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

Javad Tavakoli-Attar  
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**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**

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**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  
fulfillment 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  
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## ABSTRACT

Title of Thesis : Gas-Phase Reactions of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2/\text{C}_2\text{HCl}_3$  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 °C. Experiments were conducted isothermally,  $\pm 5$  °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 °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<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar :

$$k = 1.166E09 * \text{Exp}(-44.85/RT) \quad (1/\text{sec})$$

Methylene chloride in C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar :

$$k = 8.11E08 * \text{Exp}(-43.2/RT) \quad (1/\text{sec})$$

Trichloroethylene in C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar :

$$k = 1.13E05 * \text{Exp}(-30.67/RT) \quad (1/\text{sec})$$

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<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> system and another one with 72 reactions for mixture of C<sub>2</sub>HCl<sub>3</sub>+CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> system were found to reproduce experimental results. A rate constant for :

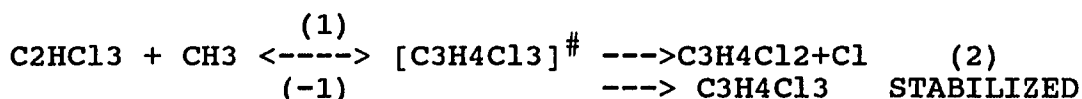
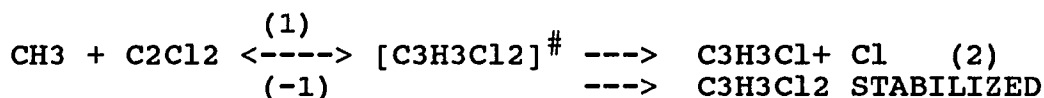
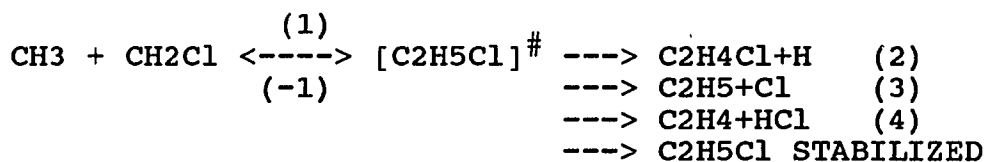
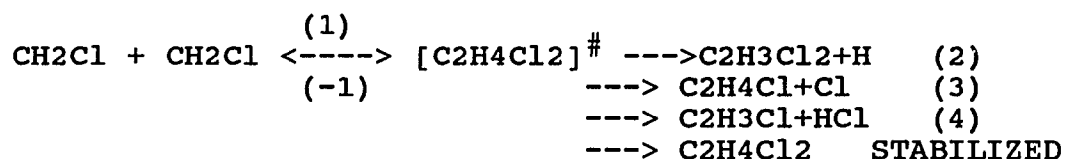


chlorine elimination from methylene chloride was found to dominate HCl elimination by 5 orders of magnitude with rate constants and E<sub>a</sub>'s was determined for this elementary reaction over our experimental conditions. The important

initial reactions in C2HCl3/CH2Cl2/CH4 system were determined as:



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



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

## **ACKNOWLEDGEMENT**

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## 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 CO<sub>2</sub> [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 of 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

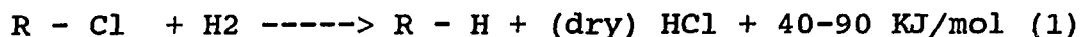
Hazardous Constituents (POHC). The mixture was composed of 2.5% carbon tetrachloride, 2.5% monochlorobenzene, 2.5% 1,1,2-trichloro-1,2,2-trifluoroethane, 2.5% trichloroethylene and 90% toluene by weight. Experiments were conducted in oxygen rich, stoichiometric and oxygen lean (pyrolysis) atmospheres. A flow reactor at a temperature as high as 1100 °C with mean residence times between 0.5-6 seconds was utilized. Results from their studies under pyrolytic conditions and at equivalence ratios of 0.06, and 1, at temperatures of 1000, to and 650 °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 H<sub>2</sub>O product.

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



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 CH<sub>4</sub> 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 CH<sub>4</sub> to the system. Benson and Weissman [39] investigated high temperature (1200-1300 °K) reaction of methyl chloride and methane. They reported C<sub>2</sub> 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.

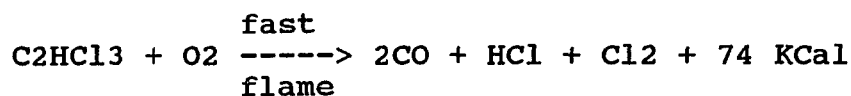
Lee et.al.[16] studied thermal (800-1500 °F) destruction rates of four organic compounds (vinyl chloride, ethyl acrylate, acrolein, and benzene) in air employing a 0.9 mm ID, 135 cm long quartz tube flow reactor. Compounds were run at 1000 ppm in air under uniform temperatures and reaction times of 0.1-1.8 seconds. They [16] reported that, at temperatures above 1450 °F, 99.8% of C<sub>2</sub>H<sub>3</sub>Cl was destroyed



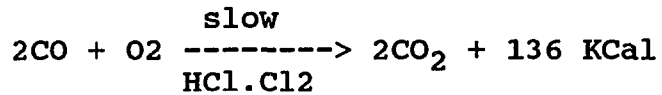
and no benzene was detected (i.e. more than 2 ppm). Higher temperature (1700-1800 °F) was required for complete destruction of ethyl acrylate and acrolein.

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 (C<sub>2</sub>HCl<sub>3</sub>) 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 Cl<sub>2</sub>. This can be shown by the following overall reaction chemistry:



The principal reaction in the second flame zone involves the slow, HCl and Cl<sub>2</sub> inhibited oxidation of CO to CO<sub>2</sub>:



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 developed 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% CO<sub>2</sub>, 11.7% Cl<sub>2</sub>, 7.14% HCl, 1.53% H<sub>2</sub>O, 23.53% O<sub>2</sub>, and 35.7% and a temperature level of 1080 °C. A cold velocity of 10 cm/s was used in the calculations. Qualitative features of the calculated profiles for O<sub>2</sub>, CO, and CO<sub>2</sub> 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 CH<sub>3</sub>Cl/CH<sub>4</sub>/O<sub>2</sub>/Ar and CH<sub>4</sub>/O<sub>2</sub>/Ar flames at atmospheric pressure. In the presence of chlorine, ample amounts of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> 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/O<sub>2</sub> mixtures will be usefull for CH<sub>4</sub> upgrading to C<sub>2</sub> unsaturates.

Sorbo et. al. [20] investigated the vaporization and combustion of droplets of pure chlorinated hydrocarbons (C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>) 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% C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> + 25% n-nonane, however, showed a long period (70 ms) of fairly steady burning. A 25% C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> + 75% nonane mixture showed complete burning (observable limit) while a 80% C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> + 20% nonane mixture showed an early flame extinction. Droplet combustion was inhibited when the Cl/H ratio approached unity. Studying a mixture of 85% C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> 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 C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>.

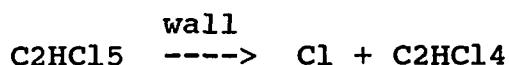
Frenklach et.al. [21] examined soot formation in shock tube pyrolysis of chlorinated methanes. The experiments were performed at temperatures ranging from 1300 to 3000 °k and pressures of 0.4-3.6 bars. Most of the experiments were

performed with approximately the same chlorinated methane concentration i.e.,  $5 \times 10^{17}$  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 ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ) 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 °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  $\text{C}_2\text{H}$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_3$  species. Where for chloromethanes with low H:Cl ratio the formation of  $\text{C}_2$  and its contribution to soot formation at high temperature becomes significant.

Louw et.al. [11] investigated thermal dechlorination of (poly) chlorinated organic compounds ( $\text{C}_6\text{H}_5\text{Cl}$ , p- and o- $\text{C}_6\text{H}_4\text{Cl}_2$ , E- $\text{CHCl}=\text{CHCl}$ ,  $\text{C}_2\text{Cl}_4$ , and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ ) in hydrogen atmosphere. Experiments were performed at 1 atm. pressure, using a quartz flow reactor and a temperature range of 500-1000 °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 °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<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>) 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<sub>6</sub>H<sub>6</sub>:H<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>Cl:H<sub>2</sub> 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<sub>2</sub>HCl<sub>5</sub> was reported to be heterogeneous (wall) C-Cl bond breaking:



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<sub>2</sub>HCl<sub>5</sub> 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<sub>2</sub>, 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 °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 °C. The major products observed above 850 °C were HCl, CH<sub>4</sub> 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 (CHCl<sub>3</sub> or C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>) is possible at temperatures near 700 °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 CHCl<sub>3</sub>/H<sub>2</sub> and CHCl<sub>2</sub>CH<sub>2</sub>Cl/H<sub>2</sub> 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 °C. They report C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, HCl and benzene as major products. No chlorinated hydrocarbons were observed in the effluent of reactor above 850 °C for reaction time of less than one second.

Several reports on dehydrochlorination of chlorocarbons at high temperature (600 - 1000°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<sub>4</sub>/H<sub>2</sub> reaction were CHCl<sub>3</sub>, HCl, and C<sub>2</sub>Cl<sub>6</sub>. Chlorine free hydrocarbons were not detected, except at temperatures over 800 °C and one second residence time. Major products reported for the CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub> reaction system above 950 °C and 1 second reaction time were CH<sub>4</sub>, HCl, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and benzene. Ritter [14] report that complete destruction of chlorobenzene in a hydrogen environment can be achieved at a temperature of 1273 °K and residence time of one second. The major products were identified as HCl, benzene, and C(s).

Reaction of H atoms with CH<sub>2</sub>Cl<sub>2</sub> were studied by Combourieu et.al. [29]. Various initial concentration ratios of [H]/[CH<sub>2</sub>Cl<sub>2</sub>], ranging from 0.39 to 12.1, were considered. A discharge-flow system on a temperature range of 298-460 °K and total pressure near 1 torr was utilized. The products were identified as HCl, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>. The rate

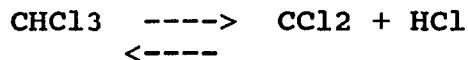
constant of the initial step:



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

Hassler and Setser [30] studied the reaction of methylene (:CH<sub>2</sub>) radical with chloromethane, using a gas phase activation technique. The CH<sub>2</sub>: radical was prepared either photochemically from compounds like CH<sub>2</sub>N<sub>2</sub> or thermally (300 °C) from CH<sub>2</sub>N<sub>2</sub>. The major product at room temperature is reported to be C<sub>2</sub>H<sub>5</sub>Cl and 1,2 C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> 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 °C for reaction times of up to 100 seconds. It was found that the presence of methane in pyrolysis of chloroform, (CH<sub>2</sub>Cl<sub>2</sub>, or CH<sub>3</sub>Cl) favored vinyl chloride formation. The vinyl chloride could be increased up to 100% of product yield by increasing reactant initial concentration ratio ([CH<sub>4</sub>]<sub>i</sub>/[CHCl<sub>3</sub>]<sub>i</sub>) to 2200 at 599 °C and 37-38 second reaction times. The first order rate constant of the initial step (HCl elimination), k<sub>1</sub>, for reaction:



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<sub>2</sub> hydrocarbons) methane. Major products at temperatures of 1260-1310 °K were reported to be ethylene and acetylene. Their yield increased as the degree of CH<sub>3</sub>Cl conversion decreased and the excess of methane increased. Changes of temperature (50 °C), pressure, or addition of HCl were reported to have little effect on reaction products. With CH<sub>4</sub> added C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> 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 CH<sub>4</sub>.

### 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 :



A second kind of unimolecular reaction is rearrangement such as cis/trans isomerization. There are different useful models that describe reaction (1) quantitatively. 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.



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.



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

$$\frac{d[\text{RX}^*]}{dt} = 0 = k_1 [\text{RX}][\text{M}] - k_2 [\text{RX}^*][\text{M}] - k_3 [\text{RX}^*] \quad <1>$$

$$[\text{RX}^*] = \frac{k_1 [\text{RX}][\text{M}]}{k_2 [\text{M}] + k_3} \quad <2>^{**}$$

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

$$\begin{aligned} \frac{-d[\text{RX}]}{dt} &= k_1 [\text{RX}][\text{M}] - k_2 [\text{RX}^*][\text{M}] \\ &= \frac{k_1 k_3 [\text{RX}][\text{M}]}{k_3 + k_2 [\text{M}]} = k_{\text{uni}} [\text{RX}] \quad <3> \end{aligned}$$

From equation <3> one can write:

$$k_{\text{uni}} = \frac{k_1 k_3 [\text{M}]}{k_3 + k_2 [\text{M}]} \quad <4>$$

At high pressure  $k_2 [\text{M}] \gg k_3$  and therefore:

$$k_{\text{inf}} = \frac{k_1 k_3}{k_2} \quad <5>$$

---

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

where  $k_{inf}$  is the high pressure rate constant. While at low pressure the limit is:

$$k_0 = k_1[M] \quad <6>$$

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 plotting  $\log(k_{uni}/k_{inf})$  vs  $\log[M]$  or  $\log P$  where  $P$  is pressure. Hence, the ratio  $k_{uni}/k_{inf}$  will be:

$$(k_{uni}/k_{inf}) = \{1 + [k_{inf}/(k_1.P)]\}^{-1} \quad <7>$$

Lindeman suggested calculation of  $k_1$  by:

$$k_1 = Z_1 \exp(-E_0/RT) \quad <8>$$

where  $Z_1$  is calculated from collision theory. The high pressure rate constant,  $k_{inf}$ , and activation energy,  $E_{inf}$  (assumed equal to critical energy,  $E_0$ ), 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 :

$$k_1 = \frac{Z_1}{(s-1)!} \frac{E_0^{(s-1)} \exp(-E_0/RT)}{RT} \quad <9>$$

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  $k_2 = Z_2 = Z_1$  (i.e. deactivation occurs with every collision), high pressure rate constant according to this theory becomes:

$$k_{inf} = (k_1 k_3 / k_2) = \frac{k_3}{(s-1)!} \frac{(E_0)^{s-1}}{RT} \exp(-E_0/RT) \quad <10>$$

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

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

where  $Z_1$  is proportional to  $T^{.5}$ .

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

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  $k_3$  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  $k_3$ , 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]

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

He defined  $K_3(E)$  as :

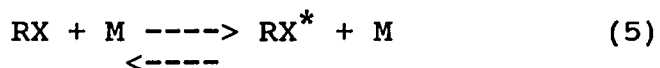
$$K_3(E) = A \frac{(E - E_0)^{s-1}}{E} = A (1 - E_0/E)^{s-1} \quad <14>$$

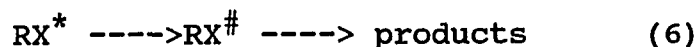
where  $A$  is high pressure  $A$  factor. Using equation <12> it can be shown [41] that :

$$k_{inf} = A \exp(-E_0/RT). \quad <15>$$

In the expressions above,  $k_1$  is calculated by Hinshelwood's expression and  $k_2$  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:





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

The RRKM theory only considers redistributable 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, overall translational energy, and rotational energies with constant angular momentum have no effect on unimolecular reaction of the molecule under consideration. Detail calculations for  $k^*$ ,  $[k]^\#$ ,  $k_1/k_2$ ,  $k_{uni}$ , and  $k_{inf}$  are given elsewhere [41].

The RRKM theory represents 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,  $\nu$ . Energies, expressed in quantized form, can be written as :

$$m = E_0/(h\nu) \quad \text{Critical Energy}$$

$$n = E/(h\nu) \quad \text{Overall Energy.}$$

Hence, the probability a chosen oscillator has energy  $> m$

quanta becomes [41] :

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

and,

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

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

The high pressure rate constant is given as:

$$k_{inf} = \sum_{n=m}^{inf} \frac{k_1(nhv) k_3(nhv)}{k_2} = A \exp(-E_0/KT) \quad <19>$$

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

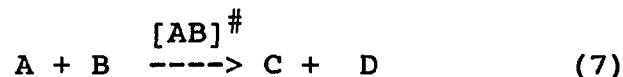
$$k_{uni}/k_{inf} = (1-\alpha)^s \sum_{p=0}^{inf} \frac{\alpha^p (p+s-1)! / [p!(s-1)!]}{1 + (A/k_2[M]) (p+m)!(p+s-1)! / [(p+m+s-1)!p!]} \quad <20>$$

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,  $e/k_p$ , 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:



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

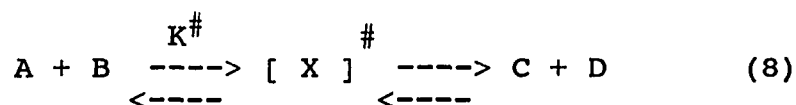
In SCT the bimolecular reaction rate is given as fraction of A and B collisions along the line-of-center which have necessary activation energy ( $e^{-E_{AB}/RT}$ ) and proper internal coordinates ( $p_{AB}$ ):

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

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 :



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

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

Employing statistical mechanics one can show that [41] :

$$k_1 = \frac{k_b T}{h} K^\ddagger \quad <23>$$

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,  $K^\ddagger$ , (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 :

$$K^\ddagger = \exp[-\Delta G^\ddagger/RT] = \exp[\Delta H^\ddagger - T \Delta S^\ddagger] \quad <24>$$

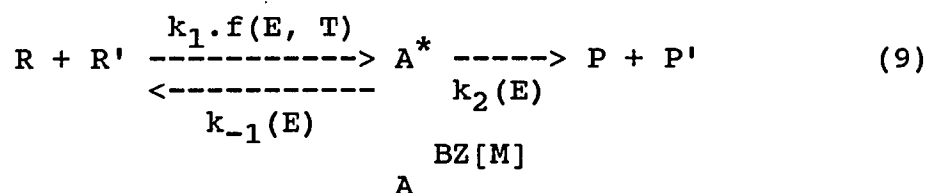
Substituting  $\Delta H^\ddagger = \Delta E^\ddagger - RT$  and combining <24> with <23> gives :

$$k_r = \frac{ek_b T}{h} \exp[\Delta S^\ddagger/R] \cdot \exp[-\Delta E^\ddagger/RT] \quad <25>$$

Del  $E^\ddagger$  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 :



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

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

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

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

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

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

where  $\langle \text{Del } E_{\text{coll}} \rangle$  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:

$$k_S = \frac{BZ[M] \cdot k_1 \cdot f(E, T)}{BZ[M] + k_{-1}(E) + k_2(E)} \quad <29>$$

$$k_R = \frac{k_2(E) * k_1 \cdot f(E, T)}{BZ[M] + k_{-1}(E) + k_2(E)} \quad <30>$$

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-pressure limit  $[M] \rightarrow 0$  and therefore:

$$\lim_{[M] \rightarrow 0} k_S = \frac{[M] \cdot B.Z. \cdot k_1 \cdot f(E, T)}{k_{-1}(E) + k_2} \quad <31>$$

$$\lim_{[M] \rightarrow 0} k_R = \frac{k_1 k_2(E) \cdot f(E, T)}{k_{-1}(E) + k_2(E)} \quad <32>$$

High-pressure limit values of  $k_S$  and  $k_R$  can be obtained from equations <29> and <30> by having  $[M] \rightarrow \infty$ . This will result in the following equations :

$$\lim_{[M] \rightarrow \infty} k_S = k_1 \quad <33>$$

$$\lim_{[M] \rightarrow \infty} k_R = \frac{1}{[M]} * \frac{k_1}{B.Z} * k_2(E) \cdot f(E, T) \quad <34>$$

It is apparent from <34> that product exit channels are pressure dependent (i. e. dependent on concentration of M). This is consistent 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 °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:

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

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

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

Where:

$k_b$  = bulk rate constant, 1/sec

$R$  = reactor diameter, cm

$D_{AB}$  = diffusion coefficient of an A-B binary system,  
cm<sup>2</sup>/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:

$$\alpha = D/(K.R^2) > 0.5 \quad <38>$$

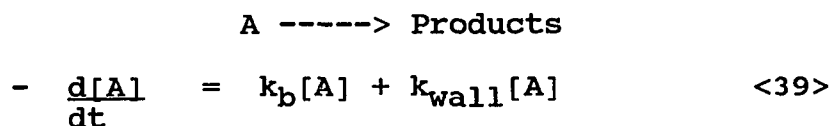
plug flow assumption for a first order reaction regime provides results within 10% accuracy. The value for alpha in this study was well above 0.5, and hence, the plug flow assumption is acceptable.



#### 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 :



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

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

where:

$$S/V = \text{surface to volume ratio, } 1/\text{cm}$$

$$k_w = \text{gamma } w/4, \text{ cm/sec}$$

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

obtains:

$$k_{\text{exp}} = k_b + k_w \cdot 2/R \quad <41>$$

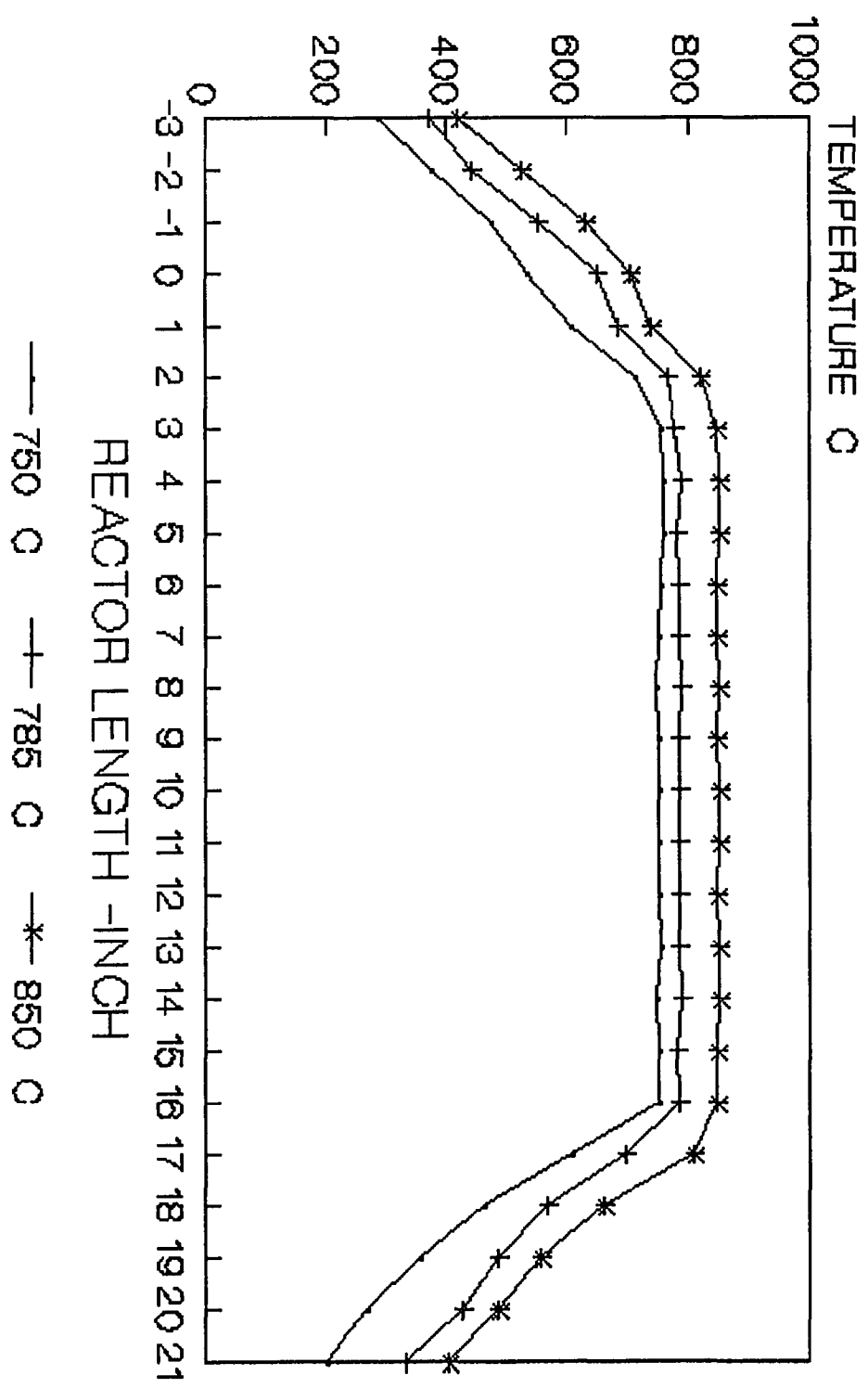
Therefore, one can easily decouple the bulk and wall rate constants simply by having global rate constants for two different reactor diameters.

#### IV. EXPERIMENTAL

A tubular flow reactor system was operated isothermally at temperatures in the range 750-1000 °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 fluxes and allowed a uniform ( $\pm 5$  °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

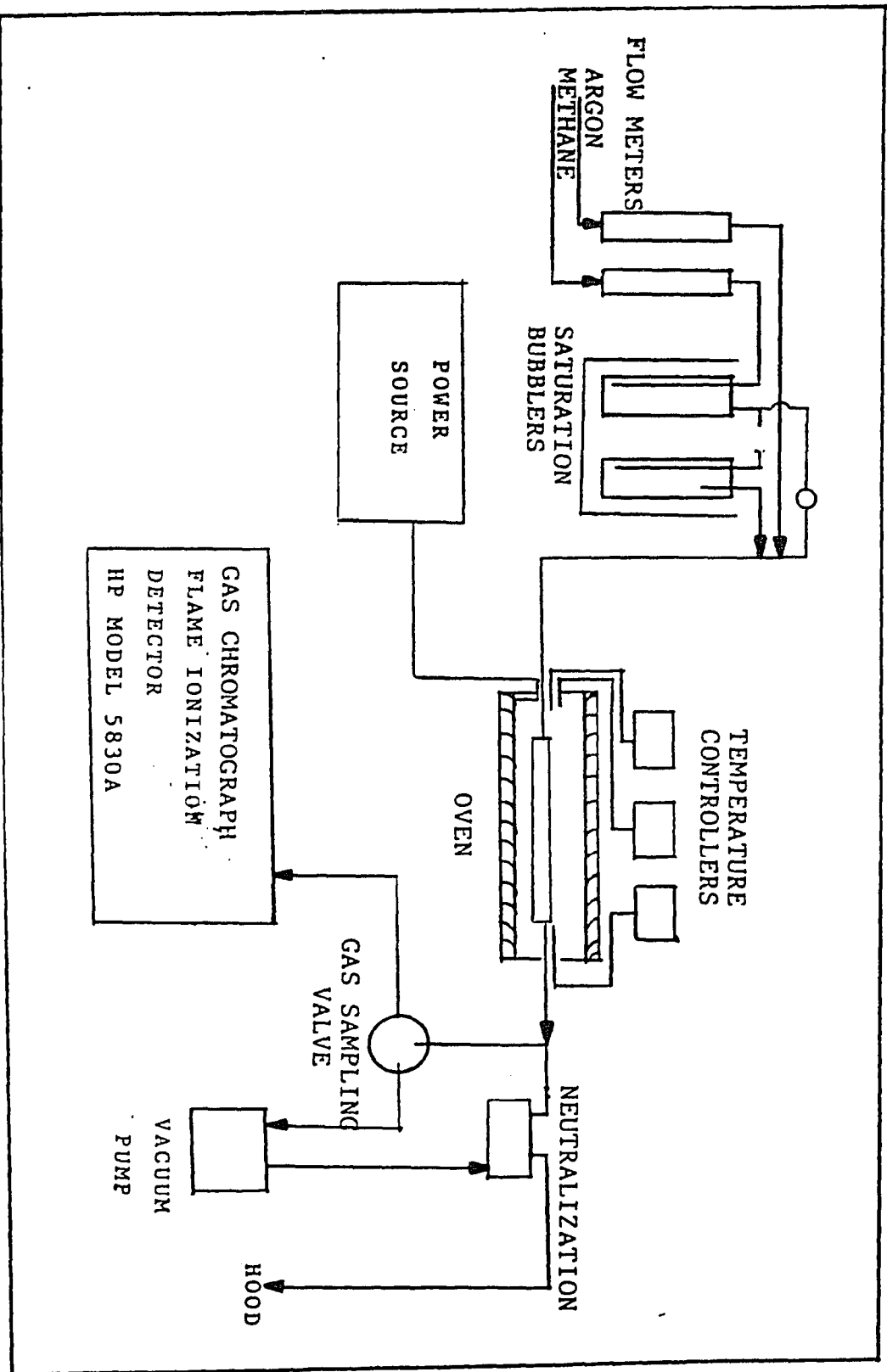


for three different temperatures 750, 785, and 850 °C illustrating the linear temperature along the reactor length.

