20.37	22.30	25.37	27.71	31.44	C	2	H	4	CL	1	0	G	1	
	Seet98[9]	22.23									C	2	H	4	CL	1	0	G	1	
	88HOL/LOS[48]	22.8 +- 2.0									C	2	H	4	CL	1	0	G	1	
	CIO/LIU97[12]	23.20	G2(isodesmic)								C	2	H	4	CL	1	0	G	1	
	CIO/LIU97[12]	21.97	B3LYP(isodesmic)								C	2	H	4	CL	1	0	G	1	
	CIO/LIU97[12]	22.16	B3LYP(adjusted)								C	2	H	4	CL	1	0	G	1	
	MELIUS93[7]	23.00									C	2	H	4	CL	1	0	G	1	
	MIYO/ROUX90[23]	21.80									C	2	H	4	CL	1	0	G	1	
	NJIT99	23.20	69.07	15.51	18.09	20.37	22.30	25.37	27.71	31.44	C	2	H	4	CL	1	0	G	1	
CH2CLCH2CL	TRC[2]	-30.31	73.12	18.54	21.95	24.96	27.45	31.16	33.78	37.64	C	2	H	4	CL	2	0	G	1	
	69STU/WES[69]	-31.00	73.66	18.99		24.74		30.32	33.06	38.79	C	2	H	4	CL	2	0	G	1	
	83KOL/PAP[55]	-32.1+- 0.3									C	2	H	4	CL	2	0	G	1	
	94Lide[33]	-30.33									C	2	H	4	CL	2	0	G	1	
	93BEN/COH[36]	-33.40	76.34								C	2	H	4	CL	2	0	G	1	
	PEDLEY86[27]	-30.33									C	2	H	4	CL	2	0	G	1	
	CHEN/BOZ98[8]	-31.05	75.05	18.23	21.54	24.39	26.70	30.25	32.89	36.94	C	2	H	4	CL	2	0	G	1	
	MELIUS93[7]	-32.40	75.05								C	2	H	4	CL	2	0	G	1	
	NJIT99	-31.22	73.12	18.54	21.95	24.96	27.45	31.16	33.78	37.64	C	2	H	4	CL	2	0	G	1	
CH3CHCL2	TRC[2]	-31.09	72.94	18.32	21.84	24.79	27.18	30.79	33.40	37.40	C	2	H	4	CL	2	0	G	1	
	69STU/WES[69]	-31.05	72.89	18.29		24.81		30.87	33.44	37.80	C	2	H	4	CL	2	0	G	1	
	CHAO74[31]	-31.10	72.88	18.24							C	2	H	4	CL	2	0	G	1	
	83KOL/PAP[55]	-31.2+- 0.7									C	2	H	4	CL	2	0	G	1	

Table 2.2 (Continued)

SPECIES	REFERENCE []	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS								
	94Lide[33]	-30.52									C	2	H	4	CL	2	0	G	1
	MELIUS93[7]	-32.10									C	2	H	4	CL	2	0	G	1
	93BEN/COH[36]	-27.90	71.82								C	2	H	4	CL	2	0	G	1
	PEDLEY86[27]	-30.52									C	2	H	4	CL	2	0	G	1
	CHEN/BOZ98[8]	-31.04	73.03	18.18	21.82	24.93	27.41	31.11	33.57	37.01	C	2	H	4	CL	2	0	G	1
	NJIT99	-31.09	72.94	18.32	21.84	24.79	27.18	30.79	33.40	37.40	C	2	H	4	CL	2	0	G	1
C2H5	TRC[2]	25.91	58.87	12.44	15.05	17.47	19.60	23.13	25.90	30.37	C	2	H	5			0	G	1
	90SANDIA[42]	28.02	60.14	11.32	13.60	15.59	18.29	22.58	25.50	29.56	C	2	H	5			0	G	1
	90CHEN[43]		59.30	12.11	14.91	17.39	19.58	23.20	25.98	30.41	C	2	H	5			0	G	1
	86TSANG[49]		59.37	12.13	14.66	17.18	19.22	22.84	25.65	30.24	C	2	H	5			0	G	1
	94BURCAT[34]	28.36	59.06	12.07							C	2	H	5			0	G	1
	92COHEN[38]		59.23	12.18	14.80	17.24	19.42	23.01	25.82	30.33	C	2	H	5			0	G	1
	LAY/BOZ95[16]	28.80	57.42	11.89	14.57	16.95	19.09	22.76	25.66		C	2	H	5			0	G	1
	Seet98[9]	28.85									C	2	H	5			0	G	1
	SEAKINS92[20]	28.92+- 0.36									C	2	H	5			0	G	1
	CIO/LIU97[12]	29.30 (this study)									C	2	H	5			0	G	1
	CIO/LIU97[12]	29.49 B3LYP(adjusted)									C	2	H	5			0	G	1
	MELIUS93[7]	28.80									C	2	H	5			0	G	1
	NICOVICH91[22]	29.10									C	2	H	5			0	G	1
	RUSS/SEET88[25]	28.68	62.14								C	2	H	5			0	G	1
	NJIT99	29.30	57.42	11.89	14.57	16.95	19.09	22.76	25.66		C	2	H	5			0	G	1
C2H5CL	JANAF[3]	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	C	2	H	5	CL	1	0	G	1
	TRC[2]	-26.84	65.94	15.04	18.54	21.66	24.28	28.38	31.43	36.17	C	2	H	5	CL	1	0	G	1
	HO/BAR92[19]	-26.83	66.03	15.06		21.67		28.43	31.47	36.27	C	2	H	5	CL	1	0	G	1
	CHAO74[31]	-26.83	65.91	14.97							C	2	H	5	CL	1	0	G	1
	88LIAS[47]	-26.79	65.96								C	2	H	5	CL	1	0	G	1
	71FLET/PIL[67]	-26.83									C	2	H	5	CL	1	0	G	1
	83KOL/PAP[55]	-26.8+- 0.2									C	2	H	5	CL	1	0	G	1
	MELIUS93[7]	-27.20									C	2	H	5	CL	1	0	G	1
	NJIT99	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	C	2	H	5	CL	1	0	G	1

Table 2.2 (Continued)											ELEMENTS									
SPECIES	REFERENCE [ ]	Hf^o_{298}	S^o_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}										
C2H6	JANAF[3]	-20.20	54.81	12.54	15.78	18.70	21.33	25.78	29.29	34.87	C	2	H	6		0	0	G	1	
	83KOL/PAP[55]	-20.1 +- 0.1									C	2	H	6		0	0	G	1	
	MELIUS93[7]	-20.80	(staggered)								C	2	H	6		0	0	G	1	
	73CHAO/WIL[64]	-20.24									C	2	H	6		0	0	G	1	
	NJIT99	-20.20	54.81	12.54	15.78	18.70	21.33	25.78	29.29	34.87	C	2	H	6		0	0	G	1	
CH3CF3	ZAC/TSANG96[15]	-180.54									C	2	H	3	F	3	0	G	1	
	CHEN/ROD75[32]	-178.20									C	2	H	3	F	3	0	G	1	
	MELIUS93[7]	-180.53									C	2	H	3	F	3	0	G	1	
	PEDLEY86[27]	-177.94									C	2	H	3	F	3	0	G	1	
	SWS[4]	-178.20									C	2	H	3	F	3	0	G	1	
CH2CF3	ZAC/TSANG96[15]	-125.86									C	2	H	2	F	3	0	G	1	
	78RODGERS[60]	-123.59									C	2	H	2	F	3	0	G	1	
	MELIUS93[7]	-125.90									C	2	H	2	F	3	0	G	1	
CH3CF2CL	MELIUS93[7]	-128.70									C	2	H	3	F	2	CL	1	G	1
	78PAP/KOL[61]	-126.60									C	2	H	3	F	2	CL	1	G	1
	THERM[6]	-127.51									C	2	H	3	F	2	CL	1	G	1
CH2CF2CL	MELIUS93[7]	-75.40									C	2	H	2	F	2	CL	1	G	1
CH3CFCL2	MELIUS93[7]	-79.67									C	2	H	3	F	1	CL	2	G	1
CH2CFCL2	MELIUS93[7]	-25.80									C	2	H	2	F	1	CL	2	G	1

| Table 2.3 | Selected Thermodynamic Property Data[a] | | | | | | | | | | | | | | | | | | |

SPECIES	REFERENCE [ ]	$H_f^\circ{}_{298}$	$S^\circ{}_{298}$	C_p^{300}	C_p^{400}	C_p^{500}	C_p^{600}	C_p^{800}	C_p^{1000}	C_p^{1500}	ELEMENTS								
*CL	JANAF[3]	28.92	39.46	5.22	5.37	5.44	5.45	5.39	5.31	5.18		0		0	CL	1	0	G	0
CL2	JANAF[3]	0.00	53.29	8.12	8.44	8.62	8.74	8.88	8.96	9.07		0		0	CL	2	0	G	0
CCL3	JANAF[3]	19.00	70.92	15.25	16.66	17.56	18.16	18.83	19.18	19.56	C	1	CL	3		0	0	G	0
CCL4	JANAF[3]	-22.94	74.02	19.98	21.92	23.09	23.82	24.64	25.05	25.47	C	1	CL	4		0	0	G	0
CF3	JANAF[3]	-113.01	63.42	11.93	13.68	15.05	16.09	17.46	18.22	19.07	C	1	F	3		0	0	G	0
CF2CL	RAYEZ94[17]	-66.02	67.72	13.17	14.73	15.93	16.83	17.98	18.59	19.25	C	1	CL	1	F	2	0	G	0
CF3CL	JANAF[3]	-169.20	68.17	16.04	18.53	20.32	21.59	23.16	24.02	24.98	C	1	CL	1	F	3	0	G	0
CFCL2	RAYEZ94[17]	-21.60	69.17	14.02	15.42	16.49	17.28	18.26	18.77	19.34	C	1	CL	2	F	1	0	G	0
CF2CL2	JANAF[3]	-117.50	71.91	17.36	19.68	21.28	22.37	23.68	24.39	25.16	C	1	CL	2	F	2	0	G	0
CFCL3	MELIUS93[7]	-67.70									C	1	CL	3	F	1	0	G	0
	TRC[2]		74.07	18.71	20.84	22.22	23.13	24.19	24.74	25.33	C	1	CL	3	F	1	0	G	0
CHCL2	89TSC/CHE[46]	23.50									C	1	H	1	CL	2	0	G	0
	KAFAFI89[24]		68.10	12.90	14.16	15.09	15.79	16.76	17.44	18.46	C	1	H	1	CL	2	0	G	0
CHCL3	SWS[4]	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86		C	1	H	1	CL	3	0	G	0
CH2CL	AVG[7,9,21,48]	27.99									C	1	H	2	CL	1	0	G	0
	MOPAC[5]		58.61	10.08	11.45	12.53	13.38	14.66	15.64	17.30	C	1	H	2	CL	1	0	G	0
CH2CL2	JANAF[3]	-22.83	64.57	12.20	14.24	15.93	17.30	19.32	20.76	22.91	C	1	H	2	CL	2	0	G	0
CH3	JANAF[3]	34.82	46.38	9.26	10.05	10.82	11.54	12.89	14.09	16.29	C	1	H	3		0	0	G	0
CH3CL	TRC[2]	-19.60	56.00	9.77	11.51	13.19	14.66	17.05	18.87	21.76	C	1	H	3	CL	1	0	G	0
C2CL3	MELIUS93[7]	54.40									C	2	CL	3		0	0	G	0
	RADICALC[72]		79.11	19.25	20.20	21.23	22.25	24.03	25.24	25.80	C	2	CL	3		0	0	G	0
C2CL4	SWS[4]	-3.40	81.41	22.43	24.86	26.66	27.95	29.40	29.95	30.78	C	2	CL	4		0	0	G	0
C2CL5	CIO/LIU97[12]	9.06	G2(isodesmic)								C	2	CL	5		0	0	G	1
	MOPAC[5]		95.68	28.56	31.13	32.72	33.75	34.93	35.54	36.20	C	2	CL	5		0	0	G	1
C2CL6	SWS[4]	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11		C	2	CL	6		0	0	G	1
CHCLCCL	MELIUS93[7]	56.00									C	2	H	1	CL	2	0	G	0
	MOPAC[5]		73.62	15.53	17.35	18.72	19.78	21.31	22.37	23.89	C	2	H	1	CL	2	0	G	0

SPECIES	REFERENCE [ ]	Hf°_{298}	S°_{298}	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}				ELEMENTS					
CCL2CH	MELIUS93[7]	62.30									C	2	H	1	CL	2	0	G	0
	MOPAC[5]		71.28	16.75	18.60	19.82	20.70	21.91	22.75	24.02	C	2	H	1	CL	2	0	G	0
C2HCL3	TRC[2]	-2.29	77.72	19.23	21.80	23.68	25.07	26.95	28.16	29.79	C	2	H	1	CL	3	0	G	0
CHCL2CCL2	CIO/LIU97[12]	6.55	G2(isodesmic)								C	2	H	1	CL	4	0	G	1
(1,1,2,2)	TRC[2]		90.65	23.88	26.74	28.78	30.23	32.15	33.32	34.89	C	2	H	1	CL	4	0	G	1
CCL3CHCL	CIO/LIU97[12]	11.28	G2(isodesmic)								C	2	H	1	CL	4	0	G	1
(1,2,2,2)	TRC[2]	12.19	88.26	25.57	28.51	30.38	31.62	33.13	34.03	35.25	C	2	H	1	CL	4	0	G	1
CHCL2CCL3	TRC[2]	-34.80	91.18	28.30	31.96	34.52	36.34	38.64	40.17	41.99	C	2	H	1	CL	5	0	G	1
CH2CCL	MELIUS93[7]	61.40									C	2	H	2	CL	1	0	G	0
	MOPAC[5]		62.77	13.00	14.82	16.27	17.44	19.26	20.61	22.76	C	2	H	2	CL	1	0	G	0
CHCHCL	MELIUS93[7]	64.80									C	2	H	2	CL	1	0	G	0
	MOPAC[5]		65.60	13.72	15.55	16.94	18.03	19.67	20.90	22.88	C	2	H	2	CL	1	0	G	0
CH2CCL2	TRC[2]	0.57	68.83	16.06	18.77	20.83	22.41	24.69	26.28	28.63	C	2	H	2	CL	2	0	G	0
CHCLCHCL	AVG[2,7,69]	-0.45									C	2	H	2	CL	2	0	G	0
(trans)	SWS[4]		69.29	15.99	18.58	20.65	22.28	24.62	26.24		C	2	H	2	CL	2	0	G	0
Z_CHCLCHCL	TRC[2]	-0.67	69.24	15.59	18.38	20.54	22.21	24.59	26.22	28.61	C	2	H	2	CL	2	0	G	0
(cis)																			
CHCL2CHCL	CIO/LIU97[12]	11.53	G2(isodesmic)								C	2	H	2	CL	3	0	G	1
(1,2,2)	TRC[2]		84.51	21.49	24.59	26.84	28.49	30.64	32.05	34.08	C	2	H	2	CL	3	0	G	1
CH2CLCCL2	CIO/LIU97[12]	7.65	G2(isodesmic)								C	2	H	2	CL	3	0	G	1
(1,1,2)	TRC[2]		84.56	21.39	24.09	26.15	27.70	29.95	31.50	33.77	C	2	H	2	CL	3	0	G	1
CCL3CH2	CIO/LIU97[12]	18.39	G2(isodesmic)								C	2	H	2	CL	3	0	G	1
(2,2,2)	TRC[2]		80.50	22.01	24.86	26.86	28.35	30.40	31.83	33.94	C	2	H	2	CL	3	0	G	1
CH2CLCCL3	TRC[2]	-35.71	85.07	24.67	28.36	31.16	33.28	36.24	38.17	40.70	C	2	H	2	CL	4	0	G	1
(1,1,1,2)																			
C2H2CL4	MELIUS93[7]	-36.00									C	2	H	2	CL	4	0	G	1
(CHCL2CHCL2)	TRC[2]		84.86	23.74	27.67	30.65	32.89	35.99	38.01	40.66	C	2	H	2	CL	4	0	G	1
(1,1,2,2)																			
C2H3	LAY/BOZ95[16]	71.64	53.79	10.10	11.93	13.57	14.97	17.22	18.95		C	2	H	3			0	0	G	0
CH2CHCL	COL/THOM97[11]	5.00									C	2	H	3	CL	1	0	G	0
	SWS[4]		63.08	12.89	15.56	17.80	19.61	22.35	24.35		C	2	H	3	CL	1	0	G	0

Table 2.3 (Continued)

Table 2.3 (Continued)																		
SPECIES	REFERENCE [ ]	$Hf°_{298}$	$S°_{298}$	Cp^{300}	Cp^{400}	Cp^{500}	Cp^{600}	Cp^{800}	Cp^{1000}	Cp^{1500}	ELEMENTS							
CH2CLCHCL	CIO/LIU97[12]	14.65	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
(1,2) a,b	TRC[2]		78.56	18.33	21.15	23.40	25.19	27.82	29.73	32.70	C	2	H	3	CL	2	0	G	1
CH3CCL2	CIO/LIU97[12]	12.43	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
(1,1) a,a	CHEN/ROUX92[18]		75.18	18.17	20.75	22.91	24.70	27.48	29.51	32.60	C	2	H	3	CL	2	0	G	1
CHCL2CH2	CIO/LIU97[12]	20.31	G2(isodesmic)								C	2	H	3	CL	2	0	G	1
(2,2) b,b	TRC[2]		74.64	18.95	21.99	24.28	26.05	28.54	30.31	33.01	C	2	H	3	CL	2	0	G	1
CH2CLCHCL2	TRC[2]	-34.80	79.71	20.40	24.47	27.74	30.29	33.85	36.15	39.29	C	2	H	3	CL	3	0	G	1
(1,1,2)																			
CH3CCL3	TRC[2]	-34.01	76.51	22.14	25.72	28.52	30.68	33.75	35.81	38.80	C	2	H	3	CL	3	0	G	1
(1,1,1)																			
C2H4	JANAF[3]	12.54	52.40	10.29	12.68	14.93	16.89	20.04	22.44	26.29	C	2	H	4		0	0	G	0
CH3CHCL	CIO/LIU97[12]	19.18	G2(isodesmic)								C	2	H	4	CL	1	0	G	1
a	CHEN/ROUX92[18]		68.86	14.84	17.57	20.00	22.05	25.29	27.72	31.51	C	2	H	4	CL	1	0	G	1
CH2CLCH2	CIO/LIU97[12]	23.20	G2(isodesmic)								C	2	H	4	CL	1	0	G	1
b	CHEN/ROUX92[18]		69.07	15.51	18.09	20.37	22.30	25.37	27.71	31.44	C	2	H	4	CL	1	0	G	1
CH2CLCH2CL	AVG[33,55]	-31.22									C	2	H	4	CL	2	0	G	1
	TRC[2]		73.12	18.54	21.95	24.96	27.45	31.16	33.78	37.64	C	2	H	4	CL	2	0	G	1
CH3CHCL2	TRC[2]	-31.09	72.94	18.32	21.84	24.79	27.18	30.79	33.40	37.40	C	2	H	4	CL	2	0	G	1
C2H5	CIO/LIU97[12]	29.30	(this study)								C	2	H	5		0	0	G	1
	LAY/BOZ95[16]		57.42	11.89	14.57	16.95	19.09	22.76	25.66		C	2	H	5		0	0	G	1
C2H5CL	JANAF[3]	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16	C	2	H	5	CL	1	0	G	1
C2H6	JANAF[3]	-20.20	54.81	12.54	15.78	18.70	21.33	25.78	29.29	34.87	C	2	H	6		0	0	G	1

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PART III

THERMOCHEMICAL AND KINETIC ANALYSIS
ON $CH_3CjO + O_2$ REACTION

CHAPTER 1

ABSTRACT FOR PART THREE

Reaction pathways and kinetics are analyzed on $CH_3CjO + O_2$ reaction system using

density functional and *ab initio* calculations to determine thermodynamic properties

of reactants, intermediate radicals, and transition state (TS) structures. Enthalpies of

formation ($\Delta H_f°_{298}$) are determined using the CBSQ composite method and also by

density functional calculations with isodesmic reactions for radical species. Entropies

($S°_{298}$) and heat capacities ($Cp°(T)$ 300 –1500 K) are determined using geometric

parameters and vibrational frequencies obtained at the HF/6-31G(d') level of theory.

Quantum Rice-Ramsperger-Kassel (QRRK) analysis is used to calculate energy

dependent rate constants, k(E). The acetyl radical CH_3CjO adds to O_2 to form a

CCOQj peroxy radical ($\Delta H_f°_{298}$ = -38.75 kcal/mole in CBSQ). The peroxy radical

can undergo dissociation back to reactants, decompose to products, $CH_2CO + HO_2$

via HO_2 elimination (Ea,rxn = 28.01 kcal/mole in CBSQ) or isomerize via hydrogen

shift (Ea,rxn = 26.93 kcal/mole in CBSQ) to form a CjCOQ isomer ($\Delta H_f°_{298}$ = -32.35

kcal/mole in CBSQ). This isomer CjCOQ can undergo β-scission to products,

$CH_2CO + HO_2$ (Ea,rxn = 31.53 kcal/mole in CBSQ) or decompose to CyCOC=O +

OH via OH elimination (Ea,rxn = 23.08 kcal/mole in CBSQ). Rate constants are

estimated as function of pressure and temperature using QRRK analysis for k(E) and

modified strong collision analysis for fall-off. Important reactions are stabilization of

CCOQj peroxy adduct at low temperature and $CH_2CO + HO_2$ and oxirane aldehyde +

OH at high temperature. Rate constants at 1atm pressure are ($k=A(T/K)^n\exp(-Ea/RT)$), A in $cm^3/(mole\text{-}s)$, Ea in kcal/mole): $k_1=(6.93\times10^{43})(T/K)^{-10.29}\,e^{-8.28/RT}$ for $CH_3CjO + O_2 \Rightarrow CCOQj$; $k_6=(3.65\times10^{18})(T/K)^{-1.78}\,e^{-6.29/RT}$ for $CH_3CjO + O_2 \Rightarrow CH_2CO + HO_2$; $k_7=(2.09\times10^{27})(T/K)^{-4.45}\,e^{-13.44/RT}$ for $CH_3CjO + O_2 \Rightarrow CyCOC{=}O + OH$; $k_8=(8.42\times10^{40})(T/K)^{-9.17}\,e^{-12.47/RT}$ for $CH_3CjO + O_2 \Rightarrow CjCOQ$

CHAPTER 2

INTRODUCTION FOR PART THREE

Important initial products from pyrolysis, oxidation, or photochemical reactions of saturated and unsaturated hydrocarbons are the corresponding radicals. The subsequent reactions of the hydrocarbon radicals with molecular oxygen are complex and difficult to study experimentally and present a source of controversy with regard to both pathway and reactions rates. These reactions, furthermore, represent the principal pathways of the radical conversion in many hydrocarbon oxidation and combustion processes[1,2] and also in atmosphere.

The currently accepted OH radical chain mechanism for oxidation of volatile organic compounds (VOC) during night-time conditions requires a source of RC•O radicals to form RCO_3 or RO_2 radicals.[3,4] The formation / pathways and kinetics of RC•O radical formation is not fully understood. Atmospheric researchers are active in areas of both experimental and modeling studies relating to these kinetic processes. Areas of focus are primarily those relative to secondary pathways, specifically the reactions of O_2 and NO with radicals formed in the primary OH abstraction or addition steps. The rate and extent of formation of secondary pollutants and photochemical oxidant, including ozone, are largely determined by these reactions. The product distributions in the photo-oxidation of VOCs under simulated troposphere conditions can be influenced by the varied reaction rates and channels (pathways) of RC•O radical interaction with oxygen.

RC•O radicals can be produced from emitted organic precursor specie such as CH$_3$CHO, in several ways , by reactions with OH, or NO$_3$ radicals or by photolysis. CH$_3$CHO is of particular interest in atmospheric chemistry since it is formed as a product of the reaction of O$_3$ and / or OH radicals with naturally occurring, non-methane hydrocarbons, especially higher olefins such as isoprene and terpene. The photo-oxidation of hydrocarbons in photochemical smog also produces acetaldehyde as a major intermediate product. Acetylperoxy radicals CCOQj(often represented as CH$_3$CO•$_3$) are formed as a result of CH$_3$CjO radical reaction with O$_2$ in the photo-oxidation of higher carbonyl compounds (acetaldehyde, acetone, methylvinylketone, methylglyoxal, etc..) play an important role in atmospheric photo-oxidation processes. In the polluted atmosphere they react with NOx and in the clean troposphere with other peroxy radicals. Acetylperoxy radicals are the precursor of peroxyacetylnitrate (PAN) an important constituent of photochemical smog and an air pollutant having important physiological effects. PAN is formed by combination with NO$_2$:

$$CH_3CO•_3 + NO_2 + M \rightarrow CH_3CO•_3 NO_2 + M$$
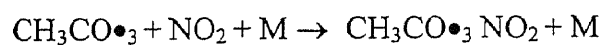
Because of its thermal stability at lower temperatures and its photochemical inertness under tropospheric conditions, PAN can act as a temporary reservoir for NOx and serve as a carrier for transport in colder regions of the troposphere.

Peroxy radicals (ROO•), particularly CH$_3$CO•$_3$, are important intermediates in the oxidation of organic compounds in the troposphere[3,4]. Their loss processes are one of the major factors influencing chain length in forming of ozone. Their reactions with NO are primarily chain propagating reactions resulting in the formation of NO$_2$,

which, on photolysis, yields O_3 NO_2, HO_2 and other peroxy radicals are, in contrast, mainly chain terminating. Hydro and alkyl - peroxy radicals are important in remote continental and marine atmospheres; they undergo reactions resulting in aldehydes, alcohols, organic acids, and hydroperoxides. There exists a need to establish structure-reactivity relationships for the different classes of radicals, due to different major reaction paths of the variety of peroxy radicals formed from VOCs and their oxidized derivatives. These relationships will allow estimation of kinetic pathways and rate constants, without required experimental data on each reactions of each molecule in a series.

Several studies have illustrated that the reactions of ethyl[5-10] and isopropyl[11] radicals at pressures from 1 to 6000 torr and temperatures from 300 to 900 K, exhibit significant negative temperature dependence (NTD) and complex fall-off with pressure. The ethyl reaction is the best characterized and is shown to produce C_2H_4 + HO_2. The rate of ethyl radical loss decreases significantly with temperature[5] and increases with pressure; this is explained by invoking reversible formation of a weakly bound adduct. The adduct, $C_2H_5OO\bullet$ is readily stabilized at low temperatures and atmospheric pressure; but dissociates back to reactants at higher temperatures. This rapid dissociation of the adduct is the origin of the observed NTD regime in hydrocarbon oxidation.

Analysis of the C_2H_5 + O_2 reaction system[12, 13] invokes formation of a chemically activated adduct, which can be stabilized or, before stabilization , can dissociate back to C_2H_5 + O_2 , react through a cyclic five-member ring intermediate to form a primary hydroperoxy alkyl radical, which can be stabilized or undergo elimination to C_2H_4 +

HO_2. The ethyl peroxy C_2H_5OO can also react directly via HO_2 elimination to $C_2H_4 +$ HO_2. The formation of epoxide + OH in this system is limited by a lower Arrhenius A factors due to the isomerization and epoxide formation transition states combined with a low Ea for direct HO_2 elimination. The results of modeling studies for loss of ethyl and production of ethylene show good agreement with experimental data [8, 9]. Important conclusions from the modeling indicate that well depth is often critical to the further reaction to new products. A deeper well provides more energy in the initially formed chemically activated adduct for forward reaction, before stabilization can occur. Isomerization, HO_2 elimination and epoxide + OH reaction A factors are much lower than that for dissociation of the complex to reactants, but the isomerization barrier height is often lower. At higher temperatures increased isomerization relative to stabilization of the activated complex leads to higher $C_2H_4 +$ HO_2 formation rates in these systems. Similar results are reported on analysis of reactions of allyl, vinyl and formyl radicals reaction with oxygen.[14,15]

There is however very little information on the important reaction of CH_3CjO radicals with O_2[16]. The oxidation process involves formation of chemically activated peroxyacetyl radical, $CH_3CO\bullet_3$, which, similar to the ethyl peroxy system. The adduct can dissociate back to reactants, undergo reaction to new products or be collisionally stabilized.

Acetaldehyde and the corresponding radical species that result via loss of hydrogen atoms from the two different carbon sites in CH_3CHO are also common products (intermediates) from oxidation processes of higher molecular weight hydrocarbon species in both combustion and in atmospheric photochemistry. The acetaldehyde and

its two radicals are also produced by molecular weight growth from C_1 carbon

combustion and mild oxidation processes where the slow reaction of methyl radical

with O_2 to $CH_3O + O$ or $CH_2O + OH$. The slow conversion of $CH_3OO\bullet$ (methyl

peroxy radical) to products, results in an equilibrium between $CH_3 + O_2$ and $CH_3OO\bullet$

where entropy favors the reactants at higher temperatures. As a result methyl radicals

often buildup in the radical pool until combination occurs forming ethane and ethyl +

H. Acetaldehyde is one of the important oxidation products of ethane and ethylene.

Acetaldehyde and acetyl radicals are important intermediates in the overall

breakdown processes of higher molecular weight and C_1 hydrocarbons to CH_2O, CO,

CO_2 and H_2O. The radical reactions with oxygen also serve as model reactions for

larger aldehydic molecule systems.

This study focuses on reaction mechanism of acetyl radical association with O_2.

Thermodynamic properties are estimated for reactants, intermediate, products and

transition states along the reaction pathway. The thermodynamic parameters are used

to calculate high-pressure limit rate constants using canonical Transition State

Theory. Rate constants as a function of temperature and pressure are estimated using

a multi frequency Quantum RRK analysis with modified strong collision analysis of

Gilbert et. al[17-19] for fall off. The data at relevant pressures and temperatures should

be useful to both atmospheric and combustion modelers.

$$CH_3CjO + O_2 + M \longrightarrow CCOQj + M \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$
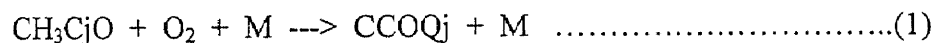
One absolute measurement of k_1 has been reported in the literature. McDade et al.[36]

determined $k_1 = (1.2 \pm 0.2) * 10^{12}$ $cm^3/(mole\text{-}s)$ in 1-4 torr total pressure of He at

298K. The high-pressure limiting value of $k_1 = (3.01 \pm 1.5) * 10^{12}$ $cm^3/(mole\text{-}s)$

recommended by the IUPAC panel is based on the absolute measurements of McDade et al.[36] and the pressure dependence of the $C_2H_5 + O_2$ reaction[37]. The results from two studies, one of the relative reactivity of CH_3CjO with O_2 and Cl_2[38], the other of the rate constant for the reaction of CH_3CjO with Cl_2[39], have been combined to give a high-pressure limiting rate constant of $k_1 = (1.9 \pm 0.4) * 10^{12}$ cm^3/(mole-s) at room temperature.

Recently, Sehested et al.[35] report on $k_1 = (2.65 \pm 0.4) * 10^{12}$ cm^3/(mole-s) at 295K and 1000 mbar total pressure of SF_6.

Tyndall et al.[40] studied the reaction of OH radical with methyl glyoxal and acetaldehyde in a low pressure (c.a. 3 torr) flow reactor at temperatures from 260 to 333 K. They report rate constants for OH abstractions from the parent molecules and also report data on further reactions of the radicals formed from the abstractions by OH. They infer that only the acetyl radical is formed and further reaction of acetyl radical with O_2 leads to noticeable regeneration of OH; from observations showing reduced loss of the OH versus time. Some chamber experiments with FTIR monitoring showed no evidence of OH radical production.

Absolute rate constants of Fluorine atom reaction with acetaldehyde were studied by Sehested and coworkers[35] using pulse radiolysis combined with transient ultraviolet absorption. They report production of two radicals - formyl methyl at 35% and acetyl at 65% (both $\pm$ 9%). We note that for reactions where chlorine atom is abstracting hydrogen atoms. Chlorine atoms usually have similiar A factors and similar or lower Ea's when the reactions are exothermic which they are in all cases in this study. In the case of acetaldehyde, for example, k_{298} for Cl atom abstraction is reported as 4.58 $\times$

10^{13}[41] at 298K, while abstraction by F atom is 5.00 x 10^{13}[42]. The H--Cl bond is 103 kcal/mole, while the carbonyl C--H and methyl C--H bonds on acetaldehyde are 88 and 94 kcal/mole respectively. Chlorine should, therefore, readily abstract from both hydrogen sites of acetaldehyde.

Michael et al.[43] studied the reaction of OH with acetaldehyde in a low pressure discharge flow reactor with resonance fluorescence monitoring. He also studied the reaction of radical(s) generated via the OH reaction with O_2. The total reaction rate constant for OH with acetaldehyde was A = 3.3 x 10^{12}, with a small negative energy of activation of 610 cal/mole. Michael et al. report near complete regeneration of OH radical in the OH + acetaldehyde experiments when O_2 was present to further react with the indicated acetyl radical formed. In separate studies with Cl atom reacting with acetaldehyde, they observed production of OH radical on further radical reaction(s) with O_2. They considered and rejected possible formation of formyl methyl radicals based on work of Gutman's research group and an assumed bond energy of the H--C bond on the methyl group of 98 kcal/mole.

Slagle and Gutman[44] studied formation of acetyl radical from acetaldehyde in reaction of Cl atoms from 1082 cm^{-1} IR multiphoton decomposition of CF_2Cl_2 of C_6F_5Cl. They monitored the radical profiles with photoionization mass spectrometry. Verification of CH_3CjO radical versus formyl methyl was by use of deuterated acetaldehyde, CH_3CHO. They observed CH_3CjO and could not detect $CjCHO$; but did not estimate lower limits of its detection.

Reaction kinetics of acetylperoxy radicals with nitric oxide and nitrogen dioxide were studies by Maricq and Szente[39], where the peroxy radicals were generated via

reaction of acetyl radical with O_2. Acetyl radicals were generated by reaction of acetaldehyde with Cl atoms and Cl atoms were produced by 351 nm eximer laser pulses ca 300 mJ/pulse. Maricq and Szente provide data on nitric oxide plus acetyl and methyl peroxy radical decay and NO_2 formation versus time for modeling comparisons.

Formyl methyl radicals, the other possible radical that may be formed by abstraction of H atoms from acetaldehyde, were generated by photodissociations of methyl-vinyl ether by Zhu and Johnston[45]. CH_3-O-C_2H_3 + hv ==> CH_3 + C_2H_3O. Here the vinoxy radical undergoes rapid electron rearrangement to the lower energy form (ca 18 kcal/mole loser in energy) formyl methyl radical. Kinetic studies on this formyl methyl radical with O_2 show slower reaction, $k_2 = 1.2 \times 10^{11}$ cm^3/mole-sec, than rate constants reported for acetyl radical $k_1 = 1 \times 10^{12}$ cm^3/mole-sec. They suggest that if formyl methyl radicals are produced in reactions of Cl atoms or OH with acetaldehyde, they will react about one tenth as fast with O_2, probably leading to small or no corrections to the faster acetyl + O_2 reactions.

Photo dissociation of PAN, (PeroxyAcetylNitrate) was used by Villalta and Howard[11] to generate acetylperoxy radicals for study of reaction kinetics with nitric oxide. Rate constants determined by this method agreed well with other reported values. This agreement of kinetic data where acetylperoxy radicals are generated by a very different and positive mechanism supports the assumption of Maricq and Szente[43], Sehested et al.[35], Tyndall et al.[40], Michael et al.[43], and Slagle and Gutman[44], that primarily acetyl radicals are generated by reaction with OH, or Cl atoms.

CHAPTER 3

CALCULATION METHOD FOR PART THREE

3.1 Determination of Enthalpies of Formation

Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) for reactants, intermediate radicals, transition states

and products are calculated using CBS-Q composite method and density functionals.

