INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book. These are also available as one exposure on a standard 35mm slide or as a 17" x 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 8825835

Gas - phase reactions of methylene chloride and methylene chloride-trichloroethylene mixture with methane in tubular flow reactor and atmospheric pressure

Tavakoli-Attar, Javad, D.Eng.Sc.

New Jersey Institute of Technology, 1988

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

GAS - PHASE REACTIONS OF METHYLENE CHLORIDE AND METHYLENE CHLORIDE-TRICHLOROETHYLENE MIXTURE WITH METHANE IN TUBULAR FLOW REACTOR AND ATMOSPHERIC PRESSURE

BY

JAVAD TAVAKOLI-ATTAR

Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fullfilment of the requirements for the degree of
Doctor of Engineering Science
1988

APPROVAL SHEET

Title of Thesis: HIGH TEMPERATURE REACTIONS OF METHYLENE CHLORIDE AND METHYLENE CHLORIDE-TRICHLOROETHYLENE MIXTURE WITH METHANE IN TUBULAR FLOW REACTOR AND ATMOSPHERIC PRESSURE

Name of Candidate: JAVAD TAVAKOLI-ATTAR
Doctor of Engineering Science, 1988.

Thesis and Abstract Approved: ______________________________
PROFESSOR JOSEPH W. BOZZELLI
FULL PROFESSOR
CHEMICAL ENGINEERING AND
CHEMISTRY DEPARTMENT

____________________ _______
Date

Signature of other members of the thesis committee.

____________________ _______
Date

____________________ _______
Date

____________________ _______
Date

VITA

Name : Javad Tavakoli-Attar

Degree and date to be conferred : PhD, 1988

Secondary education : Azar High School, 1968

Collegiate institutions :	Date	Degree	Date of Degree
1- New Jersey Institute of Technology	83-88	PhD	October, 1988
2- Illinois Institute of Technology	75-78	MS	October, 1988
3- Pahlavi University	68-73	BS	June, 1973

Major : Chemical Engineering

Publications and presentations :

"Free-Convective Mass Transfer to a Rod-Shaped Vertical Electrode", co-authored with Selman, J.R., Journal of the Electro- chemical Society, Vol.127,No.5,May 1980.

"Gas-Phase Reaction of Methylene Chloride with Methane in a Tubular Flow Reactor at Atmospheric Pressure", co-authored with Bozzelli, J. W., Central State Techincal Meeting of the Combustion Institute, May 1987.

"Combustion Echancement of Methane/Ethane Mixtures by Photodissociation of Inhibitors", co-authored with Lavid, M., and Stevens, J. G., NSF Annual Report of Phase II, August 1987.

"Combustion Enhancement of Methane/Ethane Mixtures by Photodissociation of Inhibitors", co-authored with Lavid, M., and Stevens, J. G., Eastern Section Technical Meeting of the Combustion Institute, November 1987.

"Gas-Phase Reaction of Methylene Chloride and Trichloroethylene Mixture with Methane in a Tubular Flow Reactor at Atmospheric Pressure", co-authored with Bozzelli, J. G., Central State Technical Meeting of the Combustion Institute, April 1988.

"Gas-Phase Reaction of Chlorocarbons with Methane in a Tubular Flow Reactor at Atmospheric Pressure", co-authored with Bozzelli J. W., ASME Annual Meeting, November 1988.

Positions held :

1987-1988	ENERGIA INC., Princeton, New Jersey.
1988-Present	Visiting Assistant Professor, Lafayette College, Easton, Pennsylvania
Spring of 1988	Part Time Faculty, Hudson County Community College, Instructor of General Chemistry.

ABSTRACT

Title of Thesis : Gas-Phase Reactions of CH2Cl2 and CH2Cl2/C2HCl3 Mixture with Methane in Tubular Flow Reactor and Atmospheric Pressure

Javad Tavakoli-Attar, Doctor of Engineering Science, 1988

Thesis Directed by : Professor Joseph W. Bozzelli

Reactions of methylene chloride diluted in methane and argon and a mixture of methylene chloride + trichloroethylene diluted in methane and argon are studied in three flow reactors of different surface to volume ratios 4, 10.5, and 16 mm ID , atmospheric pressure and over a temperature range of 750-1000 $^{\circ}$C. Experiments were conducted isothermally, ±5 $^{\circ}$C over central 80% of oven length using a three zone oven. Argon was added as a diluent in order to limit carbon (s) formation. The concentration ratios of methylene chloride/methane/argon and methylene chloride/trichloroethylene/methane/argon was held constant at 1:4:10 and 1:1:40:40 respectively, throughout the study. An on line gas chromatograph and GC/MS spectrometer were used for analysis of reactor products. Acetylene, ethylene, benzene, chloromethane, and HCl were observed as the major products, for temperatures above 750 $^{\circ}$K and residence times of 0.08 to 2 secs.

First order plug flow model was utilized to analyze the

experimental data. In addition the homogeneous and wall rate constants were decoupled and separately evaluated. The following overall rate equations were found to fit the reaction systems studied.

Methylene Chloride in $CH_2Cl_2/CH_4/Ar$:

$$k = 1.166E09 * Exp(-44.85/RT) \qquad (1/sec)$$

Methylene chloride in $C_2HCl_3/CH_2Cl_2/CH_4/Ar$:

$$k = 8.11E08 * Exp(-43.2/RT) \qquad (1/sec)$$

Trichloroethylene in $C_2HCl_3/CH_2Cl_2/CH_4/Ar$:

$$k = 1.13E05 * Exp(-30.67/RT) \qquad (1/sec)$$

A detailed kinetic reaction mechanism was developed and used to model the reaction systems and fit the experimentally determined product distribution. Fundamental principles in Transition State Theory and Quantum RRK theory were used in developing reaction rate constants for the model. A mechanism composed of 68 elementary reactions for CH_2Cl_2/CH_4 system and another one with 72 reactions for mixture of $C_2HCl_3+CH_2Cl_2/CH_4$ system were found to reproduce experimental results. A rate constant for :

$$CH_2Cl_2 \text{ ----> } CH_2Cl + Cl \quad \text{of} \quad k = 1.88*10^{16}*Exp(-82.8/RT)$$

chlorine elimination from methylene chloride was found to dominate HCl elimination by 5 orders of magnitude with rate constants and E_a's was determined for this elementary reaction over our experimental conditions. The important initial reactions in $C_2HCl_3/CH_2Cl_2/CH_4$ system were determined as:

$C_2HCl_3 \longrightarrow C_2Cl_2 + HCl$ $\quad k = 7.1*10^{13}*Exp(-77.61/RT)$

$C_2HCl_3 \longrightarrow C_2HCl_2. + Cl.$ $\quad k = 1.74*10^{15}*Exp(-92.1/RT)$

$CH_2Cl_2 \longrightarrow CH_2Cl. + Cl.$ $\quad k = 1.88*10^{16}*Exp(-82.8/RT)$

QRRK analysis and regression of rate constants against experimental data have lead to rate constants for the reactions:

$$CH_2Cl + CH_2Cl \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [C_2H_4Cl_2]^{\#} \begin{array}{ll} \longrightarrow C_2H_3Cl_2+H & (2) \\ \longrightarrow C_2H_4Cl+Cl & (3) \\ \longrightarrow C_2H_3Cl+HCl & (4) \\ \longrightarrow C_2H_4Cl_2 & \text{STABILIZED} \end{array}$$

$$CH_3 + CH_2Cl \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [C_2H_5Cl]^{\#} \begin{array}{ll} \longrightarrow C_2H_4Cl+H & (2) \\ \longrightarrow C_2H_5+Cl & (3) \\ \longrightarrow C_2H_4+HCl & (4) \\ \longrightarrow C_2H_5Cl & \text{STABILIZED} \end{array}$$

$$CH_3 + C_2Cl_2 \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [C_3H_3Cl_2]^{\#} \begin{array}{ll} \longrightarrow C_3H_3Cl + Cl & (2) \\ \longrightarrow C_3H_3Cl_2 & \text{STABILIZED} \end{array}$$

$$C_2HCl_3 + CH_3 \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [C_3H_4Cl_3]^{\#} \begin{array}{ll} \longrightarrow C_3H_4Cl_2+Cl & (2) \\ \longrightarrow C_3H_4Cl_3 & \text{STABILIZED} \end{array}$$

The CHEMKIN computer code was incorporated to model the kinetic schemes and good agreement was obtained between calculated and experimental resutls.

ACKNOWLEDGEMENT

I would like to thank Prof. Joseph W. Bozzelli for his guidance, patience, and encouragement. I acknowledge the careful review and productive comments of my dissertation committee members Dr. R. Ahlert, Dr. T. Gund, Dr. D. Knox, and Dr. S. Sofer.

I shall be indebted to my wife, Mojdeh, for her love, understanding, and cooperation.

I am grateful to my colleagues in Dr. Bozzelli's group, Burhan Mahmood, Edward Ritter, Dr. S. C. Chuang, Dr. S. Chang, and Yang Soo Won who shared with me their experience and helped me with GC/MS analysis.

TABLE OF CONTENTS

LIST OF TABLES

TABLE **PAGE**

LIST OF FIGURES

I. INTRODUCTION

Chlorinated hydrocarbons (ClHC) are manufactured and used on large scale in significant number of chemical industries. These industries include many which produce chlorinated vinyls, waxes and resins; solvents for drug and other chemicals manufacture, dry cleaning solvents, dyes, lacquers and varnishes. Chlorocarbons are often the key ingredient in the chemical fabric of insecticides, freons, wood preservatives and dyes, in addition. In these industries chlorocarbons are either present as one of the main constituents, produced as undesirable end products or they are used as solvents in various processes [1]. One highly noted example of undesirable chlorocarbon chemicals are the PCB's, which have had previous widespread applications, especially as transformer (electrical insulating while thermally conducting) oils [24].

Many chlorocarbons are thought to be toxic, and in some cases carcinogenic [2]. Long term exposure to even low level of these compounds is not suggested because of related health effects [3]. Since the Toxic Substances Control Act (TSCA) law was enacted in 1976, emphasizing PCBs as a hazardous group of compounds [4], disposal of chlorocarbons as industrial wastes has become more and more difficult and costly.

A number of different technologies have been developed or are under development for effective and safe destruction of chlorocarbons. One non-thermal commercially available method for treatment of PCBs is Na-based dechlorination [5]. The process, however, is costly and can not tolerate presence of water. Thermal destruction of organic pollutants in oxygen atmosphere (incineration or combustion) appears to many to be the most viable method for the required destruction, here the conversion is to carbon dioxide and water. This is especially true since The US EPA is strongly considering banning landfill of these chemicals as a disposal alternative. It is reported that combustion of chlorinated hydrocarbons under severe conditions converts all carbon to $CO2$ [6]. The EPA started its thermal destruction program of chlorocarbons in mid-1970's and it is currently the major treatment process recommended by the agency for this class if chemicals [7].

While it may appear reasonable, therefore, that incineration is presently the dominant method of chlorocarbon destruction [8]; a number of different research studies have warned of possible intolerable environmental problems with incinerators. Graham et.al. [9] demonstrated the dramatic effect, that changes in oxygen concentration had on product formation from thermal treatment of components in a mixture of Principal Organic

Hazardous Constituents (POHC). The mixture was composed of 2.5% carbon tetrachloride, 2.5% monochlorobenzene, 2.5% 1,1,2-trichloro-1,2,2-trifluoroethane,2.5% trichloroethylene and 90% toluene by weight. Experiments were conducted in oxygen rich, stoichiometric and oxygen lean (pyrolysis) atmospheres. A flow reactor at a temperature as high as 1100 ^{o}C with mean residence times between 0.5-6 seconds was utilized. Results from their studies under pyrolitic conditions and at equivalence ratios of 0.06, and 1, at temperatures of 1000, to and 650 ^{o}C, showed that more than 30 stable products were observed under each condition. Out of these products, more than 23 were halogenated carbon species. Some of the product species were believed to be more toxic than the starting compounds. This study [9] dramatically showed that the number and complexity of thermal reaction products increased by decreasing oxygen concentration. Significant quantities of halogenated and nonhalogenated polynuclear aromatic hydrocarbons were observed under pyrolytic conditions but not under oxidative conditions.

Karasek et. al. [6] and Shaub et. al. [8] have reported formation of complex halocarbons or unstable chlorine-oxygen compounds for such systems. Some investigators revealed that burning of chlorine-rich compounds require rather drastic circumstances in order to avoid emission of intolerable quantities of tetrachloro-dibenzo-p-dioxins (TCDD) [6] and polychlorinated-dibenzo-dioxins (PCDD) [11] like substances.

Even if all of the chlorocarbon parent can be destroyed by the incineration process the initial reaction products may not be all converted to carbon dioxide. With a fuel lean or oxygen rich atmosphere, there is competition for the hydrogen between the oxygen and chlorine. There is no other stable end adduct for chlorine, than HCl, in an oxygen rich atmosphere and so carbon chlorine bonds often persist. Here chlorine oxides and chlorine are not acceptable for discharge to the atmosphere, while hydrogen chloride which can be quantitatively neutralized and collected is a preferred product. In oxidizing systems, however, excess oxygen combines with hydrogen to form a more thermodynamically stable H2O product.

Utilizing a reductive, instead of oxidative, atmosphere may be an alternate pathway for conversion of chlorcarbon species:

$$R - Cl + H2 \text{ -----> } R - H + \text{(dry) } HCl + 40\text{-}90 \text{ KJ/mol} \quad (1)$$

This reaction is favorable thermochemically since reaction (1) is exothermic [10] and no oxygen is present to scavenge the hydrogen.

Louw et. al. [11] and Bozzelli et. al. [25, 26, 33, 34, 52] have reported that thermal decomposition of chlorocarbons in a reductive hydrogen atmosphere can be a promising alternative. A less expensive hydrogen source such as CH4 may, in addition, strengthen application of this concept economically. At the same time, investigation of the chlorocarbon/methane reaction system will lead to better chemical understanding of chlorinated hydrocarbon reactions and their fundamental kinetic processes at high temperatures. These reactions are also very important for upgrading methane to higher molecular weight hydrocarbons [39].

II. PREVIOUS STUDIES

Thermal treatment has received a significant amount of attention for conversion of unwanted chlorinated hydrocarbons (ClHC) in the last decade. Most of relevant studies are either in an oxygen atmosphere. Three reports were found on gas phase reaction of ClHC in a reducing atmosphere of methane. Murgulescu and Weissman [37-38] studied the effect of methane on pyrolysis of chloroform and reported that production of vinyl chloride is increased by addition of CH4 to the system. Benson and Weissman [39] investigated high temperature (1200-1300 ^{O}K) reaction of methyl chloride and methane. They reported C_2 hydrocarbons as the major products of their experiment. No research publication on high temperature reaction of methane with methylene chloride and/or trichloroethylene was found. An overall review of the related and important investigations is presented in the following paragraphs.

Lee et.al.[16] studied thermal (800-1500 ^{O}F) destruction rates of four organic compounds (vinyl chloride, ethyl acrylate, acrolein, and benzene) in air employing a 0.9 mm ID, 135 cm long quartz tube flow reactor. Compounds were run at 1000 ppm in air under uniform temperatures and reaction times of 0.1-1.8 seconds. They [16] reported that, at temperatures above 1450 ^{O}F, 99.8% of C2H3Cl was destroyed and no benzene was detected (i.e. more than 2 ppm). Higher temperature (1700-1800 ^{o}F) was required for complete destruction of ethyl acrylate and acrolein.

Valeiras et.al. [18] investigated laminar burning velocities of chlorinated methanes, trichloroethylene, and chlorobenzene in mixture with methane and air in order to obtain the overall rate of combustion where the bunsen cone method was used. The burning velocities showed a maximum in the vicinity of unit equivalence ratio for all systems studied with respect to the ClHC molecular structure. The burning velocities, however, decreased with the increasing chlorine content of the mixture and showed a simultaneous reduction of flame temperature.

Bose et.al. [17] studied premixed flame combustion of highly chlorinated hydrocarbon (C2HCl3) at 1 atm pressure using a flat-flame burner. The stable species in the flame were determined using water-cooled quartz probes, and gas-chromatography. They [17] discussed two widely separated flame zones. In the first zone, the ClHC undergoes fast oxidative reactions with the formation of mainly CO, HCl, and Cl2. This can be shown by the following overall reaction chemistry:

$$C2HCl3 + O2 \xrightarrow[\text{flame}]{\text{fast}} 2CO + HCl + Cl2 + 74\ KCal$$

The principal reaction in the second flame zone involves the slow, HCl and Cl2 inhibited oxidation of CO to CO2:

$$2CO + O2 \xrightarrow[HCl.Cl2]{slow} 2CO_2 + 136\ KCal$$

Senkan [19] numerically examined the reaction scheme of the intermediate zone of the two-stage trichloroethylene-oxygen-nitrogen flames. He incorporated a plug-flow model combined with the detailed chemical kinetics reaction mechanism for the hydrogen-catalyzed oxidation of CO deve3loped by Westbrook et.al. [35] and the elementary reactions involving chlorine and chlorinated species. The initial conditions used in the model were 15.3% CO, 5.1% CO2, 11.7% Cl2, 7.14% HCl, 1.53% H2O, 23.53% O2, and 35.7% and a temperature level of 1080 ^{o}C. A cold velocity of 10 cm/s was used in the calculations. Qualitative features of the calculated profiles for O2, CO, and CO2 mole fractions were found to be in reasonable agreement with the experimental measurements [17]. There were quantitative differences which he believed to be mostly due to errors in experimental measurements.

Karra et.al. [37] made a comparative study of the chemical structure of sooting of CH3Cl/CH4/O2/Ar and CH4/O2/Ar flames at atmospheric pressure. In the presence of chlorine, ample amounts of C2H2 and C2H4 were formed rapidly in comparison to a similar reaction system but with no chlorine.

Granada et.al. [36] have shown that reaction of 3%

oxygen, 7% chloromethane, and 90% argon at 990 °C produces significantly less carbon solids plus ethylene and acetylene as products. They suggest chlorine/O2 mixtures will be usefull for CH4 upgrading to C_2 unsaturates.

Sorbo et. al. [20] investigated the vaporization and combustion of droplets of pure chlorinated hydrocarbons (C2H2Cl4) and their mixtures with n-alkanes. They demonstrated that monodisperse droplets, with controlled spacing, of pure 1,1,2,2-tetrachloroethane injected into the post-combustion region of a flat-flame burner do not burn. A mixture of 75% C2H2Cl4 + 25% n-nonane, however, showed a long period (70 ms) of fairly steady burning. A 25% C2H2Cl4 + 75% nonane mixture showed complete burning (observable limit) while a 80% C2H2Cl4 + 20% nonane mixture showed an early flame extinction. Droplet combustion was inhibited when the Cl/H ratio approached unity. Studying a mixture of 85% C2H2Cl4 with alkanes of different volatility showed that the burning time is shortest with the least volatile alkane additive (hexadecane).The longest duration (inhibition) occured when the additive was more volatile (heptane) than C2H2Cl4.

Frenklach et.al. [21] examined soot formation in shock tube pyrolysis of chlorinated methanes. The experiments were performed at temperatures ranging from 1300 to 3000 °k and pressures of 0.4-3.6 bars. Most of the experiments were performed with approximately the same chlorinated methane concentration i.e., 5E17 atoms/cc. This was achieved by using argon as a diluent. The amounts of soot produced in pyrolysis of chlorocarbons were reported to be larger than with non-chlorinated hydrocarbons. The pyrolysis of 9.3% chloromethanes (CCl4, CHCl3, CH2Cl2, CH3Cl) in argon, for example, produced 1%, 3%, 12%, and 28% more soot, respectively, than pyrolysis of the same concentration of methane on the temperature range of 1600 - 2700 ^{o}K at a reaction time of 1 msec. The authors argue that the pathway to soot formation from chlorinated methanes and ethylenes with high H:Cl reactor influx ratios proceeds via the formation of C2H, C2H2, and C2H3 species. Where for chloromethanes with low H:Cl ratio the formation of C_2 and its contribution to soot formation at high temperature becomes significant.

Louw et.al. [11] investigated thermal dechlorination of (poly) chlorinated organic compounds (C6H5Cl, p- and o-C6H4Cl2, E-CHCl=CHCl, C2Cl4, and 1,2-C2H4Cl2) in hydrogen atmosphere. Experiments were performed at 1 atm. pressure, using a quartz flow reactor and a temperature range of 500-1000 ^{o}C. They suggested the possibility of more than 99.9% conversion in an atmosphere of excess hydrogen within a few minutes (A long time relative to incineration residence times) in a plug flow reactor at 1000 ^{o}K. Major products, for residence times of 5.9 to 10.6 seconds and various hydrogen/chlorocarbon ratios were found to be chlorine free hydrocarbons (CH_4, C_2H_4, C_2H_6, C_6H_6) or parent compounds with a smaller number of chlorine atoms. They have also postulated mechanisms for methane formation by pyrolysis of benzene and chlorobenzene in an atmosphere of hydrogen with relative concentration ratios for $C_6H_6:H_2$ and $C_6H_5Cl:H_2$ of about 1:6 [22].

Benson and Weissman [23] studied the pyrolysis of pentachloroethane to determine the kinetic parameters and elucidate elementary reactions. They reported different mechanisms for the inhibited (presence of excess toluene) and un-inhibited reaction systems. Chain initiation for uninhibited pyrolysis of C_2HCl_5 was reported to be heterogeneous (wall) C-Cl bond breaking:

$$C_2HCl_5 \xrightarrow{\text{wall}} Cl + C_2HCl_4$$

where for inhibited reaction homogeneous C-Cl bond cleavage is dominant and accounts for 50% of the reaction. The C-C bond breaking and the molecular HCl elimination pathways were reported to have comparable rates to homogeneous C-Cl bond cleavage and contribute to C_2HCl_5 consumption.

Manion et. al. [24] investigated thermolysis of PCBs (Arochlor 1248 with 48% by wt. Cl) mixed with chlorobenzene in a hydrogen atmosphere. The influx of each compound was (mmol/h): H_2, 221; PhCl,10.2; Arochlor 1248 (0.69).

Experiments were conducted in a flow reactor (3.5 m length, 46 CC volume) at a temperature range of 700-925 ^{o}C and residence times of up to 10 seconds. HCl and benzene were found to be the major products. Polychlorinatedbiphenyls (PCBs) were observed to: 1) dechlorinate and 2) dissociate by C-C bond cleavage (split) into chlorinated benzenes. In the phenyl C-C cleavage rates were reported to be about twice as fast as dechlorination.

Chuang and Bozzelli [25] studied reactions of chloroform and 1,1,2-trichloroethane with hydrogen in a tubular reactor, at atmospheric pressure, and a temperature range of 550-1100 ^{o}C. The major products observed above 850 ^{o}C were HCl, CH4 and carbon (solid). Trace levels of chlorinated species, chloromethane and vinyl chloride, were detected indicating the relative stability of these species. Complete destruction of these compounds required higher temperature or longer reaction time. Their experiments [25] demonstrated that complete destruction of parent reagent (CHCl3 or C2H3Cl3) is possible at temperatures near 700 ^{o}C and residence times of slightly over 1 second. They determined global kinetic parameters as activation energies of 48.6 KCal/mol and 48.8 KCal/mol for CHCl3/H2 and CHCl2CH2Cl/H2 reactions respective to their conditions.

Mahmood and Bozzelli [26] investigated thermal degradation of trichloroethylene in a hydrogen atmosphere utilizing tubular flow reactor, ambient pressure, and a temperature range of 550-1000 ^{o}C. They report C_2H_2, C_2H_4, CH_4, HCl and benzene as major products. No chlorinated hydrocarbons were observed in the effluent of reactor above 850 ^{o}C for reaction time of less than one second.

Several reports on dehydrochlorination of chlorocarbons at high temperature (600 - 1000^{o}C) and atmospheric pressure utilizing flow reactors have been conducted recently. Tsao studied reactions of tetrachlorocarbon and methylene chloride with hydrogen [27]. The major products of the CCl_4/H_2 reaction were $CHCl_3$, HCl, and C_2Cl_6. Chlorine free hydrocarbons were not detected, except at temperatures over 800 ^{o}C and one second residence time. Major products reported for the CH_2Cl_2/H_2 reaction system above 950 ^{o}C and 1 second reaction time were CH_4, HCl, C_2H_2, C_2H_4, C_2H_6, and benzene. Ritter [14] report that complete destruction of chlorobenzene in a hydrogen environment can be achieved at a temperature of 1273 ^{o}K and residence time of one second. The major products were identified as HCl, benzene, and C(s).

Reaction of H atoms with CH_2Cl_2 were studied by Combourieu et.al. [29]. Various initial concentration ratios of $[H]/[CH_2Cl_2]$, ranging from 0.39 to 12.1, were considered. A discharge-flow system on a temperature range of 298-460 ^{o}K and total pressure near 1 torr was utilized. The products were identified as HCl, H_2, CH_4, C_2H_2, and C_2H_4. The rate constant of the initial step:

$$H + CH2Cl2 \longrightarrow HCl + CH2Cl$$

was found to be k = 1.8*10E-11exp(-6100/RT) $cm^3\ mol^{-1}\ s^{-1}$.

Hassler and Setser [30] studied the reaction of methylene (:CH2) radical with chloromethane, using a gas phase activation technique. The CH2: radical was prepared either photochemically from compounds like CH2N2 or thermally (300 ^{o}C) from CH2N2. The major product at room temperature is reported to be C2H5Cl and 1,2 C2H4Cl2 where starting reactant energies were thought to be nearly 90 kcal/mole above the stable insertion adduct.

Murgulescu and Weissman [31, 32] investigated the influence of methane on thermal decomposition of chloroform. The temperature range varied from 520 to 600 ^{o}C for reaction times of up to 100 seconds. It was found that the presence of methane in pyrolysis of chloroform, (CH2Cl2, or CH3Cl) favored vinyl chloride formation. The vinyl chloride could be increased up to 100% of product yield by increasing reactant initial concentration ratio ([CH4]i/[CHCl3]i) to 2200 at 599 ^{o}C and 37-38 second reaction times. The first order rate constant of the initial step (HCl elimination), k1, for reaction:

$$CHCl3 \rightleftharpoons CCl2 + HCl$$

was reported to decrease with increasing contact time and initial chloroform concentration.

Benson and Weissman [39] studied the effect of methane on pyrolysis of methyl chloride in search of upgrading (conversion to C_2 hydrocarbons) methane. Major products at temperatures of 1260-1310 ^{o}K were reported to be ethylene and acetylene. Their yield increased as the degree of CH3Cl conversion decreased and the excess of methane increased. Changes of temperature (50 ^{o}C), pressure, or addition of HCl were reported to have little effect on reaction products. With CH4 added C2H4, C2H2 and C6H6 are produced and appeared to approach stationary concentrations in the system. Different routes are suggested for production of ethylene and acetylene in the presence and/or absence of CH4.

III. THEORY

A. UNIMOLECULAR REACTIONS

The simplest type of an elementary gas phase reaction can be regarded as a unimolecular reaction. One type is bond cleavage represented as :

$$RX \text{ ----> } R. + X. \qquad \text{(products)} \qquad (1)$$

A second kind of unimolecular reaction is rearrangement such as cis/trans isomerization. There are different useful models that describe reaction (1) quatitatively. Lindeman Theory, first proposed in 1922 [41], states that for this reaction to occur, the reacting molecule, RX, should accumulate enough internal energy to overcome the barrier for breaking specific bonds or undergoing internal rearrangement. In thermal processes this energy, activation energy, as termed in kinetics, is collected through irregular collisions of molecule RX with a third body. The third body can be any other gas molecule or the reactor wall.

$$RX + M \xrightarrow{k1} RX^{*} + M \qquad \text{Activation} \qquad (2)$$

These energized molecules may undergo deactivation by further collision with the gas molecules or they may decompose forming products. There is, therefore, a competition between spontaneous decomposition and deactivation.

$$RX^* + M \xrightarrow{k2} RX + M \qquad \text{Deactivation} \qquad (3)$$

$$RX^* \xrightarrow{k3} R + X \qquad \text{Decomposition} \qquad (4)$$

At the time Lindeman believed that the rate constant of reaction (4) is independent of energy content of RX^*. Assuming a steady-state concentration for RX^* in reactions (3) and (4) one can write:

$$\frac{d[RX^*]}{[dt]} = 0 = k1\,[RX][M] - k2[RX^*][M] - k3[RX^*] \qquad <1>$$

$$[RX^*] = \frac{k1[RX][M]}{k2[M] + k3} \qquad <2>^{**}$$

Also, the rate of uni-molecular reaction can be written as:

$$\frac{-d[RX]}{dt} = k1[RX][M] - k2[RX^*][M]$$

$$= \frac{k1k3[RX][M]}{k3 + k2[M]} = kuni[RX] \qquad <3>$$

From equation <3> one can write:

$$kuni = \frac{k1k3[M]}{k3 + k2[M]} \qquad <4>$$

At high pressure k2[M]>>k3 and therefore:

$$kinf = \frac{k1\;k3}{k2} \qquad <5>$$

** () represent reactions and < > is used for equations.

where kinf is the high pressure rate constant. While at low pressure the limit is:

$$k0 = k1[M] \qquad \langle 6 \rangle$$

It can be concluded from Lindeman's analysis that this process is first order at high pressure (independent of pressure) and second order at low pressure.

It is customary to check experimental vs calculated data by plotting "pressure falloff" curves. These curves are obtained by ploting log(kuni/kinf) vs log[M] or logP where P is pressure. Hence, the ratio kuni/kinf will be:

$$(kuni/kinf) = \{1 + [kinf/(k1.P)]\}^{-1} \qquad \langle 7 \rangle$$

Lindeman suggested calculation of k1 by:

$$k1 = Z1 \exp(-E0/RT) \qquad \langle 8 \rangle$$

where Z1 is calculated from collision theory. The high pressure rate constant, kinf, and activation energy, Einf (assumed equal to critical energy, E0), are obtained from experiment. Pressure falloff curves obtained from the Lindeman expression are often far different from experimental data.

Hinshelwood improved Lindeman's model by relating the critical energy accumulation of a molecule to its internal degrees of freedom (vibrational levels) [41]. Hence the corrected equation is :

$$k1 = \frac{Z1}{(s-1)!} \, \frac{E0^{(s-1)} \exp(-E0/RT)}{RT} \qquad \langle 9 \rangle$$

where s is the number of vibrational modes, s-1 is used because one vibration mode is the reaction coordinate. This is the Hinshelwood-Lindeman (H-L) expression for the low pressure limit. Assuming k2 = Z2 = Z1 (i.e. deactivation occurs with every collision), high pressure rate constant according to this theory becomes:

$$kinf = (k1*k3/k2) = \frac{k3}{(s-1)!}\left(\frac{E_0}{RT}\right)^{s-1} \exp(-E_0/RT) \qquad <10>$$

Employing the Van't Hoff Equation [50] for the activation energy of a chemical reaction to Eqns. <9> and <10>, one obtains, for :

$$E_o = E_0 - (s-3/2)RT \quad \text{(low pressure)} \qquad <11>$$

where Z1 is proportional to $T^{.5}$.

$$E = E_0 - (s-1)RT \quad \text{(high pressure)} \qquad <12>$$

Equations <11> and <12> reveal almost no dependence of activation energy on pressure. This contradicts the experimental observation that E for a unimolecular reaction decreases with pressure. Another weakness of the H-L theory is the dependence of k3 on molecule complexity but not on the energy of $[RX^*]$. According to this assumption, the fewer smaller the number of atoms in a molecule, i.e. the fewer vibrational modes, the shorter its life time.

Rice, Ramsperger, and Kassel modified Hinshelwood's expression for k3, to be a function of E, the molecule's energy content [41]. All three assumed the hypothesis that total energy E of a molecule is assumed to be distributed statistically around its structure. Hence, for any excited molecule with E greater than E_0, there is a finite statistical probability that E_0 will be found in the relevant part (vibration mode) of the molecule. The RRK theory relates the conversion rate constant of energized molecules to this probability.

Kassel showed separately [41] that classical theory calculates the probability of one oscillator having energy greater than E_0 in a molecule of s oscillators as :

probability (Prb) [energy > E_0 in one chosen oscillator]

$$\text{Prb} = \frac{(E - E_0)^{s-1}}{E} \qquad \text{<13>}$$

He defined K3(E) as :

$$K3(E) = A \frac{(E - E_0)^{s-1}}{E} = A\,(1-E_0/E)^{s-1} \qquad \text{<14>}$$

where A is high pressure A factor. Using equation <12> it can be shown [41] that :

$$\text{kinf} = A \exp(-E_0/RT). \qquad \text{<15>}$$

In the expressions above, K1 is calculated by Hinshelwood's expression and k2 by collision theory.

Marcus [41] developed a more thorough unimolecular reaction mechanism and incorporated it into the RRK theory. The new reaction scheme, i.e., the RRKM theory, is:

$$RX + M \underset{\longleftarrow}{\longrightarrow} RX^* + M \qquad (5)$$

$$RX^* \text{ ---->} RX^\# \text{ ----> products} \qquad (6)$$

The $RX^\#$ activated complex is an intermediate (transition state) between energized molecule RX^* and products. $RX^\#$ is identified as an species with configuration corresponding to the top of an energy barrier between reactant and products.

The RRKM theory only considers redistributible energies among a molecule's various degrees of freedom, in order to calculate equilibrium concentrations for RX^* and $[RX]^\#$. Hence, the zero point energy of molecular vibrations, overal translational energy, and rotational energies with constant angular momentum have no effect on unimolecular reaction of the molecule under consideration. Detail calculations for k^*, $[k]^\#$, k1/k2, kuni, and kinf are given elsewhere [41].

The RRKM theory reperesents the most realistic model of those mentioned but is a lengthy approach for analysis of a detailed kinetic model. A more straight forward method, the QRRK theory [41], with good accuracy in prediction of falloff curves is also available. Quantum RRK theory is a quantum version of Kassel's theory. This theory assumes "s" identical oscillators in the molecule, all having the same frequency, v. Energies, expressed in quantized form, can be written as :

$m = E_0/(hv)$ Critical Energy

$n = E/(hv)$ Overall Energy.

Hence, the probability a chosen oscillator has energy > m quanta becomes [41] :

$$p = \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!} \qquad \text{<16>}$$

and,

$$k_3(nhv) = A \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!} \qquad \text{<17>}$$

$$k_1(nhv) = k_2 \text{ alpha}^n(1-\text{alpha})^s \frac{(n+s-1)!}{n!(s-1)!} \qquad \text{<18>}$$

The high pressure rate constant is given as:

$$k_{inf} = \sum_{n=m}^{inf} \frac{k_1(nhv)\ k_3(nhv)}{k_2}$$

$$= A \exp(-E_o/KT) \qquad \text{<19>}$$

and the ratio k_{uni}/k_{inf} is given by :

$$k_{uni}/k_{inf} = (1-alp)^s \sum_{p=0}^{inf} \frac{alp^p(p+s-1)!/[p!(s-1)!]}{1+(A/k_2[M])(p+m)!(p+s-1)!/[(p+m+s-1)!p!]} \qquad \text{<20>}$$

where $p = (n-m)$ and alpha = exp(-hv/KT). The only input data needed are high pressure limit A factors, activation energy, E_a, Lennard-Jones parameters, e/k_b, and geometric mean frequency of dissociating energized species. In the RRKM theory, on the other hand, all distributable energies are considered and therefore the specific vibrational frequency of each mode is required. This makes calculation much more difficult and time consuming. We have used QRRK theory for calculation of energy dependent rate constants.

B. BIMOLECULAR REACTION

The simplest form of a bimolecular reaction can be represented as:

$$A + B \xrightarrow{[AB]^{\#}} C + D \qquad (7)$$

In a thermally equilibrated system reaction rate of this process has been analyzed by : Simple Collision Theory (SCT), Transition State Theory (TST), QRRK Theory.

In SCT the bimolecular reaction rate is given as fraction of A and B collisions along the line-of-center which have necessary activation energy ($e^{-EAB/RT}$) and proper internal coordinates (p_{AB}):

$$k_{AB} = p_{AB} Z_{AB} \exp(-E_{AB}/RT) \qquad <21>$$

where Z_{AB} is the collision frequency between A and B given by kinetic theory.

Comparison of experimental vs calculated values of k_{AB} by SCT has shown p-factors lying between about 10^{-3} and 10^{-1} for a large number of reactions (except for alkali metal atoms) [42].

Transition State Theory, originally developed by Eyring and Polanyi [43], proposes that molecules having an orientation for reaction and the required energy corresponding to the internal energy barrier for chemical reaction be considered in equilibrium with reactants and products :

$$A + B \underset{\longleftarrow}{\overset{K^{\#}}{\longrightarrow}} [\ X\ ]^{\#} \underset{\longleftarrow}{\longrightarrow} C + D \qquad (8)$$

In cases that products and reactants are not in equilibrium, the complex is assumed to be in equilibrium with the reactants. If $k^{\#}$ represents the specific rate constant for the passage over the barrier, the transition state, equilibrium between A + B and $X^{\#}$, may be expressed as :

$$K^{\#} = \frac{[X^{\#}]}{[A][B]} \qquad <22>$$

Employing statistical mechanics one can show that [41] :

$$k_1 = \frac{k_b\ T}{h}\ K^{\#} \qquad <23>$$

Equation <23> shows that all equilibrium rate constants can be written as a product of a universal frequency factor, $(k_b T/h)$, and a thermodynamic factor, $K^{\#}$, (an equilibrium constant) which depends only on the structure and energy of the transition state. The rate is therefore not dependent on details of the collision process.

It is known from classical thermodynamics [59] that :

$$K^{\#} = \exp[-\mathrm{Del}\ G^{\#}/RT] = \exp[\mathrm{Del}\ H^{\#} - T\ \mathrm{Del}S^{\#}] \qquad <24>$$

Substituting $\mathrm{Del}H^{\#} = \mathrm{Del}\ E^{\#} - RT$ and combining <24> with <23> gives :

$$k_{\ r} = \frac{ek_bT}{h} \exp[\mathrm{Del}\ S^{\#}/R].\ \exp[-\mathrm{Del}\ E^{\#}/RT] \qquad <25>$$

Del $E^\#$ is the internal energy of activation; a quantity similar to critical energy.

Dean et.al. [51] have employed Quantum Rice-Ramsperger-Kassel (QRRK) analysis to calculate rate constants of bimolecular, addition and recombination, reactions (formation of an energized adduct). An energized adduct can be stabilized by collision, decompose back to reactants, or result in new products by other dissociation or isomerization channels.

For an addition reaction of the general form :

$$R + R' \underset{k_{-1}(E)}{\overset{k_1.f(E,\ T)}{\rightleftarrows}} \begin{array}{c} A^* \\ \scriptstyle BZ[M] \\ A \end{array} \xrightarrow[k_2(E)]{} P + P' \qquad (9)$$

k_1 is the high-pressure-limit rate constant of excited adduct formation and f(E,T) is the energy distribution for chemical activation given by :

$$f(E,T) = \frac{k_{-1}(E)\ k(E,\ T)}{k_{-1}(E)\ k(E,\ T)} \qquad \text{<26>}$$

k(E, T) is the QRRK thermal distribution from equation <27>.

$$k(E,\ T) = alpha^{n}.(1-alpha)^{s}\frac{(n+s-1)!}{n!(s-1)!} \qquad \text{<27>}$$

B is collisional efficiency and is caculated by [55]:

$$\frac{B}{1-(B)^{1/2}} = \frac{-\langle \text{Del } E_{coll} \rangle}{F(E)\ k_b T} \qquad \langle 28 \rangle$$

where $\langle \text{Del } E_{coll} \rangle$ is the average amount of energy transferred per collision and F(E) is a factor taken to be 1.5 throughout the temperature range of this study.

Using steady state analysis the rate constants for stabilization reaction to form A, and formation of products P, P' and reactants R, R' can be written as:

$$k_s = \frac{BZ[M].\ \ k_1.f(E,\ T)}{BZ[M] + k_{-1}(E) + k_2(E)} \qquad \langle 29 \rangle$$

$$k_r = \frac{k_2(E)*\ \ k_1.f(E,T)}{BZ[M] + k_{-1}(E) + k_2(E)} \qquad \langle 30 \rangle$$

The values of calculated rate constants, however, are pressure dependent. The basic reason for change in rate constant with pressure is the variation of activation energy due to the energy distribution of the reacting molecules. At very low pressures, all energized molecules react. At high pressures, however, there is a competition between reaction of energized molecules and their collisional de-energization. A higher activation energy is, therefore, required to overcome the barrier of product channel barrier. The values for low- and high pressure limits of k_s and k_r can be obtained from equations <29> and <30>.

For low-prssure limit [M]--->0 and therefore:

$$\lim_{[M]\text{--->}0} k_s = \frac{[M].\ \ BZ.\ k_1.f(E,\ T)}{k_{-1}(E)\ +\ k_2} \qquad \text{<31>}$$

$$\lim_{[M]\text{--->}0} k_r = \frac{k_1\ k_2(E).f(E,\ T)}{k_{-1}(E)\ +\ k_2(E)} \qquad \text{<32>}$$

High-pressure limit values of k_s and k_r can be obtained from equations <29> and <30> by having [M]---> . This will result in the following equations :

$$\lim_{[M]\text{--->}} k_s = k_1 \qquad \text{<33>}$$

$$\lim_{[M]\text{--->}} k_r = \frac{1}{[M]} * \frac{k_1}{B.Z} * k_2(E).f(E,\ T) \qquad \text{<34>}$$

It is apparent from <34> that product exit channels are pressure dependent (i. e. dependent on concentration of M). This is consistant with RRKM results.

C. TUBULAR REACTOR

It is difficult to sustain operation of a laboratory scale tubular reactor at ideal plug flow conditions. Plug flow is often characterized by a Reynolds number greater than 10000 and length/diameter ratio of greater than 100 [45]. For the case of this experiment N_{Re} was well below 10000 and L/D ranged from 28 to 112.5. This implies that a well developed laminar flow regime with parabolic velocity profile was present in reactors under consideration.

Mathematical formulation of a laminar flow system in a cylindrical reactor, is not trivial. Simultaneous solution for parameters such as unequal residence time for different species, undeveloped velocity profile at the entrance, temperature variation with time at the both ends of reactor, interaction of homogeneous and heterogeneous reactions, axial and radial diffusion, variation of temperature due to imperfect radial heat transfer, etc. is difficult to realize without simplification of the problem. For laminar flow, in tubular reactors, the following assumptions are usually made: (1) no end effects; (2) single residence time for all species; (3) no pressure drop along the tube due to viscosity.

Mulcahy [46] has suggested that thermal equilibration can be greatly accelerated by preheating the gas. The mixture of reactants were preheated to 400 ^{o}C throughout this study. In small diameter (less than 1 cm) laboratory scale reactors radial diffusion is of importance because of possible heterogeneous reaction at the wall and mixing of axial diffusion is usually minimized by utilization of moderate flow rates.