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 °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,  $\text{CH}_2\text{Cl}_2/\text{CH}_4$  and  $\text{C}_2\text{HCl}_3/\text{CH}_4$ , 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 °C). Constant peak areas of  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{HCl}_3$  for 2 different flow rates exhibited complete saturation of methane. The combined methane and reagent gas flow was diluted by commercial grade argon

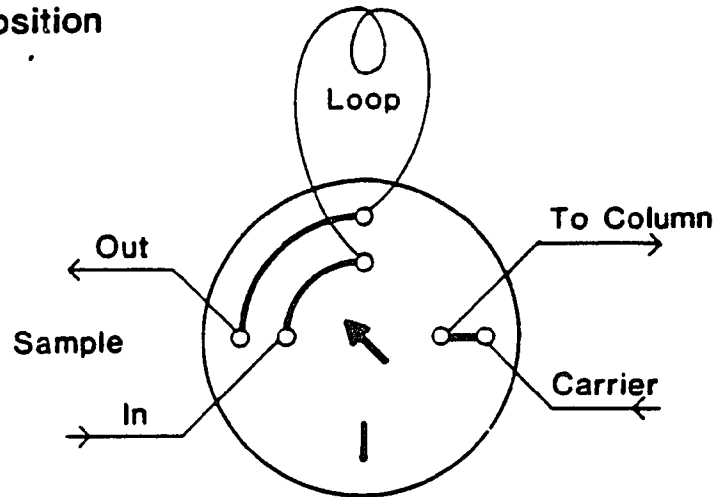
**FIGURE-2 EXPERIMENTAL SET-UP**



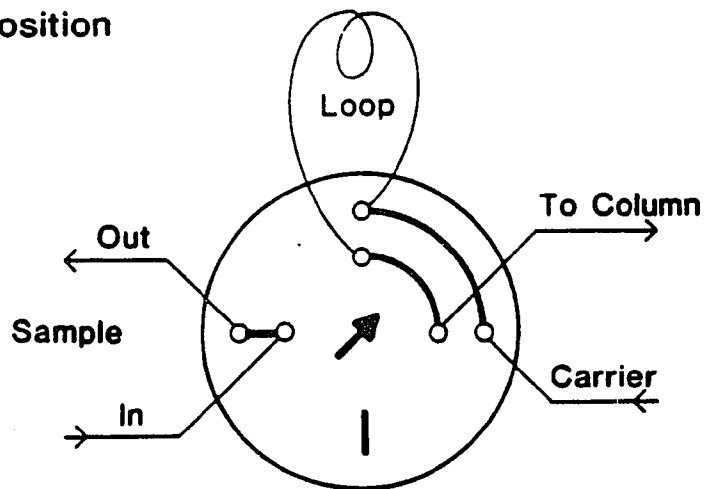
before entering the reactor. A constant molar ratio  $\text{CH}_2\text{Cl}_2:\text{CH}_4:\text{Ar}$  of 1:4:10 was maintained throughout this study. When mixture of  $\text{C}_2\text{HCl}_3$  and  $\text{CH}_2\text{Cl}_2$  was used as reagent, a constant molar ratio  $\text{C}_2\text{HCl}_3:\text{CH}_2\text{Cl}_2:\text{CH}_4:\text{Ar}$  of 1:1:40:40 was maintained through the experiments. Total gas flowrates were varied from 22 to 1395 cc/min for  $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{Ar}$  runs and 200 to 2500 cc/min for the  $\text{C}_2\text{HCl}_3/\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{Ar}$  mixture to achieve varied reaction times. All flow rates were measured by calibrated Fisher - Porter rotameters. The reagent gases were preheated up to  $450^\circ\text{C}$  before entering the reactor.

Effluent from the reactor, held at  $100^\circ\text{C}$  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 neutralization 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<sub>1</sub> chlorocarbons are close to one and for C<sub>2</sub> 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 exhaust 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 <sub>2</sub> Cl <sub>2</sub>	1.
CHCl <sub>3</sub>	1.05
CCl <sub>4</sub>	1.10
C <sub>2</sub> HCl <sub>3</sub>	2.27
C <sub>2</sub> Cl <sub>4</sub>	2.15
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> (cis)	1.90
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> (trans)	1.95
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	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 °C 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 °C, 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**

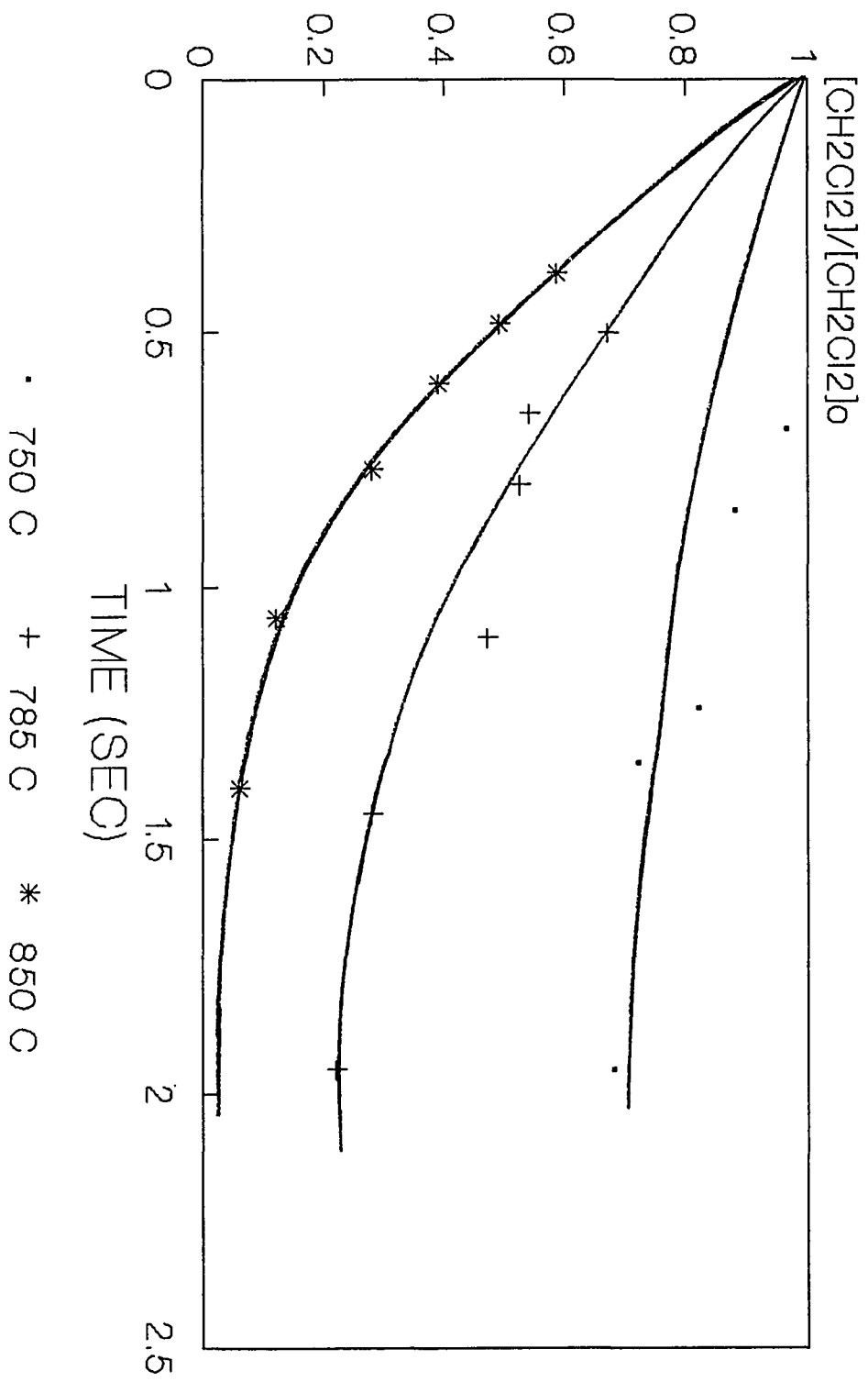


Table II- Summary of Different Runs  
CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>

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	0.118-2.22	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 CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>4</sub>:Ar of 1:4:10, showed linear decay plots ( plots of LN [C]/[C]<sub>0</sub> 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 °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 °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:

$$k'_{4 \text{ mm}} = 4.35 \text{ E}08 * \exp [-42000/(RT)] \quad \text{sec}^{-1}$$

$$k'_{10.5 \text{ mm}} = 6.7 \text{ E}09 * \exp [-48500/(RT)] \quad \text{sec}^{-1}$$

$$k'_{16 \text{ mm}} = 1.72 \text{ E}10 * \exp [-50600/(RT)] \quad \text{sec}^{-1}$$

**FIGURE-5 FIRST ORDER DECAY PLOT FOR  
CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar 10.5 mm ID REACTOR**

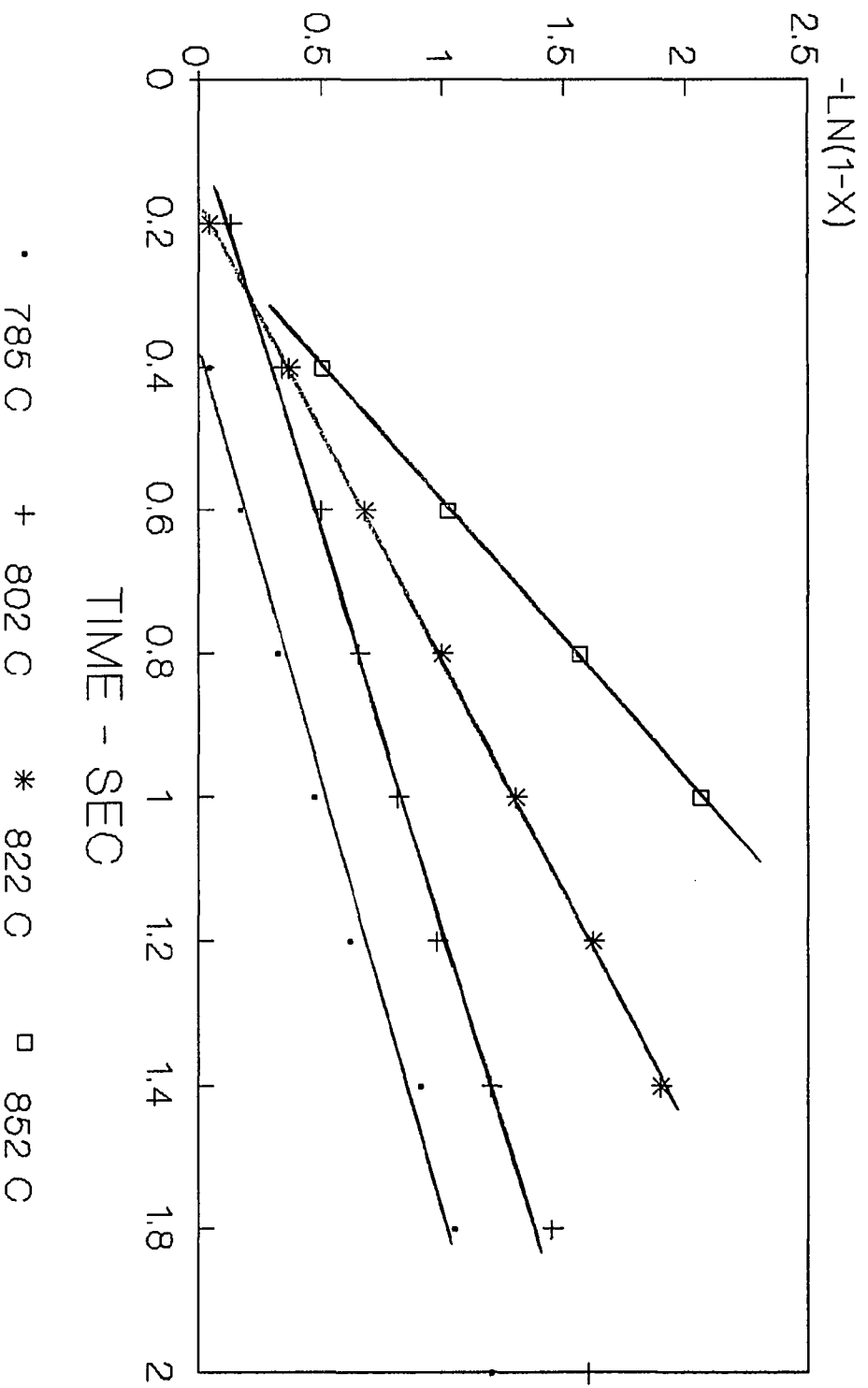


TABLE III - RATE CONSTANTS FOR CH<sub>2</sub>CL<sub>2</sub> + CH<sub>4</sub> + Ar  
 [CH<sub>2</sub>CL<sub>2</sub>]:[CH<sub>4</sub>]:[Ar] 1:4:10  
 P = 1 atm

ID (mm)	4	10.5	16		
T (K)	k'			k <sub>b</sub>	k <sub>w</sub>
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 CH<sub>2</sub>CL<sub>2</sub> in 4, 10.5, and 16 mm ID reactor

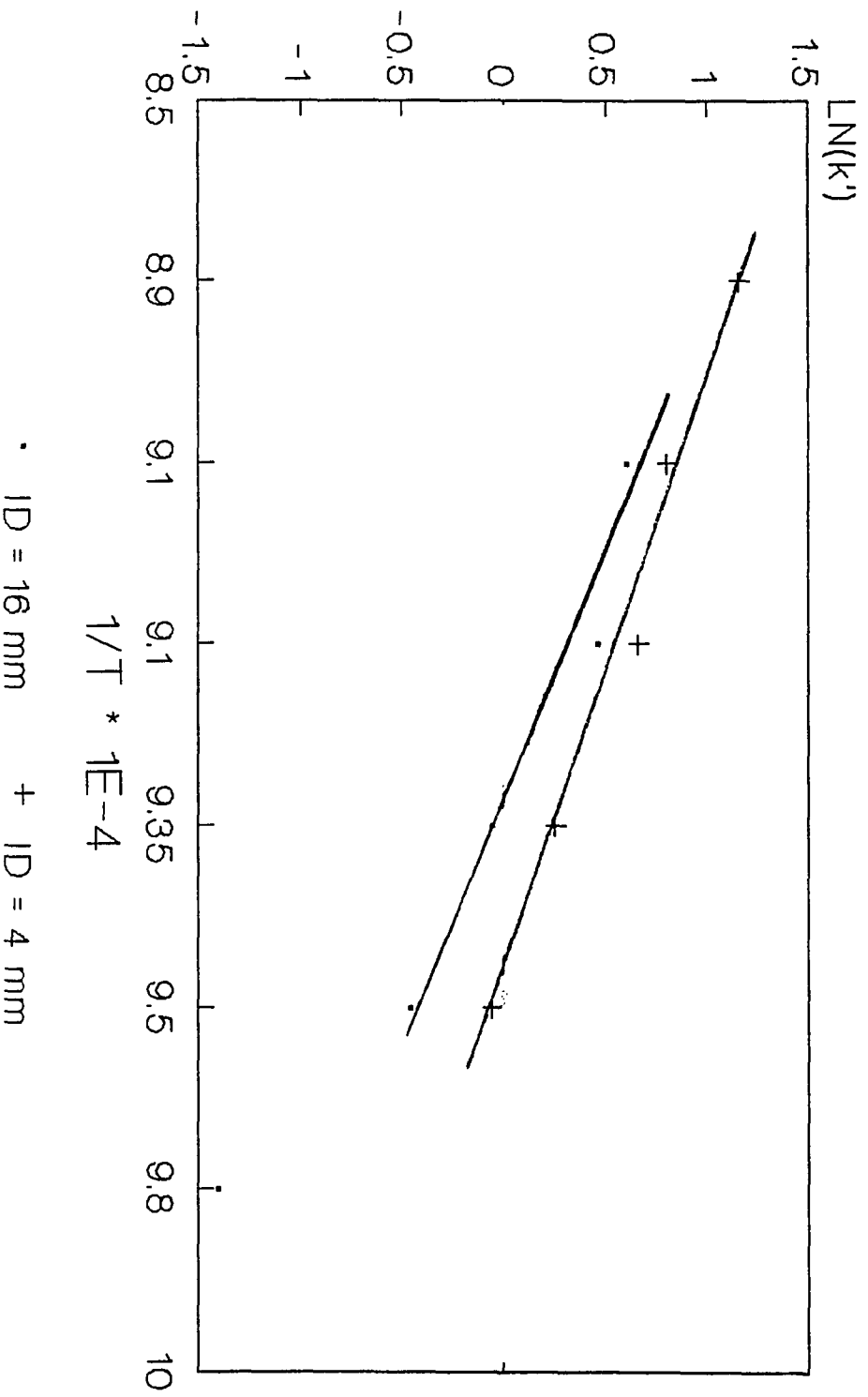
Where T is temperature in °K and R is gas constant in cal/(mol-°K). Previous studies have demonstrated that under isothermal condition, change in S/V ratio often directly affects the overall rate constants for these reactions [12-15, 25-27], because of wall reactions.

Table IV illustrates decomposition of CH<sub>2</sub>CL<sub>2</sub> in CH<sub>4</sub> + 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 CH<sub>2</sub>Cl<sub>2</sub> 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

Table-IV TEMPERATURE, DIAMETER EFFECT ON CONVERSION  
CH<sub>2</sub>Cl<sub>2</sub> / CH<sub>4</sub>

Dia / Temp (mm) / (C)	t = 1 (sec.)		
	783	822	855
	{1 - [CH <sub>2</sub> Cl <sub>2</sub> ] / [CH <sub>2</sub> Cl <sub>2</sub> ] <sub>0</sub> } X 100		
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

not important for reactor diameter greater than 10.5 mm.

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 :

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

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

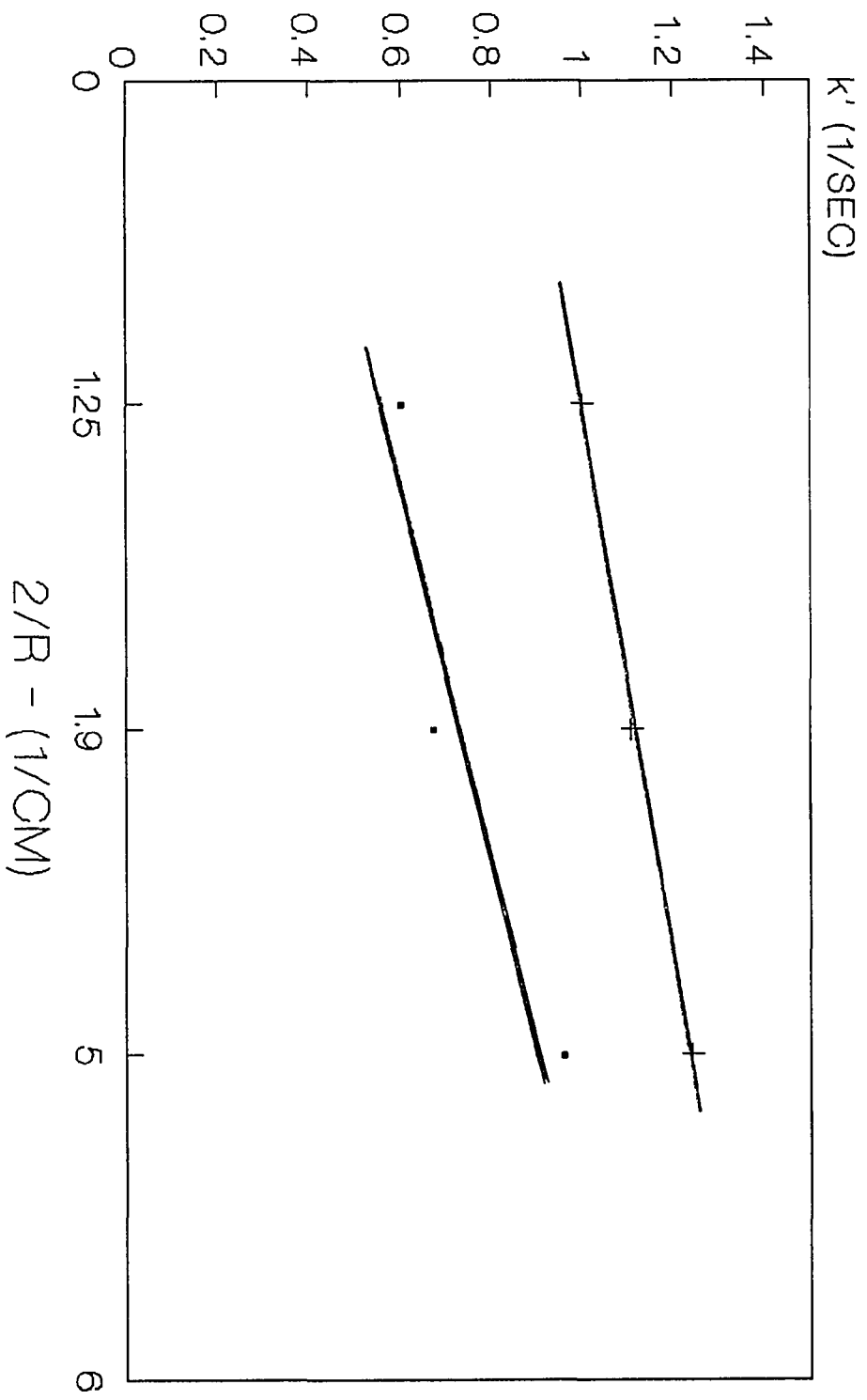
The Arrhenius form of homogeneous and heterogeneous rate constants can be written as follow :

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

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

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  $\text{CH}_2\text{Cl}_2$  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.

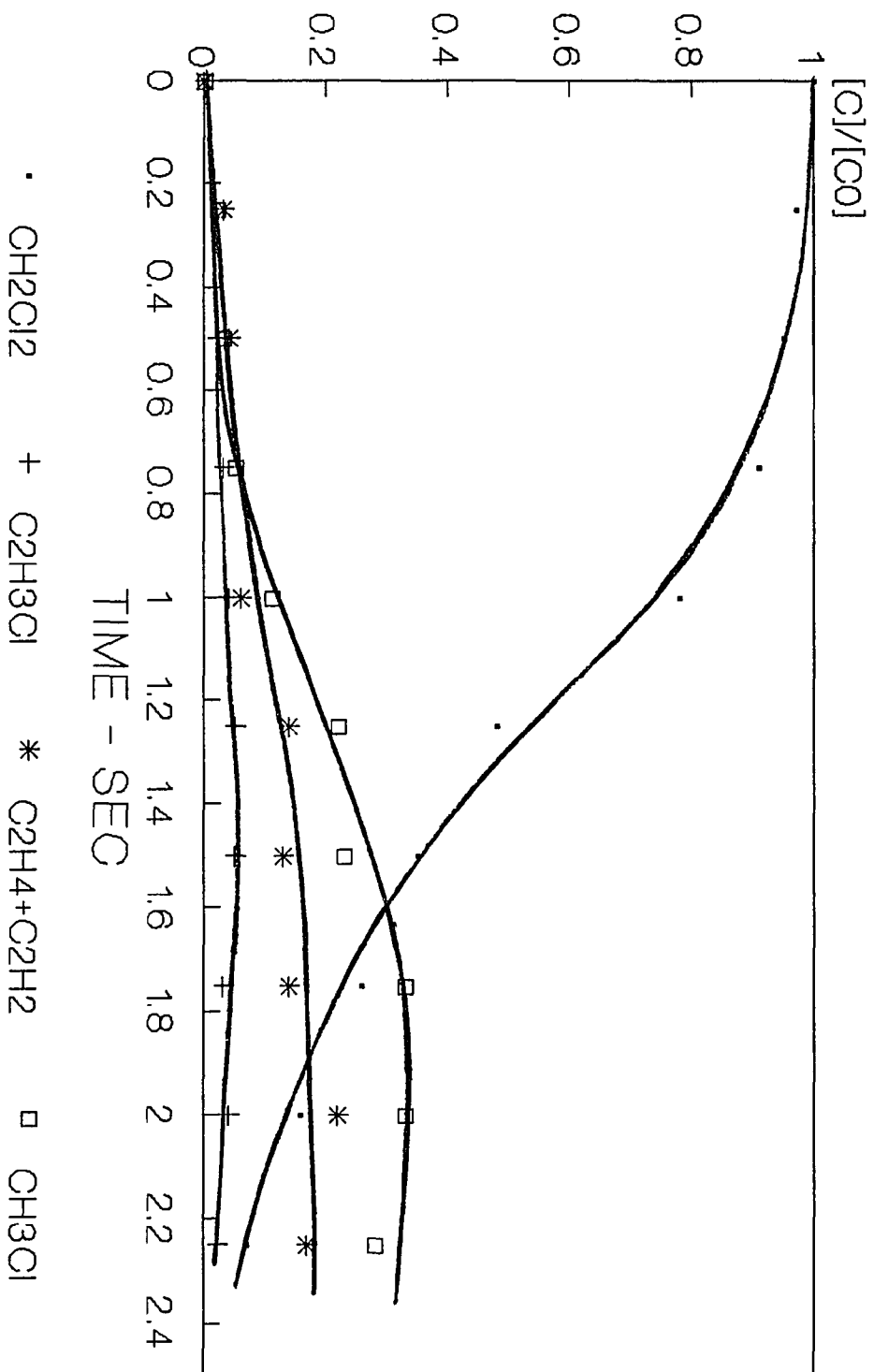
**FIGURE-7 GLOBAL RATE CONSTANT VS 2/R**



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 latter (benzene, chlorobenzene, cyclopentadiene, etc.) are more stable at higher temperatures due to their (900-1000 °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 °K/Cm) in temperature occurred. GC/MS analysis showed that traces of polychlorinated benzene is present in this residue.

The major products observed were  $C_2H_4$ ,  $C_2H_2$ ,  $C_2H_6$ ,  $CH_3Cl$ ,  $C_6H_6$ , and  $HCl$ . Figure 8 illustrates product distribution relative to initial  $CH_2Cl_2$  concentration vs

FIGURE-8 CH<sub>2</sub>Cl<sub>2</sub> DECOMPOSITION IN  
CH<sub>4</sub>/Ar AT 1075 K

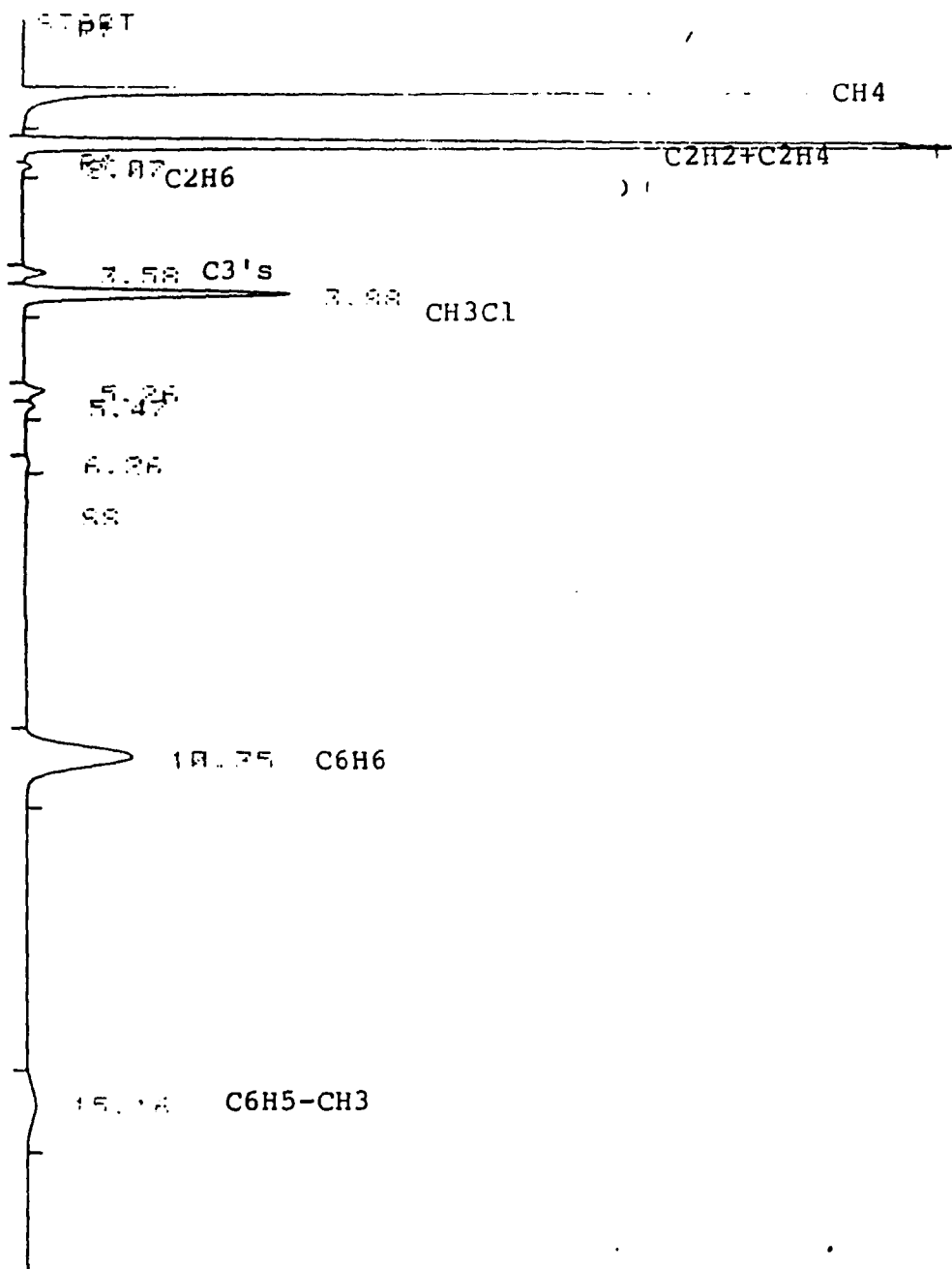


residence time for 10.5 mm ID reactor at 802 °C. Methyl chloride is the dominant initial product under above mentioned conditions; concentration of ethylene + acetylene increases with reaction time; and vinyl chloride concentration has a maximum at 1.6 sec. reaction time.