The initial structure of each compound or transition state is determined using ROHF

or UHF/PM3 in MOPAC[20], followed by optimization and vibrational frequency

calculation at HF/6-31G(d') level of theory using GAUSSIAN 94[21]. Transition State

(TS) geometries are identified by the existence of only one imaginary frequency,

structure information and the TST reaction coordinate vibration information. Zero-

point vibrational energies (ZPVE), vibrational frequencies and thermal contributions

to enthalpy from harmonic frequencies are scaled by 0.91844 as recommended by

Petersson et. al[22]. Single point energy calculation are carried out at the B3LYP/6-

31G(d'). The complete basis set (CBS-Q) method of Petersson and coworkers for

computing accurate energies[23-25] are chosen as our primary for determining

enthalpies.

The CBS-Q calculation sequence is performed on the MP2/6-31G(d') geometry and

followed by single point calculations at the theory level of QCISD(T)/6-31+G(d'),

MP4(SDQ)/CbsB4 and MP2/CBSB3 CBSExtrap=(Nmin=10,Pop).

The isodesmic reactions are used to determine the heat of formation ($\Delta H_f^\circ{}_{298}$) for intermediate radicals. For estimation of $CH_3C(=O)OOH$ [defined CCOQ, Q=OOH (hydroperoxy group)]

$$CH_3C(=O)OOH + CH_3CH_2OH <==> CH_3C(=O)OH + CH_3CH_2OOH \ldots\ldots\ldots\ldots (1)$$
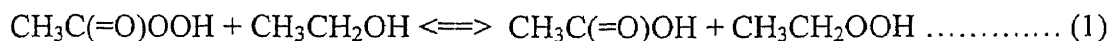
For estimation of $C\bullet H_2C(=O)OOH$ [defined CjCOQ, j : radical site]

$$CH_3C(=O)OOH + CH_3C\bullet H_2 <==> C\bullet H_2C(=O)OOH + CH_3CH_3 \ldots\ldots\ldots\ldots (2)$$
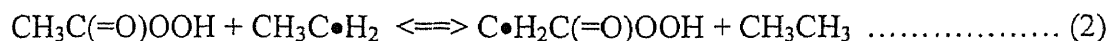
For estimation of $CH_3C(=O)OO\bullet$ [defined CCOQj, Qj : -OO$\bullet$]
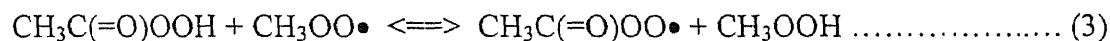
$$CH_3C(=O)OOH + CH_3OO\bullet <==> CH_3C(=O)OO\bullet + CH_3OOH \ldots\ldots\ldots\ldots (3)$$

The method of isodesmic reactions relies upon the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the *ab initio* MO calculations.[26] The basic requirement of the isodesmic reaction is that the number of bonds of each formal chemical bond type is conserved in the reaction. In reaction (1), *ab initio* calculations with ZPVE and thermal correction are performed for all of four compounds. Since $\Delta H_f^\circ{}_{298}$ of three compounds excepting CCOQ have been experimentally or theoretically calculated, the unknown $\Delta H_f^\circ{}_{298}$ of CCOQ is obtained. The remaining two radicals are calculated in the same manner.

The $\Delta H_f^\circ{}_{298}$ of transition state compounds are estimated by evaluation of $\Delta H_f^\circ{}_{298}$ of the stable radical adducts plus difference of total energies with ZPVE and thermal correction between these radical species and the transition state (TS).

TCCOQjS : A peroxy radical CCOQj isomerize to form a CjCOQ isomer via hydrogen shift.

TCCOXQE : A peroxy radical CCOQj decompose to products, $CH_2CO + HO_2$ via HO_2 elimination.

TCjCOXQ : A CjCOQ isomer undergo β-scission to products, $CH_2CO + HO_2$

TYCOCDOXOH : A CjCOQ isomer decompose to products, CyCOC=O + OH via

OH elimination.

3.2 Determination of Entropy and Heat Capacity

The contributions of external rotation and vibrations to entropies and heat capacities

are calculated from scaled vibration frequencies and moments of inertia for the

optimized HF/6-31G(d') structures. Contributions from frequencies corresponding to

hindered internal rotation are replaced with contributions calculated from the method

of Pitzer and Gwinn[27] for S and Cp(T). Number of optical isomers and spin

degeneracy of unpaired electrons are also incorporated.

3.3 High-Pressure Limit A Factors ($A_∞$) and Rate Constants ($k_∞$) Determination

For the reactions where thermodynamic properties of TS are calculated by *ab initio* or

density functional methods, $k_∞$s are fit by three parameters $A_∞$, n, and E_a over

temperature range from 298 to 2000K, $k_∞ = A_∞(T)^n exp(-E_a/RT)$ Entropy differences

between reactant and TS are used to determine the pre-exponential factor, A, via

conventional transition state theory (TST) for unimolecular and bimolecular reactions

$A = (k_bT/h_p)exp(ΔS^{\neq}/R)$ and $A = (ek_bT/h_p)exp(ΔS^{\neq}/R)$, respectively. h_p is Plank's

constant and k_b is the Boltzman constant.

3.4 Kinetic Analysis

Once the potential energy surface and thermochemical properties are evaluated,

forward or reverse rate for each, elementary reaction step are determined, Multi-

frequency Quantum Rice-Ramsperger-Kassel (QRRK) analysis is then used for k(E)

and modified strong collision analysis of Gilbert et. al[17-19] used for fall-off; to obtain

rate constants as a function of temperature and pressure. Reactions which incur a

change in number of moles, such as unimolecular dissociation, have energy of

activation calculated as delta Urxn plus an Ea for the reverse addition, where U is

internal energy.

A modified QRRK analysis we use in this srudy is described by Zhong and

Bozzelli.[34] 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,

with inclusion of one external rotation to calculate density of states $\rho(E)$.

Comparisons of ratios of these $\rho(E)/Q$ (partition function Q) with direct count $\rho(E)/Q$

are shown to be in good agreement.[34] Nonlinear Arrhenius effects resulting from

changes in the thermodynamic properties of the respective TST's relative to the

adduct with temperature are incorporated using a two parameter Arrhenius pre-

exponential factor (A, n) in AT^n.

CHAPTER 4

RESULT AND DISCUSSION FOR PART THREE

4.1 Geometries of Two Intermediate Radicals and Transition States

Figure 3.1 to 3.5 show MP2/6-31G(d') determined geometries of CCOQj, CjCOQ, TCCOQjS, TCCOXQE and TYCOCDOXOH respectively.[names are defined in section 3.1] Figure 3.1 and Figure 3.2 show the optimized geometries of two intermediate radicals, CCOQj and CjCOQ, respectively. Figure 3.3 shows TCCOQjS structure for isomerization (H shift) reaction. The H_6 atom is in a bridge structure shifting from C_1 to radical site O_5. The leaving bond length H_6-C_1 is calculated as 1.27Å with MP2/6-31G(d') determined geometry; where the H-C bond length in CCOQj is calculated as 1.09Å. The forming bond length H_6-O_5 is calculated as 1.25Å. All bond lengths are from MP2/6-31G(d') determined geometries. The normal bond length H-O in CjCOQ is calculated as 0.97Å. Figure 3.4 shows TCCOXQE structure, HO_2 elimination of CCOQj --> CH_2CO + HO_2. The leaving bond length of C_1-H_8 is calculated as 1.23Å and the C-H bond length in CCOQj is calculated as 1.09Å. The leaving bond length of C_2-O_6 is calculated as 2.02Å and the C-O bond length in CjCOQ is calculated as 1.38Å. The leaving O_6-O_7 bond length is calculated as 1.28Å and the O-O bond length in CjCOQ is calculated as 1.46Å. Again all bond lengths are from MP2/6-31G(d') determined geometries.

Figure 3.5 shows TYCOCDOXOH structure, OH elimination of CjCOQ --> CyCOC=O + OH. The leaving bond length O_4-O_7 is calculated as 1.84Å and the O-O

CCOQj [Qj = OO. (peroxy) , j : radical site]

CH₃C=O(OO.)

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.50				
O3-C2	1.44	O3-C2-C1	115.7		
O4-O3	1.31	O4-O3-O2	113.2	O4-O3-O2-C1	0.0
O5-O2	1.19	O5-C2-C1	129.0	O5-C2-C1-O3	-180.0
H6-C1	1.09	H6-C1-C2	107.2	H6-C1-C2-O3	-180.0
H7-C1	1.09	H7-C1-C2	110.7	H7-C1-C2-O3	59.5
H8-C1	1.09	H8-C1-C2	110.7	H8-C1-C2-O3	-59.5
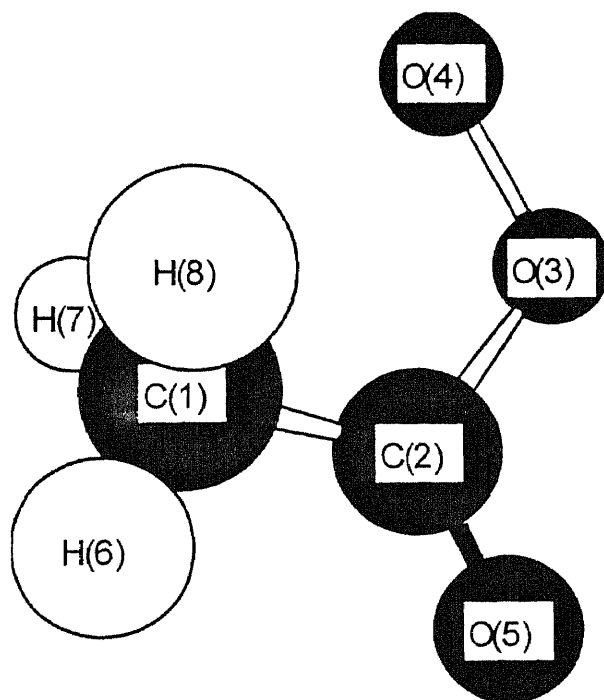
Figure 3.1 Structure for CCOQj

CjCOQ [Q = OOH (hydroperoxy group), j : radical site]

C.H₂C=O(OOH)

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.48				
O3-C2	1.38	O3-C2-C1	118.0		
O4-O3	1.46	O4-O3-O2	111.8	O4-O3-O2-C1	1.4
O5-O2	1.19	O5-C2-C1	125.4	O5-C2-C1-O3	-179.2
H6-C1	1.08	H6-C1-C2	123.6	H6-C1-C2-O3	2.5
H7-C1	1.08	H7-C1-C2	115.1	H7-C1-C2-O3	-179.1
H8-C4	0.97	H8-O4-O3	98.2	H8-O4-O3-C2	141.4
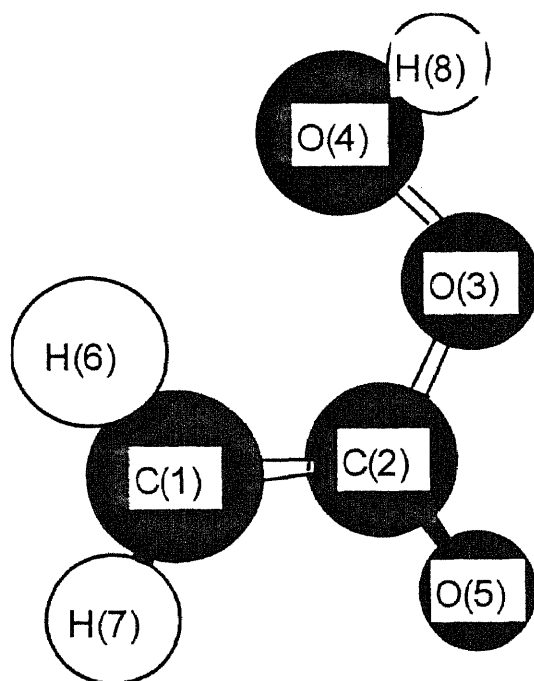
Figure 3.2 Structure for CjCOQ

TCCOQjS
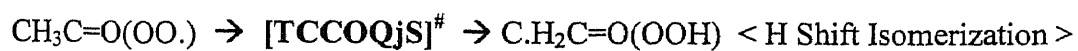
$CH_3C=O(OO.) \rightarrow$ **[TCCOQjS]**[#] $\rightarrow C.H_2C=O(OOH)$ < H Shift Isomerization >

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.52				
O3-C2	1.20	O3-C2-C1	128.6		
O4-C2	1.38	O4-C2-C1	108.8	O4-C2-C1-O3	180.0
O5-O4	1.42	O5-O4-C2	· 108.2	O5-O4-C2-C1	0.0
H6-O5	1.25	O6-O5-O4	98.2	O6-O5-O4-C2	0.0
H7-C1	1.09	O7-C1-C2	114.8	O7-C1-C2-O3	-67.3
H8-C1	1.09	H8-C1-C2	114.8	H8-C1-C2-O3	67.3
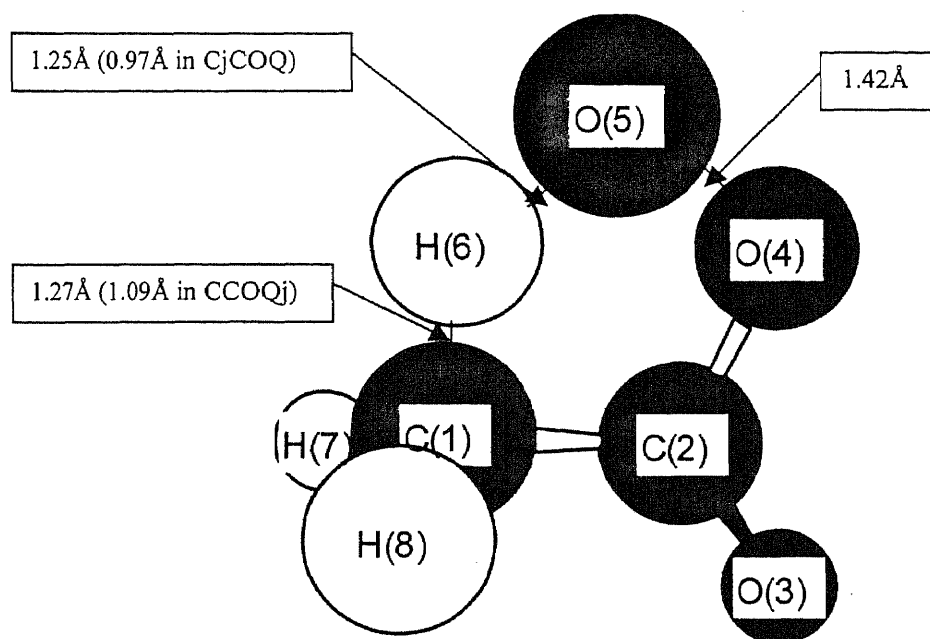
Figure 3.3 Structure for TCCOQjS

TCCOXQE
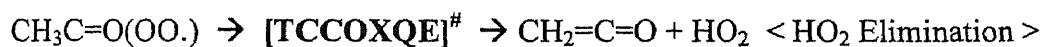
CH₃C=O(OO.) → **[TCCOXQE]**# → CH₂=C=O + HO₂ < HO₂ Elimination >

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.42				
H3-C1	1.09	H3-C1-C2	110.6		
H4-C1	1.09	H4-C1-C2	112.3	H4-C1-C2-H3	127.2
O5-C2	1.17	O5-C2-C1	157.6	O5-C2-C1-H3	-86.4
O6-O2	2.02	O6-C2-C1	95.3	O6-C2-C1-H3	99.8
O7-O6	1.28	O7-O6-C2	105.8	O7-O6-C2-C1	9.4
H8-C1	1.23	H8-C1-C2	99.3	H8-C1-C2-H3	-110.8
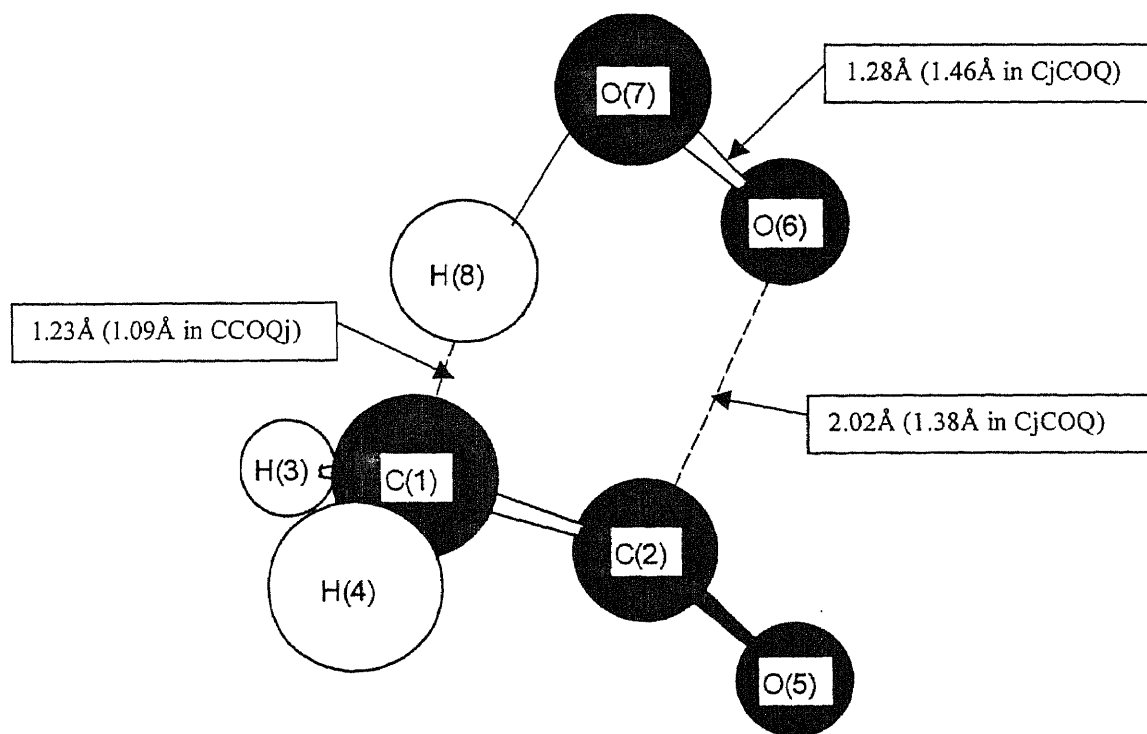
Figure 3.4 Structure for TCCOXQE

TYCOCDOXOH
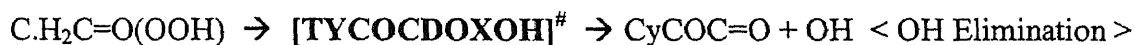
C.H$_2$C=O(OOH) → **[TYCOCDOXOH]**$^\#$ → CyCOC=O + OH   < OH Elimination >

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-O1	1.21				
C3-C2	1.47	C3-C2-O1	138.9		
O4-C2	1.31	O4-C2-O1	132.3	O4-C2-O1-C3	-180.0
H5-C3	1.08	H5-C3-C2	120.2	H5-C3-C2-O1	93.8
H6-C3	1.08	H6-C3-C2	120.2	H6-C3-C2-O1	-93.8
O7-O4	1.84	O7-O4-C2	109.1	O7-O4-C2-O1	0.0
H8-O7	0.98	H8-O7-O4	93.7	H8-O7-O4-C2	0.0
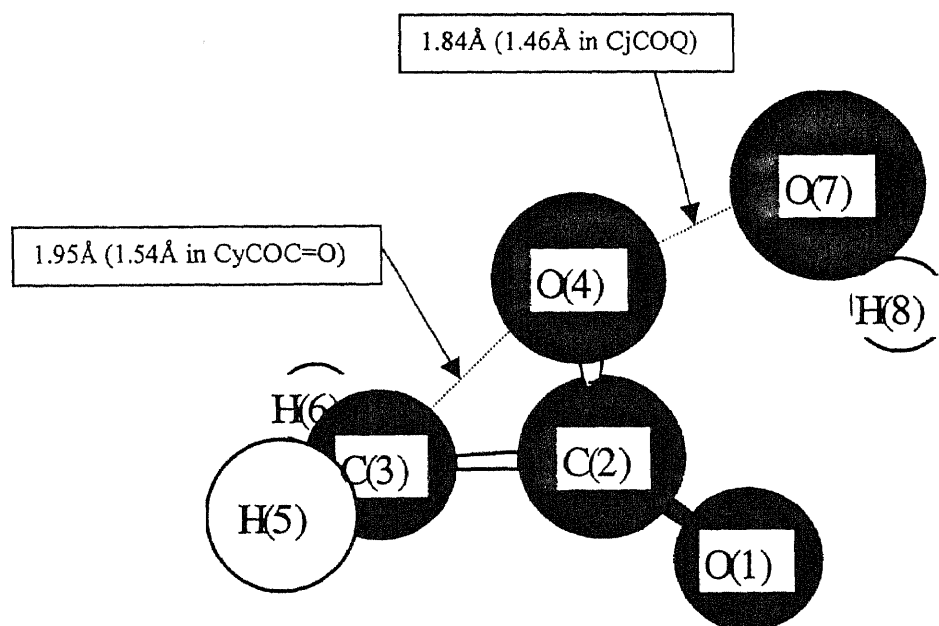
Figure 3.5 Structure for TYCOCDOXOH

bond length in CjCOQ is calculated as 1.46Å. The forming C_3-O_4 bond is calculated

as 1.95Å and the C-O bond length in CyCOC=O is calculated as 1.54Å.

4.2 Estimation of Entropy ($S^o_{(298)}$) and Heat Capacity (Cp(T)'s, 300 - 1500K)

$S^o_{(298)}$ and Cp(T)'s are calculated based on vibration frequencies and moments of

inertia of the optimized HF/6-31G(d') structures. (Table 3.1 and Table 3.2)

The calculation results using MP2/6-31G(d') determined geometries and HF/6-

31G(d') determined frequencies are summarized in Table 3.3. TVR represents the

sum of the contributions from translations, vibrations and external rotations for $S^o_{(298)}$

and Cp(T)'s. Symmetry, optical isomer and electronic spin are incorporated in

estimation of $S^o_{(298)}$ as described in Table 3.3. Contributions of internal rotation for

$S^o_{(298)}$ and Cp(T)'s are calculated based on rotational barrier heights, moments of

inertia of the rotors using the method of Pitzer and Gwinn's[26]. (Table 3.4)

4.3 Estimation of Enthalpy of Formation ($\Delta H_f^o{}_{298}$) using Total Energies and Isodesmic Reactions

The overall energy diagram for the $CH_3CjO + O_2$ reaction system is illustrated in

Figure 3.6.

CBSQ calculations are performed on the MP2/6-31G(d') determined geometries and

HF/6-31G(d') determined frequencies. Density functionals are performed on the

B3LYP/6-31G(d) determined geometries and frequencies.

Isodesmic reactions are applied to accurately estimate $\Delta H_f^o{}_{298}$ of CCOQ and two

intermediate radicals, CjCOQ and CCOQj. Zero point Vibration energies (ZPVE's)

and thermal corrections to 298.15 K are taken into account. The total energies at 0 K
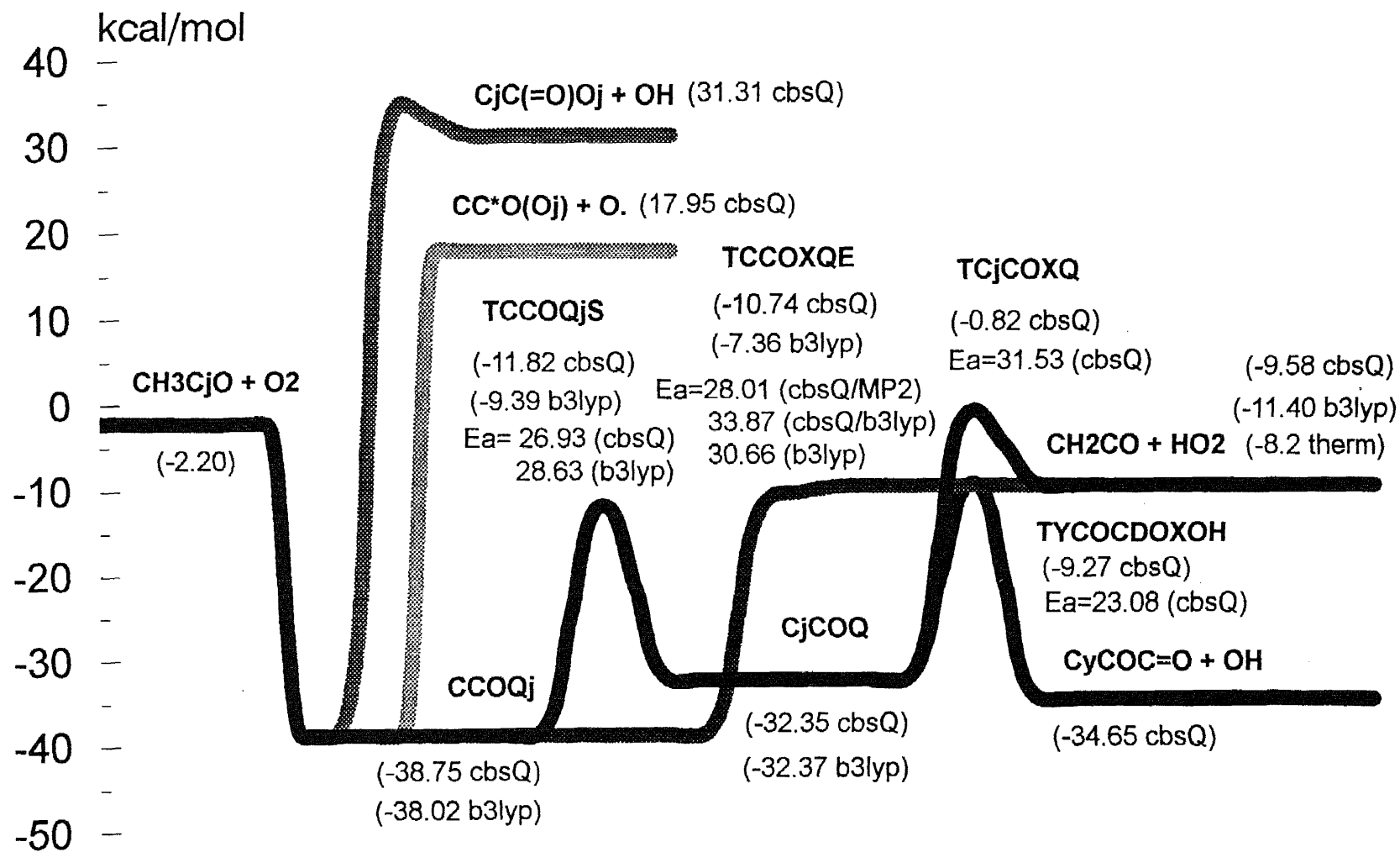
Figure 3.6 Potential Energy Diagram $CH_3CjO + O_2$

[Q=OOH, Qj=OO., j=radical site]

Table 3.1 Vibrational Frequencies[a] (ν cm^{-1}) HF/6-31G(d') level of calculation

Species	Vibrational Frequencies
CH3CHO	160 543 847 956 1223 1256 1519 1556 1598 1607 2029 3123 3190 3251 3309
CH3CjO	107 506 920 1040 1154 1502 1595 1596 2141 3199 3289 3293
CCOQ	35 175 318 346 475 672 714 998 1190 1173 1192 1425 1548 1602 1607 1677 2009 3222 3297 3336 3962
CCOQj	107 167 340 459 628 714 954 1094 1166 1252 1323 1545 1601 1607 2103 3219 3292 3337
CjCOQ	106 129 368 371 536 624 627 774 915 1096 1202 1371 1577 1631 1809 3365 3495 4113
CH2CO	492 632 690 1102 1264 1554 2381 3363 3466
TCCOQjS[b]	-1669[f] 139 274 485 543 601 690 846 934 1017 1032 1070 1165 1435 1727 1881 3136 3224
TCCOXQE[c]	-1596[f] 81 226 375 452 513 566 771 1012 1063 1182 1460 1507 1533 1868 2435 3259 3340
TCjCOXQ[d]	-877.6[f] 98 182 228 290 408 514 554 731 1015 1096 1143 1545 1626 2192 3327 3435 4059
CC*O(Oj)	52 428 594 634 933 1050 1170 1384 1534 1604 1606 2018 3214 3287 3331
CyCOC=O	542 596 839 1060 1104 1172 1257 1349 1622 2216 3315 3418
TYCOCDOXOH[e]	-671[f] 152 194 270 326 387 613 634 804 985 1012 1017 1211 1459 1898 3191 3307 3611

[a] non-scaled. [b,c,d,e] Transition State Structure described in results section.

[f] Transition State, one imaginary frequency.

Table 3.2 Moments of Inertia (amu-Bohr^2) HF/6-31G(d') level of calculation

Species	I_A	I_B	I_C	Species	I_A	I_B	I_C
CH3CHO	31.09	175.54	195.57	TCCOQjS	177.19	371.70	536.83
CH3CjO	20.77	180.48	190.17	TCCOXQE	194.75	477.79	660.74
CCOQ	191.62	383.50	562.14	TCjCOXQ	202.06	443.62	609.40
CCOQj	165.45	396.96	551.32	CC*O(Oj)	147.47	182.32	318.64
CjCOQ	170.86	382.43	553.29	CyCOC=O	67.39	218.08	273.37
CH2CO	6.30	171.66	177.96	TYCOCDOXOH	194.30	421.08	602.79

Table 3.3 Ideal Gas Phase Thermodynamic Properties Obtained
by CBSQ Calculation[a] and by Therm*

Species (s, e, OI)[g]		ΔHf°_{298}[b]	S°_{298}[c]	Cp_{300}[c]	Cp_{400}	Cp_{500}	Cp_{600}	Cp_{800}	Cp_{1000}	Cp_{1500}
CH3CHO	TVR[d]		57.97[e]	11.58	14.29	16.88	19.20	22.98	25.80	30.10
(CH3-C(=O)H)	Internal Rotor 1[f]		5.16	1.44	1.30	1.23	1.17	1.10	1.07	1.03
(3,0,1)	Total		63.13	13.02	15.59	18.11	20.37	24.08	26.87	31.13
	THERM	-39.10	63.11	12.49	15.83	18.59	20.85	24.22	26.50	29.76
CH3CjO**	TVR		58.82	11.12	13.24	15.24	17.01	19.90	22.06	25.39
(CH3-C.(=O))	Internal Rotor 1		5.24	1.62	1.41	1.29	1.21	1.12	1.08	1.03
(3,1/2,1)	Total		64.06	12.74	14.65	16.53	18.22	21.02	23.14	26.42
	THERM	-2.20	62.71	11.10	13.92	16.23	18.11	20.89	22.75	25.35
CCOQ***	TVR		66.79	15.22	18.93	22.24	25.05	29.40	32.54	37.27
(CH3-C(=O)OOH)	Internal Rotor 1,2,3		9.65	5.53	6.06	6.27	6.30	6.06	5.64	4.70
(3,0,2)	Total	-84.70	76.44	20.75	24.99	28.51	31.35	35.46	38.18	41.97
	THERM	-80.48	77.23	20.53	24.34	27.65	30.39	34.52	37.41	
CCOQj***	TVR		66.86	15.33	18.81	21.84	24.36	28.18	30.87	34.77
(CH3-C(=O)OO.)	Internal Rotor 1,2		12.69	2.72	2.46	2.30	2.21	2.12	2.08	2.03
(3,1/2,1)	Total	-38.75	79.55	18.05	21.27	24.14	26.57	30.30	32.95	36.80
	THERM	-44.38	77.45	18.48	21.50	24.10	26.30	29.80	32.44	
CjCOQ	TVR		70.45	15.79	19.14	21.85	24.01	27.19	29.43	32.85
(C.H2-C(=O)OOH)	Internal Rotor 1,2,3		8.80	6.00	6.39	6.50	6.46	6.15	5.69	4.72
(1,1/2,2)	Total	-32.35	79.25	21.79	25.53	28.35	30.47	33.34	35.12	37.57
	THERM	-38.18	74.50	20.23	23.94	26.87	29.16	32.40	34.56	
CH2CO (2,0,1)	TVR		57.57	12.26	14.10	15.61	16.85	18.81	20.29	22.61
(CH2=C=O)	Total		57.57	12.26	14.10	15.61	16.85	18.81	20.29	22.61
	THERM	-11.70	57.81	12.68	14.77	16.43	17.75	19.65	20.92	22.91
TCCOQjS	TVR		72.15	19.92	23.97	27.10	29.51	32.90	35.12	38.15
(1,1/2,2)	Total	-11.82	72.15	19.92	23.97	27.10	29.51	32.90	35.12	38.15
TCCOXQE	TVR		74.97	20.04	23.37	26.14	28.41	31.83	34.20	37.57
(1,1/2,2)	Total	-10.74	74.97	20.04	23.37	26.14	28.41	31.83	34.20	37.57
TCjCOXQ	TVR		74.11	18.14	20.96	23.20	25.00	27.76	29.80	33.03
(1,1/2,2)	Internal Rotor 1,2		5.07	3.83	4.19	4.41	4.52	4.47	4.20	3.47
	Total	-0.82	79.18	21.97	25.15	27.61	29.52	32.23	34.00	36.50
CC*O(Oj)	TVR		62.80	12.71	15.42	17.91	21.10	23.58	26.16	30.15
(CH3-C(=O)O.)	Internal Rotor 1		5.62	1.08	1.05	1.03	1.02	1.01	1.00	1.00
(3,1/2,1)	Total	-41.61	68.42	13.79	16.47	18.94	22.12	24.59	27.16	31.15
	THERM	-51.38	63.56	14.78	17.67	20.28	22.42	25.81	28.19	
CyCOC=O	TVR		62.29	11.95	14.65	17.06	19.06	22.10	24.24	27.42
(1,0,1)	Total	-44.14	62.29	11.95	14.65	17.06	19.06	22.10	24.24	27.42
TYCOCDOXOH	TVR		73.08	18.74	21.97	24.50	26.48	29.39	31.47	34.77
(1,1/2,1)	Internal Rotor 1		4.31	1.46	1.30	1.20	1.14	1.08	1.05	1.02
	Total	-9.27	77.39	20.20	23.27	25.70	27.62	30.47	32.52	35.79

* : therm values for stable species are included for comparison

** j : radical site,   *** Q = OOH (hydroperoxy group), Qj = OO.(peroxy)

a : Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiometer at 1 atm.

b : Units in kcal/mol   c : Units in cal/mol-K

d : Sum of contributions from translations, vibrations, and external rotations.

f : Contribution from internal rotation

g : Symmetry number, optical isomer and electronic spin are taken into account,
   -Rln(s), Rln2, Rln2, respectively.
   s = number of symmetry, e = electronic spin, OI = number of optical isomer

Table 3.4 Moments of Inertia (amu-A^2) and Rotational Barriers (kcal/mole)
for Internal Rotors

Species	Rotor	I_A	I_B	V	n^a
CH3CHO	CH3--C(=O)H	3.12	18.90	1.20	6
CH3CjO[b]	CH3--C.(=O)	3.12	23.81	1.20	3
CCOQ[c]	CH3--C(=O)OOH	3.12	130.14	3.18	6
	CH3C(=O)--OOH	44.19	1.56	5.46	2
	CH3C(=O)O--OH	100.00	0.92	7.15	1
CCOQj[d]	CH3--C(=O)OO.	3.12	126.74	0.70	6
	CH3C(=O)--OO.	44.19	30.84	1.00	2
CjCOQ	C.H2--C(=O)OOH	1.75	130.14	3.18	2
	C.H2C(=O)--OOH	42.44	1.56	5.46	2
	C.H2C(=O)O--OH	100.00	0.92	7.15	1
TCjCOXQ	C.H2C(=O)--OOH	42.44	1.56	5.46	2
	C.H2C(=O)O--OH	100.00	0.92	7.15	1
CC*O(Oj)[e]	CH3--C(=O)O.	3.12	38.12	0.48	6
TYCOCDOXOH	OH--CyCOC=O	0.98	61.8	1	2

[a] n : foldness

[b] "j" stands for radical site.