Chang and Bozzelli [52] have solved the continuity equation for laminar flow in a tubular reactor considering parabolic velocity profile with radial dispersion, parallel bulk and wall reactions with coupled rate constants. They showed a method to determine homogeneous and heterogeneous rate parameters simultaneously from their optimum values. They have also made comparison and reported that validity of the plug flow model for a laminar flow system depends on alpha, beta, and Z below:

$$\text{alpha} = \frac{k_b R^2}{4D_{AB}} \quad <35>$$

$$\text{beta} = \frac{k_w R}{2D_{AB}} \quad <36>$$

$$Z = 4\ D_{AB}/(V_0 R^2) \quad <37>$$

Whhere:

k_b = bulk rate constant,1/sec

R = reactor diameter, cm

D_{AB} = diffusion coefficient of an A-B binary system, cm^2/sec

Poirier and Carr [53] performed analysis of a similar system over an extended pressure range for first and second order chemical reactions showed that if:

$$\text{alpha} = D/(K.R^2) > 0.5 \qquad <38>$$

plug flow assumption for a first order reaction regime provides results within 10% accuracy. The value for alpha in this study was well above 0.5, and hence, the plug flow assumption is acceptable.

D. HOMOGENEOUS AND HETEROGENEOUS REACTIONS

Influence of surface/volume ratio on gas phase reaction rate constant of small diameter reactors (less than 1 cm) is an established phenomena [52-54]. Dependence of dehydrochlorination of halocarbons on reactor diameter, in addition to commonly accepted concentration and reactor temperature, has been shown by other investigators [12-15, 25-28].

In order to simplify the formulation of governing equations for a reactor system in which both bulk and wall reactions are present, it is usually assumed that the two reactions are parallel and independent [50]. Hence, for the first order reaction of species A one can write :

$$A \text{ -----> Products}$$

$$-\frac{d[A]}{dt} = k_b[A] + k_{wall}[A] \qquad \text{<39>}$$

Assuming a rapid radial diffusion, k_{wall} can be written as [49] :

$$k_{wall} = k_w\ (S/V) \qquad \text{<40>}$$

where:

S/V = surface to volume ratio, 1/cm

k_w = gamma w/4, cm/sec

$S/V = 2/R$ for a cylindrical reactor with R being reactor radius, gamma the fraction of collisions leading to wall reaction, and w the mean velocity. From <39> and <40> one obtains:

$$k_{exp} = k_b + k_w . 2/R \qquad <41>$$

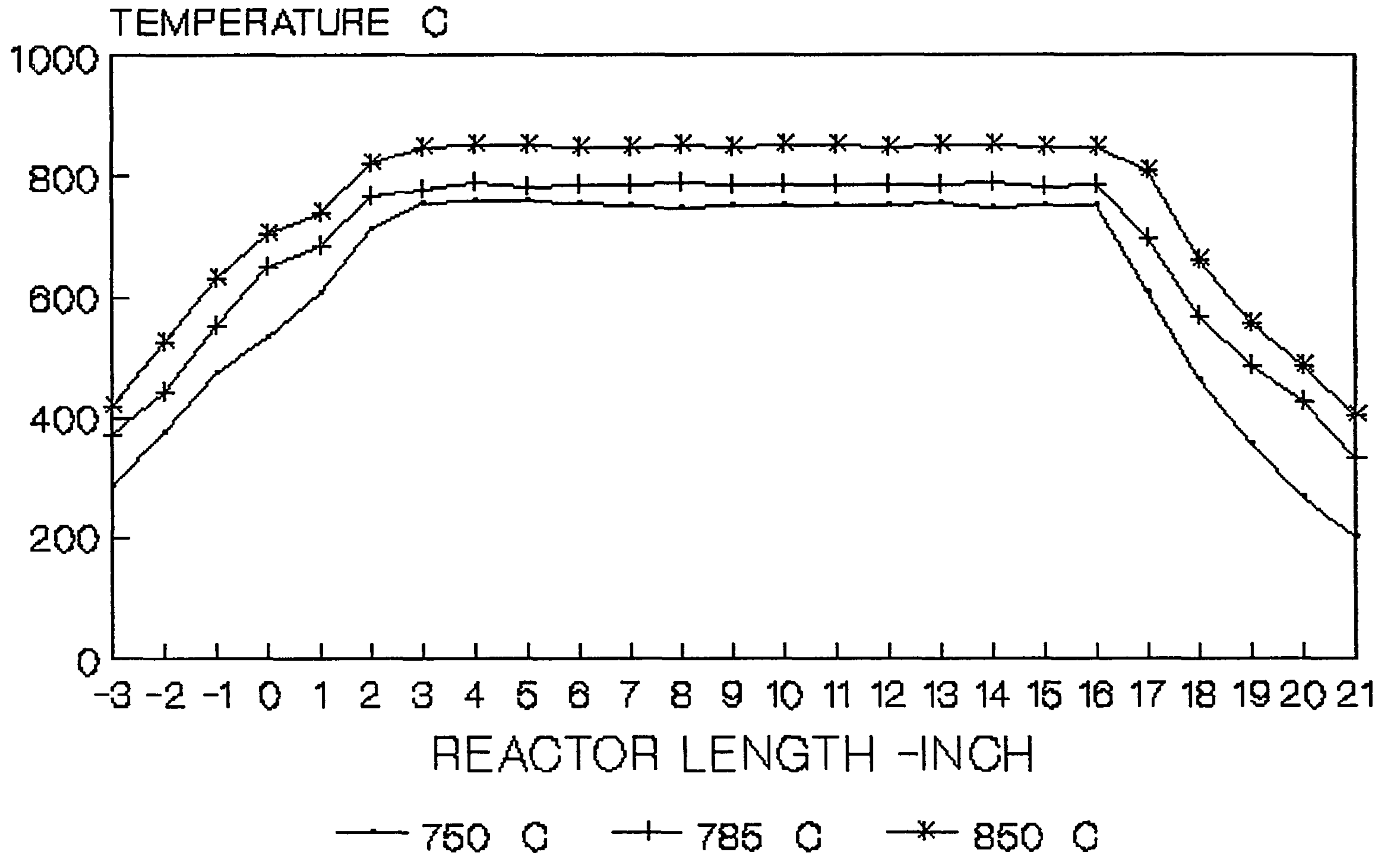
Therefore, one can easily decouple the bulk and wall rate constants simply by having global rate constants for two different reactor diameters.

IV. EXPERIMENTAL

A tubular flow reactor system was operated isothermally at temperatures in the range 750-1000 ^{o}C and atmospheric pressure. Reactors of 4, 10.5, 16 mm I.D., and 45 cm long quartz tubes were utilized. A three zone Mellen clamshell type furnace, 2 1/4 inches I.D., and 18 inches long was used for the reactor oven. Every zone was equipped with an independent Omega CN 300 PI digital temperature controller - indicator. The two end zones, 3 inches each, helped to reduce heat dissipation effects by supplying higher fluxs and allowed a uniform ($\pm$5 ^{o}C) temperature profile for the central 82-90 per cent of the reactor length.

The actual temperature inside the reactor was measured with a moveable thermocouple chromel-alumel K, which traversed the length of the reactor. Argon flowed through the reactor at rates of approximately 2000 cm/min. during temperature measurement to minimize radiation effect and to obtain temperature profile similar to experimental conditions. An Omega Type K Thermocouple Thermometer Model 650, was used for temperature readings inside the reactor, taken at one inch intervals. The The thermocouple was removed from reactor during kinetic experiments to eliminate catalytic effect of thermocouple surfaces and corrosion effect on thermocouple. Figure 1 shows temperature profile

FIGURE-1 TEMPERATURE PROFILE VS REACTOR LENGTH

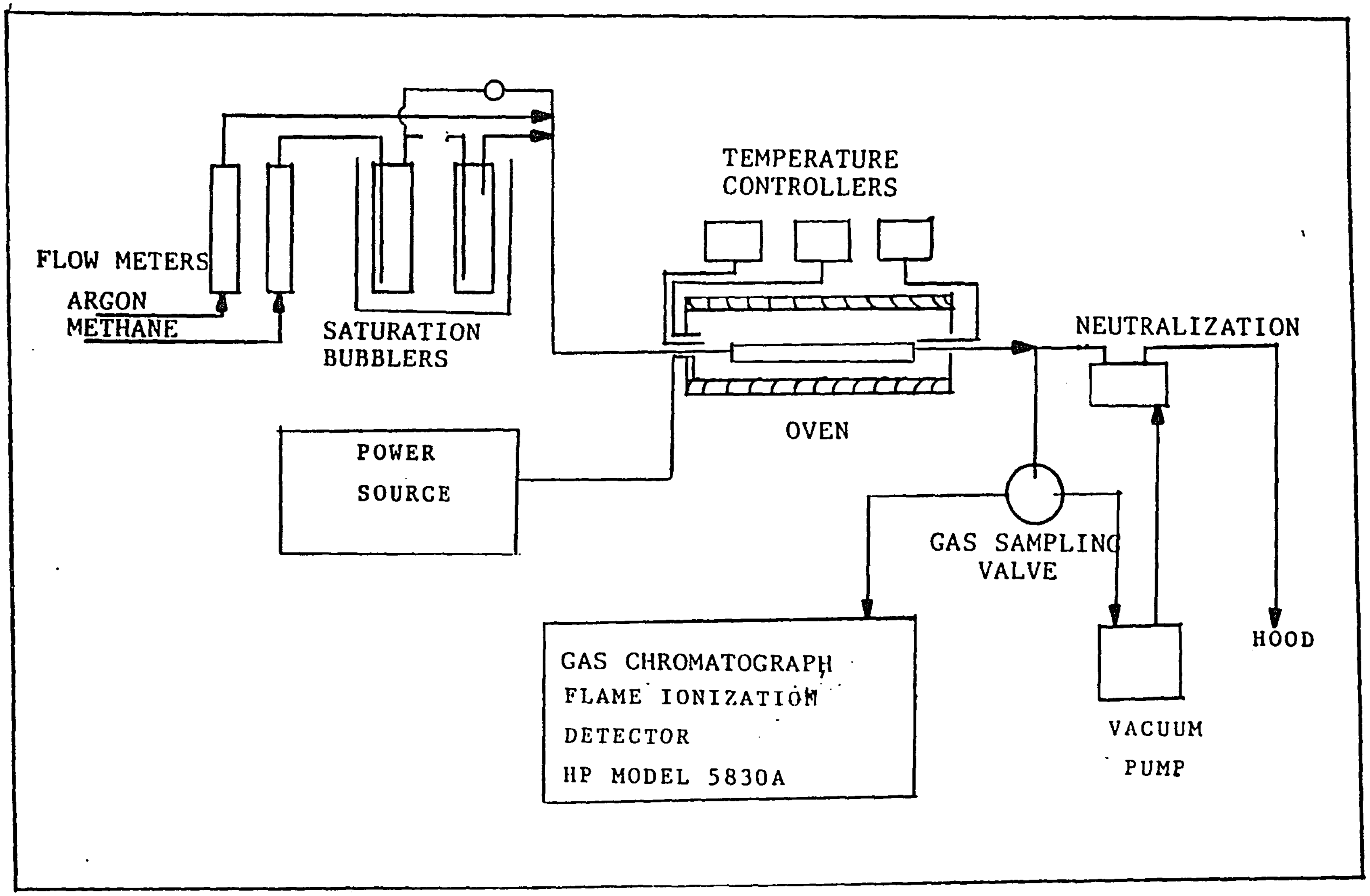


for three different temperatures 750, 785, and 850 ^{o}C illustrating the linear temperature along the reactor length.

Commercial grade methane, was used in this reaction both as carrier and reagent, passed through two sets of bubblers in parallel. Each set consisted of two saturators in series. First set of bubblers contained Aldrich HPLC 99.9 per cent pure methylene chloride. The second one filled with 99.999 per cent pure "Baker Analysed", stabilized, trichloroethylene. Both of the bubblers were kept in zero ^{o}C using an ice-water bath. The schematic diagram of experimental apparatus is shown in Figure 2. Separate saturators were utilized for trichloroethylene and methylene chloride to avoid mixing problems and keep the ratio of reagents, CH2Cl2/CH4 and C2HCl3/CH4, constant throughout the experiment. The apparatus was designed to permit easy isolation of any of two saturators from rest of the system, whenever needed.

The gas from the bubblers was tested for saturation by comparing areas of methylene chloride and trichloroethylene on a chromatogram of reactor bypass or the reactor itself at low temperature (below 400 ^{o}C). Constant peak areas of CH2Cl2 and C2HCl3 for 2 different flow rates exhibited complete saturation of methane. The combined methane and reagent gas flow was diluted by commercial grade argon

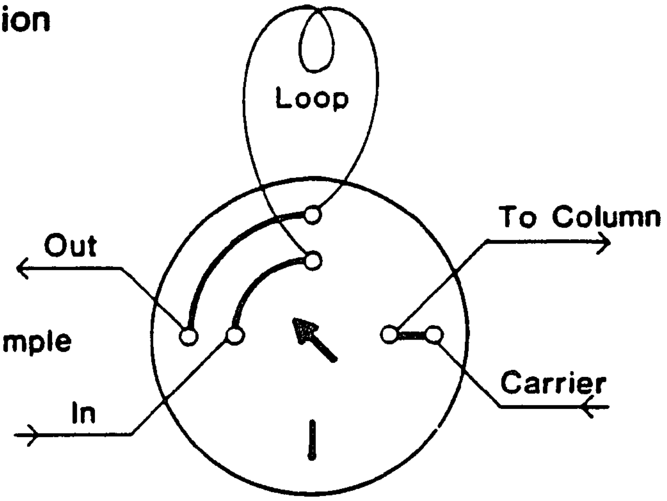
FIGURE-2 EXPERIMENTAL SET-UP



before entering the reactor. A constant molar ratio CH_2Cl_2:CH_4:Ar of 1:4:10 was maintained throughout this study. When mixture of C_2HCl_3 and CH_2Cl_2 was used as reagent, a constant molar ratio C_2HCl_3:CH_2Cl_2:CH_4:Ar of 1:1:40:40 was maintained through the experiments. Total gas flowrates were varied from 22 to 1395 cc/min for CH_2Cl_2/CH_4/Ar runs and 200 to 2500 cc/min for the C_2HCl_3/CH_2Cl_2/CH_4/Ar mixture to achieve varried reaction times. All flow rates were measured by calibrated Fisher - Porter rotameters. The reagent gases were preheated up to 450 ^oC before entering the reactor.

Effluent from the reactor, held at 100 ^oC to prevent condensation, was filtered to remove solid carbon, by passing through a pyrex wool plug. At every reactor temperature and reaction time sample, not more than 2% of reactor effluent by volume, of the gas phase reaction products was directed to a 1.05 cc volume sampling loop. The loop mounted on a six port stainless steel Valco high temperature gas sampling valve, model 6UWT (Fig. 3). Exit of the loop could be directed in two ways : to the nuetralization trap and then the hood by means of a vacuum pump operated at 750 torr pressure, position A Fig. 3; and through a packed column to a Hewlett Packard model 5830A gas chromatograph (GC) for sample analysis, position B Fig. 2. A two meter long, 1/8" O.D., stainless steel tube filled

Load Position



Inject Position

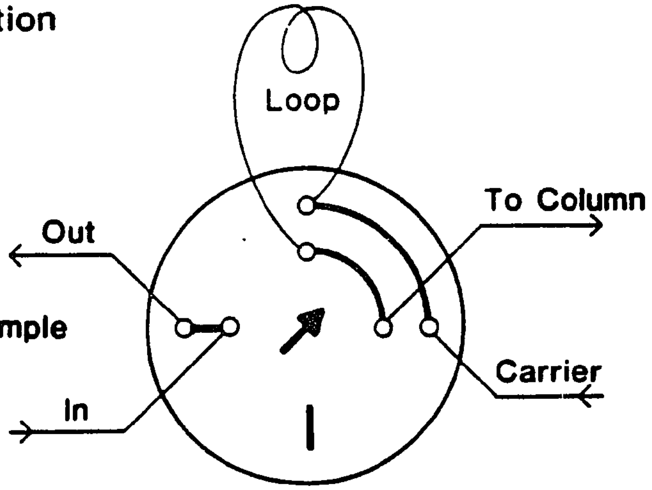


FIGURE-3 SAMPLING VALVE

Valve viewed from handle.

with Supelco Porapak Q 50/80 mesh column packing was used to separate sample species. The packing is suggested for separation of hydrocarbons and light chlorocarbons [38]. The column oven was programmed to hold at 90 °C for 3 minutes, then rise to 220 °C at a rate of 15 C/min. The initial 3 minutes period allowed enough time for distinct separation of light hydrocarbons. Qualitative analysis of reactor products was further performed by use of a Kratos MS-25 magnetic sector GC/Mass spectrometer using 25 CC batch samples collected at the reactor exit and a 30 meter 0.22 mm ID capillary column OV-101-0.1 nm thick.

The Hewlett Packard GC was equipped with a flame ionization detector (FID) and controlled by a HP 18850C programmable terminal. The terminal functioned as plotter and integrator. The FID operated at 30 CC/min hydrogen and 300 CC/min air. Nitrogen at a flowrate of 30 CC/min was used as carrier gas. Response factors for this FID (identified flows) was checked by Tsao [27] and data are shown in Table-I. The results for C_1 chlorocarbons are close to one and for C_2 compounds about 2, in good agreement with general FID principals [47]. The FID flame tip was cleaned using a solution made of 50% acetone and 50% methanol. This helped removing deposits on the jet which in turn eliminated random spiking occurred on baseline. 98.7 % of the gases exit from the reactor merged with vacuum pump exhuast and passed through a sodium-bicarbonate trap before being released into fume hood.

A heated bypass line allowed sampling of inlet reagents for determination of initial concentrations. Reproducibility of initial areas were proved for 2 consecutive samples at different flowrates before each set of runs. The integrator was programmed to reject areas less than 0.1% of this value.

Hydrogen chloride product was measured by passing the effluent of reactor through a known volume of standardized sodium hydroxide solution for a specific time period. Titration provided the amount of HCl formed at the relevant residence time and temperature of reaction.

TABLE - I

COMPOUND	RESPONSE FACTOR
CH_2Cl_2	1.
$CHCl_3$	1.05
CCl_4	1.10
C_2HCl_3	2.27
C_2Cl_4	2.15
$C_2H_2Cl_2$ (cis)	1.90
$C_2H_2Cl_2$ (trans)	1.95
$C_2H_4Cl_2$	2.30

V. RESULTS AND DISCUSSION

A. METHYLENE CHLORIDE PLUS METHANE

Methylene chloride decomposition reactions were studied in a methane and argon atmosphere, with both in excess (1:4:10 ratio, respectively) using tubular reactors of diameters 4, 10.5, 16 mm ID and 45 cm length. Reactions were carried out at temperatures of 729 to 952 ^oC and atmospheric pressure. Preliminary test runs of methane and chloroform with no argon present, produced large (intolerable) amount of solid carbon in the reactor. Therefore, when decided to study reaction of methylene chloride and methane, argon was added as diluent to limit carbon (S) formation inside the reactor. This reduced carbon deposit to a great extent. Table-II summarizes different number of runs performed for data collection at each temperature and reactor diameter.

Figure 4 shows decay plots of methylene chloride vs time for temperatures 785, 802, 852 ^oC, in the 10.5 mm ID reactor. It is apparent from this figure that a conversion of 20%, 55%, and 90% in about 1 second residence time is obtained at the respective temperatures. In addition, Fig. 4 reveals that conversion rate increases with time for higher reactor temperatures.

Methylene chloride conversion in a methane/argon

FIGURE-4 DECAY OF METHYLENE CHLORIDE VS TIME FOR 10.5 mm ID REACTOR

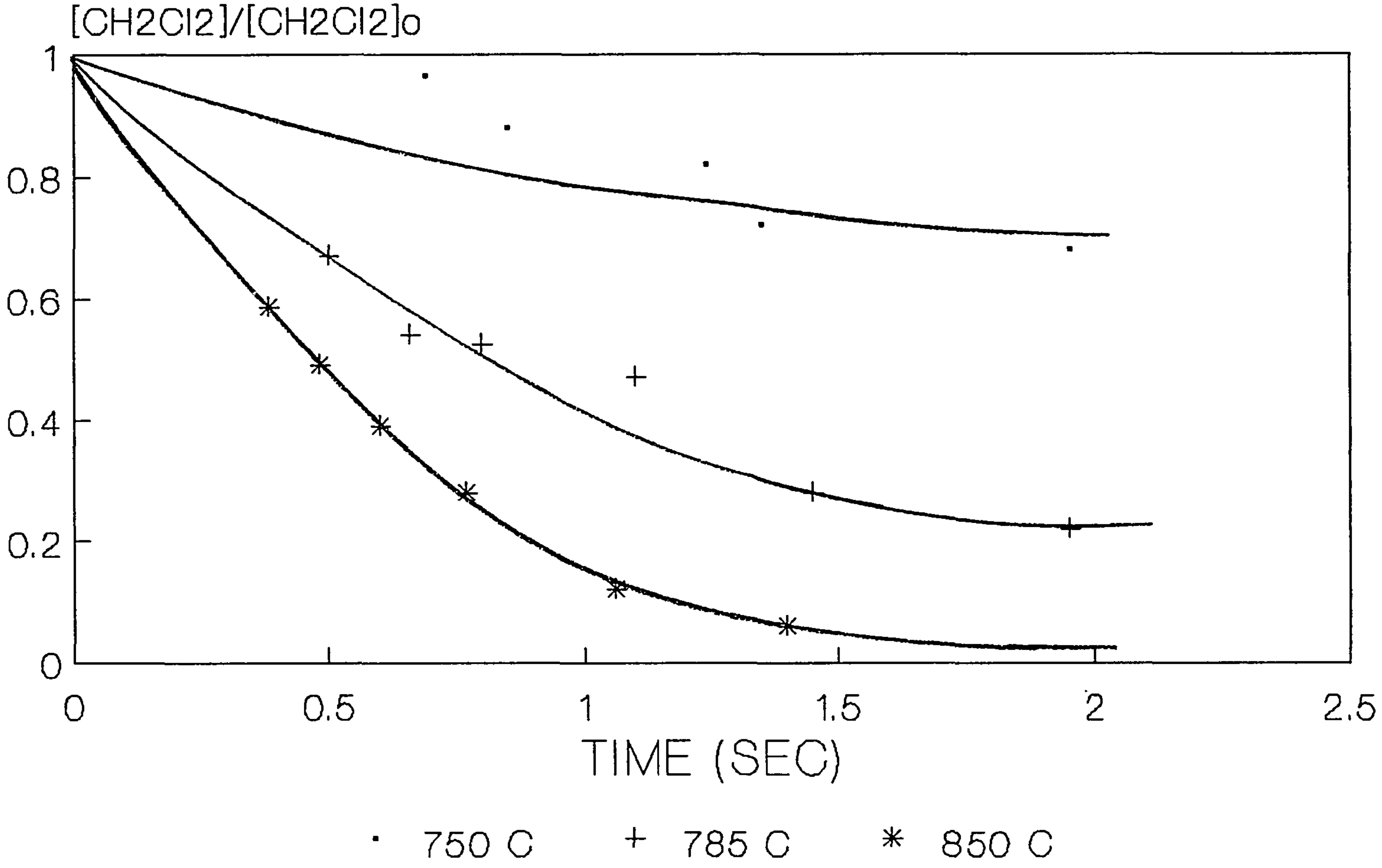


Table II- Summary of Different Runs
CH2Cl2/CH4

No.	Reactor Dia. (mm)	Temperature (K)	Range of Residence Time(sec)	No. of Residence Times
1	4	1002	0.180-1.30	9
2	4	1031	0.120-1.25	9
3	4	1056	o.118-2.22	10
4	4	1072	0.092-2.17	11
5	4	1125	0.070-1.15	10
6	4	1225	0.100-0.34	4
7	10.5	1058	0.500-4.44	7
8	10.5	1075	0.400-2.65	8
9	10.5	1095	0.350-2.61	9
10	10.5	1126	0.380-1.35	6
11	10.5	1203	0.300-1.33	3
12	16	1013	0.400-6.60	11
13	16	1053	0.380-3.34	8
14	16	1102	0.300-1.77	9
15	16	1225	0.260-1.20	4

atmosphere, at a concentration ratio for CH2Cl2:CH4:Ar of 1:4:10, showed linear decay plots (plots of LN $[C]/[C]_o$ VS time) indicating a psuedo first order reaction applies. Figure 5 illustrates several typical first order decay plots for temperatures of 785, 802, 822, and 852 ^{o}C in the 10.5 mm ID reactor, showing the good linearity obtained. This is in good agreement with reports on dehydrochlorination of other chlorocarbons [12-15, 25-27]. The plots in Fig. 5 do not pass zero because of error in calculating reaction time. The error is mainly due to the uniform temperature assumption throughout the reactor length which is not practically feasible. Table-III lists global (overall) rate constants, diameters at temperature range of 750-850 ^{o}C, obtained from the psuedo first order decay plots. The Arrhenius parameters (frequency factor, A, and activation energy, E) in Table-III were obtained by plotting global rate constants vs 1/T for different reactor size, as shown in Fig.-6. Arrhenius form of global rate constants for different reactors can be shown as follow:

$$k'_{4\ mm} = 4.35\ E08 * \exp\ [-42000/(RT)] \qquad sec^{-1}$$

$$k'_{10.5\ mm} = 6.7\ E09 * \exp\ [-48500/(RT)] \qquad sec^{-1}$$

$$k'_{16\ mm} = 1.72\ E10 * \exp\ [-50600/(RT)] \qquad sec^{-1}$$

FIGURE-5 FIRST ORDER DECAY PLOT FOR CH2Cl2/CH4/Ar 10.5 mm ID REACTOR

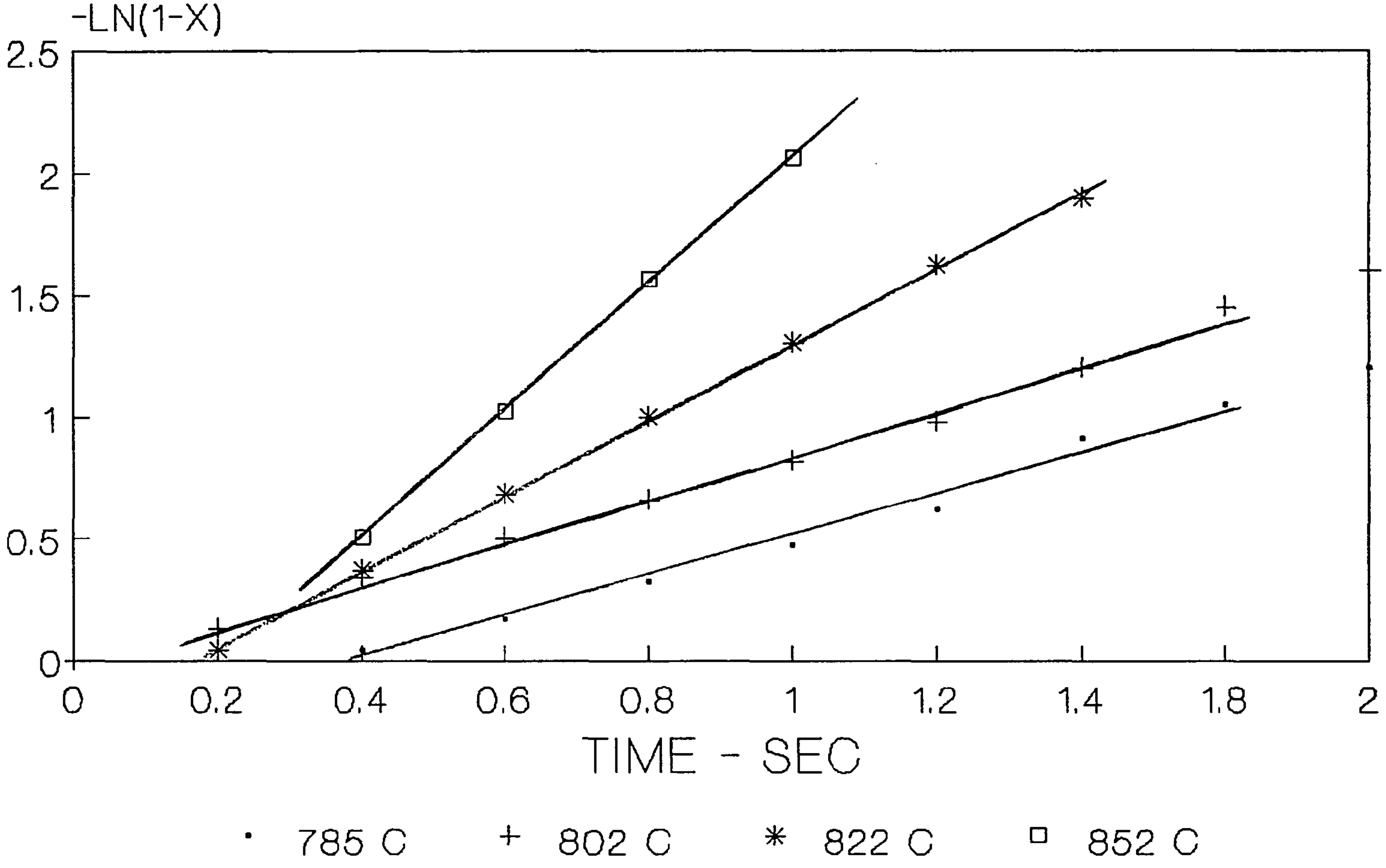


TABLE III - RATE CONSTANTS FOR CH2CL2 + CH4 + Ar
[CH2Cl2]:[CH4]:[Ar]   1:4:10
P = 1 atm

ID (mm)	4	10.5	16		
T (K)		k'		k_b	k_w
753	0.41	0.27	0.26	0.36	0.07
782	0.90	0.62	0.58	0.48	0.09
801	1.25	1.09	0.95	0.78	0.10
822	1.9	1.32	1.24	1.02	0.18
852	3.22	2.47	2.72	2.35	0.26
E	42.0	48.5	50.6	44.8	35.2
A	4.35E08	6.7E09	1.7E10	1.06E09	1.8E06

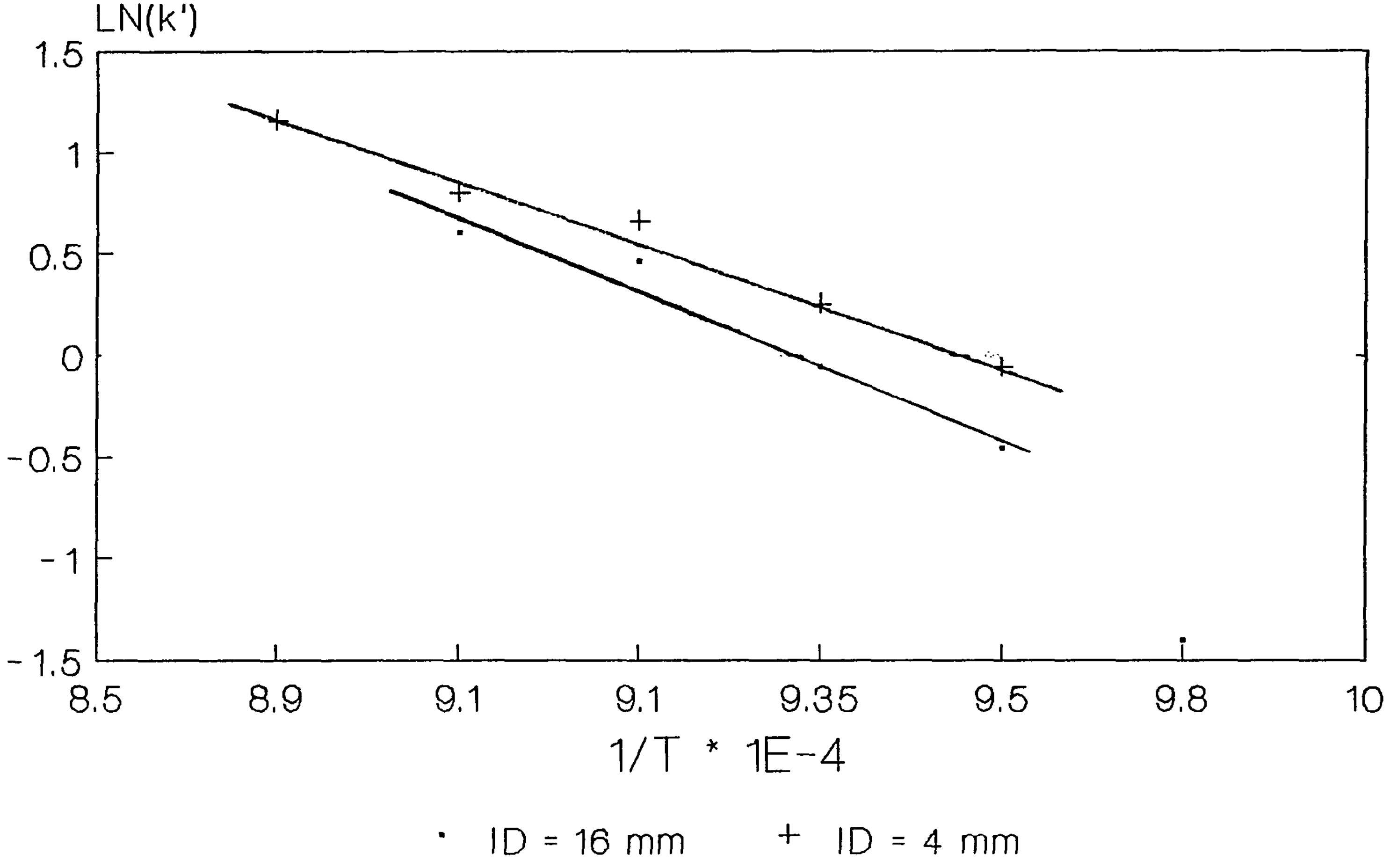
Rate constants and A factors in (1/sec.)
Activation energies in Kcal/mole.
k', for loss of CH2Cl2 in 4, 10.5, and 16 mm ID reactor

Where T is temperature in ^{o}K and R is gas constant in cal/(mol-^{o}K). Previous studies have demonstrated that under isothermal condition, change in S/V ratio often directly affects the overall rate constants for these reactions [12-15, 25-27], because of wall reactions.

Table IV illustrates decomposition of CH2Cl2 in CH4 + Ar atmosphere for few selected residence times.

It is apparent from the data listed in Table -IV that for a given reactor diameter and residence time the

FIGURE-6 ARRHENIUS PLOT FOR 4 mm ID AND 16 mm ID REACTORS



conversion rate of CH2Cl2 increases with temperature. The same data (Table-IV) reveal that at a given reaction time and temperature conversion of methylene chloride decreases by surface to volume ratio reduction of the reactor. Most of decrease is from 4 to 10.5 mm ID reactor with very little or no decrease after this, which is very similar to data available in literature [14]. This reveals that S/V ratio is not important for reactor diameter greater than 10.5 mm.

Table-IV TEMPERATURE, DIAMETER EFFECT ON CONVERSION
CH2Cl2 / CH4

	t = 1 (sec.)		
Dia / Temp (mm)/ (C)	783	822	855
	{1-[CH2Cl2]/[CH2Cl2]$_0$}X100		
4	61	79	95
10.5	35	75	85
16	38	72	NA
	t = 0.5 (sec)		
4	41	57	75
10.5	11	42	60
16	14	38	NA

Homogeneous and heterogeneous rate constants, k_b, and k_w, listed in Table-III were obtained incorporating

Kaufman's solution for a plug flow reactor [49]; bulk and wall reactions are assumed independent and parallel [50]; and reaction follows pseudo first order decay :

$$k' = k_b + (2/R) * k_w \qquad R = \text{Reactor Radius (cm)}$$

k_b and k_w were decoupled by plotting the observed rate constant, k', versus 2/R, as shown in Fig-7.

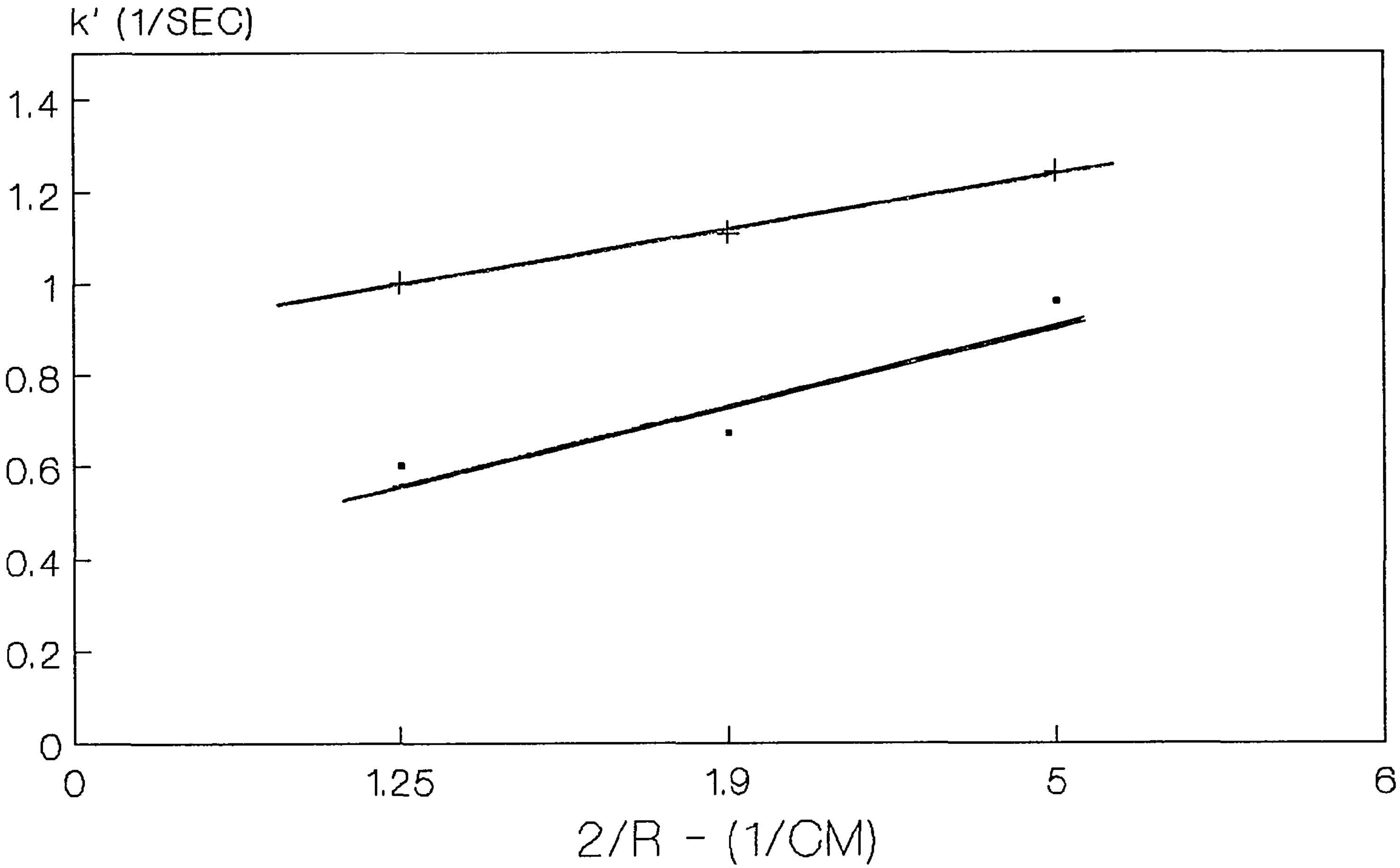
The Arrhenius form of homogeneuous and heterogeneuous rate constants can be written as follow :

$$k_b = 1.06 * 10^9 * \exp[-44800/(RT)]$$

$$k_w = 1.85 * 10^6 * \exp[-35200/(RT)]$$

It is concluded from the global bulk and wall rate constants listed in Table-III that wall reactions were less important than homogeneous ones in this system. The dominance of homogeneous reaction is also seen to increase for higher temperatures and larger diameters. Comparison of test runs between a clean wall (new) reactor and an aged (used) one revealed very little (<5%) difference in conversion of CH2Cl2 for the 10.5 mm ID reactor. New reactors were operated for several hours under low flowrate of reactants prior to data collection for consistency in results.

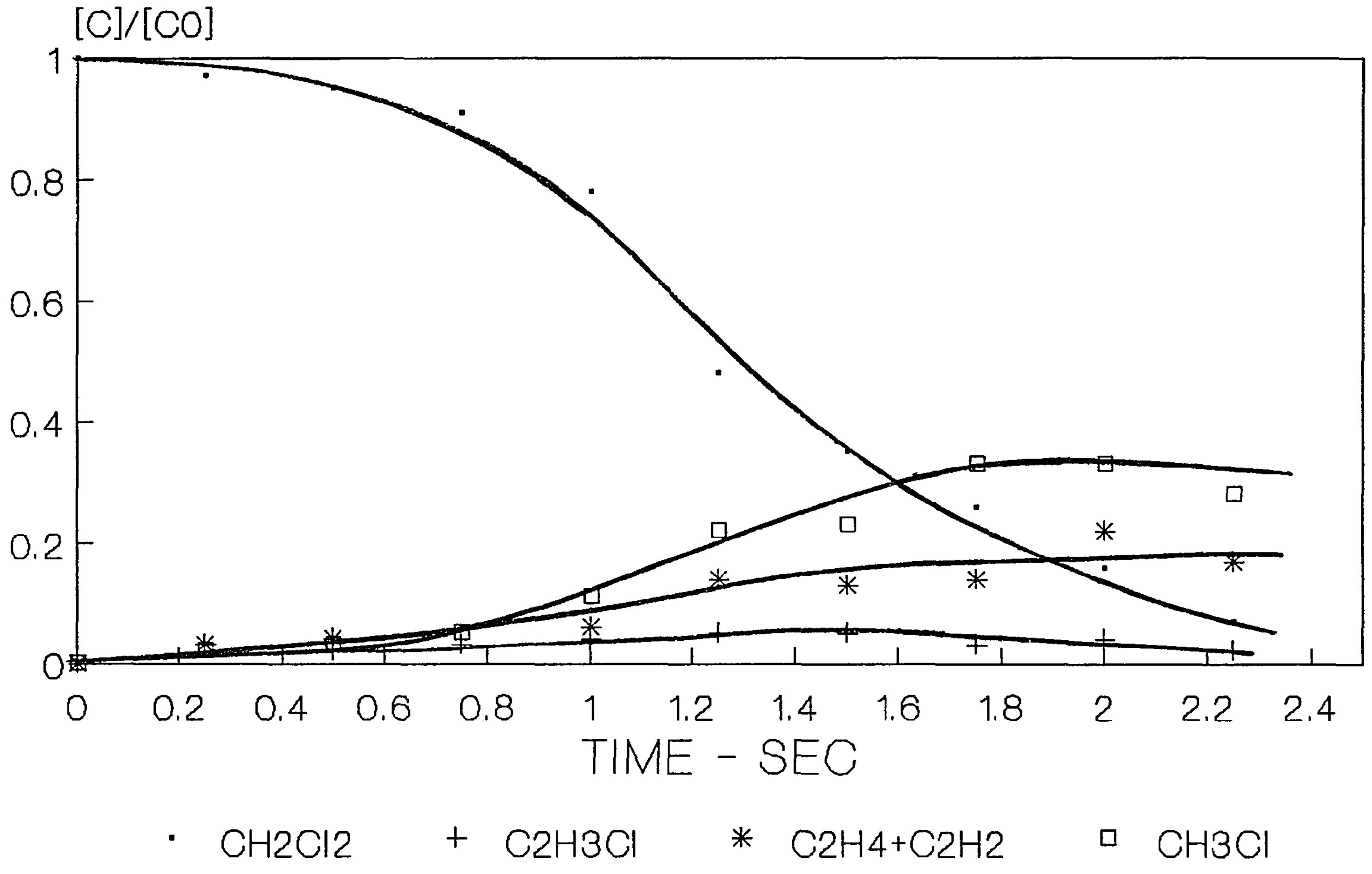
FIGURE-7 GLOBAL RATE CONSTANT VS 2/R



Wall reactions are reported to be possible source of solid carbon formation [48, 56]. Addition of argon in excess amount (250% of methane present by volume) reduced carbon solid deposition on reactor wall to less than observable limit. The presence of inert gas (Ar) enhances stabilization of lighter hydrocarbons and chlorocarbons (C_2s and C_3s) by "caging" these excited species and reducing number of collisions between them. This in addition limits combination reaction (radical-radical or radical-molecule) of small (C_2s and C_3) excited species and may be the reason for quenching formation of higher molecular weight (cyclic) hydrocarbons and chlorocarbons. The latters (benzene, chlorobenzene, cyclopentadiene, etc.) are more stable at higher temperatures due to their (900-1000 ^{o}C) thermochemical properties. The reduction in formation of high molecular weight HC and ClHC due to presence of argon in the reaction system results in limited carbon solid formation. In larger diameter (10.5, 16 mm ID) reactors carbon deposits was only observed at the reactor exit where a sharp change (decrease 150 ^{o}K/Cm) in temperature occured. GC/MS analysis showed that traces of polychlorinated benzene is present in this residue.