Small amounts of (<1%)  $CCl_4$ ,  $C_2H_2Cl_2$ ,  $C_2HCl_3$ ,  $C_2Cl_4$  were also present in the effluent product at lower reaction temperatures (below 850 °C) . Traces of heavy chlorinated compounds (hexachlorobenzene) were detected in the solid deposits at higher (950 °C) temperatures. All methylene chloride (99.9%) decomposed at 952 °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 °C, and 0.34 second reaction time. The major products are identified as acetylene + ethylene, benzene, toluene, and chloromethane.

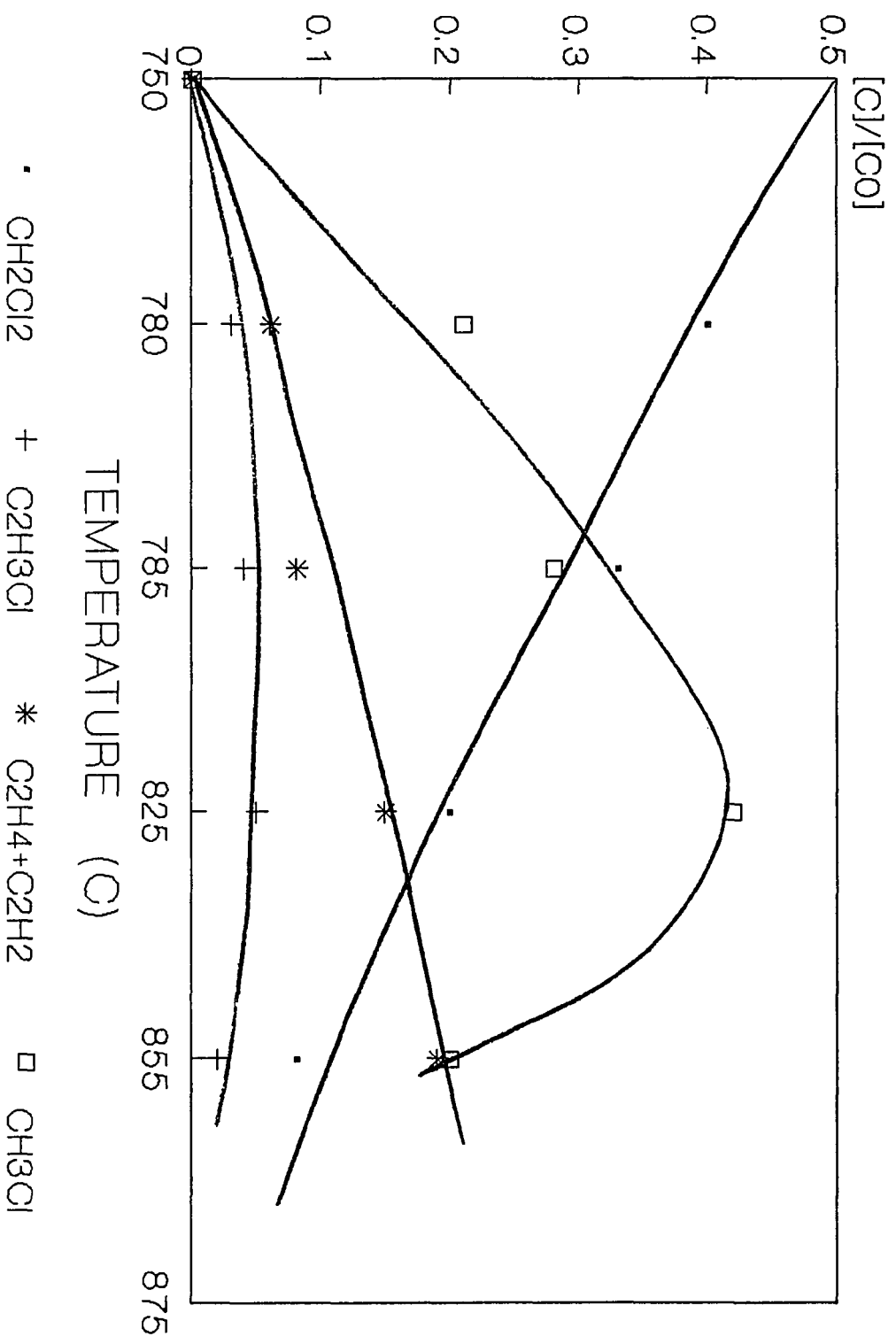
Figure 10 shows concentration of products: acetylene + ethylene, methyl chloride, and vinyl chloride, as well as methylene chloride loss relative to initial  $CH_2Cl_2$  concentration vs temperature for 10.5 mm ID reactor and resident time range of 0.88 to 0.92 sec. It is apparent from this figure that chloromethane concentration reaches a maximum at 830 °C. No chlorinated compound was detected in measurable quantities above 1050 °C.

**FIGURE-9 CHROMATOGRAM OF CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>  
1225 K 4 mm ID**





**FIGURE-10 CONCENTRATION VS TEMPERATURE**



## B. TRICHLOROETHYLENE, METHYLENE CHLORIDE AND METHANE

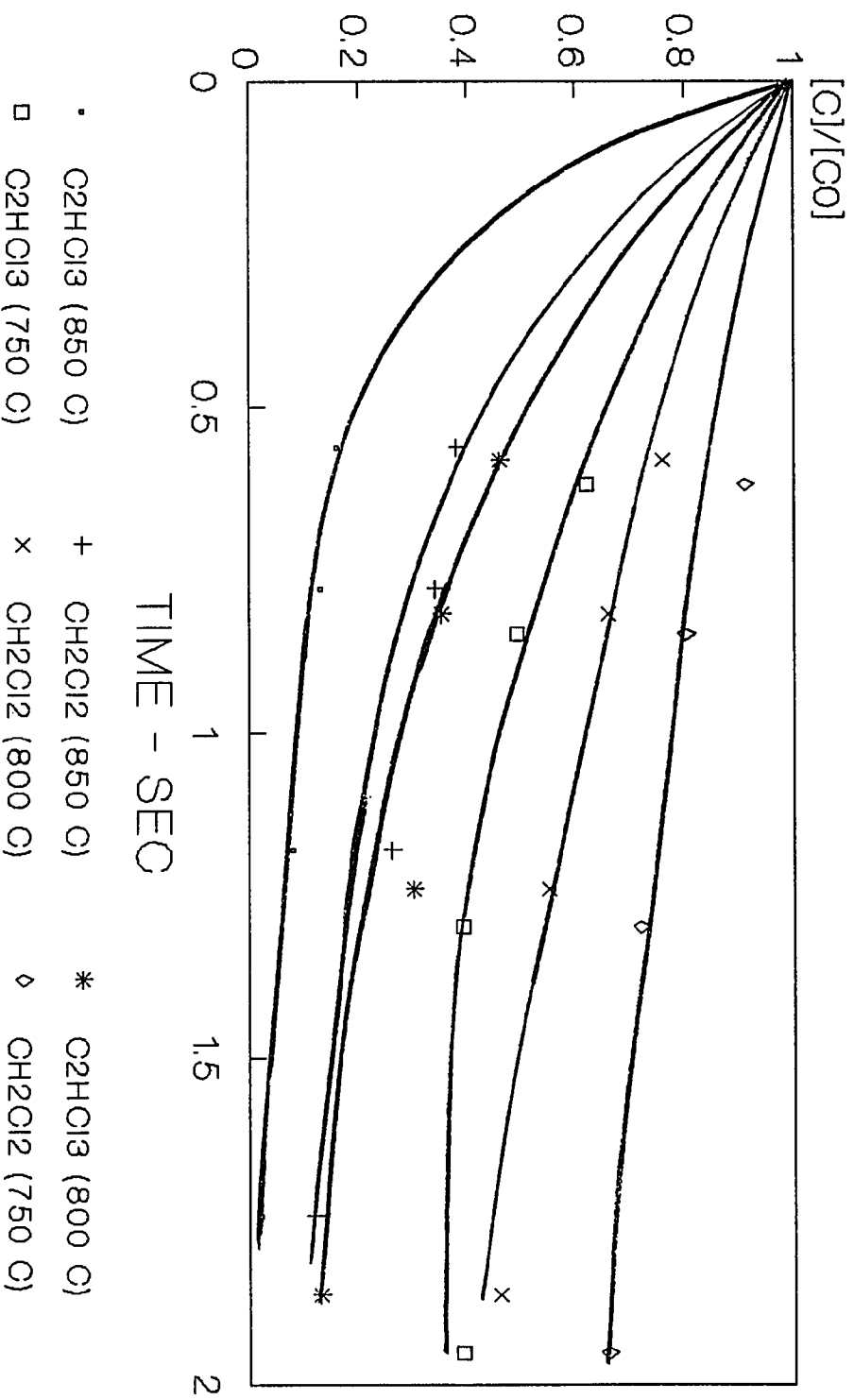
A mixture of trichloroethylene and methylene chloride in an atmosphere of excess methane and argon was studied as a second phase of this research in quartz tubular reactors of 4, 10.5, 16 mm ID and 45 cm long. Two separate streams of methane saturated with  $C_2HCl_3$  and  $CH_2Cl_2$  from separate parallel bubbler systems, both kept at  $0^\circ C$  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 occurred ( $150^\circ K/Cm$ ).

A summary of runs performed for this experiment is shown in Table V and covers the temperature range of 1025 to  $1275^\circ K$ . Figure 11 compares decay of  $C_2HCl_3$  and  $CH_2Cl_2$  at 750, 800,  $850^\circ C$  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  $C_2HCl_3:CH_4:Ar$  of

TABLE - V SUMMARY OF DIFFERENT RUNS  
C<sub>2</sub>HCl<sub>3</sub> + CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>

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 C<sub>2</sub>HCl<sub>3</sub>+CH<sub>2</sub>Cl<sub>2</sub>  
IN CH<sub>4</sub>/Ar 16 mm ID REACTOR**



1:40:40 and CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>4</sub>: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, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, 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 C<sub>2</sub>HCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> 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 C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar system:

Methylene chloride:

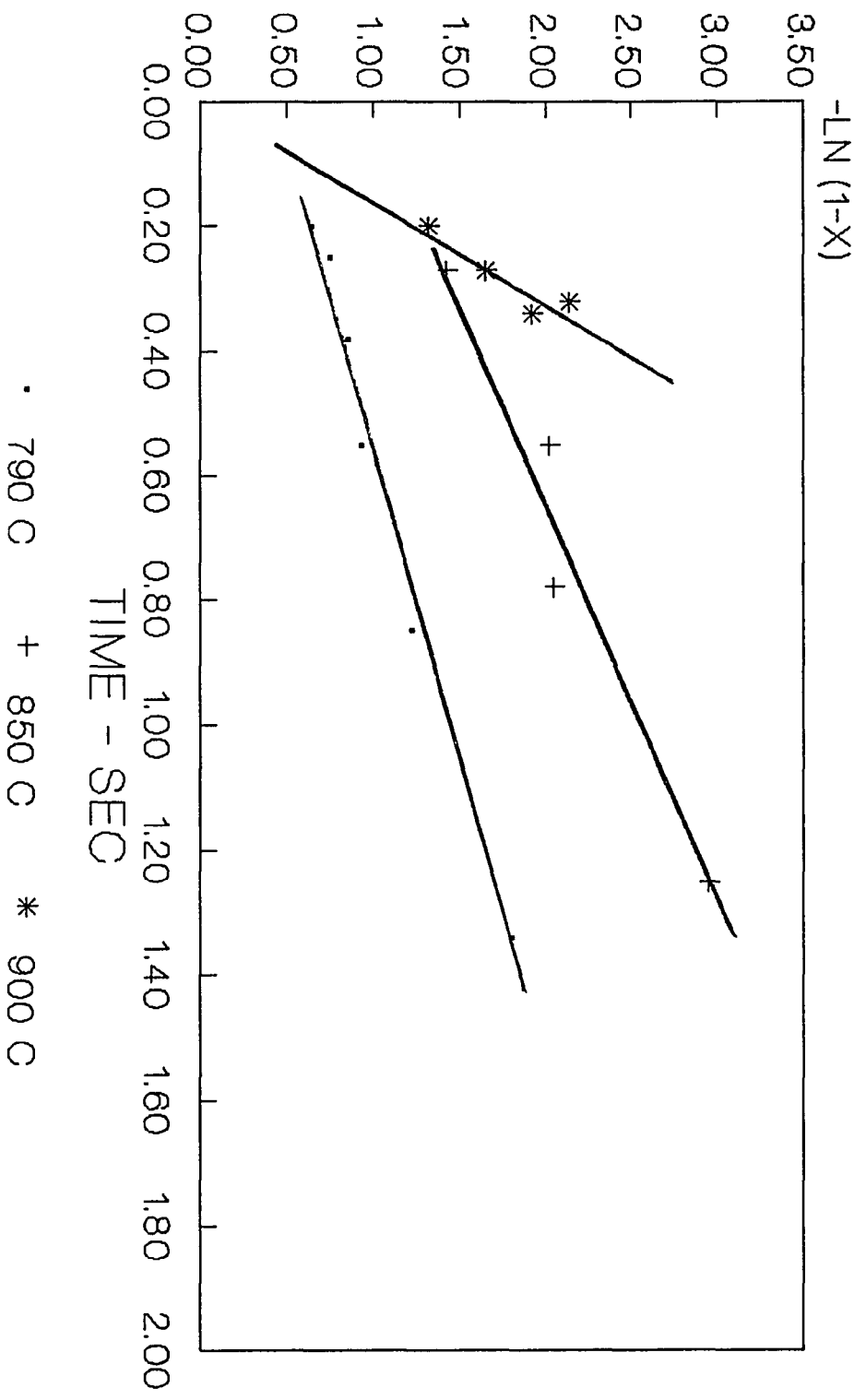
$$k = 8.11 * 10^9 * \text{Exp}(-44.85/\text{RT}) \quad (1/\text{sec.})$$

Trichloroethylene :

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

Acetylene, ethylene, benzene, chloromethane, 1,3-dichloropropene and HCl were observed to be major products of methane reaction with a mixture of C<sub>2</sub>HCl<sub>3</sub> + CH<sub>2</sub>Cl<sub>2</sub> in a CH<sub>4</sub>/Ar atmosphere, at temperatures above 750 °C. Benzene

**FIGURE-12 FIRST ORDER DECAY PLOT FOR C2HC13 IN C2HC13/CH2C12/CH4/Ar SYSTEM**



**FIGURE-13 FIRST ORDER DECAY PLOT FOR CH<sub>2</sub>Cl<sub>2</sub> IN C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar SYSTEM**

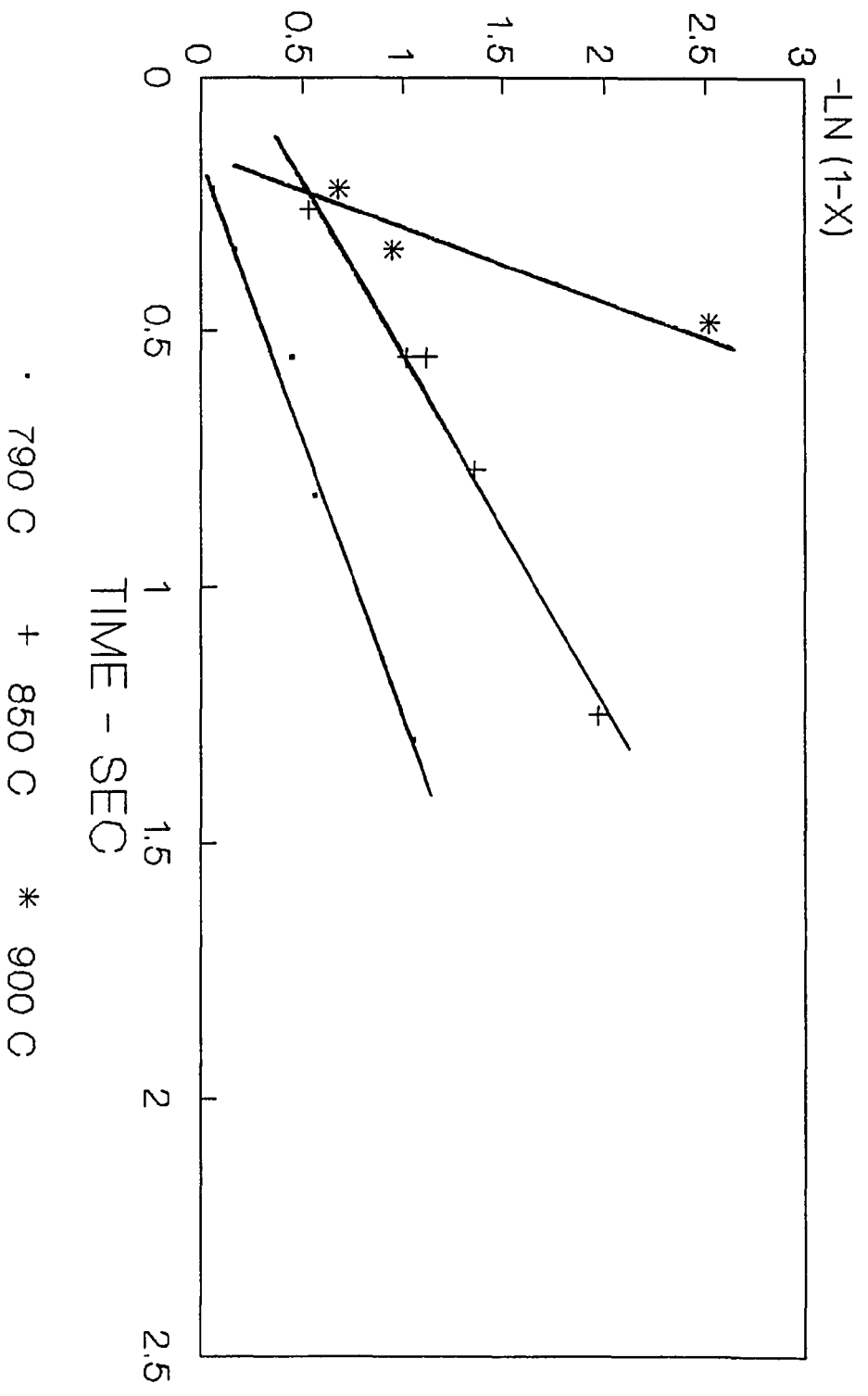


TABLE VI - RATE CONSTANTS FOR CH<sub>2</sub>Cl<sub>2</sub> IN C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar  
 [C<sub>2</sub>HCl<sub>3</sub>]:[CH<sub>2</sub>Cl<sub>2</sub>]:[CH<sub>4</sub>]:[Ar] 1:1:40:40  
 P = 1 atm

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 °C, 1.14 second residence time in 10.5 mm ID reactor, as shown in Figure 14. The products identified at 99% conversion of C<sub>2</sub>HCl<sub>3</sub> + CH<sub>2</sub>Cl<sub>2</sub>, reactants, include acetylene and ethylene, C<sub>3</sub>s, chloromethane, C<sub>4</sub>s,



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

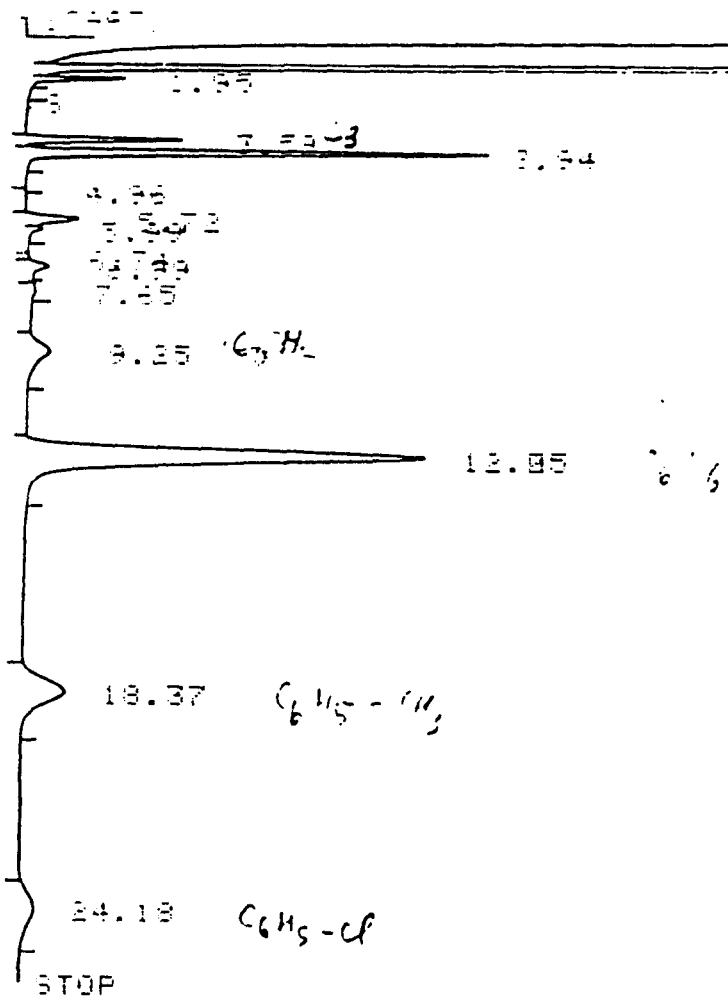


TABLE VII- RATE CONSTANTS FOR C<sub>2</sub>HCl<sub>3</sub> IN C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar  
 [C<sub>2</sub>HCl<sub>3</sub>]:[CH<sub>2</sub>Cl<sub>2</sub>]:[CH<sub>4</sub>]:[Ar] 1:1:40:40  
 P = 1 atm

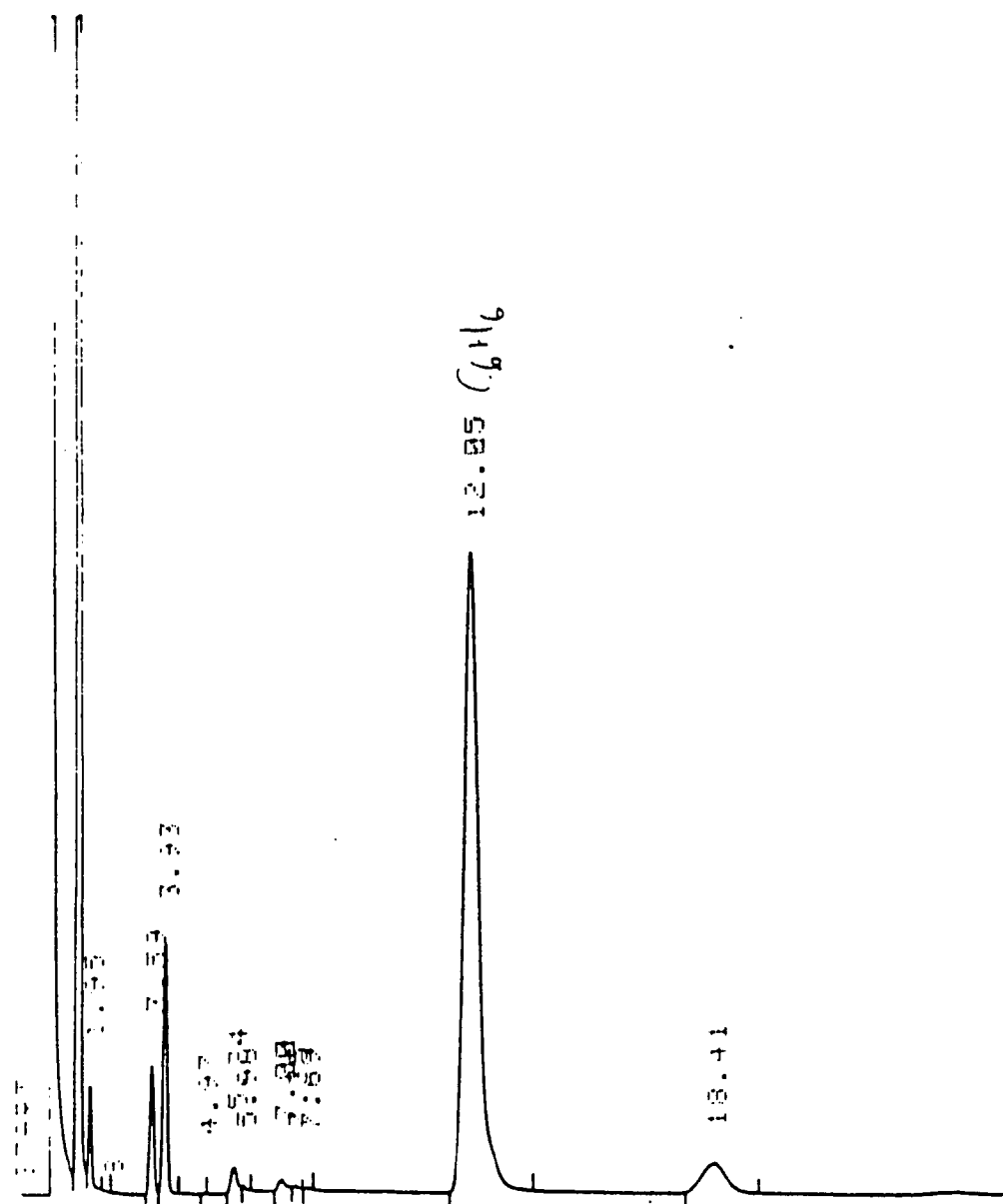
ID (mm)	4	10.5	16
T (K)	k'		
750	-	-	0.31
795	3.04	0.811	0.8
850	5.8	1.47	0.9
885	5.20	-	-
899	-	2.9	-
E	26	32	34
A	1.99E04	2.2E05	9.9E04

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

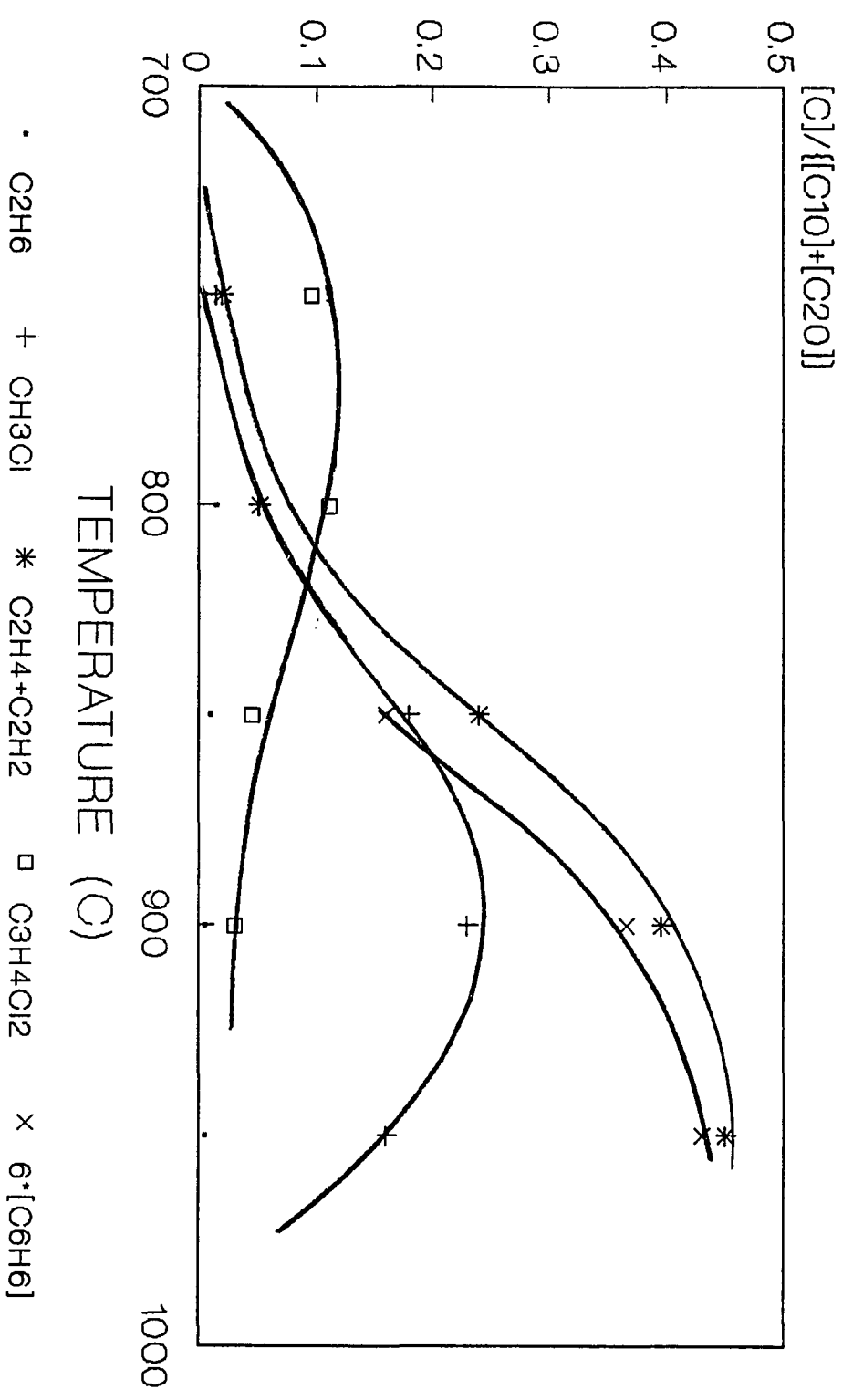
cyclopentadiene, benzene, toluene, and chlorobenzene. Figure 15 is a typical chromatogram of 10.5 mm ID reactor at 1005 °C and residence times of one second. It is observed was CH<sub>3</sub>Cl (<2%). Except for traces of polychlorinated hydrocarbons present in the effluent of reactor under these conditions, all chlorocarbons were decomposed above 1052 °C, 1.2 second residence time.