[c] "Q" stands for hydroperoxy group(OOH).

[d] "Qj" stands for peroxy (OO.).

[e] "*" stands for bouble bonding(C=O).

Table 3.5 List of Total Energy, ZPVE, and Thermal Correction of CBSQ Calculation[a]

Species	Total Energy at 0K[b]	ZPVE[c]	Thermal Correction[d]	Total Energy at 298K[b]
CH3CHO	-153.5808040	0.0596140	0.0047500	-153.5760540
CH3CjO[e]	-152.9409014	0.0463440	0.0048310	-152.9360704
CCOQ[f]	-303.8036387	0.0701660	0.0066110	-303.7970277
CCOQj[g]	-303.1591877	0.0569790	0.0059440	-303.1532437
CjCOQ	-303.1472163	0.0546810	0.0058250	-303.1413913
CH2CO	-152.3751740	0.0340450	0.0043090	-152.3708650
TCCOQjS	-303.1150471	0.0492970	0.0055420	-303.1095051
TCCOXQE	-303.1140266	0.0492960	0.0062490	-303.1077776
TCjCOXQ	-303.0980978	0.0511300	0.0069470	-303.0911508
CC*O(Oj)[h]	-228.0835228	0.0520300	0.0053120	-228.0782108
CyCOC=O	-227.5038475	0.0421240	0.0042990	-227.4995485
TYCOCDOXOH	-303.1112666	0.0480010	0.0066610	-303.1046056

[a] Unit in Hartree 1 HF=627.51 kcal/mol.

[b] Scaled ZPVE are included. Scaling factor is recommended as 0.91844 by Petersson et.al [22]

[c] Non-scaled.

[d] Non-scaled.

[e] "j" stands for radical site.

[f] "Q" stands for hydroperoxy group(OOH).

[g] "Qj" stands for peroxy(OO.).

[h] "*" stands for bouble bonding(C=O).

including scaled ZPVE's, nonscaled ZPVE's, thermal corrections to 298.15 K, and total energies at 298 K including scaled ZPVE's are shown in Table 3.5 for CBSQ calculations. Frequencies are scaled by 0.91844 for HF/6-31G(d') determined frequencies as recommended by Petersson et al.[22]

Table 3.6 Molecule Considered to Have Known $\Delta H_f^\circ{}_{298}$ for Use in Isodesmic Reactions.

Compounds	$\Delta H_f^\circ{}_{298}$ (kcal/mole)
CH_3CH_2OH	-56.17 [30]
$CH_3C(=O)OH$	-103.56 (Avg. of [30],[31],[32])
CH_3CH_2OOH	-39.9 [33]

The evaluated enthalpies of formation for the molecules considered to have known $\Delta H_f^\circ{}_{298}$ values, for use in the isodesmic reaction, are : -56.17[30], -103.56[average of 30, 31, 32], and -39.9[33] for CH_3CH_2OH, $CH_3C(=O)OH$, and CH_3CH_2OOH, respectively. A low or zero $\Delta H^\circ{}_{frxn,298}$ supports the hypothesis of group additivity and increases credibility of the calculations.

The CBSQ and density functionals determined enthalpy of reaction (1) is –2.59 and –3.88 kcal/mole, respectively. $\Delta H_f^\circ{}_{298}[CCOQ]$ is evaluated from

$$\Delta H^\circ{}_{frxn,298} = \Delta H_f^\circ{}_{298} [CH_3C(=O)OH] + \Delta H_f^\circ{}_{298} [CH_3CH_2OOH]$$

$$- \Delta H_f^\circ{}_{298} [CCOQ] - \Delta H_f^\circ{}_{298} [CH_3CH_2OH] = -2.59 \text{ or } -3.88$$

$$= -103.56 + (-39.9) - X - (-56.17) \text{ kcal/mole} \quad ....(4)$$

The enthalpy of formation of CCOQ obtained is –84.7 and –83.41 kcal/mole in CBSQ and density functionals calculations, respectively.

The enthalpy of formation of two intermediate radicals, CjCOQ and CCOQj by

CBSQ and density functionals are obtained from use of isodesmic reactions (2) and

(3) and bond dissociation energy of C_2H_5—H(101.6 kcal/mole) and CH_3OO—H(86.3

kcal/mole) The data results in enthalpy values are −32.35 and −32.37 for CjCOQ,

-38.75 and −38.02 for CCOQj, in CBSQ and density functionals calculations,

respectively.

Formation of CCOQj adduct has a well depth of 36.55 kcal/mole.

The activation energy for isomerization, TCCOQjS, is estimated from both the

reactant CCOQj and the product CjCOQ. The averaged result is 26.93 and 28.63

kcal/mole in CBSQ and density functionals, respectively. The activation energy for

direct HO_2 elimination, TCCOXQE, is estimated by taking the difference of total

energy with ZPVE and thermal correction between transition state(TS) and peroxy

reactant, resulting in 28.01 and 30.66 kcal/mole in CBSQ and density functionals,

respectively. The activation energy for HO_2 elimination from the hydroperoxide

isomer, TCjCOXQ, is estimated by taking the difference of total energy with ZPVE

and thermal correction between transition state(TS) and reactant, resulting in 31.53

kcal/mole via CBSQ. The activation energy for epoxide formation via OH

elimination, TYCOCDOXOH, is estimated by taking the difference of total energy

with ZPVE and thermal correction between transition state(TS) and hydroperoxide

isomer, resulting in 23.08 kcal/mole by CBSQ.

4.4 QRRK Calculation Results

QRRK calculations for k(E) and modified strong collision analysis of Gilbert et. al[17-19] for fall-off are performed on the $CH_3CjO + O_2$ reaction to obtain rate constants as a function of temperature and pressure and results are listed in Table 3.7. ΔE down of 400 cal/mole is used for bath gas N_2.

Plots of rate constants at 1atm pressure versus 1000/T are illustrated in Figure 3.7. Stabilization (CCOQj) is clearly important at lower temperatures, 1atm pressure, with reverse dissociation and ketene + HO_2 products via direct HO_2 elimination important at higher temperatures.

Plots of rate constants at 298 K versus pressure are illustrated in Figure 3.8. The figure illustrates that stabilization is the dominant path at high pressures, while reverse dissociation and ketene + HO_2 products via direct HO_2 elimination channel are most important at low pressures.

Plots of rate constants at 1000 K versus pressure are illustrated in Figure 3.9. The figure illustrates that stabilization decreases as pressure is decreased. Reverse dissociation and ketene + HO_2 products via direct HO_2 elimination are most important at both high and low pressures.

Table 3.7 Input Parameters[a] and High-Pressure Limit Rate Constants (K_∞)[b] for QRRK Calculations[c] and the Resulting Rate Constants (Temp=298K) : CBSQ Result (adjusted)

Input parameters for QRRK calculations

High-pressure Limit Rate Constants

Reaction	$A[S^{-1}$ or $cm^3/(mole\ s)]$	k_∞	
		n	Ea (kcal/mole)
1 $CH_3CjO + O_2 \Rightarrow CCOQj^d$	2.65E+12	0.0	0.0
-1 $CCOQj \Rightarrow CH_3CjO + O_2^e$	9.40E+13	0.0	34.66
2 $CCOQj \Rightarrow CjCOQ^f$	1.52E+5	2.22	26.25
3 $CCOQj \Rightarrow CH_2CO + HO_2^f$	9.29E+5	2.14	27.30
4 $CjCOQ \Rightarrow CyCOC=O + OH^f$	8.13E+8	0.98	23.09
5 $CjCOQ \Rightarrow CH_2CO + HO_2^f$	5.21E+10	0.81	31.77

Calculated Reaction Parameters at P = 1atm, $k=A(T/K)^n exp(-Ea/RT)$ (T=298-2000K)

Reaction	A	n	Ea (kcal/mole)	$k_{298}(s^{-1}$ or $cm^3/(mole\ s)$
1 $CH_3CjO + O_2 \Rightarrow CCOQj$	6.93E+43	-10.29	8.28	2.03E+12
6 $CH_3CjO + O_2 \Rightarrow CH_2CO + HO_2$	3.65E+18	-1.78	6.29	3.51E+09
7 $CH_3CjO + O_2 \Rightarrow CyCOC=O + OH$	2.09E+27	-4.45	13.44	2.83E+06
8 $CH_3CjO + O_2 \Rightarrow CjCOQ$	8.42E+40	-9.17	12.47	1.23E+09
2 $CCOQj \Rightarrow CjCOQ$	2.61E+40	-9.10	36.50	1.00E-09
3 $CCOQj \Rightarrow CH_2CO + HO_2$	1.07E+36	-7.53	35.97	1.00E-09
4 $CjCOQ \Rightarrow CyCOC=O + OH$	1.97E+31	-6.27	29.39	1.68E-08
5 $CjCOQ \Rightarrow CH_2CO + HO_2$	4.18E+34	-7.11	37.76	2.16E-11

[a]Geometric mean frequency (from CPFIT, Ref.[34]: 389.7 cm^{-1}(5.993); 1292.8 cm^{-1} (7.788); 2889.0 cm^{-1} (3.279). Lennard-Jones parameters: σij=5.19Å, ε/k=533.08

[b]The units of A factors and rate constants k are s^{-1} for unimolecular reactions and $cm^3/(mole\ s)$ for bimolecular reactions.

[c]ΔE down of 400 cal/mole is used.

[d]$k_{\infty,1}$: Sehested et al. [35]

[e]$k_{\infty,-1}$: thermodynamics and microscopic reversibility <MR>

[f]A is calculated using TST and entropy of transition state, ΔS^*_{298} from HF/6-31G(d') (see Table 3.3); Ea is from CBSQ calculation (see Table 3.3 and description for determination of Ea in Results section). All parameters A, n, Ea, are fit over the temperature range of 298-2000K.
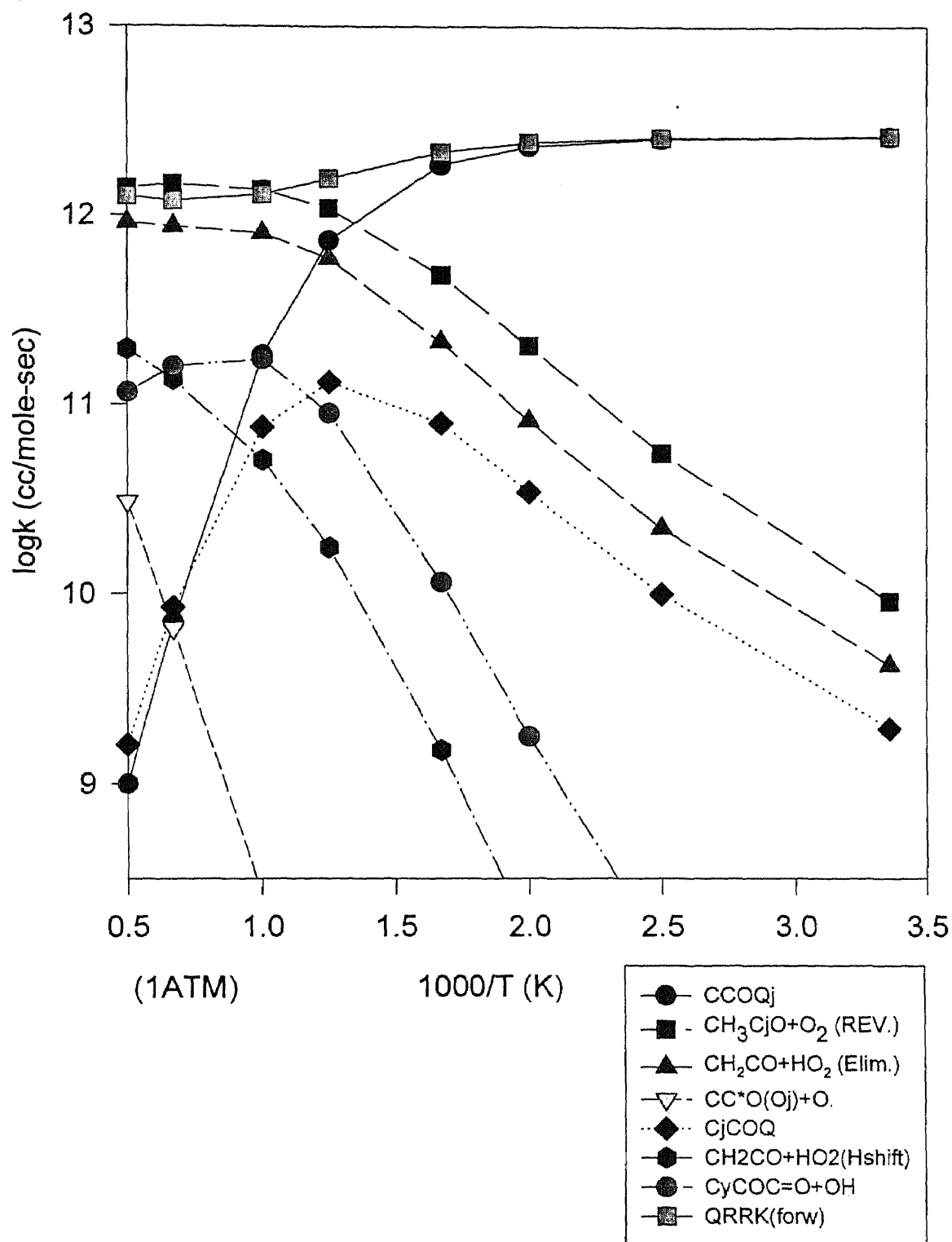
Figure 3.7 k vs. Temperature at 1atm $CH_3CjO + O_2$
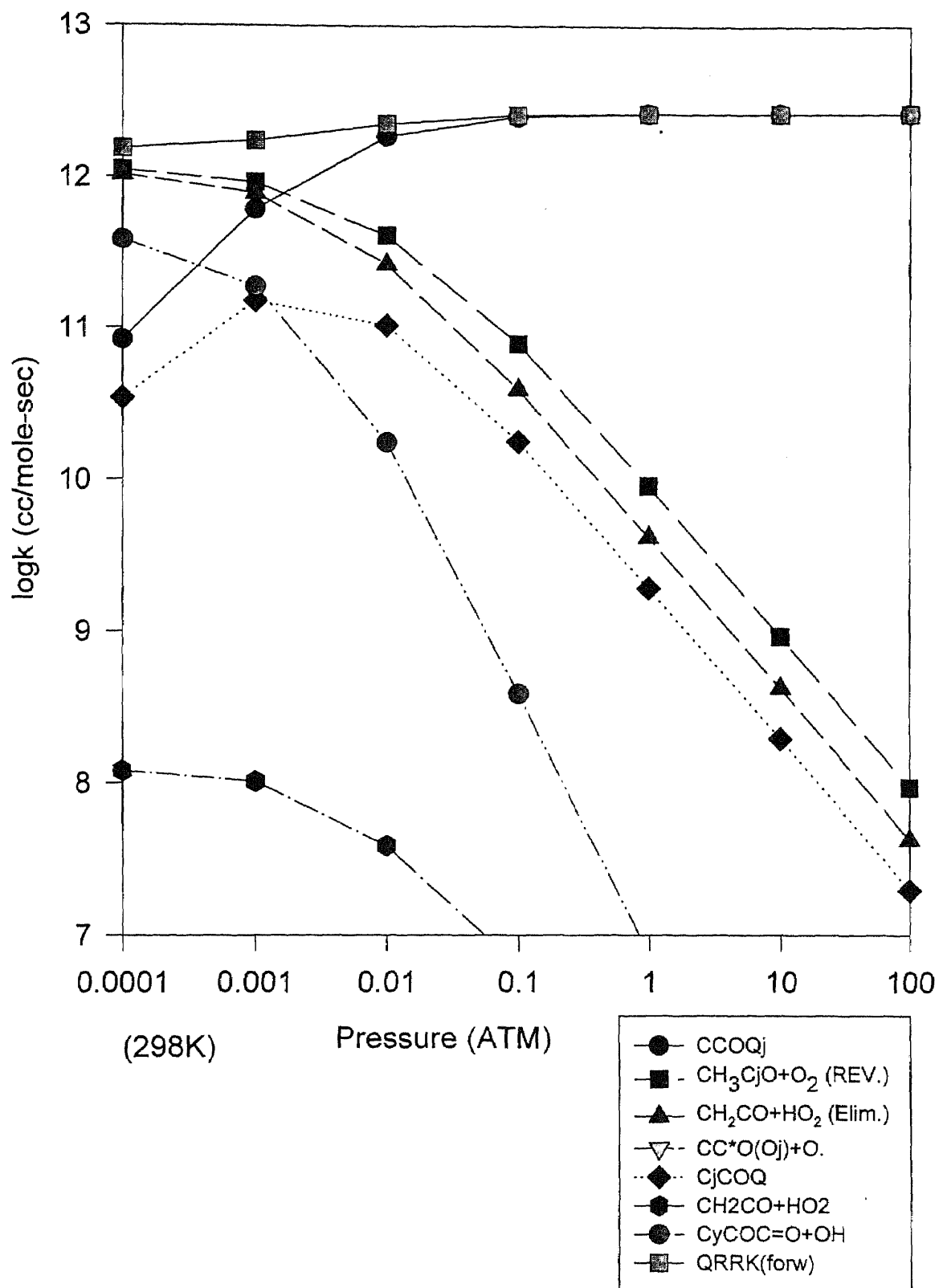
Figure 3.8 k vs. Pressure at 298K $CH_3CjO + O_2$
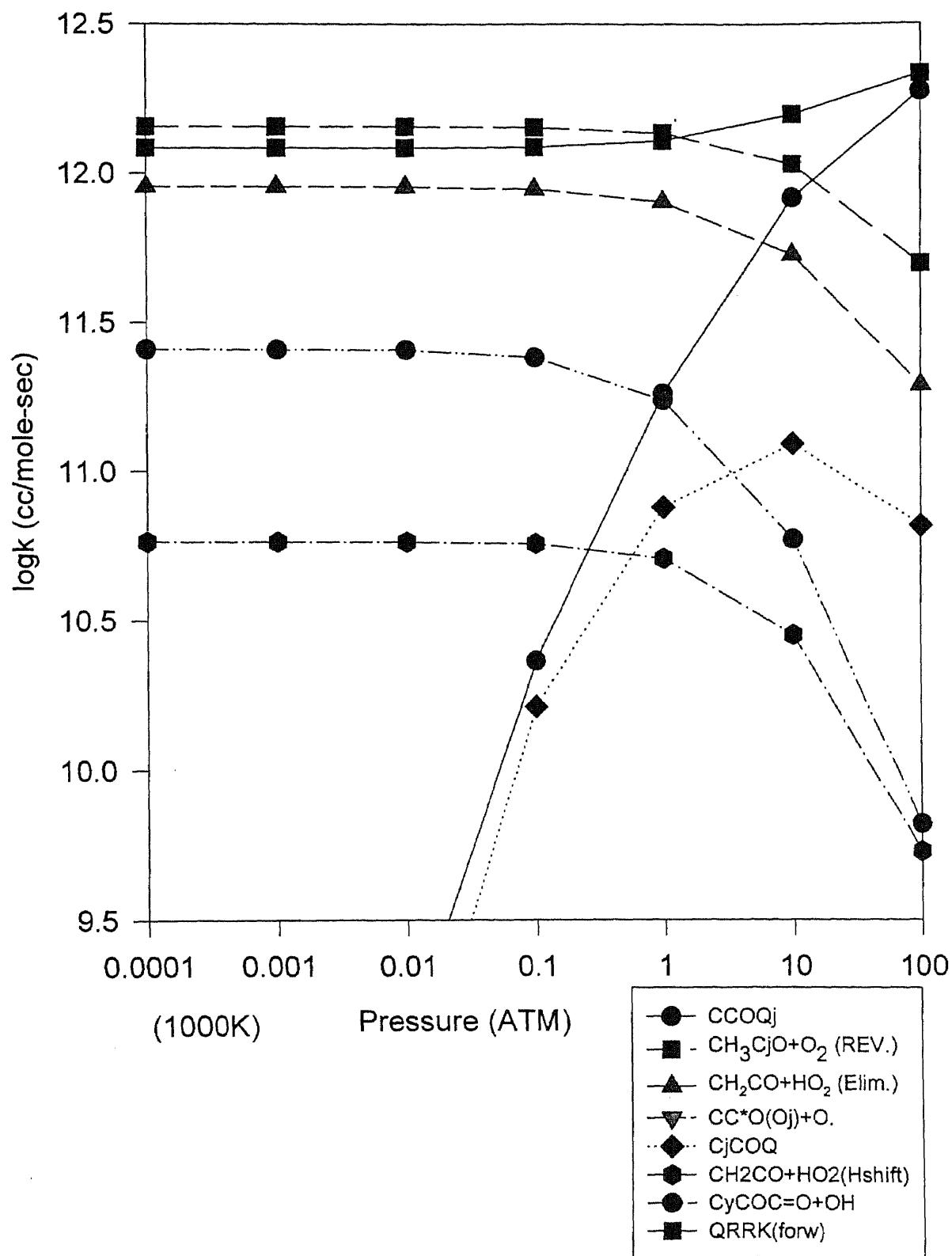
Figure 3.9 k vs. Pressure at 1000K $CH_3CjO + O_2$

CHAPTER 5

SUMMARY FOR PART THREE

Thermodynamic properties of stable radicals and transition states on $CH_3CjO + O_2$

reaction system are calculated using density functional and *ab initio* methods.

Enthalpies of formation ($\Delta H_f^{\circ}{}_{298}$) are determined using the CBSQ composite method

and density functional calculations with isodesmic reactions. Entropies ($S^{\circ}{}_{298}$) and

heat capacities (Cp(T) 300 –1500 K) are determined using geometric parameters and

vibrational frequencies obtained at the HF/6-31G(d') level of theory.

Reaction pathways and kinetics are analyzed on $CH_3CjO + O_2$ reaction system using

QRRK for k(E) and modified strong collision analysis of Gilbert et. al[17-19] for fall-off.

Major reaction paths at 1atm pressure are stabilization of CCOQj peroxy adduct at

low temperature and $CH_2CO + HO_2$ via HO_2 elimination and CyCOC=O + OH via

OH elimination at high temperature.

APPENDIX 3.1

THERMODYNAMIC ANALYSIS FOR CH3CjO + O2 REACTION

THERMODYNAMIC ANALYSIS for REACTION
Rx   CH3CJO   + O2   = CCOQJ
Hf {Kcal/mol} -2.200   .000   -38.750
S {cal/mol K} 64.060   46.630   79.550

dHr {kcal/mol} (298K) =   -36.55   dHr avg (298., 1500. K) =   -36.45
dU (dE) {kcal/mol} (") =   -35.96   dUr avg (298., 1500. K) =   -34.66
dSr {cal/mol K} (") =   -31.14   dSr avg (298., 1500. K) =   -31.35
dGr {kcal/mol} (") =   -27.27   dGr avg (298., 1500. K) =   -8.26
      Af/Ar (") = 1.039E-02 Af/Ar avg (298., 1500. K) = 2.823E-02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-3.655E+01	-3.596E+01	-3.116E+01	1.037E-02	-2.721E+01
400.00	-3.675E+01	-3.596E+01	-3.174E+01	1.032E-02	-2.406E+01
500.00	-3.686E+01	-3.587E+01	-3.198E+01	1.140E-02	-2.087E+01
600.00	-3.691E+01	-3.572E+01	-3.207E+01	1.313E-02	-1.767E+01
800.00	-3.687E+01	-3.528E+01	-3.202E+01	1.793E-02	-1.126E+01
1000.00	-3.675E+01	-3.476E+01	-3.188E+01	2.398E-02	-4.867E+00
1200.00	-3.660E+01	-3.421E+01	-3.174E+01	3.088E-02	1.496E+00
1500.00	-3.634E+01	-3.336E+01	-3.155E+01	4.244E-02	1.099E+01
2000.00	-3.591E+01	-3.193E+01	-3.130E+01	6.415E-02	2.670E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx   CCOQJ   = CC*O(OJ)   + O
Hf {Kcal/mol} -38.750   -41.590   59.560
S {cal/mol K} 79.550   68.420   38.470

dHr {kcal/mol} (298K) =   56.72   dHr avg (298., 1500. K) =   56.45
dU (dE) {kcal/mol} (") =   56.13   dUr avg (298., 1500. K) =   54.66
dSr {cal/mol K} (") =   27.34   dSr avg (298., 1500. K) =   27.12
dGr {kcal/mol} (") =   48.57   dGr avg (298., 1500. K) =   32.07
      Af/Ar (") = 1.422E+01 Af/Ar avg (298., 1500. K) = 4.217E+00

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	5.672E+01	5.613E+01	2.735E+01	1.417E+01	4.852E+01
400.00	5.677E+01	5.598E+01	2.750E+01	1.150E+01	4.577E+01
500.00	5.678E+01	5.579E+01	2.752E+01	9.278E+00	4.302E+01
600.00	5.676E+01	5.556E+01	2.747E+01	7.556E+00	4.027E+01
800.00	5.665E+01	5.506E+01	2.732E+01	5.246E+00	3.479E+01
1000.00	5.651E+01	5.452E+01	2.717E+01	3.882E+00	2.934E+01
1200.00	5.637E+01	5.399E+01	2.704E+01	3.034E+00	2.392E+01
1500.00	5.618E+01	5.320E+01	2.690E+01	2.261E+00	1.584E+01
2000.00	5.594E+01	5.197E+01	2.676E+01	1.580E+00	2.426E+00

APPENDIX 3.2

KINETIC ANALYSIS FOR $CH_3CjO + O_2$ REACTION

THERMODYNAMIC ANALYSIS for REACTION
Rx   CCOQJ   = TCCOQJS
Hf {Kcal/mol} -38.750   -11.820
S {cal/mol K} 79.550   72.150

dHr {kcal/mol} (298K) =   26.93   dHr avg (298., 1500. K) =   28.29
dU (dE) {kcal/mol} (") =   26.93   dUr avg (298., 1500. K) =   28.29
dSr {cal/mol K} (") =   -7.40   dSr avg (298., 1500. K) =   -5.46
dGr {kcal/mol} (") =   29.14   dGr avg (298., 1500. K) =   33.20
     Af/Ar (") = 2.413E-02 Af/Ar avg (298., 1500. K) = 6.417E-02
Fit Af/Ar   : A = 1.711E-06 n = 1.70 alpha = 6.111E-04 avg error 3.13 %
Fit Af/Ar w/ddU: A = 7.988E-10 n = 3.10 alpha = 1.720E-03 avg error 2.94 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.693E+01	2.693E+01	-7.388E+00	2.428E-02	2.915E+01
400.00	2.717E+01	2.717E+01	-6.726E+00	3.388E-02	2.986E+01
500.00	2.744E+01	2.744E+01	-6.119E+00	4.598E-02	3.050E+01
600.00	2.773E+01	2.773E+01	-5.592E+00	5.996E-02	3.108E+01
800.00	2.829E+01	2.829E+01	-4.779E+00	9.027E-02	3.211E+01
1000.00	2.878E+01	2.878E+01	-4.231E+00	1.189E-01	3.301E+01
1200.00	2.918E+01	2.918E+01	-3.865E+00	1.429E-01	3.382E+01
1500.00	2.965E+01	2.965E+01	-3.513E+00	1.706E-01	3.492E+01
2000.00	3.016E+01	3.016E+01	-3.216E+00	1.982E-01	3.659E+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 = 1.5209E+05   n = 2.21722   Ea = 2.6246E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.518E+11	3.107E+05	3.618E-09	3.570E-09
400.00	2.824E+11	5.879E+05	4.048E-04	4.075E-04
500.00	4.791E+11	9.643E+05	4.858E-01	4.935E-01
600.00	7.496E+11	1.445E+06	5.949E+01	6.040E+01
800.00	1.505E+12	2.734E+06	2.806E+04	2.807E+04
1000.00	2.478E+12	4.484E+06	1.270E+06	1.251E+06
1200.00	3.574E+12	6.718E+06	1.731E+07	1.694E+07
1500.00	5.333E+12	1.102E+07	2.550E+08	2.511E+08
2000.00	8.260E+12	2.085E+07	4.178E+09	4.295E+09

THERMODYNAMIC ANALYSIS for REACTION
Rx   CJCOQ   = TCCOQJS
Hf {Kcal/mol} -32.350   -11.820
S {cal/mol K} 84.120   72.150

dHr {kcal/mol} (298K) =   20.53   dHr avg (298., 1500. K) =   21.74 .
dU (dE) {kcal/mol} (") =   20.53   dUr avg (298., 1500. K) =   21.74
dSr {cal/mol K} (") =   -11.97   dSr avg (298., 1500. K) =   -10.61
dGr {kcal/mol} (") =   24.10   dGr avg (298., 1500. K) =   31.28
        Af/Ar (") = 2.420E-03   Af/Ar avg (298., 1500. K) = 4.794E-03
Fit Af/Ar   : A = 1.553E-04 n = .43 alpha =-6.148E-04 avg error   7.45 %
Fit Af/Ar w/ddU: A = 4.668E-06 n = 1.03 alpha =-5.410E-04 avg error 13.51 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.053E+01	2.053E+01	-1.197E+01	2.416E-03	2.412E+01
400.00	2.054E+01	2.054E+01	-1.195E+01	2.441E-03	2.532E+01
500.00	2.064E+01	2.064E+01	-1.173E+01	2.733E-03	2.650E+01
600.00	2.081E+01	2.081E+01	-1.143E+01	3.182E-03	2.766E+01
800.00	2.125E+01	2.125E+01	-1.079E+01	4.381E-03	2.988E+01
1000.00	2.175E+01	2.175E+01	-1.023E+01	5.804E-03	3.198E+01
1200.00	2.225E+01	2.225E+01	-9.776E+00	7.300E-03	3.398E+01
1500.00	2.296E+01	2.296E+01	-9.252E+00	9.500E-03	3.683E+01
2000.00	2.394E+01	2.394E+01	-8.683E+00	1.265E-02	4.130E+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 = 3.8474E+04   n = 2.01928   Ea =   1.9703E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.510E+10	1.005E+05	1.669E-05	1.708E-05
400.00	2.034E+10	1.796E+05	1.218E-01	1.184E-01
500.00	2.847E+10	2.818E+05	2.701E+01	2.645E+01
600.00	3.978E+10	4.073E+05	1.047E+03	1.042E+03
800.00	7.302E+10	7.280E+05	1.141E+05	1.160E+05
1000.00	1.209E+11	1.142E+06	2.128E+06	2.171E+06
1200.00	1.825E+11	1.651E+06	1.615E+07	1.638E+07
1500.00	2.969E+11	2.591E+06	1.342E+08	1.342E+08
2000.00	5.272E+11	4.631E+06	1.276E+09	1.252E+09

THERMODYNAMIC ANALYSIS for REACTION
Rx   CCOQJ   = TCCOXQE
Hf {Kcal/mol} -38.750   -10.740
S {cal/mol K}   79.550   74.970

dHr {kcal/mol} (298K) =   28.01   dHr avg (298., 1500. K) =   29.39 .
dU (dE) {kcal/mol} (") =   28.01   dUr avg (298., 1500. K) =   29.39
dSr {cal/mol K} (") =   -4.58   dSr avg (298., 1500. K) =   -2.77
dGr {kcal/mol} (") =   29.38   dGr avg (298., 1500. K) =   31.88
      Af/Ar (") = 9.976E-02   Af/Ar avg (298., 1500. K) = 2.478E-01
Fit Af/Ar   : A = 2.310E-04 n = 1.06 alpha =-8.875E-05 avg error   1.41 %
Fit Af/Ar w/ddU: A = 1.484E-06 n = 1.97 alpha = 3.886E-04 avg error   1.27 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.801E+01	2.801E+01	-4.567E+00	1.004E-01	2.938E+01
400.00	2.822E+01	2.822E+01	-3.971E+00	1.355E-01	2.981E+01
500.00	2.843E+01	2.843E+01	-3.511E+00	1.708E-01	3.018E+01
600.00	2.864E+01	2.864E+01	-3.125E+00	2.075E-01	3.051E+01
800.00	2.909E+01	2.909E+01	-2.474E+00	2.879E-01	3.107E+01
1000.00	2.958E+01	2.958E+01	-1.932E+00	3.782E-01	3.151E+01
1200.00	3.007E+01	3.007E+01	-1.482E+00	4.742E-01	3.185E+01
1500.00	3.077E+01	3.077E+01	-9.647E-01	6.154E-01	3.221E+01
2000.00	3.184E+01	3.184E+01	-3.463E-01	8.401E-01	3.253E+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 = 9.2883E+05   n = 2.14429   Ea = 2.7300E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	6.277E+11	2.050E+05	2.443E-09	2.455E-09
400.00	1.130E+12	3.798E+05	4.290E-04	4.269E-04
500.00	1.780E+12	6.129E+05	6.666E-01	6.631E-01
600.00	2.594E+12	9.061E+05	9.579E+01	9.557E+01
800.00	4.799E+12	1.679E+06	5.405E+04	5.425E+04
1000.00	7.881E+12	2.709E+06	2.701E+06	2.716E+06
1200.00	1.186E+13	4.006E+06	3.951E+07	3.965E+07
1500.00	1.923E+13	6.464E+06	6.324E+08	6.317E+08
2000.00	3.501E+13	1.198E+07	1.160E+10	1.156E+10

THERMODYNAMIC ANALYSIS for REACTION
Rx   CJCOQ   = TCJCOXQ
Hf {Kcal/mol} -32.350   -.820
S {cal/mol K} 84.120   82.960

dHr {kcal/mol} (298K) =   31.53   dHr avg (298., 1500. K) =   31.28 .
dU (dE) {kcal/mol} (") =   31.53   dUr avg (298., 1500. K) =   31.28
dSr {cal/mol K} (") =   -1.16   dSr avg (298., 1500. K) =   -1.33
dGr {kcal/mol} (") =   31.88   dGr avg (298., 1500. K) =   32.47
        Af/Ar (") = 5.578E-01   Af/Ar avg (298., 1500. K) = 5.127E-01
Fit Af/Ar   : A = 1.473E-01 n =   .27 alpha = 5.187E-04 avg error   2.71 %
Fit Af/Ar w/ddU: A = 9.832E-02 n =   .36 alpha = 8.149E-04 avg error   5.71 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	3.153E+01	3.153E+01	-1.155E+00	5.592E-01	3.188E+01
400.00	3.159E+01	3.159E+01	-9.790E-01	6.110E-01	3.198E+01
500.00	3.161E+01	3.161E+01	-9.297E-01	6.263E-01	3.208E+01
600.00	3.161E+01	3.161E+01	-9.430E-01	6.222E-01	3.217E+01
800.00	3.153E+01	3.153E+01	-1.048E+00	5.903E-01	3.237E+01
1000.00	3.141E+01	3.141E+01	-1.181E+00	5.518E-01	3.259E+01
1200.00	3.127E+01	3.127E+01	-1.314E+00	5.163E-01	3.284E+01
1500.00	3.102E+01	3.102E+01	-1.495E+00	4.712E-01	3.326E+01
2000.00	3.059E+01	3.059E+01	-1.745E+00	4.156E-01	3.408E+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 = 5.2099E+10   n = .80559   Ea = 3.1773E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.496E+12	9.898E+01	3.723E-11	3.664E-11
400.00	5.092E+12	1.248E+02	2.784E-05	2.830E-05
500.00	6.525E+12	1.494E+02	9.894E-02	1.005E-01
600.00	7.778E+12	1.730E+02	2.386E+01	2.403E+01
800.00	9.839E+12	2.181E+02	2.390E+04	2.371E+04
1000.00	1.150E+13	2.611E+02	1.568E+06	1.546E+06
1200.00	1.291E+13	3.024E+02	2.608E+07	2.572E+07
1500.00	1.473E+13	3.619E+02	4.447E+08	4.424E+08
2000.00	1.732E+13	4.563E+02	7.868E+09	8.014E+09

