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ABSTRACT

Thermal Decomposition of Dichloromethane in Absence and Presence of Added O₂ and/or CH₄

by
Hong-Ming Chiang

Thermal decomposition experiments on dichloromethane in absence and presence of added O₂ and/or CH₄ and in argon bath gas were conducted in a tubular flow reactor. The thermal reactions were studied at 1 atmosphere pressure with residence times of 0.3 - 2.0 seconds in the temperature range from 680 to 840 °C.

The degradation of dichloromethane and the decomposition product distributions were studied in both oxidative and pyrolytic reaction environments. The slowest decay of dichloromethane occurred when CH₄ was present and O₂ was absent. The concentration of all products, (except HCl, CO, and CO₂ in the oxidation), are below 10% in the reaction environments. The chlorinated products, such as C₂HCl₃, CH₃Cl, CHClCHCl, are shown to be more stable in the pyrolysis than in the oxidation. When oxygen is present, the concentration of chlorinated products decreases more rapidly above 780 °C than when no oxygen is present. Carbon mass balance in the CH₂Cl₂/Ar reaction environment was less than 60% at temperatures above 780 °C, and less than 20% at temperatures above 820 °C. This implies that the formation of high molecular species and soot are occur at higher temperatures in the absence of oxygen.

The overall (global) rate constants of CH_2Cl_2 decay in this study were found as:

- I. $\text{CH}_2\text{Cl}_2 : \text{CH}_4 : \text{O}_2 : \text{Ar} = 1 : 1 : 4 : 94$
 $k = 6.74 \times 10^{15} \times \text{EXP}(-75.84/\text{RT}) \quad (1/\text{sec})$
- II. $\text{CH}_2\text{Cl}_2 : \text{O}_2 : \text{Ar} = 1 : 4 : 95$
 $k = 1.56 \times 10^{24} \times \text{EXP}(-114.68/\text{RT}) \quad (1/\text{sec})$
- III. $\text{CH}_2\text{Cl}_2 : \text{CH}_4 : \text{Ar} = 1 : 1 : 98$
 $k = 6.46 \times 10^{13} \times \text{EXP}(-67.85/\text{RT}) \quad (1/\text{sec})$
- IV. $\text{CH}_2\text{Cl}_2 : \text{Ar} = 1 : 99$
 $k = 1.21 \times 10^{18} \times \text{EXP}(-86.92/\text{RT}) \quad (1/\text{sec})$

A detailed kinetic reaction mechanism consisting of 94 species and 382 elementary reactions based on thermochemical principles and Transition State Theory, was modified and used to model results obtained from the experimental system. The results of model prediction for dichloromethane decay were slower than experimental results. Major products (CH_3Cl and C_2HCl_3) distribution below 780 °C match the experimental results well.

**THERMAL DECOMPOSITION OF DICHLOROMETHANE IN
ABSENCE AND PRESENCE OF ADDED OXYGEN AND/OR METHANE**

**By
HONG-MING CHIANG**

**A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science
Department of Chemical Engineering, Chemistry,
and Environmental Science
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APPROVAL PAGE

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CHAPTER 1 INTRODUCTION

Controlled high-temperature incineration, in spite of the associated high costs, is an attractive organic waste reduction methodology because it represents a complete treatment and a permanent disposal method for essentially all combustible waste^{<1>}. Incineration, which is an engineered process that uses thermal decomposition via oxidation/pyrolysis to convert a waste to less bulk, nontoxic species CO₂, H₂O, HCl and ash, has developed over a number of years as a means of disposing of various types of wastes. Recently, the application of incineration to hazardous waste, such as chlorinated organic species, has been given much attention due to the consistent observation of known or suspected toxic / carcinogenic chlorocarbons or chloro-oxy carbon species in the effluent from waste and resource recovery incinerators^{<2>}. A responsible goal is therefore to try and understand these incineration processes on a fundamental basis for achieving optimal destruction and minimum pollutant effluent^{<3, 4>}.

The combustion of chlorocarbons is generally performed in an oxygen rich environment that contains excess O₂ and N₂, in addition to carbon and Cl from the halocarbons, with relatively small amounts of available hydrogen from the limiting fuel operation^{<5>}.