The major products observed were C2H4, C2H2, C2H6, CH3Cl, C6H6, and HCl. Figure 8 illustrates product distribution relative to initial CH2Cl2 concentration vs

FIGURE-8 CH2Cl2 DECOMPOSITION IN CH4/Ar AT 1075 K



residence time for 10.5 mm ID reactor at 802 ^{o}C. Methyl chloride is the dominant initial product under above mentioned conditions; concentration of ethylene + acetylene increases with reaction time; and vinyl chloride concentration has a maximum at 1.6 sec. reaction time.

Small amounts of (<1%) CCl4, C2H2Cl2, C2HCl3, C2Cl4 were also present in the effluent product at lower reaction temperatures (below 850 ^{o}C) . Traces of heavy chlorinated compounds (hexachlorobenzene) were detected in the solid deposits at higher (950 ^{o}C) temperatures. All methylene chloride (99.9%) decomposed at 952 ^{o}C in less than 1 sec residence time for all reactor diameters (4, 10.5, 16 mm ID). Figure 9 illustrates chromatogram of methylene chloride decomposition in methane + argon atmosphere for 4 mm ID reactor, 952 ^{o}C, and 0.34 second reaction time. The major products are identified as acetylene + ethylene, benzene, toluene, and chloromethane.

Figure 10 shows concentration of products: acetylene + ethylene, methyl chloride, and vinyl chloride, as well as methylene chloride loss relative to initial CH2Cl2 concentration vs temperature for 10.5 mm ID reactor and resident time range of 0.88 to 0.92 sec. It is apparent from this figure that chloromethane concentration reaches a maximum at 830 ^{o}C. No chlorinated compound was detected in measurable quantities above 1050 ^{o}C.

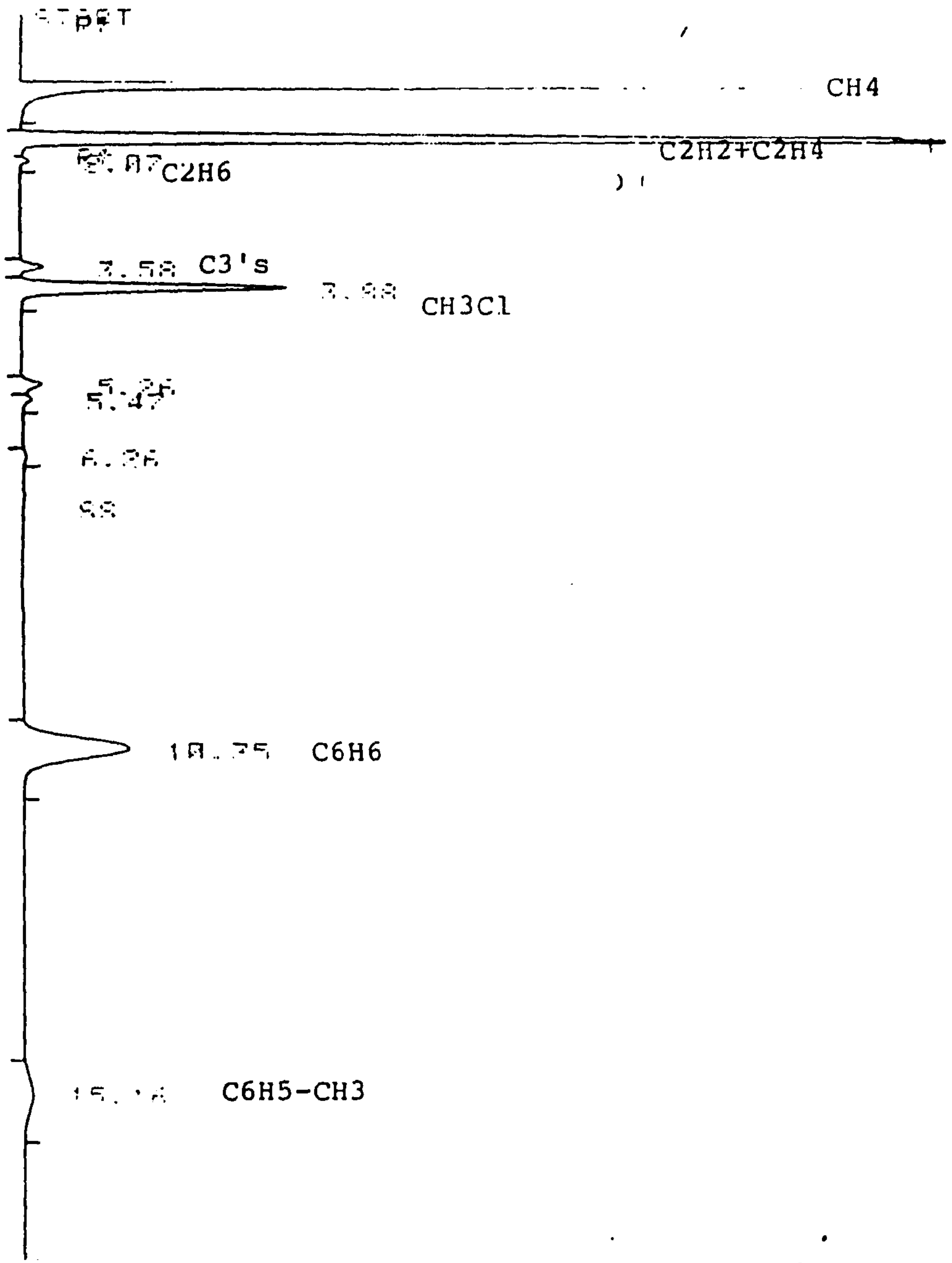
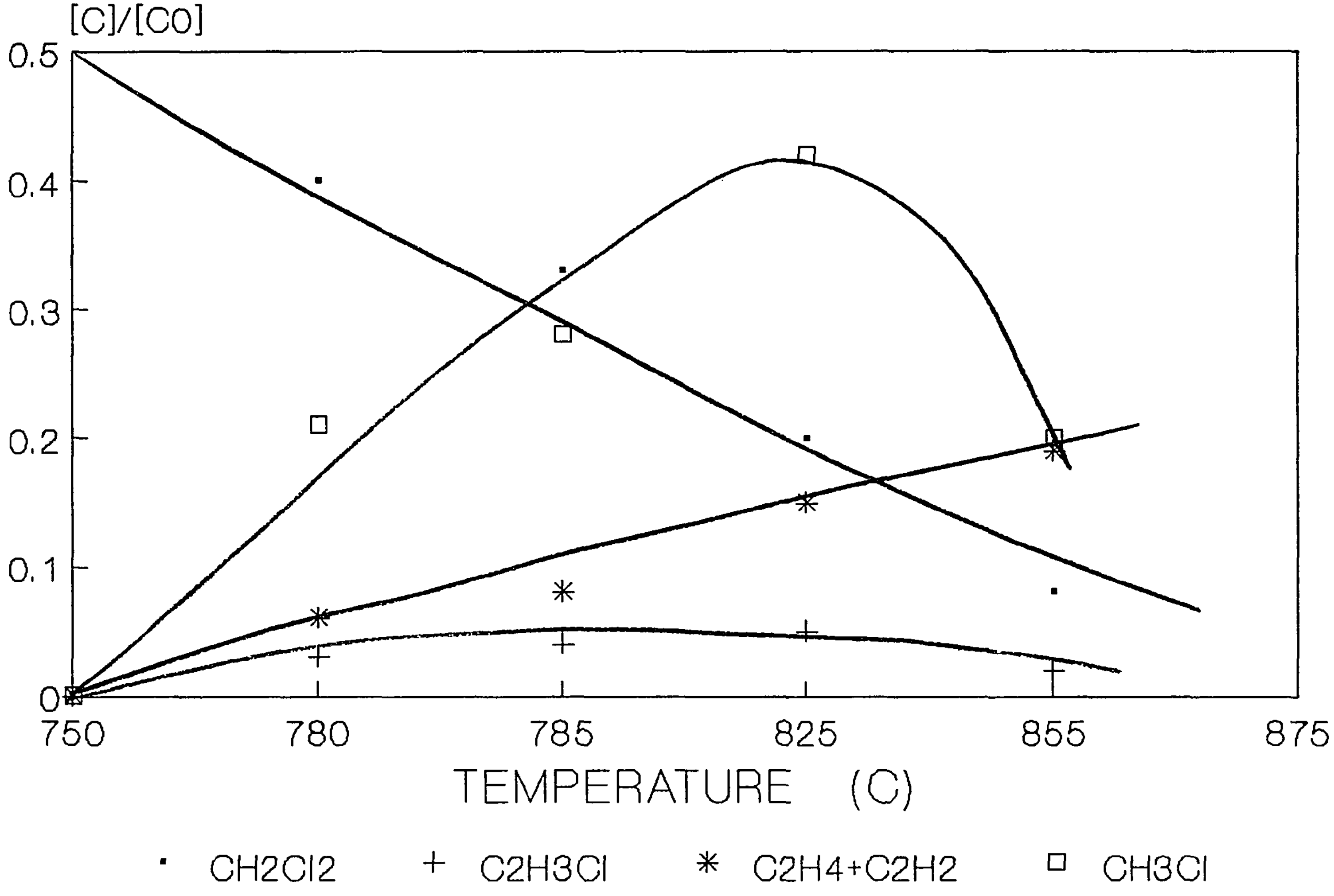


FIGURE-9 CHROMATOGRAM OF CH2Cl2/CH4
1225 K 4 mm ID

FIGURE-10 CONCENTRATION VS TEMPERATURE



B. TRICHLOROETHYLENE, METHYLENE CHLORIDE AND METHANE

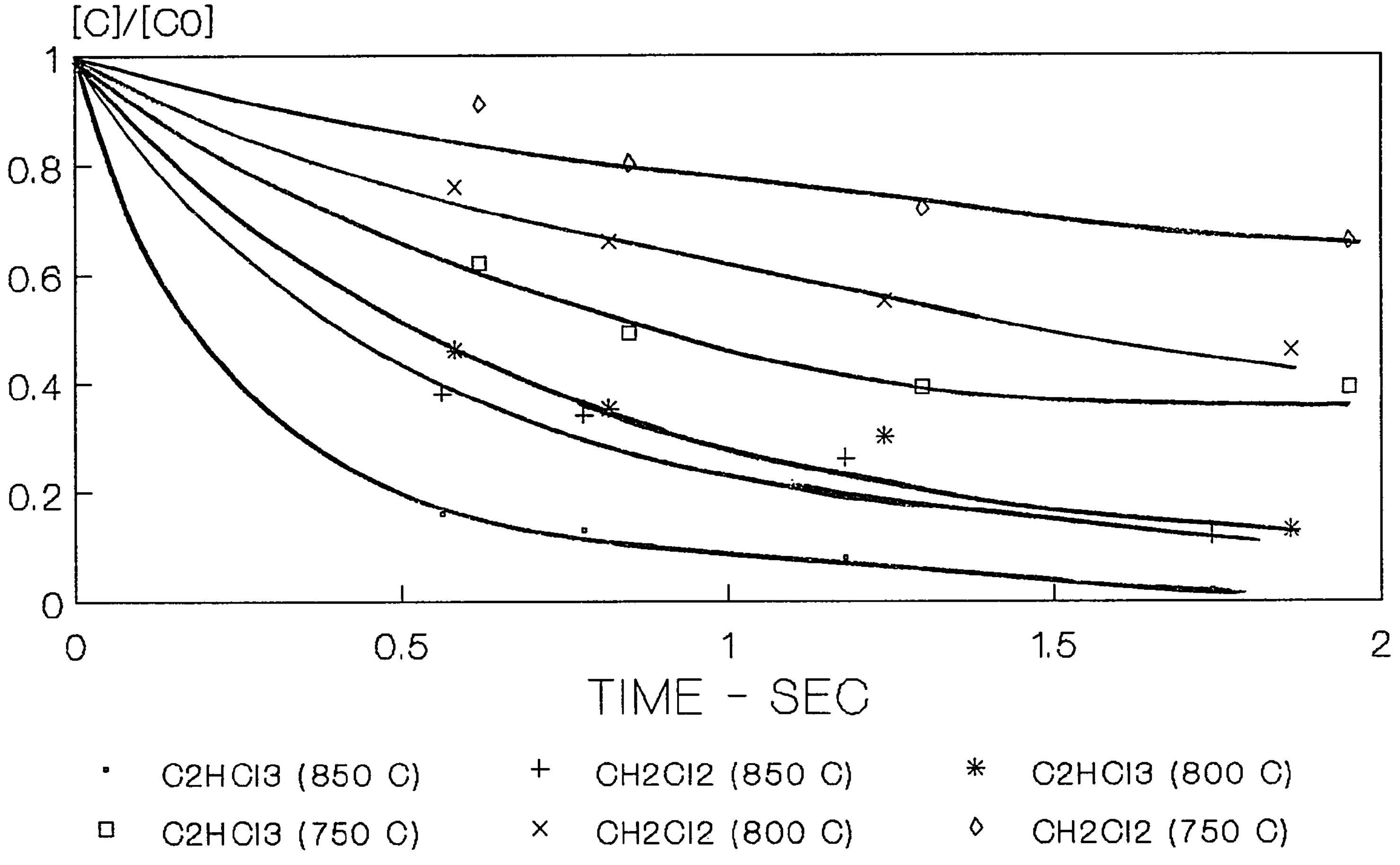
A mixture of trichloroethylene and methylene chloride in an atmosphere of excess methane and argon was studied as a second phase of this research in quartz tubular reactors of 4, 10.5, 16 mm ID and 45 cm long. Two separate streams of methane saturated with C2HCl3 and CH2Cl2 from separate parallel bubbler systems, both kept at 0 ^{o}C using an ice bath, were merged and mixed with argon before the preheat zone of the reactor. Separate saturators were used to keep the molar ratio of reagents constant. Argon was added as diluent to limit reaction and keep solid carbon formation in the reactor as low as possible. There was no observable carbon coating on the walls of 10.5 and 16 mm diameter reactors except for a small amount at the exit where a sharp reduction in temperature occured (150 ^{o}K/Cm).

A summary of runs performed for this experiment is shown in Table V and covers the temperature range of 1025 to 1275 ^{o}K. Figure 11 compares decay of C2HCl3 and CH2Cl2 at 750, 800, 850 ^{o}C temperatures in the 16 mm ID reactor. A higher rate of trichloroethylene decomposition relative to methylene chloride is apparent from the decay plot. Similar relative rates of decomposition were observed for reactors of 4mm and 10.5 mm ID. The decomposition of trichloroethylene and methylene chloride mixture in methane + argon atmosphere with molar ratios C2HCl3:CH4:Ar of

TABLE - V SUMMARY OF DIFFERENT RUNS
$C_2HCl_3 + CH_2Cl_2/CH_4$

No.	Reactor Dia. (cm)	Temperature (K)	Range of Residence Time (Sec)	No. of Residence Times
1	4	1073	0.04 - 0.47	7
2	4	1118	0.05 - 0.45	7
3	4	1158	0.05 - 0.44	7
4	10.5	1023	0.27 - 3.40	8
5	10.5	1065	0.26 - 3.30	8
6	10.5	1118	0.25 - 3.10	9
7	10.5	1172	0.24 - 1.18	7
8	10.5	1218	0.23 - 1.14	4
9	10.5	1278	0.46 - 1.0	2
10	16	1023	0.63 - 3.14	8
11	16	1073	0.60 - 3.03	8
12	16	1125	0.57 - 2.86	8
13	16	1171	0.55 - 2.75	5

**FIGURE-11 DECAY PLOT OF C2HCl3+CH2Cl2
IN CH4/Ar 16 mm ID REACTOR**



1:40:40 and CH2Cl2:CH4:Ar of 1:40:40 demonstrated linearity on a decay plot, indicating psuedo- first-order reaction conditions hold. Figures 12 and 13 show first order decay plots at temperatures 790, 850, 900 °C in the 10.5 mm ID reactor, C2HCl3 and CH2Cl2, respectively. The decay plots in Figures 12 and 13 do not pass zero because of experimental error in residence time measurement. This error, for the most part, is due to the non-uniformity of reactor temperature (±5 °C). The global (overall) rate constants, k',for decomposition of C2HCl3 and CH2Cl2 in 4, 10.5, and 16 mm ID are tabulated in Tables VI and VII. The activation energies and A factors were obtained from Arrhenius plots. Following overall rate equations were found to fit the experimental data obtained for methylene chloride and trichloroethylene loss in C2HCl3/CH2Cl2/CH4/Ar system:

Methylene chloride:

$$k = 8.11 * 10^{9} * \mathrm{Exp}(-44.85/RT) \qquad (1/\mathrm{sec.})$$

Trichloroethylene :

$$k = 1.13 * 10^{5} * \mathrm{Exp}(-30.67/RT) \qquad (1/\mathrm{ses.})$$

Acetylene, ethylene, benzene, chloromethane, 1,3-dichloropropene and HCl were observed to be major products of methane reaction with a mixture of C2HCl3 + CH2Cl2 in a CH4/Ar atmosphere, at temperatures above 750 °C. Benzene

FIGURE-12 FIRST ORDER DECAY PLOT FOR C2HCl3 IN C2HCl3/CH2Cl2/CH4/Ar SYSTEM

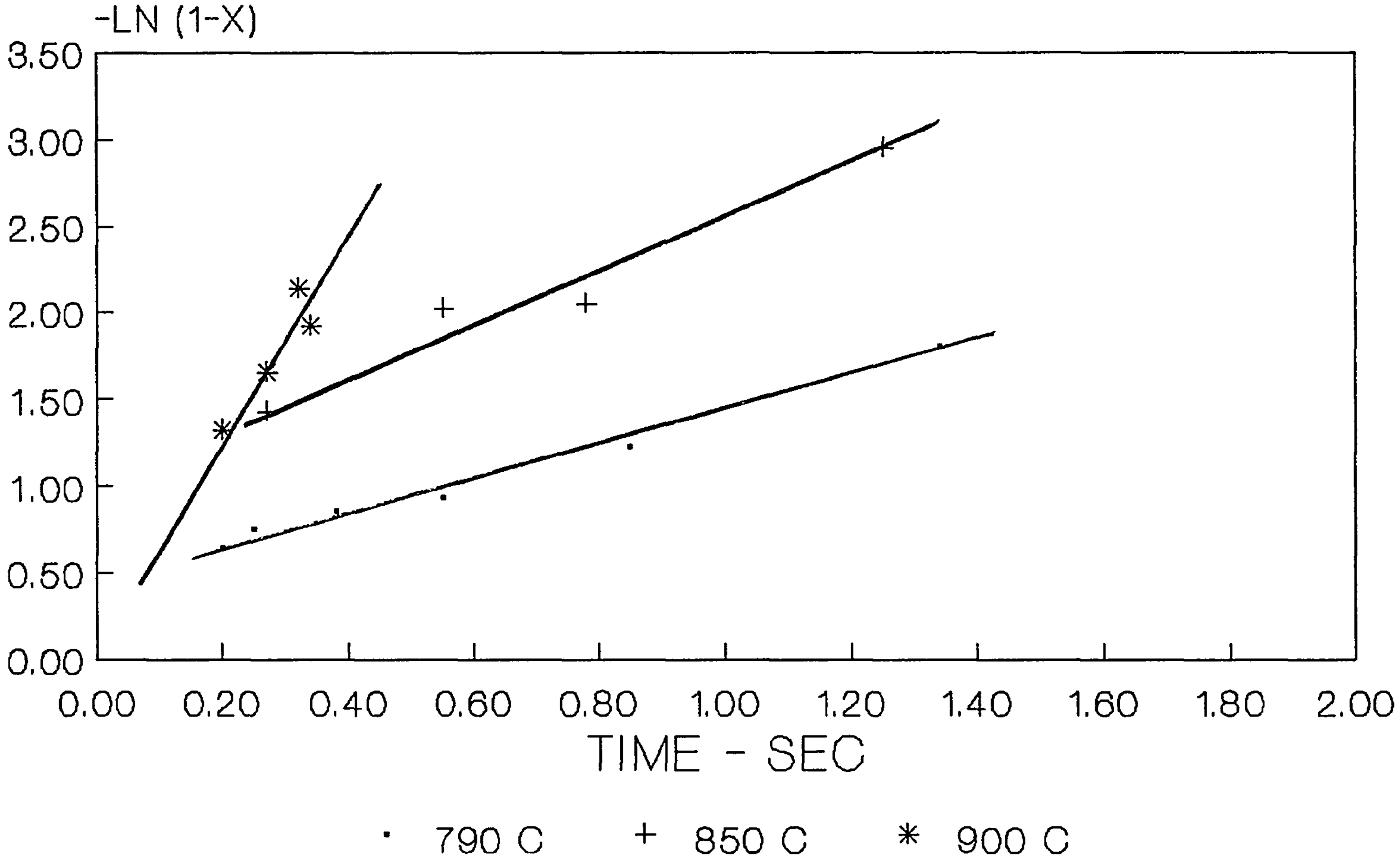


FIGURE-13 FIRST ORDER DECAY PLOT FOR CH2Cl2 IN C2HCl3/CH2Cl2/CH4/Ar SYSTEM

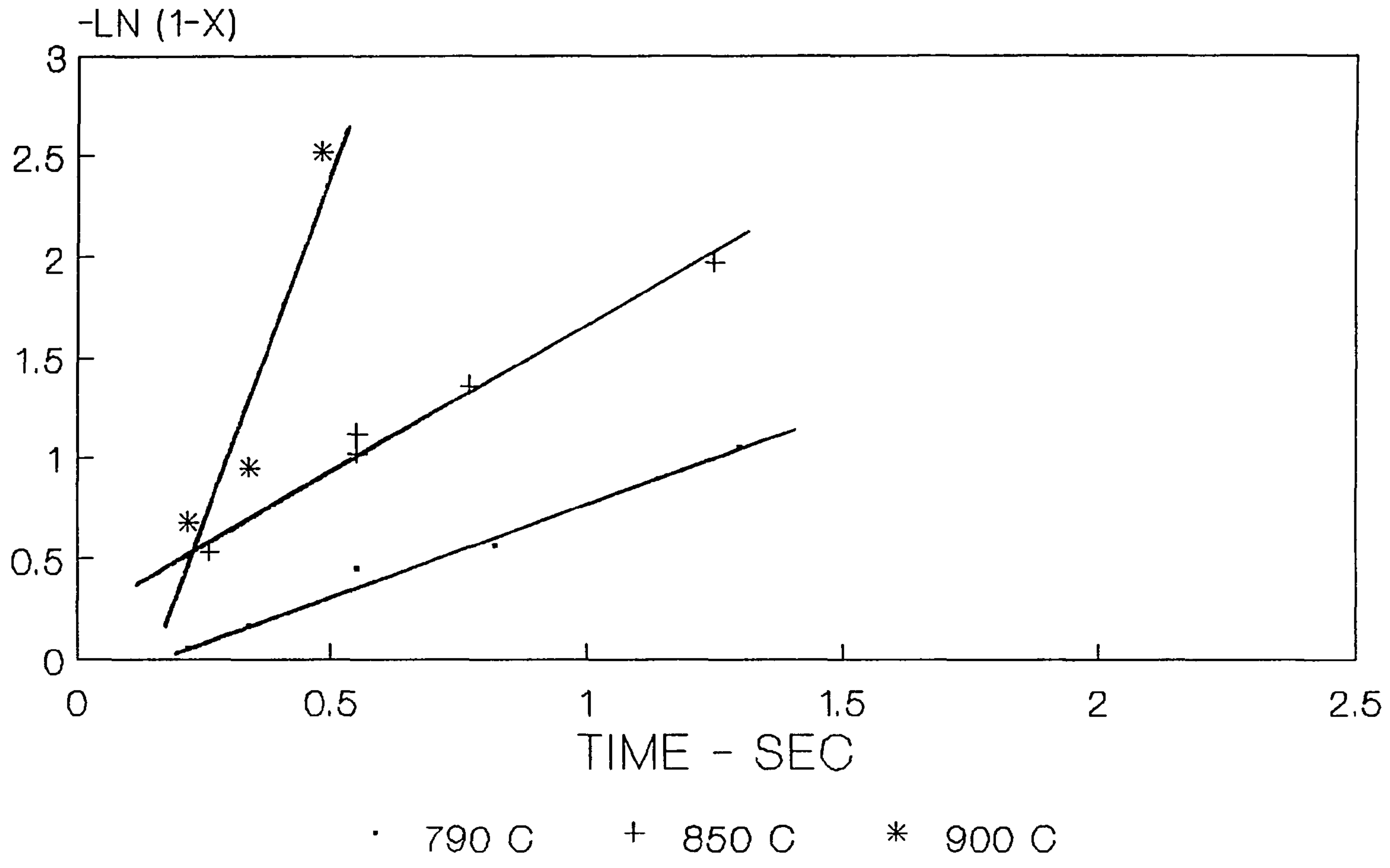


TABLE VI - RATE CONSTANTS FOR CH2Cl2 IN C2HCl3/CH2Cl2/CH4/Ar
[C2HCl3]:[CH2Cl2]:[CH4]:[Ar] 1:1:40:40
P = 1 atm

ID (mm)	4	10.5	16
T (K)		k'	
750	-	-	0.14
795	1.72	0.92	0.32
850	3.3	1.36	0.98
885	7.	-	-
899	-	7.7	-
E	44.8	40.8	44.0
A	1.97E09	1.7E08	9.0E07

Rate constants and A factors in (1/sec.)
Activation energies in Kcal/mole.

formation increases with temperature; toluene, chlorobenzene, and cyclopentadiene, were detected in smaller (<1%) amounts. More than 99% of the parent chlorocarbons were decomposed at 945 ^{o}C, 1.14 second residence time in 10.5 mm ID reactor, as shown in Figure 14. The products identified at 99% conversion of C2HCl3 + CH2Cl2, reactants, include acetylene and ethylene, C_3s, chloromethane, C_4s,

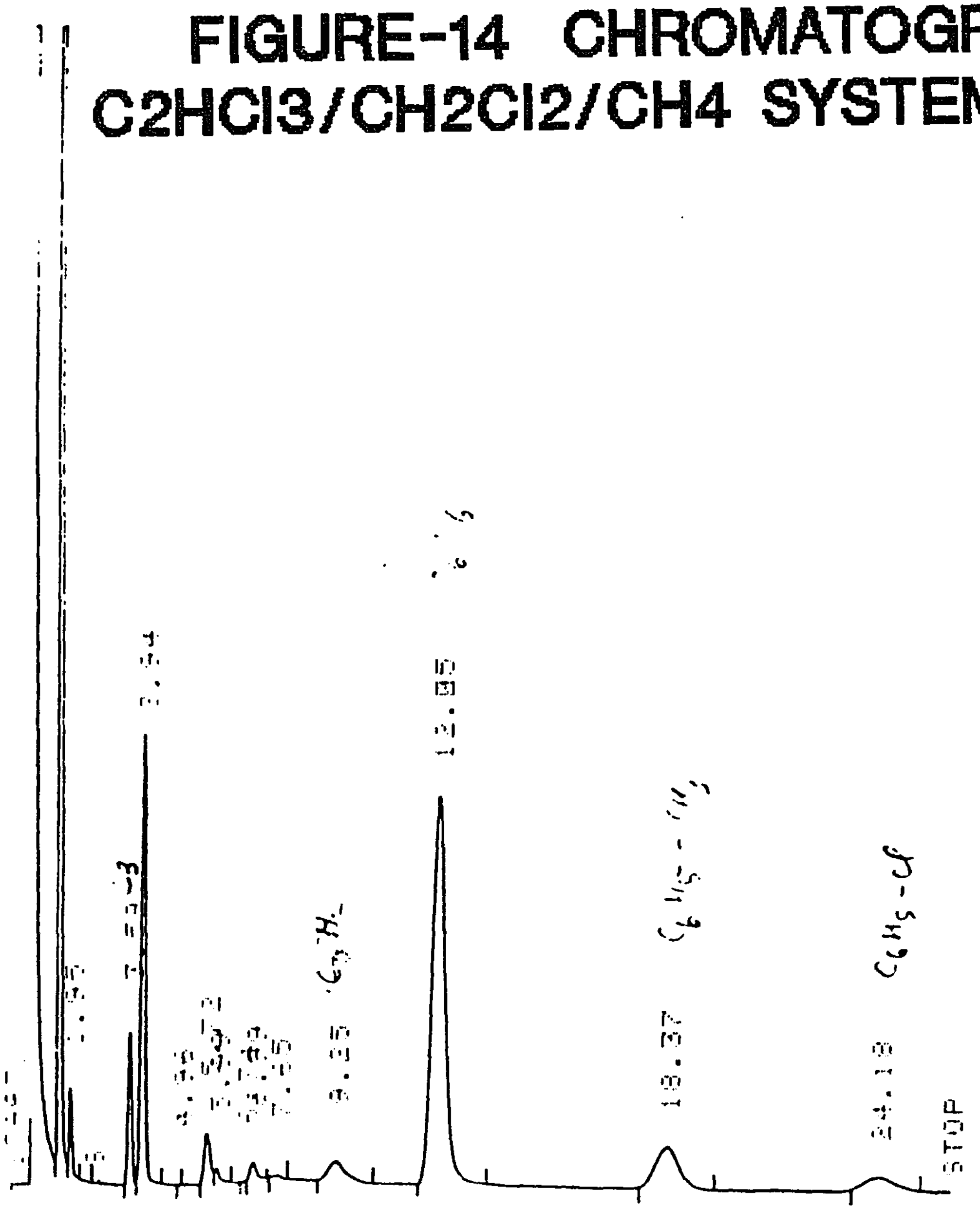


FIGURE-14 CHROMATOGRAM OF C2HCl3/CH2Cl2/CH4 SYSTEM AT 1218 K

TABLE VII- RATE CONSTANTS FOR C2HCl3 IN C2HCl3/CH2Cl2/CH4/Ar
[C2HCl3]:[CH2Cl2]:[CH4]:[Ar] 1:1:40:40
P = 1 atm

ID (mm)	4	10.5	16
T (K)		k'	
750	-	-	0.31
795	3.04	0.811	0.8
850	5.8	1.47	0.9
885	5.20	-	-
899	-	2.9	-
E	26	32	34
A	1.99E04	2.2E05	9.9E04

Rate constants and A factors in (1/sec.)
Activation energies in Kcal/mole.

cyclopentadiene, benzene, toluene, and chlorobenzene. Figure 15 is a typical chromatogram of 10.5 mm ID reactor at 1005 °C and residence times of one second. It is observed was CH3Cl (<2%). Except for traces of polychlorinated hydrocarbons present in the effluent of reactor under these conditions, all chlorocarbons were decomposed above 1052 °C, 1.2 second residence time.

Figure 16 shows relative concentrations of (relative to sum of the initial [C2HCl3] + [CH2Cl2]) acetylene +

FIGURE-15 CHROMATOGRAM OF C2HCl3/CH2Cl2/CH4 SYSTEM AT 1278 K

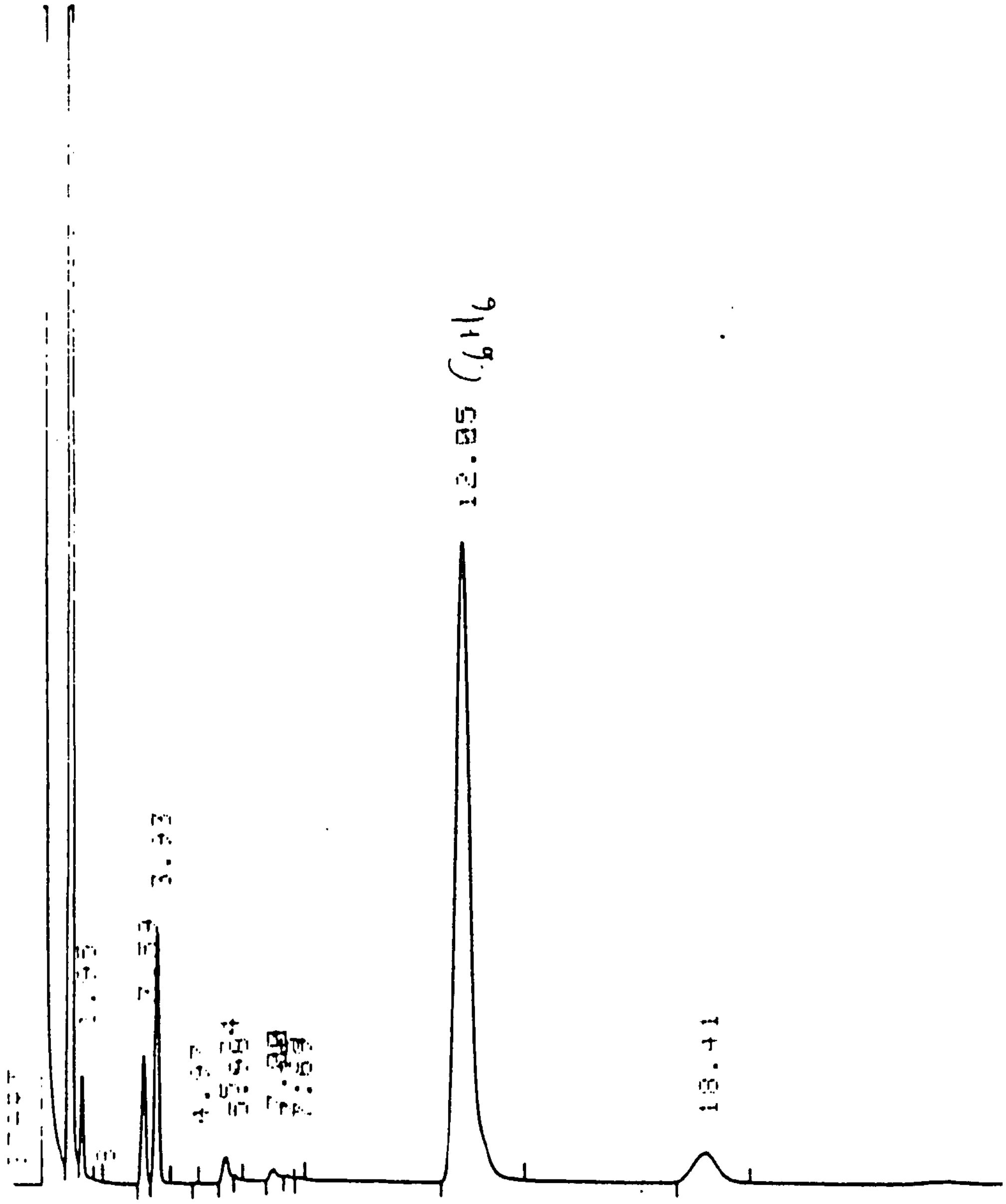
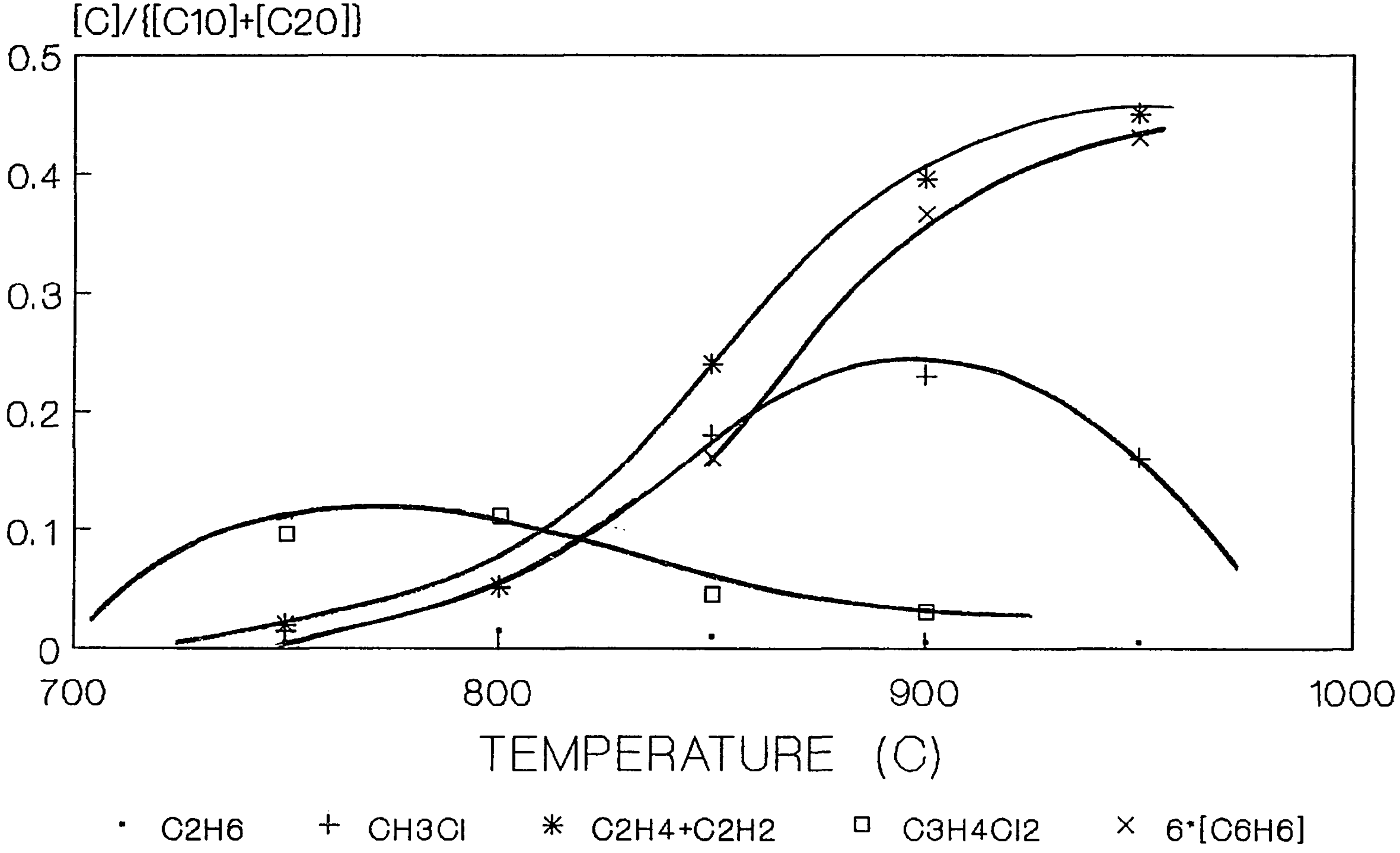


FIGURE-16 PRODUCT DISTRIBUTION
C2HCl3/CH2Cl2/CH4/Ar SYSTEM



ethylene, ethane, benzene, 1,3-dichloropropene and chloromethane, vs temperature. It is observed from this figure that acetylene + ethylene yield increases with temperature rise. Benzene starts to form, in measureable quantities (2.7%) at temperatures above 825 ^{o}C. Chloromethane and 1,3-dichloropropene concentrations show maxima at 900 and 780 ^{o}C respectively. Figure 16 illustrates that ethane remains a minor product relative to acetylene and ethylene and its concentration decreases with temperature increase.

Change in reactor diameter influenced percent conversion at selected residence times. Table-VIII shows percent conversion of C2HCl3 and CH2Cl2 for two reactor diameters (10.5 and 16 mm ID)and temperatures 750, 800, 850, and 900 ^{o}C at 0.5 and 1 sec. residence times. It is observed from the data listed in Table-VIII that the percent conversion of each reactant (C2HCl3, and CH2Cl2), relative to its initial concentration, increases with rise in temperature and reaction time for each reactor diameter at constant residence time and temperature conversion decreases with reduction of surface to volume ratio, as observed in CH2Cl2/CH4/Ar data.