THERMODYNAMIC ANALYSIS for REACTION

Rx   CJCOQ   = TYCOCDOXO

Hf {Kcal/mol} -32.350   -9.270

S {cal/mol K} 84.120   77.390

dHr {kcal/mol} (298K) =   23.08   dHr avg (298., 1500. K) =   23.05

dU (dE) {kcal/mol} (") =   23.08   dUr avg (298., 1500. K) =   23.05

dSr {cal/mol K} (") =   -6.73   dSr avg (298., 1500. K) =   -6.77

dGr {kcal/mol} (") =   25.09   dGr avg (298., 1500. K) =   29.14

     Af/Ar (") = 3.381E-02 Af/Ar avg (298., 1500. K) = 3.308E-02

Fit Af/Ar   : A = 3.270E-02 n = .01 alpha = 4.184E-05 avg error   .61 %

Fit Af/Ar w/ddU: A = 3.015E-02 n = .02 alpha = 7.455E-05 avg error   1.19 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.308E+01	2.308E+01	-6.731E+00	3.380E-02	2.510E+01
400.00	2.307E+01	2.307E+01	-6.762E+00	3.327E-02	2.577E+01
500.00	2.306E+01	2.306E+01	-6.775E+00	3.304E-02	2.645E+01
600.00	2.306E+01	2.306E+01	-6.781E+00	3.295E-02	2.713E+01
800.00	2.306E+01	2.306E+01	-6.783E+00	3.292E-02	2.849E+01
1000.00	2.306E+01	2.306E+01	-6.785E+00	3.288E-02	2.984E+01
1200.00	2.305E+01	2.305E+01	-6.793E+00	3.276E-02	3.120E+01
1500.00	2.302E+01	2.302E+01	-6.817E+00	3.236E-02	3.324E+01
2000.00	2.290E+01	2.290E+01	-6.882E+00	3.132E-02	3.666E+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 = 8.1299E+08   n = .97757   Ea =   2.3089E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.113E+11	2.640E+02	3.235E-06	3.234E-06
400.00	2.773E+11	3.497E+02	6.879E-02	6.876E-02
500.00	3.443E+11	4.349E+02	2.852E+01	2.853E+01
600.00	4.120E+11	5.198E+02	1.639E+03	1.640E+03
800.00	5.487E+11	6.886E+02	2.751E+05	2.753E+05
1000.00	6.851E+11	8.565E+02	6.256E+06	6.255E+06
1200.00	8.190E+11	1.024E+03	5.192E+07	5.185E+07
1500.00	1.012E+12	1.273E+03	4.481E+08	4.473E+08
2000.00	1.305E+12	1.687E+03	4.102E+09	4.110E+09

APPENDIX 3.3

KINETIC DATA FOR $CH_3CjO + O_2$ REACTIONS ARRHENIUS FORM

Chemical Activation CH₃CjO + O₂

CH3CO+O2	<=> CCOQJ	4.57E+36	-9.52	2923.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	13% err,	1.00 x N2
CH3CO+O2	<=> CCOQJ	3.85E+38	-9.79	3460.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	15% err,	1.00 x N2
CH3CO+O2	<=> CCOQJ	3.13E+42	-10.62	5330.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	19% err,	1.00 x N2
CH3CO+O2	<=> CCOQJ	3.61E+45	-11.16	7568.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	17% err,	1.00 x N2
CH3CO+O2	<=> CCOQJ	6.93E+43	-10.29	8278.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	24% err,	1.00 x N2
CH3CO+O2	<=> CCOQJ	2.06E+37	-8.02	7092.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	35% err,	1.00 x N2
CH3CO+O2	<=> CCOQJ	2.53E+28	-5.10	4760.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	32% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	2.10E+12	-.04	254.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	3% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	8.45E+12	-.22	590.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	1% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	2.04E+15	-.90	1977.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	4% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	8.76E+18	-1.92	4461.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	6% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	2.30E+20	-2.27	6608.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	11% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	8.34E+16	-1.18	7088.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	36% err,	1.00 x N2
CH3CO+O2	<=> CH3CO+O2	8.02E+08	1.24	5735.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	60% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	1.52E+12	-.07	-38.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	3% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	1.09E+13	-.32	449.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	5% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	8.79E+15	-1.15	2232.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	10% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	1.05E+19	-2.00	4747.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	8% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	3.65E+18	-1.78	6293.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	18% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	1.82E+13	-.15	6053.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	44% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	1.49E+04	2.57	4223.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	60% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	9.55E+12	-.04	20844.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	9.57E+12	-.04	20845.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	9.80E+12	-.04	20852.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	1.23E+13	-.07	20916.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	7.07E+13	-.28	21429.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	45% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	4.53E+15	-.77	23096.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	56% err,	1.00 x N2
CH3CO+O2	<=> CC*OOJ+O.	3.77E+13	-.09	23979.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	91% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	2.46E+33	-8.48	2472.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	18% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	5.33E+36	-9.15	3859.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	23% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	2.50E+43	-10.75	7786.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	28% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	3.80E+46	-11.26	11605.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	20% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	8.42E+40	-9.17	12465.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	43% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	6.51E+27	-4.95	10292.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	78% err,	1.00 x N2
CH3CO+O2	<=> CJCOQ	3.75E+11	.08	6449.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	85% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	2.78E+11	.13	5058.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	5% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	8.52E+11	-.01	5335.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	4% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	5.22E+14	-.81	6982.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	2% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	3.01E+20	-2.43	10960.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	6% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	2.16E+23	-3.14	15002.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	23% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	2.79E+17	-1.26	16212.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	77% err,	1.00 x N2
CH3CO+O2	<=> CH2CO+HO2	6.55E+02	3.13	13930.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	137% err,	1.00 x N2
CH3CO+O2	<=> OCYCO+OH	1.26E+16	-1.48	1158.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	2% err,	1.00 x N2
CH3CO+O2	<=> OCYCO+OH	1.79E+18	-2.10	2400.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	4% err,	1.00 x N2
CH3CO+O2	<=> OCYCO+OH	1.33E+24	-3.77	6154.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	11% err,	1.00 x N2
CH3CO+O2	<=> OCYCO+OH	1.25E+29	-5.12	10758.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	12% err,	1.00 x N2

CH3CO+O2	<=> OCYCO+OH	2.09E+27	-4.45	13442.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 46% err, 1.00 x N2
CH3CO+O2	<=> OCYCO+OH	7.34E+16	-1.24	12904.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 108% err, 1.00 x N2
CH3CO+O2	<=> OCYCO+OH	1.57E+00	3.71	9664.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 151% err, 1.00 x N2

Dissociation

CCOQJ	<=> CH3CO+O2	7.32E+38	-9.73	37889.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 15% err, 1.00 x N2
CCOQJ	<=> CH3CO+O2	5.72E+40	-9.99	38408.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 17% err, 1.00 x N2
CCOQJ	<=> CH3CO+O2	4.19E+44	-10.80	40248.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 21% err, 1.00 x N2
CCOQJ	<=> CH3CO+O2	4.84E+47	-11.35	42481.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 19% err, 1.00 x N2
CCOQJ	<=> CH3CO+O2	9.49E+45	-10.47	43193.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 24% err, 1.00 x N2
CCOQJ	<=> CH3CO+O2	2.85E+39	-8.21	42008.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 33% err, 1.00 x N2
CCOQJ	<=> CH3CO+O2	3.50E+30	-5.29	39676.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 30% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	3.02E+45	-11.70	34786.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 16% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	4.69E+47	-11.99	36613.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 16% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	1.57E+47	-11.50	37697.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 21% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	1.30E+43	-9.94	37458.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 32% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	1.07E+36	-7.53	35972.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 42% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	2.56E+27	-4.71	33715.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 41% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	8.21E+18	-1.98	31283.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 29% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	3.03E+26	-6.06	57367.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 40% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	3.04E+27	-6.06	57368.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 40% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	3.11E+28	-6.07	57374.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 40% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	3.84E+29	-6.09	57436.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 40% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	1.93E+31	-6.29	57925.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 40% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	5.79E+33	-6.68	59462.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 50% err, 1.00 x N2
CCOQJ	<=> CC*OOJ+O.	7.71E+31	-5.77	60018.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 76% err, 1.00 x N2
CCOQJ	<=> CJCOQ	1.05E+57	-15.58	37127.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 13% err, 1.00 x N2
CCOQJ	<=> CJCOQ	4.20E+58	-15.66	39020.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 17% err, 1.00 x N2
CCOQJ	<=> CJCOQ	3.69E+55	-14.34	39378.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 29% err, 1.00 x N2
CCOQJ	<=> CJCOQ	3.08E+49	-12.15	38558.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 46% err, 1.00 x N2
CCOQJ	<=> CJCOQ	2.61E+40	-9.10	36498.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 58% err, 1.00 x N2
CCOQJ	<=> CJCOQ	6.24E+29	-5.63	33648.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 53% err, 1.00 x N2
CCOQJ	<=> CJCOQ	5.33E+19	-2.40	30739.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 35% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	8.71E+32	-8.02	42632.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 11% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	3.14E+34	-8.18	42959.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 11% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	3.28E+38	-9.04	44828.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 15% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	2.52E+44	-10.39	48777.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 18% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	2.34E+44	-9.95	51548.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 34% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	5.07E+34	-6.70	50827.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 73% err, 1.00 x N2
CCOQJ	<=> CH2CO+HO2	1.66E+19	-1.85	47457.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 93% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	7.42E+45	-11.96	36987.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 19% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	1.01E+52	-13.39	40909.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 21% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	1.20E+55	-13.87	44624.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 21% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	2.14E+51	-12.35	46148.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 45% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	7.01E+40	-8.89	45045.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 84% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	1.61E+26	-4.28	42025.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 113% err, 1.00 x N2
CCOQJ	<=> OCYCO+OH	3.68E+10	.50	38140.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 106% err, 1.00 x N2

CJCOQ	<=> CCOQJ	1.32E+57	-16.22	30001.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 17% err, 1.00 x N2
CJCOQ	<=> CCOQJ	7.20E+59	-16.61	32351.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 16% err, 1.00 x N2
CJCOQ	<=> CCOQJ	1.23E+57	-15.33	32965.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 25% err, 1.00 x N2
CJCOQ	<=> CCOQJ	4.92E+50	-13.00	32199.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 43% err, 1.00 x N2
CJCOQ	<=> CCOQJ	1.03E+41	-9.73	30078.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 56% err, 1.00 x N2
CJCOQ	<=> CCOQJ	4.20E+29	-6.00	27076.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 53% err, 1.00 x N2
CJCOQ	<=> CCOQJ	9.32E+18	-2.58	24025.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 36% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	3.15E+34	-8.78	30087.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 23% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	5.71E+37	-9.43	31424.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 29% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	2.60E+44	-11.02	35301.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 34% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	8.76E+47	-11.64	39219.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 22% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	5.99E+42	-9.69	40265.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 37% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	8.33E+29	-5.54	38210.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 69% err, 1.00 x N2
CJCOQ	<=> CH3CO+O2	5.13E+13	-.51	34401.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 77% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	7.53E+46	-12.34	30200.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 28% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	1.33E+49	-12.60	33278.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 19% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	2.09E+48	-11.97	35644.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 18% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	2.85E+42	-9.85	36297.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 41% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	1.10E+31	-6.14	34752.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 75% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	1.30E+16	-1.46	31555.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 97% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	2.52E+00	3.33	27616.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 89% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	3.79E+22	-5.37	49300.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 22% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	3.89E+23	-5.38	49307.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 22% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	5.03E+24	-5.41	49373.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 22% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	4.08E+26	-5.67	49925.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 24% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	7.63E+30	-6.59	52203.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 27% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	4.08E+33	-6.99	55300.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 17% err, 1.00 x N2
CJCOQ	<=> CC*OOJ+O.	4.32E+26	-4.53	55490.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 32% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	1.12E+27	-6.21	32810.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 21% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	2.88E+28	-6.32	33048.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 22% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	3.87E+31	-6.93	34351.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 27% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	2.50E+35	-7.70	36706.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 23% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	4.18E+34	-7.11	37759.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 15% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	2.91E+28	-4.95	36702.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 21% err, 1.00 x N2
CJCOQ	<=> CH2CO+HO2	1.88E+20	-2.27	34547.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 18% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	5.56E+36	-9.27	26773.	! 1.00E-04 (1.00E-04) atm, 298-2000 K, 32% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	2.34E+40	-9.99	29023.	! 1.00E-03 (1.00E-03) atm, 298-2000 K, 28% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	1.38E+41	-9.85	30565.	! 1.00E-02 (1.00E-02) atm, 298-2000 K, 18% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	7.67E+37	-8.54	30670.	! 1.00E-01 (1.00E-01) atm, 298-2000 K, 18% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	1.97E+31	-6.27	29392.	! 1.00E+00 (1.00E+00) atm, 298-2000 K, 26% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	1.65E+23	-3.62	27305.	! 1.00E+01 (1.00E+01) atm, 298-2000 K, 26% err, 1.00 x N2
CJCOQ	<=> OCYCO+OH	8.08E+15	-1.27	25205.	! 1.00E+02 (1.00E+02) atm, 298-2000 K, 16% err, 1.00 x N2

APPENDIX 3.4

LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE
FOR $CH_3CjO + O_2$ REACTION

Chemical Activation Reaction (CH3CjO + O2) Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	10.923	12.046	12.015	-2.203	10.537	8.081	11.585	12.187
1.00E-04	400.	2.50E+00	10.281	12.062	12.027	1.201	10.009	8.997	11.603	12.175
1.00E-04	500.	2.00E+00	9.709	12.089	12.013	3.545	9.492	9.559	11.579	12.153
1.00E-04	600.	1.67E+00	9.183	12.112	11.997	5.441	8.994	9.950	11.548	12.133
1.00E-04	800.	1.25E+00	8.230	12.140	11.972	7.328	8.073	10.458	11.482	12.103
1.00E-04	1000.	1.00E+00	7.387	12.156	11.955	8.412	7.297	10.764	11.409	12.085
1.00E-04	1500.	6.67E-01	5.861	12.166	11.943	9.817	6.009	11.137	11.218	12.074
1.00E-04	2000.	5.00E-01	5.002	12.144	11.961	10.487	5.233	11.294	11.068	12.100

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	11.786	11.964	11.893	-2.203	11.176	8.012	11.272	12.238
1.00E-03	400.	2.50E+00	11.237	12.043	11.991	1.200	10.875	8.977	11.501	12.189
1.00E-03	500.	2.00E+00	10.693	12.084	12.002	3.545	10.441	9.553	11.545	12.157
1.00E-03	600.	1.67E+00	10.177	12.110	11.993	5.441	9.974	9.948	11.536	12.134
1.00E-03	800.	1.25E+00	9.229	12.140	11.971	7.328	9.069	10.458	11.480	12.104
1.00E-03	1000.	1.00E+00	8.387	12.156	11.955	8.412	8.296	10.764	11.408	12.085
1.00E-03	1500.	6.67E-01	6.861	12.166	11.943	9.817	7.008	11.137	11.218	12.074
1.00E-03	2000.	5.00E-01	6.002	12.144	11.961	10.487	6.233	11.294	11.068	12.100

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	12.268	11.613	11.422	-2.205	11.016	7.588	10.242	12.350
1.00E-02	400.	2.50E+00	11.979	11.919	11.781	1.200	11.221	8.818	10.986	12.260
1.00E-02	500.	2.00E+00	11.577	12.043	11.919	3.544	11.106	9.495	11.317	12.189
1.00E-02	600.	1.67E+00	11.126	12.097	11.962	5.441	10.813	9.927	11.443	12.146
1.00E-02	800.	1.25E+00	10.220	12.138	11.967	7.328	10.034	10.455	11.465	12.105
1.00E-02	1000.	1.00E+00	9.385	12.156	11.954	8.412	9.287	10.763	11.406	12.085
1.00E-02	1500.	6.67E-01	7.861	12.166	11.943	9.817	8.007	11.137	11.218	12.074
1.00E-02	2000.	5.00E-01	7.002	12.144	11.961	10.487	7.233	11.294	11.068	12.100

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	12.400	10.895	10.594	-2.223	10.251	6.423	8.590	12.410
1.00E-01	400.	2.50E+00	12.321	11.504	11.209	1.190	10.825	8.148	9.809	12.368
1.00E-01	500.	2.00E+00	12.147	11.840	11.587	3.540	11.115	9.157	10.578	12.292
1.00E-01	600.	1.67E+00	11.875	12.008	11.793	5.439	11.168	9.773	11.025	12.212
1.00E-01	800.	1.25E+00	11.150	12.124	11.933	7.328	10.809	10.427	11.361	12.120
1.00E-01	1000.	1.00E+00	10.366	12.154	11.948	8.412	10.213	10.758	11.381	12.088
1.00E-01	1500.	6.67E-01	8.859	12.166	11.943	9.817	8.998	11.136	11.216	12.074
1.00E-01	2000.	5.00E-01	8.002	12.144	11.961	10.487	8.230	11.294	11.068	12.100

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	12.421	9.963	9.626	-2.370	9.291	4.680	6.668	12.422
1.00E+00	400.	2.50E+00	12.409	10.747	10.350	1.108	10.001	6.784	8.127	12.414
1.00E+00	500.	2.00E+00	12.367	11.311	10.916	3.498	10.541	8.207	9.249	12.388
1.00E+00	600.	1.67E+00	12.269	11.685	11.331	5.424	10.903	9.178	10.063	12.336

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	800.	1.25E+00	11.866	12.036	11.771	7.324	11.117	10.245	10.954	12.194
1.00E+00	1000.	1.00E+00	11.260	12.135	11.905	8.411	10.880	10.708	11.237	12.109
1.00E+00	1500.	6.67E-01	9.848	12.165	11.940	9.817	9.929	11.132	11.201	12.075
1.00E+00	2000.	5.00E-01	8.999	12.144	11.960	10.487	9.208	11.293	11.064	12.100

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	12.423	8.972	8.630	-2.958	8.296	2.722	4.679	12.423
1.00E+01	400.	2.50E+00	12.422	9.800	9.376	.673	9.032	4.964	6.200	12.422
1.00E+01	500.	2.00E+00	12.416	10.477	10.015	3.216	9.658	6.643	7.488	12.418
1.00E+01	600.	1.67E+00	12.397	11.022	10.563	5.294	10.187	7.950	8.566	12.406
1.00E+01	800.	1.25E+00	12.256	11.728	11.344	7.292	10.883	9.632	10.052	12.325
1.00E+01	1000.	1.00E+00	11.919	12.031	11.728	8.403	11.092	10.453	10.773	12.198
1.00E+01	1500.	6.67E-01	10.786	12.158	11.925	9.816	10.668	11.096	11.113	12.083
1.00E+01	2000.	5.00E-01	9.983	12.142	11.958	10.487	10.102	11.283	11.041	12.101

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	12.423	7.973	7.630	-3.884	7.296	.727	2.680	12.423
1.00E+02	400.	2.50E+00	12.423	8.807	8.379	-.191	8.036	2.992	4.209	12.423
1.00E+02	500.	2.00E+00	12.422	9.507	9.031	2.456	8.676	4.740	5.535	12.423
1.00E+02	600.	1.67E+00	12.420	10.118	9.620	4.757	9.253	6.210	6.716	12.421
1.00E+02	800.	1.25E+00	12.392	11.096	10.614	7.076	10.213	8.411	8.620	12.402
1.00E+02	1000.	1.00E+00	12.274	11.697	11.287	8.330	10.818	9.729	9.821	12.333
1.00E+02	1500.	6.67E-01	11.577	12.113	11.848	9.808	11.077	10.905	10.800	12.131
1.00E+02	2000.	5.00E-01	10.913	12.132	11.940	10.484	10.797	11.214	10.919	12.112

Chemical Activation Reaction (CH₃CjO + O₂) Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	10.923	12.046	12.015	-2.203	10.537	8.081	11.585	12.187
298.	3.36E+00	1.00E-03	11.786	11.964	11.893	-2.203	11.176	8.012	11.272	12.238
298.	3.36E+00	1.00E-02	12.268	11.613	11.422	-2.205	11.016	7.588	10.242	12.350
298.	3.36E+00	1.00E-01	12.400	10.895	10.594	-2.223	10.251	6.423	8.590	12.410
298.	3.36E+00	1.00E+00	12.421	9.963	9.626	-2.370	9.291	4.680	6.668	12.422
298.	3.36E+00	1.00E+01	12.423	8.972	8.630	-2.958	8.296	2.722	4.679	12.423
298.	3.36E+00	1.00E+02	12.423	7.973	7.630	-3.884	7.296	.727	2.680	12.423

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	10.281	12.062	12.027	1.201	10.009	8.997	11.603	12.175
400.	2.50E+00	1.00E-03	11.237	12.043	11.991	1.200	10.875	8.977	11.501	12.189
400.	2.50E+00	1.00E-02	11.979	11.919	11.781	1.200	11.221	8.818	10.986	12.260
400.	2.50E+00	1.00E-01	12.321	11.504	11.209	1.190	10.825	8.148	9.809	12.368
400.	2.50E+00	1.00E+00	12.409	10.747	10.350	1.108	10.001	6.784	8.127	12.414
400.	2.50E+00	1.00E+01	12.422	9.800	9.376	.673	9.032	4.964	6.200	12.422
400.	2.50E+00	1.00E+02	12.423	8.807	8.379	-.191	8.036	2.992	4.209	12.423

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	9.709	12.089	12.013	3.545	9.492	9.559	11.579	12.153
500.	2.00E+00	1.00E-03	10.693	12.084	12.002	3.545	10.441	9.553	11.545	12.157
500.	2.00E+00	1.00E-02	11.577	12.043	11.919	3.544	11.106	9.495	11.317	12.189
500.	2.00E+00	1.00E-01	12.147	11.840	11.587	3.540	11.115	9.157	10.578	12.292
500.	2.00E+00	1.00E+00	12.367	11.311	10.916	3.498	10.541	8.207	9.249	12.388
500.	2.00E+00	1.00E+01	12.416	10.477	10.015	3.216	9.658	6.643	7.488	12.418
500.	2.00E+00	1.00E+02	12.422	9.507	9.031	2.456	8.676	4.740	5.535	12.423

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	9.183	12.112	11.997	5.441	8.994	9.950	11.548	12.133
600.	1.67E+00	1.00E-03	10.177	12.110	11.993	5.441	9.974	9.948	11.536	12.134
600.	1.67E+00	1.00E-02	11.126	12.097	11.962	5.441	10.813	9.927	11.443	12.146
600.	1.67E+00	1.00E-01	11.875	12.008	11.793	5.439	11.168	9.773	11.025	12.212
600.	1.67E+00	1.00E+00	12.269	11.685	11.331	5.424	10.903	9.178	10.063	12.336
600.	1.67E+00	1.00E+01	12.397	11.022	10.563	5.294	10.187	7.950	8.566	12.406
600.	1.67E+00	1.00E+02	12.420	10.118	9.620	4.757	9.253	6.210	6.716	12.421

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	8.230	12.140	11.972	7.328	8.073	10.458	11.482	12.103
800.	1.25E+00	1.00E-03	9.229	12.140	11.971	7.328	9.069	10.458	11.480	12.104
800.	1.25E+00	1.00E-02	10.220	12.138	11.967	7.328	10.034	10.455	11.465	12.105
800.	1.25E+00	1.00E-01	11.150	12.124	11.933	7.328	10.809	10.427	11.361	12.120
800.	1.25E+00	1.00E+00	11.866	12.036	11.771	7.324	11.117	10.245	10.954	12.194
800.	1.25E+00	1.00E+01	12.256	11.728	11.344	7.292	10.883	9.632	10.052	12.325
800.	1.25E+00	1.00E+02	12.392	11.096	10.614	7.076	10.213	8.411	8.620	12.402

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	7.387	12.156	11.955	8.412	7.297	10.764	11.409	12.085
1000.	1.00E+00	1.00E-03	8.387	12.156	11.955	8.412	8.296	10.764	11.408	12.085
1000.	1.00E+00	1.00E-02	9.385	12.156	11.954	8.412	9.287	10.763	11.406	12.085
1000.	1.00E+00	1.00E-01	10.366	12.154	11.948	8.412	10.213	10.758	11.381	12.088
1000.	1.00E+00	1.00E+00	11.260	12.135	11.905	8.411	10.880	10.708	11.237	12.109
1000.	1.00E+00	1.00E+01	11.919	12.031	11.728	8.403	11.092	10.453	10.773	12.198
1000.	1.00E+00	1.00E+02	12.274	11.697	11.287	8.330	10.818	9.729	9.821	12.333
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	5.861	12.166	11.943	9.817	6.009	11.137	11.218	12.074
1500.	6.67E-01	1.00E-03	6.861	12.166	11.943	9.817	7.008	11.137	11.218	12.074
1500.	6.67E-01	1.00E-02	7.861	12.166	11.943	9.817	8.007	11.137	11.218	12.074
1500.	6.67E-01	1.00E-01	8.859	12.166	11.943	9.817	8.998	11.136	11.216	12.074
1500.	6.67E-01	1.00E+00	9.848	12.165	11.940	9.817	9.929	11.132	11.201	12.075
1500.	6.67E-01	1.00E+01	10.786	12.158	11.925	9.816	10.668	11.096	11.113	12.083
1500.	6.67E-01	1.00E+02	11.577	12.113	11.848	9.808	11.077	10.905	10.800	12.131
T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	5.002	12.144	11.961	10.487	5.233	11.294	11.068	12.100
2000.	5.00E-01	1.00E-03	6.002	12.144	11.961	10.487	6.233	11.294	11.068	12.100
2000.	5.00E-01	1.00E-02	7.002	12.144	11.961	10.487	7.233	11.294	11.068	12.100
2000.	5.00E-01	1.00E-01	8.002	12.144	11.961	10.487	8.230	11.294	11.068	12.100
2000.	5.00E-01	1.00E+00	8.999	12.144	11.960	10.487	9.208	11.293	11.064	12.100
2000.	5.00E-01	1.00E+01	9.983	12.142	11.958	10.487	10.102	11.283	11.041	12.101
2000.	5.00E-01	1.00E+02	10.913	12.132	11.940	10.484	10.797	11.214	10.919	12.112

Adduct (CCOQj) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-13.040	-8.998	-30.463	-8.752	-18.173	-10.896	-8.555
1.00E-04	400.	2.50E+00	-7.159	-3.973	-20.822	-3.850	-11.229	-5.423	-3.600
1.00E-04	500.	2.00E+00	-3.925	-1.259	-15.220	-1.234	-7.313	-2.501	-.933
1.00E-04	600.	1.67E+00	-1.921	.376	-11.079	.285	-4.817	-.755	.652
1.00E-04	800.	1.25E+00	.274	2.054	-6.617	1.690	-1.950	1.050	2.244
1.00E-04	1000.	1.00E+00	1.312	2.719	-4.206	2.112	-.468	1.815	2.869
1.00E-04	1500.	6.67E-01	2.302	3.113	-1.260	2.034	1.167	2.373	3.269
1.00E-04	2000.	5.00E-01	2.709	3.191	.205	1.619	1.900	2.492	3.397

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-12.172	-8.850	-29.463	-8.661	-17.256	-11.160	-8.443
1.00E-03	400.	2.50E+00	-6.202	-3.593	-19.822	-3.559	-10.258	-5.187	-3.269
1.00E-03	500.	2.00E+00	-2.941	-.683	-14.220	-.735	-6.323	-1.945	-.394
1.00E-03	600.	1.67E+00	-.927	1.083	-10.079	.957	-3.821	.000	1.348
1.00E-03	800.	1.25E+00	1.273	2.906	-5.617	2.611	-.951	1.985	3.123
1.00E-03	1000.	1.00E+00	2.312	3.648	-3.206	3.159	.531	2.797	3.827
1.00E-03	1500.	6.67E-01	3.302	4.100	-.260	3.124	2.167	3.371	4.265
1.00E-03	2000.	5.00E-01	3.709	4.188	1.205	2.704	2.900	3.491	4.397

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-11.682	-8.822	-28.465	-8.644	-16.760	-11.923	-8.422
1.00E-02	400.	2.50E+00	-5.455	-3.452	-18.823	-3.450	-9.479	-5.535	-3.146
1.00E-02	500.	2.00E+00	-2.055	-.363	-13.221	-.459	-5.418	-1.896	-.095
1.00E-02	600.	1.67E+00	.023	1.577	-9.080	1.413	-2.861	.356	1.826
1.00E-02	800.	1.25E+00	2.264	3.638	-4.617	3.344	.041	2.714	3.860
1.00E-02	1000.	1.00E+00	3.310	4.501	-2.206	4.069	1.529	3.690	4.702
1.00E-02	1500.	6.67E-01	4.302	5.060	.740	4.246	3.166	4.355	5.247
1.00E-02	2000.	5.00E-01	4.709	5.175	2.205	3.894	3.900	4.487	5.393

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	-11.547	-8.818	-27.483	-8.642	-17.071	-12.877	-8.420
1.00E-01	400.	2.50E+00	-5.110	-3.421	-17.832	-3.426	-9.337	-6.303	-3.118
1.00E-01	500.	2.00E+00	-1.483	-.246	-12.225	-.354	-4.923	-2.357	.020
1.00E-01	600.	1.67E+00	.773	1.834	-8.082	1.657	-2.134	.220	2.084
1.00E-01	800.	1.25E+00	3.194	4.186	-3.617	3.898	.972	3.094	4.416
1.00E-01	1000.	1.00E+00	4.292	5.243	-1.206	4.846	2.510	4.366	5.460
1.00E-01	1500.	6.67E-01	5.300	5.986	1.740	5.285	4.164	5.274	6.194
1.00E-01	2000.	5.00E-01	5.708	6.150	3.205	5.048	4.899	5.459	6.381

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	-11.526	-8.818	-26.629	-8.641	-17.903	-13.871	-8.419
1.00E+00	400.	2.50E+00	-5.022	-3.417	-16.913	-3.423	-9.902	-7.248	-3.113
1.00E+00	500.	2.00E+00	-1.263	-.220	-11.271	-.331	-5.145	-3.157	.051
1.00E+00	600.	1.67E+00	1.168	1.922	-7.101	1.742	-2.012	-.348	2.187

1.00E+00	800.	1.25E+00	3.911	4.506	-2.622	4.232	1.601	3.044	4.766
1.00E+00	1000.	1.00E+00	5.185	5.808	-.208	5.449	3.370	4.716	6.054
1.00E+00	1500.	6.67E-01	6.288	6.852	2.739	6.263	5.141	6.052	7.085
1.00E+00	2000.	5.00E-01	6.706	7.103	4.205	6.195	5.891	6.365	7.351

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	-11.523	-8.818	-26.214	-8.641	-18.880	-14.871	-8.419
1.00E+01	400.	2.50E+00	-5.009	-3.416	-16.345	-3.422	-10.809	-8.240	-3.113
1.00E+01	500.	2.00E+00	-1.213	-.216	-10.570	-.328	-5.895	-4.110	.057
1.00E+01	600.	1.67E+00	1.295	1.941	-6.255	1.760	-2.524	-1.194	2.217
1.00E+01	800.	1.25E+00	4.301	4.642	-1.666	4.373	1.644	2.584	4.944
1.00E+01	1000.	1.00E+00	5.845	6.155	.779	5.823	3.842	4.670	6.455
1.00E+01	1500.	6.67E-01	7.227	7.603	3.738	7.113	6.003	6.594	7.874
1.00E+01	2000.	5.00E-01	7.689	8.006	5.204	7.294	6.837	7.131	8.280

P (ATM)	T (K)	1000/T	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	-11.523	-8.818	-26.139	-8.641	-19.877	-15.871	-8.419
1.00E+02	400.	2.50E+00	-5.007	-3.416	-16.209	-3.422	-11.797	-9.240	-3.113
1.00E+02	500.	2.00E+00	-1.207	-.216	-10.345	-.328	-6.851	-5.103	.057
1.00E+02	600.	1.67E+00	1.319	1.944	-5.845	1.762	-3.399	-2.162	2.222
1.00E+02	800.	1.25E+00	4.437	4.680	-.937	4.412	1.113	1.800	5.005
1.00E+02	1000.	1.00E+00	6.200	6.316	1.672	5.997	3.746	4.217	6.669
1.00E+02	1500.	6.67E-01	8.018	8.181	4.723	7.755	6.550	6.805	8.509
1.00E+02	2000.	5.00E-01	8.619	8.812	6.199	8.251	7.609	7.662	9.124

Adduct (CCOQj) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-13.040	-8.998	-30.463	-8.752	-18.173	-10.896	-8.555
298.	3.36E+00	1.00E-03	-12.172	-8.850	-29.463	-8.661	-17.256	-11.160	-8.443
298.	3.36E+00	1.00E-02	-11.682	-8.822	-28.465	-8.644	-16.760	-11.923	-8.422
298.	3.36E+00	1.00E-01	-11.547	-8.818	-27.483	-8.642	-17.071	-12.877	-8.420
298.	3.36E+00	1.00E+00	-11.526	-8.818	-26.629	-8.641	-17.903	-13.871	-8.419
298.	3.36E+00	1.00E+01	-11.523	-8.818	-26.214	-8.641	-18.880	-14.871	-8.419
298.	3.36E+00	1.00E+02	-11.523	-8.818	-26.139	-8.641	-19.877	-15.871	-8.419

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-7.159	-3.973	-20.822	-3.850	-11.229	-5.423	-3.600
400.	2.50E+00	1.00E-03	-6.202	-3.593	-19.822	-3.559	-10.258	-5.187	-3.269
400.	2.50E+00	1.00E-02	-5.455	-3.452	-18.823	-3.450	-9.479	-5.535	-3.146
400.	2.50E+00	1.00E-01	-5.110	-3.421	-17.832	-3.426	-9.337	-6.303	-3.118
400.	2.50E+00	1.00E+00	-5.022	-3.417	-16.913	-3.423	-9.902	-7.248	-3.113
400.	2.50E+00	1.00E+01	-5.009	-3.416	-16.345	-3.422	-10.809	-8.240	-3.113
400.	2.50E+00	1.00E+02	-5.007	-3.416	-16.209	-3.422	-11.797	-9.240	-3.113

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	-3.925	-1.259	-15.220	-1.234	-7.313	-2.501	-.933
500.	2.00E+00	1.00E-03	-2.941	-.683	-14.220	-.735	-6.323	-1.945	-.394
500.	2.00E+00	1.00E-02	-2.055	-.363	-13.221	-.459	-5.418	-1.896	-.095
500.	2.00E+00	1.00E-01	-1.483	-.246	-12.225	-.354	-4.923	-2.357	.020
500.	2.00E+00	1.00E+00	-1.263	-.220	-11.271	-.331	-5.145	-3.157	.051
500.	2.00E+00	1.00E+01	-1.213	-.216	-10.570	-.328	-5.895	-4.110	.057
500.	2.00E+00	1.00E+02	-1.207	-.216	-10.345	-.328	-6.851	-5.103	.057

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	-1.921	.376	-11.079	.285	-4.817	-.755	.652
600.	1.67E+00	1.00E-03	-.927	1.083	-10.079	.957	-3.821	.000	1.348
600.	1.67E+00	1.00E-02	.023	1.577	-9.080	1.413	-2.861	.356	1.826
600.	1.67E+00	1.00E-01	.773	1.834	-8.082	1.657	-2.134	.220	2.084
600.	1.67E+00	1.00E+00	1.168	1.922	-7.101	1.742	-2.012	-.348	2.187
600.	1.67E+00	1.00E+01	1.295	1.941	-6.255	1.760	-2.524	-1.194	2.217
600.	1.67E+00	1.00E+02	1.319	1.944	-5.845	1.762	-3.399	-2.162	2.222

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	.274	2.054	-6.617	1.690	-1.950	1.050	2.244
800.	1.25E+00	1.00E-03	1.273	2.906	-5.617	2.611	-.951	1.985	3.123
800.	1.25E+00	1.00E-02	2.264	3.638	-4.617	3.344	.041	2.714	3.860
800.	1.25E+00	1.00E-01	3.194	4.186	-3.617	3.898	.972	3.094	4.416
800.	1.25E+00	1.00E+00	3.911	4.506	-2.622	4.232	1.601	3.044	4.766
800.	1.25E+00	1.00E+01	4.301	4.642	-1.666	4.373	1.644	2.584	4.944
800.	1.25E+00	1.00E+02	4.437	4.680	-.937	4.412	1.113	1.800	5.005