Figure 16 shows relative concentrations of (relative to sum of the initial [C<sub>2</sub>HCl<sub>3</sub>] + [CH<sub>2</sub>Cl<sub>2</sub>]) acetylene +

**FIGURE-15 CHROMATOGRAM OF  
C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> SYSTEM AT 1278 K**



**FIGURE-16 PRODUCT DISTRIBUTION  
C2HC13/CH2C12/CH4/Ar SYSTEM**

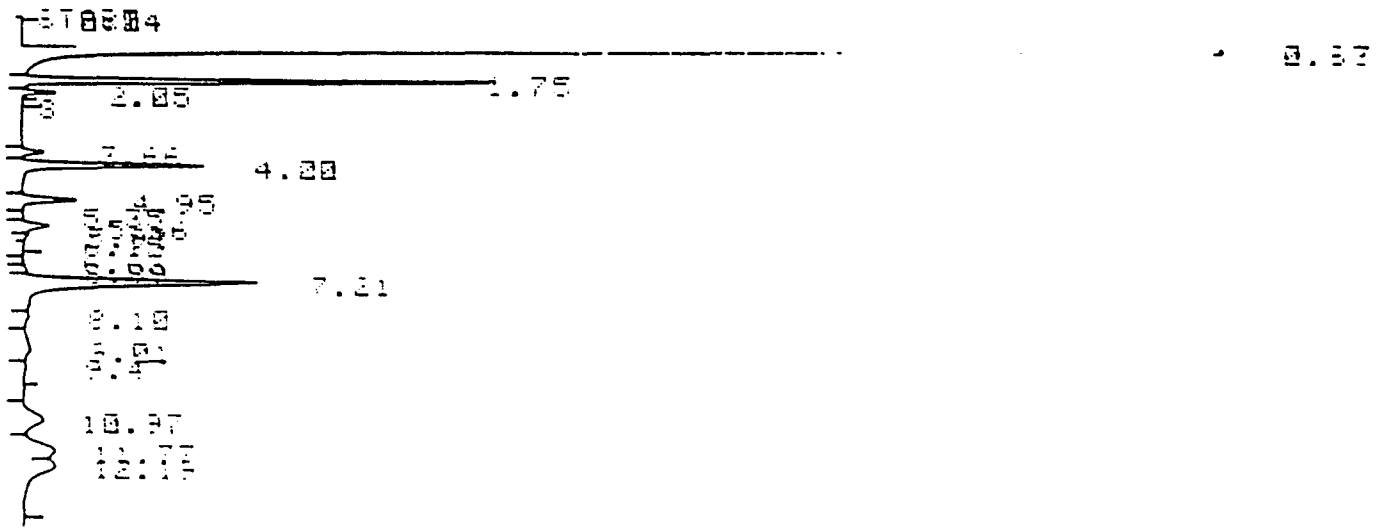


ethylene, ethane, benzene, 1,3-dichloropropene and chloromethane, vs temperature. It is observed from this figure that acetylene + ethylene yield increases with temperature rise. Benzene starts to form, in measureable quantities (2.7%) at temperatures above 825 °C. Chloromethane and 1,3-dichloropropene concentrations show maxima at 900 and 780 °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  $C_2HCl_3$  and  $CH_2Cl_2$  for two reactor diameters (10.5 and 16 mm ID) and temperatures 750, 800, 850, and 900 °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 ( $C_2HCl_3$ , and  $CH_2Cl_2$ ), 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  $CH_2Cl_2/CH_4/Ar$  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 °C. The comparison of major products

**FIGURE-17A C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> SYSTEM  
.45 SEC 1123 K 4 mm ID**



**FIGURE-17B C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> SYSTEM  
1.2 SEC 1123 K 1.6 mm ID**

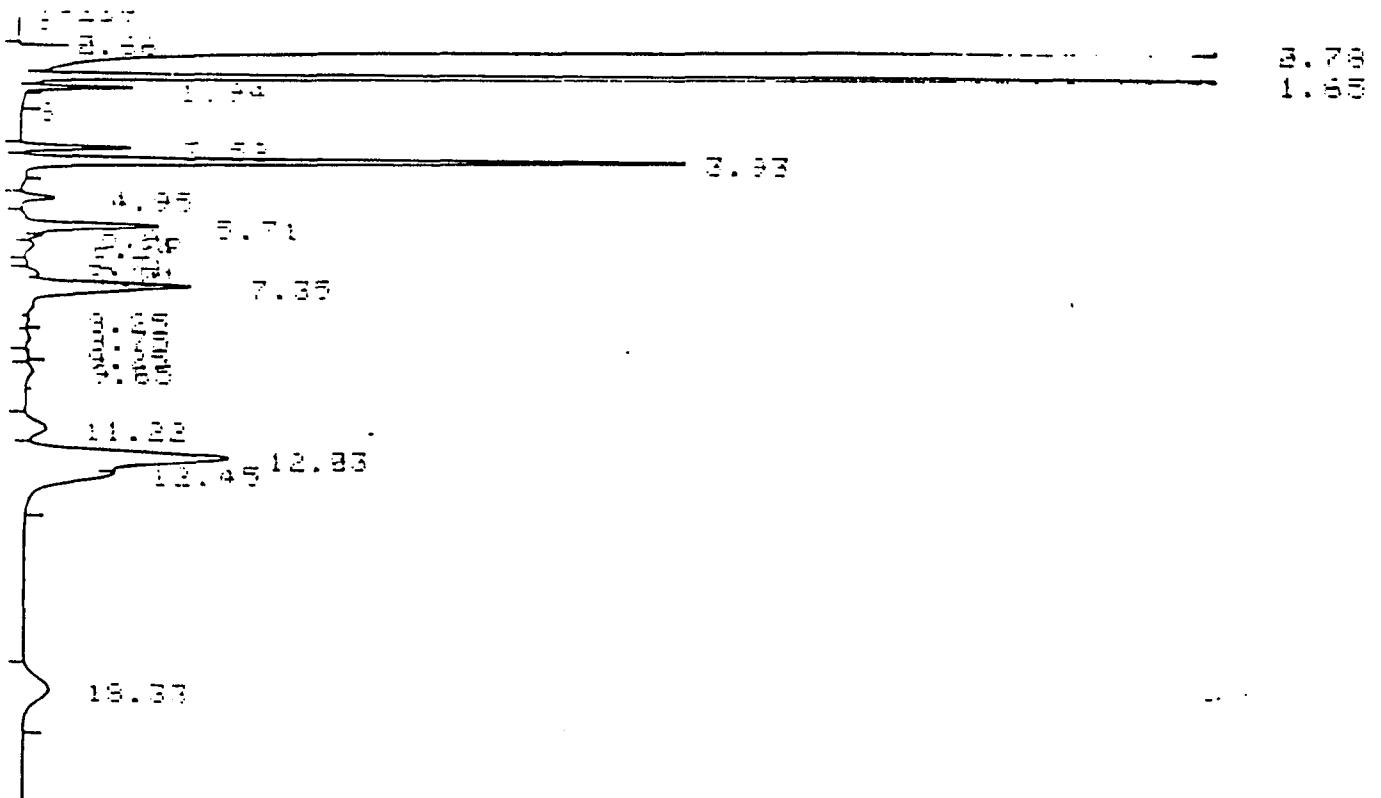


TABLE VIII-TEMPERATURE, DIAMETER EFFECT ON CONVERSION  
 $C_2HCl_3 + CH_2Cl_2 / CH_4$

		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.

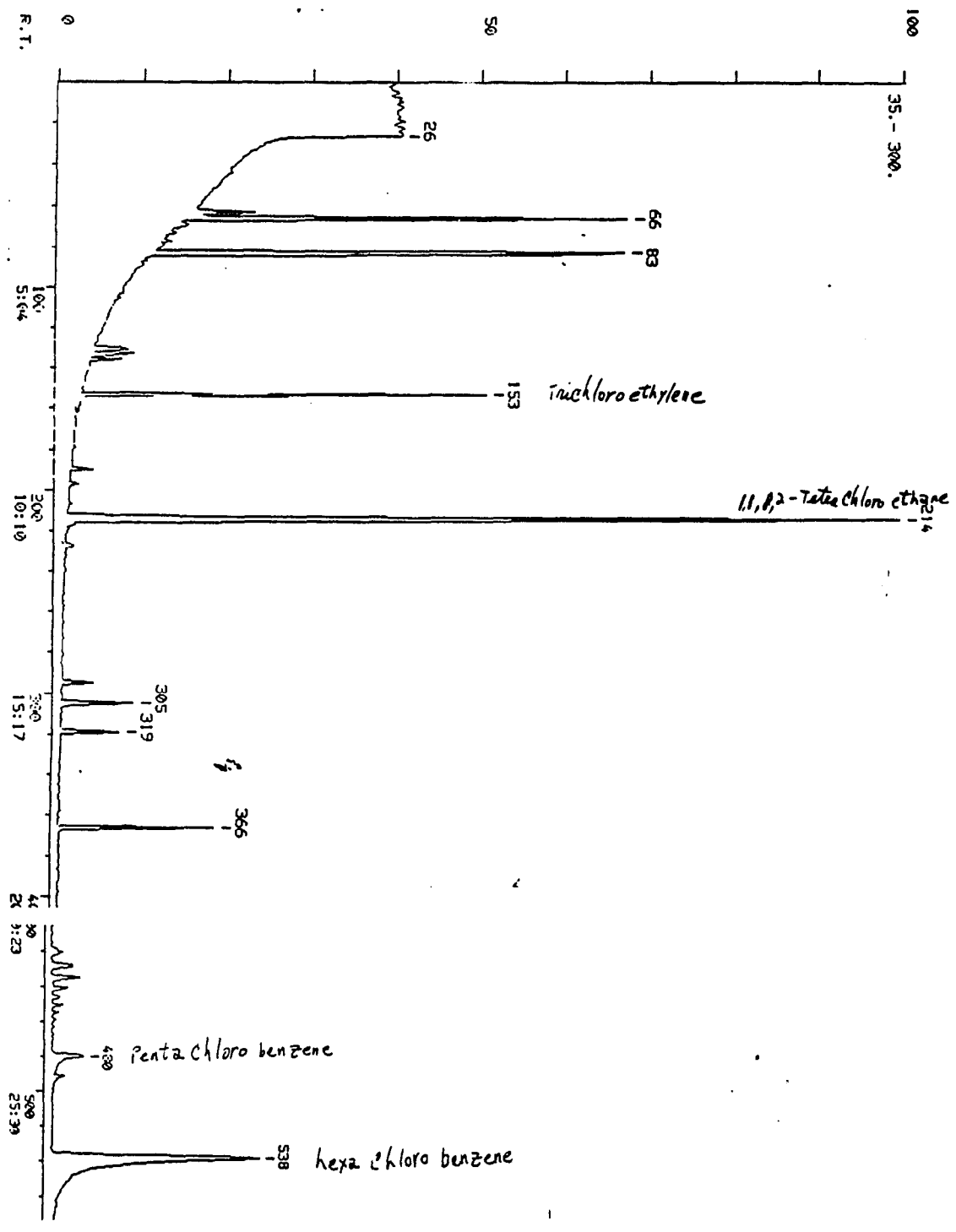
The effect of lack of CH<sub>4</sub> and hydrogen addition to the reactor on product distribution was studied in a series of experiments where all parameters but the carrier gas were held constant (10.5 mm ID reactor, 875 °C, and 0.51 sec). The gas phase reaction of trichloroethylene and methylene chloride 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 C<sub>2</sub>HCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> 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 C<sub>2</sub>HCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> mixture in hydrogen atmosphere under similar conditions, however, produced



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

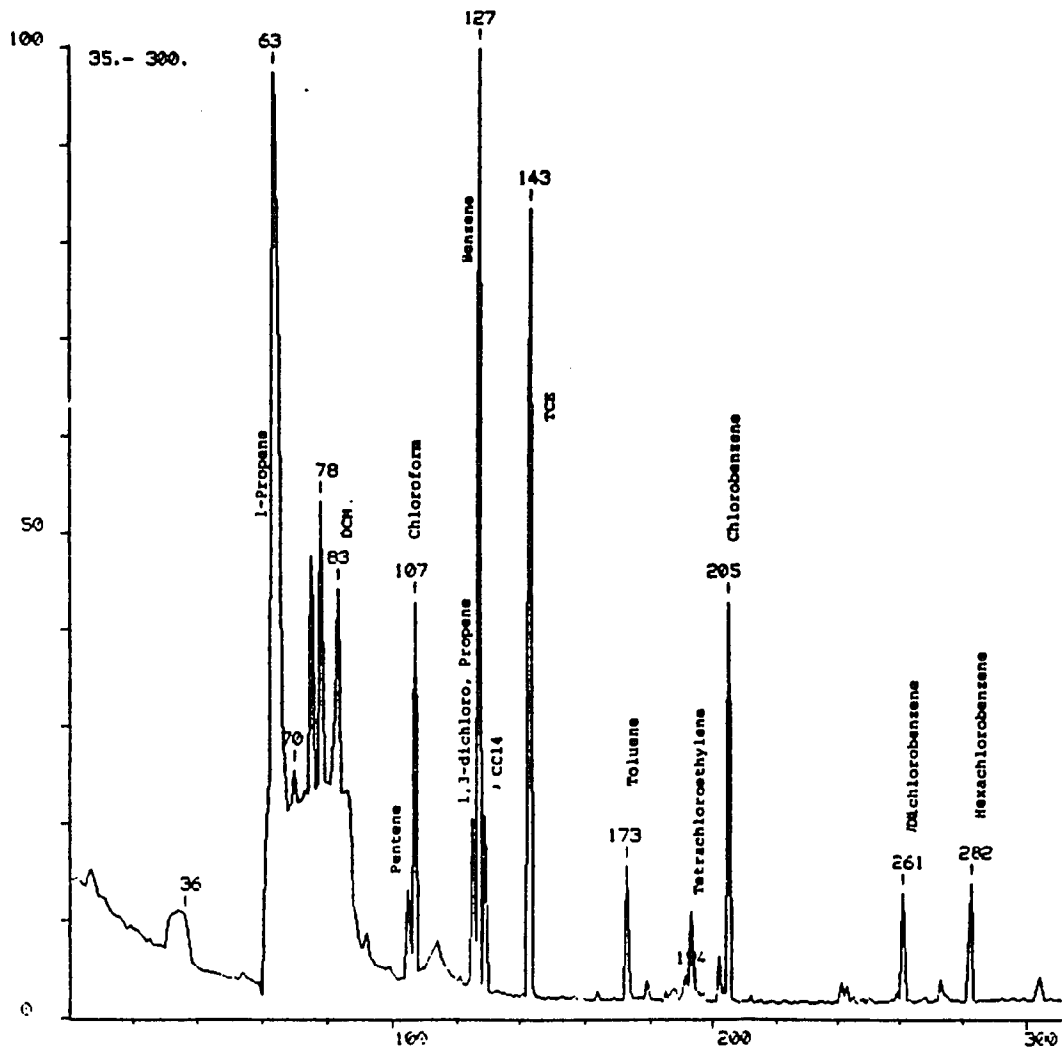


mainly light, chlorine free hydrocarbons with methane, ethane, ethylene, acetylene, chloromethane, and benzene observed to be major products. Quantifiable amounts of chlorobenzene, chloroform, carbon tetrachloride, and 1,3 dichloropropene were also detected (Fig. 19).

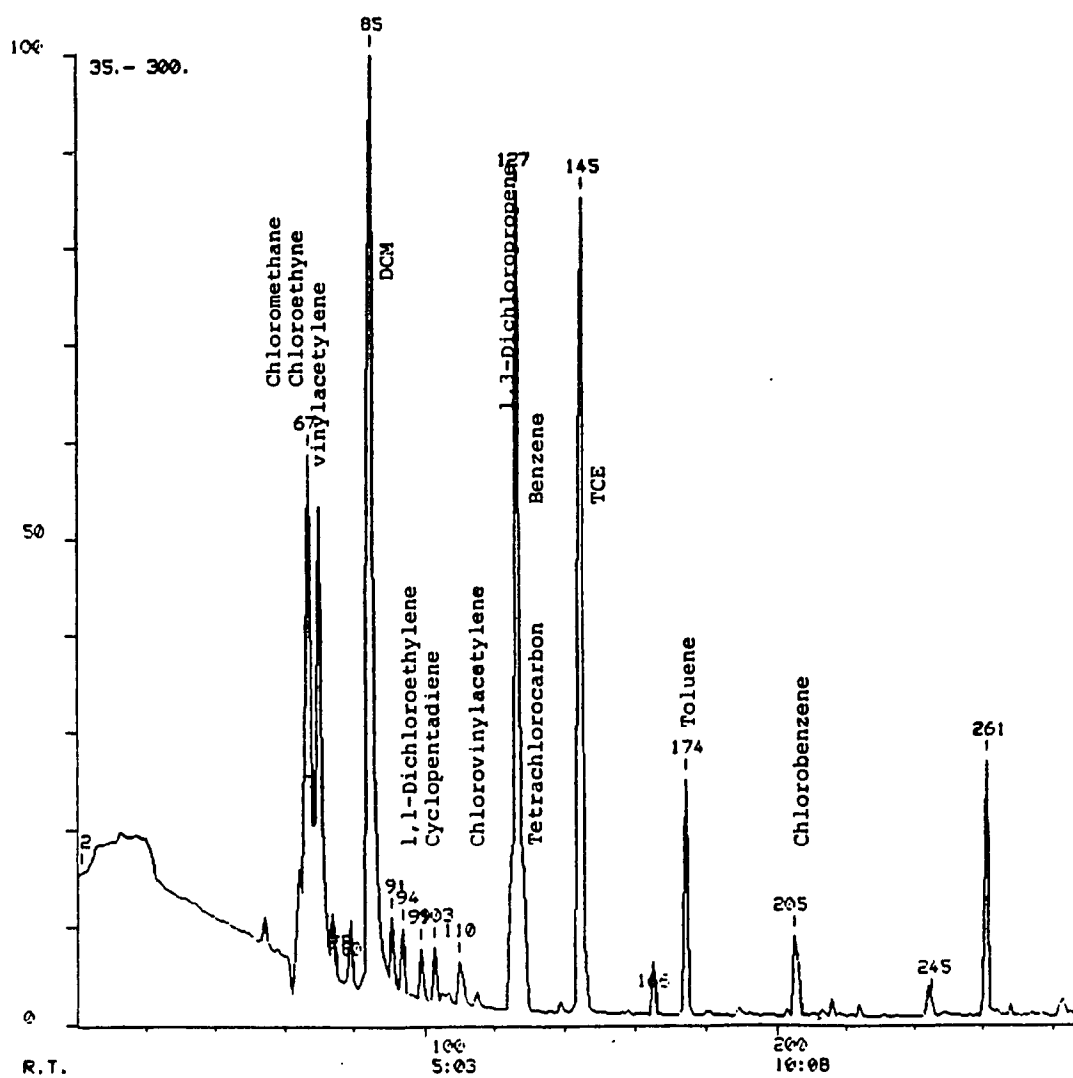
A comparison of product distribution for high temperature reactions of  $C_2HCl_3 + CH_2Cl_2$  in methane and methane + argon atmospheres, Figures 20 and 21, demonstrate inert (argon in this study) addition to the reaction system studied. It has enhanced production of chlorine free hydrocarbons (e.g. 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

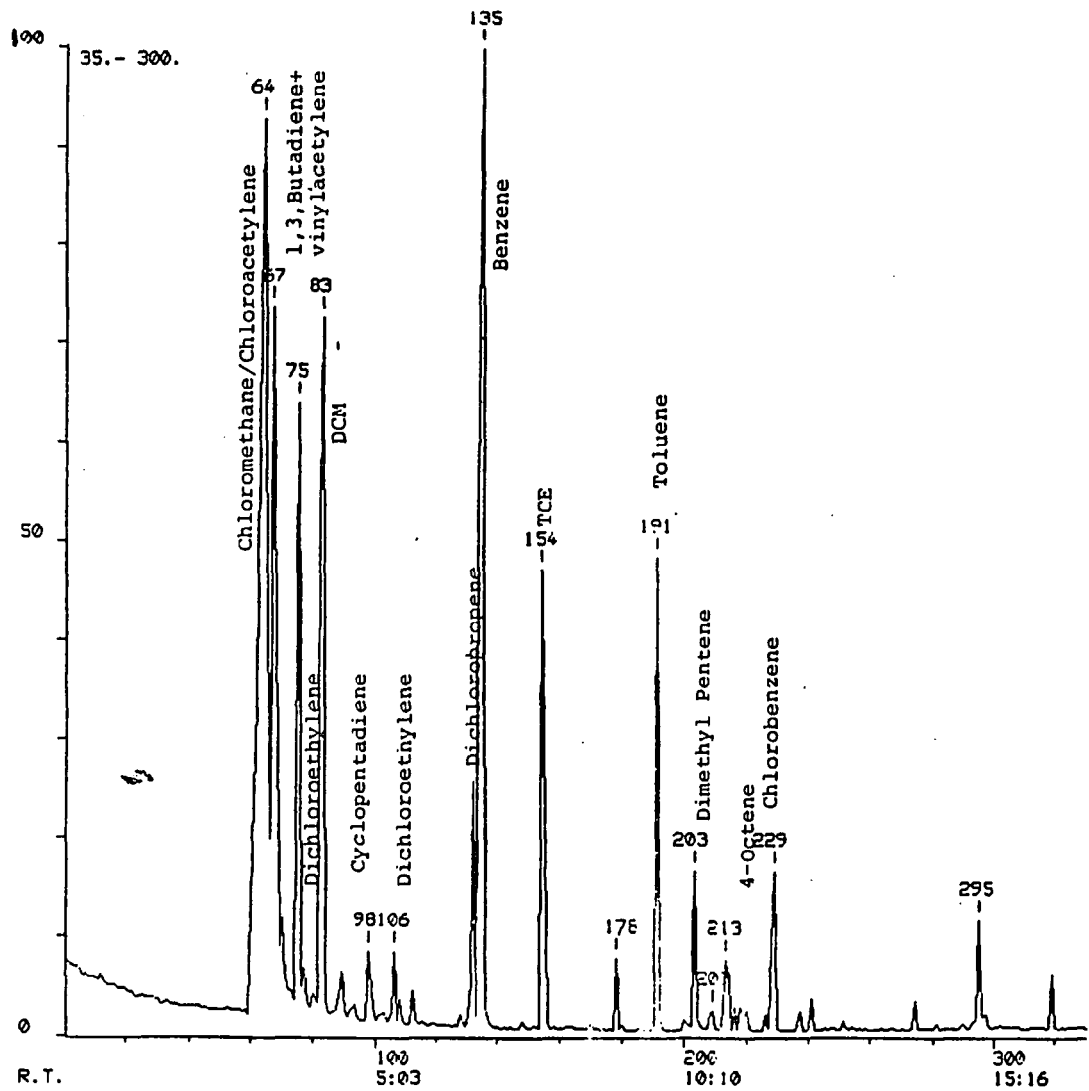
**FIGURE-19 GC/MS CHROMATOGRAM  
C2HCl3/CH2Cl2 PYROLYSIS IN H2 AT 875 C**



# 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 noticeable difference was higher reactor temperature requirement (100 °C) for chlorinated hydrocarbon conversion in methane atmosphere compared to that of hydrogen bath [25-27].

Table-IX MATERIAL BALANCE 500 MOLES [Cl]  
 C<sub>2</sub>HCl<sub>3</sub> + CH<sub>2</sub>Cl<sub>2</sub> / CH<sub>4</sub>  
 REACTOR DIAMETER : 10.5 mm ID  
 RESIDENCE TIME : 0.48-0.56 SEC.

Compound / Temp. (C)	750	792	854	899
CH <sub>3</sub> Cl	4.5	20	90	94.5
CH <sub>2</sub> Cl <sub>2</sub>	200	124	70	16
C <sub>2</sub> HCl	X	X	X	X
C <sub>3</sub> H <sub>2</sub> Cl <sub>2</sub>	X	X	X	X
C <sub>2</sub> HCl <sub>3</sub>	210	117	30	--
C <sub>4</sub> H <sub>3</sub> Cl	X	X	X	X
C <sub>6</sub> H <sub>5</sub> Cl	NA	NA	NA	1.91
HCl	46.7	207.2	290.9	376.8
C <sub>3</sub> H <sub>4</sub> Cl <sub>2</sub>	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<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> system and another one with 72 reactions for mixture of C<sub>2</sub>HCl<sub>3</sub> + CH<sub>2</sub>Cl<sub>2</sub> / CH<sub>4</sub> system were found to reproduce experimental results.

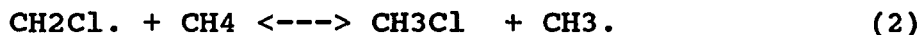
These kinetic schemes were formulated considering all reaction products detected by GC and GC/MS at varied stages of conversion (0.05 to 0.9). Rate constants and reaction channels were developed from literature values, fundamental principals in Transition State Theory [44] and thermodynamic parameters 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

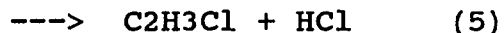
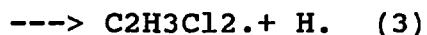
According to our experimental results methyl chloride is the first and major stable product from reaction of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>4</sub> at temperatures below 900 °C. CH<sub>3</sub>Cl is formed

from reaction of CH<sub>2</sub>Cl with methane, which also produces methyl radicals, (1) and (2) below. CH<sub>2</sub>Cl is formed from unimolecular decomposition of the parent compound, CH<sub>2</sub>Cl<sub>2</sub> :



**Recombination of Chloromethyl Radicals- CH<sub>2</sub>Cl.+CH<sub>2</sub>Cl.:**

Vinyl chloride, another major product of this system at temperatures below 800 °C, arises from several channels. One of which is recombination of CH<sub>2</sub>Cl radicals into an activated complex:



# 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 CH<sub>2</sub>Cl+CH<sub>2</sub>Cl for temperature range of 900-1400 °K and pressure range of 0.001-10 atm,



show that the rate constant for exit channel C<sub>2</sub>H<sub>3</sub>Cl+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 °K and different pressures are tabulated in Table X and shown schematically in Figure 23. The C<sub>2</sub>H<sub>4</sub>Cl radical, from channel 2 in Fig. 22, can further react by undergoing beta scission to C<sub>2</sub>H<sub>4</sub> + Cl or C<sub>2</sub>H<sub>3</sub>Cl + H and the stabilized [C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>] (adduct) can split out HCl forming vinyl chloride at temperatures and conditions of our experiment.