Figures 17a and 17b show chromatograms of 4 and 16 mm ID reactors at 0.450, 1.2 seconds reaction time respectively, and 850 ^{o}C. The comparison of major products

FIGURE-17A C2HCl3/CH2Cl2/CH4 SYSTEM
.45 SEC 1123 K 4 mm ID

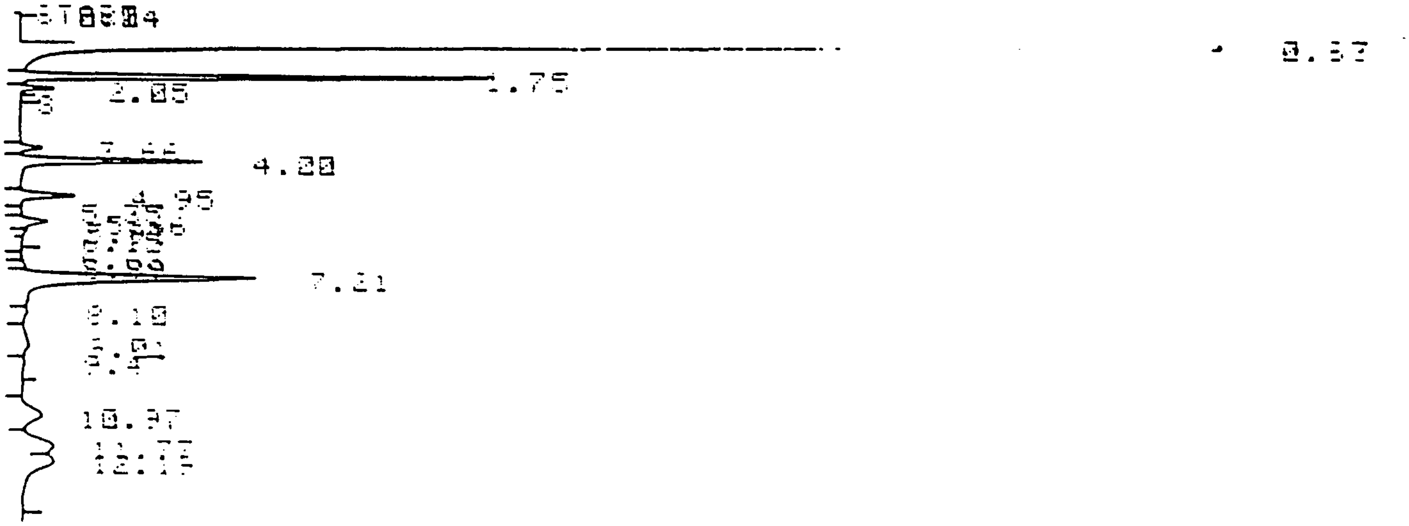


FIGURE-17B C2HCl3/CH2Cl2/CH4 SYSTEM
1.2 SEC 1123 K 1.6 mm ID

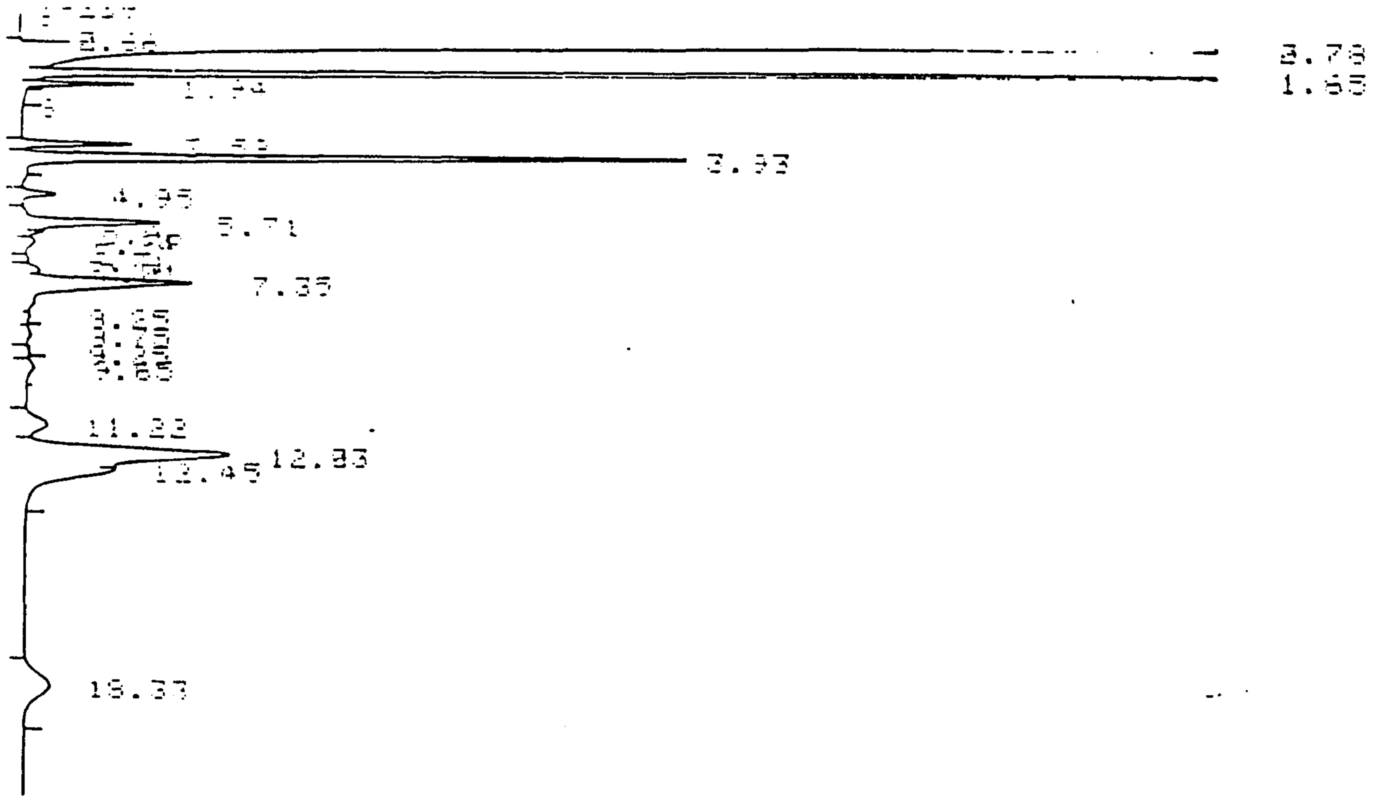


TABLE VIII-TEMPERATURE, DIAMETER EFFECT ON CONVERSION
$C_2HCl_3 + CH_2Cl_2 / CH_4$

		t = 0.5 sec.			
Temperature (C)		750	800	850	900
Compound	Dia. (MM)	PERCENT CONVERSION			
C_2HCl_3	10.5	38	62	85	99
CH_2Cl_2	10.5	3	32	63	89
C_2HCl_3	16	32	55	80	--
CH_2Cl_2	16	5	20	56	--
		t = 1. sec.			
C_2HCl_3	10.5	60	76	95	--
CH_2Cl_2	10.5	15	52	83	--
C_2HCl_3	16	51	68	91	--
CH_2Cl_2	16	19	38	74	--

identified on both chromatographs (C_2H_2 + C_2H_4, CH_3Cl, 1,3-$C_3H_4Cl_2$, C_6H_6, C_2HCl_3, C_6H_5-CH_3) indicates that change in reactor diameter did not significantly affect product distribution at constant temperature.

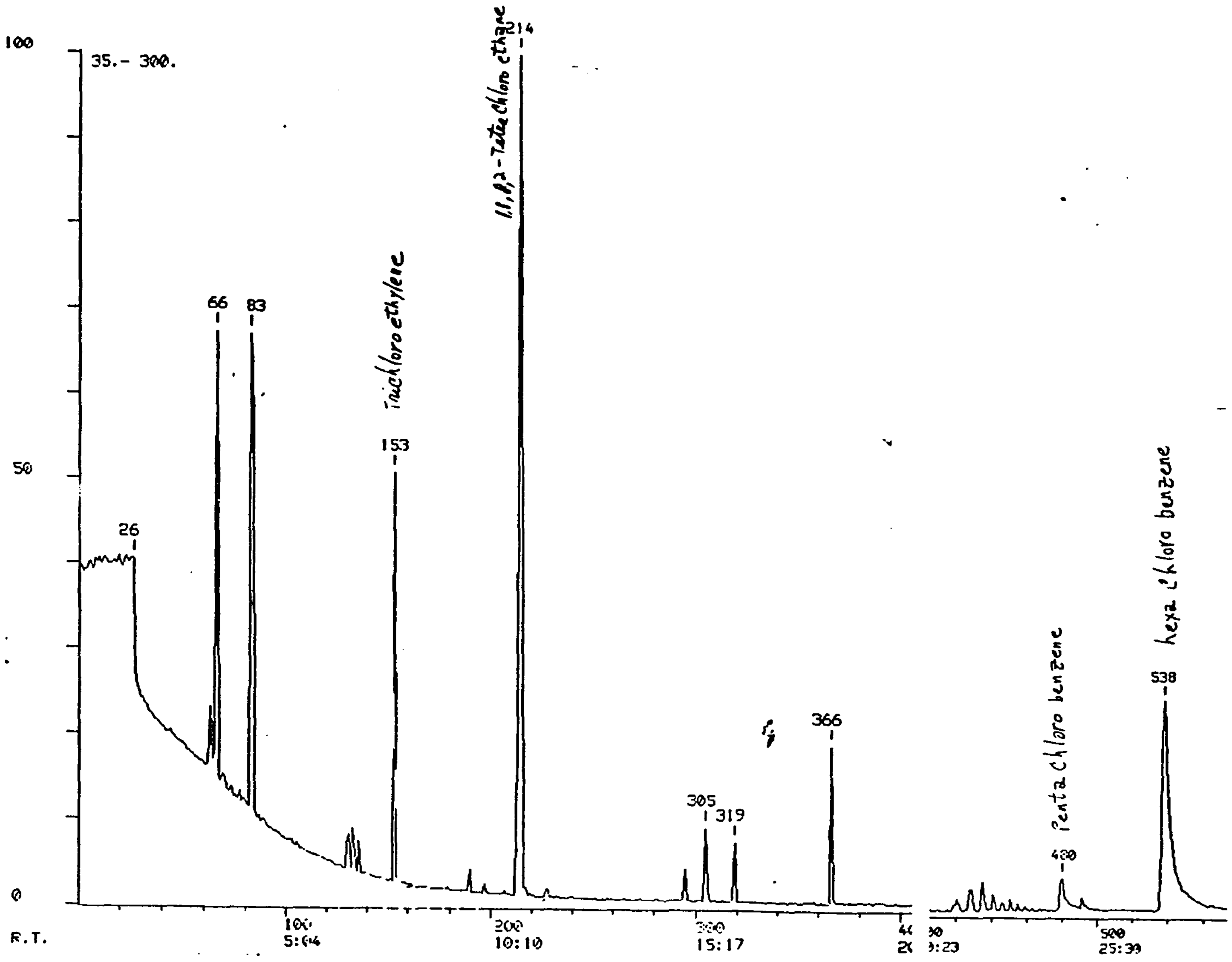
GC/MS analysis has identified the following compounds at 845 °C: dimethylcyclopentane, cyclopentadiene, chloroacetylene, 1,3-butadiene, vinyl acetylene, dichloroethylene, 4-octene, and propene. Table-IX shows the material balance for 500 moles of chlorine atoms at different temperatures in the residence time range of 0.48-0.56 seconds. The data indicate a dramatic increase in HCl formation at higher temperatures. Hydrochloric acid counts for more than 75% of chlorine at 900 °C.

The effect of lack of CH4 and hydrogen addition to the reactor on product distribution was studied in a series of experiments where all parameters but the carrier gas were held constant (10.5 mm ID reactor, 875 °C, and 0.51 sec). The gas phase reaction of trichloroethylene and methylene chloride mixture in argon, hydrogen, methane, and methane + argon (argon used as diluent) atmospheres were analyzed. Figures 18 - 21 illustrate GC/MS graphs of these reaction systems.

Pyrolysis of C2HCl3 and CH2Cl2 mixture in an inert atmosphere, argon, produced significant quantities polychlorinated hydrocarbons such as: hexachlorobenzene, pentachlorobenzene, hexachloroethane, tetrachlorobutadiene, tetrachloroethylene, dichloroacetylen. No measurable amount of chlorine free hydrocarbon was detected (Fig. 18).

The reaction of C2HCl3 and CH2Cl2 mixture in hydrogen atmosphere under similar conditions, however, produced

FIGURE-18 GC/MS CHROMATOGRAM C2HCl3/CH2Cl2 PYROLYSIS IN Ar AT 875 C



mainly light, chlorine free hydrocarbons with methane, ethane, ethylene, acetylene, chloromethane, and benzene observed to be major products. Quantifiable amounts of chlorobenzene, chloroform, carbon tetrachloride, and 1,3 dichloropropene were also detected (Fig. 19).

A comparison of product distribution for high temperature reactions of C_2HCl_3 + CH_2Cl_2 in methane and methane + argon atmospheres, Figures 20 and 21, demonstrate inert (argon in this study) addition to the reaction system studied. It has enhanced production of chlorine free hydrocarbons (e.g. benzene, toluene, cyclopentadiene) when all other experimental conditions were similar (10.5 mm ID reactor, 875 °C, and .51 sec). Quantitative analysis of gas chromatograms showed that concentration of lighter hydrocarbons (C_2H_2+C_2H_4, C_2H_6) increased by % when argon added as diluent to the reaction system. The comparison of GC/MS chromatograms of $C_2HCl_3/CH_2Cl_2/CH_4$ system, Fig. 20, and $C_2HCl_3/CH_2Cl_2/CH_4/Ar$, Fig. 21, reveals that concentrations of chlorocarbons with high chlorine/hydrogen ratio (e.g. CCl_4) dramatically reduce in reactor effluent when diluent, argon, is present.

The study of product distribution for reaction systems CH_2Cl_2/CH_4 and $C_2HCl_3/CH_2Cl_2/CH_4$ in tubular flow reactor have revealed that methane is a good substitute for hydrogen in hydrodechlorination of chlorocarbons. The primary

FIGURE-19 GC/MS CHROMATOGRAM
C2HCl3/CH2Cl2 PYROLYSIS IN H2 AT 875 C

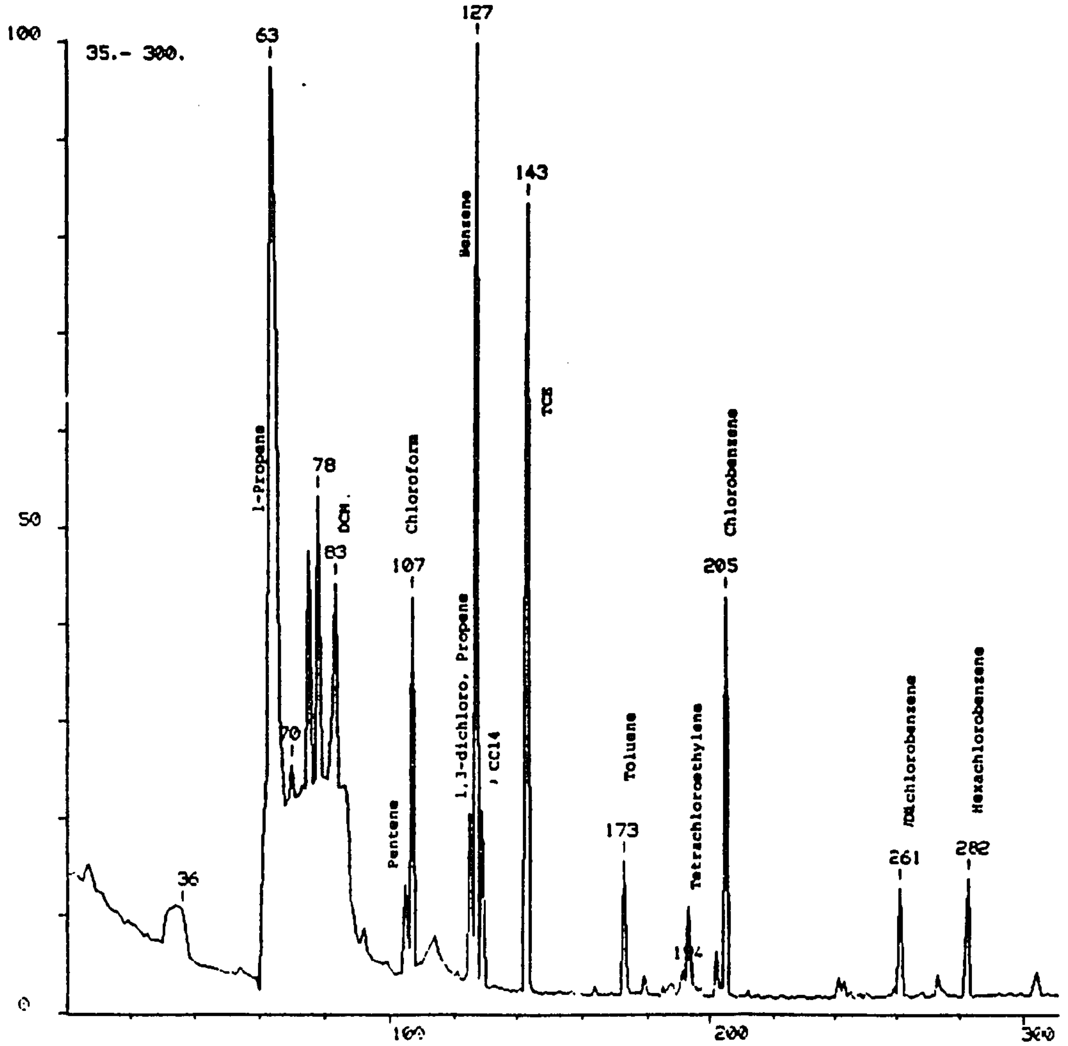


FIGURE-20 GC/MS CHROMATOGRAM
C2HCl3/CH2Cl2 PYROLYSIS IN CH4 AT 875 C

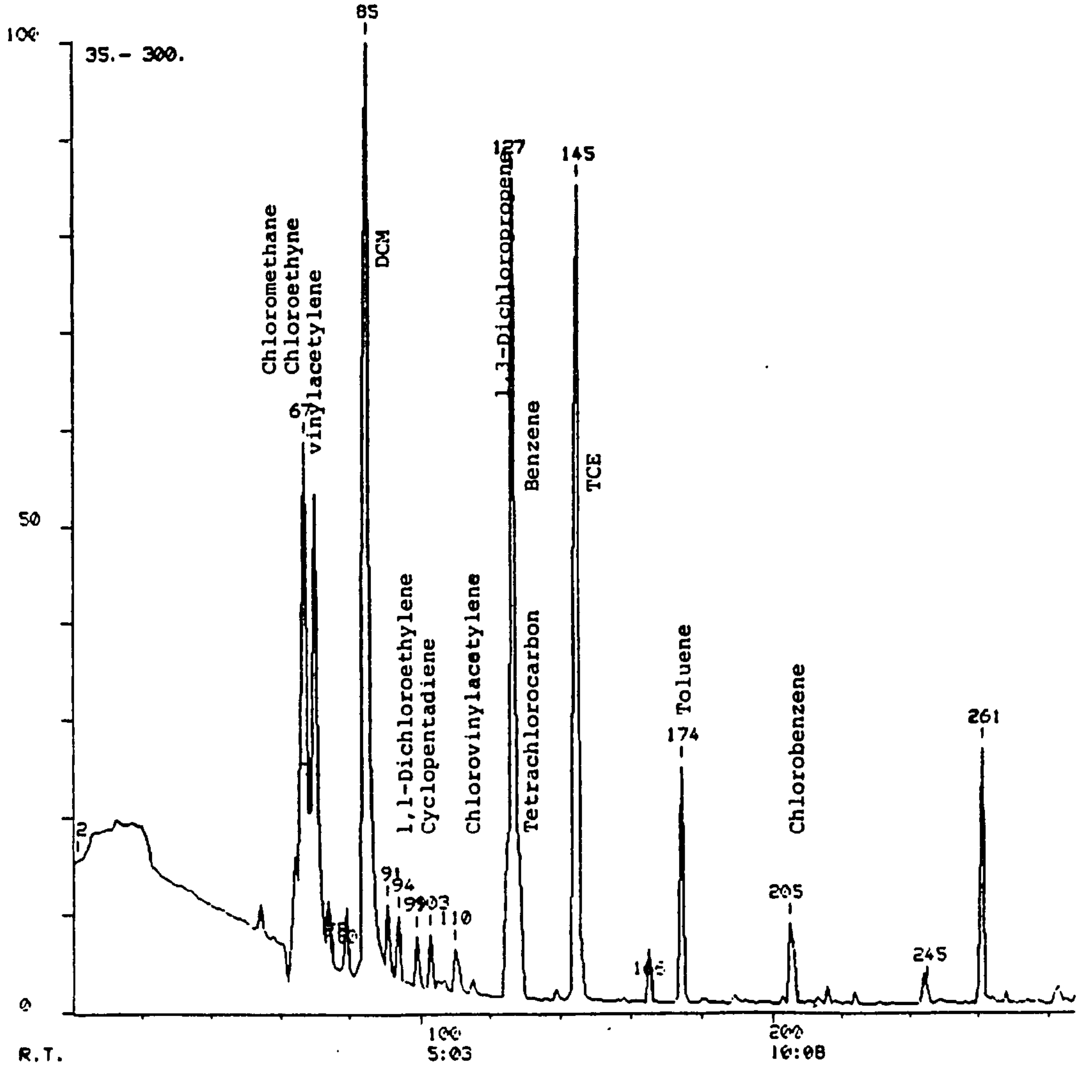
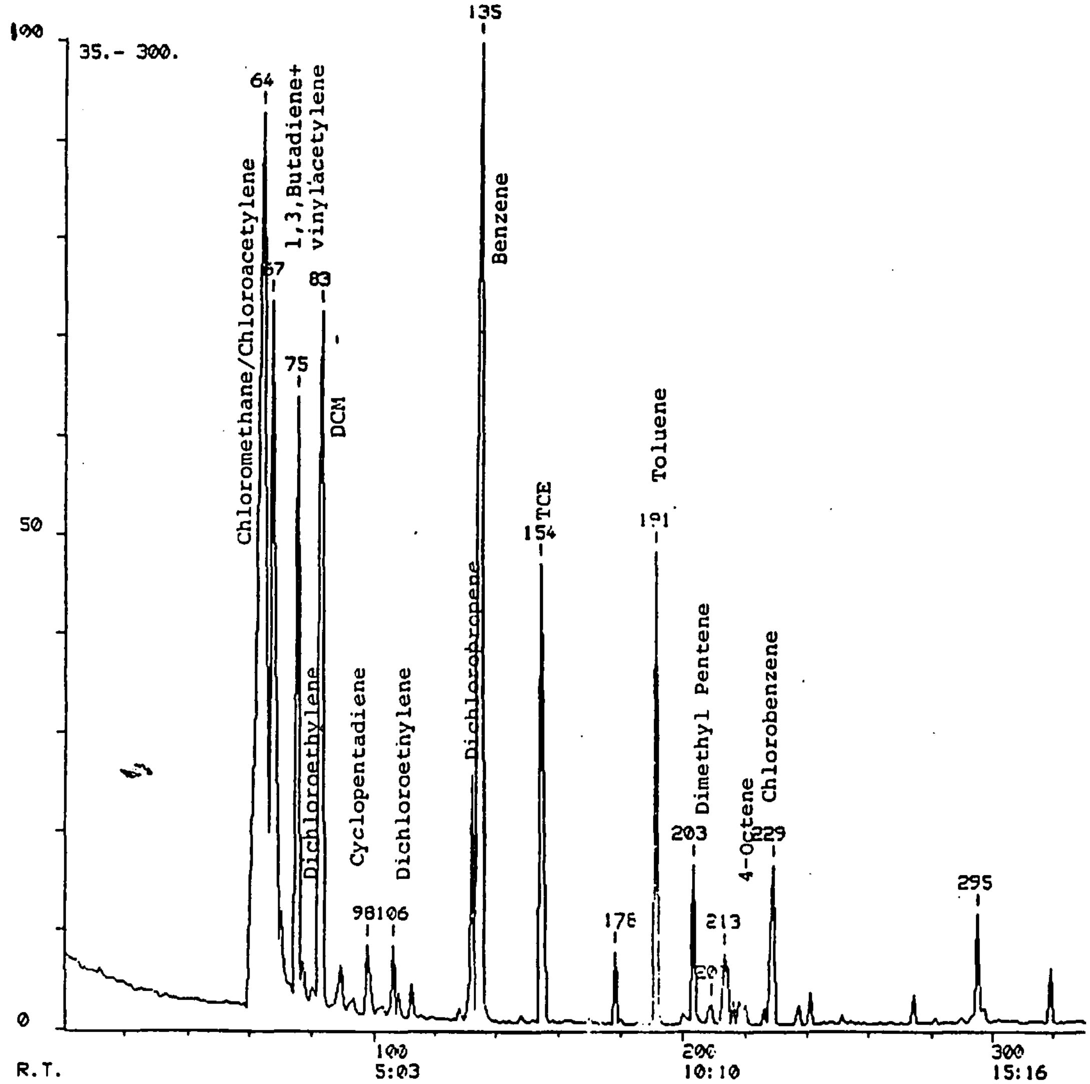


FIGURE-21 GC/MS CHROMATOGRAM
C2HCl3/CH2Cl2 PYROLYSIS IN CH4+Ar



difference observed was that in presence of methane ethylene and acetylene were dominant products compared to methane formation in systems with hydrogen bath. Another noticable difference was higher reactor temperature requirement (100 ^{o}C) for chlorinated hydrocarbon conversion in methane atmosphere compared to that of hydrogen bath [25-27].

Table-IX MATERIAL BALANCE 500 MOLES [Cl]
C2HCl3 + CH2Cl2 / CH4
REACTOR DIAMETER : 10.5 mm ID
RESIDENCE TIME : 0.48-0.56 SEC.

Compound / Temp. (C)	750	792	854	899
CH_3Cl	4.5	20	90	94.5
CH_2Cl_2	200	124	70	16
C_2HCl	X	X	X	X
$C_3H_2Cl_2$	X	X	X	X
C_2HCl_3	210	117	30	--
C_4H_3Cl	X	X	X	X
C_6H_5Cl	NA	NA	NA	1.91
HCl	46.7	207.2	290.9	376.8
$C_3H_4Cl_2$	X	X	X	X
Total	461.2	468.2	480.9	489.1

VI. DETAILED KINETIC MECHANISM AND MODELING

A detailed kinetic mechanism was developed to describe the system of reactions studied. A mechanism composed of 68 elementary reactions, for CH_2Cl_2/CH_4 system and another one with 72 reactions for mixture of $C_2HCl_3 + CH_2Cl_2 / CH_4$ system were found to reproduce experimental results.

These kinetic schemes were formulated considering all reaction products detected by GC and GC/MS at varied stages of conversion (0.05 to 0.9). Rate constants and reaction channels were developed from literature values, fundamental principals in Transition State Theory [44] and thermodynamic parameters for each specific elementary reaction. Activated Complex/QRRK Theory [51], was utilized to evaluate addition, recombination and unimolecular decay reactions at relevant temperatures and pressure. The CHEMKIN computer code [28] is used in interpreting and integrating the detailed reaction mechanisms (models) in the mode which utilizes thermodynamic calculation of the equilibrium constants for determination of reverse reaction rate constants.

A. MECHANISM

i. METHYLENE CHLORIDE AND METHANE

According to our experimental results methyl chloride is the first and major stable product from reaction of CH_2Cl_2 and CH_4 at temperatures below 900 ^{o}C. CH_3Cl is formed from reaction of CH2Cl with methane, which also produces methyl radicals, (1) and (2) below. CH2Cl is formed from unimolecular decomposition of the parent compound, CH2Cl2 :

$$\mathrm{CH2Cl2} \;\texttt{<--->}\; \mathrm{CH2Cl.} + \mathrm{Cl.} \qquad (1)$$

$$\mathrm{CH2Cl.} + \mathrm{CH4} \;\texttt{<--->}\; \mathrm{CH3Cl} + \mathrm{CH3.} \qquad (2)$$

Recombination of Chloromethyl Radicals- CH2Cl.+CH2Cl.:

Vinyl chloride, another major product of this system at temperatures below 800 ^{o}C, arises from several channels. One of which is recombination of CH2Cl radicals into an activated complex:

$$\mathrm{CH2Cl.} + \mathrm{CH2Cl.} \;\texttt{<--->}\; [\mathrm{CH2ClCH2Cl}]^{\#} \begin{array}{ll} \texttt{--->}\; \mathrm{C2H3Cl2.} + \mathrm{H.} & (3) \\ \texttt{--->}\; \mathrm{C2H4Cl.} + \mathrm{Cl.} & (4) \\ \texttt{--->}\; \mathrm{C2H3Cl} + \mathrm{HCl} & (5) \\ \texttt{--->}\; \mathrm{C2H4Cl2}\ \mathrm{STABILIZED} & (6) \end{array}$$

# denotes energized complex

where the energized complex further decomposes as shown in equations (3) - (6). An energy diagram of reactions (3) - (6) is illustrated in Figure 22. Reaction (3) does not occur due to thermodynamic limitations, (endothermic), while reaction (5) is the thermodynamically most favorable exit channel (low energy barrier), next to stabilization.

The QRRK calculations on CH2Cl+CH2Cl for temperature range of 900-1400 ^{o}K and pressure range of 0.001-10 atm, show that the rate constant for exit channel C2H3Cl+HCl is dominant by two to three order of magnitude. At pressures above 10 atm stabilization of activated complex competes with this channel. Results of the QRRK calculation for 1100 ^{O}K and different pressures are tabulated in Table X and shown schematically in Figure 23. The C2H4Cl radical, from channel 2 in Fig. 22, can further react by undergoing beta scission to C2H4 + Cl or C2H3Cl + H and the stabilized [C2H4Cl2] (adduct) can split out HCl forming vinyl chloride at temperatures and conditions of our experiment.

TABLE-X RESULTS OF ACTIVATED COMPLEX THEORY CALCULATION FOR RATE CONSTANTS AT 1100 K

		CH2Cl + CH2Cl	cc/sec-mole
P(Atm)	C2H4Cl+Cl	C2H3Cl+HCl	C2H4Cl2 (stabilize)
0.001	1.11E07	9.98E09	1.26E06
0.01	1.11E07	9.97E09	1.26E07
0.1	1.10E07	9.85E09	1.24E08
1.0	1.03E07	8.88E09	1.10E09
10.0	6.30E06	4.64E09	6.06E09

QRRK Utilization:

The Quantum Rice, Ramsberger, Kassel (QRRK) computer code [51] was utilized to determine the energy dependent

FIGURE-22 ENERGY DIAGRAM FOR REACTION CH2Cl+CH2Cl

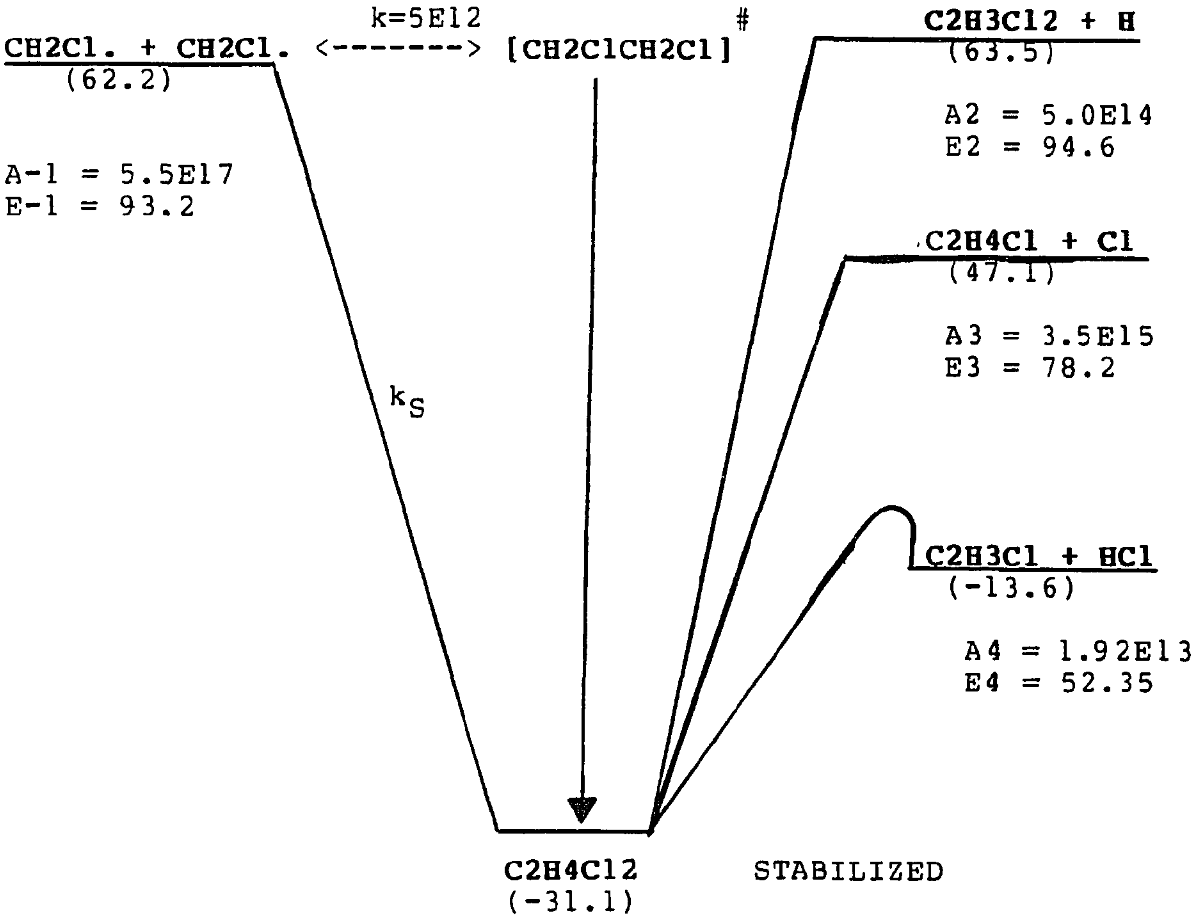
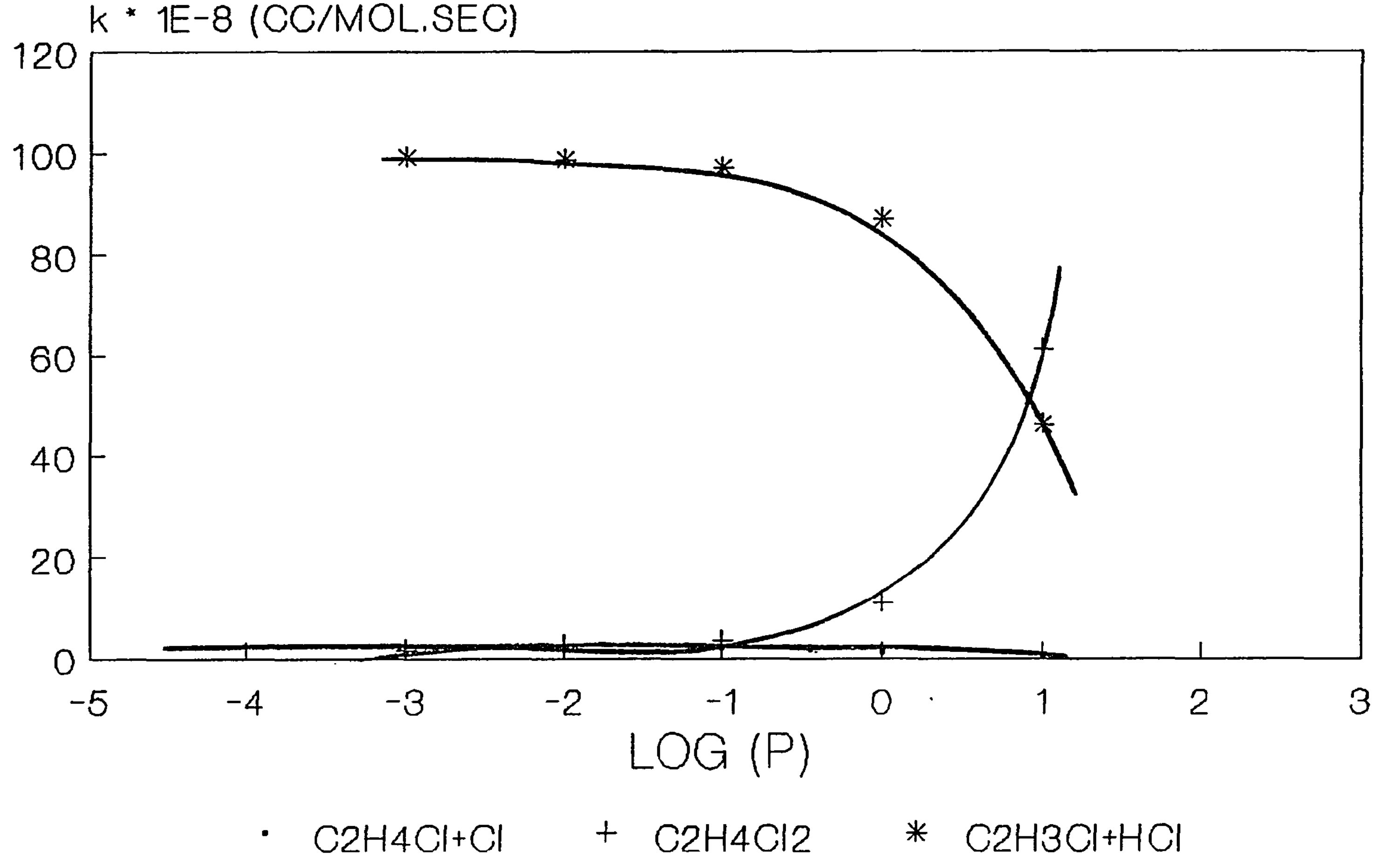


FIGURE-23 RESULTS OF ACTIVATED COMPLEX THEORY CALCULATION FOR CH2Cl+CH2CCl



rate constants, for possible exit channels of all radical-radical recombination reactions. These represent approximately 28% of reactions in the mechanism, Table IX. The program incorporates Quantum RRK theory to calculate rate constants as function of temperature and pressure. An example format of input and output QRRK data is listed in Appendix I. The input data required include the high pressure limit A factors and activation energies, E_A, for the combination reaction, and for reaction of the energized complex to each product channel as well as its dissociation back to reactants. It also utilizes Lennard Jones parameters, sigma and e/k, for the complex and the third body (bath gas), geometric mean frequency and the number of vibrational oscillators of the complex.

The A factors and E_As were taken from literature, calculated by fundamental principals in transition state theory [44], or from equilibrium and the reverse rate constants. The reverse rate constants are also calculated by a computer code that utilizes the CHEMKIN subroutines are listed in Appendix II. The Lennard Jones parameters when not available in literature, were calculated by equations using critical constants given in Reid, Prauznits and Sherwood [57] :

$$\text{sigma}\ (P_C/T_C)^{1/3} = 2.3551 - 0.087\text{omega}$$

$$e/kT_C = 0.7915 + 0.1693 \text{ omega}$$

where :

omega = accentric factor

sigma = potential length constant, A (similar to a reactive diameter or cross section)

P_C = critical pressure, atm

T_C = critical temperature, ^{o}K

e = potential-energy constant, ergs

k = Boltzmann's constant = 1.3805E-16, ergs/^{o}k

The number of vibrational degrees of freedom (oscillators), N, are given by the following equations [41]:

$N = 3n - 6$ Non-linear molecules

$N = 3n - 5$ Linear molecules

where n represents the number of atoms in the complex. The geometric mean of the adduct's vibrational frequencies, <v>, was available from literature [60].

The deactivation rate, k_s, is determined from [51] and references therein:

$$k_s = B.Z.[M]$$

where Z is collisional frequency rate constant given by:

$$Z = 2.708\ k_{HS}(e/kT)^{1/3}.$$

The hard sphere collision factor, k_{HS}, is given by Benson [44] and Forst [58], e/k is Lennard Jones parameter, and T is temperature in degrees Kelvin. [M] is any specified third body concentration represented by pressure of the system ,

P. The collision efficiency, B, a temperature dependent factor, is obtained from Troe's [55] correlation :

$$\frac{B}{1-B^{1/2}} = \frac{-<Del.E_{col}>}{F(E).k.T}$$

where :

$<Del.E_{col}>$ = Average amount of energy transferred per collision

F(E) = 1.15, a constant [55]

k_b = Boltzman's constant

T = Temperature, ^{o}K

The QRRK program incorporates sigma, e/k_b, and mass for third bodies relevant to the system of study, argon in our system.

Recombination of Methyl Radicals with CH2Cl:

The combination reaction of primary radicals, CH3 and CH2Cl, is similar but will produce different end products as shown in reactions (7) to (10) :

$$\mathrm{CH3 + CH2Cl}\ [65.9] \longrightarrow [\mathrm{C2H5Cl}]^{\#} \longrightarrow \mathrm{C2H4Cl + H}\ [70.3] \quad (7)$$

$$[\mathrm{C2H5Cl}]^{\#} \longrightarrow \mathrm{C2H5 + Cl}\ [54.4] \quad (8)$$

$$[\mathrm{C2H5Cl}]^{\#} \longrightarrow \mathrm{C2H4 + HCl}\ [17.2] \quad (9)$$

$$[\mathrm{C2H5Cl}]^{\#} \longrightarrow \mathrm{C2H5Cl}\ [-26.7] \quad \mathrm{STABILIZED} \quad (10)$$

The energy diagram for this combination reaction is illustrated in Figure 24. The activated complex , $[C2H5Cl]^{\#}$, can be stabilized, react further through one or more of the three exit channels to produce C2H4Cl + H, C2H5 + Cl, and C2H4 + HCl, or dissociate back to original reagents. The dominant exit channel for the reaction of CH3 + CH2Cl at the experimental condition of this study predicted by QRRK is C2H5 + Cl. The pressure dependence of k_s as predicted by QRRK is shown in Figure 25. It is apparent from this figure that the C2H5 + Cl exit channel dominates over the C2H4 + HCl channel by 2.5 times at atmospheric pressure and 1100 ^{o}K, and over stabilization of the activated complex by more than two orders of magnitude up to 8 atm. The apparent rate for the high energy exit channel C2H4Cl + H, was almost three orders of magnitude lower at 1 atm and temperature of this study.

The detailed mechanism developed for CH2Cl2/CH4/Ar reaction system is shown in Table XI.