The destruction of organic compounds in high tempera-

ture environments involves the combination of pyrolytic and oxidative processes. The mechanisms in both cases are generally free radical in nature^{<6>}. The pyrolysis process is initially one of continuous degradation to smaller and more unsaturated species. At some stages in the decomposition process, the levels of unsaturated molecules begin to combine, leading ultimately to molecular weight growth soot or heavy carbonized compounds. Under oxidation, the breakdown process is enhanced. Carbon-containing radicals rapidly react or combine with oxygen, and the many higher molecular weight unsaturated structures have little chance to form. The oxidation process is highly exothermic in nature, along with chain induced decomposition, there is significant increase in temperature, more radicals are created and the reaction is driven to completion^{<7>}.

Chlorinated compounds are well recognized because of their chemical inhibition characteristics in hydrocarbon combustion process in normal air. They are often reported to require the use of either oxygen-enriched air or an auxiliary fuel. In this study, we use methane as an auxiliary fuel in order to try to establish stable burning. The advantages of using methane are: (a) it is widely available and relatively inexpensive, (b) it has a sufficiently high heat of combustion, and (c) it has a high hydrogen content. An auxiliary fuel (hydrocarbon) is often required to produce desired and thermodynamically favorable products such as HCl from a chlorocarbon conversion proc-

ess^{<8>}. Methane, because of its high hydrogen content, insures the formation of HCl as the primary chlorinated combustion product instead of Cl₂. The formation of HCl is more desirable because it is relatively easier to remove from combustion effluent gases by simple aqueous scrubbing^{<9>}.

In our study, the basic objectives are to :

- . Characterize the reagent decay and product formation as functions of both temperature and residence time.
- . Determine the initiation rate constant of CH₂Cl₂ decomposition.
- . Develop a detailed reaction mechanism based on fundamental thermodynamic and kinetic principles to describe the reaction.
- . Determine the important reaction pathways using sensitivity analysis.
- . Improve and/or optimize oxidation/pyrolysis of chlorocarbons using the model as a predictive tool.

A comprehensive data base of kinetics and reactant and product concentration profiles available in the Kinetics Research Group at NJIT (Research Group of Professor Bozzelli) will be used to construct and calibrate a detailed reaction model for the separate chlorocarbon pyrolysis and oxidation reaction systems. The model will then be used for optimization of kinetic parameters effecting reductions of unwanted chlorocarbon species. The model

predictions will be verified in both lab scale experiments at NJIT, as well in pilot and full scale incinerators. The thermodynamic parameters, rate constants and computer codes to run the models are already available. This work is not model development, but model validation and use of validated models for optimization.

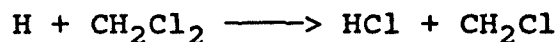
CHAPTER 2 PREVIOUS STUDIES

The investigations of the thermal decomposition of chlorinated hydrocarbons has received significant attention for the past several decades. This study focuses on CH_2Cl_2 , and we are specifically interested in CH_2Cl_2 and CH_3Cl oxidative and pyrolytic reaction studies. Benson and Weissman^{<10>} studied high temperature (1200-1300 K) reaction of methyl chloride and methane and that CH_3Cl . They reported C_2 hydrocarbons as the major products of their experiment, and that CH_3Cl was a sort of catalyst for C_2 formation from CH_4 .

Karra et.al.^{<11>} made a comparative study of the chemical structure of sooting of $\text{CH}_3\text{Cl}/\text{CH}_4/\text{O}_2/\text{Ar}$ and $\text{CH}_4/\text{O}_2/\text{Ar}$ flames at atmospheric pressure. In the presence of chlorine, ample amounts of C_2H_2 and C_2H_4 were formed rapidly in comparison to a no chlorine reaction system. They concluded that the oxidative pyrolysis of CH_3Cl , (1-2% O_2) which presents the second stage in chlorine-catalyzed oxidative pyrolysis of CH_4 , was shown to result in the formation of decreased levels of carbonaceous deposits, while allowing the formation of C_2H_2 and C_2H_4 with combined yields as high as 60% at about 30% conversion of CH_2Cl . The chlorine-catalyzed oxidative pyrolysis process proceeds in a controllable manner, without the formation of flames because of the well-known flame inhibition

characteristics of chlorine and chlorinated compounds.