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	1.312	2.719	-4.206	2.112	-.468	1.815	2.869
1000.	1.00E+00	1.00E-03	2.312	3.648	-3.206	3.159	.531	2.797	3.827
1000.	1.00E+00	1.00E-02	3.310	4.501	-2.206	4.069	1.529	3.690	4.702
1000.	1.00E+00	1.00E-01	4.292	5.243	-1.206	4.846	2.510	4.366	5.460
1000.	1.00E+00	1.00E+00	5.185	5.808	-.208	5.449	3.370	4.716	6.054
1000.	1.00E+00	1.00E+01	5.845	6.155	.779	5.823	3.842	4.670	6.455
1000.	1.00E+00	1.00E+02	6.200	6.316	1.672	5.997	3.746	4.217	6.669

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	2.302	3.113	-1.260	2.034	1.167	2.373	3.269
1500.	6.67E-01	1.00E-03	3.302	4.100	-.260	3.124	2.167	3.371	4.265
1500.	6.67E-01	1.00E-02	4.302	5.060	.740	4.246	3.166	4.355	5.247
1500.	6.67E-01	1.00E-01	5.300	5.986	1.740	5.285	4.164	5.274	6.194
1500.	6.67E-01	1.00E+00	6.288	6.852	2.739	6.263	5.141	6.052	7.085
1500.	6.67E-01	1.00E+01	7.227	7.603	3.738	7.113	6.003	6.594	7.874
1500.	6.67E-01	1.00E+02	8.018	8.181	4.723	7.755	6.550	6.805	8.509

T (K)	1000/T	P (ATM)	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CJCOQ	CH2CO+HO2	OCYCO+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	2.709	3.191	.205	1.619	1.900	2.492	3.397
2000.	5.00E-01	1.00E-03	3.709	4.188	1.205	2.704	2.900	3.491	4.397
2000.	5.00E-01	1.00E-02	4.709	5.175	2.205	3.894	3.900	4.487	5.393
2000.	5.00E-01	1.00E-01	5.708	6.150	3.205	5.048	4.899	5.459	6.381
2000.	5.00E-01	1.00E+00	6.706	7.103	4.205	6.195	5.891	6.365	7.351
2000.	5.00E-01	1.00E+01	7.689	8.006	5.204	7.294	6.837	7.131	8.280
2000.	5.00E-01	1.00E+02	8.619	8.812	6.199	8.251	7.609	7.662	9.124

Adduct (CjCOQ) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-5.046	-9.369	-5.876	-26.948	-12.441	-5.943	-4.941
1.00E-04	400.	2.50E+00	-1.500	-4.732	-1.703	-18.298	-6.983	-1.936	-1.200
1.00E-04	500.	2.00E+00	.277	-2.257	.474	-13.389	-3.959	.142	.797
1.00E-04	600.	1.67E+00	1.210	-.775	1.706	-10.233	-2.070	1.327	1.947
1.00E-04	800.	1.25E+00	1.848	.756	2.792	-6.521	.037	2.451	2.991
1.00E-04	1000.	1.00E+00	1.799	1.444	3.095	-4.454	1.127	2.888	3.327
1.00E-04	1500.	6.67E-01	1.112	2.128	3.134	-1.771	2.463	3.268	3.563
1.00E-04	2000.	5.00E-01	.408	2.362	3.018	-.422	3.099	3.378	3.692

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-4.928	-8.715	-6.488	-25.949	-11.501	-5.717	-4.852
1.00E-03	400.	2.50E+00	-1.146	-3.859	-1.884	-17.299	-6.002	-1.463	-.924
1.00E-03	500.	2.00E+00	.863	-1.305	.612	-12.390	-2.966	.821	1.257
1.00E-03	600.	1.67E+00	1.984	.206	2.076	-9.233	-1.073	2.149	2.554
1.00E-03	800.	1.25E+00	2.876	1.752	3.473	-5.521	1.037	3.407	3.802
1.00E-03	1000.	1.00E+00	2.939	2.443	3.946	-3.454	2.127	3.877	4.247
1.00E-03	1500.	6.67E-01	2.266	3.128	4.106	-.771	3.463	4.267	4.552
1.00E-03	2000.	5.00E-01	1.550	3.362	4.011	.578	4.099	4.378	4.690

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-4.904	-8.850	-7.366	-24.967	-10.848	-5.661	-4.833
1.00E-02	400.	2.50E+00	-1.005	-3.491	-2.432	-16.305	-5.151	-1.264	-.803
1.00E-02	500.	2.00E+00	1.200	-.624	.417	-11.392	-2.026	1.210	1.543
1.00E-02	600.	1.67E+00	2.519	1.055	2.166	-8.234	-.098	2.719	3.006
1.00E-02	800.	1.25E+00	3.714	2.720	3.937	-4.522	2.032	4.228	4.496
1.00E-02	1000.	1.00E+00	3.969	3.435	4.625	-2.454	3.126	4.811	5.080
1.00E-02	1500.	6.67E-01	3.507	4.127	5.008	.229	4.463	5.259	5.517
1.00E-02	2000.	5.00E-01	2.860	4.362	4.977	1.578	5.099	5.376	5.683

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	-4.901	-9.601	-8.344	-24.114	-10.641	-5.653	-4.830
1.00E-01	400.	2.50E+00	-.972	-3.860	-3.273	-15.363	-4.699	-1.214	-.773
1.00E-01	500.	2.00E+00	1.335	-.584	-.158	-10.417	-1.350	1.366	1.662
1.00E-01	600.	1.67E+00	2.819	1.438	1.891	-7.245	.732	3.029	3.264
1.00E-01	800.	1.25E+00	4.355	3.511	4.150	-3.524	2.992	4.837	5.040
1.00E-01	1000.	1.00E+00	4.848	4.368	5.133	-1.455	4.115	5.611	5.813
1.00E-01	1500.	6.67E-01	4.671	5.119	5.826	1.229	5.461	6.217	6.445
1.00E-01	2000.	5.00E-01	4.151	5.360	5.905	2.578	6.099	6.365	6.664

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	-4.901	-10.557	-9.341	-23.794	-10.611	-5.653	-4.830
1.00E+00	400.	2.50E+00	-.967	-4.671	-4.238	-14.743	-4.591	-1.207	-.769
1.00E+00	500.	2.00E+00	1.368	-1.134	-1.004	-9.614	-1.091	1.402	1.688
1.00E+00	600.	1.67E+00	2.931	1.203	1.254	-6.343	1.185	3.138	3.357

P (ATM)	T (K)	1000/T							
1.00E+00	800.	1.25E+00	4.758	3.849	4.004	-2.549	3.767	5.199	5.377
1.00E+00	1000.	1.00E+00	5.545	5.057	5.378	-.463	5.033	6.210	6.386
1.00E+00	1500.	6.67E-01	5.765	6.057	6.525	2.228	6.449	7.090	7.305
1.00E+00	2000.	5.00E-01	5.425	6.340	6.769	3.577	7.095	7.319	7.619

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	-4.901	-11.552	-10.341	-24.243	-10.608	-5.653	-4.830
1.00E+01	400.	2.50E+00	-.966	-5.636	-5.233	-14.875	-4.577	-1.206	-.769
1.00E+01	500.	2.00E+00	1.373	-2.009	-1.968	-9.428	-1.042	1.407	1.692
1.00E+01	600.	1.67E+00	2.957	.503	.381	-5.880	1.313	3.159	3.375
1.00E+01	800.	1.25E+00	4.938	3.640	3.495	-1.741	4.178	5.342	5.517
1.00E+01	1000.	1.00E+00	5.988	5.295	5.272	.470	5.707	6.562	6.741
1.00E+01	1500.	6.67E-01	6.714	6.812	7.016	3.216	7.365	7.803	8.036
1.00E+01	2000.	5.00E-01	6.629	7.241	7.506	4.573	8.064	8.185	8.509

P (ATM)	T (K)	1000/T	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	-4.901	-12.551	-11.341	-25.138	-10.608	-5.653	-4.830
1.00E+02	400.	2.50E+00	-.966	-6.632	-6.233	-15.645	-4.575	-1.206	-.769
1.00E+02	500.	2.00E+00	1.373	-2.988	-2.964	-10.007	-1.037	1.407	1.692
1.00E+02	600.	1.67E+00	2.961	-.426	-.593	-6.210	1.333	3.161	3.378
1.00E+02	800.	1.25E+00	4.990	2.984	2.693	-1.525	4.299	5.374	5.551
1.00E+02	1000.	1.00E+00	6.196	5.039	4.794	1.074	6.031	6.698	6.892
1.00E+02	1500.	6.67E-01	7.419	7.238	7.205	4.117	8.070	8.284	8.567
1.00E+02	2000.	5.00E-01	7.650	7.947	8.027	5.530	8.920	8.882	9.264

Adduct (CjCOQ) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-5.046	-9.369	-5.876	-26.948	-12.441	-5.943	-4.941
298.	3.36E+00	1.00E-03	-4.928	-8.715	-6.488	-25.949	-11.501	-5.717	-4.852
298.	3.36E+00	1.00E-02	-4.904	-8.850	-7.366	-24.967	-10.848	-5.661	-4.833
298.	3.36E+00	1.00E-01	-4.901	-9.601	-8.344	-24.114	-10.641	-5.653	-4.830
298.	3.36E+00	1.00E+00	-4.901	-10.557	-9.341	-23.794	-10.611	-5.653	-4.830
298.	3.36E+00	1.00E+01	-4.901	-11.552	-10.341	-24.243	-10.608	-5.653	-4.830
298.	3.36E+00	1.00E+02	-4.901	-12.551	-11.341	-25.138	-10.608	-5.653	-4.830

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-1.500	-4.732	-1.703	-18.298	-6.983	-1.936	-1.200
400.	2.50E+00	1.00E-03	-1.146	-3.859	-1.884	-17.299	-6.002	-1.463	-.924
400.	2.50E+00	1.00E-02	-1.005	-3.491	-2.432	-16.305	-5.151	-1.264	-.803
400.	2.50E+00	1.00E-01	-.972	-3.860	-3.273	-15.363	-4.699	-1.214	-.773
400.	2.50E+00	1.00E+00	-.967	-4.671	-4.238	-14.743	-4.591	-1.207	-.769
400.	2.50E+00	1.00E+01	-.966	-5.636	-5.233	-14.875	-4.577	-1.206	-.769
400.	2.50E+00	1.00E+02	-.966	-6.632	-6.233	-15.645	-4.575	-1.206	-.769

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	.277	-2.257	.474	-13.389	-3.959	.142	.797
500.	2.00E+00	1.00E-03	.863	-1.305	.612	-12.390	-2.966	.821	1.257
500.	2.00E+00	1.00E-02	1.200	-.624	.417	-11.392	-2.026	1.210	1.543
500.	2.00E+00	1.00E-01	1.335	-.584	-.158	-10.417	-1.350	1.366	1.662
500.	2.00E+00	1.00E+00	1.368	-1.134	-1.004	-9.614	-1.091	1.402	1.688
500.	2.00E+00	1.00E+01	1.373	-2.009	-1.968	-9.428	-1.042	1.407	1.692
500.	2.00E+00	1.00E+02	1.373	-2.988	-2.964	-10.007	-1.037	1.407	1.692

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	1.210	-.775	1.706	-10.233	-2.070	1.327	1.947
600.	1.67E+00	1.00E-03	1.984	.206	2.076	-9.233	-1.073	2.149	2.554
600.	1.67E+00	1.00E-02	2.519	1.055	2.166	-8.234	-.098	2.719	3.006
600.	1.67E+00	1.00E-01	2.819	1.438	1.891	-7.245	.732	3.029	3.264
600.	1.67E+00	1.00E+00	2.931	1.203	1.254	-6.343	1.185	3.138	3.357
600.	1.67E+00	1.00E+01	2.957	.503	.381	-5.880	1.313	3.159	3.375
600.	1.67E+00	1.00E+02	2.961	-.426	-.593	-6.210	1.333	3.161	3.378

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	1.848	.756	2.792	-6.521	.037	2.451	2.991
800.	1.25E+00	1.00E-03	2.876	1.752	3.473	-5.521	1.037	3.407	3.802
800.	1.25E+00	1.00E-02	3.714	2.720	3.937	-4.522	2.032	4.228	4.496
800.	1.25E+00	1.00E-01	4.355	3.511	4.150	-3.524	2.992	4.837	5.040
800.	1.25E+00	1.00E+00	4.758	3.849	4.004	-2.549	3.767	5.199	5.377
800.	1.25E+00	1.00E+01	4.938	3.640	3.495	-1.741	4.178	5.342	5.517
800.	1.25E+00	1.00E+02	4.990	2.984	2.693	-1.525	4.299	5.374	5.551

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	1.799	1.444	3.095	-4.454	1.127	2.888	3.327
1000.	1.00E+00	1.00E-03	2.939	2.443	3.946	~3.454	2.127	3.877	4.247
1000.	1.00E+00	1.00E-02	3.969	3.435	4.625	-2.454	3.126	4.811	5.080
1000.	1.00E+00	1.00E-01	4.848	4.368	5.133	-1.455	4.115	5.611	5.813
1000.	1.00E+00	1.00E+00	5.545	5.057	5.378	-.463	5.033	6.210	6.386
1000.	1.00E+00	1.00E+01	5.988	5.295	5.272	.470	5.707	6.562	6.741
1000.	1.00E+00	1.00E+02	6.196	5.039	4.794	1.074	6.031	6.698	6.892

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	1.112	2.128	3.134	-1.771	2.463	3.268	3.563
1500.	6.67E-01	1.00E-03	2.266	3.128	4.106	-.771	3.463	4.267	4.552
1500.	6.67E-01	1.00E-02	3.507	4.127	5.008	.229	4.463	5.259	5.517
1500.	6.67E-01	1.00E-01	4.671	5.119	5.826	1.229	5.461	6.217	6.445
1500.	6.67E-01	1.00E+00	5.765	6.057	6.525	2.228	6.449	7.090	7.305
1500.	6.67E-01	1.00E+01	6.714	6.812	7.016	3.216	7.365	7.803	8.036
1500.	6.67E-01	1.00E+02	7.419	7.238	7.205	4.117	8.070	8.284	8.567

T (K)	1000/T	P (ATM)	CCOQJ	CH3CO+O2	CH2CO+HO2	CC*OOJ+O.	CH2CO+HO2	OCYCO+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	.408	2.362	3.018	-.422	3.099	3.378	3.692
2000.	5.00E-01	1.00E-03	1.550	3.362	4.011	.578	4.099	4.378	4.690
2000.	5.00E-01	1.00E-02	2.860	4.362	4.977	1.578	5.099	5.376	5.683
2000.	5.00E-01	1.00E-01	4.151	5.360	5.905	2.578	6.099	6.365	6.664
2000.	5.00E-01	1.00E+00	5.425	6.340	6.769	3.577	7.095	7.319	7.619
2000.	5.00E-01	1.00E+01	6.629	7.241	7.506	4.573	8.064	8.185	8.509
2000.	5.00E-01	1.00E+02	7.650	7.947	8.027	5.530	8.920	8.882	9.264

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PART IV

THERMOCHEMICAL AND KINETIC ANALYSIS
ON CjCHO + O$_2$ REACTION

CHAPTER 1

ABSTRACT FOR PART FOUR

Reaction pathways and kinetics are analyzed on CjCHO + O_2 reaction system using density functional and *ab initio* calculations to determine thermodynamic properties of reactants, intermediate radicals, and transition state (TS) structures. Enthalpies of formation ($\Delta H_f^{\circ}{}_{298}$) are determined using the CBSQ composite method and also by density functional calculations with isodesmic reactions for radical species. Entropies ($S^{\circ}{}_{298}$) and heat capacities ($Cp^{\circ}(T)$ 300 –1500 K) are determined using geometric parameters and vibrational frequencies obtained at the HF/6-31G(d') level of theory. Quantum Rice-Ramsperger-Kassel (QRRK) analysis is used to calculate energy dependent rate constants, k(E). The formyl methyl radical CjCHO adds to O_2 to form a CQjCHO peroxy radical ($\Delta H_f^{\circ}{}_{298}$ = -21.01 kcal/mole in CBSQ). The peroxy radical can undergo dissociation back to reactants, decompose to products, CH_2CO + HO_2 via HO_2 elimination (Ea,rxn = 48.2 kcal/mole in CBSQ) or isomerize via hydrogen shift (Ea,rxn = 19.39 kcal/mole in CBSQ) to form a CQCjO isomer ($\Delta H_f^{\circ}{}_{298}$ = -21.81 kcal/mole in CBSQ). This isomer CQCjO can undergo β-scission to products, CH_2CO + HO_2 (Ea,rxn = 24.32 kcal/mole in CBSQ) or decompose to CO + CH_2O + OH (Ea,rxn = 9.57 kcal/mole in CBSQ). Rate constants are estimated as function of pressure and temperature using QRRK analysis for k(E) and modified strong collision analysis for fall-off. Important reactions are stabilization of CQjCHO peroxy adduct at low temperature and CO + CH_2O + OH products via H shift and ketene + HO_2

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products via H shift at high temperature. Rate constants at 1atm pressure are

$(k=A(T/K)^n \exp(-Ea/RT)$, A in $cm^3/(mole\text{-}s)$, Ea in kcal/mole): $k_1=(2.87 \times 10^{37})(T/K)^{-8.73} e^{-6.42/RT}$ for $CjCHO + O_2 \Rightarrow CQjCHO$; $k_6=(2.68 \times 10^{-6})(T/K)^{5.46} e^{-21.76/RT}$ for

$CjCHO + O_2 \Rightarrow CH_2CO + HO_2$; $k_7=(1.25 \times 10^{14})(T/K)^{-1.05} e^{-4.99/RT}$ for $CjCHO + O_2 \Rightarrow CO + CH_2O + OH$; $k_8=(2.07 \times 10^{14})(T/K)^{-3.74} e^{-2.71/RT}$ for $CjCHO + O_2 \Rightarrow CQCjO$

CHAPTER 2

INTRODUCTION FOR PART FOUR

Important initial products from pyrolysis, oxidation, or photochemical reactions of

saturated and unsaturated hydrocarbons are the corresponding radicals.

The subsequent reactions of the hydrocarbon radicals with molecular oxygen are

complex and difficult to study experimentally and present a source of controversy

with regard to both pathway and reactions rates. These reactions, furthermore,

represent the principal pathways of the radical conversion in many hydrocarbon

oxidation and combustion processes[1,2] and also in atmosphere. Acetaldehyde and the

corresponding radical species that result via loss of hydrogen atoms from the two

different carbon sites in CH_3CHO are also common products (intermediates) from

oxidation processes of higher molecular weight hydrocarbon species in both

combustion and in atmospheric photochemistry. The acetaldehyde and its two

radicals are also produced by molecular weight growth from C_1 carbon combustion

and mild oxidation processes where the slow reaction of methyl radical with O_2 to

$CH_3O + O$ or $CH_2O + OH$. The slow conversion of $CH_3OO\bullet$(methyl peroxy radical)

to products, results in an equilibrium between $CH_3 + O_2$ and $CH_3OO\bullet$ where entropy

favors the reactants at higher temperatures. As a result methyl radicals often buildup

in the radical pool until combination occurs forming ethane and ethyl + H.

Acetaldehyde is one of the important oxidation products of ethane and ethylene.

Acetaldehyde and acetyl radicals are important intermediates in the overall

breakdown processes of higher molecular weight and C_1 hydrocarbons to CH_2O, CO, CO_2 and H_2O. The radical reactions with oxygen also serve as model reactions for larger aldehydic molecule systems.

Tyndall et al.[3] studied the reaction of OH radical with methyl glyoxal and acetaldehyde in a low pressure (c.a. 3 torr) flow reactor at temperatures from 260 to 333 K. They report rate constants for OH abstractions from the parent molecules and also report data on further reactions of the radicals formed from the abstractions by OH. They infer that only the acetyl radical is formed and further reaction of acetyl radical with O_2 leads to noticeable regeneration of OH; from observations showing reduced loss of the OH versus time. Some chamber experiments with FTIR monitoring showed no evidence of OH radical production. Absolute rate constants of Fluorine atom reaction with acetaldehyde were studied by Sehested and coworkers[4] using pulse radiolysis combined with transient ultraviolet absorption. They report production of two radicals - formyl methyl at 35% and acetyl at 65% (both ± 9%). We note that for reactions where chlorine atom is abstracting hydrogen atoms. Chlorine atoms usually have similiar A factors and similar or lower Ea's when the reactions are exothermic which they are in all cases in this study. In the case of acetaldehyde, for example, k_{298} for Cl atom abstraction is reported as 4.58×10^{13}[5] at 298K, while abstraction by F atom is 5.00×10^{13}[6]. The H--Cl bond is 103 kcal/mole, while the carbonyl C--H and methyl C--H bonds on acetaldehyde are 88 and 94 kcal/mole respectively. Chlorine should, therefore, readily abstract from both hydrogen sites of acetaldehyde. Michael et al.[7] studied the reaction of OH with acetaldehyde in a low pressure discharge flow reactor with resonance fluorescence

monitoring. He also studied the reaction of radical(s) generated via the OH reaction

with O_2. The total reaction rate constant for OH with acetaldehyde was A = 3.3 x

10^{12}, with a small negative energy of activation of 610 cal/mole. Michael et al. report

near complete regeneration of OH radical in the OH + acetaldehyde experiments

when O_2 was present to further react with the indicated acetyl radical formed. In

separate studies with Cl atom reacting with acetaldehyde, they observed production of

OH radical on further radical reaction(s) with O_2. They considered and rejected

possible formation of formyl methyl radicals based on work of Gutman's research

group and an assumed bond energy of the H--C bond on the methyl group of 98

kcal/mole. Slagle and Gutman[8] studied formation of acetyl radical from acetaldehyde

in reaction of Cl atoms from 1082 cm^{-1} IR multiphoton decomposition of CF_2Cl_2 of

C_6F_5Cl. They monitored the radical profiles with photoionization mass spectrometry.

Verification of CH_3CjO radical versus formyl methyl was by use of deuterated

acetaldehyde, CH_3CHO. They observed CH_3CjO and could not detect $CjCHO$; but

did not estimate lower limits of its detection. Reaction kinetics of acetylperoxy

radicals with nitric oxide and nitrogen dioxide were studies by Maricq and Szente[9],

where the peroxy radicals were generated via reaction of acetyl radical with O_2.

Acetyl radicals were generated by reaction of acetaldehyde with Cl atoms and Cl

atoms were produced by 351 nm eximer laser pulses ca 300 mJ/pulse. Maricq and

Szente provide data on nitric oxide plus acetyl and methyl peroxy radical decay and

NO_2 formation versus time for modeling comparisons.

Formyl methyl radicals, the other possible radical that may be formed by abstraction

of H atoms from acetaldehyde, were generated by photodissociations of methyl-vinyl

ether by Zhu and Johnston[10]. $CH_3-O-C_2H_3 + hv ==> CH_3 + C_2H_3O$. Here the vinoxy radical undergoes rapid electron rearrangement to the lower energy form (ca 18 kcal/mole loser in energy) formyl methyl radical. Kinetic studies on this formyl methyl radical with O_2 show slower reaction, $k_2 = 1.2 \times 10^{11}$ cm^3/mole-sec, than rate constants reported for acetyl radical $k_1 = 1 \times 10^{12}$ cm^3/mole-sec. They suggest that if formyl methyl radicals are produced in reactions of Cl atoms or OH with acetaldehyde, they will react about one tenth as fast with O_2, probably leading to small or no corrections to the faster acetyl + O_2 reactions.

Photo dissociation of PAN, (PeroxyAcetylNitrate) was used by Villalta and Howard[11] to generate acetylperoxy radicals for study of reaction kinetics with nitric oxide. Rate constants determined by this method agreed well with other reported values. This agreement of kinetic data where acetylperoxy radicals are generated by a very different and positive mechanism supports the assumption of Maricq and Szente[7], Sehested et al.[4], Tyndall et al.[3], Michael et al.[7], and Slagle and Gutman[8], that primarily acetyl radicals are generated by reaction with OH, or Cl atoms.

This study focuses on reaction mechanism of formyl methyl radical association with O_2. Thermodynamic properties are estimated for reactants, intermediate, products and transition states along the reaction pathway. The thermodynamic parameters are used to calculate high-pressure limit rate constants using canonical Transition State Theory. Rate constants as a function of temperature and pressure are estimated using a multi frequency Quantum RRK analysis with modified strong collision analysis of Gilbert et al.[12-14] for fall off. The data at relevant pressures and temperatures should be useful to both atmospheric and combustion modelers.

CHAPTER 3

CALCULATION METHOD FOR PART FOUR

3.1 Determination of Enthalpies of Formation

Enthalpies of formation ($\Delta H_f^{\circ}{}_{298}$) for reactants, intermediate radicals, transition states and products are calculated using CBS-Q composite method and density functionals. The initial structure of each compound or transition state is determined using ROHF or UHF/PM3 in MOPAC[15], followed by optimization and vibrational frequency calculation at HF/6-31G(d') level of theory using GAUSSIAN 94[16]. Transition State (TS) geometries are identified by the existence of only one imaginary frequency, structure information and the TST reaction coordinate vibration information. Zero-point vibrational energies (ZPVE), vibrational frequencies and thermal contributions to enthalpy from harmonic frequencies are scaled by 0.91844 as recommended by Petersson et al.[17]. Single point energy calculation are carried out at the B3LYP/6-31G(d'). The complete basis set (CBS-Q) method of Petersson and coworkers for computing accurate energies[18-20] are chosen as our primary for determining enthalpies.

The CBS-Q calculation sequence is performed on the MP2/6-31G(d') geometry and followed by single point calculations at the theory level of QCISD(T)/6-31+G(d'), MP4(SDQ)/CbsB4 and MP2/CBSB3 CBSExtrap=(Nmin=10,Pop).

The isodesmic reactions are used to determine the heat of formation ($\Delta H_f°_{298}$) for intermediate radicals. For estimation of $C(OOH)H_2C(=O)H$ [defined CQCHO, Q=OOH (hydroperoxy group)]

$$C(OOH)H_2C(=O)H + CH_3CH_3 \Longleftrightarrow CH_3C(=O)H + CH_3CH_2OOH \ldots\ldots\ldots(1)$$
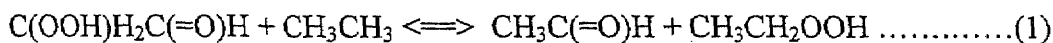
For estimation of $C(OOH)H_2C\bullet(=O)$ [defined CQCjO, j : radical site]

$$C(OOH)H_2C(=O)H + CH_3C\bullet H_2 \Longleftrightarrow C(OOH)H_2C\bullet(=O) + CH_3CH_3 \ldots\ldots (2)$$
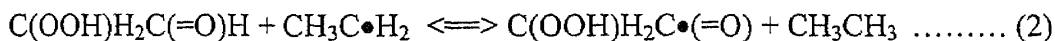
For estimation of $C(OO\bullet)H_2C(=O)H$ [defined CQjCHO, Qj : -OO$\bullet$]
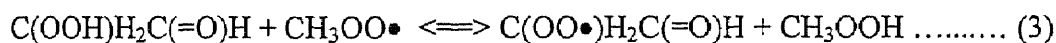
$$C(OOH)H_2C(=O)H + CH_3OO\bullet \Longleftrightarrow C(OO\bullet)H_2C(=O)H + CH_3OOH \ldots\ldots (3)$$

The method of isodesmic reactions relies upon the similarity of bonding environment in the reactants and products that leads to cancellation of systematic errors in the *ab initio* MO calculations.[21] The basic requirement of the isodesmic reaction is that the number of bonds of each formal chemical bond type is conserved in the reaction. In reaction (1), *ab initio* calculations with ZPVE and thermal correction are performed for all of four compounds. Since $\Delta H_f°_{298}$ of three compounds excepting CQCHO have been experimentally or theoretically calculated, the unknown $\Delta H_f°_{298}$ of CQCHO is obtained. The remaining two radicals are calculated in the same manner.

The $\Delta H_f°_{298}$ of transition state compounds are estimated by evaluation of $\Delta H_f°_{298}$ of the stable radical adducts plus difference of total energies with ZPVE and thermal correction between these radical species and the transition state (TS).

TCQjCHOS : A peroxy radical CQjCHO isomerize to form a CQCjO isomer via hydrogen shift.

TCQjCHOE : A peroxy radical CQjCHO decompose to products, $CH_2CO + HO_2$ via HO_2 elimination.

TCXQCjO : A CQCjO isomer undergo β-scission to products, $CH_2CO + HO_2$

TCQXCjO : A CQCjO isomer undergo β-scission to products, $CO + CH_2O + OH$

3.2 Determination of Entropy and Heat Capacity

The contributions of external rotation and vibrations to entropies and heat capacities are calculated from scaled vibration frequencies and moments of inertia for the optimized HF/6-31G(d') structures. Contributions from frequencies corresponding to hindered internal rotation are replaced with contributions calculated from the method of Pitzer and Gwinn[22] for S and Cp(T). Number of optical isomers and spin degeneracy of unpaired electrons are also incorporated.

3.3 High-Pressure Limit A Factors (A_∞) and Rate Constants (k_∞) Determination

For the reactions where thermodynamic properties of TS are calculated by *ab initio* or density functional methods, k_∞s are fit by three parameters A_∞, n, and E_a over temperature range from 298 to 2000K, $k_\infty = A_\infty(T)^n \exp(-E_a/RT)$ Entropy differences between reactant and TS are used to determine the pre-exponential factor, A, via conventional transition state theory (TST) for unimolecular and bimolecular reactions $A = (k_b T/h_p)\exp(\Delta S^{\neq}/R)$ and $A = (ek_b T/h_p)\exp(\Delta S^{\neq}/R)$, respectively. h_p is Plank's constant and k_b is the Boltzman constant.

3.4 Kinetic Analysis

Once the potential energy surface and thermochemical properties are evaluated,
forward or reverse rate for each, elementary reaction step are determined, Multi-
frequency Quantum Rice-Ramsperger-Kassel (QRRK) analysis is then used for $k(E)$
and modified strong collision analysis of Gilbert et. al[12-14] used for fall-off, to obtain
rate constants as a function of temperature and pressure. Reactions which incur a
change in number of moles, such as unimolecular dissociation, have energy of
activation calculated as delta Urxn plus an Ea for the reverse addition, where U is
internal energy.

A modified QRRK analysis we use in this srudy is described by Zhong and
Bozzelli.[23] 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,
with inclusion of one external rotation to calculate density of states $\rho(E)$.
Comparisons of ratios of these $\rho(E)/Q$ (partition function Q) with direct count $\rho(E)/Q$
are shown to be in good agreement.[23] Nonlinear Arrhenius effects resulting from
changes in the thermodynamic properties of the respective TST's relative to the
adduct with temperature are incorporated using a two parameter Arrhenius pre-
exponential factor (A, n) in AT^n.

CHAPTER 4

RESULT AND DISCUSSION FOR PART FOUR

4.1 Geometries of Two Intermediate Radicals and Transition States

Figure 4.1 to 4.5 show MP2/6-31G(d') determined geometries of CQjCHO, CQCjO,

TCQjCHOS, TCQjCHOE and TCQXCjO respectively.[names are defined in section

3.1] Figure 4.1 and Figure 4.2 show the optimized geometries of two intermediate

radicals, CQjCHO and CQCjO, respectively. Figure 4.3 shows TCQjCHOS structure

for isomerization (H shift) reaction. The H_4 atom is in a bridge structure shifting from

C_2 to radical site O_5. The leaving bond length H_4-C_2 is calculated as 1.29Å with

MP2/6-31G(d') determined geometry; where the H-C bond length in CQjCHO is

calculated as 1.11Å. The forming bond length H_4-O_5 is calculated as 1.36Å. All bond

lengths are from MP2/6-31G(d') determined geometries. The normal bond length H-

O in CQCjO is calculated as 0.97Å. Figure 4.4 shows TCQjCHOE structure, HO_2

elimination of CQjCHO --> CH_2CO + HO_2. The leaving bond length of C_2-H_6 is

calculated as 1.31Å and the C-H bond length in CQjCHO is calculated as 1.11Å. The

leaving bond length of C_1-O_7 is calculated as 2.31Å and the C-O bond length in

CQjCHO is calculated as 1.45Å. The leaving O_7-O_8 bond length is calculated as

1.26Å and the O-O bond length in CQCjO is calculated as 1.45Å. Again all bond

lengths are from MP2/6-31G(d') determined geometries.