FIGURE-24 ENERGY DIAGRAM FOR REACTION CH3+CH2Cl

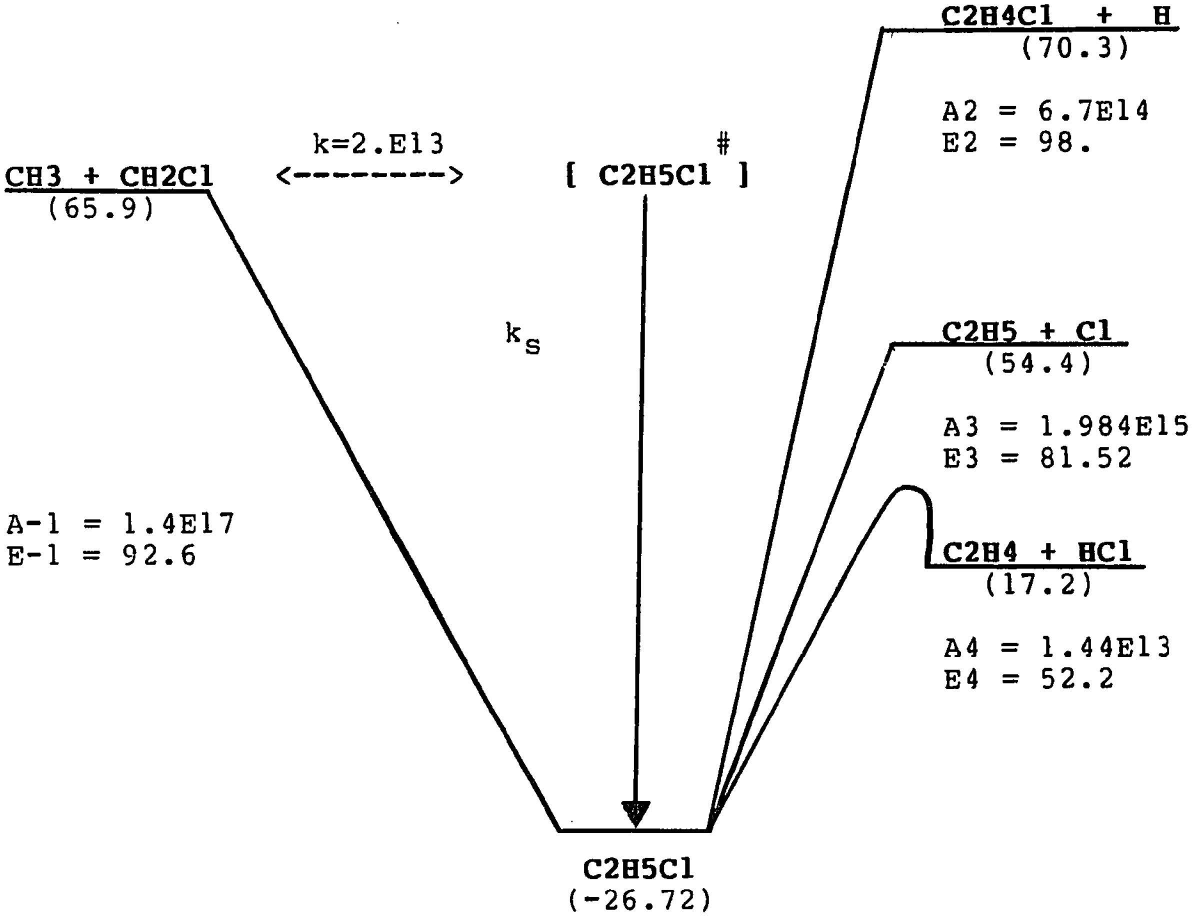


FIGURE-25 RESULTS OF ACTIVATED COMPLEX THEORY CALCULATION FOR CH3+CH2Cl

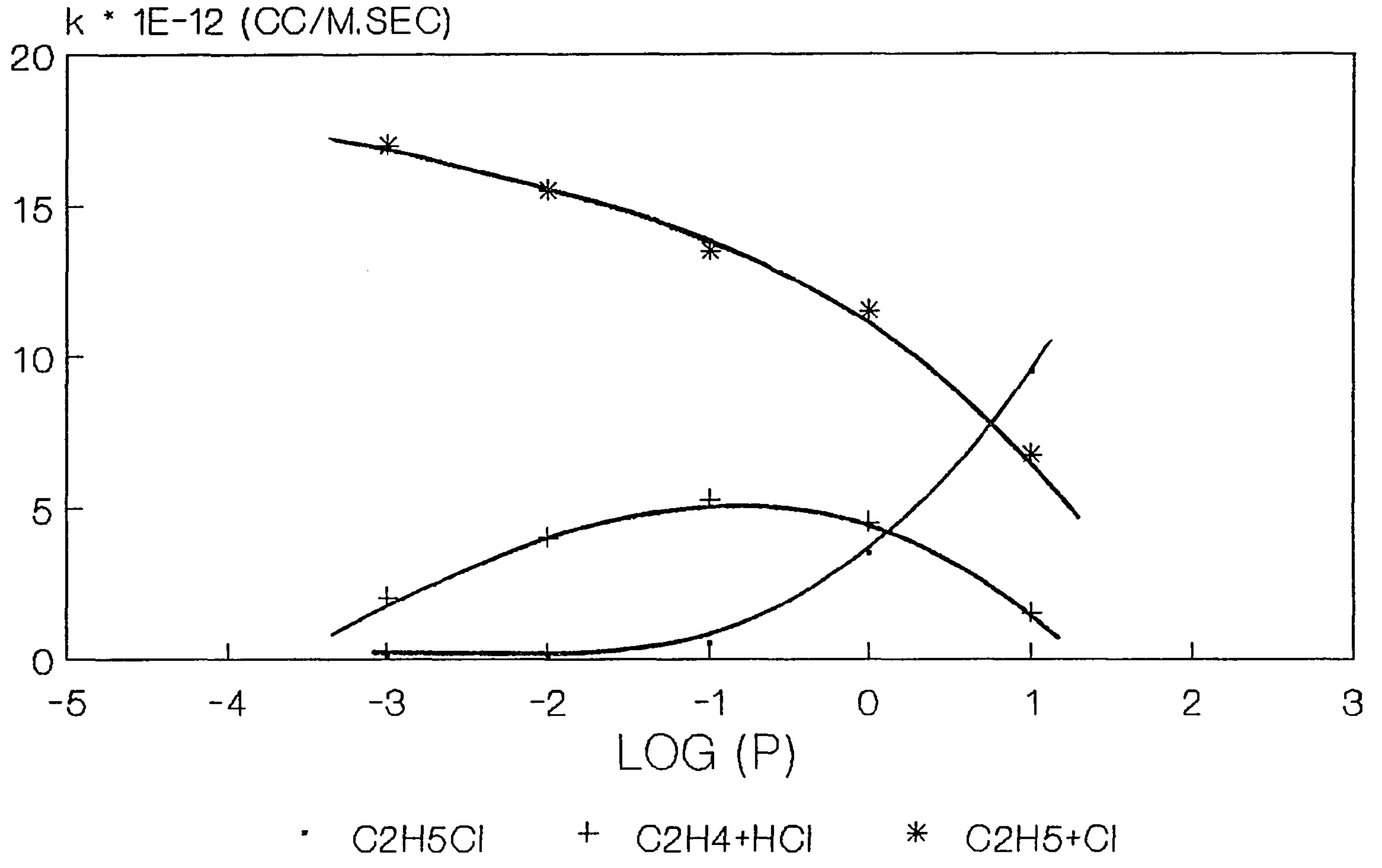


TABLE XI- DETAILED MECHANISM FOR CH2CL2/CH4/Ar
REACTION SYSTEM

REACTION	A	E_a	SOURCE
1. CH2Cl2 = CH2Cl + Cl	1.88E16	82.8	1
2. CH2Cl2 = CHCl + HCl	1.42E14	111.0	2
3. CH4 = CH3 + H	1.00E16	104.8	3
4. CH3Cl = CH3 + Cl	1.88E15	84.4	4
5. Cl + CH4 = HCl + CH3	3.10E13	3.6	7
6. Cl + C2H6 = HCl + C2H5	1.20E14	1.0	7
7. Cl + C2H4 = C2H4Cl	2.90E10	-8.0	8
8. Cl + C2H4 = C2H3 + HCl	1.00E13	5.1	7
9. Cl + CH2Cl2 = CH2Cl + Cl2	1.00E14	21.4	7
10. Cl + CH2Cl2 = CHCl2 + HCl	2.50E13	3.1	9
11. Cl + CH3Cl = CH3 + Cl2	1.00E14	25.0	7
12. Cl + CH3Cl = CH2Cl + HCl	3.10E13	3.6	9
13. Cl + C2H3Cl3 = C2H2Cl3 + HCl	3.16E13	3.5	7
14. Cl + C2H5Cl = C2H4Cl + HCl	2.00E13	1.5	7
15. Cl + C2H2Cl4 = C2HCl4 + HCl	1.41E12	2.5	7
16. Cl + H2 = H + HCl	4.80E13	1.3	11
17. Cl2 = Cl + Cl	7.69E08	55.6	11
18. HCl = H + Cl	6.09E08	97.3	11
19. H + CH4 = CH3 + H2	2.40E11	7.0	5
20. H + Cl2 = Cl + HCl	4.57E12	1.4	11
21. H2 = H + H	5.26E08	105.0	11
22. H + CH2Cl2 = HCl + CH2Cl	1.02E13	6.1	7

23. H + CH3Cl = HCl + CH3	9.00E13	7.7	33
24. H + C2H3Cl = HCl + C2H3	1.00E13	6.5	7
25. CH3 + CHCl2 = C2H4Cl2	7.35E10	-6.29	8
26. CH3 + CHCl2 = C2H4Cl + Cl	7.92E12	4.71	8
27. CH3 + CHCl2 = C2H3Cl + HCl	4.02E12	0.0447	8
28. CH3+C2H3Cl3=C2H3Cl2 + CH3Cl	2.00E11	1.08	9
29. CH3 + C2H5Cl = C2H5 + CH3Cl	1.06E12	2.36	12
30. CH3 + CHCl = C2H4Cl	7.30E08	-4.17	8
31. CH3 + CHCl = C2H4 + Cl	1.46E13	-0.107	8
32. CH3 + CH2Cl = C2H5Cl	2.79E11	-5.31	8
33. CH3 + CH2Cl = C2H4 + HCl	1.56E13	0.502	8
34. CH3 + CH2Cl = C2H5 + Cl	1.67E13	5.66	8
35. CH3 + CH2Cl = C2H4Cl + H	5.47E11	12.50	8
36. C2H6 = CH3 + CH3	7.94E16	89.4	3
37. C2H6 = C2H5 + H	1.26E16	98.0	3
38. CH3 + CH2Cl2 = CHCl2 + CH4	6.76E10	7.2	7
39. CH3 + CH2Cl2 = CH2Cl + CH3Cl	1.40E11	4.9	7
40. CH3 + C2H3Cl = C2H3 + CH3Cl	1.38E11	11.97	7
41. CH3 + CH3Cl = CH2Cl + CH4	3.31E11	9.4	7
42. C2H5 = C2H4 + H	4.00E13	40.9	3
43. C2H3 = C2H2 + H	1.58E12	38.3	13
44. C2H3 + CH4 = C2H4 + CH3	8.92E11	20.5	16
45. C2H6 + CH3 = C2H5 + CH4	1.58E12	11.7	14
46. CH2Cl + CH2Cl = C2H4Cl2	3.92E10	-6.32	8
47. CH2Cl + CH2Cl = C2H4Cl + Cl	6.12E12	4.68	8

48.	CH2Cl + CH2Cl = C2H3Cl + HCl	2.59E12	0.0477	8
49.	CHCl2 + CH2Cl = C2H3Cl3	9.26E09	-6.63	8
50.	CHCl2 + CH2Cl = C2H3Cl2 + Cl	2.33E12	6.31	8
51.	CHCl2 + CH2Cl = C2H2Cl2 + HCl	2.27E12	0.197	8
52.	C2H2Cl + CH4 = C2H3Cl + CH3	7.94E11	10.1	15
53.	C2H3Cl3 = C2H3Cl2 + Cl	2.40E16	73.2	17
54.	C2H3Cl3 = C2H2Cl2 + HCl	3.80E13	49.09	17
55.	C2H3Cl = C2H3 + Cl	3.66E15	87.6	18
56.	C2H3Cl = C2H2 + HCl	3.55E13	68.73	19
57.	C2H2Cl2 = C2H2Cl + Cl	1.04E16	89.17	20
58.	C2H2Cl2 = C2HCl + HCl	7.10E13	69.11	21
59.	C2H4Cl2 = C2H4Cl + Cl	6.00E15	77.42	22
60.	C2H4Cl2 = C2H3Cl + HCl	2.88E13	54.35	23
61.	C2HCl3 = C2HCl2 + Cl	1.74E15	92.1	24
62.	C2HCl3 = C2Cl2 + HCl	7.10E13	77.61	25
63.	C2HCl2 + CH3 = C2HCl + CH3Cl	1.26E12	1.50	26
64.	CHCl2 + CHCl2 = C2H2Cl4	4.95E09	-6.93	8
65.	CHCl2 + CHCl2 = C2HCl3 + HCl	3.91E11	-0.404	8
66.	CHCl2 + CHCl2 = C2H2Cl3 + Cl	1.69E12	4.65	8
67.	C2H2Cl4 = C2HCl3 + HCl	1.00E14	56.0	34
68.	C2H5Cl = C2H4 + HCl	1.44E13	52.2	35

SOURCE

[1] A factor is based on Del S for reverse reaction, A_{-1}; A_{-1} is taken as twice of CH3+C2H5 (A=2E13), [33]; E_a = Del H.

[2] A = $10^{13.55}$*4; E_a = Del H + 40 [34].

[3] Dean, A. M., J. Phys. Chem., Vol. 89, 4600 (1985).

[4] A factor is based on A_{-1}; A_{-1}=4E13 taken as 2*A for CH3+C2H5 [33]; E_a=Del H.

[5] Robaugh, D., and Tsang, W., J. Phys. Chem., Vol. 90, 4159 (1986).

[6] Herman, I. P., Magnotta, F., Buss, R. J., and Lee Y. T., J. Chem. Phys., Vol. 79(4), 1789 (1983).

[7] Kerr, J. A., and Moss, S. J., HANDBOOK OF BIOMOLECULAR AND TERMOLECULAR GAS REACTIONS, Vol. I, CRC Press, 1981.

[8] Calculated by GISOQRRK computer program.

[9] Kerr, J. A., and Moss, S. J., HANDBOOK OF BIMOLECULAR AND TERMOLECULAR GAS REACTIONS, Vol. I, CRC Press, 1981.

[10] A taken as for rreaction C3H7+CH3 (A=1.26E12), [33]; E=0. [33].

[11] Ritter, E, Bozzelli, J. W., and Dean, A. M., J. Phys. Chem., (1988).

[12] A factor taken as 2/3 for C2H6+CH3 (A=1.5E12), [33]; E = Del H+2. [33].

[13] A factor from [3]; E_a from [3].

[14] A factor and E from [33], table 42 .

[15] A factor taken from reaction 53; E=Del H+E_{-1}.

[16] A factor taken for C2H5+CH4 (A=1.58E12) and E_a as of C3H5+C2H6 [33].

[17] Won, Y. S., Master Thesis, NJIT, 1988.

[18] A factor is based on A_{-1}; A_{-1}=2E13, taken for C3H7+CH3 [33]; E_a=Del H.

[19] A = $10^{13.55}$; E_a=Del H+45 [35].

[20] A factor is based on A_{-1}; A_{-1}=2E13, taken for C3H7+CH3; E_a=Del H.

[21] $A = 10^{13.55}*4$; E_a=Del H+45

[22] A factor is based on A_{-1}; A_{-1}=2.66E13 taken as 2*2/3 for CH3+C2H5 [33]; E_a=Del H.

[23] $A = 10^{13.55} * 6$; E_a = Del H+37, [34].

[24] A is based on A_{-1}; A_{-1}=1.E13, taken as 1/2 for C3H7+CH3 [33]; E_a= Del H.

[25] $A = 10^{13.55} * 3$; E_a = Del H + 45

[26] A factor taken as 2*1/2 for C3H5+C2H5 [33]; E_a=Del H+1.5, [7].

[27] Allara, D. L., and Shaw, R., J. Phys. Chem. Ref. Data, Vol. 9, No. 3, 1980.

[28] Setser, D. W., and Hassler, J. C., J. Chem. Phys., Vol. 45, 3237 (1966).

[29] Skinner, Unpublished paper.

[30] Weissman, M., and Benson, S. W., Int'l J. of Chem. Kin., Vol.16, 307 (1984).

[31] Benson, S. W., Thermochemical Kinetics, John Wiley, 1976.

[32] Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., The Properties of Gases and liquids 3rd. Ed., McGraw Hill, 1977.

[33] Baulch, J. Chem. Ref. Data, Vol. 10, Suppl. 1, 1981.

[34] $A = 10^{13.55}*10^{-4/4.6}*6$; E_a=Del H+35.

[35] $A = 10^{13.55}*10^{-4/4.6}*3$; E_a=Del H+35.

ii. TRICHLOROETHYLENE + METHYLENE CHLORIDE AND METHANE

A detailed kinetic scheme for pyrolysis of trichloroethylene plus methylene chloride mixture in methane bath is discussed in this section. A constant ratio C2HCl3:CH2Cl2:CH4:Ar of 1:1:40:40 was held throughout the experiment. Tubular flow reactors of different surface to volume ratios (4, 10.5, and 16 mm ID) were utilized. The important initial reactions are unimolecular decomposition of C2HCl3 and CH2Cl2 :

			A (1/s)	E (Kcal/mol)	
C2HCl3	---->	C2HCl2 + Cl	3.16E15	88.5	(11)
C2HCl3	---->	C2Cl2 + HCl	5.E13	72	(12)
CH2Cl2	---->	CH2Cl + Cl	2.5E16	82.2	(13)
CH2Cl2	---->	CHCl + HCl	1.2E14	105	(14)

Table XII shows the specific decomposition rate constants for reactions (11) to (14) at temperatures of 900-1200 ^{O}K. It is observed from the values listed in table IX that reactions (12) and (13) are the most important initiation reactions at temperature range of this study (1000 - 1250 ^{O}K). Decomposition of trichloroethylene proceeds primarily via path C2Cl2 + HCl because this channel has the lowest E_a for this parent. About four percent of the trichloroethylene is converted through reaction (11). Pathway (14) is the least probable one since its rate

TABLE-XII RATE CONSTANTS FOR UNIMOLECULAR DECOMPOSITION REACTIONS OF C2HCl3 AND CH2Cl2

REACTION CHANNEL	C2HCl2+Cl (11)	C2Cl2+HCl (12)	CH2Cl+Cl (13)	CHCl+HCl (14)
T (K)		k (1/s)		
900	1.01E-06	1.64E-04	2.73E-04	3.80E-12
1000	1.43E-04	9.16E-03	2.70E-02	1.35E-09
1100	8.22E-03	2.47E-01	1.16	1.64E-07
1200	2.42E-01	3.85	2.67E+01	9.01E-06

constant is smaller than reactions (11)-(13) by five order of magnitude (at 1100 ^{O}K).

The presence of CH4 accelerates initiation steps via formation of methyl radical:

Cl + CH4 = HCl + .CH3 (15)

Metathetical reaction of CH3 with initial chlorocarbon reagents to chloromethane or any other stable chlorinated intermediate, is fast because of low activation energy (less than 5 Kcal/mol) and high A factors (about 2E11).

CH2Cl2 + .CH3 = CH2Cl. + CH3Cl (16)

C2HCl3 + .CH3 = C2HCl2. + CH3Cl (17)

C2H2Cl2 + .CH3 = C2H2Cl. + CH3Cl (18)

Radicals formed by above Cl-transfer reactions can then abstract hydrogen from excess available methane in the system and produce less chlorinated hydrocarbons:

.CH2Cl + CH4 = CH3Cl + .CH3 (19)

.C2HCl2 + CH4 = C2H2Cl2 + .CH3 (20)

.C2H2Cl + CH4 = C2H3Cl + .CH3 (21)

We note that with the methane excess entropy drives these exothermic reaction set.

In addition to pathway (15) reactions (19) - (21) are other channels for formation of the methyl radicals. CH3 plays a key role in propagating reactions toward final stable products. The methyl radical, for example, has a catalytic role in production of ethylene, one of the major products, via vinyl chloride :

C2H3Cl + .CH3 = C2H3. + CH3Cl (22)

C2H3. + CH4 = C2H4 + .CH3 (23)

C2H3Cl + CH4 = C2H4 + CH3Cl OVERALL (24)

In addition to reactions (3)-(6) another pathway for formation of vinyl chloride is a set of consecutive metathetical reactions starting with C2HCl3, and methyl radical with radical chlorocarbon species then converting CH4 to CH3.

C2HCl3 + .CH3 = C2HCl.Cl + CH3Cl (25)

.C2HCl2 + CH4 = C2H2Cl2 + .CH3 (26)

C2H2Cl2 + .CH3 = C2H2Cl. + CH3Cl (27)

C2H2Cl. + CH4 = C2H3Cl + .CH3 (28)

C2HCl3 + 2CH4 = C2H3Cl + 2CH3Cl OVERALL (29)

Both of trichloroethylene decomposition reactions, (11) and (12), are calculated to be important in our reaction system, with current rate analysis predicting that the four center elimination to dichloroacetylene + HCl (12) is about a factor of 10 faster than reaction (11) or (13). Transition state principles [44] would calculate an A factor of 2E13 sec^{-1} and generic estimates of the energy of activation would be 45 Kcal/mole above the enthalpies of reaction (12). The fraction of reactions that do proceed through simple unimolecular fission channels produce Cl atoms which then rapidly generates methyl radicals through reaction (15).

The C2Cl2 from reaction (12) however, is not detected in measurable quantity by our GC analysis. This may be due to rapid formation of more stable adducts by rapid addition reactions of the reactive C2Cl2 with CH3, Cl, and to a lesser extent H; for example:

C2Cl2 +.CH3 <---> $[CH3CCl=C.Cl]^{\#}$ ---> CH3CCl=C.Cl (31)

(Stabilized)

---> CH3C≡CCl +.Cl (32)

CH3CCl=C.Cl + CH4 ---> C3H4Cl2 + .CH3 (33)

Reactions (31), (32), and (33) are exothermic and (33) is further driven by excess CH4 in the system.

The products observed in the experiment at highest concentrations are, C2H2 and C2H4, CH3Cl and to a smaller extent benzene.

The C2H4, ethylene and vinyl chloride are produced in a similar manner as that described above for pure methylene chloride reaction in methane; i.e. from recombination of methyl and chloromethyl radicals as illustrated in reactions (5), (9), or metathetical reactions of C2HCl3 with CH3. and CH4 as indicated by reactions (23), and (28).

Acetylene is produced by beta scission of vinyl and vinylchloro radicals which are produced by reaction of chlorine atoms abstracting a hydrogen from ethylene or vinylchloride, reactions (35) and (36) respectively.

Cl. + C2H4 <---> HCl + C2H3. (35)

Cl. + C2H3Cl <---> HCl + C2H2Cl. (36)

C2H3. <---> H + C2H2 (37)

C2H2Cl. <---> Cl + C2H2 (38)

Addition reaction of methyl radical to unsaturated chlorinated hydrocarbons is also thermodynamically favored.

.CH3 + CHCl=CCl2 ---> CH3-CH=CCl2 + Cl. (30)

Production of less chlorinated hydrocarbon plus chlorine is more preferred exit channel under the experimental conditions of this study. The Cl atom generated reacts with excess methane which creats more CH3. This further stimulates the progress of reactions toward chlorine free hydrocarbons plus HCl.

In reactions which involve radical-radical recombination or radical addition to an unsaturated molecule, an energized complex is formed. A competition between stabilization of this complex and its dissociation back to reactants or further reaction to products, is possible. These chemical reactions, therefore, should not be considered as one step, elementary, reactions. Consequently, the extrapolation of their experimentally obtained kinetic parameters, obtained at low pressure and temperature, to other practical conditions could result in incorrect values.

The QQRK energized complex analysis [51] was used for determination of Arrhenius parameters of radical addition and recombination reactions at temperature and pressure of this study. The input data required are:

-High pressure limit pre exponential factors (A factors), which are obtained from literature, for each reaction step thermodynamic data developed at NJIT [14] , or method of Benson [44].

-Energies of Activation, taken from literature or calculated from thermodynamic heats of formation for the species involved and by analogy of similar reaction.

-Number of vibrational degrees of freedom :

$N = 3n - 6$ Non-linear molecules

$N = 3n - 5$ Linear molecules

where n represnts the number of atoms in the adduct; and the geometric mean vibrational frequency of the energized complex avialable from literature [60].

-Lennard Jones transport properties, sigma and e/k, required for both, energized adduct and the bath gas, taken from literature or calculated by the equations and critical factors given in [57].

As a detailed example the input parameters for addition reaction of methyl radical to dichloroacetylene are listed in Table XIII. In addition to stabilization of the adduct, another possible exit channel is CH3C≡CCl+Cl. Table XII shows the QRRK calculation results for this reaction. It is observed from the values listed in Table XIV that formation of products CH3C≡CCl+Cl, dominate the stabilized complex, C3H3Cl2, at pressures lower than 0.1 atmosphere. At the experimental conditions of this study (1000-1250 ^{o} C and atmospheric pressure), however, the complex adduct stabilization starts to compete with the product exit channel. The C3H3Cl2 radical can further react with excess available CH4 to produce dichloropropene, one of out major observed products under 800 ^{o}C.

TABLE-XIII

$$\mathrm{CH_3 + C_2Cl_2} \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [\mathrm{C_3H_3Cl_2}]^{\#} \begin{array}{l} \longrightarrow \mathrm{CH_3C{\equiv}CCl + Cl} \quad (2) \\ \longrightarrow \mathrm{C_3H_3Cl_2}\ \text{STABILIZED} \end{array}$$

k	A	E_a	Ref.
1	6.30E11	0.0	a
-1	4.26E13	47.10	a
2	3.24E09	0.0	b

<v> = 1040. /cm c

LJ PARAMETERS : d

sigma = 5.575 A e/k = 483.7 cal

a
A_1 taken as of $\mathrm{CH_3+C_2H_2}$ (A=6.3E11), [3]; E=7.7 [3].
A_{-1} from thermodynamics; E_{-1}=Del H+7.2, [3].

b
A_2 based on A_{-2}; A_{-2} taken as of Cl+C=CCl(A=1.58E13),[3]; E_2=Del H.

c
<V> taken as <V> for $\mathrm{C_3H_3Cl_4}$ -200; <V> for $\mathrm{C_3H_3Cl_4}$ calculated by averaging twice the value for $\mathrm{C_2HCl_3}$, and $\mathrm{C_2H_4Cl_2}$.
Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

d
Taken as of the values for $\mathrm{C_3H_5Cl_2}$. The valuse for $\mathrm{C_3H_5Cl_2}$ is calculated by the equations and critical factors given in [32].

The primary process to $C_3H_4Cl_2$ formation, however, is from the combination reaction of CH_3 with C_2HCl_3 (reagent) by addition of methyl to the double bond and then the activated complex undergoing beta elimination:

TABLE XIV RESULTS OF ACTIVATED COMPLEX THEORY CALCULATION FOR RATE CONSTANTS AT 1050 K

	$CH_3 + C_2Cl_2$	
P (atm)	C_3H_3Cl+Cl	$C_3H_3Cl_2$ (STABILIZED)
0.001	5.92E11	1.84E8
0.01	5.91E11	1.84E9
0.1	5.75E11	1.79E10
1.0	4.57E11	1.42E11
10.0	4.68E11	1.50E11

$$CH_3 + C_2HCl_3 \longrightarrow [C_3H_4Cl_3]^{\#} \longrightarrow C_3H_4Cl_2 + Cl. \qquad (34)$$

Reaction (34) is the major channel for dichloropropene formation, because the trichloroethylene is present in higher concentration than the dichloracetylene. Dichloropropene is one of the major products in this experiment below 800°C, as illustrated in Figure 16. This Figure clearly shows that the dichloropropene further decomposes at the higher temperatures.

The information required for QQRk analysis of methyl radical addition to trichloroethylene is listed in Table XV and the results in Table XVI. It is observed from the tabulated results of this calculation that the product formation, C3H4CL2+Cl, dominates stabilization of complex adduct for all pressure range, from 0.001 to 10 atm.

The detail mechanism developed for C2HCl3/CH2Cl2/CH4 system is listed in Table XVII. This kinetic scheme includes the important reactions invoving C2HCl3 in addition to 72 elementary steps tabulated for CH2Cl2/CH4 system in Table XI.

TABLE XVI RESULTS OF ACTIVATED COMPLEX THEORY
CALCULATION FOR RATE CONSTANTS AT TEMPERATURE 1050 K

P (atm)	C3H4Cl2+Cl	C3H4Cl3 (STABILIZED)
0.001	2.31E10	1.49E04
0.01	2.31E10	1.49E05
0.1	2.31E10	1.49E06
1.0	2.31E10	1.49E07
10.0	2.31E10	1.49E08

TABLE-XV

$$C_2HCl_3 + CH_3 \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [C_3H_4Cl_3]^{\#} \longrightarrow C_3H_4Cl_2+Cl \quad (2)$$

$$\longrightarrow C_3H_4Cl_3 \quad \text{STABILIZED}$$

k	A	E_a	Ref.
1	2.00E11	0.0	a
-1	5.65E13	34.92	a
2	5.95E14	18.9	b

<v> =1100. /cm d

LJ PARAMETERS : e

sigma = 5.94 A e/k = 534.4 cal

---

a
A_1 factor taken as 1/2 of $CH_3+C_2H_4$ [27];
A_{-1} from thermodynamics; E_{-1}=Del H.

b
A_2 is based on A_{-2}; A_{-2} taken as of $Cl+HC\equiv CCl$ (A=1.58E13) [7]; E_2=Del H.

c
<V> estimated from the average <V> of $C_2H_2Cl_4$, and 2*<V> of $C_2H_3Cl_3$.
Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

e
Taken as of the values for $C_3H_5Cl_3$. The values for $C_3H_5CL_3$ calculated by the equations and critical factors given in [32].

TABLE XVII- DETAILED MECHANISM FOR CH2CL2/CH4/Ar REACTION SYSTEM

REACTION	A	E_a	SOURCE
1. CH2Cl2 = CH2Cl + Cl	1.88E16	82.8	1
2. CH2Cl2 = CHCl + HCl	1.42E14	111.0	2
3. CH4 = CH3 + H	1.00E16	104.8	3
4. CH3Cl = CH3 + Cl	1.88E15	84.4	4
5. Cl + CH4 = HCl + CH3	3.10E13	3.6	7
6. Cl + C2H6 = HCl + C2H5	1.20E14	1.0	7
7. Cl + C2H4 = C2H4Cl	2.90E10	-8.0	8
8. Cl + C2H4 = C2H3 + HCl	1.00E13	5.1	7
9. Cl + CH2Cl2 = CH2Cl + Cl2	1.00E14	21.4	7
10. Cl + CH2Cl2 = CHCl2 + HCl	2.50E13	3.1	9
11. Cl + CH3Cl = CH3 + Cl2	1.00E14	25.0	7
12. Cl + CH3Cl = CH2Cl + HCl	3.10E13	3.6	9
13. Cl + C2H3Cl3 = C2H2Cl3 + HCl	3.16E13	3.5	7
14. Cl + C2H5Cl = C2H4Cl + HCl	2.00E13	1.5	7
15. Cl + C2H2Cl4 = C2HCl4 + HCl	1.41E12	2.5	7
16. Cl + H2 = H + HCl	4.80E13	1.3	11
17. Cl2 = Cl + Cl	7.69E08	55.6	11
18. HCl = H + Cl	6.09E08	97.3	11
19. H + CH4 = CH3 + H2	2.40E11	7.0	5
20. H + Cl2 = Cl + HCl	4.57E12	1.4	11
21. H2 = H + H	5.26E08	105.0	11
22. H + CH2Cl2 = HCl + CH2Cl	1.02E13	6.1	7

23. H + CH3Cl = HCl + CH3	9.00E13	7.7	33
24. H + C2H3Cl = HCl + C2H3	1.00E13	6.5	7
25. CH3 + CHCl2 = C2H4Cl2	7.35E10	-6.29	8
26. CH3 + CHCl2 = C2H4Cl + Cl	7.92E12	4.71	8
27. CH3 + CHCl2 = C2H3Cl + HCl	4.02E12	0.0447	8
28. CH3+C2H3Cl3=C2H3Cl2 + CH3Cl	2.00E11	1.08	9
29. CH3 + C2H5Cl = C2H5 + CH3Cl	1.06E12	2.36	12
30. CH3 + CHCl = C2H4Cl	7.30E08	-4.17	8
31. CH3 + CHCl = C2H4 + Cl	1.46E13	-0.107	8
32. CH3 + CH2Cl = C2H5Cl	2.79E11	-5.31	8
33. CH3 + CH2Cl = C2H4 + HCl	1.56E13	0.502	8
34. CH3 + CH2Cl = C2H5 + Cl	1.67E13	5.66	8
35. CH3 + CH2Cl = C2H4Cl + H	5.47E11	12.50	8
36. C2H6 = CH3 + CH3	7.94E16	89.4	3
37. C2H6 = C2H5 + H	1.26E16	98.0	3
38. CH3 + CH2Cl2 = CHCl2 + CH4	6.76E10	7.2	7
39. CH3 + CH2Cl2 = CH2Cl + CH3Cl	1.40E11	4.9	7
40. CH3 + C2H3Cl = C2H3 + CH3Cl	1.38E11	11.97	7
41. CH3 + CH3Cl = CH2Cl + CH4	3.31E11	9.4	7
42. C2H5 = C2H4 + H	4.00E13	40.9	3
43. C2H3 = C2H2 + H	1.58E12	38.3	13
44. C2H3 + CH4 = C2H4 + CH3	8.92E11	20.5	16
45. C2H6 + CH3 = C2H5 + CH4	1.58E12	11.7	14
46. CH2Cl + CH2Cl = C2H4Cl2	3.92E10	-6.32	8
47. CH2Cl + CH2Cl = C2H4Cl + Cl	6.12E12	4.68	8

48. CH2Cl + CH2Cl = C2H3Cl + HCl	2.59E12	0.0477	8
49. CHCl2 + CH2Cl = C2H3Cl3	9.26E09	-6.63	8
50. CHCl2 + CH2Cl = C2H3Cl2 + Cl	2.33E12	6.31	8
51. CHCl2 + CH2Cl = C2H2Cl2 + HCl	2.27E12	0.197	8
52. C2H2Cl + CH4 = C2H3Cl + CH3	7.94E11	10.1	15
53. C2H3Cl3 = C2H3Cl2 + Cl	2.40E16	73.2	17
54. C2H3Cl3 = C2H2Cl2 + HCl	3.80E13	49.09	17
55. C2H3Cl = C2H3 + Cl	3.66E15	87.6	18
56. C2H3Cl = C2H2 + HCl	3.55E13	68.73	19
57. C2H2Cl2 = C2H2Cl + Cl	1.04E16	89.17	20
58. C2H2Cl2 = C2HCl + HCl	7.10E13	69.11	21
59. C2H4Cl2 = C2H4Cl + Cl	6.00E15	77.42	22
60. C2H4Cl2 = C2H3Cl + HCl	2.88E13	54.35	23
61. C2HCl3 = C2HCl2 + Cl	1.74E15	92.1	24
62. C2HCl3 = C2Cl2 + HCl	7.10E13	77.61	25
63. C2HCl2 + CH3 = C2HCl + CH3Cl	1.26E12	1.50	26
64. CHCl2 + CHCl2 = C2H2Cl4	4.95E09	-6.93	8
65. CHCl2 + CHCl2 = C2HCl3 + HCl	3.91E11	-0.404	8
66. CHCl2 + CHCl2 = C2H2Cl3 + Cl	1.69E12	4.65	8
67. C2H2Cl4 = C2HCl3 + HCl	1.00E14	56.0	34
68. C2H5Cl = C2H4 + HCl	1.44E13	52.2	35
69. C2HCl3 + CH3 = C3H4Cl3	2.12E06	-3.93	8
70. C2HCl3 + CH3 = C3H4Cl2+Cl	2.00E11	4.51	8
71. C2Cl2 + CH3 = C3H3Cl2	3.38E10	2.65	8
72. C2Cl2 + CH3 = C3H3Cl+Cl	5.25E11	0.334	8

SOURCE

[1] A factor is based on Del S for reverse reaction, A_{-1}; A_{-1} is taken as twice of CH3+C2H5 (A=2E13), [33]; E_a = Del H.

[2] A = 10 $^{13.55}$*4; E_a = Del H + 40 [34].

[3] Dean, A. M., J. Phys. Chem., Vol. 89, 4600 (1985).

[4] A factor is based on A_{-1}; A_{-1}=4E13 taken as 2*A for CH3+C2H5 [33]; E_a=Del H.

[5] Robaugh, D., and Tsang, W., J. Phys. Chem., Vol. 90, 4159 (1986).

[6] Herman, I. P., Magnotta, F., Buss, R. J., and Lee Y. T., J. Chem. Phys., Vol. 79(4), 1789 (1983).

[7] Kerr, J. A., and Moss, S. J., HANDBOOK OF BIOMOLECULAR AND TERMOLECULAR GAS REACTIONS, Vol. I, CRC Press, 1981.

[8] Calculated by GISOQRRK computer program.

[9] Kerr, J. A., and Moss, S. J., HANDBOOK OF BIMOLECULAR AND TERMOLECULAR GAS REACTIONS, Vol. I, CRC Press, 1981.

[10] A taken as for rreaction C3H7+CH3 (A=1.26E12), [33]; E=0. [33].

[11] Ritter, E, Bozzelli, J. W., and Dean, A. M., J. Phys. Chem., (1988).

[12] A factor taken as 2/3 for C2H6+CH3 (A=1.5E12), [33]; E = Del H+2. [33].

[13] A factor from [3]; E_a from [3].

[14] A factor and E from [33], table 42 .

[15] A factor taken from reaction 53; E=Del H+E_{-1}.

[16] A factor taken for C2H5+CH4 (A=1.58E12) and E_a as of C3H5+C2H6 [33].

[17] Won, Y. S., Master Thesis, NJIT, 1988.

[18] A factor is based on A_{-1}; A_{-1}=2E13, taken for C3H7+CH3 [33]; E_a=Del H.

[19] A = $10^{13.55}$; E_a=Del H+45 [35].

[20] A factor is based on A_{-1}; A_{-1}=2E13, taken for C3H7+CH3; E_a=Del H.

[21] $A = 10^{13.55}*4$; E_a=Del H+45

[22] A factor is based on A_{-1}; A_{-1}=2.66E13 taken as 2*2/3 for CH3+C2H5 [33]; E_a=Del H.

[23] $A = 10^{13.55} * 6$; E_a = Del H+37, [34].

[24] A is based on A_{-1}; A_{-1}=1.E13, taken as 1/2 for C3H7+CH3 [33]; E_a= Del H.

[25] $A = 10^{13.55} * 3$; E_a = Del H + 45

[26] A factor taken as 2*1/2 for C3H5+C2H5 [33]; E_a=Del H+1.5, [7].

[27] Allara, D. L., and Shaw, R., J. Phys. Chem. Ref. Data, Vol. 9, No. 3, 1980.

[28] Setser, D. W., and Hassler, J. C., J. Chem. Phys., Vol. 45, 3237 (1966).

[29] Skinner, Unpublished paper.

[30] Weissman, M., and Benson, S. W., Int'l J. of Chem. Kin., Vol.16, 307 (1984).

[31] Benson, S. W., Thermochemical Kinetics, John Wiley, 1976.

[32] Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., The Properties of Gases and liquids 3rd. Ed., McGraw Hill, 1977.

[33] Baulch, J. Chem. Ref. Data, Vol. 10, Suppl. 1, 1981.

[34] $A = 10^{13.55}*10^{-4/4.6}*6$; E_a=Del H+35.

[35] $A = 10^{13.55}*10^{-4/4.6}*3$; E_a=Del H+35.

B. MODELING

Numerical calculations were carried out using the CHEMKIN computer code [28]. The CHEMKIN program, Fig.-26, is composed of four important pieces: the interpreter which reads the user's symbolic description of the reaction mechanism; the thermodynamic data base, which has the appropriate thermodynamic information and mass for all species present in mechanism with a format similar to the one used by the NASA complex chemical equilibrium code; the linking file which contains all the pertinent and current information on the elements, species, and reactions in the mechanism; and finally the CHEMKIN gas phase subroutines, which can be called to return information on the elements, species, reactions, equation of state, thermodynamic properties, chemical production rates, and derivatives of thermodynamic properties relative to any time in the integration. Generally the input to these subroutines are the state variables of the gas pressure or density, temperature and the species composition. All routines can be called with the species composition defined in terms of mass fractions or molar concentrations.

The CHEMKIN program does not provide a means to solve the governing equation; hence, selection and implementation of a solution method is chosen by the user. By addition of

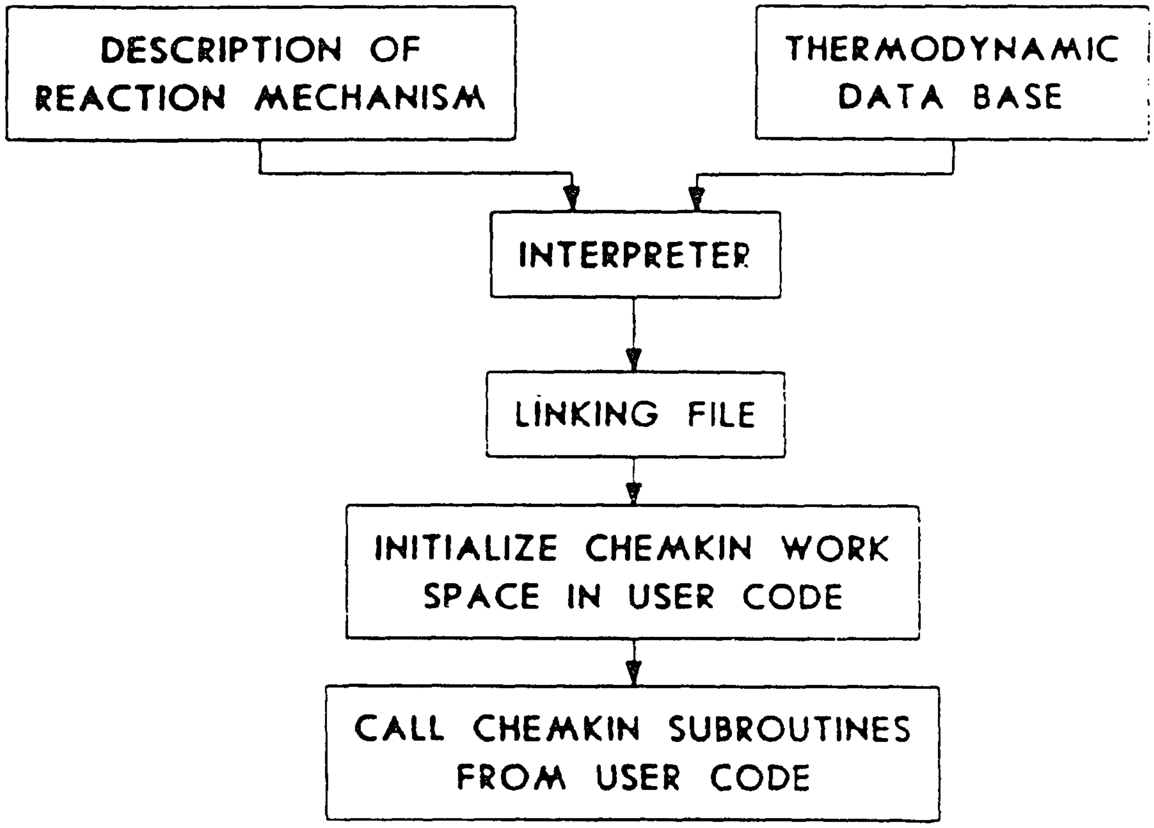


FIGURE-26 STRUCTURE OF THE CHEMKIN PACKAGE a FORTRAN code to describe the governing equations, mass conservations in this case, CHEMKIN package calculates reverse rate constants for each reaction step and species composition change with time utilizing thermodynamic properties and micro reversibility. The LSODE (Livermore Solver for Ordinary Differential Equations) program package was incorporated to solve the stiff system of first order differential equations.

The input data requirement to run CHEMKIN program include:

- Detailed reaction mechanism
- Mole fraction of all gases present in the reaction system
- Pressure and temperature at which the reaction system being studied
- Time increment at which the concentration of species present in the system be reported.