Reaction of H atoms with CH_2Cl_2 were studied by Combourieu et.al.^{<12>}. Initial concentration ratios of $[\text{H}]/[\text{CH}_2\text{Cl}_2]$, 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_2 , CH_4 , C_2H_2 , and C_2H_4 . They concluded by reporting the rate constant of the initial step:



as $k = 1.8 * 10\text{E}-11 * \exp(-6100/\text{RT})$ (1/sec)

Several investigations on the thermal decomposition of dichloromethane have been conducted in this laboratory. Javad^{<13>} investigated the reaction of $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{Ar}$ and $\text{CH}_2\text{Cl}_2/\text{C}_2\text{HCl}_3/\text{CH}_4/\text{Ar}$ at atmospheric pressure and over a temperature range of 1023-1273 K in a tubular flow reactor. Acetylene, ethylene, benzene, chloromethane, and HCl were observed as the major products, for temperatures above 1023 K and residence times of 0.08 to 2.0 seconds. They reported experimental data on the pyrolysis and a detailed mechanism.

Huang^{<14>} studied the kinetics of the reaction of atomic hydrogen with dichloromethane in a flow system at pressures of 2.1 to 2.7 torr and room temperature. The

major products observed were HCl and methane. The extent of conversion of dichloromethane increases first to a maximum and then decreases with increasing concentration of dichloromethane. A mechanism was developed to explain the data.

Tsao^{<15>} examined the thermal reaction of dichloromethane with hydrogen over the temperature range of 973-1173 K, in a 1 atm pressure tubular flow reactor. The major products in this reaction system were methane and methyl chloride. The minor products were ethylene, acetylene and HCl. Trace amounts of ethane, chloroethylene, 1,2-dichloroethylene, trichloroethylene, and benzene were also observed. No chlorocarbons were found over 1223 K at 1.0 second residence time where the only products were methane, HCl, acetylene, ethane and benzene.

Won^{<16>} investigated the thermal reaction of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CCl}_3$ mixtures in a hydrogen bath gas over the temperature range 748-1083 K at 1 atm pressure in a flow reactor. Won demonstrated that selective formation of HCl can result from thermal reaction of chlorocarbon mixture and showed that effects of 1,1,1-trichloroethane decomposition accelerate the rate of dichloromethane decomposition. There is significant interaction of decay products from 1,1,1-trichloroethane with parent dichloromethane.

Ho^{<17>} studied the thermal decomposition of dichloromethane in H_2/O_2 mixtures and argon bath gas. The reaction was carried out at 1 atmosphere total pressure over tem-

perature range 883-1093 K with average residence times from 0.1 to 2.0 second in tubular flow reactor. The major products observed were methyl chloride, methane, CO, and HCl. Oxygen had almost no effect on the decay of dichloromethane when conversion was below 50% and/or the initial oxygen concentration is below 5%. When conversion is above 90%, the major products are HCl and non-chlorinated hydrocarbons: CH₄, C₂H₂, C₂H₄, CO, and CO₂. The higher the ratio of O₂ to H₂, the lower the temperature needed to observe the formation of CO and CO₂.

Several investigations on using methane as a fuel source. Benson and Weissman^{<34>} studied the effect of methyl chloride on pyrolysis of methane in search of upgrading (conversion to C₂ hydrocarbons) methane. Major products at temperatures of 1260-1310 K were reported to be ethylene and acetylene. With CH₄ added C₂H₄, C₂H₂ and C₂H₆ are produced and appeared to approach stationary concentrations in the system. Different routes are suggested for production of ethylene and acetylene in the presence and/or absence of CH₄.