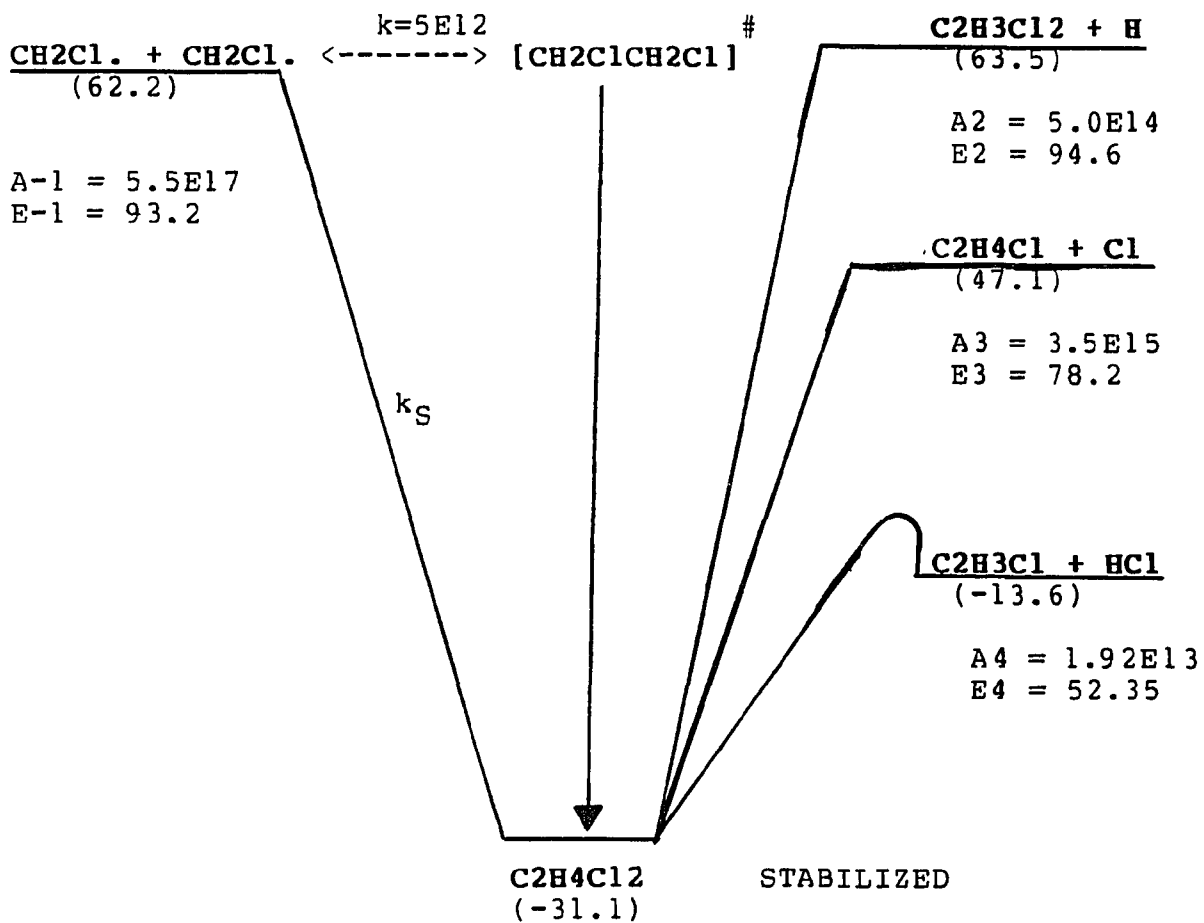
**TABLE-X RESULTS OF ACTIVATED COMPLEX THEORY  
CALCULATION FOR RATE CONSTANTS AT 1100 K**

P(Atm)	CH <sub>2</sub> Cl + CH <sub>2</sub> Cl		cc/sec-mole
	C <sub>2</sub> H <sub>4</sub> Cl+Cl	C <sub>2</sub> H <sub>3</sub> Cl+HCl	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (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

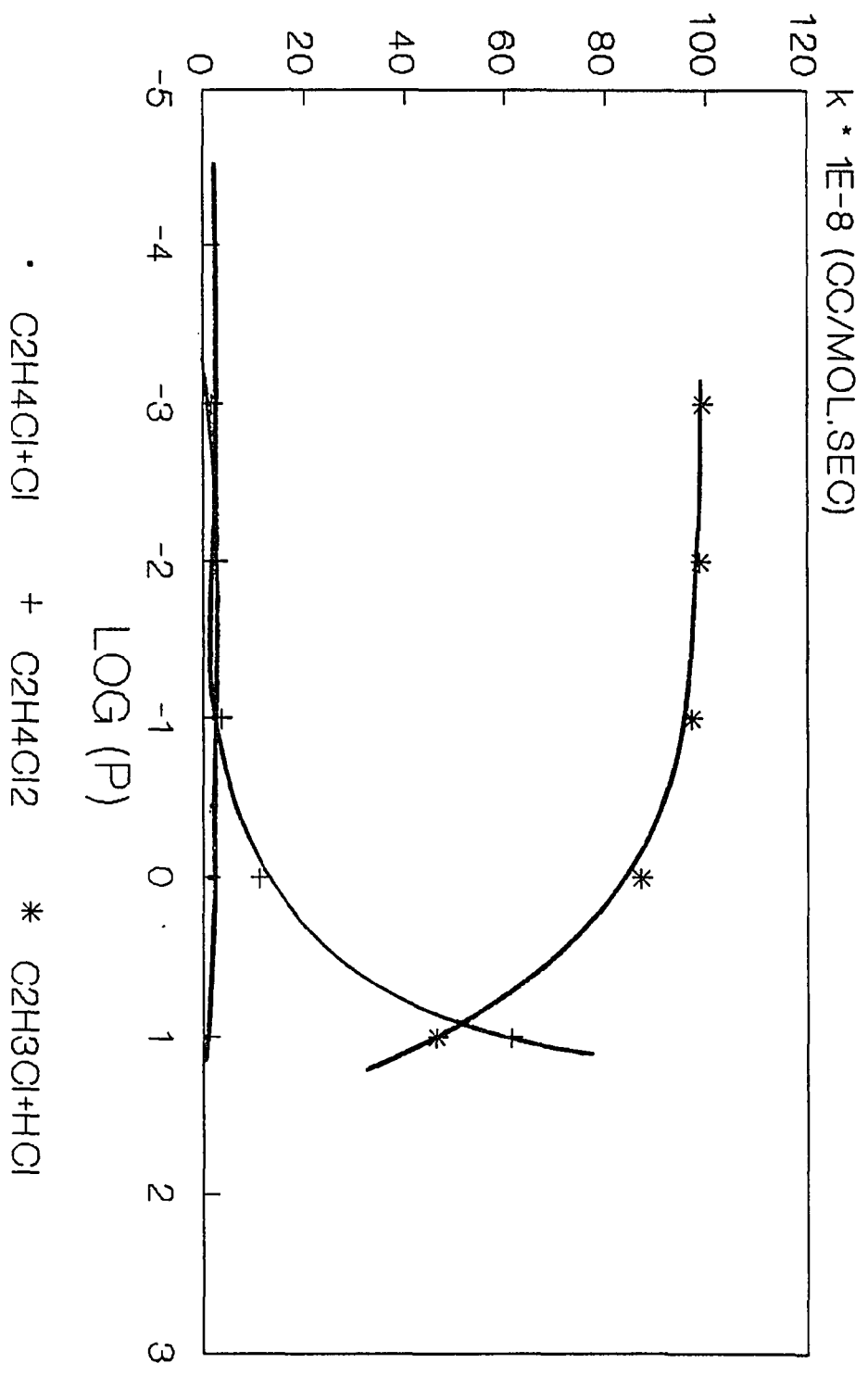
**QRRK Utilization:**

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

# FIGURE-22 ENERGY DIAGRAM FOR REACTION CH<sub>2</sub>Cl + CH<sub>2</sub>Cl



**FIGURE-23 RESULTS OF ACTIVATED COMPLEX THEORY CALCULATION FOR CH<sub>2</sub>Cl+CH<sub>2</sub>CCl**



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  $E_A$ s 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 = acentric factor

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

$P_C$  = critical pressure, atm

$T_C$  = critical temperature, °K

e = potential-energy constant, ergs

k = Boltzmann's constant =  $1.3805E-16$ , ergs/°k

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

$$N = 3n - 6 \quad \text{Non-linear molecules}$$

$$N = 3n - 5 \quad \text{Linear molecules}$$

where n represents the number of atoms in the complex. The geometric mean of the adduct's vibrational frequencies,  $\langle \nu \rangle$ , 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 :

$$\frac{B}{1-B^{1/2}} = \frac{-\langle \text{Del.}E_{\text{col}} \rangle}{F(E) \cdot k_b \cdot T}$$

where :

$\langle \text{Del.}E_{\text{col}} \rangle$  = Average amount of energy transferred per collision

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

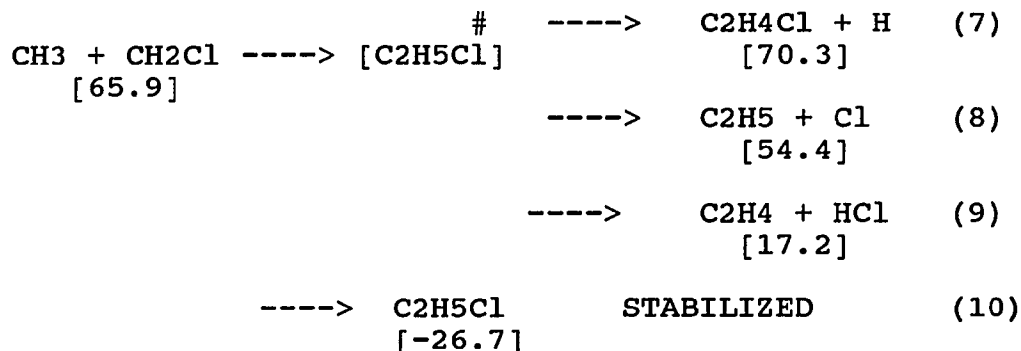
$k_b$  = Boltzman's constant

$T$  = Temperature, °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 CH<sub>2</sub>Cl:

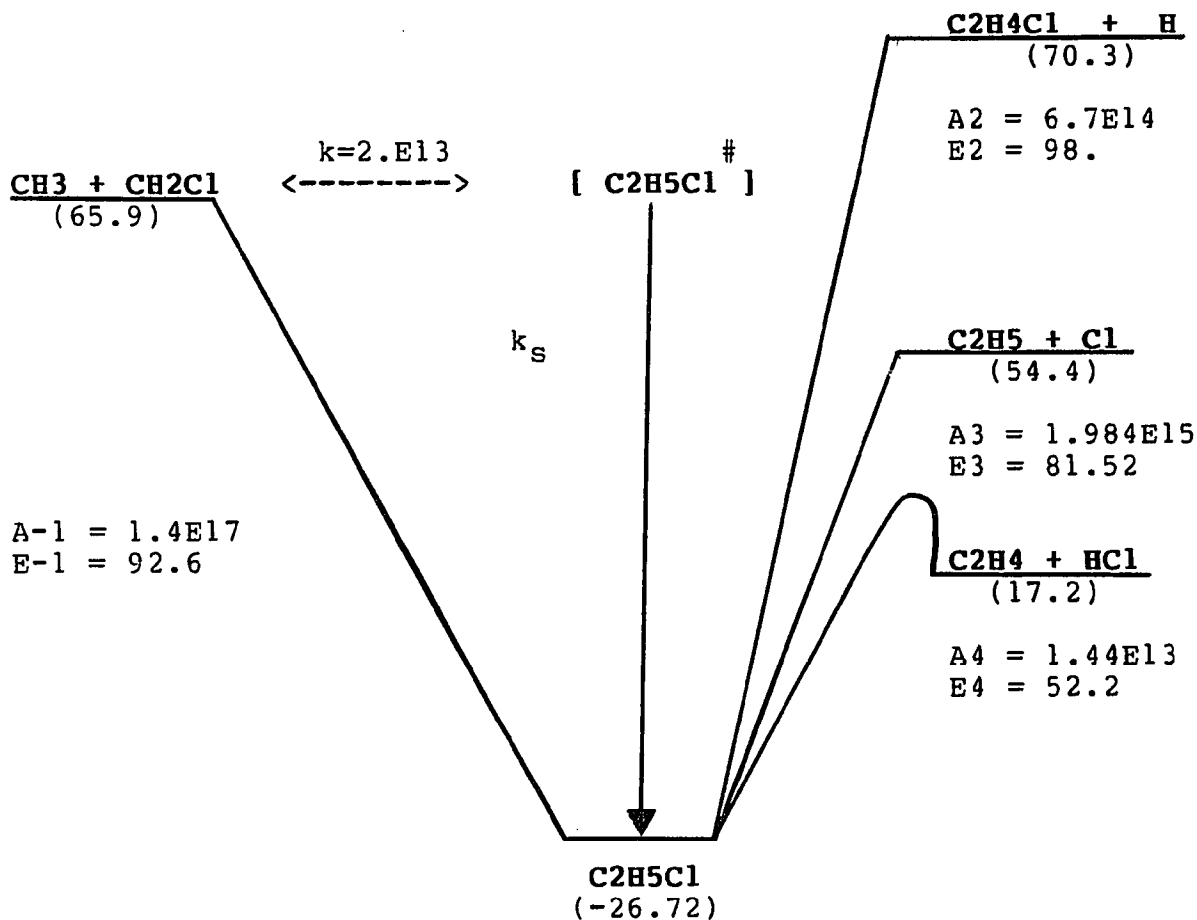
The combination reaction of primary radicals, CH<sub>3</sub> and CH<sub>2</sub>Cl, is similar but will produce different end products as shown in reactions (7) to (10) :



The energy diagram for this combination reaction is illustrated in Figure 24. The activated complex,  $[C_2H_5Cl]^\ddagger$ , can be stabilized, react further through one or more of the three exit channels to produce  $C_2H_4Cl + H$ ,  $C_2H_5 + Cl$ , and  $C_2H_4 + HCl$ , or dissociate back to original reagents. The dominant exit channel for the reaction of  $CH_3 + CH_2Cl$  at the experimental condition of this study predicted by QRRK is  $C_2H_5 + Cl$ . The pressure dependence of  $k_s$  as predicted by QRRK is shown in Figure 25. It is apparent from this figure that the  $C_2H_5 + Cl$  exit channel dominates over the  $C_2H_4 + HCl$  channel by 2.5 times at atmospheric pressure and 1100 °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  $C_2H_4Cl + H$ , was almost three orders of magnitude lower at 1 atm and temperature of this study.

The detailed mechanism developed for  $CH_2Cl_2/CH_4/Ar$  reaction system is shown in Table XI.

**FIGURE-24 ENERGY DIAGRAM FOR  
REACTION CH<sub>3</sub>+CH<sub>2</sub>Cl**





**FIGURE-25 RESULTS OF ACTIVATED COMPLEX  
THEORY CALCULATION FOR CH<sub>3</sub>+CH<sub>2</sub>Cl**

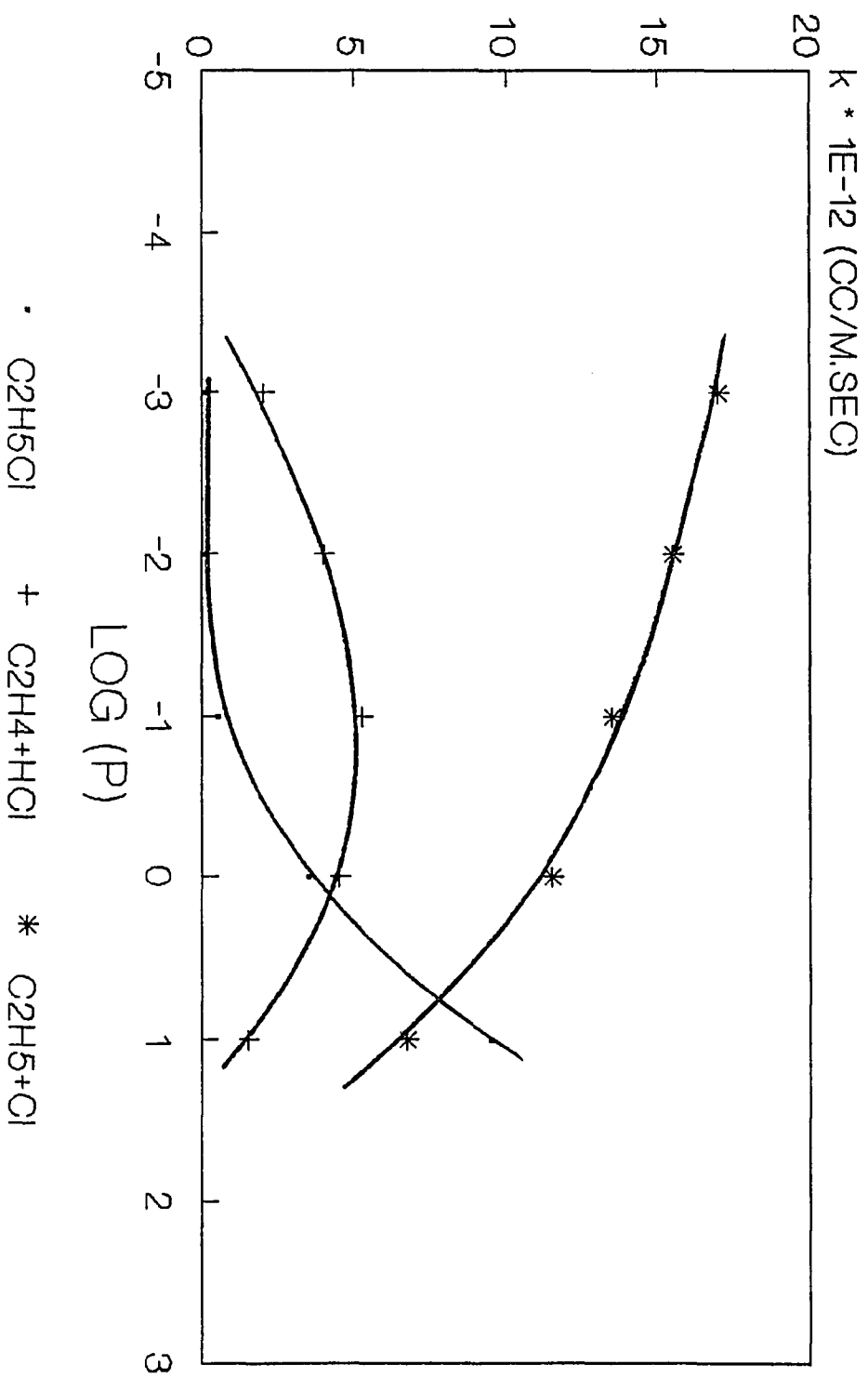


TABLE XI- DETAILED MECHANISM FOR CH<sub>2</sub>CL<sub>2</sub>/CH<sub>4</sub>/Ar  
REACTION SYSTEM

REACTION	A	E <sub>a</sub>	SOURCE
1. CH <sub>2</sub> CL <sub>2</sub> = CH <sub>2</sub> Cl + Cl	1.88E16	82.8	1
2. CH <sub>2</sub> CL <sub>2</sub> = CHCl + HCl	1.42E14	111.0	2
3. CH <sub>4</sub> = CH <sub>3</sub> + H	1.00E16	104.8	3
4. CH <sub>3</sub> Cl = CH <sub>3</sub> + Cl	1.88E15	84.4	4
5. Cl + CH <sub>4</sub> = HCl + CH <sub>3</sub>	3.10E13	3.6	7
6. Cl + C <sub>2</sub> H <sub>6</sub> = HCl + C <sub>2</sub> H <sub>5</sub>	1.20E14	1.0	7
7. Cl + C <sub>2</sub> H <sub>4</sub> = C <sub>2</sub> H <sub>4</sub> Cl	2.90E10	-8.0	8
8. Cl + C <sub>2</sub> H <sub>4</sub> = C <sub>2</sub> H <sub>3</sub> + HCl	1.00E13	5.1	7
9. Cl + CH <sub>2</sub> CL <sub>2</sub> = CH <sub>2</sub> Cl + Cl <sub>2</sub>	1.00E14	21.4	7
10. Cl + CH <sub>2</sub> CL <sub>2</sub> = CHCl <sub>2</sub> + HCl	2.50E13	3.1	9
11. Cl + CH <sub>3</sub> Cl = CH <sub>3</sub> + Cl <sub>2</sub>	1.00E14	25.0	7
12. Cl + CH <sub>3</sub> Cl = CH <sub>2</sub> Cl + HCl	3.10E13	3.6	9
13. Cl + C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub> = C <sub>2</sub> H <sub>2</sub> Cl <sub>3</sub> + HCl	3.16E13	3.5	7
14. Cl + C <sub>2</sub> H <sub>5</sub> Cl = C <sub>2</sub> H <sub>4</sub> Cl + HCl	2.00E13	1.5	7
15. Cl + C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub> = C <sub>2</sub> HCl <sub>4</sub> + HCl	1.41E12	2.5	7
16. Cl + H <sub>2</sub> = H + HCl	4.80E13	1.3	11
17. Cl <sub>2</sub> = Cl + Cl	7.69E08	55.6	11
18. HCl = H + Cl	6.09E08	97.3	11
19. H + CH <sub>4</sub> = CH <sub>3</sub> + H <sub>2</sub>	2.40E11	7.0	5
20. H + Cl <sub>2</sub> = Cl + HCl	4.57E12	1.4	11
21. H <sub>2</sub> = H + H	5.26E08	105.0	11
22. H + CH <sub>2</sub> CL <sub>2</sub> = HCl + CH <sub>2</sub> Cl	1.02E13	6.1	7

23.	$\text{H} + \text{CH}_3\text{Cl} = \text{HCl} + \text{CH}_3$	9.00E13	7.7	33
24.	$\text{H} + \text{C}_2\text{H}_3\text{Cl} = \text{HCl} + \text{C}_2\text{H}_3$	1.00E13	6.5	7
25.	$\text{CH}_3 + \text{CHCl}_2 = \text{C}_2\text{H}_4\text{Cl}_2$	7.35E10	-6.29	8
26.	$\text{CH}_3 + \text{CHCl}_2 = \text{C}_2\text{H}_4\text{Cl} + \text{Cl}$	7.92E12	4.71	8
27.	$\text{CH}_3 + \text{CHCl}_2 = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	4.02E12	0.0447	8
28.	$\text{CH}_3 + \text{C}_2\text{H}_3\text{Cl}_3 = \text{C}_2\text{H}_3\text{Cl}_2 + \text{CH}_3\text{Cl}$	2.00E11	1.08	9
29.	$\text{CH}_3 + \text{C}_2\text{H}_5\text{Cl} = \text{C}_2\text{H}_5 + \text{CH}_3\text{Cl}$	1.06E12	2.36	12
30.	$\text{CH}_3 + \text{CHCl} = \text{C}_2\text{H}_4\text{Cl}$	7.30E08	-4.17	8
31.	$\text{CH}_3 + \text{CHCl} = \text{C}_2\text{H}_4 + \text{Cl}$	1.46E13	-0.107	8
32.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_5\text{Cl}$	2.79E11	-5.31	8
33.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4 + \text{HCl}$	1.56E13	0.502	8
34.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_5 + \text{Cl}$	1.67E13	5.66	8
35.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4\text{Cl} + \text{H}$	5.47E11	12.50	8
36.	$\text{C}_2\text{H}_6 = \text{CH}_3 + \text{CH}_3$	7.94E16	89.4	3
37.	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_5 + \text{H}$	1.26E16	98.0	3
38.	$\text{CH}_3 + \text{CH}_2\text{Cl}_2 = \text{CHCl}_2 + \text{CH}_4$	6.76E10	7.2	7
39.	$\text{CH}_3 + \text{CH}_2\text{Cl}_2 = \text{CH}_2\text{Cl} + \text{CH}_3\text{Cl}$	1.40E11	4.9	7
40.	$\text{CH}_3 + \text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_3 + \text{CH}_3\text{Cl}$	1.38E11	11.97	7
41.	$\text{CH}_3 + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl} + \text{CH}_4$	3.31E11	9.4	7
42.	$\text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H}$	4.00E13	40.9	3
43.	$\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H}$	1.58E12	38.3	13
44.	$\text{C}_2\text{H}_3 + \text{CH}_4 = \text{C}_2\text{H}_4 + \text{CH}_3$	8.92E11	20.5	16
45.	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	1.58E12	11.7	14
46.	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4\text{Cl}_2$	3.92E10	-6.32	8
47.	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4\text{Cl} + \text{Cl}$	6.12E12	4.68	8

48.	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	2.59E12	0.0477	8
49.	$\text{CHCl}_2 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl}_3$	9.26E09	-6.63	8
50.	$\text{CHCl}_2 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}$	2.33E12	6.31	8
51.	$\text{CHCl}_2 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$	2.27E12	0.197	8
52.	$\text{C}_2\text{H}_2\text{Cl} + \text{CH}_4 = \text{C}_2\text{H}_3\text{Cl} + \text{CH}_3$	7.94E11	10.1	15
53.	$\text{C}_2\text{H}_3\text{Cl}_3 = \text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}$	2.40E16	73.2	17
54.	$\text{C}_2\text{H}_3\text{Cl}_3 = \text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$	3.80E13	49.09	17
55.	$\text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_3 + \text{Cl}$	3.66E15	87.6	18
56.	$\text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_2 + \text{HCl}$	3.55E13	68.73	19
57.	$\text{C}_2\text{H}_2\text{Cl}_2 = \text{C}_2\text{H}_2\text{Cl} + \text{Cl}$	1.04E16	89.17	20
58.	$\text{C}_2\text{H}_2\text{Cl}_2 = \text{C}_2\text{HCl} + \text{HCl}$	7.10E13	69.11	21
59.	$\text{C}_2\text{H}_4\text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl} + \text{Cl}$	6.00E15	77.42	22
60.	$\text{C}_2\text{H}_4\text{Cl}_2 = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	2.88E13	54.35	23
61.	$\text{C}_2\text{HCl}_3 = \text{C}_2\text{HCl}_2 + \text{Cl}$	1.74E15	92.1	24
62.	$\text{C}_2\text{HCl}_3 = \text{C}_2\text{Cl}_2 + \text{HCl}$	7.10E13	77.61	25
63.	$\text{C}_2\text{HCl}_2 + \text{CH}_3 = \text{C}_2\text{HCl} + \text{CH}_3\text{Cl}$	1.26E12	1.50	26
64.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{H}_2\text{Cl}_4$	4.95E09	-6.93	8
65.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{HCl}_3 + \text{HCl}$	3.91E11	-0.404	8
66.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}$	1.69E12	4.65	8
67.	$\text{C}_2\text{H}_2\text{Cl}_4 = \text{C}_2\text{HCl}_3 + \text{HCl}$	1.00E14	56.0	34
68.	$\text{C}_2\text{H}_5\text{Cl} = \text{C}_2\text{H}_4 + \text{HCl}$	1.44E13	52.2	35

## SOURCE

- [1] A factor is based on  $\Delta S$  for reverse reaction,  $A_{-1}$ ;  $A_{-1}$  is taken as twice of  $\text{CH}_3+\text{C}_2\text{H}_5$  ( $A=2\text{E}13$ ), [33];  $E_a = \Delta H$ .
- [2]  $A = 10^{13.55*4}$ ;  $E_a = \Delta H + 40$  [34].
- [3] Dean, A. M., J. Phys. Chem., Vol. 89, 4600 (1985).
- [4] A factor is based on  $A_{-1}$ ;  $A_{-1}=4\text{E}13$  taken as  $2*A$  for  $\text{CH}_3+\text{C}_2\text{H}_5$  [33];  $E_a=\Delta H$ .
- [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  $\text{C}_3\text{H}_7+\text{CH}_3$  ( $A=1.26\text{E}12$ ), [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  $\text{C}_2\text{H}_6+\text{CH}_3$  ( $A=1.5\text{E}12$ ), [33];  $E = \Delta H+2$ . [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;  $E=\Delta H+E_{-1}$ .
- [16] A factor taken for  $\text{C}_2\text{H}_5+\text{CH}_4$  ( $A=1.58\text{E}12$ ) and  $E_a$  as of  $\text{C}_3\text{H}_5+\text{C}_2\text{H}_6$  [33].
- [17] Won, Y. S., Master Thesis, NJIT, 1988.
- [18] A factor is based on  $A_{-1}$ ;  $A_{-1}=2\text{E}13$ , taken for  $\text{C}_3\text{H}_7+\text{CH}_3$  [33];  $E_a=\Delta H$ .
- [19]  $A = 10^{13.55}$ ;  $E_a=\Delta H+45$  [35].