A Thermodynamic Data Base for species with C/H/Cl elements is developed at NJIT and used for modeling of the kinetic scheme of reaction systems investigated. For those species that thermodynamic information were not available in the data base, a thermo data was generated utilizing JANAFIT program. This program requires heat of formation and entropy of species at room temperature, and heat capacities in the temperature range of interest, as input. Heat of formations and entropies, as well as heat capacities, were calculated by group additivity method of Benson [44] when not available in literature. The calculated values for a number of C3 chlorocarbons are listed in Table XVI.

Figures 27 compares the experimental and calculated results for CH2Cl2 decomposition in methane/Ar atmosphere at 1025, 1075, 1125 °K in 4 and 10.5 mm ID reactors. This Figure 27 shows good agreement between calculated and experimental results for decay of parent reagent in the range of temperature and reactor diameters studied (4 to 16 mm ID).

TABLE XVIII THERMODYNAMIC PROPERTIES OF C_3 CHLOROCARBONS

SPECIES	H_f	S	C_p				
			300	500	800	1000	1500
C3H4Cl2	-3.41	80.48	21.75	28.31	35.27	38.22	43.2
C3H4Cl	43.21	74.07	18.05	24.40	30.39	33.02	37.86
C3H3Cl	9.66	46.50	17.10	23.74	28.87	30.99	34.96
C3H3Cl2	45.61	80.77	21.55	27.40	32.69	34.92	38.76
C3H3Cl3	-9.71	87.87	24.46	31.41	37.55	40.15	45.82
C3H2Cl2	9.06	53.21	20.60	26.74	31.17	32.89	35.86
C3H4Cl3	10.17	90.52	27.79	35.64	42.11	44.81	49.39

Figure 28 demonstrates concentration of products

FIGURE-27 DECAY PLOT OF CH2Cl2 IN CH2Cl2/CH4/Ar SYSTEM

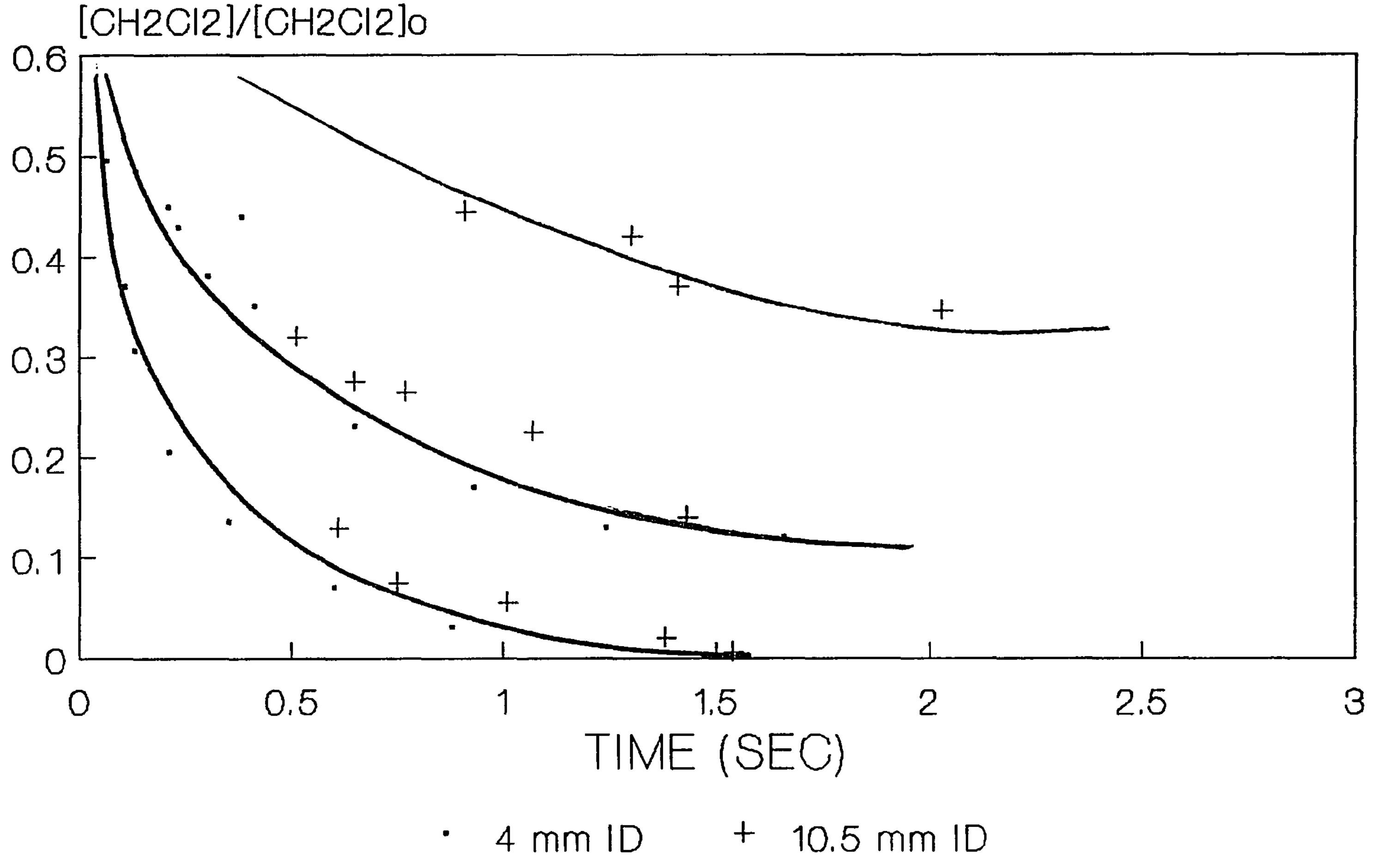
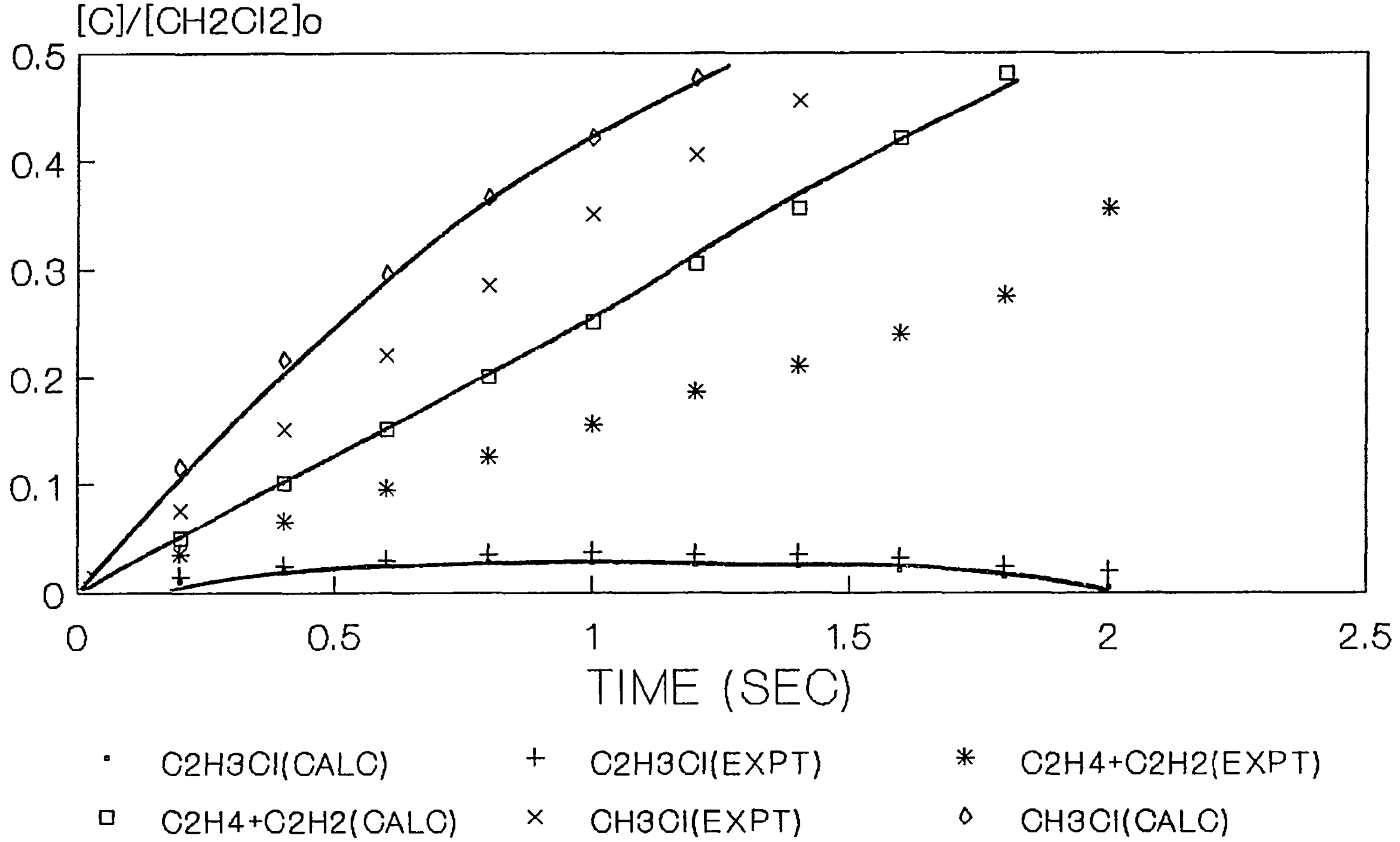


FIGURE-28 PRODUCT DISTRIBUTION VS TIME IN CH2Cl2/CH4/Ar SYSTEM AT 1075 K



C2H2+C2H4, CH3Cl, and C2H3Cl versus reaction time for CH2Cl2/CH4/Ar system at temperature of 1075 ^{o}K. The difference seen between calculated and experimental values for various product compounds could be due to the fact that our kinetic scheme does not include all species present in the reaction system. Therfore, generation of a higher numerical concentration values by CHEMKIN for existing hydrocarbons (or chlorocarbons) in the mechanism, is expectable.

Figure 29 illustrates change of concentration for major products, methylchloride, vinyl chloride and ethylene plus acetylene versus temperature for calculated and experimental values. Computational results indicate that ethylene concentration exceeds acetylene in temperature range of this experiment (1000 to 1250 ^{o}K). It is interesting to note, however, that the ratio [C2H2]/[C2H4] increases with temperature rise. This complies with our experimental result even though separate quantitative analysis of ethylene and acetylene was accomplished. The reason for such a conclusion is benzene formation at higher temperature range of (above 1125 ^{o}K) our experiment.

The CHEMKIN computer code was utilized to model the detail kinetic scheme developed for C2HCl3/CH2Cl2/CH4 system. Figures 30 and 31 compare experimental and calculated values of trichloroethylene and methylene chloride decomposition at temperatures 1075 and 1125 ^{o}K. It is apparent from these figures that the model reproduces the experimental data.

FIGURE-29 PRODUCT DISTRIBUTION VS TEMPERATURE IN CH2Cl2/CH4/Ar SYSTEM

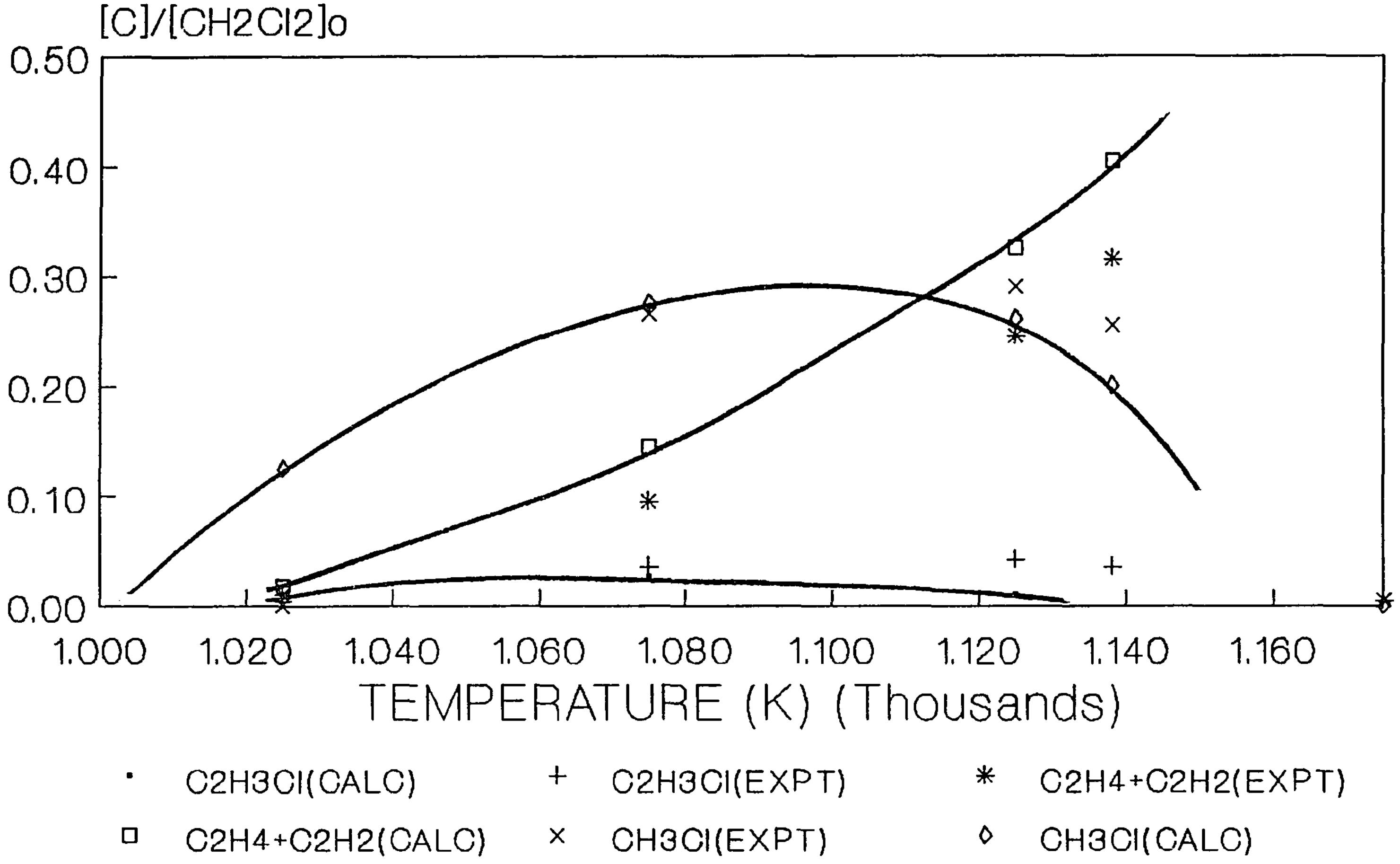


FIGURE-30 DECAY PLOT OF CH2Cl2 IN C2HCl3/CH2Cl2/CH4/Ar SYSTEM

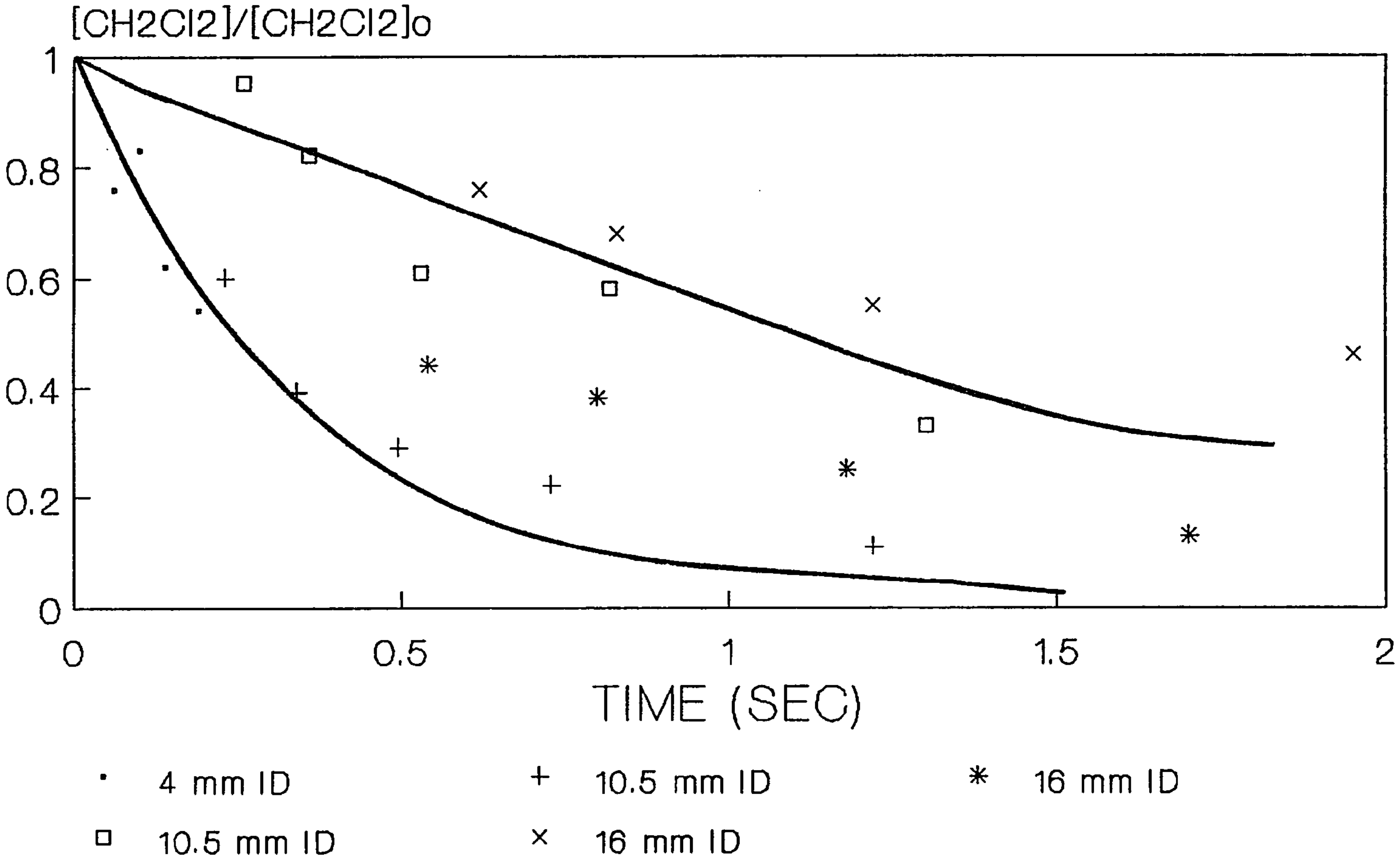
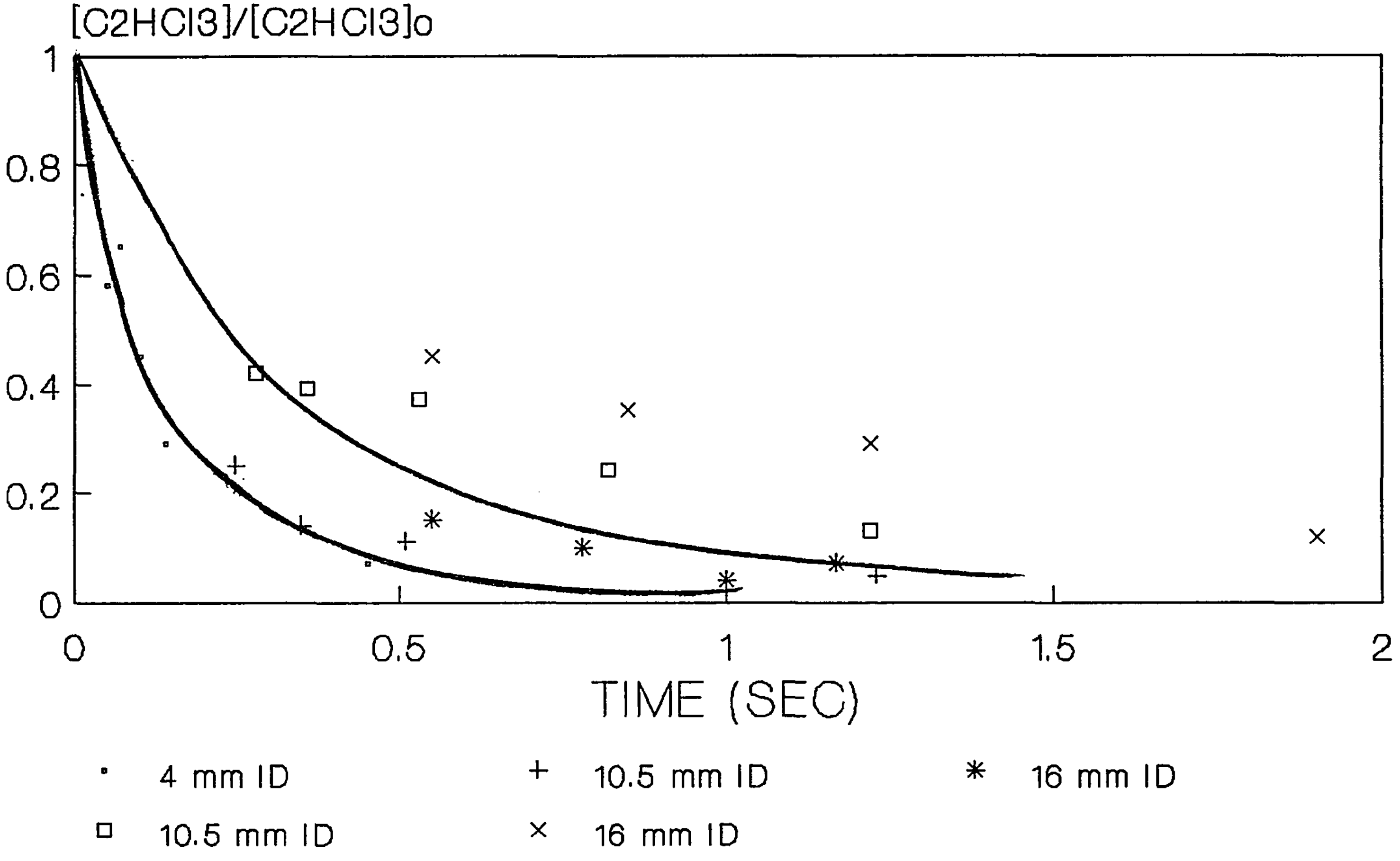


FIGURE-31 DECAY PLOT OF C2HCl3 IN C2HCl3/CH2Cl2/CH4/Ar SYSTEM



APPENDIX

TABLE-I

$$\begin{array}{lll} \mathrm{CH2Cl + CH2Cl} \xleftrightarrow[(-1)]{(1)} [\mathrm{C2H4Cl2}]^{\#} & \longrightarrow \mathrm{C2H3Cl2+H} & (2) \\ & \longrightarrow \mathrm{C2H4Cl+Cl} & (3) \\ & \longrightarrow \mathrm{C2H3Cl+HCl} & (4) \\ & \longrightarrow \mathrm{C2H4Cl2} & \mathrm{STABILIZED} \end{array}$$

k	A	E_a	Ref.
1	5.00E12	0.0	a
-1	5.50E17	93.2	a
2	5.00E14	94.6	b
3	3.55E15	78.11	c
4	1.92E13	52.35	d
-4	1.00E13	100.0	d
<v> = 797.2 /cm			e
LJ PARAMETERS :			f
sigma = 5.116 A		e/k = 472. cal	

---

[a] A_1 taken as of 1/2 the value given in [36] for CH2Cl+CH2Cl, (A=1E13); A_{-1} from thermodynamics; E_{-1}=Del H.

[b] A_2 is based on A_{-2}; A_{-2} taken as 2 of CH3+C2H5 (A=2E13) [33]; E_2=Del H.

[c] A_3 is based on A_{-3}; A_{-3} taken as Cl+C=CCl (A=1.58E13), [33]; E_a=Del H.

[d] $A_4=10^{13.55}*10^{-4/4.6}*4$ [37]; E_4=Del H+35 [34].

[e] Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

[f] Calculated by the equations and critical factors given in [38].

TABLE-II

$$\mathrm{CH3 + CH2Cl} \underset{(-1)}{\overset{(1)}{\longleftarrow\!\!\!\longrightarrow}} [\mathrm{C2H5Cl}]^{\#} \begin{array}{lll} \longrightarrow & \mathrm{C2H4Cl+H} & (2) \\ \longrightarrow & \mathrm{C2H5+Cl} & (3) \\ \longrightarrow & \mathrm{C2H4+HCl} & (4) \\ \longrightarrow & \mathrm{C2H5Cl\ STABILIZED} & \end{array}$$

k	A	E_a	Ref.
1	2.00E13	0.0	a
-1	1.40E17	92.60	a
2	6.70E14	98.00	b
3	1.98E15	81.52	c
4	1.44E13	52.20	d
-4	1.00E13	100.00	d
<v> =1265.3 /cm			e
LJ PARAMETERS :			f
sigma = 4.9 A		e/k = 400.cal	

---

[a] A_1 taken as 2/5 of the value given in [36] (A=5E13); A_{-1} from thermodynamics; E_{-1}=Del H.

[b] A_2 based on A_{-2}; A_{-2} taken as 2/3 of H+C2H5 (A=4E13), [33]; E_a=Del H.

[c] A_3 based on A_{-3}; A_{-3}=2.E13 as for CH3+C2H5 [33]; E_3=Del H.

[d] $A_4=10^{13.55}*10^{-4/4.6}*3$ [33]; E_4=Del H+35 [34].

[e] Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

[f] Calculated by the equations and critical factors given in [38].

TABLE-III

$$\mathrm{CHCl2 + CHCl2} \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [\mathrm{C2H2Cl4}]^{\#} \begin{array}{l} \longrightarrow \mathrm{C2H2Cl3+Cl} \quad (2)\\ \longrightarrow \mathrm{C2HCl3+HCl} \quad (3)\\ \longrightarrow \mathrm{C2H2Cl4} \quad \text{STABILIZED} \end{array}$$

k	A	E_a	Ref.
1	9.91E11	0.0	a
-1	5.90E17	88.6	a
2	6.66E15	74.6	b
3	1.91E13	48.74	c

<v> = 578.0 /cm　　d

LJ PARAMETERS :　　e

sigma = 5.91 A　　e/k = 525.9 cal

---

a
A factor taken as of 1/4 of C3H7+C3H7 (A=4E12) [33];
A_{-1} from thermodynamics (Del S); E_{-1}=Del H.

b
A_2 is based on A_{-2}; A_{-2} taken as 1/4 ofCH3+C2H5 (A=2E13) [33];
E_2=Del H.

c
$A_3=10^{13.55}*10^{-4/4.6}*4$ [37]; E_3=Del H+35 [34].

d
Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

e
Calculated by the equations and critical factors given in [38].

TABLE-IV

$$\begin{array}{lll}
\text{CHCl2 + CH2Cl} \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [\text{C2H3Cl3}]^{\#} & \longrightarrow \text{C2H3Cl2+Cl} & (2) \\
 & \longrightarrow \text{C2H2Cl2+HCl} & (3) \\
 & \longrightarrow \text{C2H3Cl3} & \text{STABILIZED}
\end{array}$$

k	A	E_a	Ref.
1	2.65E12	0.0	a
-1	3.03E17	92.2	a
2	2.20E15	77.7	b
3	3.35E13	49.07	c
<v> = 687.7 /cm			d
LJ PARAMETERS :			e
sigma = 5.71 A		e/k = 498.9 cal	

---

[a] A_1 taken as 1/3 of C2H5+C3H7 (A=7.94E12) [33]; A_{-1} from thermodynamics (Del S); E_{-1}=Del H.

[b] A_2 is based on A_{-2}; A_{-2} taken as of CH3+C4H9 (A=2E13) [33]; E_2=Del H.

[c] $A_3=10^{13.55}*10^{-4/4.6}*(9+5)/2$ [37]; E_3=Del H+35 [34].

[d] Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

[e] Calculated by the equations and critical factors given in [38].

TABLE-V

$$\text{C2HCl3 + CH3} \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [\text{C3H4Cl3}]^{\#} \longrightarrow \text{C3H4Cl2+Cl} \quad (2)$$
$$\longrightarrow \text{C3H4Cl3} \quad \text{STABILIZED}$$

k	A	E_a	Ref.
1	2.00E11	0.0	a
-1	5.65E13	34.92	a
2	5.95E14	18.9	b
<v> =1100. /cm			d
LJ PARAMETERS :			e
sigma = 5.94 A		e/k = 534.4 cal	

a
A_1 factor taken as 1/2 of CH3+C2H4 [33];
A_{-1} from thermodynamics; E_{-1}=Del H.

b
A_2 is based on A_{-2}; A_{-2} taken as of Cl+C=CCl (A=1.58E13) [7]; E_2=Del H.

c
<V> estimated from the average <V> of C2H2Cl4, and 2*<V> of C2H3Cl3.
Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

e
Taken as of the vlues for C3H5Cl3. The values for C3H5CL3 calculated by the equations and critical factors given in [38].

TABLE-VI

$$\begin{array}{llll} \mathrm{CH_3 + C_2Cl_2} \underset{(-1)}{\overset{(1)}{\longleftrightarrow}} [\mathrm{C_3H_3Cl_2}]^{\#} & \longrightarrow & \mathrm{C_3H_3Cl + Cl} & (2) \\ & \longrightarrow & \mathrm{C_3H_3Cl_2}\ \text{STABILIZED} & \end{array}$$

k	A	E_a	Ref.
1	6.30E11	7.7	a
-1	4.26E13	47.10	a
2	3.26E09	0.0	b

<v> = 1040. /cm [c]

LJ PARAMETERS : [d]

sigma = 5.575 A e/k = 483.7 cal

---

[a] A_1 taken as of CH3+C2H2 (A=6.3E11), [3]; E=7.7 [3]. A_{-1} from thermodynamics; E_{-1}=Del H+7.2, [3].

[b] A_2 based on A_{-2}; A_{-2} taken as of Cl+C=CCl (A=1.58E13),[3]; E_2=Del H.

[c] <V> taken as <V> for C3H3Cl4 -200; <V> for C3H3Cl4 calculated by averaging twice the value for C2HCl3, and C2H4Cl2.
Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.