Won^{<8>} examined the thermal decomposition of chloroform in absence and presence of added O₂ and/or CH₄. The reactions were studied in tubular flow reactor at a total pressure of 1 atm with residence times of 0.3-2.0 second in the temperature range 808-1073 K. Chloroform decay and product distribution were distinctly different in the

absence and presence of added O_2 and/or CH_4 . Increases in O_2 were observed to speed reagent loss. Won demonstrated that almost all major chlorinated products (C_2Cl_4 , CH_2CCl_2 , and C_2HCl_3) were C_2 compound.

CHAPTER 3 RESEARCH BACKGROUND

3.1 Reaction Mechanism of Chlorinated Hydrocarbons (CHCs) in Combustion Process

Relatively little fundamental research has been conducted on the high-temperature oxidation kinetics of chlorinated hydrocarbons. Most of the previous studies I written were pyrolysis only. This is not surprising since chlorinated hydrocarbons are not desirable as an energy source because of the corrosive and toxic nature of their combustion end-products, e.g., Cl_2 , HCl .

In the incineration process, almost all organic molecules will decompose into smaller molecules and atoms, CO_2 , H_2O and HCl hopefully. When oxygen is added, this process is expedited by the thermodynamic stability of the end-products, H_2O and CO_2 . The most thorough way to fully describe such a process is in terms of elementary reactions. It is important to distinguish this approach from the more empirical or global approach of simply describing the system in terms of the directly observed input and output. This traditional and essentially empirical approach is, in spirit, that which is used in most of the present day studies on incineration. For the optimization of a large scale reactor, this may still be the most cost efficient method; but times are rapidly changing. The emissions of toxic organic products depend however on

complex reaction mechanisms. The current data base on products formation is very limited, and such data is not transferable, therefore the conditions where total destruction are achieved in a particular incinerator may not have the same consequences in other situations^{<18>}.

There are two types of reactions, unimolecular and bimolecular processes, which will lead to destruction of organic compounds in the gas phase. The former can be considered to be more dependent on temperature than the bimolecular process. The physical situation is that of a molecule receiving energy from the heat bath until some reaction threshold is surpassed and decomposition occurs. Bimolecular destruction mechanisms usually involve a radical attacking the molecule of interest. This can lead to the direct abstraction of an atom or addition to a site of unsaturation. In both cases the consequences are the formation of a radical which can rapidly decompose in the incineration environment. Although a large number of radicals are formed during the degradation of most organic compounds, it is known that a few radicals, principally OH, O, H and Cl, contribute significantly to the destruction mechanism. Many of the organic radicals that are formed rapidly decompose under the high temperature conditions of an incinerator. They have, therefore, little or no time to attack other species. In addition, most of the larger organic radicals are not particularly reactive (compared to OH, O, H and Cl) except for reaction with

urated sites. Therefore the presence of large quantities of chlorinated waste opens up other bimolecular decomposition pathways. Chlorine in incineration systems is rapidly converted to hydrogen chloride. This ties up a great number of the hydrogen atoms. It also produces significant quantities of HCl which can now interact with free radicals in the system. The OH radical and H atoms react rapidly with HCl. The concentration of these two species are thus reduced. The overall chemistry rapidly becomes that found when chlorinated fire suppressants are added to a combustion system. The weakness of the Cl-Cl bond means that there is a very high barrier to the direct chlorine abstraction of chlorine ($\text{Cl} + \text{RCl} \rightarrow \text{R} + \text{Cl}_2$)^{<18>}. Thus fully chlorinated compounds in highly chlorinated systems have an extra degree of stability in so far as bimolecular decompositions are concerned.

3.2 Methods for The Estimation of Thermochemical Data

Thermochemical data are required to determine the energy balance in chemical reactions and in determining the Gibbs Free Energy of a reaction as a function of temperature. The data also provide a convenient way to determine reverse reaction rate constants from the calculated equilibrium constant of the reaction and the known forward rate.^{<21>}

other radicals. They are thus rapidly removed from the system^{<19>}.