- [20] A factor is based on  $A_{-1}$ ;  $A_{-1}=2E13$ , taken for  $C_3H_7+CH_3$ ;  $E_a=Del\ H$ .
- [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  $CH_3+C_2H_5$  [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  $C_3H_7+CH_3$  [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  $C_3H_5+C_2H_5$  [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.
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- [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  $C_2HCl_3:CH_2Cl_2:CH_4:Ar$  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  $C_2HCl_3$  and  $CH_2Cl_2$  :

			A (1/s)	E (Kcal/mol)	
$C_2HCl_3$	---->	$C_2HCl_2 + Cl$	$3.16E15$	88.5	(11)
$C_2HCl_3$	---->	$C_2Cl_2 + HCl$	$5.E13$	72	(12)
$CH_2Cl_2$	---->	$CH_2Cl + Cl$	$2.5E16$	82.2	(13)
$CH_2Cl_2$	---->	$CHCl + HCl$	$1.2E14$	105	(14)

Table XII shows the specific decomposition rate constants for reactions (11) to (14) at temperatures of 900-1200 °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 °K). Decomposition of trichloroethylene proceeds primarily via path  $C_2Cl_2 + HCl$  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 C<sub>2</sub>HCl<sub>3</sub> AND CH<sub>2</sub>Cl<sub>2</sub>

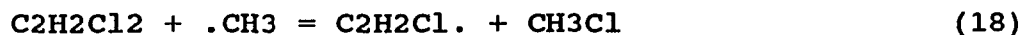
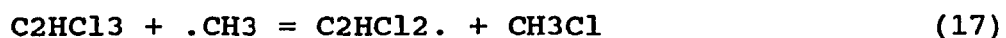
REACTION CHANNEL	C <sub>2</sub> HCl <sub>2</sub> +Cl (11)	C <sub>2</sub> Cl <sub>2</sub> +HCl (12)	CH <sub>2</sub> Cl+Cl (13)	CHCl+HCl (14)
T (K)	k (1/s)			
900	1.01E-06	1.64E-04	2.73E-04	3.80E-12
1000	1.43E-04	9.16E-03	2.70E-02	1.35E-09
1100	8.22E-03	2.47E-01	1.16	1.64E-07
1200	2.42E-01	3.85	2.67E+01	9.01E-06

constant is smaller than reactions (11)-(13) by five order of magnitude (at 1100 °K).

The presence of CH<sub>4</sub> accelerates initiation steps via formation of methyl radical:



Metathetical reaction of CH<sub>3</sub> 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).



Radicals formed by above Cl-transfer reactions can then

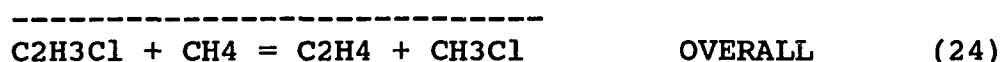
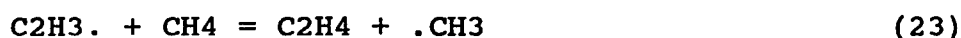


abstract hydrogen from excess available methane in the system and produce less chlorinated hydrocarbons:

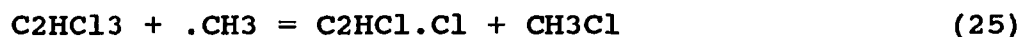


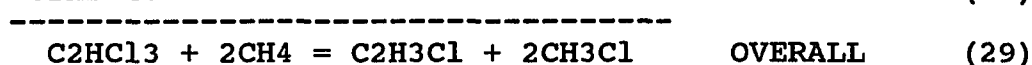
We note that with the methane excess entropy drives these exothermic reaction set.

In addition to pathway (15) reactions (19) - (21) are other channels for formation of the methyl radicals.  $CH_3$  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 :



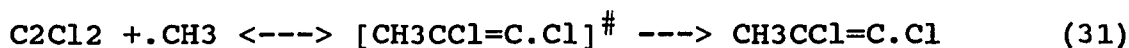
In addition to reactions (3)-(6) another pathway for formation of vinyl chloride is a set of consecutive metathetical reactions starting with  $C_2HCl_3$ , and methyl radical with radical chlorocarbon species then converting  $CH_4$  to  $CH_3$ .





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  $2\text{E}13 \text{ sec}^{-1}$  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  $\text{C}_2\text{Cl}_2$  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  $\text{C}_2\text{Cl}_2$  with  $\text{CH}_3$ , Cl, and to a lesser extent H; for example:



(Stabilized)

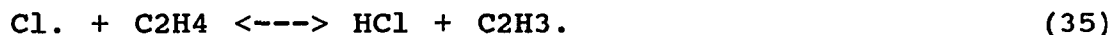


Reactions (31), (32), and (33) are exothermic and (33) is further driven by excess CH<sub>4</sub> in the system.

The products observed in the experiment at highest concentrations are, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>Cl and to a smaller extent benzene.

The C<sub>2</sub>H<sub>4</sub>, 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 C<sub>2</sub>HCl<sub>3</sub> with CH<sub>3</sub>. and CH<sub>4</sub> 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.



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



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 creates more CH<sub>3</sub>. 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 :

$$N = 3n - 6 \quad \text{Non-linear molecules}$$

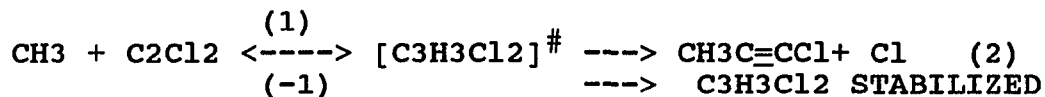
$$N = 3n - 5 \quad \text{Linear molecules}$$

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

-Lennard Jones transport properties,  $\sigma$  and  $\epsilon/k$ , 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  $\text{CH}_3\text{C}=\text{CCl}+\text{Cl}$ . Table XII shows the QRRK calculation results for this reaction. It is observed from the values listed in Table XIV that formation of products  $\text{CH}_3\text{C}=\text{CCl}+\text{Cl}$ , dominate the stabilized complex,  $\text{C}_3\text{H}_3\text{Cl}_2$ , at pressures lower than 0.1 atmosphere. At the experimental conditions of this study (1000-1250 °C and atmospheric pressure), however, the complex adduct stabilization starts to compete with the product exit channel. The  $\text{C}_3\text{H}_3\text{Cl}_2$  radical can further react with excess available  $\text{CH}_4$  to produce dichloropropene, one of our major observed products under 800 °C.

TABLE-XIII



k	A	E <sub>a</sub>	Ref.
1	6.30E11	0.0	a
-1	4.26E13	47.10	a
2	3.24E09	0.0	b
<hr/>			
<v> = 1040. /cm			c
LJ PARAMETERS :			d
sigma = 5.575 A		e/k = 483.7 cal	

a

A<sub>1</sub> taken as of CH<sub>3</sub>+C<sub>2</sub>H<sub>2</sub> (A=6.3E11), [3]; E=7.7 [3].  
 A<sub>-1</sub> from thermodynamics; E<sub>-1</sub>=Del H+7.2, [3].

b

A<sub>2</sub> based on A<sub>-2</sub>; A<sub>-2</sub> taken as of Cl+C=CCl (A=1.58E13), [3];  
 E<sub>2</sub>=Del H.

c

<V> taken as <V> for C<sub>3</sub>H<sub>3</sub>Cl<sub>4</sub> -200; <V> for C<sub>3</sub>H<sub>3</sub>Cl<sub>4</sub> calculated by averaging twice the value for C<sub>2</sub>HCl<sub>3</sub>, and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

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

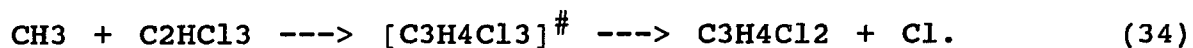
d

Taken as of the values for C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub>. The value for C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub> is calculated by the equations and critical factors given in [32].

The primary process to C<sub>3</sub>H<sub>4</sub>Cl<sub>2</sub> formation, however, is from the combination reaction of CH<sub>3</sub> with C<sub>2</sub>HCl<sub>3</sub> (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 <sub>3</sub> + C <sub>2</sub> Cl <sub>2</sub>		
P (atm)	C <sub>3</sub> H <sub>3</sub> Cl+Cl	C <sub>3</sub> H <sub>3</sub> Cl <sub>2</sub> (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



Reaction (34) is the major channel for dichloropropene formation, because the trichloroethylene is present in higher concentration than the dichloroethylene. 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,  $C_3H_4Cl_2+Cl$ , dominates stabilization of complex adduct for all pressure range, from 0.001 to 10 atm.

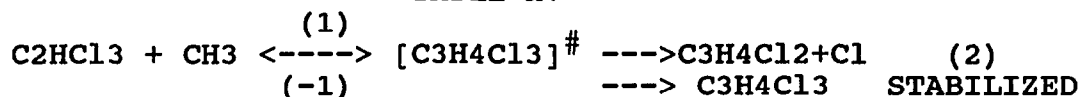
The detail mechanism developed for  $C_2HCl_3/CH_2Cl_2/CH_4$  system is listed in Table XVII. This kinetic scheme includes the important reactions involving  $C_2HCl_3$  in addition to 72 elementary steps tabulated for  $CH_2Cl_2/CH_4$  system in Table XI.

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

P (atm)	$C_3H_4Cl_2+Cl$	$C_3H_4Cl_3$ (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



k	A	E <sub>a</sub>	Ref.
1	2.00E11	0.0	a
-1	5.65E13	34.92	a
2	5.95E14	18.9	b
$\langle v \rangle = 1100. \text{ /cm}$			d
LJ PARAMETERS :			e
sigma = 5.94 A		e/k = 534.4 cal	

a

A<sub>1</sub> factor taken as 1/2 of CH<sub>3</sub>+C<sub>2</sub>H<sub>4</sub> [27];  
A<sub>-1</sub> from thermodynamics; E<sub>-1</sub>=Del H.

b

A<sub>2</sub> is based on A<sub>-2</sub>; A<sub>-2</sub> taken as of Cl+HC≡CCl (A=1.58E13)  
[7]; E<sub>2</sub>=Del H.

c

$\langle V \rangle$  estimated from the average  $\langle V \rangle$  of C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, and 2\* $\langle V \rangle$  of C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>.

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<sub>3</sub>H<sub>5</sub>Cl<sub>3</sub>. The values for C<sub>3</sub>H<sub>5</sub>Cl<sub>3</sub> calculated by the equations and critical factors given in [32].

TABLE XVII- DETAILED MECHANISM FOR CH<sub>2</sub>CL<sub>2</sub>/CH<sub>4</sub>/Ar  
REACTION SYSTEM

REACTION	A	E <sub>a</sub>	SOURCE
1. CH <sub>2</sub> CL <sub>2</sub> = CH <sub>2</sub> CL + CL	1.88E16	82.8	1
2. CH <sub>2</sub> CL <sub>2</sub> = CHCL + HCL	1.42E14	111.0	2
3. CH <sub>4</sub> = CH <sub>3</sub> + H	1.00E16	104.8	3
4. CH <sub>3</sub> CL = CH <sub>3</sub> + CL	1.88E15	84.4	4
5. CL + CH <sub>4</sub> = HCL + CH <sub>3</sub>	3.10E13	3.6	7
6. CL + C <sub>2</sub> H <sub>6</sub> = HCL + C <sub>2</sub> H <sub>5</sub>	1.20E14	1.0	7
7. CL + C <sub>2</sub> H <sub>4</sub> = C <sub>2</sub> H <sub>4</sub> CL	2.90E10	-8.0	8
8. CL + C <sub>2</sub> H <sub>4</sub> = C <sub>2</sub> H <sub>3</sub> + HCL	1.00E13	5.1	7
9. CL + CH <sub>2</sub> CL <sub>2</sub> = CH <sub>2</sub> CL + CL <sub>2</sub>	1.00E14	21.4	7
10. CL + CH <sub>2</sub> CL <sub>2</sub> = CHCL <sub>2</sub> + HCL	2.50E13	3.1	9
11. CL + CH <sub>3</sub> CL = CH <sub>3</sub> + CL <sub>2</sub>	1.00E14	25.0	7
12. CL + CH <sub>3</sub> CL = CH <sub>2</sub> CL + HCL	3.10E13	3.6	9
13. CL + C <sub>2</sub> H <sub>3</sub> CL <sub>3</sub> = C <sub>2</sub> H <sub>2</sub> CL <sub>3</sub> + HCL	3.16E13	3.5	7
14. CL + C <sub>2</sub> H <sub>5</sub> CL = C <sub>2</sub> H <sub>4</sub> CL + HCL	2.00E13	1.5	7
15. CL + C <sub>2</sub> H <sub>2</sub> CL <sub>4</sub> = C <sub>2</sub> HCL <sub>4</sub> + HCL	1.41E12	2.5	7
16. CL + H <sub>2</sub> = H + HCL	4.80E13	1.3	11
17. CL <sub>2</sub> = CL + CL	7.69E08	55.6	11
18. HCL = H + CL	6.09E08	97.3	11
19. H + CH <sub>4</sub> = CH <sub>3</sub> + H <sub>2</sub>	2.40E11	7.0	5
20. H + CL <sub>2</sub> = CL + HCL	4.57E12	1.4	11
21. H <sub>2</sub> = H + H	5.26E08	105.0	11
22. H + CH <sub>2</sub> CL <sub>2</sub> = HCL + CH <sub>2</sub> CL	1.02E13	6.1	7

23.	$\text{H} + \text{CH}_3\text{Cl} = \text{HCl} + \text{CH}_3$	9.00E13	7.7	33
24.	$\text{H} + \text{C}_2\text{H}_3\text{Cl} = \text{HCl} + \text{C}_2\text{H}_3$	1.00E13	6.5	7
25.	$\text{CH}_3 + \text{CHCl}_2 = \text{C}_2\text{H}_4\text{Cl}_2$	7.35E10	-6.29	8
26.	$\text{CH}_3 + \text{CHCl}_2 = \text{C}_2\text{H}_4\text{Cl} + \text{Cl}$	7.92E12	4.71	8
27.	$\text{CH}_3 + \text{CHCl}_2 = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	4.02E12	0.0447	8
28.	$\text{CH}_3 + \text{C}_2\text{H}_3\text{Cl}_3 = \text{C}_2\text{H}_3\text{Cl}_2 + \text{CH}_3\text{Cl}$	2.00E11	1.08	9
29.	$\text{CH}_3 + \text{C}_2\text{H}_5\text{Cl} = \text{C}_2\text{H}_5 + \text{CH}_3\text{Cl}$	1.06E12	2.36	12
30.	$\text{CH}_3 + \text{CHCl} = \text{C}_2\text{H}_4\text{Cl}$	7.30E08	-4.17	8
31.	$\text{CH}_3 + \text{CHCl} = \text{C}_2\text{H}_4 + \text{Cl}$	1.46E13	-0.107	8
32.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_5\text{Cl}$	2.79E11	-5.31	8
33.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4 + \text{HCl}$	1.56E13	0.502	8
34.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_5 + \text{Cl}$	1.67E13	5.66	8
35.	$\text{CH}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4\text{Cl} + \text{H}$	5.47E11	12.50	8
36.	$\text{C}_2\text{H}_6 = \text{CH}_3 + \text{CH}_3$	7.94E16	89.4	3
37.	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_5 + \text{H}$	1.26E16	98.0	3
38.	$\text{CH}_3 + \text{CH}_2\text{Cl}_2 = \text{CHCl}_2 + \text{CH}_4$	6.76E10	7.2	7
39.	$\text{CH}_3 + \text{CH}_2\text{Cl}_2 = \text{CH}_2\text{Cl} + \text{CH}_3\text{Cl}$	1.40E11	4.9	7
40.	$\text{CH}_3 + \text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_3 + \text{CH}_3\text{Cl}$	1.38E11	11.97	7
41.	$\text{CH}_3 + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl} + \text{CH}_4$	3.31E11	9.4	7
42.	$\text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H}$	4.00E13	40.9	3
43.	$\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H}$	1.58E12	38.3	13
44.	$\text{C}_2\text{H}_3 + \text{CH}_4 = \text{C}_2\text{H}_4 + \text{CH}_3$	8.92E11	20.5	16
45.	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	1.58E12	11.7	14
46.	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4\text{Cl}_2$	3.92E10	-6.32	8
47.	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_4\text{Cl} + \text{Cl}$	6.12E12	4.68	8

48.	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	2.59E12	0.0477	8
49.	$\text{CHCl}_2 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl}_3$	9.26E09	-6.63	8
50.	$\text{CHCl}_2 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}$	2.33E12	6.31	8
51.	$\text{CHCl}_2 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$	2.27E12	0.197	8
52.	$\text{C}_2\text{H}_2\text{Cl} + \text{CH}_4 = \text{C}_2\text{H}_3\text{Cl} + \text{CH}_3$	7.94E11	10.1	15
53.	$\text{C}_2\text{H}_3\text{Cl}_3 = \text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}$	2.40E16	73.2	17
54.	$\text{C}_2\text{H}_3\text{Cl}_3 = \text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$	3.80E13	49.09	17
55.	$\text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_3 + \text{Cl}$	3.66E15	87.6	18
56.	$\text{C}_2\text{H}_3\text{Cl} = \text{C}_2\text{H}_2 + \text{HCl}$	3.55E13	68.73	19
57.	$\text{C}_2\text{H}_2\text{Cl}_2 = \text{C}_2\text{H}_2\text{Cl} + \text{Cl}$	1.04E16	89.17	20
58.	$\text{C}_2\text{H}_2\text{Cl}_2 = \text{C}_2\text{HCl} + \text{HCl}$	7.10E13	69.11	21
59.	$\text{C}_2\text{H}_4\text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl} + \text{Cl}$	6.00E15	77.42	22
60.	$\text{C}_2\text{H}_4\text{Cl}_2 = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	2.88E13	54.35	23
61.	$\text{C}_2\text{HCl}_3 = \text{C}_2\text{HCl}_2 + \text{Cl}$	1.74E15	92.1	24
62.	$\text{C}_2\text{HCl}_3 = \text{C}_2\text{Cl}_2 + \text{HCl}$	7.10E13	77.61	25
63.	$\text{C}_2\text{HCl}_2 + \text{CH}_3 = \text{C}_2\text{HCl} + \text{CH}_3\text{Cl}$	1.26E12	1.50	26
64.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{H}_2\text{Cl}_4$	4.95E09	-6.93	8
65.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{HCl}_3 + \text{HCl}$	3.91E11	-0.404	8
66.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}$	1.69E12	4.65	8
67.	$\text{C}_2\text{H}_2\text{Cl}_4 = \text{C}_2\text{HCl}_3 + \text{HCl}$	1.00E14	56.0	34
68.	$\text{C}_2\text{H}_5\text{Cl} = \text{C}_2\text{H}_4 + \text{HCl}$	1.44E13	52.2	35
69.	$\text{C}_2\text{HCl}_3 + \text{CH}_3 = \text{C}_3\text{H}_4\text{Cl}_3$	2.12E06	-3.93	8
70.	$\text{C}_2\text{HCl}_3 + \text{CH}_3 = \text{C}_3\text{H}_4\text{Cl}_2 + \text{Cl}$	2.00E11	4.51	8
71.	$\text{C}_2\text{Cl}_2 + \text{CH}_3 = \text{C}_3\text{H}_3\text{Cl}_2$	3.38E10	2.65	8
72.	$\text{C}_2\text{Cl}_2 + \text{CH}_3 = \text{C}_3\text{H}_3\text{Cl} + \text{Cl}$	5.25E11	0.334	8

## SOURCE

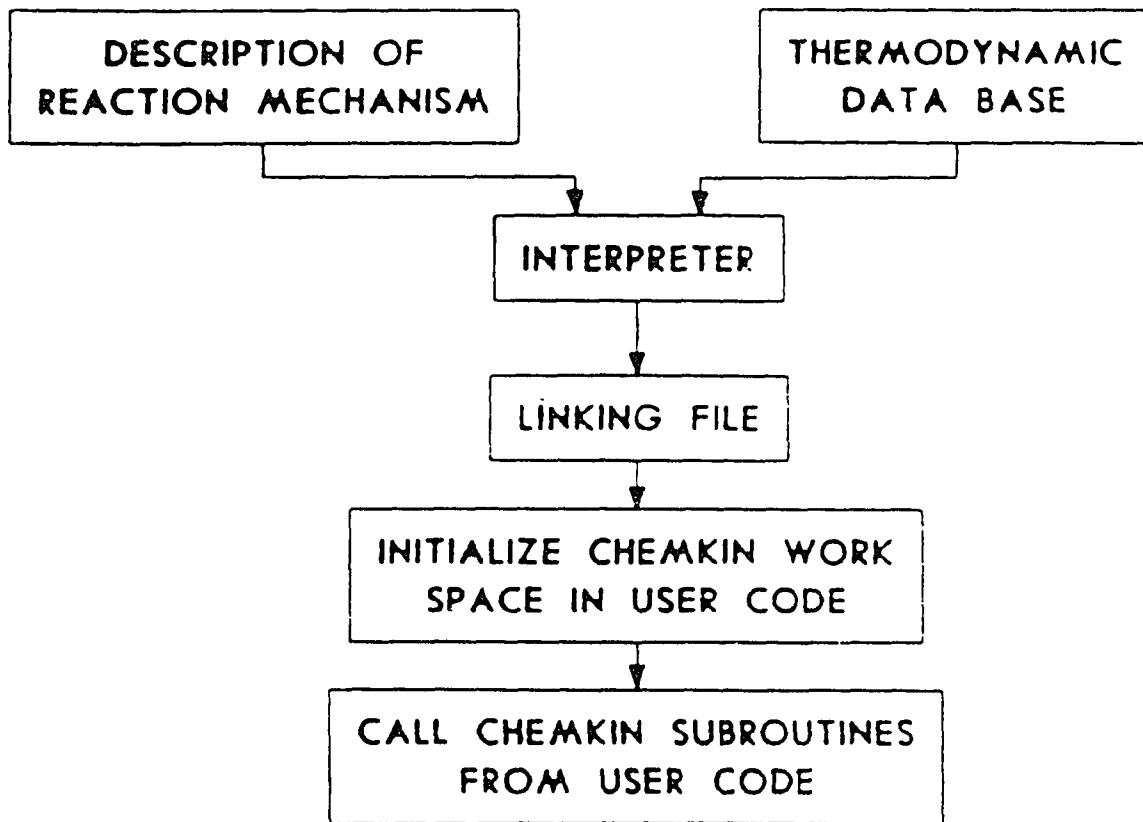
- [1] A factor is based on  $\Delta S$  for reverse reaction,  $A_{-1}$ ;  $A_{-1}$  is taken as twice of  $\text{CH}_3+\text{C}_2\text{H}_5$  ( $A=2\text{E}13$ ), [33];  $E_a = \Delta H$ .
- [2]  $A = 10^{13.55} \cdot 4$ ;  $E_a = \Delta H + 40$  [34].
- [3] Dean, A. M., J. Phys. Chem., Vol. 89, 4600 (1985).
- [4] A factor is based on  $A_{-1}$ ;  $A_{-1}=4\text{E}13$  taken as  $2 \cdot A$  for  $\text{CH}_3+\text{C}_2\text{H}_5$  [33];  $E_a = \Delta H$ .
- [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 BIOMOLECULAR AND TERMOLECULAR GAS REACTIONS, Vol. I, CRC Press, 1981.
- [10] A taken as for rreaction  $\text{C}_3\text{H}_7+\text{CH}_3$  ( $A=1.26\text{E}12$ ), [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  $\text{C}_2\text{H}_6+\text{CH}_3$  ( $A=1.5\text{E}12$ ), [33];  $E = \Delta H+2$ . [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;  $E = \Delta H + E_{-1}$ .
- [16] A factor taken for  $\text{C}_2\text{H}_5+\text{CH}_4$  ( $A=1.58\text{E}12$ ) and  $E_a$  as of  $\text{C}_3\text{H}_5+\text{C}_2\text{H}_6$  [33].
- [17] Won, Y. S., Master Thesis, NJIT, 1988.
- [18] A factor is based on  $A_{-1}$ ;  $A_{-1}=2\text{E}13$ , taken for  $\text{C}_3\text{H}_7+\text{CH}_3$  [33];  $E_a = \Delta H$ .
- [19]  $A = 10^{13.55}$ ;  $E_a = \Delta H + 45$  [35].

- [20] A factor is based on  $A_{-1}$ ;  $A_{-1}=2E13$ , taken for  $C_3H_7+CH_3$ ;  $E_a=Del\ H$ .
- [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  $CH_3+C_2H_5$  [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  $C_3H_7+CH_3$  [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  $C_3H_5+C_2H_5$  [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.
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- [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.