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CQjCHO   [Qj = OO. (peroxy) , j : radical site]

C(OO.)H₂C(=O)H

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-O1	1.21				
C3-C2	1.52	C3-C2-O1	121.7		
O4-C3	1.45	O4-C3-C2	111.1	O4-C3-C2-O1	179.5
O5-O4	1.30	O5-O4-C3	110.0	O5-O4-C3-C2	-65.1
H6-C2	1.11	H6-C2-O5	122.9	H6-C2-O5-C3	-179.6
H7-C3	1.10	H7-C3-C2	110.6	H7-C3-C2-O1	58.3
H8-C3	1.10	H8-C3-C2	110.7	H8-C3-C2-O1	-63.8
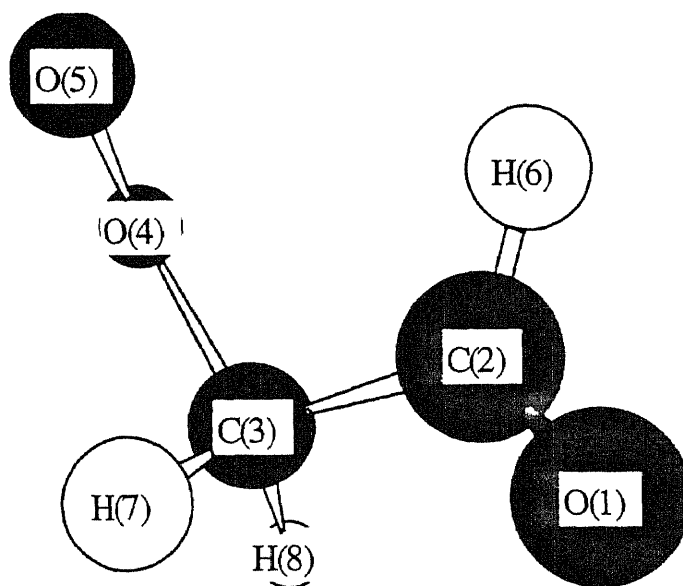
Figure 4.1 Structure for CQjCHO

CQCjO [Q = OOH (hydroperoxy group), j : radical site]

C(OOH)H₂C.(=O)

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.54				
O3-C2	1.41	O3-C2-C1	112.3		
O4-O3	1.45	O4-O3-C2	105.1	O4-O3-C2-C1	66.8
O5-C1	1.19	O5-C1-C2	125.9	O5-C1-C2-O3	178.4
H6-C2	1.10	H6-C2-C1	109.1	H6-C2-C1-O3	-116.4
H7-C2	1.10	H7-C2-C1	108.7	H7-C2-C1-O3	123.7
H8-O4	0.97	H8-O4-O3	100.3	H8-O4-O3-C2	-105.2
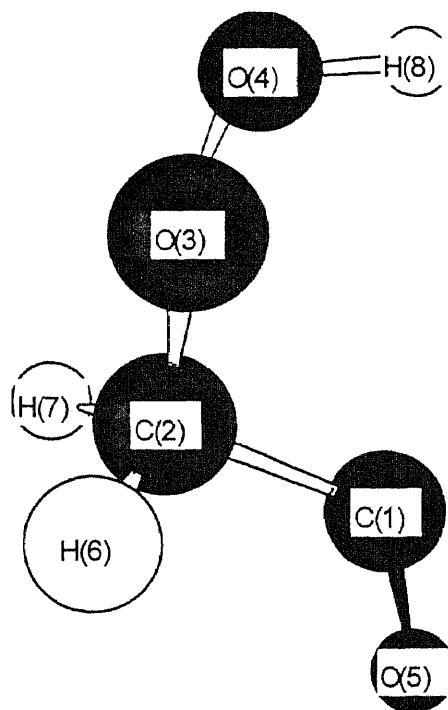
Figure 4.2 Structure for CQCjO

TCQjCHOS
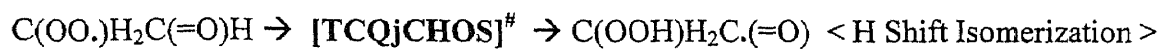
C(OO.)H$_2$C(=O)H → **[TCQjCHOS]**$^{#}$ → C(OOH)H$_2$C.(=O) < H Shift Isomerization >

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.60				
O3-C2	1.18	O3-C2-C1	131.6		
H4-C2	1.29	H4-C2-C1	90.9	H4-C2-C1-O3	-176.2
O5-H4	1.36	O5-H4-C2	126.8	O5-H4-C2-C1	3.3
O6-O5	1.37	O6-O5-H4	92.2	O6-O5-H4-C2	-31.1
H7-C1	1.09	O7-C1-C2	114.5	O7-C1-C2-O3	-39.8
H8-C1	1.10	H8-C1-C2	104.9	H8-C1-C2-O3	84.7
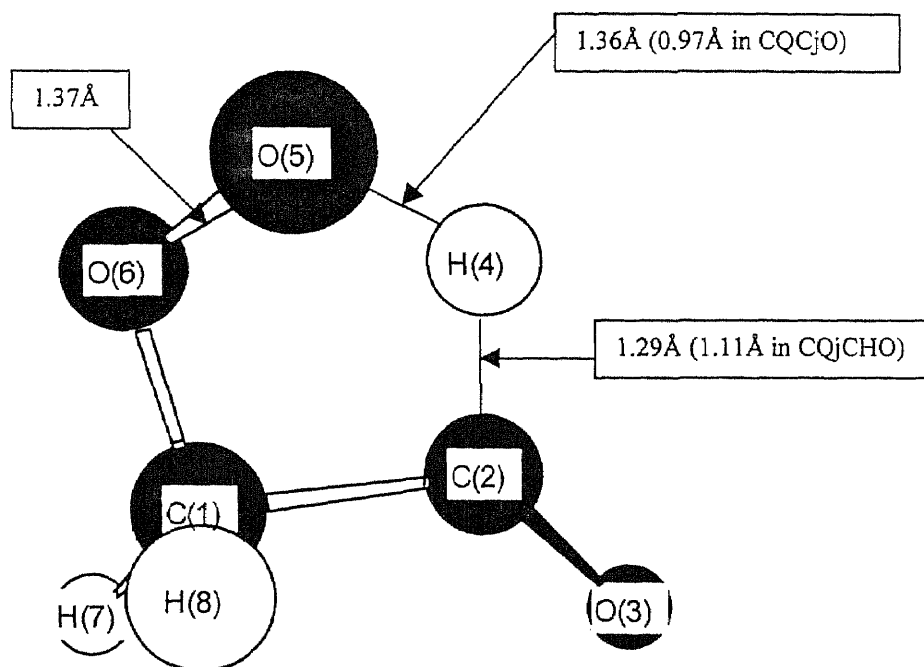
Figure 4.3 Structure for TCQjCHOS

TCQjCHOE
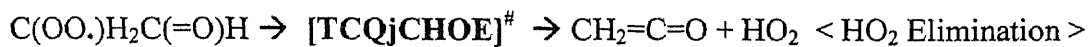
C(OO.)H$_2$C(=O)H $\rightarrow$ **[TCQjCHOE]**$^{\#}$ $\rightarrow$ CH$_2$=C=O + HO$_2$ < HO$_2$ Elimination >

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	1.39				
H3-C1	1.08	H3-C1-C2	120.8		
H4-C1	1.08	H4-C1-C2	120.8	H4-C1-C2-H3	-174.9
O5-C2	1.20	O5-C2-C1	146.9	O5-C2-C1-H3	-92.7
H6-O2	1.31	H6-C2-C1	97.6	H6-C2-C1-H3	87.4
O7-H6	1.97	O7-H6-C2	113.0	O7-H6-C2-C1	0.0
O8-O7	1.26	O8-O7-H6	42.9	O8-O7-C2-C2	180.0
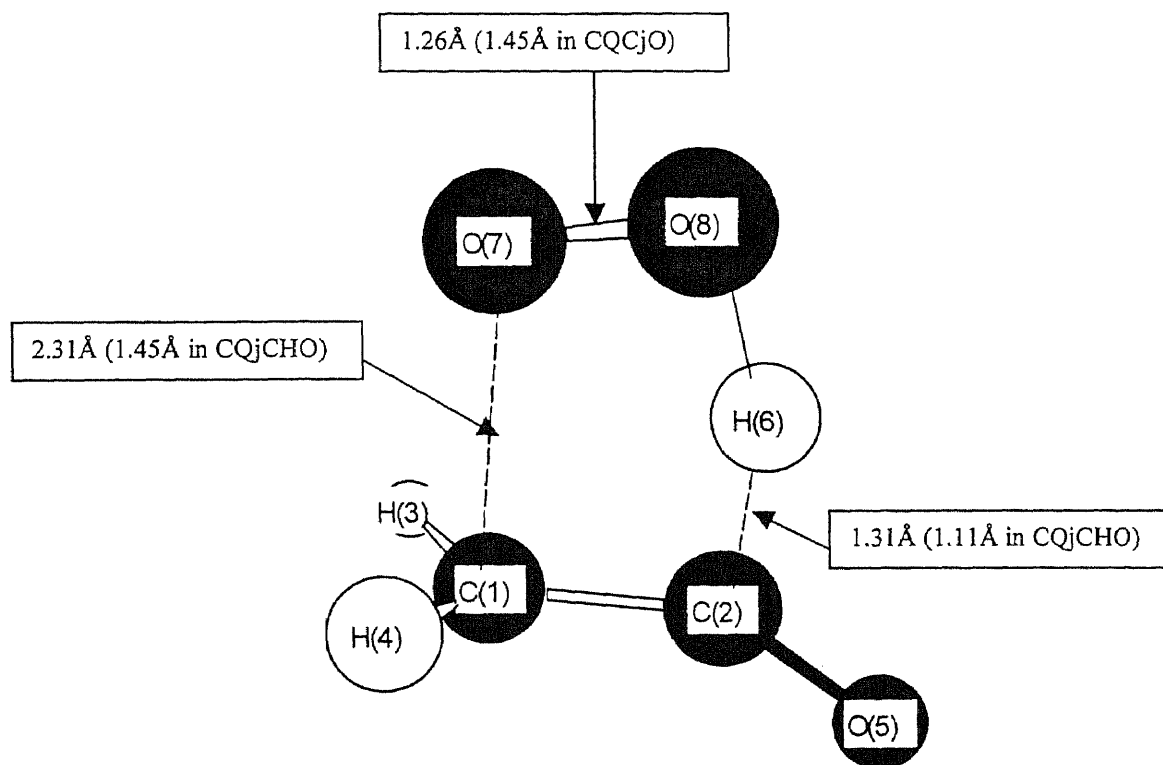
Figure 4.4 Structure for TCQjCHOE

TCQXCjO

C(OOH)H₂C.(=O)→ [TCQXCjO]# → CO + CH₂OOH

$C(OOH)H_2C.(=O) \rightarrow [TCQXCjO]^{\#} \rightarrow CO + CH_2OOH$

Geometry optimization at the MP2/6-31G(d') level of theory.

	Bond Length (Å)		Bond Angle (deg)		Dihedral Angle (deg)
C2-C1	2.32				
O3-C2	1.36	O3-C2-C1	103.4		
O4-O3	1.45	O4-O3-C2	108.6	O4-O3-C2-C1	-73.8
O5-C1	1.16	O5-C1-C2	106.8	O5-C1-C2-O3	19.3
H6-C2	1.09	H6-C2-C1	99.5	H6-C2-C1-O3	-120.7
H7-C2	1.09	H7-O2-C1	103.1	H7-O2-C1-O3	114.9
H8-O4	0.98	H8-O4-O3	99.6	H8-O4-O3-C2	92.2
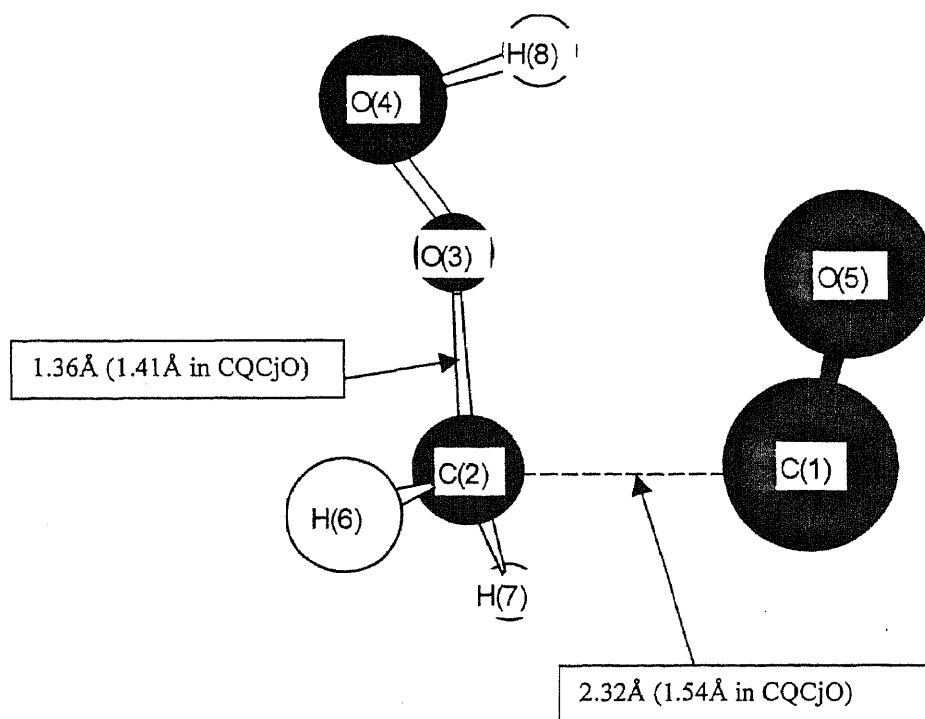
Figure 4.5 Structure for TCQXCjO

Figure 4.5 shows TCQXCjO structure, β-scission of CQCjO --> CO + CH$_2$OOH. The

leaving bond length C$_1$-C$_2$ is calculated as 2.32Å and the C-C bond length in CQCjO

is calculated as 1.54Å. The C$_2$-O$_3$ bond is calculated as 1.36Å and the C-O bond

length in CQCjO is calculated as 1.41Å.

4.2 Estimation of Entropy (S°$_{(298)}$) and Heat Capacity (Cp(T)'s, 300 - 1500K)

S°$_{(298)}$ and Cp(T)'s are calculated based on vibration frequencies and moments of

inertia of the optimized HF/6-31G(d') structures. (Table 4.1 and Table 4.2)

The calculation results using MP2/6-31G(d') determined geometries and HF/6-

31G(d') determined frequencies are summarized in Table 4.3. TVR represents the

sum of the contributions from translations, vibrations and external rotations for S°$_{(298)}$

and Cp(T)'s. Symmetry, optical isomer and electronic spin are incorporated in

estimation of S°$_{(298)}$ as described in Table 4.3. Contributions of internal rotation for

S°$_{(298)}$ and Cp(T)'s are calculated based on rotational barrier heights, moments of

inertia of the rotors using the method of Pitzer and Gwinn's[22]. (Table 4.4)

4.3 Estimation of Enthalpy of Formation (ΔH$_f$°$_{298}$) using Total Energies and Isodesmic Reactions

The overall energy diagram for the CjCHO + O$_2$ reaction system is illustrated in

Figure 4.6.

CBSQ calculations are performed on the MP2/6-31G(d') determined geometries and

HF/6-31G(d') determined frequencies. Density functionals are performed on the

B3LYP/6-31G(d) determined geometries and frequencies.
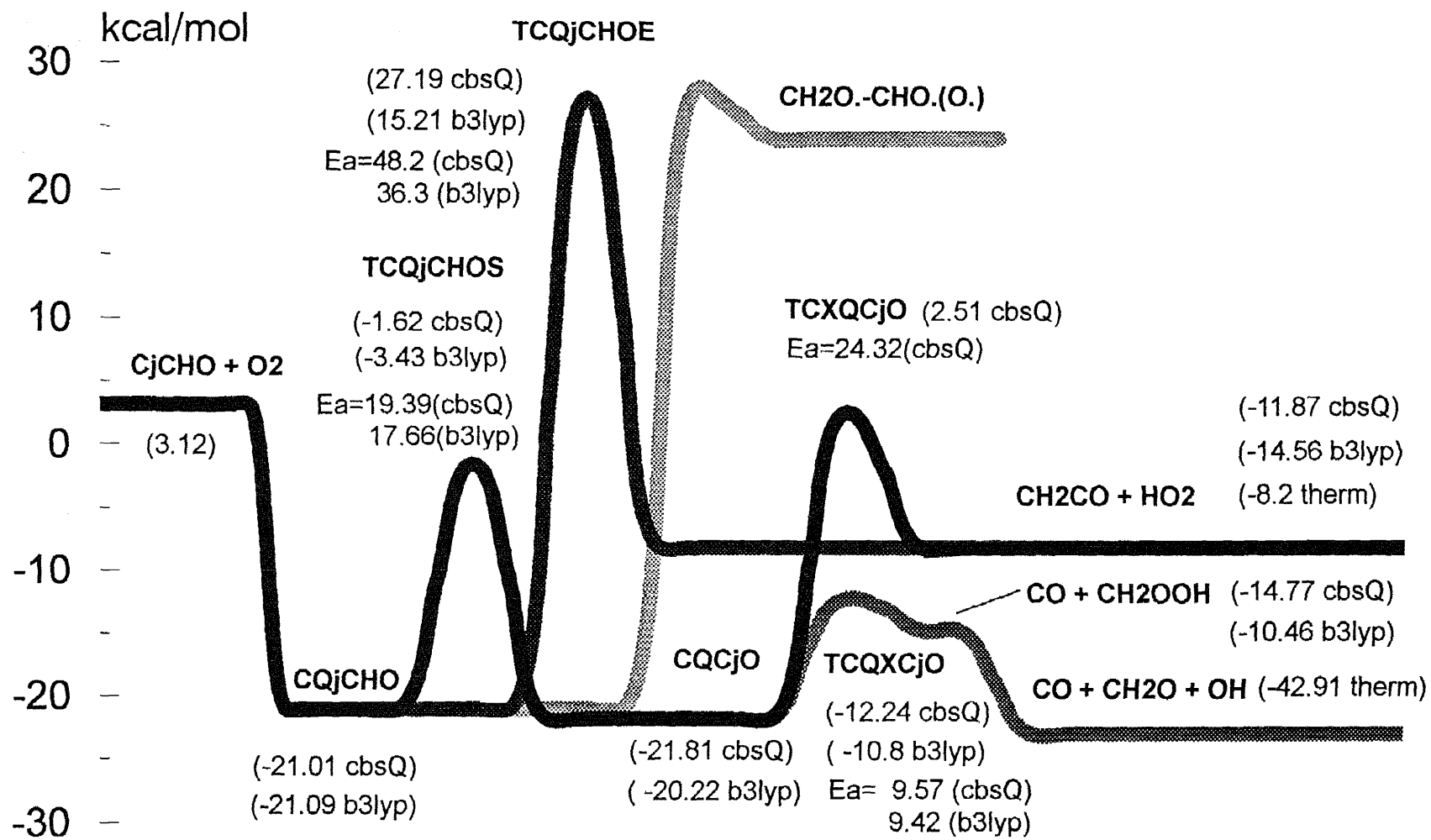
Figure 4.6 Potential Energy Diagram CjCHO + O₂

[Q=OOH, Qj=OO., j=radical site]

Table 4.1 Vibrational Frequencies[a] (v cm^{-1}) HF/6-31G(d') level of calculation

Species				Vibrational	Frequencies													
CjCHO	522	536	769	1015	1051	1214	1424	1546	1599	3223	3325	3437						
CQCHO	74	86	181	336	459	620	810	1047	1134	1230	1246	1394	1468	1540	1588	1612	2035	3170
	3239	3298	4113															
CQjCHO	70	132	336	476	637	811	1088	1126	1240	1280	1400	1470	1542	1591	2038	3172	3258	3322
CQCjO	110	188	242	341	452	622	938	978	1067	1258	1388	1475	1576	1592	2156	3236	3305	4094
TCQjCHOS[b]	-3103.6[f]	216	389	413	587	743	881	998	1062	1207	1215	1347	1427	1597	1826	2174	3226	3325
TCQjCHOE[c]	-3393.3[f]	64	111	164	274	350	422	617	783	879	1023	1159	1412	1551	1623	2110	3313	3420
TCXQCjO[d]	-761.3[f]	54	141	288	391	435	496	725	989	1085	1145	1188	1556	1602	2255	3316	3408	4060
TCQXCjO[e]	-858.9[f]	19	30	40	87	101	252	362	439	899	1209	1243	1381	1566	2423	3296	3433	4097
CH2OOH	160.8[f]	282	526	853	1045	1289	1314	1560	1620	3302	3440	4105						

[a] non-scaled. [b,c,d,e] Transition State Structure described in results section.

[f] Transition State, one imaginary frequency.

Table 4.2 Moments of Inertia (amu-Bohr^2) HF/6-31G(d') level of calculation

Species	I_A	I_B	I_C	Species	I_A	I_B	I_C
CjCHO	26.75	155.67	182.43	TCQjCHOE	196.29	651.84	835.95
CQCHO	120.40	607.17	672.79	TCXQCjO	177.37	566.48	690.74
CQjCHO	103.48	609.46	665.24	TCQXCjO	158.53	945.93	1092.42
CQCjO	111.26	609.24	678.83	CH2OOH	31.28	154.47	181.22
TCQjCHOS	133.47	485.29	589.56				

Table 4.3 Ideal Gas Phase Thermodynamic Properties Obtained
by CBSQ Calculation[a] and by Therm*

Species (s, e, OI)[g]		ΔHf°_{298}[b]	S°_{298}[c]	Cp_{300}[c]	Cp_{400}	Cp_{500}	Cp_{600}	Cp_{800}	Cp_{1000}	Cp_{1500}
CjCHO**	TVR[d]		61.25	11.77	14.21	16.32	18.07	20.76	22.71	25.71
(C.H2-C(=O)H)	Internal Rotor 1[f]		4.69	1.64	1.42	1.30	1.21	1.12	1.08	1.03
(1,1/2,1)	Total		65.94	13.41	15.63	17.62	19.28	21.88	23.79	26.74
	THERM	3.12	61.79	12.93	15.35	17.44	19.24	22.10	24.17	27.14
CQCHO***	TVR		69.25	15.10	18.82	22.20	25.05	29.44	32.58	37.30
(C(OOH)H2-C(=O)H)	Internal Rotor 1,2,3		13.56	3.99	5.82	5.92	5.93	5.84	5.68	5.20
(1,0,2)	Total	-56.61	82.81	19.09	24.64	28.12	30.98	35.28	38.26	42.50
	THERM	-57.15	82.24	22.34	25.60	28.29	30.68	34.77	37.81	
CQjCHO***	TVR		68.79	14.86	18.37	21.49	24.10	28.06	30.81	34.77
(C(OO.)H2-C(=O)H)	Internal Rotor 1,2		11.34	1.99	1.94	1.80	1.66	1.44	1.32	1.15
(1,1/2,1)	Total	-21.01	80.13	16.85	20.31	23.29	25.76	29.50	32.13	35.92
	THERM	-21.05	82.46	20.29	22.76	24.74	26.59	30.05	32.84	
CQCjO	TVR		70.40	14.64	17.81	20.58	22.89	26.39	28.88	32.62
(C(OOH)H2-C.(=O))	Internal Rotor 1,2,3		11.38	5.90	6.35	6.49	6.45	6.09	5.59	4.59
(1,1/2,2)	Total	-21.81	81.78	20.54	24.16	27.07	29.34	32.48	34.47	37.21
	THERM	-20.25	80.85	22.15	24.75	26.70	28.47	31.56	33.92	
TCQjCHOS	TVR		70.09	17.85	21.71	24.96	27.58	31.41	33.98	37.51
(1,1/2,2)	Total	-1.62	70.09	17.85	21.71	24.96	27.58	31.41	33.98	37.51
TCQjCHOE	TVR		81.23	22.66	25.70	28.18	30.17	33.12	35.15	38.05
(1,1/2,2)	Total	27.19	81.23	22.66	25.70	28.18	30.17	33.12	35.15	38.05
TCXQCjO	TVR		70.81	16.98	19.98	22.41	24.37	27.35	29.52	32.89
(1,1/2,2)	Internal Rotor 1,2		5.34	3.60	4.06	4.33	4.46	4.37	4.07	3.33
	Total	2.51	76.15	20.58	24.04	26.74	28.83	31.72	33.59	36.22
TCQXCjO	TVR		85.82	20.33	22.39	24.17	25.69	28.12	30.01	33.10
(1,1/2,2)	Internal Rotor 1,2,3		11.38	5.90	6.35	6.49	6.45	6.09	5.59	4.59
	Total	-12.24	97.20	26.23	28.74	30.66	32.14	34.21	35.60	37.69
CH2OOH	TVR		61.46	11.15	13.22	15.05	16.57	18.93	20.68	23.52
(1,1/2,2)	Internal Rotor 1,2		4.77	3.61	4.05	4.33	4.48	4.45	4.19	3.44
	Total		66.23	14.76	17.27	19.38	21.05	23.38	24.87	26.96
	THERM	15.20	65.41	15.60	18.12	20.15	21.79	24.14	25.65	27.65

* : therm values for stable species are included for comparison
** j : radical site, *** Q = OOH (hydroperoxy group), Qj = OO.(peroxy)
a : Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiometer at 1 atm.
b : Units in kcal/mol   c : Units in cal/mol-K
d : Sum of contributions from translations, vibrations, and external rotations.
f : Contribution from internal rotation
g : Symmetry number, optical isomer and electronic spin are taken into account,
  -Rln(s), Rln2, Rln2, respectively.
  s = number of symmetry, e = electronic spin, OI = number of optical isomer

Table 4.4 Moments of Inertia (amu-A^2) and Rotational Barriers (kcal/mole) for Internal Rotors

Species	Rotor	I_A	I_B	V	n^a
CjCHO[b]	C.H2--C(=O)H	1.75	18.90	1.20	2
CQCHO[c]	CHO--C(OOH)H2	18.90	114.36	13.00	6
	CHOC(H2)--OOH	114.63	1.56	2.50	3
	CHOC(H2)O--OH	120.00	0.86	6.38	1
CQjCHO[d]	CHO--C(OO.)H2	18.90	108.88	13.00	6
	CHOC(H2)--OO.	114.63	1.47	2.50	3
CQCjO	C.O--C(OOH)H2	23.81	114.36	3.26	3
	C(C.O)H2--OOH	116.71	1.56	5.40	3
	C(C.O)H2O--OH	100.00	0.86	6.38	1
TCXQCjO	C(C.O)H2--OOH	116.71	1.56	5.40	3
	C(C.O)H2O--OH	100.00	0.86	6.38	1
TCQXCjO	C.O--C(OOH)H2	23.81	114.36	3.26	3
	C(C.O)H2--OOH	116.71	1.56	5.40	3
	C(C.O)H2O--OH	100.00	0.86	6.38	1
CH2OOH	C.H2--OOH	1.75	1.56	6.46	2
	C.H2O--OH	27.44	1.10	5.98	1

[a] n : foldness

[b] "j" stands for radical site.

[c] "Q" stands for hydroperoxy group(OOH).

[d] "Qj" stands for peroxy (OO.).

Table 4.5 List of Total Energy, ZPVE, and Thermal Correction of CBSQ Calculation[a]

Species	Total Energy at 0K[b]	ZPVE[c]	Thermal Correction[d]	Total Energy at 298K[b]
CjCHO[e]	-152.9289585	0.0447890	0.0043670	-152.9245915
CQCHO[f]	-303.7676261	0.0698900	0.0068810	-303.7607451
CQjCHO[g]	-303.1306731	0.0569290	0.0061780	-303.1244951
CQCjO	-303.1274466	0.0569890	0.0065010	-303.1209456
TCQjCHOS	-303.0965504	0.0515610	0.0053710	-303.0911794
TCQjCHOE	-303.0514196	0.0439090	0.0073810	-303.0440386
TCXQCjO	-303.0889178	0.0526960	0.0067360	-303.0821818
TCQXCjO	-303.1128718	0.0483070	0.0071840	-303.1056878
CH2OOH	-189.9367183	0.0444130	0.0051750	-189.9315433

[a] Unit in Hartree 1 HF=627.51 kcal/mol.

[b] Scaled ZPVE are included. Scaling factor is recommended as 0.91844 by Petersson et.al [22]

[c] Non-scaled.

[d] Non-scaled.

[e] "j" stands for radical site.

[f] "Q" stands for hydroperoxy group(OOH).

[g] "Qj" stands for peroxy(OO.).

Isodesmic reactions are applied to accurately estimate $\Delta H_f^\circ{}_{298}$ of CQCHO and two

intermediate radicals, CQCjO and CQjCHO. *Zero point Vibration energies (ZPVE's)*

and thermal corrections to 298.15 K are taken into account. The total energies at 0 K

including scaled ZPVE's, nonscaled ZPVE's, thermal corrections to 298.15 K, and

total energies at 298 K including scaled ZPVE's are shown in Table 4.5 for CBSQ

calculations. Frequencies are scaled by 0.91844 for HF/6-31G(d') determined

frequencies as recommended by Petersson et al.[17]

Table 4.6 Molecule Considered to Have Known $\Delta H_f^\circ{}_{298}$
for Use in Isodesmic Reactions.

Compounds	$\Delta H_f^\circ{}_{298}$ (kcal/mole) [reference]
CH_3CH_3	-20.03 [24]
$CH_3C(=O)H$	-39.72 [24]
CH_3CH_2OOH	-39.9 [25]

The evaluated enthalpies of formation for the molecules considered to have known

$\Delta H_f^\circ{}_{298}$ values, for use in the isodesmic reaction, are: -20.03[24], -39.72[24], and

-39.9[25] for CH_3CH_3, $CH_3C(=O)H$, and CH_3CH_2OOH, respectively. A low or zero

$\Delta H^\circ{}_{frxn,298}$ supports the hypothesis of group additivity and increases credibility of the

calculations.

The CBSQ and density functionals determined enthalpy of reaction (1) is −2.98 and

−3.16 kcal/mole, respectively. $\Delta H_f^\circ{}_{298}$[CQCHO] is evaluated from

$$\Delta H^\circ{}_{frxn,298} = \Delta H_f^\circ{}_{298} \, [CH_3C(=O)H] + \Delta H_f^\circ{}_{298} \, [CH_3CH_2OOH]$$

$$- \Delta H_f^\circ{}_{298} \, [CQCHO] - \Delta H_f^\circ{}_{298} \, [CH_3CH_3] = -2.98 \text{ or } -3.16$$

$$= -39.72 + (-39.9) - X - (-20.03) \text{ kcal/mole} \quad\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The enthalpy of formation of CCOQ obtained is –56.61 and –56.43 kcal/mole in CBSQ and density functionals calculations, respectively.

The enthalpy of formation of two intermediate radicals, CQCjO and CQjCHO by CBSQ and density functionals are obtained from use of isodesmic reactions (2) and (3) and bond dissociation energy of C_2H_5—H(101.6 kcal/mole) and CH_3OO—H(86.3 kcal/mole) The data results in enthalpy values are –21.81 and –20.22 for CQCjO, -21.01 and –21.09 for CQjCHO, in CBSQ and density functionals calculations, respectively.

Formation of CQjCHO adduct has a well depth of 24.13 kcal/mole.

The activation energy for isomerization, TCQjCHOS, is estimated from both the reactant CQjCHO and the product CQCjO. The averaged result is 19.39 and 17.66 kcal/mole in CBSQ and density functionals, respectively. The activation energy for direct HO_2 elimination, TCQjCHOE, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and peroxy reactant, resulting in 27.19 and 15.21 kcal/mole in CBSQ and density functionals, respectively. The activation energy for HO_2 elimination from the hydroperoxide isomer, TCXQCjO, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and reactant, resulting in 24.32 kcal/mole via CBSQ. The activation energy for β-scission to $CO + CH_2OOH$, TCQXCjO, is estimated by taking the difference of total energy with ZPVE and thermal correction between transition state(TS) and hydroperoxide isomer, resulting in 9.57 and 9.42 kcal/mole in CBSQ and density functionals, respectively.

4.4 QRRK Calculation Results

QRRK calculations for k(E) and modified strong collision analysis of Gilbert et. al[12-14] for fall-off are performed on the CjCHO + O_2 reaction to obtain rate constants as a function of temperature and pressure and results are listed in Table 4.7. ΔE down of 400 cal/mole is used for bath gas N_2.

Plots of rate constants at 1atm pressure versus 1000/T are illustrated in Figure 4.7. Stabilization (CQjCHO), reverse dissociation, and CO + CH_2O + OH products via H shift are important at lower temperatures, 1atm pressure, with reverse dissociation, CO + CH_2O + OH products via H shift and ketene + HO_2 products via H shift important at higher temperatures.

Plots of rate constants at 298 K versus pressure are illustrated in Figure 4.8.

The figure illustrates that stabilization is the dominant path at high pressures, while stabilization (CQjCHO), reverse dissociation, and CO + CH_2O + OH products via H shift are important at low pressures.

Plots of rate constants at 1000 K versus pressure are illustrated in Figure 4.9.

The figure illustrates that stabilization decreases as pressure is decreased. Reverse dissociation and CO + CH_2O + OH products via H shift are most important at both high and low pressures.

Table 4.7 Input Parameters[a] and High-Pressure Limit Rate Constants (K_∞)[b] for QRRK Calculations[c] and the Resulting Rate Constants (Temp=298K) : CBSQ Result (adjusted)

Input parameters for QRRK calculations

	High-pressure Limit Rate Constants		
		k_∞	
Reaction	$A[S^{-1}$ or $cm^3/(mole\ s)]$	n	Ea (kcal/mole)
1 CjCHO + O_2 => CQjCHO[d]	1.57E+11	0.0	0.0
-1 CQjCHO => CjCHO + O_2[e]	1.96E+13	0.0	23.03
2 CQjCHO => CQCjO[f]	5.00E+5	2.14	18.57
3 CQjCHO => CH_2CO + HO_2[f]	4.99E+5	2.74	47.48
4 CQCjO => CO +CH_2O + OH[f]	8.47E+10	2.04	9.40
5 CQCjO => CH_2CO + HO_2[f]	1.47E+10	0.65	24.61

Calculated Reaction Parameters at P = 1atm, $k=A(T/K)^n exp(-Ea/RT)$ (T=298-2000K)

Reaction	A	n	Ea (kcal/mole)	$k_{298}(s^{-1}$ or $cm^3/(mole\ s)$
1 CjCHO + O_2 => CQjCHO	2.87E+37	-8.73	6.42	1.41E+11
6 CjCHO + O_2 => CH_2CO + HO_2	2.68E-06	5.46	21.76	9.00E-09
7 CjCHO + O_2 => CO +CH_2O + OH	1.25E+14	-1.05	4.99	6.90E+07
8 CjCHO + O_2 => CQCjO	2.07E+14	-3.74	2.71	1.19E+03
2 CQjCHO => CQCjO	3.11E+29	-8.48	22.88	5.00E-09
3 CQjCHO => CH_2CO + HO_2	1.02E+16	-1.64	48.33	3.19E-24
4 CQCjO => CO +CH_2O + OH	3.44E+18	-2.90	6.93	1.90E+06
5 CQCjO => CH_2CO + HO_2	5.57E+09	-1.92	21.86	9.17E-12

[a]Geometric mean frequency (from CPFIT, Ref.[34]: 529.0 cm^{-1}(6.962); 1518.5 cm^{-1} (8.074); 3999.8 cm^{-1} (1.964). Lennard-Jones parameters: σij=5.19Å, ε/k=533.08

[b]The units of A factors and rate constants k are s^{-1} for unimolecular reactions and $cm^3/(mole\ s)$ for bimolecular reactions.

[c]ΔE down of 400 cal/mole is used.