Under incineration conditions, organic molecules will decompose via pyrolytic and oxidative processes. Free radicals are important intermediates. For pyrolysis, the process involves degradation to smaller and more unsaturated species. At some stage in the decomposition process the unsaturated molecules begin to condense, leading ultimately to highly carbonized structures or soot. Under oxidation, the breakdown process is enhanced. Carbon atoms are bonded to oxygen, and many of the unsaturated structures have little or no chance to form^{<20>}. Furthermore, the oxidation process is highly exothermic, therefore, along with the chain induced decomposition, there are sharp increases in temperatures. More radicals are created and the reaction is driven to completion. During any stage of these processes if the reaction is stopped, through quenching at the cold walls or mixing with cold gases or if the temperature of a given plug of gas is never hot enough to drive the reaction to completion, then the remaining organic compounds are the products of incomplete combustion.^{<8>}

Hazardous waste incineration involving chlorine compounds merits special attention. As a result of thermochemical consideration, chlorine atoms are extremely reactive. They rapidly abstract hydrogen and add to unsat-

The thermodynamic data base, entropy (S), enthalpy of formation (Hf) and heat capacity Cp, is based upon the best currently available thermochemical data. When experimentally based thermochemical data were not available, the values were estimated using the THERM computer code^{<22>}, which is based on the group additivity techniques^{<23>}.

3.2.1 Benson Group Additivity Method

The group-additivity method is applicable for Cp, Hf₂₉₈, S₂₉₈. A group is defined as a polyvalent atom (ligancy ≥ 2), in a molecule together with all of its ligands. Molecules such as HOH, CH₃Cl, and CH₄ that contain only one such atoms (i.e., one group), are irreducible entities and do not need to be treated by group additivity. For each group, the key atom is given then followed by notation specifying other atoms bonded to the key atom.

Example: Estimate of CH₃CH₂OH by group additivity method

Gr #	- Group ID	- Quantity
1	C/C/H ₃	- 1
2	C/C/H ₂ /O	- 1
3	O/C/H	- 1

Other information includes:

No. of Rotors = 2 No. of Symmetry = 3

For radicals, an average Cp can be calculated from values for adjacent saturated and olefinic hydrocarbons to obtain a value for the intermediate radical, for example :

$$C_p(\text{CCC}\cdot) = 1/2 [C_p(\text{CCC}) + C_p(\text{C}=\text{CC})]$$

In calculating entropies by using the group additivity method, correction factors are considered for: symmetry number, optical isomers, degenerate spin of the electron etc. For example:

$$S_p = S_{\text{(int.)}} - R \ln \sigma_p + R \ln \text{OI}$$

$$S_r = S_p + R \ln \sigma_p - R \ln \sigma_r + R \ln 2 - 0.1 - 2.6$$

S_p : Parent molecule entropy

$S_{\text{int.}}$: Intrinsic parent molecule entropy

σ_p : Number of parent molecule symmetry

σ_r : Number of radical symmetry

R : Gas constant

S_r : Radical entropy

OI : Optical Isomer

. Add $R \ln 2$ for free radical electron spin

. Subtract 0.1 for loss of H atom

. Subtract 2.6, if loss of an O-H, N-H or C-H rotor,

compare

with parent molecule

3.2.2 Method of Bond Energy^{<8>}

When required properties for various Benson groups were not available, estimates were made based on reasonable modifications of groups which were available for similar compounds, or from properties of a series of species for the same chemical functional group. Items considered were: structure (e.g. double or triple bond, primary, secondary

or tertiary bond dissociation, resonance), number of chlorines, effect of Cl atom on intra-molecular bond strength, etc.

After estimating the data, we try to verify if the data are reasonable. In comparisons most of the estimated data are consistent with recently published experimental data. If the experimentally measured data is unavailable, verification by two different estimation methods is used. It is important to note that improvements in the accuracy of the thermodynamic properties for molecules and radicals are critical to improvements in reaction mechanisms. A listing of thermochemical data used in this study is included in APPENDIX 1. An example follows:

(Method 1)

Estimation of H-CX₂OOH Bond Energy (units : Kcal/mol),

X = H or Cl

	Bond Energy	Δ	Source
CH ₃ -H	105.0		Reference No. 24, 36
CH ₂ Cl-H	100.8	4.2	Reference No. 24, 36
CHCl ₂ -H	98.4	2.6	Reference No. 24, 36

Assumption: Δ (difference between bond energies of species of chlorine content) may be decreased in the peroxy functional group by multiplicative factor of 0.5. One C-H of CH₄ is replaced by a C-OOH. This will effect the C-H bond energy of H-CH₂OOH.