Figure 27 compares the experimental and calculated results for CH<sub>2</sub>Cl<sub>2</sub> decomposition in methane/Ar atmosphere at

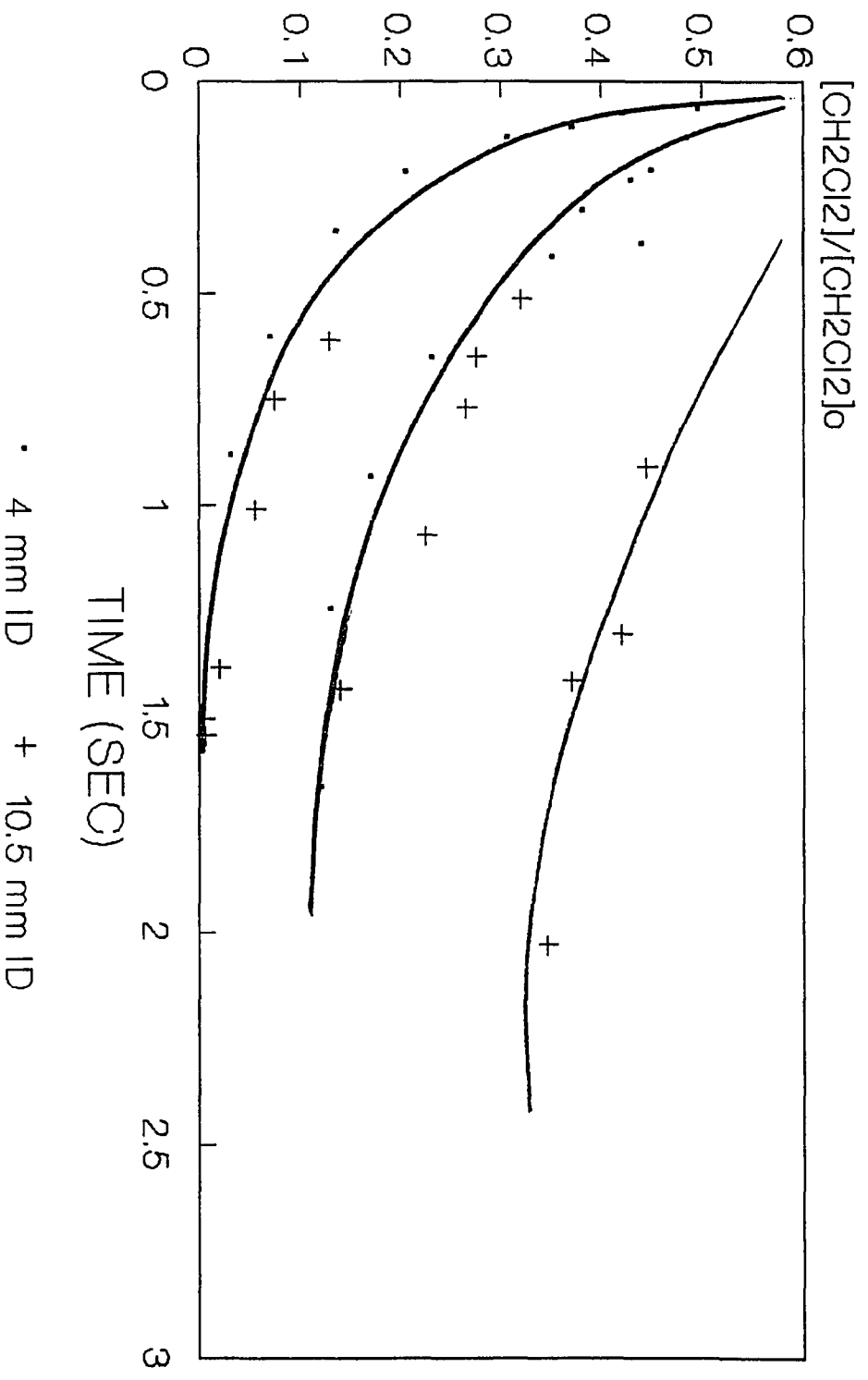
TABLE XVIII THERMODYNAMIC PROPERTIES OF C<sub>3</sub> CHLOROCARBONS

SPECIES	H <sub>f</sub>	S	C <sub>p</sub>				
			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

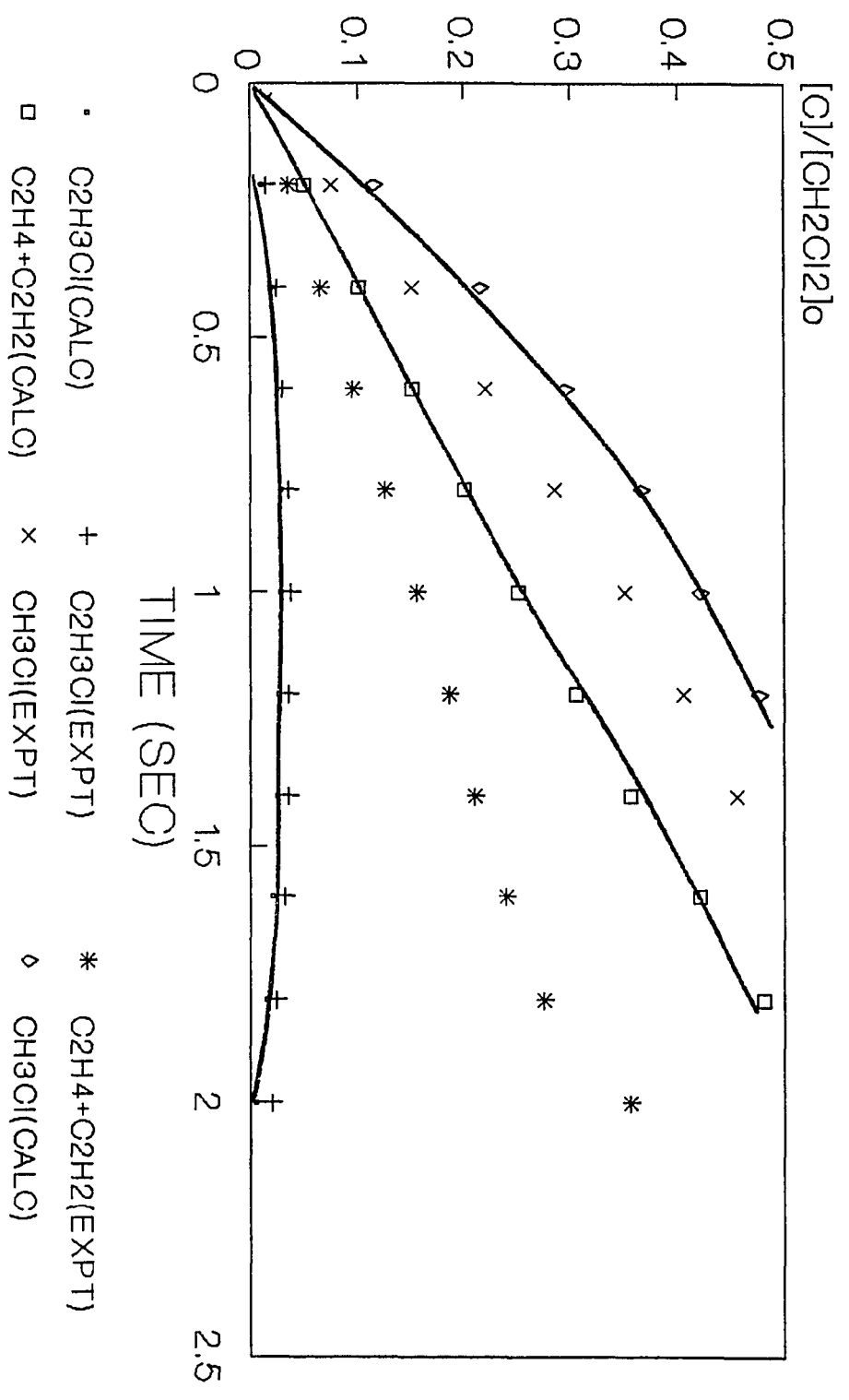
1025, 1075, 1125 °K in 4 and 10.5 mm ID reactors. This Figure 27 shows good agreement between calculated and experimental results for decay of parent reagent in the range of temperature and reactor diameters studied (4 to 16 mm ID).

Figure 28 demonstrates concentration of products

**FIGURE-27 DECAY PLOT OF CH<sub>2</sub>Cl<sub>2</sub> IN  
CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar SYSTEM**



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



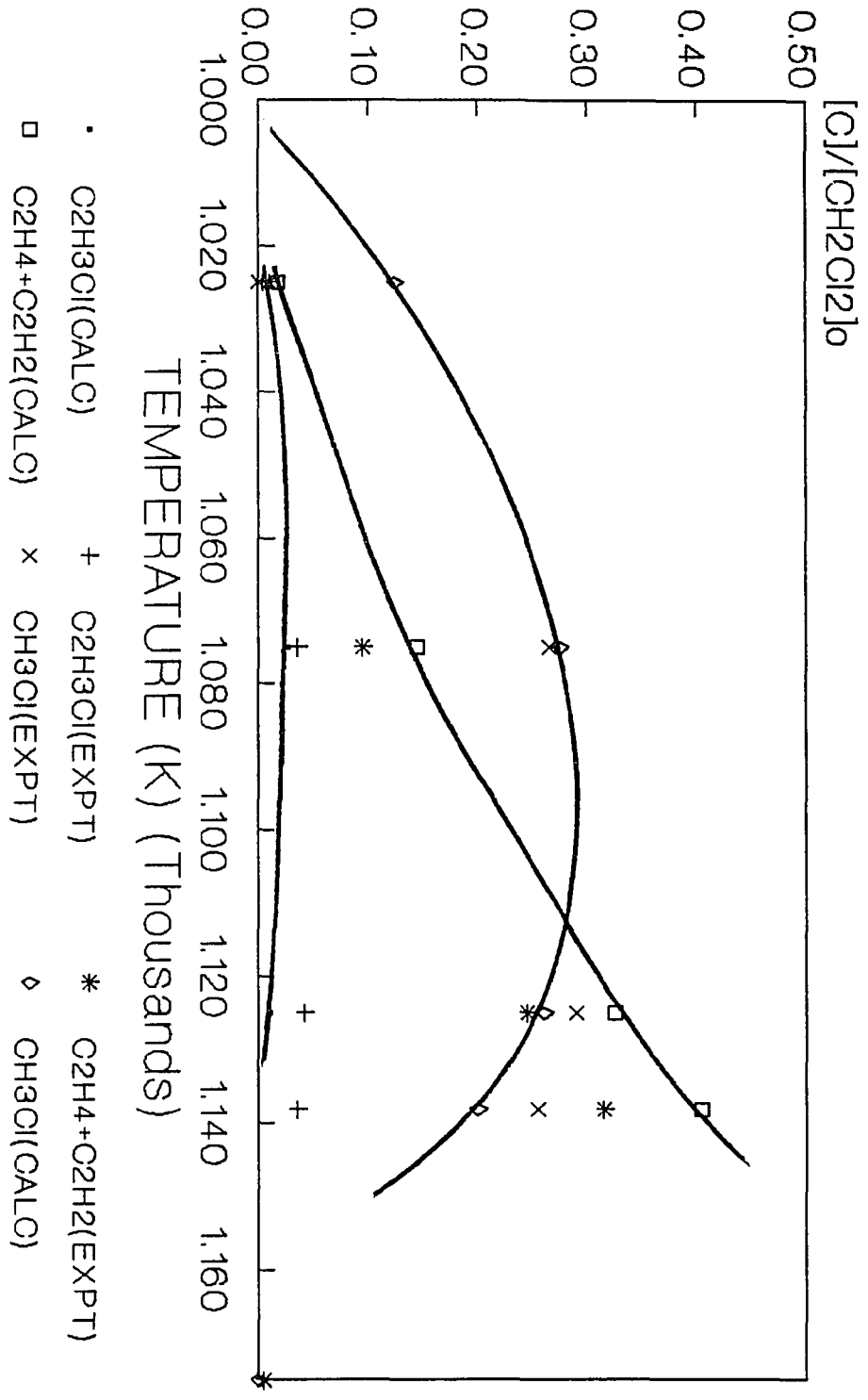
C<sub>2</sub>H<sub>2</sub>+C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>Cl, and C<sub>2</sub>H<sub>3</sub>Cl versus reaction time for CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar system at temperature of 1075 °K. The difference seen between calculated and experimental values for various product compounds could be due to the fact that our kinetic scheme does not include all species present in the reaction system. Therefore, 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 °K). It is interesting to note, however, that the ratio [C<sub>2</sub>H<sub>2</sub>]/[C<sub>2</sub>H<sub>4</sub>] 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 °K) our experiment.

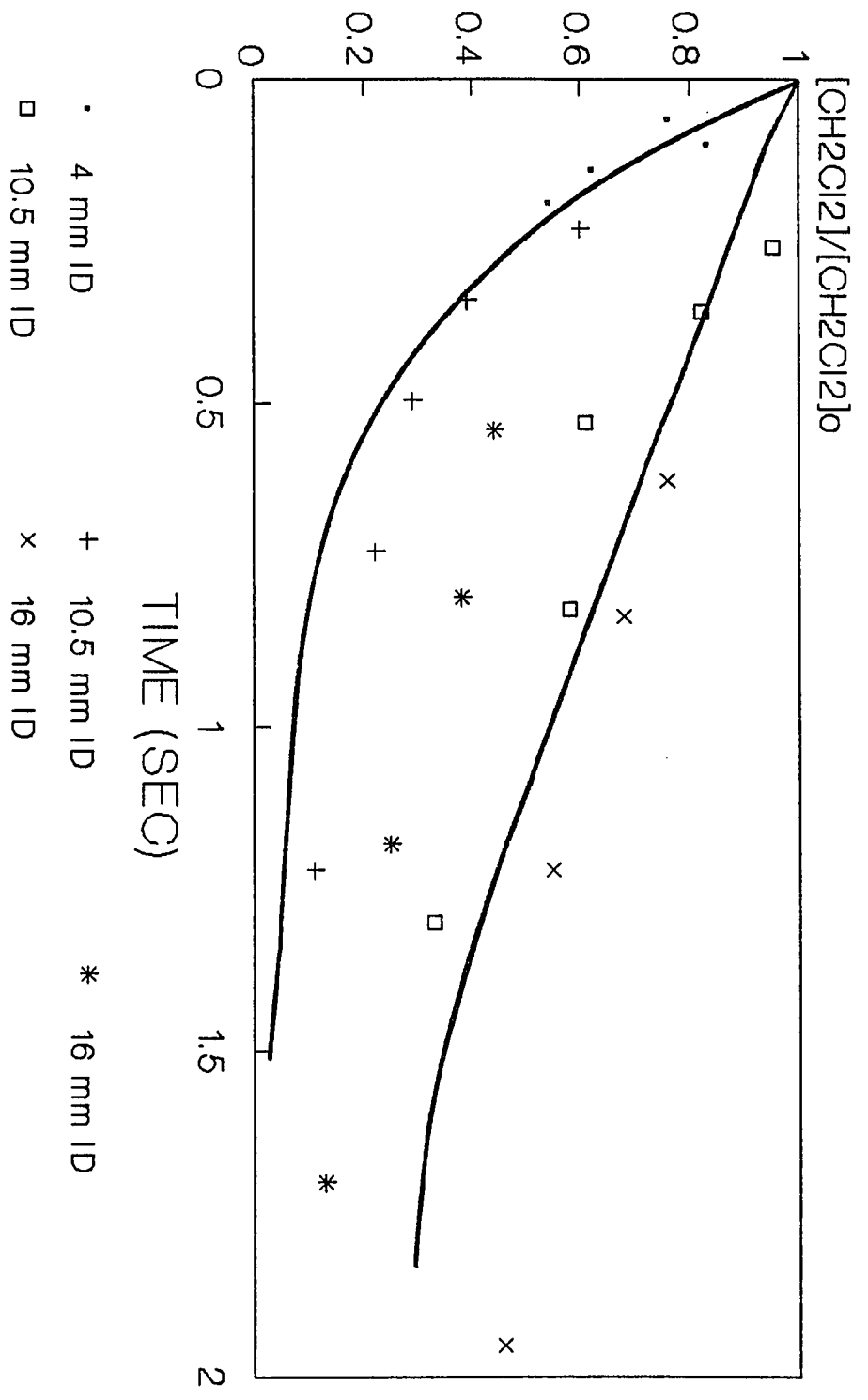
The CHEMKIN computer code was utilized to model the detail kinetic scheme developed for C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub> system. Figures 30 and 31 compare experimental and calculated values of trichloroethylene and methylene

chloride decomposition at temperatures 1075 and 1125 °K. It is apparent from these figures that the model reproduces the experimental data.

**FIGURE-29 PRODUCT DISTRIBUTION VS TEMPERATURE IN CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar SYSTEM**

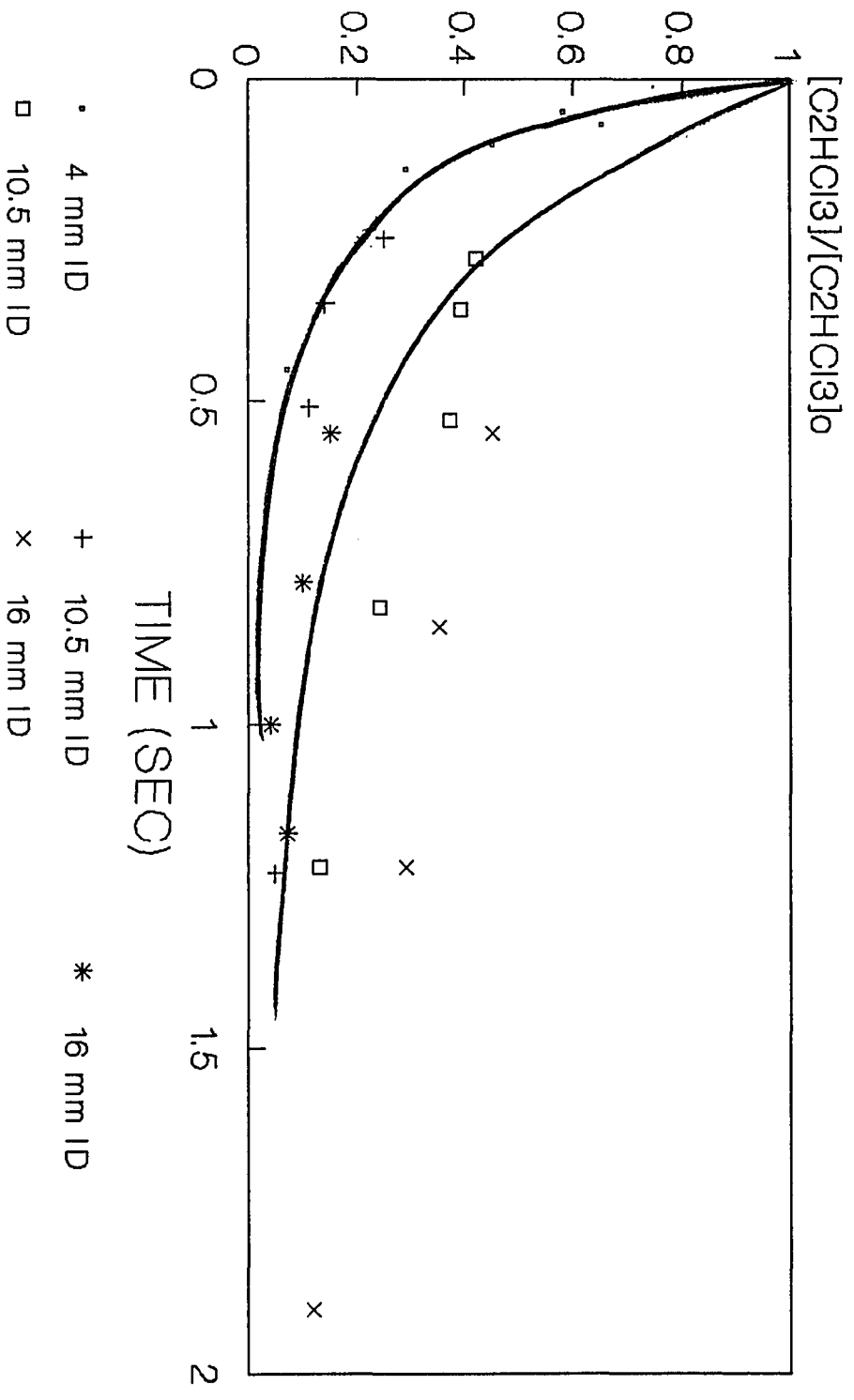


**FIGURE-30 DECAY PLOT OF CH<sub>2</sub>Cl<sub>2</sub> IN  
C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar SYSTEM**





**FIGURE-31 DECAY PLOT OF C<sub>2</sub>HCl<sub>3</sub> IN  
C<sub>2</sub>HCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>4</sub>/Ar SYSTEM**

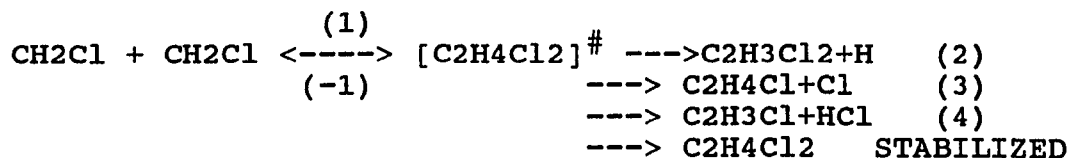


## APPENDIX

SAMPLE OF GISOQRRK INPUT/OUTPUT DATA Page 121

KINETIC PARAMETERS OF REVERSE REACTIONS Page 146

TABLE-I



k	A	E <sub>a</sub>	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

$\langle v \rangle = 797.2 \text{ /cm}$

e

LJ PARAMETERS :

f

sigma = 5.116 A

e/k = 472. cal

a

A<sub>1</sub> taken as of 1/2 the value given in [36] for CH<sub>2</sub>Cl+CH<sub>2</sub>Cl, (A=1E13); A<sub>-1</sub> from thermodynamics;

E<sub>-1</sub>=Del H.

b

A<sub>2</sub> is based on A<sub>-2</sub>; A<sub>-2</sub> taken as 2 of CH<sub>3</sub>+C<sub>2</sub>H<sub>5</sub> (A=2E13) [33]; E<sub>2</sub>=Del H.

c

A<sub>3</sub> is based on A<sub>-3</sub>; A<sub>-3</sub> taken as Cl+C=CCl (A=1.58E13), [33]; E<sub>a</sub>=Del H.

d

A<sub>4</sub>=10<sup>13.55</sup>\*10<sup>-4/4.6\*4</sup> [37]; E<sub>4</sub>=Del H+35 [34].

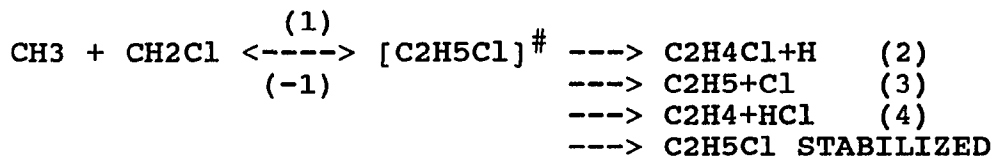
e

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



k	A	E <sub>a</sub>	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<sub>1</sub> taken as 2/5 of the value given in [36] (A=5E13);  
A<sub>-1</sub> from thermodynamics; E<sub>-1</sub>=Del H.

b

A<sub>2</sub> based on A<sub>-2</sub>; A<sub>-2</sub> taken as 2/3 of H+C<sub>2</sub>H<sub>5</sub> (A=4E13), [33];  
E<sub>a</sub>=Del H.

c

A<sub>3</sub> based on A<sub>-3</sub>; A<sub>-3</sub>=2.E13 as for CH<sub>3</sub>+C<sub>2</sub>H<sub>5</sub> [33]; E<sub>3</sub>=Del H.

d

A<sub>4</sub>=10<sup>13.55</sup>\*10<sup>-4/4.6</sup>\*3 [33]; E<sub>4</sub>=Del H+35 [34].

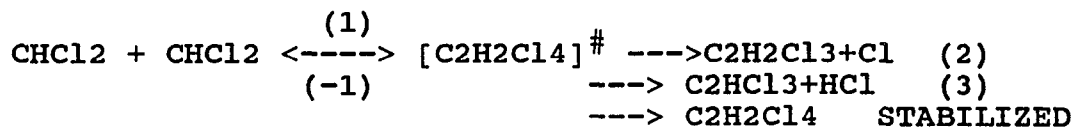
e

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



k	A	E <sub>a</sub>	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
<hr/>			
<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 C<sub>3</sub>H<sub>7</sub>+C<sub>3</sub>H<sub>7</sub> (A=4E12) [33];  
A<sub>-1</sub> from thermodynamics (Del S); E<sub>-1</sub>=Del H.

b

A<sub>2</sub> is based on A<sub>-2</sub>; A<sub>-2</sub> taken as 1/4 of CH<sub>3</sub>+C<sub>2</sub>H<sub>5</sub> (A=2E13) [33];  
E<sub>2</sub>=Del H.

c

A<sub>3</sub>=10<sup>13.55</sup>\*10<sup>-4/4.6</sup>\*4 [37]; E<sub>3</sub>=Del H+35 [34].

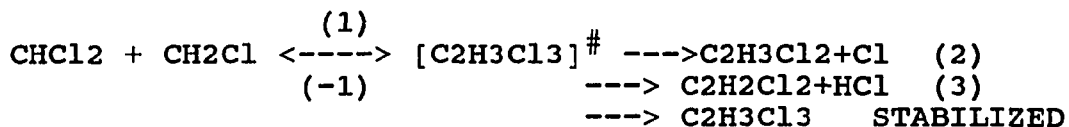
d

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



k	A	E <sub>a</sub>	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
$\langle v \rangle = 687.7 \text{ /cm}$			d
LJ PARAMETERS :			e
sigma = 5.71 A		e/k = 498.9 cal	

a

A<sub>1</sub> taken as 1/3 of C<sub>2</sub>H<sub>5</sub>+C<sub>3</sub>H<sub>7</sub> (A=7.94E12) [33];  
A<sub>-1</sub> from thermodynamics (Del S); E<sub>-1</sub>=Del H.

b

A<sub>2</sub> is based on A<sub>-2</sub>; A<sub>-2</sub> taken as of CH<sub>3</sub>+C<sub>4</sub>H<sub>9</sub> (A=2E13) [33];  
E<sub>2</sub>=Del H.

c

A<sub>3</sub>=10<sup>13.55</sup>\*10<sup>-4/4.6</sup>\*(9+5)/2 [37]; E<sub>3</sub>=Del H+35 [34].

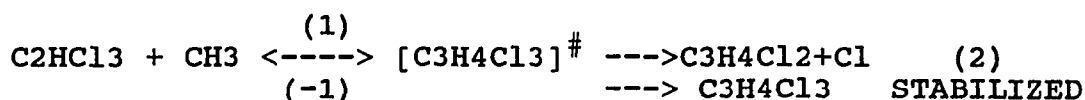
d

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



k	A	E <sub>a</sub>	Ref.
1	2.00E11	0.0	a
-1	5.65E13	34.92	a
2	5.95E14	18.9	b
$\langle v \rangle = 1100. \text{ /cm}$			d
LJ PARAMETERS :			e
sigma = 5.94 A		e/k = 534.4 cal	

a

A<sub>1</sub> factor taken as 1/2 of CH<sub>3</sub>+C<sub>2</sub>H<sub>4</sub> [33];  
A<sub>-1</sub> from thermodynamics; E<sub>-1</sub>=Del H.

b

A<sub>2</sub> is based on A<sub>-2</sub>; A<sub>-2</sub> taken as of Cl+C=CCl (A=1.58E13)  
[7]; E<sub>2</sub>=Del H.

c

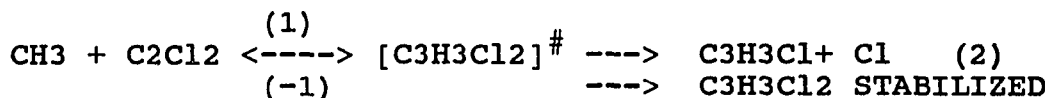
$\langle V \rangle$  estimated from the average  $\langle V \rangle$  of C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, and 2\* $\langle V \rangle$  of C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>.

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 C<sub>3</sub>H<sub>5</sub>Cl<sub>3</sub>. The values for C<sub>3</sub>H<sub>5</sub>Cl<sub>3</sub> calculated by the equations and critical factors given in [38].

TABLE-VI



k	A	E <sub>a</sub>	Ref.
1	6.30E11	7.7	a
-1	4.26E13	47.10	a
2	3.26E09	0.0	b
<hr/>			
<v> = 1040. /cm			c
LJ PARAMETERS :			d
sigma = 5.575 A		e/k = 483.7 cal	

a

A<sub>1</sub> taken as of CH<sub>3</sub>+C<sub>2</sub>H<sub>2</sub> (A=6.3E11), [3]; E=7.7 [3].  
 A<sub>-1</sub> from thermodynamics; E<sub>-1</sub>=Del H+7.2, [3].

b

A<sub>2</sub> based on A<sub>-2</sub>; A<sub>-2</sub> taken as of Cl+C=CCl (A=1.58E13), [3];  
 E<sub>2</sub>=Del H.

c

<V> taken as <V> for C<sub>3</sub>H<sub>3</sub>Cl<sub>4</sub> -200; <V> for C<sub>3</sub>H<sub>3</sub>Cl<sub>4</sub> calculated by averaging twice the value for C<sub>2</sub>HCl<sub>3</sub>, and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

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

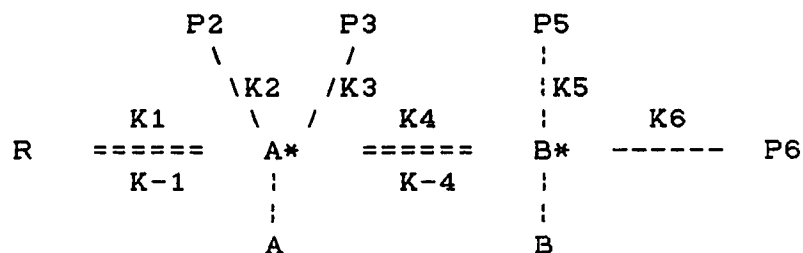
Taken as of the values for C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub>. The value for C<sub>3</sub>H<sub>5</sub>Cl<sub>2</sub> is calculated by the equations and critical factors given in [32].