[d] $k_{\infty,1}$: Baulch et al. [26]

[e] $k_{\infty,-1}$: thermodynamics and microscopic reversibility <MR>

[f] A is calculated using TST and entropy of transition state, $\Delta S^{\neq}_{298}$ from HF/6-31G(d') (see Table 4.3); Ea is from CBSQ calculation (see Table 4.3 and description for determination of Ea in Results section). All parameters A, n, Ea, are fit over the temperature range of 298-2000K.
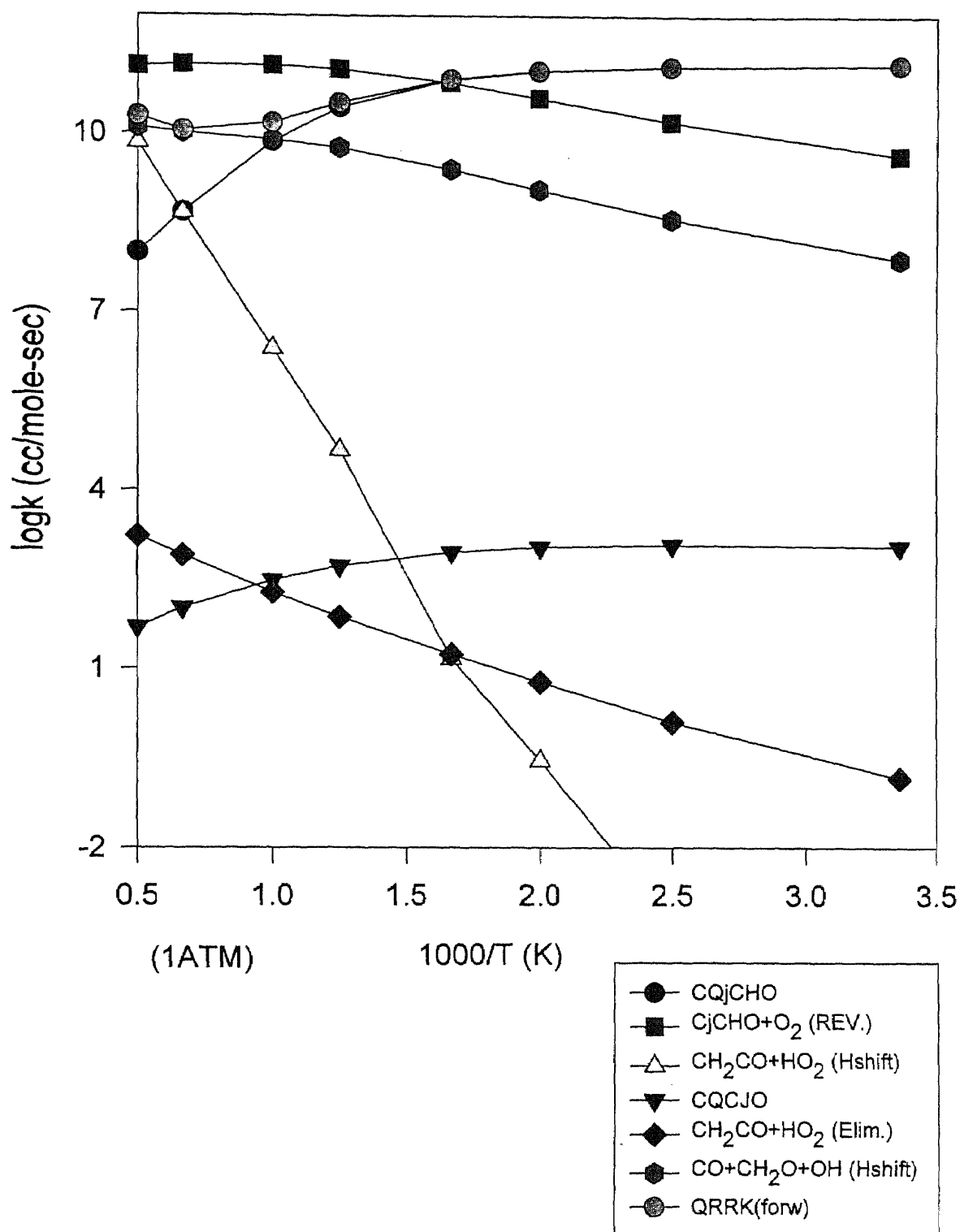
Figure 4.7 k vs. Temperature at 1atm CjCHO + O_2
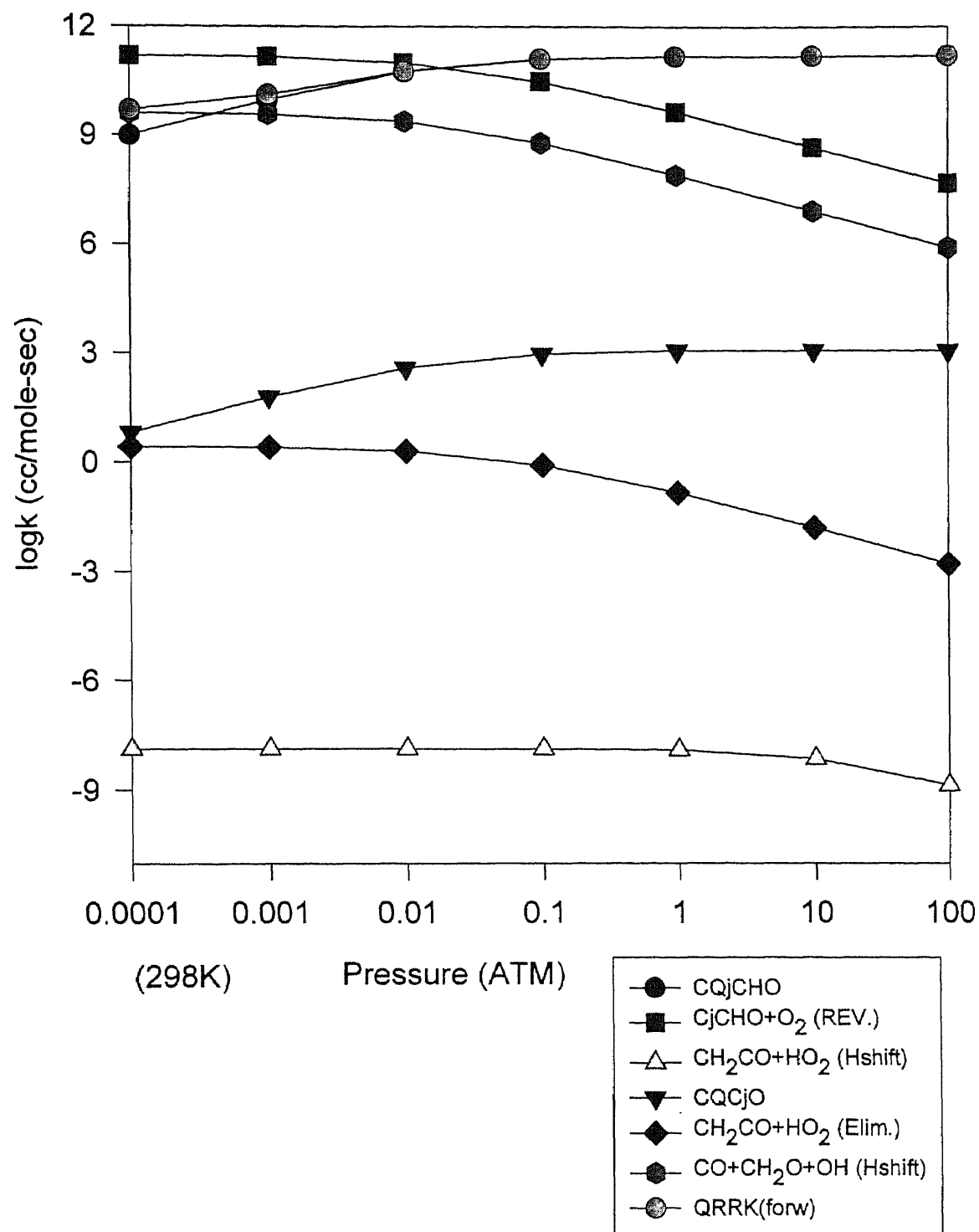
Figure 4.8 k vs. Pressure at 298K CjCHO + O$_2$
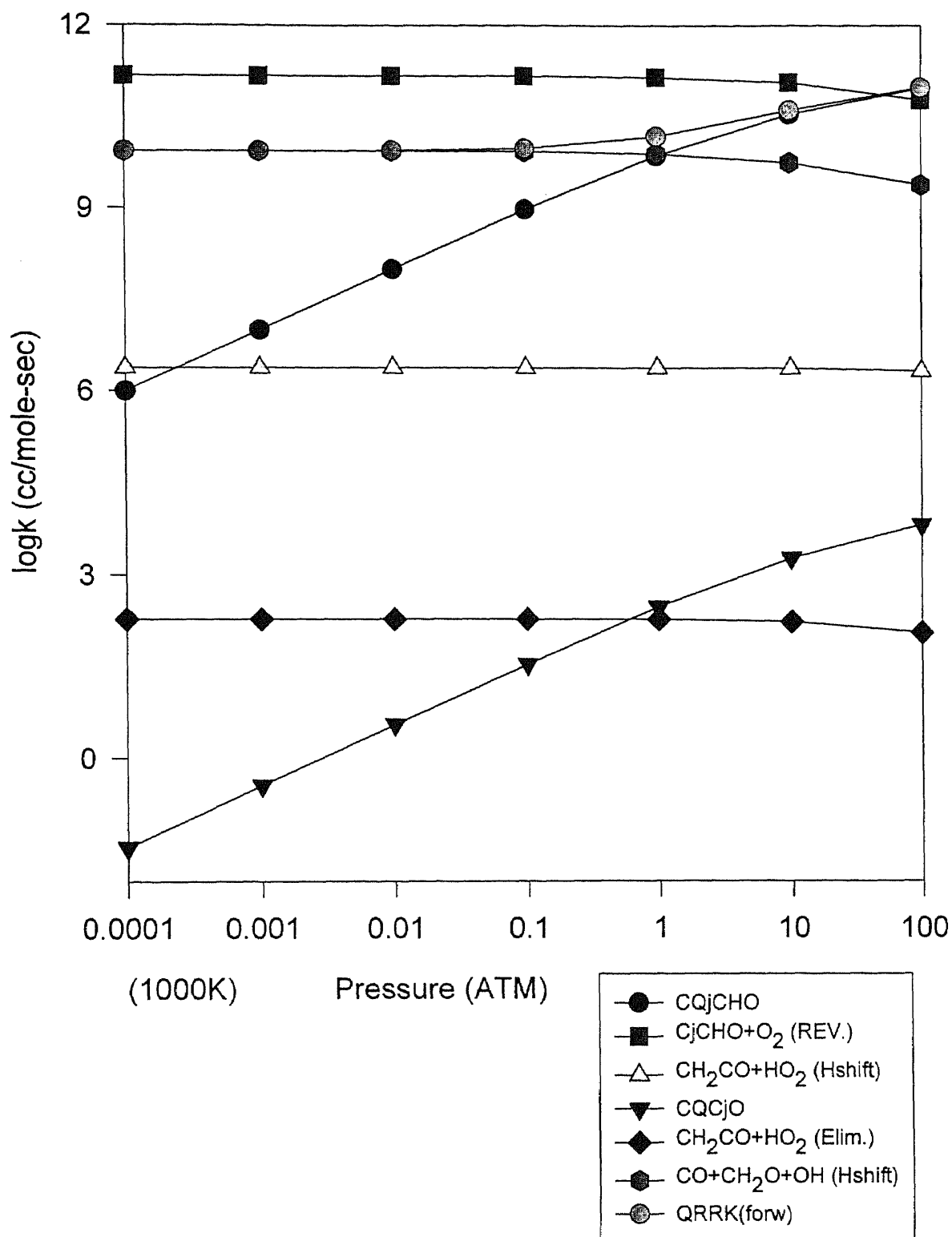
Fifure 4.9 k vs. Pressure at 1000K CjCHO + O$_2$

CHAPTER 5

SUMMARY FOR PART FOUR

Thermodynamic properties of stable radicals and transition states on CjCHO + O_2

reaction system are calculated using density functional and *ab initio* methods.

Enthalpies of formation ($\Delta H_f^\circ{}_{298}$) are determined using the CBSQ composite method

and density functional calculations with isodesmic reactions. Entropies ($S^\circ{}_{298}$) and

heat capacities (Cp(T) 300 –1500 K) are determined using geometric parameters and

vibrational frequencies obtained at the HF/6-31G(d') level of theory.

Reaction pathways and kinetics are analyzed on CjCHO + O_2 reaction system using

QRRK for k(E) and modified strong collision analysis of Gilbert et. al[12-14] for fall-off.

Major reaction paths at 1 atm pressure are stabilization of CQjCHO peroxy adduct at

low temperature and CO + CH_2O + OH products via H shift and ketene + HO_2

products via H shift at high temperature.

APPENDIX 4.1

THERMODYNAMIC ANALYSIS FOR CjCHO + O_2 REACTION

THERMODYNAMIC ANALYSIS for REACTION
Rx   CJCHO   + O2   = CQJCHO
Hf {Kcal/mol} 3.120   .000 -21.010
S {cal/mol K} 65.940   46.630   80.130

dHr {kcal/mol} (298K) =   -24.13   dHr avg (298., 1500. K) =   -24.82
dU (dE) {kcal/mol} (") =   -23.54   dUr avg (298., 1500. K) =   -23.03
dSr {cal/mol K} (") =   -32.44   dSr avg (298., 1500. K) =   -33.85
dGr {kcal/mol} (") =   -14.46   dGr avg (298., 1500. K) =   5.61
      Af/Ar (") = 5.401E-03   Af/Ar avg (298., 1500. K) = 8.024E-03

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	-2.414E+01	-2.354E+01	-3.247E+01	5.359E-03	-1.440E+01
400.00	-2.453E+01	-2.374E+01	-3.360E+01	4.032E-03	-1.109E+01
500.00	-2.483E+01	-2.383E+01	-3.427E+01	3.613E-03	-7.693E+00
600.00	-2.504E+01	-2.385E+01	-3.466E+01	3.550E-03	-4.245E+00
800.00	-2.531E+01	-2.372E+01	-3.505E+01	3.895E-03	2.733E+00
1000.00	-2.543E+01	-2.344E+01	-3.519E+01	4.539E-03	9.760E+00
1200.00	-2.548E+01	-2.310E+01	-3.524E+01	5.319E-03	1.680E+01
1500.00	-2.550E+01	-2.252E+01	-3.525E+01	6.595E-03	2.738E+01
2000.00	-2.545E+01	-2.148E+01	-3.522E+01	8.920E-03	4.500E+01

KINETIC ANALYSIS FOR CjCHO + O_2 REACTION

THERMODYNAMIC ANALYSIS for REACTION
Rx   CQJCHO   = TCQJCHOS
Hf {Kcal/mol} -21.010   -1.620
S {cal/mol K} 80.130   70.090

dHr {kcal/mol} (298K) =   19.39   dHr avg (298., 1500. K) =   20.79
dU (dE) {kcal/mol} (") =   19.39   dUr avg (298., 1500. K) =   20.79
dSr {cal/mol K} (") =   -10.04   dSr avg (298., 1500. K) =   -8.36
dGr {kcal/mol} (") =   22.38   dGr avg (298., 1500. K) =   28.31
      Af/Ar (") = 6.391E-03   Af/Ar avg (298., 1500. K) = 1.488E-02
Fit Af/Ar   : A = 1.380E-04 n = .63 alpha =-5.650E-04 avg error   3.62 %
Fit Af/Ar w/ddU: A = 2.963E-06 n = 1.31 alpha =-4.459E-04 avg error   5.51 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	1.939E+01	1.939E+01	-1.003E+01	6.411E-03	2.240E+01
400.00	1.951E+01	1.951E+01	-9.694E+00	7.608E-03	2.339E+01
500.00	1.966E+01	1.966E+01	-9.352E+00	9.035E-03	2.434E+01
600.00	1.985E+01	1.985E+01	-9.015E+00	1.071E-02	2.526E+01
800.00	2.030E+01	2.030E+01	-8.373E+00	1.479E-02	2.700E+01
1000.00	2.082E+01	2.082E+01	-7.795E+00	1.978E-02	2.861E+01
1200.00	2.137E+01	2.137E+01	-7.293E+00	2.547E-02	3.012E+01
1500.00	2.219E+01	2.219E+01	-6.681E+00	3.466E-02	3.221E+01
2000.00	2.350E+01	2.350E+01	-5.926E+00	5.067E-02	3.535E+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 = 5.0008E+04   n = 2.14395   Ea = 1.8566E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	4.008E+10	2.046E+05	2.984E-04	3.041E-04
400.00	6.341E+10	3.790E+05	1.384E+00	1.357E+00
500.00	9.413E+10	6.116E+05	2.386E+02	2.341E+02
600.00	1.338E+11	9.041E+05	7.864E+03	7.796E+03
800.00	2.465E+11	1.675E+06	7.016E+05	7.089E+05
1000.00	4.122E+11	2.703E+06	1.162E+07	1.183E+07
1200.00	6.369E+11	3.996E+06	8.165E+07	8.297E+07
1500.00	1.083E+12	6.447E+06	6.327E+08	6.354E+08
2000.00	2.112E+12	1.195E+07	5.706E+09	5.588E+09

THERMODYNAMIC ANALYSIS for REACTION
Rx   CQCJO   = TCQJCHOS
Hf {Kcal/mol} -21.810   -1.620
S {cal/mol K} 81.780   70.090

dHr {kcal/mol} (298K) =   20.19   dHr avg (298., 1500. K) =   20.14
dU (dE) {kcal/mol} (") =   20.19   dUr avg (298., 1500. K) =   20.14
dSr {cal/mol K} (") =   -11.69   dSr avg (298., 1500. K) =   -12.31
dGr {kcal/mol} (") =   23.68   dGr avg (298., 1500. K) =   31.21
        Af/Ar (") = 2.786E-03   Af/Ar avg (298., 1500. K) = 2.038E-03
Fit Af/Ar   : A = 3.897E+01 n = -1.78 alpha =-1.860E-03 avg error   4.41 %
Fit Af/Ar w/ddU: A = 1.595E+04 n = -2.94 alpha =-3.409E-03 avg error   12.67 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.018E+01	2.018E+01	-1.171E+01	2.762E-03	2.370E+01
400.00	1.992E+01	1.992E+01	-1.246E+01	1.891E-03	2.491E+01
500.00	1.970E+01	1.970E+01	-1.295E+01	1.475E-03	2.618E+01
600.00	1.953E+01	1.953E+01	-1.326E+01	1.262E-03	2.749E+01
800.00	1.937E+01	1.937E+01	-1.351E+01	1.116E-03	3.018E+01
1000.00	1.942E+01	1.942E+01	-1.346E+01	1.144E-03	3.288E+01
1200.00	1.962E+01	1.962E+01	-1.327E+01	1.256E-03	3.555E+01
1500.00	2.008E+01	2.008E+01	-1.293E+01	1.491E-03	3.948E+01
2000.00	2.108E+01	2.108E+01	-1.236E+01	1.987E-03	4.580E+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 = 1.1349E+08   n = .82014   Ea = 1.9946E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.726E+10	1.075E+02	3.398E-05	3.586E-05
400.00	1.576E+10	1.362E+02	2.045E-01	1.950E-01
500.00	1.536E+10	1.635E+02	3.745E+01	3.543E+01
600.00	1.578E+10	1.899E+02	1.208E+03	1.168E+03
800.00	1.860E+10	2.404E+02	9.493E+04	9.692E+04
1000.00	2.384E+10	2.887E+02	1.359E+06	1.431E+06
1200.00	3.141E+10	3.352E+02	8.371E+06	8.858E+06
1500.00	4.660E+10	4.026E+02	5.520E+07	5.667E+07
2000.00	8.279E+10	5.097E+02	4.113E+08	3.823E+08

THERMODYNAMIC ANALYSIS for REACTION
Rx   CQJCHO   = TCQJCHOE
Hf {Kcal/mol} -21.010   27.190
S {cal/mol K} 80.130   81.230

dHr {kcal/mol} (298K) =   48.20. dHr avg (298., 1500. K) =   50.17
dU (dE) {kcal/mol} (") =   48.20   dUr avg (298., 1500. K) =   50.17
dSr {cal/mol K} (") =   1.10   dSr avg (298., 1500. K) =   4.21
dGr {kcal/mol} (") =   47.87   dGr avg (298., 1500. K) =   46.39
        Af/Ar (") = 1.740E+00   Af/Ar avg (298., 1500. K) = 8.327E+00
Fit Af/Ar   : A = 7.022E-08 n = 3.08 alpha = 1.545E-03 avg error   4.29 %
Fit Af/Ar w/ddU: A = 3.717E-13 n = 5.35 alpha = 3.562E-03 avg error 15.55 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	4.821E+01	4.821E+01	1.136E+00	1.772E+00	4.787E+01
400.00	4.877E+01	4.877E+01	2.746E+00	3.983E+00	4.767E+01
500.00	4.927E+01	4.927E+01	3.866E+00	6.999E+00	4.734E+01
600.00	4.972E+01	4.972E+01	4.682E+00	1.055E+01	4.691E+01
800.00	5.047E+01	5.047E+01	5.766E+00	1.821E+01	4.585E+01
1000.00	5.106E+01	5.106E+01	6.432E+00	2.546E+01	4.463E+01
1200.00	5.155E+01	5.155E+01	6.875E+00	3.182E+01	4.329E+01
1500.00	5.214E+01	5.214E+01	7.323E+00	3.986E+01	4.116E+01
2000.00	5.289E+01	5.289E+01	7.753E+00	4.950E+01	3.738E+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 = 4.9884E+05   n = 2.74176   Ea =   4.7476E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.107E+13	6.190E+06	8.314E-23	7.955E-23
400.00	3.320E+13	1.362E+07	7.460E-14	7.770E-14
500.00	7.291E+13	2.511E+07	2.114E-08	2.210E-08
600.00	1.319E+14	4.140E+07	1.022E-04	1.048E-04
800.00	3.035E+14	9.111E+07	4.948E+00	4.860E+00
1000.00	5.305E+14	1.680E+08	3.669E+03	3.520E+03
1200.00	7.957E+14	2.769E+08	3.253E+05	3.112E+05
1500.00	1.246E+15	5.106E+08	3.143E+07	3.078E+07
2000.00	2.063E+15	1.124E+09	3.427E+09	3.633E+09

THERMODYNAMIC ANALYSIS for REACTION
Rx   CQCJO   = TCXQCJO
Hf {Kcal/mol} -21.810   2.510
S {cal/mol K}   81.780   76.150

dHr {kcal/mol} (298K) =   24.32   dHr avg (298., 1500. K) =   23.89
dU (dE) {kcal/mol} (") =   24.32   dUr avg (298., 1500. K) =   23.89
dSr {cal/mol K} (") =   -5.63   dSr avg (298., 1500. K) =   -6.09
dGr {kcal/mol} (") =   26.00   dGr avg (298., 1500. K) =   29.37
        Af/Ar (") = 5.881E-02   Af/Ar avg (298., 1500. K) = 4.656E-02
Fit Af/Ar   : A = 8.471E-02 n = -.04 alpha = 3.522E-04 avg error   1.56 %
Fit Af/Ar w/ddU: A = 1.711E-01 n = -.15 alpha = 4.561E-04 avg error   2.80 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.432E+01	2.432E+01	-5.629E+00	5.884E-02	2.601E+01
400.00	2.432E+01	2.432E+01	-5.637E+00	5.860E-02	2.657E+01
500.00	2.428E+01	2.428E+01	-5.708E+00	5.654E-02	2.714E+01
600.00	2.423E+01	2.423E+01	-5.804E+00	5.389E-02	2.771E+01
800.00	2.409E+01	2.409E+01	-6.005E+00	4.869E-02	2.889E+01
1000.00	2.393E+01	2.393E+01	-6.188E+00	4.441E-02	3.011E+01
1200.00	2.375E+01	2.375E+01	-6.347E+00	4.099E-02	3.137E+01
1500.00	2.347E+01	2.347E+01	-6.558E+00	3.687E-02	3.330E+01
2000.00	2.289E+01	2.289E+01	-6.887E+00	3.125E-02	3.667E+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 = 1.4687E+10   n = .64845   Ea =   2.4611E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.678E+11	4.039E+01	7.028E-07	6.958E-07
400.00	4.884E+11	4.867E+01	2.522E-02	2.548E-02
500.00	5.890E+11	5.625E+01	1.428E+01	1.441E+01
600.00	6.737E+11	6.331E+01	1.003E+03	1.007E+03
800.00	8.116E+11	7.629E+01	2.126E+05	2.116E+05
1000.00	9.253E+11	8.817E+01	5.454E+06	5.408E+06
1200.00	1.025E+12	9.924E+01	4.836E+07	4.797E+07
1500.00	1.152E+12	1.147E+02	4.385E+08	4.368E+08
2000.00	1.302E+12	1.382E+02	4.101E+09	4.148E+09

THERMODYNAMIC ANALYSIS for REACTION
Rx   CQCJO   = TCQXCJO
Hf {Kcal/mol} -21.810   -12.240
S {cal/mol K} 81.780   97.200

dHr {kcal/mol} (298K) =   9.57   dHr avg (298., 1500. K) =   10.72
dU (dE) {kcal/mol} (") =   9.57   dUr avg (298., 1500. K) =   10.72
dSr {cal/mol K} (") =   15.42   dSr avg (298., 1500. K) =   17.53
dGr {kcal/mol} (") =   4.97   dGr avg (298., 1500. K) =   -5.04
      Af/Ar (") = 2.346E+03 Af/Ar avg (298., 1500. K) = 6.790E+03
Fit Af/Ar   : A = 2.001E-03 n = 2.57 alpha = 1.720E-03 avg error 8.13 %
Fit Af/Ar w/ddU: A = 2.173E-07 n = 4.30 alpha = 3.502E-03 avg error 22.46 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	9.581E+00	9.581E+00	1.546E+01	2.388E+03	4.944E+00
400.00	1.009E+01	1.009E+01	1.692E+01	4.991E+03	3.319E+00
500.00	1.049E+01	1.049E+01	1.782E+01	7.842E+03	1.579E+00
600.00	1.080E+01	1.080E+01	1.840E+01	1.049E+04	-2.341E-01
800.00	1.124E+01	1.124E+01	1.904E+01	1.449E+04	-3.986E+00
1000.00	1.152E+01	1.152E+01	1.935E+01	1.693E+04	-7.828E+00
1200.00	1.170E+01	1.170E+01	1.951E+01	1.839E+04	-1.171E+01
1500.00	1.188E+01	1.188E+01	1.964E+01	1.966E+04	-1.759E+01
2000.00	1.205E+01	1.205E+01	1.974E+01	2.067E+04	-2.744E+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 = 8.4672E+10   n = 2.04186   Ea = 9.3533E+03

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.493E+16	1.143E+05	1.563E+09	1.483E+09
400.00	4.159E+16	2.056E+05	1.280E+11	1.349E+11
500.00	8.170E+16	3.243E+05	2.127E+12	2.239E+12
600.00	1.311E+17	4.705E+05	1.521E+13	1.560E+13
800.00	2.415E+17	8.466E+05	2.046E+14	1.995E+14
1000.00	3.527E+17	1.335E+06	1.071E+15	1.021E+15
1200.00	4.597E+17	1.938E+06	3.402E+15	3.246E+15
1500.00	6.143E+17	3.056E+06	1.143E+16	1.122E+16
2000.00	8.615E+17	5.498E+06	4.157E+16	4.424E+16

APPENDIX 4.3

KINETIC DATA FOR CjCHO + O_2 REACTIONS ARRHENIUS FORM

Chemical Activation CjCHO + O$_2$

CJCHO+O2	<=> CQJCHO	1.08E+32	-8.43	2907.	! 1.00E-04	(1.00E-04) atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=> CQJCHO	1.63E+33	-8.48	3021.	! 1.00E-03	(1.00E-03) atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=> CQJCHO	2.06E+35	-8.79	3762.	! 1.00E-02	(1.00E-02) atm,	298-2000 K,	19% err,	1.00 x N2
CJCHO+O2	<=> CQJCHO	9.57E+37	-9.24	5435.	! 1.00E-01	(1.00E-01) atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=> CQJCHO	2.87E+37	-8.73	6423.	! 1.00E+00	(1.00E+00) atm,	298-2000 K,	14% err,	1.00 x N2
CJCHO+O2	<=> CQJCHO	3.54E+32	-6.94	5815.	! 1.00E+01	(1.00E+01) atm,	298-2000 K,	19% err,	1.00 x N2
CJCHO+O2	<=> CQJCHO	8.79E+24	-4.41	3987.	! 1.00E+02	(1.00E+02) atm,	298-2000 K,	20% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	2.95E+11	-.10	74.	! 1.00E-04	(1.00E-04) atm,	298-2000 K,	1% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	4.22E+11	-.14	165.	! 1.00E-03	(1.00E-03) atm,	298-2000 K,	1% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	4.55E+12	-.44	784.	! 1.00E-02	(1.00E-02) atm,	298-2000 K,	2% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	2.02E+15	-1.18	2569.	! 1.00E-01	(1.00E-01) atm,	298-2000 K,	3% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	2.55E+17	-1.74	4762.	! 1.00E+00	(1.00E+00) atm,	298-2000 K,	7% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	4.13E+15	-1.14	5804.	! 1.00E+01	(1.00E+01) atm,	298-2000 K,	27% err,	1.00 x N2
CJCHO+O2	<=> CJCHO+O2	8.80E+08	.88	4968.	! 1.00E+02	(1.00E+02) atm,	298-2000 K,	51% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.81E-06	5.50	21640.	! 1.00E-04	(1.00E-04) atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.81E-06	5.50	21640.	! 1.00E-03	(1.00E-03) atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.82E-06	5.50	21641.	! 1.00E-02	(1.00E-02) atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.89E-06	5.50	21653.	! 1.00E-01	(1.00E-01) atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	2.68E-06	5.46	21760.	! 1.00E+00	(1.00E+00) atm,	298-2000 K,	79% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	2.16E-05	5.20	22475.	! 1.00E+01	(1.00E+01) atm,	298-2000 K,	80% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	2.97E-05	5.22	23754.	! 1.00E+02	(1.00E+02) atm,	298-2000 K,	99% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	1.21E+07	-2.91	-1374.	! 1.00E-04	(1.00E-04) atm,	298-2000 K,	16% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	1.82E+08	-2.96	-1265.	! 1.00E-03	(1.00E-03) atm,	298-2000 K,	17% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	2.34E+10	-3.28	-545.	! 1.00E-02	(1.00E-02) atm,	298-2000 K,	18% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	2.95E+13	-3.85	1228.	! 1.00E-01	(1.00E-01) atm,	298-2000 K,	16% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	2.07E+14	-3.74	2711.	! 1.00E+00	(1.00E+00) atm,	298-2000 K,	3% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	6.03E+10	-2.34	2695.	! 1.00E+01	(1.00E+01) atm,	298-2000 K,	17% err,	1.00 x N2
CJCHO+O2	<=> CQCJO	3.56E+03	.11	1146.	! 1.00E+02	(1.00E+02) atm,	298-2000 K,	30% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.40E-09	3.67	-180.	! 1.00E-04	(1.00E-04) atm,	298-2000 K,	12% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.77E-09	3.64	-123.	! 1.00E-03	(1.00E-03) atm,	298-2000 K,	11% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	9.74E-09	3.43	297.	! 1.00E-02	(1.00E-02) atm,	298-2000 K,	9% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	2.72E-06	2.73	1777.	! 1.00E-01	(1.00E-01) atm,	298-2000 K,	5% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	5.40E-03	1.81	4208.	! 1.00E+00	(1.00E+00) atm,	298-2000 K,	6% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	1.77E-02	1.73	6059.	! 1.00E+01	(1.00E+01) atm,	298-2000 K,	24% err,	1.00 x N2
CJCHO+O2	<=> CH2CO+HO2	2.92E-07	3.21	6000.	! 1.00E+02	(1.00E+02) atm,	298-2000 K,	55% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	5.19E+09	.13	558.	! 1.00E-04	(1.00E-04) atm,	298-2000 K,	5% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	7.76E+09	.08	664.	! 1.00E-03	(1.00E-03) atm,	298-2000 K,	6% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	1.02E+11	-.24	1372.	! 1.00E-02	(1.00E-02) atm,	298-2000 K,	7% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	2.33E+13	-.90	3200.	! 1.00E-01	(1.00E-01) atm,	298-2000 K,	6% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	1.25E+14	-1.05	4991.	! 1.00E+00	(1.00E+00) atm,	298-2000 K,	10% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	4.62E+10	.04	5421.	! 1.00E+01	(1.00E+01) atm,	298-2000 K,	30% err,	1.00 x N2
CJCHO+O2	<=> CO+CH2O+OH	1.11E+03	2.33	4177.	! 1.00E+02	(1.00E+02) atm,	298-2000 K,	50% err,	1.00 x N2

Dissociation

CQJCHO	<=> CJCHO+O2	1.49E+34	-8.46	25999.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	21% err,	1.00 x N2
CQJCHO	<=> CJCHO+O2	2.21E+35	-8.51	26108.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=> CJCHO+O2	2.61E+37	-8.82	26829.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=> CJCHO+O2	1.25E+40	-9.27	28497.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	20% err,	1.00 x N2
CQJCHO	<=> CJCHO+O2	3.97E+39	-8.76	29493.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	14% err,	1.00 x N2
CQJCHO	<=> CJCHO+O2	5.00E+34	-6.98	28888.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	16% err,	1.00 x N2
CQJCHO	<=> CJCHO+O2	1.25E+27	-4.45	27061.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	17% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	6.84E+11	-1.59	48214.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	6.84E+12	-1.59	48214.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	6.87E+13	-1.59	48215.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	7.14E+14	-1.60	48226.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	1.02E+16	-1.64	48330.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	22% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	1.03E+18	-1.92	49047.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	8.48E+19	-2.15	50550.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	16% err,	1.00 x N2
CQJCHO	<=> CQCJO	9.81E+35	-12.88	22341.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	33% err,	1.00 x N2
CQJCHO	<=> CQCJO	3.41E+40	-13.57	24714.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	26% err,	1.00 x N2
CQJCHO	<=> CQCJO	9.53E+39	-12.75	25462.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	9% err,	1.00 x N2
CQJCHO	<=> CQCJO	1.05E+35	-10.67	24395.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	8% err,	1.00 x N2
CQJCHO	<=> CQCJO	3.11E+29	-8.48	22875.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	9% err,	1.00 x N2
CQJCHO	<=> CQCJO	6.81E+23	-6.29	21177.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	8% err,	1.00 x N2
CQJCHO	<=> CQCJO	1.27E+18	-4.11	19297.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	7% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	1.81E+08	-3.21	23315.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	24% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	2.57E+09	-3.25	23406.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	24% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	2.71E+11	-3.55	24038.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	26% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	7.91E+14	-4.24	25820.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	27% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	1.53E+17	-4.55	27767.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	19% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	1.83E+15	-3.62	28378.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	16% err,	1.00 x N2
CQJCHO	<=> CH2CO+HO2	7.67E+08	-1.40	27215.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	6.98E+40	-10.72	24722.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	28% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	4.21E+44	-11.48	27150.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	25% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	4.45E+43	-10.82	28115.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	20% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	1.73E+38	-8.89	27311.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	19% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	6.07E+31	-6.68	25971.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	21% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	3.46E+24	-4.27	24253.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	23% err,	1.00 x N2
CQJCHO	<=> CO+CH2O+OH	5.13E+16	-1.72	22146.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	18% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+27	-9.98	10836.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+29	-9.98	10836.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+31	-9.98	10836.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+33	-9.98	10836.	!	1.00E-01 (1.00E-01) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+35	-9.98	10836.	!	1.00E+00 (1.00E+00) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+37	-9.98	10836.	!	1.00E+01 (1.00E+01) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CQJCHO	2.87E+39	-9.98	10836.	!	1.00E+02 (1.00E+02) atm,	298-2000 K,	15% err,	1.00 x N2
CQCJO	<=> CJCHO+O2	7.01E+11	-4.09	22120.	!	1.00E-04 (1.00E-04) atm,	298-2000 K,	24% err,	1.00 x N2
CQCJO	<=> CJCHO+O2	1.05E+13	-4.14	22225.	!	1.00E-03 (1.00E-03) atm,	298-2000 K,	24% err,	1.00 x N2
CQCJO	<=> CJCHO+O2	1.36E+15	-4.45	22929.	!	1.00E-02 (1.00E-02) atm,	298-2000 K,	26% err,	1.00 x N2

CQCJO	<=> CJCHO+O2	3.08E+18	-5.11	24751.	! 1.00E-01 (1.00E-01) atm,	298-2000 K,	25% err,	1.00 x N2
CQCJO	<=> CJCHO+O2	1.61E+20	-5.25	26533.	! 1.00E+00 (1.00E+00) atm,	298-2000 K,	11% err,	1.00 x N2
CQCJO	<=> CJCHO+O2	5.06E+17	-4.15	26929.	! 1.00E+01 (1.00E+01) atm,	298-2000 K,	9% err,	1.00 x N2
CQCJO	<=> CJCHO+O2	1.03E+11	-1.84	25636.	! 1.00E+02 (1.00E+02) atm,	298-2000 K,	25% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	3.52E-01	-.01	46342.	! 1.00E-04 (1.00E-04) atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	3.53E+00	-.01	46342.	! 1.00E-03 (1.00E-03) atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	3.54E+01	-.01	46343.	! 1.00E-02 (1.00E-02) atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	3.68E+02	-.01	46354.	! 1.00E-01 (1.00E-01) atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.31E+03	-.06	46459.	! 1.00E+00 (1.00E+00) atm,	298-2000 K,	19% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.68E+05	-.35	47184.	! 1.00E+01 (1.00E+01) atm,	298-2000 K,	20% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	6.69E+07	-.62	48744.	! 1.00E+02 (1.00E+02) atm,	298-2000 K,	12% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.57E+05	-1.92	21863.	! 1.00E-04 (1.00E-04) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.57E+06	-1.92	21863.	! 1.00E-03 (1.00E-03) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.57E+07	-1.92	21863.	! 1.00E-02 (1.00E-02) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.57E+08	-1.92	21863.	! 1.00E-01 (1.00E-01) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.57E+09	-1.92	21863.	! 1.00E+00 (1.00E+00) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.58E+10	-1.92	21863.	! 1.00E+01 (1.00E+01) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CH2CO+HO2	5.63E+11	-1.92	21865.	! 1.00E+02 (1.00E+02) atm,	298-2000 K,	16% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	3.39E+14	-2.90	6929.	! 1.00E-04 (1.00E-04) atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	3.39E+15	-2.90	6929.	! 1.00E-03 (1.00E-03) atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	3.39E+16	-2.90	6929.	! 1.00E-02 (1.00E-02) atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	3.40E+17	-2.90	6929.	! 1.00E-01 (1.00E-01) atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	3.44E+18	-2.90	6932.	! 1.00E+00 (1.00E+00) atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	3.91E+19	-2.91	6963.	! 1.00E+01 (1.00E+01) atm,	298-2000 K,	29% err,	1.00 x N2
CQCJO	<=> CO+CH2O+OH	1.20E+21	-3.05	7233.	! 1.00E+02 (1.00E+02) atm,	298-2000 K,	31% err,	1.00 x N2