[d] Taken as of the values for C3H5Cl2. The valuse for C3H5Cl2 is calculated by the equations and critical factors given in [32].

```
          ***** GISOQRRK : USES NON-INTEGER VALUES FOR
                   THE NUMBER OF QUANTA *****

               **** GAMMA FUNCTION EVALUATION ****
                    STERLING ASYMTOTIC SERIES

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK


            P2       P3         P5
             \       /          |
              \K2   /K3         |K5
        K1     \   /      K4    |      K6
   R   ======   A*   ======     B*   ------   P6
       K-1      |         K-4   |
                |               |
                A               B


R (REACTANTS)
 CH2Cl + CHCl2

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
 C2H3CL3             C2H3CL2 + Cl         C2H2CL2 + HCl

B* (ISOMER STABIL)  P5 (1ST B* DECOMP)  P6 (2ND B* DECOMP)


  FREQ  687.70 CM-1           VIB MODES 18

 A1  2.650D+12      TN  0.000D+00      EA    .00D+00 (K1)

 MASS  133.50      SIGMA 5.71 A       WELL 498.90 CAL

 MASS   39.95      SIGMA  3.330 A

 WELL136.00 CAL     E COLL  630.00 CAL    3RD BODY

  A-1   3.030D+17      EA  92.20 (K-1)

  A2    2.200D+15      EA  77.70 (K2 )

  A3    3.350D+13      EA  49.07 (K3 )

  A4    0.000D+00      EA    .00 (K4 )

  A-4   0.000D+00      EA    .00 (K-4)

  A5    0.000D+00      EA    .00 (K5 )
```

```
 A6    0.000D+00       EA     .00 (K6 )

DEL H (K4)    .00       XLAM    .0


# T s    6     T s  KELVIN   750.  850.  950. 1050. 1150. 1250.


#P s    6      P s TORR       .760    7.60  76.00  760.0  2000.0

 T DIST   950.            P DIST    760.000           DIST OPT  -1

  -1  -  DISTRIBUTION ONLY FOR Tdist and Pdist
   0  -  ALL DISTRIBUTIONS & CHANNEL SUMMARIES
   1  -  DISTRIBUTION AT Tdist AND ALL PRESSURES
   2  -  DISTRIBUTION AT Pdist AND ALL TEMPERATURES
   3  -  CHANNEL SUMMARY ONLY: ALL TEMP & PRESSURES
   4  -  CHANNEL SUMMARY ONLY FOR Tdist & Pdist ONLY
   5  -  CHANNEL SUMMARY FOR Tdist AND ALL PRESSURES
   6  -  CHANNEL SUMMARY FOR Pdist AND ALL TEMPERATURES
   7  -  SUPPRESS ALL DISTRIBUTIONS AND CHANNEL SUMMARIES

    BARRIERS IN TERMS OF # OF QUANTA (INTEGER/DECIMAL)
    DECIMAL VALUES ARE USED IN THIS CALCULATION
    INTEGER VALUES ARE FOR COMPARISON ONLY

***** FOR INTEGER QUANTA USE GISOMACT *****


E-1  47  46.894     E2  40  39.519     E3  25  24.958


E4   0    .000     E-4   0    .000


E5   0    .000     E6   0    .000


DELTA H iso    0     .000
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E-01TORR

 CH2Cl + CHCl2    =   C2H3CL3           T  750. K TO 1250. K
0                           NON-LINEAR REGRESSION RESULTS
  9.830E+28 * (T^   -6.49) exp( -    4.52 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)        %err
   1       750.00        1.04373E+09    1.04175E+09     -.19
   2       850.00        6.58485E+08    6.60844E+08      .36
   3       950.00        4.25205E+08    4.25663E+08      .11
   4      1050.00        2.80064E+08    2.79328E+08     -.26
   5      1150.00        1.87456E+08    1.86899E+08     -.30
   6      1250.00        1.27102E+08    1.27465E+08      .29
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
P =   7.60E-01 TORR

0 CH2Cl + CHCl2    =   C2H3CL3           T  750. K TO 1250. K
                 A =   6.21E+06     E = -7.79E+00 KCAL
           T            K EXP            K CALC          PERENT ERROR
             750.         1.04E+09         1.16E+09           -9.8
             850.         6.58E+08         6.26E+08            5.2
             950.         4.25E+08         3.85E+08           10.4
            1050.         2.80E+08         2.60E+08            7.7
            1150.         1.87E+08         1.88E+08            -.2
            1250.         1.27E+08         1.43E+08          -11.1
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E-01TORR

 CH2Cl + CHCl2    =   C2H3CL2 + Cl      T  750. K TO 1250. K
0                           NON-LINEAR REGRESSION RESULTS
  2.288E+12 * (T^    -.03) exp( -    5.71 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)        %err
   1       750.00        4.09359E+10    4.06946E+10     -.59
   2       850.00        6.29091E+10    6.36535E+10     1.18
   3       950.00        9.04060E+10    9.05830E+10      .20
   4      1050.00        1.21477E+11    1.20492E+11     -.81
   5      1150.00        1.53641E+11    1.52479E+11     -.76
   6      1250.00        1.84319E+11    1.85787E+11      .80
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E-01 TORR

0 CH2Cl + CHCl2    =   C2H3CL2 + Cl      T  750. K TO 1250. K
                 A =   1.81E+12      E =  5.66E+00 KCAL
            T            K EXP            K CALC          PERENT ERROR
              750.        4.09E+10          4.07E+10                .5
              850.        6.29E+10          6.36E+10              -1.1
              950.        9.04E+10          9.05E+10               -.1
             1050.        1.21E+11          1.20E+11                .9
             1150.        1.54E+11          1.52E+11                .8
             1250.        1.84E+11          1.86E+11               -.8
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E-01TORR

 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
0                           NON-LINEAR REGRESSION RESULTS
  3.204E+19 * (T^  -2.14) exp( -    3.28 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00       2.59122E+12    2.58301E+12      -.32
   2      850.00       2.54578E+12    2.56123E+12       .61
   3      950.00       2.47350E+12    2.47763E+12       .17
   4     1050.00       2.37125E+12    2.36078E+12      -.44
   5     1150.00       2.23933E+12    2.22861E+12      -.48
   6     1250.00       2.08223E+12    2.09198E+12       .47
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E-01 TORR

0 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
                 A =   1.59E+12      E = -7.74E-01 KCAL
            T            K EXP            K CALC          PERENT ERROR
              750.        2.59E+12          2.67E+12              -3.1
              850.        2.55E+12          2.52E+12               1.2
              950.        2.47E+12          2.40E+12               3.2
             1050.        2.37E+12          2.31E+12               2.8
             1150.        2.24E+12          2.23E+12                .3
             1250.        2.08E+12          2.17E+12              -4.2
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E-01TORR

 K-1(T) COMPLEX A DISSOC  T  750. K TO 1250. K
0                                NON-LINEAR REGRESSION RESULTS
  5.610E+11 * (T^    .55) exp( -   10.67 KCAL/RT)

  NO    TEM (K)         KI (EXP)       KI (CAL)       %err
   1      750.00       1.67971E+10    1.66472E+10     -.89
   2      850.00       4.06533E+10    4.14311E+10     1.91
   3      950.00       8.56703E+10    8.56872E+10      .02
   4     1050.00       1.56998E+11    1.55166E+11    -1.17
   5     1150.00       2.56838E+11    2.54572E+11     -.88
   6     1250.00       3.83328E+11    3.87339E+11     1.05


1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR   P =  7.60E-01 TORR

 K-1(T) COMPLEX A DISSOC  T  750. K TO 1250. K
                 A =  4.30E+13      E =  1.17E+01 KCAL
           T           K EXP           K CALC          PERENT ERROR
             750.        1.68E+10        1.65E+10             1.8
             850.        4.07E+10        4.16E+10            -2.3
             950.        8.57E+10        8.64E+10             -.9
            1050.        1.57E+11        1.56E+11              .6
            1150.        2.57E+11        2.54E+11              .9
            1250.        3.83E+11        3.84E+11             -.1


 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+00TORR

 CH2Cl + CHCl2   =  C2H3CL3          T  750. K TO 1250. K
0                                NON-LINEAR REGRESSION RESULTS
  1.110E+30 * (T^  -6.50) exp( -    4.56 KCAL/RT)

  NO    TEM (K)         KI (EXP)       KI (CAL)       %err
   1      750.00       1.03889E+10    1.03694E+10     -.19
   2      850.00       6.56442E+09    6.58775E+09      .36
   3      950.00       4.24299E+09    4.24754E+09      .11
   4     1050.00       2.79645E+09    2.78915E+09     -.26
   5     1150.00       1.87254E+09    1.86701E+09     -.30
   6     1250.00       1.27002E+09    1.27362E+09      .28
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+00 TORR

0 CH2Cl + CHCl2    =   C2H3CL3           T  750. K TO 1250. K
                A =   6.24E+07      E = -7.78E+00 KCAL
           T            K EXP            K CALC          PERENT ERROR
             750.        1.04E+10         1.15E+10             -9.9
             850.        6.56E+09         6.24E+09              5.2
             950.        4.24E+09         3.84E+09             10.4
            1050.        2.80E+09         2.60E+09              7.7
            1150.        1.87E+09         1.88E+09              -.2
            1250.        1.27E+09         1.43E+09            -11.2
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+00TORR

 CH2Cl + CHCl2    =  C2H3CL2 + Cl      T  750. K TO 1250. K
0                                    NON-LINEAR REGRESSION RESULTS
  2.481E+12 * (T^    -.04) exp( -    5.74 KCAL/RT)

  NO    TEM (K)         KI (EXP)       KI (CAL)        %err
   1      750.00      4.08472E+10    4.06069E+10     -.59
   2      850.00      6.28257E+10    6.35673E+10     1.18
   3      950.00      9.03300E+10    9.05064E+10      .20
   4     1050.00      1.21410E+11    1.20427E+11     -.81
   5     1150.00      1.53584E+11    1.52425E+11     -.75
   6     1250.00      1.84272E+11    1.85735E+11      .79
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+00 TORR

0 CH2Cl + CHCl2    =   C2H3CL2 + Cl      T  750. K TO 1250. K
                A =   1.82E+12      E =  5.66E+00 KCAL
           T            K EXP            K CALC          PERENT ERROR
             750.        4.08E+10         4.06E+10               .5
             850.        6.28E+10         6.35E+10             -1.1
             950.        9.03E+10         9.05E+10              -.1
            1050.        1.21E+11         1.20E+11               .9
            1150.        1.54E+11         1.52E+11               .8
            1250.        1.84E+11         1.86E+11              -.9
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+00TORR

 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
0                                NON-LINEAR REGRESSION RESULTS
  3.594E+19 * (T^  -2.15) exp( -    3.32 KCAL/RT)

  NO    TEM (K)        KI (EXP)      KI (CAL)       %err
   1      750.00      2.58199E+12   2.57385E+12     -.32
   2      850.00      2.53999E+12   2.55532E+12      .60
   3      950.00      2.46980E+12   2.47391E+12      .17
   4     1050.00      2.36885E+12   2.35845E+12     -.44
   5     1150.00      2.23776E+12   2.22709E+12     -.48
   6     1250.00      2.08119E+12   2.09089E+12      .47
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR   P =  7.60E+00 TORR

0 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
                A =  1.60E+12      E = -7.62E-01 KCAL
           T            K EXP           K CALC          PERENT ERROR
             750.        2.58E+12        2.67E+12           -3.1
             850.        2.54E+12        2.51E+12            1.2
             950.        2.47E+12        2.39E+12            3.2
            1050.        2.37E+12        2.30E+12            2.9
            1150.        2.24E+12        2.23E+12             .3
            1250.        2.08E+12        2.17E+12           -4.2
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+00TORR

K-1(T) COMPLEX A DISSOC  T  750. K TO 1250. K
0                                NON-LINEAR REGRESSION RESULTS
  5.869E+11 * (T^    .55) exp( -  10.69 KCAL/RT)

  NO    TEM (K)        KI (EXP)      KI (CAL)       %err
   1      750.00      1.67760E+10   1.66264E+10     -.89
   2      850.00      4.06216E+10   4.13984E+10     1.91
   3      950.00      8.56283E+10   8.56449E+10      .02
   4     1050.00      1.56948E+11   1.55118E+11    -1.17
   5     1150.00      2.56783E+11   2.54520E+11     -.88
   6     1250.00      3.83272E+11   3.87279E+11     1.05
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+01 TORR

 K-1(T) COMPLEX A DISSOC  T  750. K TO 1250. K
                  A =  4.31E+13        E =  1.17E+01 KCAL
             T             K EXP             K CALC           PERENT ERROR
                750.      1.66E+10         1.65E+10                1.6
                850.      4.06E+10         4.16E+10               -2.3
                950.      8.56E+10         8.64E+10                -.9
               1050.      1.57E+11         1.56E+11                 .6
               1150.      2.57E+11         2.54E+11                 .9
               1250.      3.83E+11         3.84E+11                -.1
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+01TORR

 CH2Cl + CHCl2    =   C2H3CL3            T  750. K TO 1250. K
0                               NON-LINEAR REGRESSION RESULTS
  3.393E+31 * (T^  -6.64) exp( -    4.96 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)        %err
   1      750.00       9.93407E+10    9.91654E+10     -.18
   2      850.00       6.36881E+10    6.39003E+10      .33
   3      950.00       4.15519E+10    4.15944E+10      .10
   4     1050.00       2.75543E+10    2.74868E+10     -.25
   5     1150.00       1.85270E+10    1.84751E+10     -.28
   6     1250.00       1.26011E+10    1.26348E+10      .27
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+01 TORR

0 CH2Cl + CHCl2    =   C2H3CL3          T  750. K TO 1250. K
                 A =   6.56E+08     E = -7.64E+00 KCAL
            T            K EXP           K CALC           PERENT ERROR
               750.       9.93E+10        1.10E+11             -10.1
               850.       6.37E+10        6.04E+10               5.4
               950.       4.16E+10        3.75E+10              10.7
              1050.       2.76E+10        2.55E+10               7.9
              1150.       1.85E+10        1.86E+10               -.3
              1250.       1.26E+10        1.42E+10             -11.4
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+01TORR

 CH2Cl + CHCl2    =  C2H3CL2 + Cl      T  750. K TO 1250. K
0                             NON-LINEAR REGRESSION RESULTS
  5.383E+12 * (T^    -.13) exp( -    5.99 KCAL/RT)

  NO    TEM (K)          KI (EXP)      KI (CAL)       %err
   1      750.00        3.99875E+10   3.97574E+10     -.58
   2      850.00        6.20083E+10   6.27242E+10     1.15
   3      950.00        8.95800E+10   8.97512E+10      .19
   4     1050.00        1.20745E+11   1.19790E+11     -.79
   5     1150.00        1.53013E+11   1.51883E+11     -.74
   6     1250.00        1.83797E+11   1.85225E+11      .78
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+01 TORR

0 CH2Cl + CHCl2    =   C2H3CL2 + Cl      T  750. K TO 1250. K
                A =   1.87E+12      E =  5.73E+00 KCAL
             T           K EXP            K CALC          PERENT ERROR
                750.       4.00E+10         3.98E+10                .4
                850.       6.20E+10         6.27E+10              -1.0
                950.       8.96E+10         8.96E+10                .0
               1050.       1.21E+11         1.20E+11                .9
               1150.       1.53E+11         1.52E+11                .7
               1250.       1.84E+11         1.86E+11              -1.0
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+01TORR

  CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
0                             NON-LINEAR REGRESSION RESULTS
  1.052E+20 * (T^  -2.28) exp( -    3.67 KCAL/RT)

  NO    TEM (K)          KI (EXP)      KI (CAL)       %err
   1      750.00        2.49410E+12   2.48660E+12     -.30
   2      850.00        2.48399E+12   2.49829E+12      .58
   3      950.00        2.43366E+12   2.43758E+12      .16
   4     1050.00        2.34525E+12   2.33542E+12     -.42
   5     1150.00        2.22222E+12   2.21203E+12     -.46
   6     1250.00        2.07089E+12   2.08014E+12      .45
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =   7.60E+01 TORR

0 CH2Cl + CHCl2     =     C2H2CL2 + HCl     T  750. K TO 1250. K
                 A =   1.67E+12        E = -6.52E-01 KCAL
           T            K EXP              K CALC            PERENT ERROR
            750.          2.49E+12           2.58E+12              -3.3
            850.          2.48E+12           2.45E+12               1.3
            950.          2.43E+12           2.35E+12               3.4
           1050.          2.35E+12           2.28E+12               3.0
           1150.          2.22E+12           2.22E+12                .3
           1250.          2.07E+12           2.17E+12              -4.4


 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+01TORR

K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
0                             NON-LINEAR REGRESSION RESULTS
  9.117E+11 * (T^     .49) exp( -   10.83 KCAL/RT)

  NO    TEM (K)           KI (EXP)        KI (CAL)        %err
   1      750.00        1.65689E+10     1.64220E+10       -.89
   2      850.00        4.03086E+10     4.10755E+10       1.90
   3      950.00        8.52117E+10     8.52250E+10        .02
   4     1050.00        1.56450E+11     1.54638E+11      -1.16
   5     1150.00        2.56239E+11     2.54002E+11       -.87
   6     1250.00        3.82717E+11     3.86687E+11       1.04


1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =   7.60E+01 TORR

 K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
                 A =   4.38E+13        E =   1.18E+01 KCAL
           T            K EXP              K CALC            PERENT ERROR
            750.          1.66E+10           1.63E+10               1.7
            850.          4.03E+10           4.12E+10              -2.3
            950.          8.52E+10           8.59E+10               -.8
           1050.          1.56E+11           1.55E+11                .6
           1150.          2.56E+11           2.54E+11                .9
           1250.          3.83E+11           3.83E+11               -.2
```

```
0         P=  7.600E+02 TORR       T=    950.0 K
0      DEACTIVATION K = 5.50E+14      COLL  EFFICIENCY =  1.70E-01
       DEACT K*M=  1.20E+09
      LEVEL
      ABOVE
         E(1)     F(E)        K-1(E)          K2(E)        K3(E)         K4(E)
          0     3.97E-04    2.27E+02      8.83E+05     1.23E+09      0.00E+
          1     2.52E-03    3.01E+03      1.97E+06     1.59E+09      0.00E+
          2     8.45E-03    2.12E+04      4.12E+06     2.01E+09      0.00E+
          3     1.99E-02    1.06E+05      8.11E+06     2.53E+09      0.00E+
          4     3.68E-02    4.16E+05      1.52E+07     3.13E+09      0.00E+
          5     5.71E-02    1.38E+06      2.71E+07     3.85E+09      0.00E+
          6     7.73E-02    4.00E+06      4.66E+07     4.69E+09      0.00E+
          7     9.35E-02    1.04E+07      7.73E+07     5.66E+09      0.00E+
          8     1.03E-01    2.49E+07      1.24E+08     6.77E+09      0.00E+
          9     1.05E-01    5.51E+07      1.94E+08     8.05E+09      0.00E+
         10     1.00E-01    1.14E+08      2.96E+08     9.49E+09      0.00E+
         11     9.00E-02    2.25E+08      4.40E+08     1.11E+10      0.00E+
         12     7.67E-02    4.22E+08      6.42E+08     1.30E+10      0.00E+
         13     6.25E-02    7.59E+08      9.17E+08     1.50E+10      0.00E+
         14     4.88E-02    1.31E+09      1.29E+09     1.73E+10      0.00E+
         15     3.67E-02    2.20E+09      1.78E+09     1.98E+10      0.00E+
         16     2.67E-02    3.57E+09      2.42E+09     2.26E+10      0.00E+
         17     1.89E-02    5.64E+09      3.24E+09     2.56E+10      0.00E+
         18     1.29E-02    8.69E+09      4.29E+09     2.89E+10      0.00E+
         19     8.66E-03    1.31E+10      5.60E+09     3.26E+10      0.00E+
         20     5.65E-03    1.93E+10      7.24E+09     3.65E+10      0.00E+
         21     3.61E-03    2.80E+10      9.26E+09     4.07E+10      0.00E+
         22     2.26E-03    3.98E+10      1.17E+10     4.53E+10      0.00E+
         23     1.38E-03    5.56E+10      1.47E+10     5.02E+10      0.00E+
         24     8.35E-04    7.66E+10      1.83E+10     5.55E+10      0.00E+


            T =    950. K      Kinf =    .27E+13
            KA   =   3.48E+11      KA/Kinf   =   1.31E-01
            K-1  =   8.13E+10      K-1/Kinf  =   3.07E-02
            KP2  =   8.30E+10      KP2/Kinf  =   3.13E-02
            KP3  =   2.14E+12      KP3/Kinf  =   8.07E-01
            Kiso=    0.00E+00      Kiso/Kinf=    0.00E+00
            KB   =   0.00E+00      KB/Kinf   =   0.00E+00
            K-4  =   0.00E+00      K-4/Kinf  =   0.00E+00
            KP5  =   0.00E+00      KP5/Kinf  =   0.00E+00
            KP6  =   0.00E+00      KP6/Kinf  =   0.00E+00

                 SUM of Ki/Kinf =    .10E+01
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+02TORR

 CH2Cl + CHCl2     =  C2H3CL3            T  750. K TO 1250. K
0                               NON-LINEAR REGRESSION RESULTS
  9.470E+34 * (T^  -7.31) exp( -    7.24 KCAL/RT)

  NO    TEM (K)          KI (EXP)        KI (CAL)        %err
   1      750.00        7.06335E+11     7.05075E+11     -.18
   2      850.00        4.98347E+11     5.00059E+11      .34
   3      950.00        3.47881E+11     3.48185E+11      .09
   4     1050.00        2.41952E+11     2.41355E+11     -.25
   5     1150.00        1.68265E+11     1.67821E+11     -.26
   6     1250.00        1.17232E+11     1.17536E+11      .26
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR   P =   7.60E+02 TORR

0 CH2Cl + CHCl2     =   C2H3CL3            T  750. K TO 1250. K
                A =   9.26E+09      E = -6.63E+00 KCAL
             T          K EXP            K CALC          PERENT ERROR
               750.        7.06E+11         7.94E+11           -11.1
               850.        4.98E+11         4.70E+11             5.9
               950.        3.48E+11         3.11E+11            11.8
              1050.        2.42E+11         2.23E+11             8.7
              1150.        1.68E+11         1.69E+11             -.3
              1250.        1.17E+11         1.34E+11           -12.4
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+02TORR

 CH2Cl + CHCl2     =  C2H3CL2 + Cl      T  750. K TO 1250. K
0                               NON-LINEAR REGRESSION RESULTS
  1.307E+15 * (T^   -.80) exp( -    7.84 KCAL/RT)

  NO    TEM (K)          KI (EXP)        KI (CAL)        %err
   1      750.00        3.33743E+10     3.32014E+10     -.52
   2      850.00        5.51667E+10     5.57427E+10     1.04
   3      950.00        8.29512E+10     8.30829E+10      .16
   4     1050.00        1.14658E+11     1.13845E+11     -.71
   5     1150.00        1.47666E+11     1.46700E+11     -.65
   6     1250.00        1.79268E+11     1.80508E+11      .69
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+02 TORR

0 CH2Cl + CHCl2    =   C2H3CL2 + Cl      T  750. K TO 1250. K
                A =  2.33E+12      E =  6.31E+00 KCAL
           T            K EXP            K CALC          PERENT ERROR
            750.          3.34E+10         3.36E+10              -.8
            850.          5.52E+10         5.54E+10              -.4
            950.          8.30E+10         8.21E+10              1.1
           1050.          1.15E+11         1.13E+11              1.6
           1150.          1.48E+11         1.47E+11               .6
           1250.          1.79E+11         1.83E+11             -2.1
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+02TORR

 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
0                            NON-LINEAR REGRESSION RESULTS
  6.011E+22 * (T^  -3.05) exp( -    5.98 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)        %err
   1      750.00       1.89548E+12    1.89037E+12     -.27
   2      850.00       2.05899E+12    2.06969E+12      .52
   3      950.00       2.13782E+12    2.14069E+12      .13
   4     1050.00       2.14166E+12    2.13365E+12     -.37
   5     1150.00       2.08307E+12    2.07474E+12     -.40
   6     1250.00       1.97618E+12    1.98396E+12      .39
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+02 TORR

0 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
                A =  2.27E+12      E =  1.97E-01 KCAL
           T            K EXP            K CALC          PERENT ERROR
            750.          1.90E+12         1.99E+12             -4.6
            850.          2.06E+12         2.02E+12              2.1
            950.          2.14E+12         2.04E+12              4.7
           1050.          2.14E+12         2.06E+12              3.8
           1150.          2.08E+12         2.08E+12               .2
           1250.          1.98E+12         2.09E+12             -5.6
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+02TORR
 K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
0                               NON-LINEAR REGRESSION RESULTS
  3.174E+13 * (T^    .06) exp( -   12.02 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00       1.48076E+10    1.46799E+10     -.86
   2      850.00       3.74996E+10    3.81985E+10     1.86
   3      950.00       8.13443E+10    8.13294E+10     -.02
   4     1050.00       1.51730E+11    1.50034E+11    -1.12
   5     1150.00       2.50998E+11    2.48939E+11     -.82
   6     1250.00       3.77319E+11    3.81056E+11      .99
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR   P =  7.60E+02 TORR

 K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
                A =  5.03E+13     E =  1.21E+01 KCAL
             T          K EXP            K CALC           PERENT ERROR
               750.       1.48E+10         1.47E+10              1.0
               850.       3.75E+10         3.82E+10             -1.9
               950.       8.13E+10         8.14E+10              -.1
              1050.       1.52E+11         1.50E+11              1.1
              1150.       2.51E+11         2.49E+11               .8
              1250.       3.77E+11         3.81E+11              -.9
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  2.00E+03TORR
  CH2Cl + CHCl2   =  C2H3CL3          T  750. K TO 1250. K
0                               NON-LINEAR REGRESSION RESULTS
  1.574E+36 * (T^  -7.50) exp( -   8.67 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00       1.25434E+12    1.25097E+12     -.27
   2      850.00       9.64275E+11    9.69394E+11      .53
   3      950.00       7.21374E+11    7.22137E+11      .11
   4     1050.00       5.29652E+11    5.27674E+11     -.37
   5     1150.00       3.84022E+11    3.82630E+11     -.36
   6     1250.00       2.76193E+11    2.77222E+11      .37
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =   2.00E+03 TORR

0 CH2Cl + CHCl2    =   C2H3CL3          T  750. K TO 1250. K
                A =   3.36E+10      E = -5.57E+00 KCAL
           T           K EXP           K CALC          PERENT ERROR
             750.        1.25E+12        1.41E+12           -11.3
             850.        9.64E+11        9.10E+11             5.9
             950.        7.21E+11        6.43E+11            12.1
            1050.        5.30E+11        4.86E+11             9.1
            1150.        3.84E+11        3.85E+11             -.3
            1250.        2.76E+11        3.17E+11           -12.8


 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   2.00E+03TORR

 CH2Cl + CHCl2    =   C2H3CL2 + Cl      T  750. K TO 1250. K
0                            NON-LINEAR REGRESSION RESULTS
  1.746E+17 * (T^   -1.39) exp( -    9.70 KCAL/RT)

  NO    TEM (K)         KI (EXP)        KI (CAL)        %err
   1     750.00       2.61793E+10    2.60399E+10      -.53
   2     850.00       4.65649E+10    4.70710E+10      1.09
   3     950.00       7.37342E+10    7.38314E+10       .13
   4    1050.00       1.05581E+11    1.04816E+11      -.72
   5    1150.00       1.39290E+11    1.38400E+11      -.64
   6    1250.00       1.71922E+11    1.73111E+11       .69


1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =   2.00E+03 TORR

0 CH2Cl + CHCl2    =   C2H3CL2 + Cl     T  750. K TO 1250. K
                A =   3.05E+12      E =  7.07E+00 KCAL
           T           K EXP           K CALC          PERENT ERROR
             750.        2.62E+10        2.66E+10            -1.7
             850.        4.66E+10        4.65E+10              .1
             950.        7.37E+10        7.23E+10             2.0
            1050.        1.06E+11        1.03E+11             2.3
            1150.        1.39E+11        1.39E+11              .5
            1250.        1.72E+11        1.77E+11            -3.1
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   2.00E+03TORR

 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
0                            NON-LINEAR REGRESSION RESULTS
  2.585E+24 * (T^  -3.48) exp( -    7.78 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00       1.35694E+12    1.35238E+12     -.34
   2      850.00       1.60567E+12    1.61630E+12      .66
   3      950.00       1.77946E+12    1.78184E+12      .13
   4     1050.00       1.87061E+12    1.86191E+12     -.46
   5     1150.00       1.88436E+12    1.87578E+12     -.46
   6     1250.00       1.83370E+12    1.84226E+12      .47



1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR   P =   2.00E+03 TORR

0 CH2Cl + CHCl2    =    C2H2CL2 + HCl    T  750. K TO 1250. K
               A =   3.14E+12      E =   1.17E+00 KCAL
           T             K EXP           K CALC          PERENT ERROR
             750.          1.36E+12         1.43E+12              -5.2
             850.          1.61E+12         1.57E+12               2.3
             950.          1.78E+12         1.69E+12               5.4
            1050.          1.87E+12         1.79E+12               4.4
            1150.          1.88E+12         1.88E+12                .2
            1250.          1.83E+12         1.96E+12              -6.4



 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   2.00E+03TORR

K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
0                            NON-LINEAR REGRESSION RESULTS
  1.750E+15 * (T^   -.43) exp( -   13.47 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00       1.25418E+10    1.24313E+10     -.88
   2      850.00       3.34920E+10    3.41358E+10     1.92
   3      950.00       7.54274E+10    7.53798E+10     -.06
   4     1050.00       1.44162E+11    1.42532E+11    -1.13
   5     1150.00       2.42323E+11    2.40393E+11     -.80
   6     1250.00       3.68181E+11    3.71812E+11      .99
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  2.00E+03 TORR

 K-1(T) COMPLEX A DISSOC  T  750. K TO 1250. K
                   A =   6.13E+13      E =  1.27E+01 KCAL
              T           K EXP            K CALC          PERENT ERROR
                750.        1.25E+10         1.25E+10                 .2
                850.        3.35E+10         3.40E+10               -1.5
                950.        7.54E+10         7.49E+10                 .7
               1050.        1.44E+11         1.42E+11                1.6
               1150.        2.42E+11         2.40E+11                 .8
               1250.        3.68E+11         3.75E+11               -1.7
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =  7.60E+03TORR

 CH2Cl + CHCl2    =  C2H3CL3            T  750. K TO 1250. K
0                                NON-LINEAR REGRESSION RESULTS
  1.233E+34 * (T^  -6.66) exp( -    9.02 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)        %err
   1      750.00        2.00629E+12    1.99639E+12     -.49
   2      850.00        1.75033E+12    1.76738E+12      .97
   3      950.00        1.47490E+12    1.47785E+12      .20
   4     1050.00        1.20408E+12    1.19580E+12     -.69
   5     1150.00        9.56265E+11    9.49893E+11     -.67
   6     1250.00        7.42263E+11    7.47358E+11      .69
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+03 TORR

0 CH2Cl + CHCl2    =   C2H3CL3            T  750. K TO 1250. K
                   A =  1.96E+11      E = -3.62E+00 KCAL
              T           K EXP            K CALC          PERENT ERROR
                750.        2.01E+12         2.22E+12               -9.8
                850.        1.75E+12         1.67E+12                4.7
                950.        1.47E+12         1.33E+12               10.6
               1050.        1.20E+12         1.11E+12                8.4
               1150.        9.56E+11         9.55E+11                 .1
               1250.        7.42E+11         8.41E+11              -11.8
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+03TORR

 CH2Cl + CHCl2    =   C2H3CL2 + Cl       T  750. K TO 1250. K
0                            NON-LINEAR REGRESSION RESULTS
  5.988E+18 * (T^  -1.77) exp( -   12.22 KCAL/RT)

  NO   TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00        1.39142E+10    1.38072E+10     -.77
   2      850.00        2.85857E+10    2.90425E+10     1.60
   3      950.00        5.10345E+10    5.11047E+10      .14
   4     1050.00        8.01659E+10    7.93300E+10    -1.04
   5     1150.00        1.13394E+11    1.12419E+11     -.86
   6     1250.00        1.47403E+11    1.48826E+11      .97
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =   7.60E+03 TORR

0 CH2Cl + CHCl2    =   C2H3CL2 + Cl       T  750. K TO 1250. K
                A =   5.46E+12      E =   8.87E+00 KCAL
            T            K EXP           K CALC          PERENT ERROR
               750.        1.39E+10        1.42E+10             -2.1
               850.        2.86E+10        2.86E+10              -.1
               950.        5.10E+10        4.97E+10              2.6
              1050.        8.02E+10        7.78E+10              3.0
              1150.        1.13E+11        1.13E+11               .7
              1250.        1.47E+11        1.54E+11             -4.0
```

```
 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
 FOR P =   7.60E+03TORR

 CH2Cl + CHCl2    =   C2H2CL2 + HCl    T  750. K TO 1250. K
0                            NON-LINEAR REGRESSION RESULTS
  3.563E+23 * (T^  -3.16) exp( -    9.16 KCAL/RT)

  NO   TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00        6.22093E+11    6.18382E+11     -.60
   2      850.00        8.47803E+11    8.57912E+11     1.19
   3      950.00        1.06593E+12    1.06819E+12      .21
   4     1050.00        1.24607E+12    1.23574E+12     -.83
   5     1150.00        1.36828E+12    1.35773E+12     -.77
   6     1250.00        1.42588E+12    1.43745E+12      .81
```

```
1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+03 TORR

0 CH2C1 + CHC12    =    C2H2CL2 + HC1    T  750. K TO 1250. K
                 A =  5.43E+12       E =  3.16E+00 KCAL
           T             K EXP            K CALC           PERENT ERROR
             750.         6.22E+11         6.51E+11              -4.4
             850.         8.48E+11         8.35E+11               1.5
             950.         1.07E+12         1.02E+12               4.8
            1050.         1.25E+12         1.19E+12               4.4
            1150.         1.37E+12         1.36E+12                .5
            1250.         1.43E+12         1.52E+12              -6.2


 MODIFIED ARRHENIUS PARAMETERS FOR APPARANT RATE CONSTANTS
FOR P =   7.60E+03TORR

 K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
0                                NON-LINEAR REGRESSION RESULTS
  3.859E+17 * (T^  -1.05) exp( -   16.12 KCAL/RT)

  NO    TEM (K)          KI (EXP)       KI (CAL)       %err
   1      750.00        7.70394E+09   7.61655E+09   -1.13
   2      850.00        2.32823E+10   2.38678E+10    2.51
   3      950.00        5.81377E+10   5.80497E+10    -.15
   4     1050.00        1.19682E+11   1.17952E+11   -1.44
   5     1150.00        2.12059E+11   2.10038E+11    -.95
   6     1250.00        3.34449E+11   3.38559E+11    1.23


1ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS
FOR    P =  7.60E+03 TORR

 K-1(T) COMPLEX A DISSOC   T  750. K TO 1250. K
                 A =  1.02E+14       E =  1.41E+01 KCAL
           T             K EXP            K CALC           PERENT ERROR
             750.         7.70E+09         7.75E+09               -.6
             850.         2.33E+10         2.37E+10              -1.6
             950.         5.81E+10         5.71E+10               1.8
            1050.         1.20E+11         1.17E+11               2.6
            1150.         2.12E+11         2.10E+11                .9
            1250.         3.34E+11         3.45E+11              -3.0
```