\*\*\*\*\* GISOQRRK : USES NON-INTEGGER VALUES FOR  
THE NUMBER OF QUANTA \*\*\*\*\*

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

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK



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

CH2C1 + CHC12 = 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 CH2C1 + CHC12 = 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

CH2C1 + CHC12 = C2H3CL2 + C1 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 CH2C1 + CHC12 = C2H3CL2 + C1 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

CH2C1 + CHC12 = C2H2CL2 + HC1 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
3.204E+19 \* (T<sup>-2.14</sup>) 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 CH2C1 + CHC12 = C2H2CL2 + HC1 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  
NON-LINEAR REGRESSION RESULTS  
0 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

CH2C1 + CHC12 = C2H3CL3 T 750. K TO 1250. K  
NON-LINEAR REGRESSION RESULTS  
0 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

CH2C1 + CHC12 = C2H2CL2 + HC1 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
3.594E+19 \* (T<sup>-2.15</sup>) 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 CH2C1 + CHC12 = C2H2CL2 + HC1 T 750. K TO 1250. K  
A = 1.60E+12 E = -7.62E-01 KCAL

T	K EXP	K CALC	PERCENT 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<sup>.55</sup>) 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

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

K-1171) COMPLEX A DISSOC T 750. K TO 1250. K  
A = 4.31E+10 E = 11.7E+01 KCAL

T	K EXP	K CALC	PERCENT ERROR
750.	1.66E+11	1.65E+11	1.0
850.	4.06E+10	4.18E+10	-2.9
950.	9.96E+10	9.64E+10	1.9
1050.	1.97E+11	1.96E+11	1.0
1150.	2.97E+11	2.94E+11	1.0
1250.	3.83E+11	3.84E+11	1.1

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

CH2Cl + CHCl2 = C2H3Cl3 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
3.393E+31 \* (T<sup>-6.64</sup>) 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	PERCENT 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

CH2C1 + CHC12 = C2H3CL2 + C1 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 CH2C1 + CHC12 = C2H3CL2 + C1 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

CH2C1 + CHC12 = 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<sup>.49</sup>) 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  
0

P= 7.600E+02 TORR      T= 950.0 K  
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

CH2C1 + CHC12 = C2H3CL3 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
9.470E+34 \* (T<sup>-7.31</sup>) 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 CH2C1 + CHC12 = 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

CH2C1 + CHC12 = C2H3CL2 + C1 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
1.307E+15 \* (T<sup>-.80</sup>) 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<sup>.06</sup>) 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<sup>-7.50</sup>) 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 CH2C1 + CHC12 = 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

CH2C1 + CHC12 = C2H3CL2 + C1 T 750. K TO 1250. K  
 0 NON-LINEAR REGRESSION RESULTS  
 1.746E+17 \* (T<sup>-1.39</sup>) 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 CH2C1 + CHC12 = C2H3CL2 + C1 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

CH2C1 + CHC12 = C2H2CL2 + HC1 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
2.585E+24 \* (T<sup>-3.48</sup>) 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 CH2C1 + CHC12 = C2H2CL2 + HC1 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<sup>-.43</sup>) 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

CH2C1 + CHC12 = C2H3CL3 T 750. K TO 1250. K  
NON-LINEAR REGRESSION RESULTS  
1.233E+34 \* (T<sup>-6.66</sup>) 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 CH2C1 + CHC12 = 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

CH2C1 + CHC12 = C2H3CL2 + C1 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
5.988E+18 \* (T<sup>-1.77</sup>) 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 CH2C1 + CHC12 = C2H3CL2 + C1 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

CH2C1 + CHC12 = C2H2CL2 + HC1 T 750. K TO 1250. K  
0 NON-LINEAR REGRESSION RESULTS  
3.563E+23 \* (T<sup>-3.16</sup>) 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 CH2Cl + CHCl2 = C2H2CL2 + HCl 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



\*\*\*\*\* # 12 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.322E+00 CAL/DEG/MOLE  
DELTA H = 0.399E+03  
DELTA H = -0.272E+04

\*\*\*\*\* # 13 FL+CH3FL=CH2FL+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 4.369E+02 CAL/MOLE  
DELTA H = 0.414E+01  
DELTA H = -0.272E+04

\*\*\*\*\* # 14 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.233E+03 CAL/MOLE  
DELTA H = 0.211E+04  
DELTA H = -0.601E+04

\*\*\*\*\* # 15 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = -2.275E+04 CAL/MOLE  
DELTA H = -0.205E+05  
DELTA H = -0.671E+04

\*\*\*\*\* # 16 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = -2.368E+01 CAL/DEG/MOLE  
DELTA H = -0.205E+05  
DELTA H = -0.671E+04

\*\*\*\*\* # 17 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 9.329E+00 CAL/DEG/MOLE  
DELTA H = 0.671E+04  
DELTA H = -0.272E+04

\*\*\*\*\* # 18 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 7.382E+00 CAL/DEG/MOLE  
DELTA H = -0.601E+04  
DELTA H = -0.361E+01

\*\*\*\*\* # 19 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.046E+00 CAL/DEG/MOLE  
DELTA H = -0.272E+04  
DELTA H = -0.361E+01

\*\*\*\*\* # 20 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.046E+00 CAL/DEG/MOLE  
DELTA H = -0.272E+04  
DELTA H = -0.361E+01

\*\*\*\*\* # 21 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.046E+00 CAL/DEG/MOLE  
DELTA H = -0.272E+04  
DELTA H = -0.361E+01

\*\*\*\*\* # 22 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.046E+00 CAL/DEG/MOLE  
DELTA H = -0.272E+04  
DELTA H = -0.361E+01

\*\*\*\*\* # 23 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.046E+00 CAL/DEG/MOLE  
DELTA H = -0.272E+04  
DELTA H = -0.361E+01

\*\*\*\*\* # 24 FL+CH6=CH3+HCL  
CAL/MOLE  
DELTA S (T = 950. K) = 8.046E+00 CAL/DEG/MOLE  
DELTA H = -0.272E+04  
DELTA H = -0.361E+01

INCN. -0.5944E+04 0.3644E+01 0.5665353E+03 0.666E+03 0.433E+12 0.64E+09  
11CN. -0.611E+04 0.357E+01 0.517369E+03 0.522E+03 0.447E+12 0.91E+09  
12CN. -0.629E+04 0.352E+01 0.416744E+03 0.422E+03 0.52E+12 0.12E+10

FCALCUTTUW # 10 FL+G2H3C13=C2H2CL3+HCL

DELTA N = 0 DELTA HGT = 950. K) = -6.256E+03 CAL/MOLE DELTA S (T = 950. K) = 6.254E+00 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.306E+01 DELTA H = -0.645E+04

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.627E+04 0.315E+01 0.645195E+03 0.655E+03 0.49E+13 0.77E+10  
11CN. -0.640E+04 0.308E+01 0.468735E+03 0.47E+03 0.59E+13 0.13E+11  
12CN. -0.653E+04 0.302E+01 0.357989E+03 0.36E+03 0.68E+13 0.19E+11

13CN. -0.667E+04 0.296E+01 0.284089E+03 0.28E+03 0.77E+13 0.27E+11

FCALCUTTUW # 20 FL+G2H5C1=C2H4CL+HCL

DELTA N = 0 DELTA HGT = 950. K) = -6.373E+03 CAL/MOLE DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.294E+01 DELTA H = -0.656E+04

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.637E+04 0.303E+01 0.606387E+03 0.61E+03 0.90E+13 0.15E+11  
11CN. -0.650E+04 0.296E+01 0.458245E+03 0.44E+03 0.97E+13 0.22E+11  
12CN. -0.665E+04 0.290E+01 0.333227E+03 0.33E+03 0.10E+14 0.31E+11

13CN. -0.681E+04 0.283E+01 0.263298E+03 0.26E+03 0.11E+14 0.42E+11

FCALCUTTUW # 30 H+G2H2C1=C2H2C1+HCL

DELTA N = 0 DELTA HGT = 950. K) = -2.192E+04 CAL/MOLE DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.455E+01 DELTA H = -0.222E+05

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.719E+05 0.470E+01 0.122335E+08 0.12E+08 0.40E+12 0.33E+05  
11CN. -0.722E+05 0.458E+01 0.402270E+07 0.40E+07 0.55E+12 0.14E+06  
12CN. -0.724E+05 0.446E+01 0.159054E+07 0.16E+07 0.71E+12 0.44E+06

13CN. -0.727E+05 0.442E+01 0.724704E+06 0.73E+06 0.87E+12 0.12E+07

FCALCUTTUW # 40 H+G2H3C1=C2H3+HCL

DELTA N = 0 DELTA HGT = 950. K) = -1.919E+04 CAL/MOLE DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.339E+01 DELTA H = -0.195E+05

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.192E+05 0.355E+01 0.907619E+06 0.91E+06 0.15E+13 0.17E+07  
11CN. -0.194E+05 0.344E+01 0.342744E+06 0.34E+06 0.22E+13 0.66E+07  
12CN. -0.196E+05 0.333E+01 0.151892E+06 0.15E+06 0.31E+13 0.20E+08

13CN. -0.198E+05 0.323E+01 0.760408E+05 0.76E+05 0.41E+13 0.53E+08

FCALCUTTUW # 50 H+G2H3C1=C2H3+HCL

DELTA N = 0 DELTA HGT = 950. K) = -1.359E+04 CAL/MOLE DELTA S (T = 950. K) = 8.113E+00 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.388E+01 DELTA H = -0.140E+05

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.134E+05 0.408E+01 0.796124E+05 0.80E+05 0.32E+12 0.40E+07  
11CN. -0.139E+05 0.398E+01 0.398039E+05 0.44E+05 0.44E+12 0.11E+08  
12CN. -0.142E+05 0.380E+01 0.221787E+05 0.22E+05 0.58E+12 0.26E+08

13CN. -0.145E+05 0.367E+01 0.134290E+05 0.14E+05 0.73E+12 0.54E+08

FCALCUTTUW # 60 H+G2H3C1=C2H3+HCL

DELTA N = 0 DELTA HGT = 950. K) = -9.174E+04 CAL/MOLE DELTA S (T = 950. K) = -4.092E+01 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.812E+01 DELTA H = -0.895E+05

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.899E+05 0.114637E+18 0.11E+18 0.11E+18 0.21E+13 0.18E-04

FCALCUTTUW # 70 H+G2H3C1=C2H3+HCL

DELTA N = 0 DELTA HGT = 950. K) = -9.174E+04 CAL/MOLE DELTA S (T = 950. K) = -4.092E+01 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.812E+01 DELTA H = -0.895E+05

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.899E+05 0.114637E+18 0.11E+18 0.11E+18 0.21E+13 0.18E-04

FCALCUTTUW # 80 H+G2H3C1=C2H3+HCL

DELTA N = 0 DELTA HGT = 950. K) = -9.174E+04 CAL/MOLE DELTA S (T = 950. K) = -4.092E+01 CAL/DEG/MOLE  
TRVW- DELTA N = 0 DELTA S/R = 0.812E+01 DELTA H = -0.895E+05

FF-PRFV LN AF/AREV KEQ FIT K FORWARD K REVERSE  
INCN. -0.899E+05 0.114637E+18 0.11E+18 0.11E+18 0.21E+13 0.18E-04

----- # 10  
DELTA N = 0  
DELTA S (T = 950. K) = 6.254E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -1.359E+04 CAL/MOLE  
DELTA N = 0.388E+01  
DELTA H = -0.140E+05  
DELTA S (T = 950. K) = 8.113E+00 CAL/DEG/MOLE  
DELTA H = -0.895E+05  
DELTA S (T = 950. K) = -4.092E+01 CAL/DEG/MOLE

----- # 9  
DELTA N = 0  
DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -3.174E+04 CAL/MOLE  
DELTA N = 0.308E+01  
DELTA H = -0.645E+04  
DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
DELTA H = -0.222E+05  
DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE

----- # 8  
DELTA N = 0  
DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -3.174E+04 CAL/MOLE  
DELTA N = 0.290E+01  
DELTA H = -0.656E+04  
DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
DELTA H = -0.222E+05  
DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE

----- # 7  
DELTA N = 0  
DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -3.174E+04 CAL/MOLE  
DELTA N = 0.283E+01  
DELTA H = -0.656E+04  
DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
DELTA H = -0.222E+05  
DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE

----- # 6  
DELTA N = 0  
DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -3.174E+04 CAL/MOLE  
DELTA N = 0.275E+01  
DELTA H = -0.656E+04  
DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
DELTA H = -0.222E+05  
DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE

----- # 5  
DELTA N = 0  
DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -3.174E+04 CAL/MOLE  
DELTA N = 0.267E+01  
DELTA H = -0.656E+04  
DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
DELTA H = -0.222E+05  
DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE

----- # 4  
DELTA N = 0  
DELTA S (T = 950. K) = 6.018E+00 CAL/DEG/MOLE  
DELTA H (T = 950. K) = -3.174E+04 CAL/MOLE  
DELTA N = 0.259E+01  
DELTA H = -0.656E+04  
DELTA S (T = 950. K) = 9.340E+00 CAL/DEG/MOLE  
DELTA H = -0.222E+05  
DELTA S (T = 950. K) = 7.049E+00 CAL/DEG/MOLE



----- # 25  
FCAL2=FCAL3+CL  
FCAL M = N NPITA HGT = 950. K) = -1.340E+04 CAL/MOLE DELTA S (T = 950. K) = -7.429E+00 CAL/DEG/MOLE  
----- VALUES TN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)  
----- TN 1250. DELTA S/R - DELTA N = -0.353E+01 DELTA H = -0.132E+05  
T FF-FRFV LN AF/AREV KEQ K EQ FIT K FORWARD K REVERSE  
OCN. -0.174E+05 -0.374E+01 0.287671E+02 0.29E+02 0.65E+12 0.23E+11  
10CN. -0.173E+05 -0.368E+01 0.146735E+02 0.15E+02 0.83E+12 0.56E+11  
11CN. -0.171E+05 -0.362E+01 0.845812E+01 0.85E+01 0.10E+13 0.12E+12  
12CN. -0.170E+05 -0.356E+01 0.534907E+01 0.53E+01 0.12E+13 0.22E+12

----- # 26  
FCAL2=FCAL3+CL  
FCAL M = N NPITA HGT = 950. K) = -7.453E+04 CAL/MOLE DELTA S (T = 950. K) = -6.986E+00 CAL/DEG/MOLE  
----- VALUES TN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)  
----- TN 1250. DELTA S/R - DELTA N = -0.353E+01 DELTA H = -0.746E+05  
T FF-FRFV LN AF/AREV KEQ K EQ FIT K FORWARD K REVERSE  
OCN. -0.745E+05 -0.352E+01 0.422932E+16 0.42E+16 0.39E+13 0.40E-03  
10CN. -0.745E+05 -0.353E+01 0.982661E+14 0.98E+14 0.39E+13 0.40E-01  
11CN. -0.744E+05 -0.354E+01 0.438789E+13 0.44E+13 0.39E+13 0.90E+00  
12CN. -0.744E+05 -0.356E+01 0.321809E+12 0.32E+12 0.39E+13 0.12E+02

----- # 27  
FCAL2=FCAL3+CL  
FCAL M = N NPITA HGT = 950. K) = -8.545E+04 CAL/MOLE DELTA S (T = 950. K) = -4.684E+01 CAL/DEG/MOLE  
----- VALUES TN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)  
----- TN 1250. DELTA S/R - DELTA N = -0.111E+02 DELTA H = -0.841E+05  
T FF-FRFV LN AF/AREV KEQ K EQ FIT K FORWARD K REVERSE  
OCN. -0.844E+05 -0.113E+02 0.352171E+15 0.35E+15 0.19E+12 0.55E-03  
10CN. -0.842E+05 -0.111E+02 0.497766E+13 0.50E+13 0.14E+12 0.28E-01  
11CN. -0.839E+05 -0.110E+02 0.149713E+12 0.15E+12 0.10E+12 0.69E+00  
12CN. -0.834E+05 -0.109E+02 0.797430E+10 0.79E+10 0.81E+11 0.10E+02

----- # 28  
FCAL2=FCAL3+CL  
FCAL M = N NPITA HGT = 950. K) = -7.434E+04 CAL/MOLE DELTA S (T = 950. K) = -1.160E+01 CAL/DEG/MOLE  
----- VALUES TN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)  
----- TN 1250. DELTA S/R - DELTA N = -0.591E+01 DELTA H = -0.745E+05  
T FF-FRFV LN AF/AREV KEQ K EQ FIT K FORWARD K REVERSE  
OCN. -0.743E+05 -0.584E+01 0.375601E+15 0.38E+15 0.48E+12 0.13E-02  
10CN. -0.744E+05 -0.584E+01 0.979874E+13 0.88E+13 0.47E+12 0.54E-01  
11CN. -0.744E+05 -0.594E+01 0.394227E+12 0.39E+12 0.47E+12 0.12E+01  
12CN. -0.747E+05 -0.601E+01 0.208749E+11 0.29E+11 0.46E+12 0.16E+02

----- # 29  
FCAL2=FCAL3+CL  
FCAL M = N NPITA HGT = 950. K) = -1.183E+04 CAL/MOLE DELTA S (T = 950. K) = -1.070E+01 CAL/DEG/MOLE  
----- VALUES TN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)  
----- TN 1250. DELTA S/R - DELTA N = -0.532E+01 DELTA H = -0.117E+05  
T FF-FRFV LN AF/AREV KEQ K EQ FIT K FORWARD K REVERSE  
OCN. -0.118E+05 -0.539E+01 0.241481E+01 0.24E+01 0.14E+12 0.60E+11  
10CN. -0.117E+05 -0.533E+01 0.133277E+01 0.13E+01 0.18E+12 0.14E+12  
11CN. -0.114E+05 -0.530E+01 0.818919E+00 0.82E+00 0.22E+12 0.27E+12  
12CN. -0.114E+05 -0.527E+01 0.545190E+00 0.54E+00 0.26E+12 0.48E+12

----- # 30  
FCAL2=FCAL3+CL  
FCAL M = N NPITA HGT = 950. K) = -9.105E+04 CAL/MOLE DELTA S (T = 950. K) = -4.384E+01 CAL/DEG/MOLE  
----- VALUES TN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)  
----- TN 1250. DELTA S/R - DELTA N = -0.958E+01 DELTA H = -0.887E+05  
T FF-FRFV LN AF/AREV KEQ K EQ FIT K FORWARD K REVERSE  
OCN. -0.958E+05 -0.980E+01 0.182611E+17 0.18E+17 0.31E+12 0.17E-04



DELTA HGT = 950. K) = -9.955E+03 CAL/MOLE  
DELTA S (T = 950. K) = 9.312E-02 CAL/DEG/MOLE  
DELTA H = -0.903E+04  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = 5.603E+03 CAL/MOLE  
DELTA S (T = 950. K) = 1.064E+00 CAL/DEG/MOLE  
DELTA H = 0.551E+04  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -1.736E+03 CAL/MOLE  
DELTA S (T = 950. K) = 8.645E-02 CAL/DEG/MOLE  
DELTA H = -0.171E+04  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -9.251E+04 CAL/MOLE  
DELTA S (T = 950. K) = -4.033E+01 CAL/DEG/MOLE  
DELTA H = -0.902E+05  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.803E+01  
DELTA S (T = 950. K) = 0.23E+18  
DELTA H = 0.23E+18  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.901E+05  
DELTA S (T = 950. K) = 0.36E+13  
DELTA H = 0.36E+13  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.758E+05  
DELTA S (T = 950. K) = 0.51E+14  
DELTA H = 0.51E+14  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.754E+05  
DELTA S (T = 950. K) = 0.12E+14  
DELTA H = 0.12E+14  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.459E+01  
DELTA S (T = 950. K) = 0.22E+13  
DELTA H = 0.22E+13  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.459E+01  
DELTA S (T = 950. K) = 0.157E+12  
DELTA H = 0.157E+12  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.184E+03 CAL/MOLE  
DELTA S (T = 950. K) = -8.076E+00 CAL/DEG/MOLE  
DELTA H = -0.804E+04  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.399E+01  
DELTA S (T = 950. K) = 0.131E+12  
DELTA H = 0.131E+12  
KEQ FIT  
K FORWARD  
K REVERSE

DELTA HGT = 950. K) = -0.406E+01  
DELTA S (T = 950. K) = 0.93E+12  
DELTA H = 0.93E+12  
KEQ FIT  
K FORWARD  
K REVERSE



0.422E+04 0.120E+00 0.111500E+00 0.11E+00 0.33E+10 0.29E+11  
0.42E+04 0.136E+00 0.136558E+00 0.14E+00 0.53E+10 0.39E+11  
0.42E+04 0.141E+00 0.161917E+00 0.16E+00 0.80E+10 0.50E+11

DELTA HGT = 950. K) = 1.059E+02 CAL/MOLE DELTA S (T = 950. K) = 1.352E+00 CAL/DEG/MOLE  
DELTA H = 0.517E+00 KEQ FIT  
LN AF/AREV LN AF/AREV KEQ KEQ FIT K FORWARD K REVERSE  
0.680E+00 0.186736E+01 0.19E+01 0.38E+10 0.20E+10  
-0.11E+03 0.571E+00 0.186789E+01 0.19E+01 0.63E+10 0.34E+10  
-0.37E+03 0.449E+00 0.184951E+01 0.18E+01 0.96E+10 0.52E+10  
-0.60E+03 0.318E+00 0.181556E+01 0.18E+01 0.14E+11 0.75E+10

DELTA HGT = 950. K) = 3.796E+04 CAL/MOLE DELTA S (T = 950. K) = 2.492E+01 CAL/DEG/MOLE  
DELTA H = 0.359E+05 KEQ FIT  
LN AF/AREV LN AF/AREV KEQ KEQ FIT K FORWARD K REVERSE  
0.279E+00 0.696148E-08 0.70E-08 0.16E+05 0.22E+13  
0.263E+05 0.421598E-07 0.43E-07 0.12E+06 0.29E+13  
0.35E+05 0.191208E-06 0.19E-06 0.67E+06 0.35E+13  
0.35E+05 0.5711293E-06 0.67E-06 0.28E+07 0.42E+13

DELTA HGT = 950. K) = 1.211E+04 CAL/MOLE DELTA S (T = 950. K) = 3.525E+01 CAL/DEG/MOLE  
DELTA H = 0.517E+01 KEQ FIT  
LN AF/AREV LN AF/AREV KEQ KEQ FIT K FORWARD K REVERSE  
0.54E+05 0.106653E+01 0.11E+01 0.13E+02 0.12E+02  
0.07E+04 0.525E+01 0.176765E+01 0.17E+01 0.22E+03 0.12E+03  
0.03E+04 0.50E+01 0.263322E+01 0.26E+01 0.23E+04 0.86E+03  
0.08E+04 0.48E+01 0.362099E+01 0.37E+01 0.16E+05 0.45E+04

DELTA HGT = 950. K) = 1.721E+04 CAL/MOLE DELTA S (T = 950. K) = 3.394E+01 CAL/DEG/MOLE  
DELTA H = 0.459E+01 KEQ FIT  
LN AF/AREV LN AF/AREV KEQ KEQ FIT K FORWARD K REVERSE  
0.48E+01 0.368931E-01 0.37E-01 0.90E+01 0.24E+03  
0.15E+05 0.44E+01 0.793572E-01 0.19E-01 0.18E+04 0.18E+04  
0.14E+05 0.44E+01 0.147312E+00 0.15E+00 0.13E+04 0.92E+04  
0.14E+05 0.44E+01 0.244430E+00 0.25E+00 0.90E+04 0.37E+05

DELTA HGT = 950. K) = 7.835E+04 CAL/MOLE DELTA S (T = 950. K) = 3.350E+01 CAL/DEG/MOLE  
DELTA H = 0.762E+05 KEQ FIT  
LN AF/AREV LN AF/AREV KEQ KEQ FIT K FORWARD K REVERSE  
0.45E+01 0.250941E-15 0.25E-15 0.92E-02 0.37E+14  
0.74E+05 0.44E+01 0.118500E-13 0.12E-13 0.46E+00 0.39E+14  
0.74E+05 0.44E+01 0.283960E-12 0.28E-12 0.12E+02 0.41E+14  
0.74E+05 0.44E+01 0.4404239E-11 0.44E-11 0.17E+03 0.43E+14

DELTA HGT = 950. K) = 1.709E+04 CAL/MOLE DELTA S (T = 950. K) = 3.121E+01 CAL/DEG/MOLE  
DELTA H = 0.147E+05 KEQ FIT  
LN AF/AREV LN AF/AREV KEQ KEQ FIT K FORWARD K REVERSE  
0.15E+05 0.346E+01 0.996287E-02 0.10E-01 0.14E+02 0.14E+04

DATA N = 1 DELTA HGT = 950. KJ = 1.175E+04 CAL/MOLE DELTA S (T = 950. K) = 3.218E+01 CAL/DEG/MOLE  
FF-FRFRV LN AF/AREV KEQ DELTA H = 0.114E+05 K FORWARD K REVERSE  
0.110E+05 0.393E+01 0.951414E-01 0.96E-01 0.18E+04 0.19E+05 0.10E+06  
0.11E+05 0.375E+01 0.171665E+00 0.17E+00 0.17E+05 0.11E+06 0.40E+06  
0.11E+05 0.358E+01 0.275262E+00 0.27E+00 0.11E+06 0.11E+06 0.40E+06  
0.107E+05 0.341E+01 0.403802E+00 0.41E+00 0.54E+06 0.13E+07 0.13E+07

DATA N = 1 DELTA HGT = 950. KJ = 7.635E+04 CAL/MOLE DELTA S (T = 950. K) = 3.311E+01 CAL/DEG/MOLE  
FF-FRFRV LN AF/AREV KEQ DELTA H = 0.749E+05 K FORWARD K REVERSE  
0.440E+01 0.433551E-15 0.44E-15 0.35E+00 0.80E+15  
0.429E+01 0.190638E-13 0.19E-13 0.14E+02 0.73E+15  
0.766E+05 0.420E+01 0.4302291E-12 0.43E-12 0.29E+03 0.68E+15  
0.746E+05 0.410E+01 0.585335E-11 0.59E-11 0.38E+04 0.65E+15

DATA N = 1 DELTA HGT = 950. KJ = 2.472E+04 CAL/MOLE DELTA S (T = 950. K) = 3.188E+01 CAL/DEG/MOLE  
FF-FRFRV LN AF/AREV KEQ DELTA H = 0.225E+05 K FORWARD K REVERSE  
0.378E+05 0.244759E-03 0.25E-03 0.54E-02 0.22E+02  
0.22E+05 0.366E+01 0.770544E-03 0.77E-03 0.17E+00 0.22E+03  
0.22E+05 0.354E+01 0.196605E-02 0.20E-02 0.30E+01 0.15E+04  
0.22E+05 0.342E+01 0.427738E-02 0.43E-02 0.34E+02 0.79E+04

DATA N = 1 DELTA HGT = 950. KJ = 9.151E+04 CAL/MOLE DELTA S (T = 950. K) = 3.408E+01 CAL/DEG/MOLE  
FF-FRFRV LN AF/AREV KEQ DELTA H = 0.893E+05 K FORWARD K REVERSE  
0.894E+05 0.489E+01 0.315292E-18 0.32E-18 0.26E-04 0.81E+14  
0.894E+05 0.477E+01 0.288321E-16 0.29E-16 0.21E-02 0.74E+14  
0.891E+05 0.446E+01 0.119501E-14 0.12E-14 0.82E-01 0.69E+14  
0.888E+05 0.456E+01 0.270123E-13 0.27E-13 0.18E+01 0.65E+14

DATA N = 1 DELTA HGT = 950. KJ = 9.030E+04 CAL/MOLE DELTA S (T = 950. K) = 3.626E+01 CAL/DEG/MOLE  
FF-FRFRV LN AF/AREV KEQ DELTA H = 0.885E+05 K FORWARD K REVERSE  
0.884E+05 0.59E+01 0.178735E-17 0.18E-17 0.32E-04 0.18E+14  
0.884E+05 0.6151E+01 0.155157E-15 0.16E-15 0.29E-02 0.18E+14  
0.885E+05 0.605E+01 0.621369E-14 0.62E-14 0.12E+00 0.19E+14  
0.882E+05 0.609E+01 0.138338E-12 0.14E-12 0.27E+01 0.19E+14

DATA N = 1 DELTA HGT = 950. KJ = 2.467E+04 CAL/MOLE DELTA S (T = 950. K) = 3.505E+01 CAL/DEG/MOLE  
FF-FRFRV LN AF/AREV KEQ DELTA H = 0.224E+05 K FORWARD K REVERSE  
0.779E+05 0.59E+01 0.178735E-17 0.18E-17 0.32E-04 0.18E+14  
0.779E+05 0.6151E+01 0.155157E-15 0.16E-15 0.29E-02 0.18E+14  
0.779E+05 0.605E+01 0.621369E-14 0.62E-14 0.12E+00 0.19E+14  
0.779E+05 0.609E+01 0.138338E-12 0.14E-12 0.27E+01 0.19E+14

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DATA N = 1 DELTA HGT = 950. KJ = 0.517E+01 DELTA H = 0.13E-02 K FORWARD K REVERSE  
0.517E+01 0.538E+01 0.124698E-02 0.13E-02 0.99E-02 0.72E+01

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE

DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE  
DELTA H = -0.273E+04  
DELTA S (T = 950. K) = 3.622E+01 CAL/DEG/MOLE





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