APPENDIX 4.4

LOG RATE CONSTANTS VS PRESSURE AND TEMPERATURE
FOR CjCHO + O_2 REACTION

Chemical Activation Reaction (CjCHO + O₂) Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	8.990	11.182	-7.875	.808	.414	9.596	9.692
1.00E-04	400.	2.50E+00	8.515	11.179	-3.201	.340	.768	9.752	9.777
1.00E-04	500.	2.00E+00	8.063	11.176	-.539	-.094	1.092	9.834	9.842
1.00E-04	600.	1.67E+00	7.618	11.174	1.166	-.480	1.385	9.878	9.881
1.00E-04	800.	1.25E+00	6.760	11.173	4.662	-1.067	1.885	9.915	9.915
1.00E-04	1000.	1.00E+00	5.998	11.171	6.373	-1.448	2.276	9.936	9.936
1.00E-04	1500.	6.67E-01	4.698	11.165	8.663	-1.984	2.897	10.012	10.031
1.00E-04	2000.	5.00E-01	4.004	11.139	9.836	-2.314	3.224	10.099	10.288

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	9.958	11.159	-7.875	1.778	.399	9.568	10.107
1.00E-03	400.	2.50E+00	9.501	11.171	-3.201	1.328	.765	9.741	9.938
1.00E-03	500.	2.00E+00	9.056	11.173	-.539	.900	1.091	9.830	9.897
1.00E-03	600.	1.67E+00	8.615	11.173	1.166	.517	1.385	9.876	9.899
1.00E-03	800.	1.25E+00	7.759	11.172	4.662	-.068	1.885	9.915	9.918
1.00E-03	1000.	1.00E+00	6.998	11.171	6.373	-.448	2.276	9.936	9.936
1.00E-03	1500.	6.67E-01	5.698	11.165	8.663	-.984	2.897	10.012	10.031
1.00E-03	2000.	5.00E-01	5.004	11.139	9.836	-1.314	3.224	10.099	10.288

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	10.741	10.998	-7.875	2.576	.295	9.374	10.760
1.00E-02	400.	2.50E+00	10.390	11.107	-3.201	2.229	.734	9.651	10.463
1.00E-02	500.	2.00E+00	9.999	11.149	-.539	1.853	1.082	9.789	10.208
1.00E-02	600.	1.67E+00	9.586	11.164	1.166	1.495	1.382	9.858	10.044
1.00E-02	800.	1.25E+00	8.751	11.171	4.662	.928	1.884	9.911	9.940
1.00E-02	1000.	1.00E+00	7.996	11.171	6.373	.551	2.276	9.935	9.940
1.00E-02	1500.	6.67E-01	6.698	11.165	8.663	.015	2.897	10.012	10.031
1.00E-02	2000.	5.00E-01	6.004	11.139	9.836	-.314	3.224	10.099	10.288

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	11.100	10.483	-7.879	2.966	-.091	8.784	11.102
1.00E-01	400.	2.50E+00	10.945	10.826	-3.203	2.830	.569	9.280	10.954
1.00E-01	500.	2.00E+00	10.708	11.009	-.540	2.609	1.019	9.574	10.739
1.00E-01	600.	1.67E+00	10.405	11.100	1.166	2.355	1.360	9.743	10.491
1.00E-01	800.	1.25E+00	9.690	11.160	4.662	1.888	1.882	9.884	10.099
1.00E-01	1000.	1.00E+00	8.975	11.169	6.373	1.540	2.276	9.929	9.975
1.00E-01	1500.	6.67E-01	7.695	11.165	8.663	1.015	2.897	10.011	10.032
1.00E-01	2000.	5.00E-01	7.004	11.139	9.836	.686	3.224	10.099	10.289

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	11.183	9.645	-7.911	3.067	-.838	7.898	11.184
1.00E+00	400.	2.50E+00	11.148	10.207	-3.220	3.080	.100	8.565	11.149
1.00E+00	500.	2.00E+00	11.063	10.605	-.550	3.038	.766	9.055	11.067
1.00E+00	600.	1.67E+00	10.913	10.862	1.160	2.950	1.238	9.396	10.926
1.00E+00	800.	1.25E+00	10.439	11.093	4.660	2.716	1.859	9.758	10.521
1.00E+00	1000.	1.00E+00	9.859	11.152	6.372	2.476	2.271	9.890	10.176
1.00E+00	1500.	6.67E-01	8.675	11.164	8.663	2.008	2.897	10.009	10.047
1.00E+00	2000.	5.00E-01	7.999	11.138	9.836	1.685	3.224	10.099	10.290

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	11.195	8.673	-8.149	3.081	-1.786	6.915	11.195
1.00E+01	400.	2.50E+00	11.190	9.321	-3.362	3.140	-.705	7.639	11.190
1.00E+01	500.	2.00E+00	11.174	9.876	-.637	3.194	.171	8.248	11.175
1.00E+01	600.	1.67E+00	11.132	10.318	1.106	3.247	.850	8.753	11.134
1.00E+01	800.	1.25E+00	10.917	10.855	4.648	3.308	1.734	9.427	10.931
1.00E+01	1000.	1.00E+00	10.545	11.066	6.368	3.270	2.236	9.748	10.609
1.00E+01	1500.	6.67E-01	9.588	11.155	8.662	2.973	2.893	9.991	10.150
1.00E+01	2000.	5.00E-01	8.971	11.136	9.836	2.677	3.223	10.095	10.306

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	11.196	7.676	-8.866	3.082	-2.780	5.917	11.196
1.00E+02	400.	2.50E+00	11.195	8.339	-3.940	3.148	-1.669	6.650	11.195
1.00E+02	500.	2.00E+00	11.193	8.940	-1.085	3.225	-.712	7.290	11.193
1.00E+02	600.	1.67E+00	11.187	9.479	.771	3.333	.105	7.868	11.187
1.00E+02	800.	1.25E+00	11.133	10.313	4.544	3.613	1.336	8.803	11.135
1.00E+02	1000.	1.00E+00	10.974	10.780	6.333	3.823	2.065	9.386	10.985
1.00E+02	1500.	6.67E-01	10.357	11.099	8.655	3.843	2.866	9.908	10.495
1.00E+02	2000.	5.00E-01	9.871	11.118	9.832	3.631	3.213	10.068	10.413

Chemical Activation Reaction (CjCHO + O₂) Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	8.990	11.182	-7.875	.808	.414	9.596	9.692
298.	3.36E+00	1.00E-03	9.958	11.159	-7.875	1.778	.399	9.568	10.107
298.	3.36E+00	1.00E-02	10.741	10.998	-7.875	2.576	.295	9.374	10.760
298.	3.36E+00	1.00E-01	11.100	10.483	-7.879	2.966	-.091	8.784	11.102
298.	3.36E+00	1.00E+00	11.183	9.645	-7.911	3.067	-.838	7.898	11.184
298.	3.36E+00	1.00E+01	11.195	8.673	-8.149	3.081	-1.786	6.915	11.195
298.	3.36E+00	1.00E+02	11.196	7.676	-8.866	3.082	-2.780	5.917	11.196

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	8.515	11.179	-3.201	.340	.768	9.752	9.777
400.	2.50E+00	1.00E-03	9.501	11.171	-3.201	1.328	.765	9.741	9.938
400.	2.50E+00	1.00E-02	10.390	11.107	-3.201	2.229	.734	9.651	10.463
400.	2.50E+00	1.00E-01	10.945	10.826	-3.203	2.830	.569	9.280	10.954
400.	2.50E+00	1.00E+00	11.148	10.207	-3.220	3.080	.100	8.565	11.149
400.	2.50E+00	1.00E+01	11.190	9.321	-3.362	3.140	-.705	7.639	11.190
400.	2.50E+00	1.00E+02	11.195	8.339	-3.940	3.148	-1.669	6.650	11.195

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	8.063	11.176	-.539	-.094	1.092	9.834	9.842
500.	2.00E+00	1.00E-03	9.056	11.173	-.539	.900	1.091	9.830	9.897
500.	2.00E+00	1.00E-02	9.999	11.149	-.539	1.853	1.082	9.789	10.208
500.	2.00E+00	1.00E-01	10.708	11.009	-.540	2.609	1.019	9.574	10.739
500.	2.00E+00	1.00E+00	11.063	10.605	-.550	3.038	.766	9.055	11.067
500.	2.00E+00	1.00E+01	11.174	9.876	-.637	3.194	.171	8.248	11.175
500.	2.00E+00	1.00E+02	11.193	8.940	-1.085	3.225	-.712	7.290	11.193

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	7.618	11.174	1.166	-.480	1.385	9.878	9.881
600.	1.67E+00	1.00E-03	8.615	11.173	1.166	.517	1.385	9.876	9.899
600.	1.67E+00	1.00E-02	9.586	11.164	1.166	1.495	1.382	9.858	10.044
600.	1.67E+00	1.00E-01	10.405	11.100	1.166	2.355	1.360	9.743	10.491
600.	1.67E+00	1.00E+00	10.913	10.862	1.160	2.950	1.238	9.396	10.926
600.	1.67E+00	1.00E+01	11.132	10.318	1.106	3.247	.850	8.753	11.134
600.	1.67E+00	1.00E+02	11.187	9.479	.771	3.333	.105	7.868	11.187

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	6.760	11.173	4.662	-1.067	1.885	9.915	9.915
800.	1.25E+00	1.00E-03	7.759	11.172	4.662	-.068	1.885	9.915	9.918
800.	1.25E+00	1.00E-02	8.751	11.171	4.662	.928	1.884	9.911	9.940

T (K)	1000/T	P (ATM)							
800.	1.25E+00	1.00E-01	9.690	11.160	4.662	1.888	1.882	9.884	10.099
800.	1.25E+00	1.00E+00	10.439	11.093	4.660	2.716	1.859	9.758	10.521
800.	1.25E+00	1.00E+01	10.917	10.855	4.648	3.308	1.734	9.427	10.931
800.	1.25E+00	1.00E+02	11.133	10.313	4.544	3.613	1.336	8.803	11.135

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	5.998	11.171	6.373	-1.448	2.276	9.936	9.936
1000.	1.00E+00	1.00E-03	6.998	11.171	6.373	-.448	2.276	9.936	9.936
1000.	1.00E+00	1.00E-02	7.996	11.171	6.373	.551	2.276	9.935	9.940
1000.	1.00E+00	1.00E-01	8.975	11.169	6.373	1.540	2.276	9.929	9.975
1000.	1.00E+00	1.00E+00	9.859	11.152	6.372	2.476	2.271	9.890	10.176
1000.	1.00E+00	1.00E+01	10.545	11.066	6.368	3.270	2.236	9.748	10.609
1000.	1.00E+00	1.00E+02	10.974	10.780	6.333	3.823	2.065	9.386	10.985

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	4.698	11.165	8.663	-1.984	2.897	10.012	10.031
1500.	6.67E-01	1.00E-03	5.698	11.165	8.663	-.984	2.897	10.012	10.031
1500.	6.67E-01	1.00E-02	6.698	11.165	8.663	.015	2.897	10.012	10.031
1500.	6.67E-01	1.00E-01	7.695	11.165	8.663	1.015	2.897	10.011	10.032
1500.	6.67E-01	1.00E+00	8.675	11.164	8.663	2.008	2.897	10.009	10.047
1500.	6.67E-01	1.00E+01	9.588	11.155	8.662	2.973	2.893	9.991	10.150
1500.	6.67E-01	1.00E+02	10.357	11.099	8.655	3.843	2.866	9.908	10.495

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	4.004	11.139	9.836	-2.314	3.224	10.099	10.288
2000.	5.00E-01	1.00E-03	5.004	11.139	9.836	-1.314	3.224	10.099	10.288
2000.	5.00E-01	1.00E-02	6.004	11.139	9.836	-.314	3.224	10.099	10.288
2000.	5.00E-01	1.00E-01	7.004	11.139	9.836	.686	3.224	10.099	10.289
2000.	5.00E-01	1.00E+00	7.999	11.138	9.836	1.685	3.224	10.099	10.290
2000.	5.00E-01	1.00E+01	8.971	11.136	9.836	2.677	3.223	10.095	10.306
2000.	5.00E-01	1.00E+02	9.871	11.118	9.832	3.631	3.213	10.068	10.413

Adduct (CQjCHO) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-5.900	-27.540	-12.398	-16.867	-3.895	-3.891
1.00E-04	400.	2.50E+00	-2.030	-18.608	-9.626	-12.778	-.513	-.500
1.00E-04	500.	2.00E+00	.040	-13.455	-8.402	-10.504	1.204	1.233
1.00E-04	600.	1.67E+00	1.267	-10.080	-7.859	-9.078	2.148	2.201
1.00E-04	800.	1.25E+00	2.488	-5.991	-7.606	-7.469	2.946	3.076
1.00E-04	1000.	1.00E+00	2.974	-3.616	-7.730	-6.612	3.131	3.361
1.00E-04	1500.	6.67E-01	3.369	-.349	-8.274	-5.444	3.028	3.533
1.00E-04	2000.	5.00E-01	3.532	1.434	-8.822	-4.750	2.931	3.631

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-4.930	-26.540	-11.252	-15.891	-3.736	-3.709
1.00E-03	400.	2.50E+00	-1.044	-17.608	-8.244	-11.787	-.103	-.056
1.00E-03	500.	2.00E+00	1.034	-12.455	-6.787	-9.507	1.848	1.910
1.00E-03	600.	1.67E+00	2.264	-9.080	-6.074	-8.079	2.954	3.035
1.00E-03	800.	1.25E+00	3.487	-4.991	-5.663	-6.469	3.897	4.040
1.00E-03	1000.	1.00E+00	3.974	-2.616	-5.746	-5.612	4.118	4.353
1.00E-03	1500.	6.67E-01	4.369	.651	-6.276	-4.444	4.027	4.532
1.00E-03	2000.	5.00E-01	4.532	2.434	-6.822	-3.750	3.931	4.631

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-4.141	-25.540	-10.229	-15.060	-3.708	-3.572
1.00E-02	400.	2.50E+00	-.152	-16.609	-7.147	-10.860	.011	.238
1.00E-02	500.	2.00E+00	1.978	-11.455	-5.553	-8.539	2.113	2.352
1.00E-02	600.	1.67E+00	3.236	-8.080	-4.667	-7.092	3.400	3.626
1.00E-02	800.	1.25E+00	4.479	-3.991	-3.948	-5.471	4.647	4.872
1.00E-02	1000.	1.00E+00	4.972	-1.616	-3.865	-4.612	5.021	5.298
1.00E-02	1500.	6.67E-01	5.369	1.651	-4.298	-3.444	5.013	5.528
1.00E-02	2000.	5.00E-01	5.531	3.434	-4.830	-2.750	4.928	5.631

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	-3.777	-24.544	-9.224	-14.606	-3.701	-3.436
1.00E-01	400.	2.50E+00	.409	-15.610	-6.117	-10.183	.055	.568
1.00E-01	500.	2.00E+00	2.692	-10.455	-4.473	-7.714	2.223	2.819
1.00E-01	600.	1.67E+00	4.059	-7.080	-3.512	-6.181	3.600	4.188
1.00E-01	800.	1.25E+00	5.419	-2.991	-2.573	-4.490	5.083	5.584
1.00E-01	1000.	1.00E+00	5.952	-.616	-2.263	-3.616	5.685	6.139
1.00E-01	1500.	6.67E-01	6.367	2.651	-2.425	-2.444	5.932	6.503
1.00E-01	2000.	5.00E-01	6.531	4.434	-2.882	-1.750	5.908	6.627

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	-3.692	-23.574	-8.223	-14.469	-3.699	-3.394
1.00E+00	400.	2.50E+00	.613	-14.624	-5.107	-9.856	.073	.723
1.00E+00	500.	2.00E+00	3.048	-9.463	-3.432	-7.184	2.291	3.118
1.00E+00	600.	1.67E+00	4.568	-6.084	-2.418	-5.482	3.745	4.629
1.00E+00	800.	1.25E+00	6.170	-1.992	-1.342	-3.592	5.402	6.238
1.00E+00	1000.	1.00E+00	6.837	.384	-.886	-2.647	6.168	6.921
1.00E+00	1500.	6.67E-01	7.347	3.651	-.745	-1.447	6.728	7.441
1.00E+00	2000.	5.00E-01	7.526	5.434	-1.041	-.750	6.844	7.611

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	-3.681	-22.796	-7.223	-14.447	-3.699	-3.389
1.00E+01	400.	2.50E+00	.656	-13.747	-4.105	-9.767	.077	.757
1.00E+01	500.	2.00E+00	3.160	-8.530	-2.421	-6.964	2.312	3.218
1.00E+01	600.	1.67E+00	4.788	-5.121	-1.380	-5.094	3.812	4.832
1.00E+01	800.	1.25E+00	6.649	-1.004	-.191	-2.898	5.635	6.689
1.00E+01	1000.	1.00E+00	7.523	1.379	.408	-1.778	6.582	7.570
1.00E+01	1500.	6.67E-01	8.259	4.650	.829	-.466	7.454	8.323
1.00E+01	2000.	5.00E-01	8.498	6.433	.717	.245	7.733	8.570

P (ATM)	T (K)	1000/T	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	-3.680	-22.492	-6.224	-14.445	-3.700	-3.388
1.00E+02	400.	2.50E+00	.661	-13.279	-3.105	-9.754	.077	.762
1.00E+02	500.	2.00E+00	3.179	-7.910	-1.419	-6.916	2.315	3.235
1.00E+02	600.	1.67E+00	4.843	-4.374	-.372	-4.968	3.827	4.883
1.00E+02	800.	1.25E+00	6.865	-.103	.868	-2.512	5.738	6.896
1.00E+02	1000.	1.00E+00	7.953	2.340	1.579	-1.139	6.847	7.985
1.00E+02	1500.	6.67E-01	9.028	5.640	2.298	.441	8.072	9.074
1.00E+02	2000.	5.00E-01	9.398	7.428	2.391	1.211	8.544	9.459

Adduct (CQjCHO) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-5.900	-27.540	-12.398	-16.867	-3.895	-3.891
298.	3.36E+00	1.00E-03	-4.930	-26.540	-11.252	-15.891	-3.736	-3.709
298.	3.36E+00	1.00E-02	-4.141	-25.540	-10.229	-15.060	-3.708	-3.572
298.	3.36E+00	1.00E-01	-3.777	-24.544	-9.224	-14.606	-3.701	-3.436
298.	3.36E+00	1.00E+00	-3.692	-23.574	-8.223	-14.469	-3.699	-3.394
298.	3.36E+00	1.00E+01	-3.681	-22.796	-7.223	-14.447	-3.699	-3.389
298.	3.36E+00	1.00E+02	-3.680	-22.492	-6.224	-14.445	-3.700	-3.388

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-2.030	-18.608	-9.626	-12.778	-.513	-.500
400.	2.50E+00	1.00E-03	-1.044	-17.608	-8.244	-11.787	-.103	-.056
400.	2.50E+00	1.00E-02	-.152	-16.609	-7.147	-10.860	.011	.238
400.	2.50E+00	1.00E-01	.409	-15.610	-6.117	-10.183	.055	.568
400.	2.50E+00	1.00E+00	.613	-14.624	-5.107	-9.856	.073	.723
400.	2.50E+00	1.00E+01	.656	-13.747	-4.105	-9.767	.077	.757
400.	2.50E+00	1.00E+02	.661	-13.279	-3.105	-9.754	.077	.762

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	.040	-13.455	-8.402	-10.504	1.204	1.233
500.	2.00E+00	1.00E-03	1.034	-12.455	-6.787	-9.507	1.848	1.910
500.	2.00E+00	1.00E-02	1.978	-11.455	-5.553	-8.539	2.113	2.352
500.	2.00E+00	1.00E-01	2.692	-10.455	-4.473	-7.714	2.223	2.819
500.	2.00E+00	1.00E+00	3.048	-9.463	-3.432	-7.184	2.291	3.118
500.	2.00E+00	1.00E+01	3.160	-8.530	-2.421	-6.964	2.312	3.218
500.	2.00E+00	1.00E+02	3.179	-7.910	-1.419	-6.916	2.315	3.235

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	1.267	-10.080	-7.859	-9.078	2.148	2.201
600.	1.67E+00	1.00E-03	2.264	-9.080	-6.074	-8.079	2.954	3.035
600.	1.67E+00	1.00E-02	3.236	-8.080	-4.667	-7.092	3.400	3.626
600.	1.67E+00	1.00E-01	4.059	-7.080	-3.512	-6.181	3.600	4.188
600.	1.67E+00	1.00E+00	4.568	-6.084	-2.418	-5.482	3.745	4.629
600.	1.67E+00	1.00E+01	4.788	-5.121	-1.380	-5.094	3.812	4.832
600.	1.67E+00	1.00E+02	4.843	-4.374	-.372	-4.968	3.827	4.883

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	2.488	-5.991	-7.606	-7.469	2.946	3.076
800.	1.25E+00	1.00E-03	3.487	-4.991	-5.663	-6.469	3.897	4.040
800.	1.25E+00	1.00E-02	4.479	-3.991	-3.948	-5.471	4.647	4.872

800.	1.25E+00	1.00E-01	5.419	-2.991	-2.573	-4.490	5.083	5.584
800.	1.25E+00	1.00E+00	6.170	-1.992	-1.342	-3.592	5.402	6.238
800.	1.25E+00	1.00E+01	6.649	-1.004	-.191	-2.898	5.635	6.689
800.	1.25E+00	1.00E+02	6.865	-.103	.868	-2.512	5.738	6.896

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	2.974	-3.616	-7.730	-6.612	3.131	3.361
1000.	1.00E+00	1.00E-03	3.974	-2.616	-5.746	-5.612	4.118	4.353
1000.	1.00E+00	1.00E-02	4.972	-1.616	-3.865	-4.612	5.021	5.298
1000.	1.00E+00	1.00E-01	5.952	-.616	-2.263	-3.616	5.685	6.139
1000.	1.00E+00	1.00E+00	6.837	.384	-.886	-2.647	6.168	6.921
1000.	1.00E+00	1.00E+01	7.523	1.379	.408	-1.778	6.582	7.570
1000.	1.00E+00	1.00E+02	7.953	2.340	1.579	-1.139	6.847	7.985

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	3.369	-.349	-8.274	-5.444	3.028	3.533
1500.	6.67E-01	1.00E-03	4.369	.651	-6.276	-4.444	4.027	4.532
1500.	6.67E-01	1.00E-02	5.369	1.651	-4.298	-3.444	5.013	5.528
1500.	6.67E-01	1.00E-01	6.367	2.651	-2.425	-2.444	5.932	6.503
1500.	6.67E-01	1.00E+00	7.347	3.651	-.745	-1.447	6.728	7.441
1500.	6.67E-01	1.00E+01	8.259	4.650	.829	-.466	7.454	8.323
1500.	6.67E-01	1.00E+02	9.028	5.640	2.298	.441	8.072	9.074

T (K)	1000/T	P (ATM)	CJCHO+O2	CH2CO+HO2	CQCJO	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	3.532	1.434	-8.822	-4.750	2.931	3.631
2000.	5.00E-01	1.00E-03	4.532	2.434	-6.822	-3.750	3.931	4.631
2000.	5.00E-01	1.00E-02	5.531	3.434	-4.830	-2.750	4.928	5.631
2000.	5.00E-01	1.00E-01	6.531	4.434	-2.882	-1.750	5.908	6.627
2000.	5.00E-01	1.00E+00	7.526	5.434	-1.041	-.750	6.844	7.611
2000.	5.00E-01	1.00E+01	8.498	6.433	.717	.245	7.733	8.570
2000.	5.00E-01	1.00E+02	9.398	7.428	2.391	1.211	8.544	9.459

Adduct (CQCjO) Dissociation Reaction Rate Constants : log rate constants vs Temperature at specified Pressures

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-04	298.	3.36E+00	-5.241	-14.595	-34.554	-15.114	2.160	2.160
1.00E-04	400.	2.50E+00	-4.354	-10.751	-25.690	-11.095	3.339	3.339
1.00E-04	500.	2.00E+00	-4.126	-8.734	-20.638	-8.905	3.817	3.817
1.00E-04	600.	1.67E+00	-4.167	-7.525	-17.335	-7.530	4.012	4.012
1.00E-04	800.	1.25E+00	-4.523	-6.159	-13.233	-5.876	4.125	4.125
1.00E-04	1000.	1.00E+00	-4.941	-5.380	-10.716	-4.875	4.170	4.170
1.00E-04	1500.	6.67E-01	-5.822	-4.373	-7.216	-3.524	4.279	4.279
1.00E-04	2000.	5.00E-01	-6.593	-3.967	-5.491	-2.924	4.331	4.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-03	298.	3.36E+00	-3.241	-13.623	-33.554	-14.114	3.160	3.160
1.00E-03	400.	2.50E+00	-2.354	-9.762	-24.690	-10.095	4.339	4.339
1.00E-03	500.	2.00E+00	-2.126	-7.739	-19.638	-7.905	4.817	4.817
1.00E-03	600.	1.67E+00	-2.167	-6.527	-16.335	-6.530	5.012	5.012
1.00E-03	800.	1.25E+00	-2.523	-5.159	-12.233	-4.876	5.125	5.125
1.00E-03	1000.	1.00E+00	-2.941	-4.380	-9.716	-3.875	5.170	5.170
1.00E-03	1500.	6.67E-01	-3.822	-3.373	-6.216	-2.524	5.279	5.279
1.00E-03	2000.	5.00E-01	-4.593	-2.967	-4.491	-1.924	5.331	5.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-02	298.	3.36E+00	-1.241	-12.816	-32.555	-13.114	4.160	4.160
1.00E-02	400.	2.50E+00	-.354	-8.851	-23.690	-9.095	5.339	5.339
1.00E-02	500.	2.00E+00	-.126	-6.780	-18.638	-6.905	5.817	5.817
1.00E-02	600.	1.67E+00	-.167	-5.545	-15.335	-5.530	6.012	6.012
1.00E-02	800.	1.25E+00	-.523	-4.162	-11.233	-3.876	6.125	6.125
1.00E-02	1000.	1.00E+00	-.941	-3.381	-8.716	-2.875	6.170	6.170
1.00E-02	1500.	6.67E-01	-1.822	-2.373	-5.216	-1.524	6.279	6.279
1.00E-02	2000.	5.00E-01	-2.593	-1.967	-3.491	-.924	6.331	6.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E-01	298.	3.36E+00	.759	-12.404	-31.558	-12.114	5.160	5.160
1.00E-01	400.	2.50E+00	1.646	-8.219	-22.691	-8.095	6.339	6.339
1.00E-01	500.	2.00E+00	1.874	-5.992	-17.639	-5.905	6.817	6.817
1.00E-01	600.	1.67E+00	1.833	-4.658	-14.336	-4.530	7.012	7.012
1.00E-01	800.	1.25E+00	1.477	-3.190	-10.233	-2.876	7.125	7.125
1.00E-01	1000.	1.00E+00	1.059	-2.387	-7.716	-1.875	7.170	7.170
1.00E-01	1500.	6.67E-01	.178	-1.373	-4.216	-.524	7.279	7.279
1.00E-01	2000.	5.00E-01	-.593	-.967	-2.491	.076	7.331	7.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+00	298.	3.36E+00	2.759	-12.289	-30.588	-11.114	6.160	6.160
1.00E+00	400.	2.50E+00	3.646	-7.933	-21.706	-7.095	7.339	7.339
1.00E+00	500.	2.00E+00	3.874	-5.510	-16.646	-4.905	7.817	7.817
1.00E+00	600.	1.67E+00	3.833	-4.005	-13.340	-3.530	8.012	8.012
1.00E+00	800.	1.25E+00	3.477	-2.317	-9.234	-1.876	8.125	8.125
1.00E+00	1000.	1.00E+00	3.059	-1.427	-6.717	-.875	8.170	8.170
1.00E+00	1500.	6.67E-01	2.178	-.377	-3.216	.476	8.279	8.279
1.00E+00	2000.	5.00E-01	1.407	.032	-1.491	1.076	8.331	8.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+01	298.	3.36E+00	4.759	-12.271	-29.809	-10.114	7.152	7.154
1.00E+01	400.	2.50E+00	5.646	-7.858	-20.826	-6.095	8.337	8.338
1.00E+01	500.	2.00E+00	5.874	-5.317	-15.711	-3.905	8.817	8.817
1.00E+01	600.	1.67E+00	5.833	-3.651	-12.375	-2.530	9.012	9.012
1.00E+01	800.	1.25E+00	5.477	-1.656	-8.244	-.876	9.125	9.125
1.00E+01	1000.	1.00E+00	5.059	-.579	-5.721	.125	9.170	9.170
1.00E+01	1500.	6.67E-01	4.178	.602	-2.217	1.476	9.279	9.279
1.00E+01	2000.	5.00E-01	3.407	1.027	-.491	2.076	9.331	9.331

P (ATM)	T (K)	1000/T	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1.00E+02	298.	3.36E+00	6.759	-12.270	-29.504	-9.115	8.086	8.106
1.00E+02	400.	2.50E+00	7.646	-7.847	-20.353	-5.095	9.322	9.331
1.00E+02	500.	2.00E+00	7.874	-5.276	-15.082	-2.905	9.813	9.818
1.00E+02	600.	1.67E+00	7.833	-3.539	-11.617	-1.530	10.010	10.013
1.00E+02	800.	1.25E+00	7.477	-1.293	-7.334	.124	10.125	10.126
1.00E+02	1000.	1.00E+00	7.059	.038	-4.755	1.125	10.170	10.171
1.00E+02	1500.	6.67E-01	6.178	1.504	-1.224	2.476	10.279	10.279
1.00E+02	2000.	5.00E-01	5.407	1.994	.505	3.076	10.331	10.331

Adduct (CQCjO) Dissociation Reaction Rate Constants : log rate constants vs Pressure at specified Temperatures

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
298.	3.36E+00	1.00E-04	-5.241	-14.595	-34.554	-15.114	2.160	2.160
298.	3.36E+00	1.00E-03	-3.241	-13.623	-33.554	-14.114	3.160	3.160
298.	3.36E+00	1.00E-02	-1.241	-12.816	-32.555	-13.114	4.160	4.160
298.	3.36E+00	1.00E-01	.759	-12.404	-31.558	-12.114	5.160	5.160
298.	3.36E+00	1.00E+00	2.759	-12.289	-30.588	-11.114	6.160	6.160
298.	3.36E+00	1.00E+01	4.759	-12.271	-29.809	-10.114	7.152	7.154
298.	3.36E+00	1.00E+02	6.759	-12.270	-29.504	-9.115	8.086	8.106

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
400.	2.50E+00	1.00E-04	-4.354	-10.751	-25.690	-11.095	3.339	3.339
400.	2.50E+00	1.00E-03	-2.354	-9.762	-24.690	-10.095	4.339	4.339
400.	2.50E+00	1.00E-02	-.354	-8.851	-23.690	-9.095	5.339	5.339
400.	2.50E+00	1.00E-01	1.646	-8.219	-22.691	-8.095	6.339	6.339
400.	2.50E+00	1.00E+00	3.646	-7.933	-21.706	-7.095	7.339	7.339
400.	2.50E+00	1.00E+01	5.646	-7.858	-20.826	-6.095	8.337	8.338
400.	2.50E+00	1.00E+02	7.646	-7.847	-20.353	-5.095	9.322	9.331

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
500.	2.00E+00	1.00E-04	-4.126	-8.734	-20.638	-8.905	3.817	3.817
500.	2.00E+00	1.00E-03	-2.126	-7.739	-19.638	-7.905	4.817	4.817
500.	2.00E+00	1.00E-02	-.126	-6.780	-18.638	-6.905	5.817	5.817
500.	2.00E+00	1.00E-01	1.874	-5.992	-17.639	-5.905	6.817	6.817
500.	2.00E+00	1.00E+00	3.874	-5.510	-16.646	-4.905	7.817	7.817
500.	2.00E+00	1.00E+01	5.874	-5.317	-15.711	-3.905	8.817	8.817
500.	2.00E+00	1.00E+02	7.874	-5.276	-15.082	-2.905	9.813	9.818

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
600.	1.67E+00	1.00E-04	-4.167	-7.525	-17.335	-7.530	4.012	4.012
600.	1.67E+00	1.00E-03	-2.167	-6.527	-16.335	-6.530	5.012	5.012
600.	1.67E+00	1.00E-02	-.167	-5.545	-15.335	-5.530	6.012	6.012
600.	1.67E+00	1.00E-01	1.833	-4.658	-14.336	-4.530	7.012	7.012
600.	1.67E+00	1.00E+00	3.833	-4.005	-13.340	-3.530	8.012	8.012
600.	1.67E+00	1.00E+01	5.833	-3.651	-12.375	-2.530	9.012	9.012
600.	1.67E+00	1.00E+02	7.833	-3.539	-11.617	-1.530	10.010	10.013

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
800.	1.25E+00	1.00E-04	-4.523	-6.159	-13.233	-5.876	4.125	4.125
800.	1.25E+00	1.00E-03	-2.523	-5.159	-12.233	-4.876	5.125	5.125
800.	1.25E+00	1.00E-02	-.523	-4.162	-11.233	-3.876	6.125	6.125

800.	1.25E+00	1.00E-01	1.477	-3.190	-10.233	-2.876	7.125	7.125
800.	1.25E+00	1.00E+00	3.477	-2.317	-9.234	-1.876	8.125	8.125
800.	1.25E+00	1.00E+01	5.477	-1.656	-8.244	-.876	9.125	9.125
800.	1.25E+00	1.00E+02	7.477	-1.293	-7.334	.124	10.125	10.126

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1000.	1.00E+00	1.00E-04	-4.941	-5.380	-10.716	-4.875	4.170	4.170
1000.	1.00E+00	1.00E-03	-2.941	-4.380	-9.716	-3.875	5.170	5.170
1000.	1.00E+00	1.00E-02	-.941	-3.381	-8.716	-2.875	6.170	6.170
1000.	1.00E+00	1.00E-01	1.059	-2.387	-7.716	-1.875	7.170	7.170
1000.	1.00E+00	1.00E+00	3.059	-1.427	-6.717	-.875	8.170	8.170
1000.	1.00E+00	1.00E+01	5.059	-.579	-5.721	.125	9.170	9.170
1000.	1.00E+00	1.00E+02	7.059	.038	-4.755	1.125	10.170	10.171

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
1500.	6.67E-01	1.00E-04	-5.822	-4.373	-7.216	-3.524	4.279	4.279
1500.	6.67E-01	1.00E-03	-3.822	-3.373	-6.216	-2.524	5.279	5.279
1500.	6.67E-01	1.00E-02	-1.822	-2.373	-5.216	-1.524	6.279	6.279
1500.	6.67E-01	1.00E-01	.178	-1.373	-4.216	-.524	7.279	7.279
1500.	6.67E-01	1.00E+00	2.178	-.377	-3.216	.476	8.279	8.279
1500.	6.67E-01	1.00E+01	4.178	.602	-2.217	1.476	9.279	9.279
1500.	6.67E-01	1.00E+02	6.178	1.504	-1.224	2.476	10.279	10.279

T (K)	1000/T	P (ATM)	CQJCHO	CJCHO+O2	CH2CO+HO2	CH2CO+HO2	CO+CH2O+OH	QRRK (forw)
2000.	5.00E-01	1.00E-04	-6.593	-3.967	-5.491	-2.924	4.331	4.331
2000.	5.00E-01	1.00E-03	-4.593	-2.967	-4.491	-1.924	5.331	5.331
2000.	5.00E-01	1.00E-02	-2.593	-1.967	-3.491	-.924	6.331	6.331
2000.	5.00E-01	1.00E-01	-.593	-.967	-2.491	.076	7.331	7.331
2000.	5.00E-01	1.00E+00	1.407	.032	-1.491	1.076	8.331	8.331
2000.	5.00E-01	1.00E+01	3.407	1.027	-.491	2.076	9.331	9.331
2000.	5.00E-01	1.00E+02	5.407	1.994	.505	3.076	10.331	10.331

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