APPENDIX II

THERMODYNAMIC DATA DEL H_{rxn}, DEL S_{rxn}

FORWARD/REVERSE RATE CONSTANTS VERSUS TEMPERATURE

```
P= 1.00ATM      KEQ IN MOLE CC UNITS

REACTION #  1      CL+H2=H+HCL
DELTA N =   0   DELTA H(T =  950. K)=  9.556E+02 CAL/MOLE      DELTA S (T =  950. K) =  9.725E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.101E+03      DELTA H=-0.246E+06
       T          FF-FREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
     950.         0.956E+03        0.489E+00      0.262394E+13      0.55E+13          0.24E+14       0.25E+14
    1050.         0.961E+03        0.492E+00      0.544740E+09      0.22E+08          0.26E+14       0.25E+14
    1150.         0.984E+03        0.503E+00      0.690754E+01      0.77E+03          0.27E+14       0.25E+14
    1250.         0.103E+04        0.520E+00      0.111299E+01      0.14E+00          0.28E+14       0.26E+14

REACTION #  2      H+CL2=CL+HCL
DELTA N =   0   DELTA H(T =  950. K)= -4.602E+04 CAL/MOLE      DELTA S (T =  950. K) =  2.078E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.969E+00      DELTA H=-0.462E+05
       T          FF-FREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
     950.        -0.440E+05        0.105E+01      0.111254E+12      0.11E+12          0.22E+13       0.20E+02
    1050.        -0.441E+05        0.988E+00      0.108723E+11      0.11E+11          0.23E+13       0.21E+03
    1150.        -0.442E+05        0.938E+00      0.158473E+10      0.16E+10          0.25E+13       0.16E+04
    1250.        -0.443E+05        0.897E+00      0.313210E+09      0.31E+09          0.26E+13       0.83E+04

REACTION #  3      HCL=H+CL
DELTA N =   1   DELTA H(T =  950. K)=  1.051E+05 CAL/MOLE      DELTA S (T =  950. K) =  2.597E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.855E+00      DELTA H= 0.103E+06
       T          FF-FREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
     950.         0.103E+06        0.804E+00      0.396021E-23      0.40E-23          0.25E-13       0.63E+10
    1050.         0.103E+06        0.841E+00      0.725752E-21      0.73E-21          0.34E-11       0.47E+10
    1150.         0.103E+06        0.866E+00      0.538812E-19      0.54E-19          0.20E-09       0.36E+10
    1250.         0.103E+06        0.883E+00      0.201149E-17      0.20E-17          0.59E-08       0.29E+10

REACTION #  4      CL2=2CL
DELTA N =   1   DELTA H(T =  950. K)=  5.997E+04 CAL/MOLE      DELTA S (T =  950. K) =  2.804E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.182E+01      DELTA H= 0.571E+05
       T          FF-FREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
     950          0.572E+05        0.185E+01      0.440587E-12      0.44E-12          0.12E-03       0.28E+09
    1050          0.571E+05        0.183E+01      0.789058E-11      0.79E-11          0.21E-02       0.26E+09
    1150          0.571E+05        0.180E+01      0.853873E-10      0.85E-10          0.21E-01       0.24E+09
    1250          0.570E+05        0.178E+01      0.630020E-09      0.63E-09          0.15E+00       0.23E+09

REACTION #  5      H2=2H
DELTA N =   1   DELTA H(T =  950. K)=  1.060E+05 CAL/MOLE      DELTA S (T =  950. K) =  2.694E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.135E+01      DELTA H= 0.104E+06
       T          FF-FREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
     950          0.104E+06        0.129E+01      0.389401E-23      0.39E-23          0.37E-15       0.94E+08
    1050          0.104E+06        0.133E+01      0.748935E-21      0.75E-21          0.73E-13       0.98E+08
    1150.         0.104E+06        0.137E+01      0.579994E-19      0.58E-19          0.58E-11       0.10E+09
    1250          0.104E+06        0.140E+01      0.223878E-17      0.22E-17          0.23E-09       0.10E+09

REACTION #  6      CH4=CH3+H
DELTA N =   1   DELTA H(T =  950. K)=  1.073E+05 CAL/MOLE      DELTA S (T =  950. K) =  3.420E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.494E+01      DELTA H= 0.105E+06
       T          FF-FREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
     950.         0.105E+06        0.495E+01      0.765464E-22      0.77E-22          0.77E-08       0.10E+15
```

```
     1050.       -0.234E+04      0.421E+01      0.210067E+03     0.21E+03        0.57E+13      0.27E+11
     1150.       -0.240E+04      0.419E+01      0.190192E+03     0.19E+03        0.64E+13      0.34E+11
     1250.       -0.244E+04      0.418E+01      0.174722E+03     0.17E+03        0.72E+13      0.41E+11

REACTION # 13     CL+CH3CL=CH2CL+HCL
DELTA N =   0   DELTA H(T =  950. K)=  4.969E+02 CAL/MOLE     DELTA S (T =  950. K) =  8.322E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.414E+01     DELTA H= 0.399E+03
       T          FF-FREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       0.497E+03      0.419E+01      0.507380E+02     0.51E+02        0.46E+13      0.91E+11
     1050.       0.418E+03      0.415E+01      0.519241E+02     0.52E+02        0.55E+13      0.11E+12
     1150.       0.352E+03      0.412E+01      0.527653E+02     0.53E+02        0.64E+13      0.12E+12
     1250.       0.296E+03      0.409E+01      0.533682E+02     0.53E+02        0.73E+13      0.14E+12

REACTION # 14     CL+CH4=CH3+HCL
DELTA N =   0   DELTA H(T =  950. K)=  2.233E+03 CAL/MOLE     DELTA S (T =  950. K) =  8.236E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.408E+01     DELTA H= 0.211E+04
       T          FF-FREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       0.223E+04      0.414E+01      0.193541E+02     0.19E+02        0.46E+13      0.24E+12
     1050.       0.215E+04      0.410E+01      0.216215E+02     0.22E+02        0.55E+13      0.26E+12
     1150.       0.204E+04      0.405E+01      0.235985E+02     0.24E+02        0.64E+13      0.27E+12
     1250.       0.192E+04      0.400E+01      0.252944E+02     0.25E+02        0.73E+13      0.29E+12

REACTION # 15     CL+C2H4=CH2CH2CL
DELTA N -  -1   DELTA H(T =  950. K)= -2.275E+04 CAL/MOLE     DELTA S (T =  950. K) = -2.368E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.524E+00     DELTA H=-0.205E+05
       T          FF-FREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.      -0.209E+05      0.346E+00      0.892499E+05     0.89E+05        0.20E+13      0.23E+08
     1050.      -0.206E+05      0.478E+00      0.313333E+05     0.32E+05        0.13E+13      0.43E+08
     1150.      -0.203E+05      0.600E+00      0.133432E+05     0.13E+05        0.96E+12      0.72E+08
     1250.      -0.201E+05      0.715E+00      0.657573E+04     0.65E+04        0.73E+12      0.11E+09

REACTION # 16     CL+C2H4=C2H3+HCL
DELTA N =   0   DELTA H(T =  950. K)=  6.906E+03 CAL/MOLE     DELTA S (T =  950. K) =  9.329E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.459E+01     DELTA H= 0.671E+04
       T          FF-FREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       0.691E+04      0.470E+01      0.282123E+01     0.28E+01        0.67E+12      0.24E+12
     1050.       0.676E+04      0.462E+01      0.398398E+01     0.40E+01        0.87E+12      0.22E+12
     1150.       0.660E+04      0.455E+01      0.526440E+01     0.52E+01        0.11E+13      0.20E+12
     1250.       0.642E+04      0.447E+01      0.661379E+01     0.66E+01        0.13E+13      0.19E+12

REACTION # 17     CL+C2H6=C2H5+HCL
DELTA N -   0   DELTA H(T =  950. K)= -2.542E+03 CAL/MOLF     DELTA S (T =  950. K) =  8.046E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINF HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.396E+01     DELTA H=-0.272E+04
       T          FF-FREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.      -0.254E+04      0.405E+01      0.220974E+03     0.22E+03        0.71E+14      0.32E+12
     1050.      -0.268E+04      0.398E+01      0.193741E+03     0.19E+03        0.74E+14      0.38E+12
     1150.      -0.281E+04      0.392E+01      0.172810E+03     0.17E+03        0.77E+14      0.45E+12
     1250.      -0.295E+04      0.386E+01      0.156218E+03     0.16E+03        0.80E+14      0.51E+12

REACTION # 18     CL+C2H2CL4=C2HCL4+HCL
DELTA N -   0   DELTA H(T =  950. K)= -5.813F+03 CAL/MOLE     DELTA S (T =  950. K) =  7.382E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINF HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.361E+01     DELTA H=-0.601E+04
       T          FF-FREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950       -0.581E+04      0.372E+01      0.895504E+03     0.90E+03        0.38E+12      0.42E+03
```

```
   1050.       -0.596E+04      0.364E+01       0.665353E+03     0.66E+03          0.43E+12       0.64E+09
   1150.       -0.611E+04      0.357E+01       0.517369E+03     0.52E+03          0.47E+12       0.91E+09
   1250.       -0.625E+04      0.352E+01       0.416744E+03     0.42E+03          0.52E+12       0.12E+10

REACTION # 19      CL+C2H3CL3=C2H2CL3+HCL
DELTA N =    0     DELTA H(T =   950. K)= -6.256E+03 CAL/MOLE      DELTA S (T =  950. K) =  6.254E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.306E+01      DELTA H=-0.645E+04
       T           FF-FREV         LN AF/AREV         KEQ           KEQ FIT           K FORWARD      K REVERSE
    950.       -0.627E+04      0.315E+01       0.645185E+03     0.65E+03          0.49E+13       0.77E+10
   1050.       -0.640E+04      0.308E+01       0.468735E+03     0.47E+03          0.59E+13       0.13E+11
   1150.       -0.653E+04      0.302E+01       0.357989E+03     0.36E+03          0.68E+13       0.19E+11
   1250.       -0.667E+04      0.296E+01       0.284089E+03     0.28E+03          0.77E+13       0.27E+11

REACTION # 20      CL+C2H5CL=C2H4CL+HCL
DELTA N =    0     DELTA H(T =   950. K)= -6.373E+03 CAL/MOLE      DELTA S (T =  950. K) =  6.018E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.294E+01      DELTA H=-0.656E+04
       T           FF-FREV         LN AF/AREV         KEQ           KEQ FIT           K FORWARD      K REVERSE
    950.       -0.637E+04      0.303E+01       0.606387E+03     0.61E+03          0.90E+13       0.15E+11
   1050.       -0.650E+04      0.296E+01       0.438245E+03     0.44E+03          0.97E+13       0.22E+11
   1150.       -0.665E+04      0.290E+01       0.333227E+03     0.33E+03          0.10E+14       0.31E+11
   1250.       -0.681E+04      0.283E+01       0.263298E+03     0.26E+03          0.11E+14       0.42E+11

REACTION # 21      H+CH2CL2=CH2CL+HCL
DELTA N =    0     DELTA H(T =   950. K)= -2.192E+04 CAL/MOLE      DELTA S (T =  950. K) =  9.340E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.455E+01      DELTA H=-0.222E+05
       T           FF-FREV         LN AF/AREV         KEQ           KEQ FIT           K FORWARD      K REVERSE
    950.       -0.219E+05      0.470E+01       0.122335E+08     0.12E+08          0.40E+12       0.33E+05
   1050.       -0.222E+05      0.458E+01       0.402270E+07     0.40E+07          0.55E+12       0.14E+06
   1150.       -0.224E+05      0.449E+01       0.159054E+07     0.16E+07          0.71E+12       0.44E+06
   1250.       -0.225E+05      0.442E+01       0.724704E+06     0.73E+06          0.87E+12       0.12E+07

REACTION # 22      H+CH3CL=CH3+HCL
DELTA N =    0     DELTA H(T =   950. K)= -1.919E+04 CAL/MOLE      DELTA S (T =  950. K) =  7.049E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.339E+01      DELTA H=-0.195E+05
       T           FF-FREV         LN AF/AREV         KEQ           KEQ FIT           K FORWARD      K REVERSE
    950.       -0.192E+05      0.355E+01       0.907619E+06     0.91E+06          0.15E+13       0.17E+07
   1050.       -0.194E+05      0.344E+01       0.342744E+06     0.34E+06          0.22E+13       0.66E+07
   1150.       -0.196E+05      0.333E+01       0.151892E+06     0.15E+06          0.31E+13       0.20E+08
   1250.       -0.199E+05      0.323E+01       0.760408E+05     0.76E+05          0.41E+13       0.53E+08

REACTION # 23      H+C2H3CL=C2H3+HCL
DELTA N =    0     DELTA H(T =   950. K)= -1.359E+04 CAL/MOLE      DELTA S (T =  950. K) =  8.113E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.388E+01      DELTA H=-0.140E+05
       T           FF-FREV         LN AF/AREV         KEQ           KEQ FIT           K FORWARD      K REVERSE
    950.       -0.136E+05      0.408E+01       0.796124E+05     0.80E+05          0.32E+12       0.40E+07
   1050.       -0.139E+05      0.393E+01       0.398099E+05     0.40E+05          0.44E+12       0.11E+08
   1150.       -0.142E+05      0.380E+01       0.221787E+05     0.22E+05          0.58E+12       0.26E+08
   1250.       -0.145E+05      0.367E+01       0.134290E+05     0.14E+05          0.73E+12       0.54E+08

REACTION # 24      CHCL2+CH3=C2H4CL2
DELTA N =   -1     DELTA H(T =   950. K)= -9.174E+04 CAL/MOLE      DELTA S (T =  950. K) = -4.092E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.812E+01      DELTA H=-0.895E+05
       T           FF-FREV         LN AF/AREV         KEQ           KEQ FIT           K FORWARD      K REVERSE
    950.       -0.899E+05     -0.833E+01       0.114637E+18     0.11E+18          0.21E+13       0.18E-04
```

```
  1050.     -0.596E+04      0.364E+01     0.665353E+03     0.66E+03          0.43E+12      0.64E+09
  1150.     -0.611E+04      0.357E+01     0.517369E+03     0.52E+03          0.47E+12      0.91E+09
  1250.     -0.625E+04      0.352E+01     0.416744E+03     0.42E+03          0.52E+12      0.12E+10

REACTION # 19      CL+C2H3CL3=C2H2CL3+HCL
DELTA N =   0    DELTA H(T =  950. K)= -6.256E+03 CAL/MOLE      DELTA S (T =  950. K) =  6.254E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.306E+01      DELTA H=-0.645E+04
      T           FF-FREV          LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
   950.     -0.627E+04      0.315E+01     0.645185E+03     0.65E+03          0.49E+13      0.77E+10
  1050.     -0.640E+04      0.308E+01     0.468735E+03     0.47E+03          0.59E+13      0.13E+11
  1150.     -0.653E+04      0.302E+01     0.357989E+03     0.36E+03          0.68E+13      0.19E+11
  1250.     -0.667E+04      0.296E+01     0.284089E+03     0.29E+03          0.77E+13      0.27E+11

REACTION # 20      CL+C2H5CL=C2H4CL+HCL
DELTA N =   0    DELTA H(T =  950. K)= -6.373E+03 CAL/MOLE      DELTA S (T =  950. K) =  6.018E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.294E+01      DELTA H=-0.656E+04
      T           FF-FREV          LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
   950.     -0.637E+04      0.303E+01     0.606387E+03     0.61E+03          0.90E+13      0.15E+11
  1050.     -0.650E+04      0.296E+01     0.438245E+03     0.44E+03          0.97E+13      0.22E+11
  1150.     -0.665E+04      0.290E+01     0.333227E+03     0.33E+03          0.10E+14      0.31E+11
  1250.     -0.681E+04      0.283E+01     0.263288E+03     0.26E+03          0.11E+14      0.42E+11

REACTION # 21      H+CH2CL2=CH2CL+HCL
DELTA N =   0    DELTA H(T =  950. K)= -2.192E+04 CAL/MOLE      DELTA S (T =  950. K) =  9.340E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.455E+01      DELTA H=-0.222E+05
      T           FF-FREV          LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
   950.     -0.219E+05      0.470E+01     0.122335E+08     0.12E+08          0.40E+12      0.33E+05
  1050.     -0.222E+05      0.458E+01     0.402270E+07     0.40E+07          0.55E+12      0.14E+06
  1150.     -0.224E+05      0.449E+01     0.159054E+07     0.16E+07          0.71E+12      0.44E+06
  1250.     -0.225E+05      0.442E+01     0.724704E+06     0.73E+06          0.87E+12      0.12E+07

REACTION # 22      H+CH3CL=CH3+HCL
DELTA N =   0    DELTA H(T =  950. K)= -1.919E+04 CAL/MOLE      DELTA S (T =  950. K) =  7.049E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.339E+01      DELTA H=-0.195E+05
      T           FF-FREV          LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
   950.     -0.192E+05      0.355E+01     0.907619E+06     0.91E+06          0.15E+13      0.17E+07
  1050.     -0.194E+05      0.344E+01     0.342744E+06     0.34E+06          0.22E+13      0.66E+07
  1150.     -0.196E+05      0.333E+01     0.151892E+06     0.15E+06          0.31E+13      0.20E+08
  1250.     -0.199E+05      0.323E+01     0.760408E+05     0.76E+05          0.41E+13      0.53E+08

REACTION # 23      H+C2H3CL=C2H3+HCL
DELTA N =   0    DELTA H(T =  950. K)= -1.359E+04 CAL/MOLE      DELTA S (T =  950. K) =  8.113E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.388E+01      DELTA H=-0.140E+05
      T           FF-FREV          LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
   950.     -0.136E+05      0.408E+01     0.796124E+05     0.80E+05          0.32E+12      0.40E+07
  1050.     -0.139E+05      0.393E+01     0.398039E+05     0.40E+05          0.44E+12      0.11E+08
  1150.     -0.142E+05      0.380E+01     0.221787E+05     0.22E+05          0.58E+12      0.26E+08
  1250.     -0.145E+05      0.367E+01     0.134290E+05     0.14E+05          0.73E+12      0.54E+08

REACTION # 24      CHCL2+CH3=C2H4CL2
DELTA N =  -1    DELTA H(T =  950. K)= -9.174E+04 CAL/MOLE      DELTA S (T =  950. K) = -4.092E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.812E+01      DELTA H=-0.895E+05
      T           FF-FREV          LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
   950.     -0.899E+05     -0.833E+01     0.114637E+18     0.11E+18          0.21E+13      0.18E-04
```

```
   1050.      -0.894E+05      -0.818E+01      0.123827E+16     0.12E+16          0.15E+13       0.12E-02
   1150.      -0.892E+05      -0.803E+01      0.297863E+14     0.30E+14          0.12E+13       0.39E-01
   1250.      -0.889E+05      -0.788E+01      0.131657E+13     0.13E+13          0.92E+12       0.70E+00

REACTION # 25      CHCL2+CH3=C2H4CL+CL
DELTA N =   0   DELTA H(T =  950. K)= -1.340E+04 CAL/MOLE      DELTA S (T =  950. K) = -7.429E+00 CAL/DEG/MOLE
(STANDARD VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.365E+01      DELTA H=-0.132E+05
      T           EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
    950.      -0.134E+05      -0.374E+01      0.287671E+02     0.29E+02          0.65E+12       0.23E+11
   1050.      -0.133E+05      -0.368E+01      0.146735E+02     0.15E+02          0.83E+12       0.56E+11
   1150.      -0.131E+05      -0.362E+01      0.845812E+01     0.85E+01          0.10E+13       0.12E+12
   1250.      -0.130E+05      -0.356E+01      0.534907E+01     0.53E+01          0.12E+13       0.22E+12

REACTION # 26      CHCL2+CH3=C2H3CL+HCL
DELTA N =   0   DELTA H(T =  950. K)= -7.453E+04 CAL/MOLE      DELTA S (T =  950. K) = -6.986E+00 CAL/DEG/MOLE
(STANDARD VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.353E+01      DELTA H=-0.746E+05
      T           EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
    950.      -0.745E+05      -0.352E+01      0.422332E+16     0.42E+16          0.39E+13       0.93E-03
   1050.      -0.745E+05      -0.353E+01      0.982661E+14     0.98E+14          0.39E+13       0.40E-01
   1150.      -0.746E+05      -0.354E+01      0.438789E+13     0.44E+13          0.39E+13       0.90E+00
   1250.      -0.746E+05      -0.356E+01      0.321809E+12     0.32E+12          0.39E+13       0.12E+02

REACTION # 27      2CHCL2=C2H2CL4
DELTA N = -1   DELTA H(T =  950. K)= -8.645E+04 CAL/MOLE      DELTA S (T =  950. K) = -4.684E+01 CAL/DEG/MOLE
(STANDARD VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.111E+02      DELTA H=-0.841E+05
      T           EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
    950.      -0.846E+05      -0.113E+02      0.352171E+15     0.35E+15          0.19E+12       0.55E-03
   1050.      -0.842E+05      -0.111E+02      0.497766E+13     0.50E+13          0.14E+12       0.28E-01
   1150.      -0.839E+05      -0.110E+02      0.149713E+12     0.15E+12          0.10E+12       0.69E+00
   1250.      -0.836E+05      -0.109E+02      0.797430E+10     0.79E+10          0.81E+11       0.10E+02

REACTION # 28      2CHCL2=C2HCL3+HCL
DELTA N =   0   DELTA H(T =  950. K)= -7.434E+04 CAL/MOLE      DELTA S (T =  950. K) = -1.160E+01 CAL/DEG/MOLE
(STANDARD VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.591E+01      DELTA H=-0.745E+05
      T           EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
    950.      -0.743E+05      -0.584E+01      0.375601E+15     0.38E+15          0.48E+12       0.13E-02
   1050.      -0.744E+05      -0.588E+01      0.879874E+13     0.88E+13          0.47E+12       0.54E-01
   1150.      -0.746E+05      -0.594E+01      0.394227E+12     0.39E+12          0.47E+12       0.12E+01
   1250.      -0.747E+05      -0.601E+01      0.288749E+11     0.29E+11          0.46E+12       0.16E+02

REACTION # 29      2CHCL2=C2H2CL3+CL
DELTA N =   0   DELTA H(T =  950. K)= -1.183E+04 CAL/MOLE      DELTA S (T =  950. K) = -1.070E+01 CAL/DEG/MOLE
(STANDARD VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.532E+01      DELTA H=-0.117E+05
      T           EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
    950.      -0.118E+05      -0.539E+01      0.241481E+01     0.24E+01          0.14E+12       0.60E+11
   1050.      -0.117E+05      -0.533E+01      0.133277E+01     0.13E+01          0.18E+12       0.14E+12
   1150.      -0.116E+05      -0.530E+01      0.818919E+00     0.82E+00          0.22E+12       0.27E+12
   1250.      -0.116E+05      -0.527E+01      0.545190E+00     0.54E+00          0.26E+12       0.48E+12

REACTION # 30      CHCL2+CH2CL=C2H3CL3
DELTA N = -1   DELTA H(T =  950. K)= -9.105E+04 CAL/MOLE      DELTA S (T =  950. K) = -4.384E+01 CAL/DEG/MOLE
(STANDARD VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.958E+01      DELTA H=-0.887E+05
      T           EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
    950       -0.892E+05      -0.980E+01      0.182611E+17     0.18E+17          0.31E+12       0.17E-04
```

```
   1050.      -0.888E+05     -0.962E+01     0.204588E+15     0.21E+15        0.22E+12      0.11E-02
   1150.      -0.885E+05     -0.948E+01     0.507671E+13     0.51E+13        0.17E+12      0.33E-01
   1250.      -0.882E+05     -0.935E+01     0.230018E+12     0.23E+12        0.13E+12      0.58E+00

REACTION # 31      CHCL2+CH2CL=C2H2CL2+HCL
DELTA N =    0    DELTA H(T =  950. K)= -7.730E+04 CAL/MOLE      DELTA S (T =  950. K) = -1.167E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.589E+01      DELTA H=-0.774E+05
       T            EF-EREV          LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     950.       -0.773E+05       -0.587E+01     0.173738E+16     0.17E+16        0.20E+13      0.12E-02
    1050.       -0.773E+05       -0.587E+01     0.351201E+14     0.35E+14        0.21E+13      0.59E-01
    1150.       -0.774E+05       -0.590E+01     0.139742E+13     0.14E+13        0.21E+13      0.15E+01
    1250.       -0.775E+05       -0.594E+01     0.928818E+11     0.93E+11        0.21E+13      0.23E+02

REACTION # 32      CHCL2+CH2CL=C2H3CL2+CL
DELTA N =    0    DELTA H(T =  950. K)= -1.410E+04 CAL/MOLE      DELTA S (T =  950. K) = -1.073E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.532E+01      DELTA H=-0.139E+05
       T            EF-EREV          LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     950.       -0.141E+05       -0.540E+01     0.791709E+01     0.79E+01        0.82E+11      0.10E+11
    1050.       -0.140E+05       -0.533E+01     0.390023E+01     0.39E+01        0.11E+12      0.29E+11
    1150.       -0.139E+05       -0.528E+01     0.218446E+01     0.22E+01        0.15E+12      0.67E+11
    1250.       -0.138E+05       -0.525E+01     0.134637E+01     0.13E+01        0.18E+12      0.14E+12

REACTION # 33      2CH2CL=C2H4CL2
DELTA N =   -1    DELTA H(T =  950. K)= -9.182E+04 CAL/MOLE      DELTA S (T =  950. K) = -4.312E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.921E+01      DELTA H=-0.895E+05
       T            EF-EREV          LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     950.       -0.899E+05       -0.944E+01     0.396224E+17     0.39E+17        0.11E+13      0.28E-04
    1050.       -0.896E+05       -0.926E+01     0.426833E+15     0.43E+15        0.81E+12      0.19E-02
    1150.       -0.893E+05       -0.911E+01     0.102523E+14     0.10E+14        0.62E+12      0.61E-01
    1250.       -0.889E+05       -0.898E+01     0.452266E+12     0.45E+12        0.50E+12      0.11E+01

REACTION # 34      2CH2CL=C2H3CL+HCL
DELTA N =    0    DELTA H(T =  950. K)= -7.461E+04 CAL/MOLE      DELTA S (T =  950. K) = -9.177E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.462E+01      DELTA H=-0.746E+05
       T            EF-EREV          LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     950.       -0.746E+05       -0.462E+01     0.146179E+16     0.15E+16        0.25E+13      0.17E-02
    1050.       -0.746E+05       -0.461E+01     0.338723E+14     0.34E+14        0.25E+13      0.75E-01
    1150.       -0.746E+05       -0.462E+01     0.151029E+13     0.15E+13        0.25E+13      0.17E+01
    1250.       -0.747E+05       -0.465E+01     0.110548E+12     0.11E+12        0.25E+13      0.23E+02

REACTION # 35      2CH2CL=CH2CH2CL+CL
DELTA N =    0    DELTA H(T =  950. K)= -1.276E+04 CAL/MOLE      DELTA S (T =  950. K) = -8.107E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N =-0.396E+01      DELTA H=-0.125E+05
       T            EF-EREV          LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     950.       -0.128E+05       -0.408E+01     0.145799E+02     0.15E+02        0.51E+12      0.35E+11

    1050.       -0.126E+05       -0.398E+01     0.769686E+01     0.77E+01        0.65E+12      0.84E+11
    1150.       -0.124E+05       -0.391E+01     0.457451E+01     0.46E+01        0.79E+12      0.17E+12
    1250.       -0.123E+05       -0.386E+01     0.296896E+01     0.30E+01        0.93E+12      0.31E+12

REACTION # 36      CH4+H=H2+CH3
DELTA N =    0    DELTA H(T =  950. K)=  1.278E+03 CAL/MOLE      DELTA S (T =  950. K) =  7.263E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  950. TO 1250.  DELTA S/R - DELTA N = 0.358E+01      DELTA H= 0.114E+04
       T            EF-EREV          LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     950.        0.128E+04        0.366E+01     0.196831E+02     0.20E+02        0.59E+10      0.30E+09
```

```
     1050        0.119E+04       0.361E+01      0.209522E+02      0.21E+02          0.84E+10      0.40E+09
     1150        0.106E+04       0.355E+01      0.219608E+02      0.22E+02          0.11E+11      0.51E+09
     1250.       0.890E+03       0.348E+01      0.227264E+02      0.23E+02          0.14E+11      0.63E+09

REACTION # 37      CH3+C2H3CL3=C2H3CL2+CH3CL
DELTA N -    0    DELTA H(T =  950. K)= -8.955E+03 CAL/MOLE     DELTA S (T =  950. K) =  9.312E-02 CAL/DEG/MOLE
 (THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.104E-01     DELTA H=-0.903E+04
       T            EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       -0.895E+04       0.469E-01      0.120620E+03      0.12E+03          0.11E+12      0.94E+09
     1050.       -0.901E+04       0.165E-01      0.766394E+02      0.77E+02          0.12E+12      0.16E+10
     1150.       -0.906E+04      -0.264E-02      0.525799E+02      0.53E+02          0.12E+12      0.24E+10
     1250.       -0.909E+04      -0.146E-01      0.382683E+02      0.38E+02          0.13E+12      0.34E+10

REACTION # 38      CH3+C2H3CL=C2H3+CH3CL
DELTA N -    0    DELTA H(T =  950. K)=  5.603E+03 CAL/MOLE     DELTA S (T =  950. K) =  1.064E+00 CAL/DEG/MOLE
 (THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.484E+00     DELTA H= 0.551E+04
       T            EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.        0.560E+04       0.535E+00      0.877157E-01      0.88E-01          0.24E+09      0.28E+10
     1050.        0.552E+04       0.495E+00      0.116151E+00      0.12E+00          0.44E+09      0.38E+10
     1150.        0.546E+04       0.465E+00      0.146026E+00      0.15E+00          0.73E+09      0.50E+10
     1250.        0.540E+04       0.441E+00      0.176602E+00      0.18E+00          0.11E+10      0.63E+10

REACTION # 39      CH3+CH3CL=CH2CL+CH4
DELTA N -    0    DELTA H(T =  950. K)= -1.736E+03 CAL/MOLE     DELTA S (T =  950. K) =  8.645E-02 CAL/DEG/MOLE
 (THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.573E-01     DELTA H=-0.171E+04
       T            EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       -0.174E+04       0.435E-01      0.262156E+01      0.26E+01          0.23E+10      0.87E+09
     1050.       -0.173E+04       0.462E-01      0.240151E+01      0.24E+01          0.37E+10      0.15E+10
     1150.       -0.169E+04       0.653E-01      0.223596E+01      0.22E+01          0.54E+10      0.24E+10
     1250.       -0.162E+04       0.941E-01      0.210988E+01      0.21E+01          0.75E+10      0.36E+10

REACTION # 40      CH3+CH2CL=C2H5CL
DELTA N -   -1    DELTA H(T =  950. K)= -9.251E+04 CAL/MOLE     DELTA S (T =  950. K) = -4.033E+01 CAL/DEG/MOLE
 (THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.779E+01     DELTA H=-0.902E+05
       T            EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       -0.906E+05      -0.803E+01      0.231459E+18      0.23E+18          0.46E+13      0.20E-04
     1050.       -0.903E+05      -0.785E+01      0.240918E+16      0.24E+16          0.36E+13      0.15E-02
     1150.       -0.899E+05      -0.768E+01      0.563308E+14      0.57E+14          0.28E+13      0.51E-01
     1250.       -0.895E+05      -0.751E+01      0.243509E+13      0.24E+13          0.24E+13      0.97E+00

REACTION # 41      CH3+CH2CL=C2H4+HCL
DELTA N -    0    DELTA H(T =  950. K)= -7.541E+04 CAL/MOLE     DELTA S (T =  950. K) = -9.121E+00 CAL/DEG/MOLE
 (THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.459E+01     DELTA H=-0.754E+05
       T            EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       -0.754E+05      -0.459E+01      0.230600E+16      0.23E+16          0.12E+14      0.52E-02
     1050.       -0.754E+05      -0.459E+01      0.512764E+14      0.51E+14          0.12E+14      0.24E+00
     1150        -0.754E+05      -0.459E+01      0.221051E+13      0.22E+13          0.13E+14      0.57E+01
     1250.       -0.754E+05      -0.459E+01      0.157535E+12      0.16E+12          0.13E+14      0.81E+02

REACTION # 42      CH3+CH2CL=C2H5+CL
DELTA N -    0    DELTA H(T =  950. K)= -8.184E+03 CAL/MOLE     DELTA S (T =  950. K) = -8.076E+00 CAL/DEG/MOLE
 (THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.399E+01     DELTA H=-0.804E+04
       T            EF-EREV         LV AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.       -0.818E+04      -0.406E+01      0.131192E+01      0.13E+01          0.83E+12      0.63E+12
```

```
   1050.      -0.807E+04    -0.401E+01     0.870303E+00    0.87E+00        0.11E+13     0.13E+13
   1150.      -0.797E+04    -0.396E+01     0.522906E+00    0.62E+00        0.14E+13     0.23E+13
   1250.      -0.787E+04    -0.392E+01     0.472045E+00    0.47E+00        0.17E+13     0.36E+13

REACTION # 63     CH3+CH2CL=C2H4CL+H
DELTA N -    0    DELTA H(T =  950. K)=  6.212E+03 CAL/MOLE     DELTA S (T =  950. K) = -8.348E+00 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.400E+01     DELTA H= 0.661E+04
      T          FF-FREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
     950.        0.621E+04      -0.420E+01     0.555830E-03    0.55E-03         0.73E+09      0.13E+13
    1050.        0.652E+04      -0.405E+01     0.766258E-03    0.77E-03         0.14E+10      0.18E+13
    1150.        0.680E+04      -0.392E+01     0.101140E-02    0.10E-02         0.23E+10      0.23E+13
    1250.        0.708E+04      -0.380E+01     0.129963E-02    0.13E-02         0.36E+10      0.28E+13

REACTION # 64     C2H6=2CH3
DELTA N -    1    DELTA H(T =  950. K)=  9.105E+04 CAL/MOLE     DELTA S (T =  950. K) =  4.082E+01 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.306E+01     DELTA H= 0.888E+05
      T          FF-FREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
     950.        0.892E+05       0.828E+01     0.119331E-16    0.12E-16         0.21E-03      0.18E+14
    1050.        0.888E+05       0.812E+01     0.106645E-14    0.11E-14         0.20E-01      0.18E+14
    1150.        0.885E+05       0.796E+01     0.430268E-13    0.43E-13         0.81E+00      0.19E+14
    1250.        0.881E+05       0.780E+01     0.948485E-12    0.96E-12         0.19E+02      0.20E+14

REACTION # 65     C2H6=C2H5+H
DELTA N -    1    DELTA H(T =  950. K)=  1.025E+05 CAL/MOLE     DELTA S (T =  950. K) =  3.401E+01 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.481E+01     DELTA H= 0.101E+06
      T          FF-FREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
     950.        0.101E+06       0.485E+01     0.875103E-21    0.88E-21         0.36E-06      0.41E+15
    1050.        0.101E+06       0.482E+01     0.140608E-18    0.14E-18         0.50E-04      0.36E+15
    1150.        0.101E+06       0.478E+01     0.931120E-17    0.93E-17         0.30E-02      0.32E+15
    1250.        0.100E+06       0.474E+01     0.314231E-15    0.31E-15         0.92E-01      0.29E+15

REACTION # 66     C2H3=C2H2+H
DELTA N -    1    DELTA H(T =  950. K)=  3.831E+04 CAL/MOLE     DELTA S (T =  950. K) =  2.377E+01 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.265E+00     DELTA H= 0.365E+05
      T          FF-FREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
     950.        0.364E+05      -0.302E+00     0.307451E-08    0.31E-08         0.24E+04      0.79E+12
    1050.        0.365E+05      -0.274E+00     0.193556E-07    0.19E-07         0.17E+05      0.87E+12
    1150.        0.365E+05      -0.259E+00     0.886457E-07    0.89E-07         0.83E+05      0.94E+12
    1250.        0.365E+05      -0.253E+00     0.318519E-06    0.32E-06         0.32E+06      0.10E+13

REACTION # 67     C2H3+CH4=C2H4+CH3
DELTA N -    0    DELTA H(T =  950. K)= -4.673E+03 CAL/MOLE     DELTA S (T =  950. K) = -1.094E+00 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.511E+00     DELTA H=-0.460E+04
      T          FF-FREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
     950.       -0.467E+04      -0.550E+00     0.586018E+01    0.69E+01         0.17E+08      0.25E+07
    1050.       -0.461E+04      -0.520E+00     0.542710E+01    0.54E+01         0.48E+08      0.89E+07
    1150.       -0.456E+04      -0.495E+00     0.448266E+01    0.45E+01         0.11E+09      0.25E+08
    1250.       -0.451E+04      -0.474E+00     0.382449E+01    0.38E+01         0.23E+09      0.61E+08

REACTION # 68     C2H5+CH4=C2H6+CH3
DELTA N =    0    DELTA H(T =  950. K)=  4.775E+03 CAL/MOLE     DELTA S (T =  950. K) =  1.900E-01 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.124E+00     DELTA H= 0.483E+04
      T          FF-FREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
     950.        0.478E+04       0.956E-01     0.875856E-01    0.88E-01         0.18E+10      0.21E+11
```

```
   1050.      0.682E+04      0.120E+00     0.111500E+00     0.11E+00        0.33E+10     0.29E+11
   1150.      0.685E+04      0.134E+00     0.136558E+00     0.14E+00        0.53E+10     0.39E+11
   1250.      0.687E+04      0.141E+00     0.161917E+00     0.16E+00        0.80E+10     0.50E+11

REACTION # 49       C2H2CL+CH4=C2H3CL+CH3
DELTA N =   0    DELTA H(T =  950. K)=  1.059E+02 CAL/MOLE     DELTA S (T =  950. K) =  1.352E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.517E+00      DELTA H=-0.213E+03
      T          EF-EREV         LN AF/AREV      KEQ            KEQ FIT          K FORWARD     K REVERSE
    950.        0.106E+03       0.680E+00     0.186736E+01     0.19E+01        0.38E+10     0.20E+10
   1050.       -0.111E+03       0.571E+00     0.186789E+01     0.19E+01        0.63E+10     0.34E+10
   1150.       -0.379E+03       0.449E+00     0.184951E+01     0.18E+01        0.96E+10     0.52E+10
   1250.       -0.691E+03       0.318E+00     0.181556E+01     0.18E+01        0.14E+11     0.75E+10

REACTION # 50       C2H5=C2H4+H
DELTA N =   1    DELTA H(T =  950. K)=  3.796E+04 CAL/MOLE     DELTA S (T =  950. K) =  2.492E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.256E+00      DELTA H= 0.359E+05
      T          EF-EREV         LN AF/AREV      KEQ            KEQ FIT          K FORWARD     K REVERSE
    950.        0.360E+05       0.279E+00     0.696148E-08     0.70E-08        0.16E+05     0.22E+13
   1050.        0.359E+05       0.263E+00     0.427598E-07     0.43E-07        0.12E+06     0.29E+13
   1150.        0.359E+05       0.238E+00     0.191208E-06     0.19E-06        0.67E+06     0.35E+13
   1250.        0.358E+05       0.206E+00     0.571293E-06     0.67E-06        0.28E+07     0.42E+13

REACTION # 51       C2H2CL4=C2HCL3+HCL
DELTA N =   1    DELTA H(T =  950. K)=  1.211E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.525E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.517E+01      DELTA H= 0.963E+04
      T          EF-EREV         LN AF/AREV      KEQ            KEQ FIT          K FORWARD     K REVERSE
    950.        0.102E+05       0.547E+01     0.106653E+01     0.11E+01        0.13E+02     0.12E+02
   1050.        0.978E+04       0.525E+01     0.176765E+01     0.17E+01        0.22E+03     0.12E+03
   1150.        0.932E+04       0.504E+01     0.263322E+01     0.26E+01        0.23E+04     0.86E+03
   1250.        0.885E+04       0.485E+01     0.362099E+01     0.37E+01        0.16E+05     0.45E+04

REACTION # 52       C2H4CL2=C2H3CL+HCL
DELTA N -   1    DELTA H(T =  950. K)=  1.721E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.394E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.459E+01      DELTA H= 0.149E+05
      T          EF-EREV         LN AF/AREV      KEQ            KEQ FIT          K FORWARD     K REVERSE
    950.        0.153E+05       0.482E+01     0.368931E-01     0.37E-01        0.90E+01     0.24E+03
   1050.        0.150E+05       0.465E+01     0.793572E-01     0.79E-01        0.14E+03     0.18E+04
   1150.        0.146E+05       0.449E+01     0.147312E+00     0.15E+00        0.13E+04     0.92E+04
   1250.        0.142E+05       0.432E+01     0.244430E+00     0.25E+00        0.90E+04     0.37E+05

REACTION # 53       C2H4CL2=C2H4CL+CL
DELTA N -   1    DELTA H(T =  950. K)=  7.835E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.350E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.447E+01      DELTA H= 0.762E+05
      T          EF-EREV         LN AF/AREV      KEQ            KEQ FIT          K FORWARD     K REVERSE
    950.        0.765E+05       0.459E+01     0.250941E-15     0.25E-15        0.92E-02     0.37E+14
   1050.        0.763E+05       0.450E+01     0.118500E-13     0.12E-13        0.46E+00     0.39E+14
   1150.        0.761E+05       0.461E+01     0.283960E-12     0.28E-12        0.12E+02     0.41E+14
   1250.        0.759E+05       0.432E+01     0.406299E-11     0.41E-11        0.17E+03     0.43E+14

REACTION # 54       C2H5CL=C2H4+HCL
DELTA N -   1    DELTA H(T =  950. K)=  1.709E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.121E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.320E+01      DELTA H= 0.147E+05
      T          EF-EREV         LN AF/AREV      KEQ            KEQ FIT          K FORWARD     K REVERSE
    950         0.152E+05       0.344E+01     0.996287E-02     0.10E-01        0.14E+02     0.14E+04
```

```
    1050.       0.149E+05     0.327E+01     0.212838E-01    0.21E-01        0.19E+03     0.90E+04
    1150.       0.145E+05     0.309E+01     0.392415E-01    0.39E-01        0.17E+04     0.43E+05
    1250.       0.141E+05     0.292E+01     0.646938E-01    0.65E-01        0.10E+05     0.16E+06

REACTION # 55     C2H3CL3=C2H2CL2+HCL
DELTA N =   1    DELTA H(T =   950. K)=  1.375E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.218E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.368E+01     DELTA H= 0.114E+05
       T         EF-EREV      LN AF/AREV       KEQ         KEQ FIT         K FORWARD     K REVERSE
     950.       0.119E+05     0.393E+01     0.951414E-01    0.96E-01        0.18E+04     0.19E+05
    1050.       0.115E+05     0.375E+01     0.171663E+00    0.17E+00        0.17E+05     0.10E+06
    1150.       0.111E+05     0.358E+01     0.275262E+00    0.27E+00        0.11E+06     0.40E+06
    1250.       0.107E+05     0.341E+01     0.403802E+00    0.41E+00        0.54E+06     0.13E+07

REACTION # 56     C2H3CL3=C2H3CL2+CL
DELTA N =   1    DELTA H(T =   950. K)=  7.695E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.311E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.426E+01     DELTA H= 0.748E+05
       T         EF-EREV      LN AF/AREV       KEQ         KEQ FIT         K FORWARD     K REVERSE
     950.       0.751E+05     0.440E+01     0.433551E-15    0.44E-15        0.35E+00     0.80E+15
    1050.       0.749E+05     0.429E+01     0.190638E-13    0.19E-13        0.14E+02     0.73E+15
    1150.       0.746E+05     0.420E+01     0.430291E-12    0.43E-12        0.29E+03     0.68E+15
    1250.       0.744E+05     0.410E+01     0.585335E-11    0.59E-11        0.38E+04     0.65E+15

REACTION # 57     C2H3CL=C2H2+HCL
DELTA N =   1    DELTA H(T =   950. K)=  2.472E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.188E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.361E+01     DELTA H= 0.225E+05
       T         EF-EREV      LN AF/AREV       KEQ         KEQ FIT         K FORWARD     K REVERSE
     950.       0.228E+05     0.378E+01     0.244759E-03    0.25E-03        0.54E-02     0.22E+02
    1050.       0.226E+05     0.366E+01     0.770544E-03    0.77E-03        0.17E+00     0.22E+03
    1150.       0.223E+05     0.354E+01     0.196605E-02    0.20E-02        0.30E+01     0.15E+04
    1250.       0.220E+05     0.342E+01     0.427738E-02    0.43E-02        0.34E+02     0.79E+04

REACTION # 58     C2H3CL=C2H3+CL
DELTA N =   1    DELTA H(T =   950. K)=  9.151E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.408E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.473E+01     DELTA H= 0.893E+05
       T         EF-EREV      LN AF/AREV       KEQ         KEQ FIT         K FORWARD     K REVERSE
     950.       0.896E+05     0.489E+01     0.315282E-18    0.32E-18        0.26E-04     0.81E+14
    1050.       0.894E+05     0.477E+01     0.288921E-16    0.29E-16        0.21E-02     0.74E+14
    1150.       0.891E+05     0.466E+01     0.119501E-14    0.12E-14        0.82E-01     0.69E+14
    1250.       0.889E+05     0.456E+01     0.270123E-13    0.27E-13        0.18E+01     0.65E+14

REACTION # 59     C2H2CL2=C2H2CL+CL
DELTA N =   1    DELTA H(T =   950. K)=  9.030E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.626E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.603E+01     DELTA H= 0.885E+05
       T         EF-EREV      LN AF/AREV       KEQ         KEQ FIT         K FORWARD     K REVERSE
     950.       0.884E+05     0.598E+01     0.178735E-17    0.18E-17        0.32E-04     0.18E+14
    1050.       0.885E+05     0.601E+01     0.155157E-15    0.16E-15        0.29E-02     0.18E+14
    1150.       0.885E+05     0.605E+01     0.621369E-14    0.62E-14        0.12E+00     0.19E+14
    1250.       0.887E+05     0.609E+01     0.138338E-12    0.14E-12        0.27E+01     0.19E+14

REACTION # 60     C2H2CL2=C2HCL+HCL
DELTA N =   1    DELTA H(T =   950. K)=  2.467E+04 CAL/MOLE     DELTA S (T =  950. K) =  3.505E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.517E+01     DELTA H= 0.224E+05
       T         EF-EREV      LN AF/AREV       KEQ         KEQ FIT         K FORWARD     K REVERSE
     950.       0.228E+05     0.538E+01     0.124698E-02    0.13E-02        0.89E-02     0.72E+01
```

```
    1050.      0.225E+05     0.522E+01     0.390816E-02     0.39E-02        0.29E+00      0.75E+02
    1150.      0.222E+05     0.508E+01     0.991174E-02     0.99E-02        0.52E+01      0.52E+03
    1250.      0.218E+05     0.494E+01     0.214175E-01     0.22E-01        0.58E+02      0.27E+04

REACTION # 41     C2HCL3=C2HCL2+CL
DELTA N =   1    DELTA H(T =  950. K)=  9.127E+04 CAL/MOLE      DELTA S (T =  950. K) =  3.622E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.615E+01      DELTA H= 0.898E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.      0.894E+05     0.596E+01     0.104635E-17     0.10E-17        0.11E-05      0.11E+13
     1050.      0.896E+05     0.609E+01     0.958961E-16     0.97E-15        0.12E-03      0.12E+13
     1150.      0.899E+05     0.622E+01     0.405042E-14     0.41E-14        0.54E-02      0.13E+13
     1250.      0.902E+05     0.634E+01     0.943091E-13     0.94E-13        0.14E+00      0.14E+13

REACTION # 42     C2HCL2+CH3=C2HCL+CH3CL
DELTA N =   0    DELTA H(T =  950. K)= -6.998E+04 CAL/MOLE      DELTA S (T =  950. K) = -7.365E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.402E+01      DELTA H=-0.706E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.     -0.700E+05    -0.371E+01     0.314343E+15     0.32E+15        0.57E+12      0.18E-02
     1050.     -0.704E+05    -0.394E+01     0.908859E+13     0.90E+13        0.61E+12      0.68E-01
     1150.     -0.709E+05    -0.414E+01     0.477615E+12     0.47E+12        0.65E+12      0.14E+01
     1250.     -0.713E+05    -0.432E+01     0.395985E+11     0.40E+11        0.69E+12      0.17E+02

REACTION # 43     C2HCL3=C2CL2+HCL
DELTA N =   1    DELTA H(T =  950. K)=  1.943E+04 CAL/MOLE      DELTA S (T =  950. K) =  3.186E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.358E+01      DELTA H= 0.172E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.      0.175E+05     0.377E+01     0.401261E-02     0.40E-02        0.99E-04      0.25E-01
     1050.      0.173E+05     0.363E+01     0.965899E-02     0.96E-02        0.50E-02      0.51E+00
     1150.      0.170E+05     0.350E+01     0.197262E-01     0.20E-01        0.13E+00      0.64E+01
     1250.      0.167E+05     0.339E+01     0.355913E-01     0.36E-01        0.19E+01      0.54E+02

REACTION # 44     CH3+C2H5CL=CH3CL+C2H5
DELTA N =   0    DELTA H(T =  950. K)= -1.581E+03 CAL/MOLE      DELTA S (T =  950. K) = -7.594E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.452E+00      DELTA H=-0.172E+04
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.     -0.158E+04    -0.382E+00     0.157681E+01     0.16E+01        0.30E+12      0.19E+12
     1050.     -0.168E+04    -0.433E+00     0.145226E+01     0.14E+01        0.34E+12      0.24E+12
     1150.     -0.178E+04    -0.478E+00     0.135125E+01     0.13E+01        0.38E+12      0.28E+12
     1250.     -0.188E+04    -0.522E+00     0.126737E+01     0.13E+01        0.41E+12      0.32E+12

REACTION # 45     CH3+CH2CL2=CH3CL+CH2CL
DELTA N =   0    DELTA H(T =  950. K)= -2.732E+03 CAL/MOLE      DELTA S (T =  950. K) =  2.291E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.116E+01      DELTA H=-0.273E+04
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.     -0.273E+04     0.115E+01     0.134787E+02     0.13E+02        0.26E+10      0.20E+09
     1050.     -0.274E+04     0.115E+01     0.117368E+02     0.12E+02        0.38E+10      0.33E+09
     1150.     -0.272E+04     0.116E+01     0.104722E+02     0.10E+02        0.53E+10      0.50E+09
     1250.     -0.266E+04     0.118E+01     0.953045E+01     0.95E+01        0.68E+10      0.72E+09

REACTION # 46     CH3+CHCL=C2H4CL
DELTA N =  -1    DELTA H(T =  950. K)= -8.805E+04 CAL/MOLE      DELTA S (T =  950. K) = -3.658E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.121E+03      DELTA H= 0.210E+06
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD     K REVERSE
      950.     -0.862E+05    -0.615E+01     0.983285E+00     0.16E+05        0.73E+09      0.74E+09
```

```
      1050.       -0.859E+05      -0.601E+01      0.187150E+16      0.63E+03          0.73E+09       0.39E-06
      1150.       -0.856E+05      -0.589E+01      0.523833E+14      0.40E+13          0.73E+09       0.14E-04
      1250.       -0.853E+05      -0.577E+01      0.262394E+13      0.62E+16          0.73E+09       0.28E-03

REACTION # 47      CH3+CHCL=C2H4+CL
DELTA N =    0    DELTA H(T =  950. K)= -6.458E+04 CAL/MOLE     DELTA S (T =  950. K) = -1.139E+01 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N = 0.995E+01     DELTA H=-0.171E+05
        T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
      950.        -0.646E+05      -0.573E+01      0.236439E+13      0.18E+09          0.15E+14       0.62E+01
     1050.        -0.645E+05      -0.571E+01      0.103194E+01      0.75E+08          0.15E+14       0.14E+14
     1150.        -0.645E+05      -0.569E+01      0.516878E+10      0.37E+08          0.15E+14       0.24E+04
     1250.        -0.645E+05      -0.568E+01      0.544740E+09      0.20E+08          0.15E+14       0.23E+05

REACTION # 48      CH3+CH2CL2=CHCL2+CH4
DELTA N =    0    DELTA H(T =  950. K)= -4.546E+03 CAL/MOLE     DELTA S (T =  950. K) =  1.853E-01 CAL/DEG/MOLE
(SECOND VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)-  950. TO 1250.  DELTA S/R - DELTA N =-0.293E+01     DELTA H=-0.100E+05
        T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
      950.        -0.455E+04      0.933E-01       0.122130E+02      0.11E+02          0.67E+11       0.55E+10
     1050.        -0.451E+04      0.110E+00       0.971557E+01      0.65E+01          0.67E+11       0.69E+10
     1150.        -0.445E+04      0.140E+00       0.107458E+01      0.43E+01          0.67E+11       0.63E+11
     1250.        -0.436E+04      0.178E+00       0.690754E+01      0.30E+01          0.67E+11       0.98E+10
```

VIII. SELECTED BIBLIOGRAPHY

[1] Sittig, M., Hazardous and Toxic Effects of Industrial Chemicals, Noyes Data Corporation (1979).

[2] Handbook of Chemistry and Physics, 63 rd Edition, CRC, pp.D-132 (1982-83).

[3] Kebbekus, B.B., and Bozzelli, J.W., " Determination of Selected Toxic Organic Vapors in Air by Adsorbent Trapping and Capillary Gas Chromatography", J. Environ. Sci. Health, A17(5), 713, (1982).

[4] Kraus, R., " Enviromental Carcinogenesis : Regulation on the Frontiers of Science ", Enviromental Law, vol.7, No.1, 83 (1976).

[5] Sworzn, E. M., and Ackerman, D. G., " Interim Guidelines for the Disposal/Destruction of PCB's and PCB Items by Non-thermal Methods ", EPA - 60/2 - 82 - 069, NTIS PB82 - 217498 (1982).

[6] Karasek, F. W., Clement, R.E., and Viau, A. C., J. Chromatography, Vol.239, 173 (1982).

[7] Gerber, C. R., " EPA's Hazardous Waste Research Programs : 1985 ", J. Air Pollution Control Ass., Vol. 35, 7, 749 (1985).

[8] Shaub, W. M., and Tsang, W., " Dioxin Formation in Incinerators ", Environ. Sci. Technol., Vol.17, 12,

721 (1983).

[9] Graham, J. L., Hall, L. H., and Dellinger, B., " Laboratory Investigation of Thermal Degradation of a Mixture of Hazardous Organic Compounds 1. ", Environ. Sci. Technol., Vol. 20, 703 (1986).

[10] Stull, D. R., Westrum, Jr., E. F., and Sinke, G. C., " The Chemical Thermodynamics of Organic Compounds", New York Wiley (1969).

[11] Louw, R., Dijks, H., and Mulder, P., " Thermal Hydro- dichlorination of (poly) Chlorinated Organic Compounds ", Chemistry and Industry, 19, 759 (1983).

[12] Mahmood, B., M.S. Thesis, NJIT, 1985.

[13] Mingta Hu, M.S. Thesis, NJIT, 1987.

[14] Ritter, E., M.S. Thesis, NJIT, 1986.

[15] Lee, W., M.S. Thesis, NJIT, 1986.

[16] Lee, K. C., Jahnes, H. J., Macauley, D. C., " Thermal Oxidation Kinetics of Selected Organic Compounds", J. Air Pollution Control Ass., Vol. 29, 7, 749 (1979).

[17] Bose, D., and Senkan, S. M., " On the Combustion of Chlorinated Hydrocarbons I. Trichloroethylene ", Comb. Sci. Tech., Vol. 35, 187 (1983).

[18] Valeiras, H., Gupta, A. K., Senkan, S. M., " Laminar Burning Velocities of Chlorinated Hydrocarbon-Methane-Air Flames ", Comb. Sci. Tech., 123 (1984).

[19] Senkan, S. M., " On the Combustion of Chlorinated Hydrocarbons II. Detailed Chemical Kinetic Modeling of the Intermediate Zone of the Two-Stage Trichloroethylene-Oxygen-Nitrogen Flame ", Comb. Sci. Tech., 333 (1984).

[20] Sorbo, N. W., Steeper, R. R., Chang, D. P. Y., and Law, C. K., " Incineration of Liquid Hazardous Wastes: Vaporization and Combustion of Dropletsof Chlorinated Hydrocarbons " , Technical Meeting of the Central States Section of the Combustion Institute, Argonne, ILL (1987).

[21] Frenklash, M., Hsu, J. P., Miller, D. L., and Matula, R. A., " Shock - Tube Pyrolysis of Chlorinated Hydrocarbons : Formation of Soot ", Comb. and Flame, Vol. 64, 141 (1986).

[22] Louw, R., Dijks, H. M., and Mulder, P., " Pyrolysis of Benzene and Chlorobenzene in an Atmosphere of Hydrogen; Formation of Methane", J. of the Royal Netherland Chemical Soc., 103/10, 271 (1984).

[23] Benson, S. W., Weissman, M., " Mechanism of the Pyrolysis of C2HCl5, Molecular and Radical Steps", Int'l J. of Chem. Kin., Vol. 14, 1287 (1982).

[24] Manion, J. A., Mulder, P., and Louw, R., " Gas-Phase Hydrogenolysis of Polychlorobiphenyls", Environ. Sci. Technol., Vol.19, 280 (1985).

[25] Chuang, S.C., and Bozzelli, J. W., " Gas-Phase Reactions of Chloroform and 1,1,2-Trichloroethane With Hydrogen in a Tubular Flow Reactor", Ind. Eng. Chem. Process Des. Dev., Vol. 25, 317 (1986).

[26] Mahmood, R., and Bozzelli, J.W., Ind. Eng. Chem., Accepted for Publication.

[27] Tsao Hu, M.S. Thesis, NJIT, (1987).

[28] Kee, R. J., Miller, T. H., Jefferson, T. H., "CHEMKIN: A General-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package", SANDIA Report, 1980.

[29] Combourieu J., Le Bras, G., and Paty C., " Reaction of H Atom with CH2Cl2 Application to the inhibition of Flames", Forteenth Int'l Symposium on Combustion (1973).

[30] Hassler, J. C., and Setser, D. W.," Reaction of Methylene with Dichloromethane and Nonequilibrium Unimolecular Elimination Reactions of 1,1-C2H4Cl2 and 1,1,2 C2H3Cl3 Molecules", J. Chem. Phys., Vol. 45, No. 9, 3237 (1966).

[31] Murgulescu, I. G., and Weissman M., " The Effect of Methane on the Thermal Decomposition of Chloroform; I. The First Three Reaction Steps", Rev. Roum. Chem., Vol. 21, No. 9-10, 1275 (1976).

[32] Murgulescu, I. G., and Weissman M., " The Effect

of Methane on the Thermal Decomposition of Chloroform; II. The Fourth Reaction Step", Rev. Roum. Chem., Vol. 21, No. 11-12, 1435 (1976).

[33] Tavakoli, J. and Bozzelli, J. W., "Gas-Phase reaction of Methylene Chloride with Methane in a Tubular Flow Reactor at Atmospheric Pressure", Central State Technical Meeting of The Combustion Institute, 1987.

[34] Ritter, E. and Bozzelli, J. W., " Thermal Decomposition of Chlorobenzene in H2 and He Atmospheres", Central State Technical Meeting of The Combustion Institute, 1987.

[35] Westbrook, C. K., Creighton, J., Lund, C., and Dryer, F. L., "A Numerical Model of Chemical Kinetics of Combustion in a Turbulant Flow Reactor", J.Phys. Chem., Vol. 81, 2542, (1977).

[36] Granada, A., Karra, S. B., and Senkan, S. M., "Conversion of CH4 into C2H2 and C2H4 by the Chlorine-Catalyzed Oxidative-Pyrolysis (CCOP) Process. I. Oxidative Pyrolysis of CH3Cl", Ind. Eng. Chem. Res., Vol. 26, No.9, 1901 (1987).

[37] Kara,S. B., Senkan, S. M., "Chemical Structure of Sooting CH3Cl/CH4/O2/Ar and CH4/O2/Ar Flame",Central States Technical Meeting of The Combustion Institute, 1987.

[38] Supelco Chromatography Supplies, Catalog 21, 1983.

[39] Benson S. W., and Weissman, M., " Pyrolysis of Methyl Chloride, a Pathway in the Chlorine-Catalyzed Polymerization of Methane," Int'l J. Chem. Kin., Vol. 16, 307 (1984).

[40] Dean, A. M., " Predictions of Pressure and Temperature Effects Upon Radical Addition and Recombination reactions", J. Phys. Chem., Vol. 89, 4600 (1985).

[41] Robinson, P. J., and Holbrook, K. A., Unimolecular Reactions, Wiley-Interscience, London (1975).

[42] Gardiner Jr., W. C., Rate and Mechanisms of Chemical Reactions, W. A. Benjamin Inc., New York (1969).

[43] Laidler, K. J., Theories of Chemical Reaction Rates, McGraw-Hill Bool Co., New York (1969).

[44] Benson, S. W., Thermochemical Kinetics, John Wiley & Sons Inc. (1976).

[45] Come, G. M., Pyrolysis, Theory and Industrial Practice, Chap. 11, Academic Press (1983)

[46] Mulcahy, M. F. R., Gas Kinetics, Nelson, London (1973).

[47] Leathard, D. A. and Shwlock, Identification Techniques in Gas Chromatography, John & Wiley,

1970.

[48] Back, M. H., and Back, R. A., Pyrolysis, Theory and Industrial Practice, Chap. 1, Academic Press (1983).

[49] Kaufman, F., Progress in Reaction Kinetics, Ed. Porter, G., Vol. 1, Chap.1, (1961).

[50] Levenspiel, O., Chemical Reaction Engineering, John & Wiley (1972).

[51] Westmoreland, P. R., Howard, J. B., Longwell, J. P., and Dean, A. M.," Prediction of Rate Constants for Combustion and Pyrolysis Reactions by Bimolecular QRRK ", AIChe J., Vol. 32, No. 12, 1971 (1986).

[52] Chang, S. H., and Bozzelli, J. W., "Kinetic Parameters for Coupled Bulk and Wall Reactions in a Tubular Flow Reactor", AIChE J., Vol. 33, No.7, 1207 (1987).

[53] Poirier, R. V., and Carr Jr., R. W., "The Use of Tubular Flow Reactors for Kinetic Studies over Extended pressure Ranges", The J. Phys. Chem., Vol. 75, No. 10, 1593 (1971).

[54] Albright, L. F., and Tsai, T. C., Theory and Industrial Practice, Chap. 10, Academic Press (1983).

[55] Troe, J., "Theory of Thermal Unimolecular

Reactions at Low Pressures. I. Solutions of the Master Equation. II. Strong Collision Rate Constants. Applications," J. Chem. Phys., Vol. 66, 4745 and 4758 (1977).

[56] Semenov, N. N., Some Problems in Chemical Kinetics and Reactivity, Princeton University Press (1958).

[57] Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., The Properties of Gases and Liquids, 3rd Ed., McGraw-Hill Book Co., New Yor (1977).

[58] Forst, W., Theory of Unimolecular Reactions, Academic Press, New York (1973).

[59] Smith, J. M., and Van Ness, H. C., Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, New York (1975).

[60] Shimanouchi, T., "Tables of Molecular Vibration Frequencies, Consolidated Vol.I"; Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39.