H-CH ₂ OOH	96.6	THERM Database
H-CHClOOH	94.5	BE1
H-CCl ₂ OOH	93.2	BE2

where

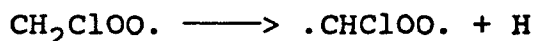
$$BE1 = BE_{H-CH_2OOH} - (BE_{CH_3-H} - BE_{CH_2Cl-H}) * 0.5$$

$$BE2 = BE_{H-CH_2OOH} - (BE_{CH_3-H} - BE_{CHCl_2-H}) * 0.5$$

Assignments are now made to these group additivity elements, CXJOOH = 94.5 and CX2JOOH = 93.2 for the corresponding C-H bond energies.

Example of .CHClOO. estimation (diradical)

The estimation of the heat of formation of the diradical .CHClOO. is based on CH₂ClOO., the reaction is shown as:



Heat of reaction (BE) = $\Sigma H_{products}$ - $\Sigma H_{reactants}$

CHClOO (X) can be calculated as follow :

$$BE(94.5) = X + H(52.1) - CH_2ClOO.(-1.9)$$

(CH₂ClOO. Hf₂₉₈ = -1.9 Kcal/mol, Ref: Russel et al. 23rd Symposium on Comb., The Comb. Ins. 1991)

Estimate result: Hf(CHClOO) = 40.5 Kcal/mol

.CHClOO. can be calculated knowing the appropriate C-H bond energy, and Hf of CH₂ClOO. and H.

(Method 2)

The bond energy of H-CHClOO. was estimated to be that of CH₃CH₂Cl \longrightarrow CH₃CHCl + H because the C-H bond broken in both compounds has the same structure for the "CH₂Cl" side. The "OO." in CH₂ClOO. has a weak effect on the H

bond breaking. This bond energy(94.5) is consistent with that estimated for the H-CHClOOH bond by method 1. The Hf of .CHClOO. was estimated by Benson's group additivity method based upon the above estimated bond energy (CXJOOH=94.5). The calculated value was compared with the group additivity method based on CXJOOH, and varified that it is reasonably accurate.

The two estimated results for .CHClOO., by using the bond dissociation energy method and the group additivity method are in good agreement.

3.3 Estimation of Quantitative Kinetic Data

3.3.1 Unimolecular Dissociation

(a). Simple fission

In this study, the estimation of kinetic parameters for the simple fission is based on the thermochemical principles. Benson^{<23>} noted that at low pressure the simple fission becomes a bimolecular process, since it is controlled primary by the rate of accumulation of internal energy by collision. Its rate is also controlled by the bond being broken.

These simple fission reactions usually have a high average A factor, but are also accompanied by high activation energy (Ea).

Table 3.1 and 3.2 present the examples of simple fission reaction:

Table 3.1 C-H Rupture in Hydrocarbon molecules

Reaction	logA	Ea(Kcal)	ΔH (Kcal)
$\text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}$	15.4	105.0	104.8
$\text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}$	15.3	100.7	100.7
$\text{C}_3\text{H}_8 \longrightarrow \text{n-C}_3\text{H}_7 + \text{H}$	15.4	100.7	100.7
$\text{n-C}_4\text{H}_{10} \longrightarrow \text{n-C}_4\text{H}_9 + \text{H}$	15.4	100.7	100.7

Suggested values: $A = 3 * 10^{15}$, $E_a = \Delta H$

(Ref: Dean, A.M., J. Phys. Chem., 89, 4600, 1985)

Table 3.2 C-C Rupture in Hydrocarbon Molecules

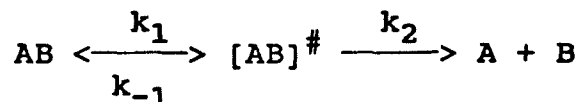
Reaction	logA	Ea(Kcal)	ΔH (Kcal)
$\text{C}_2\text{H}_6 \longrightarrow \text{CH}_3 + \text{CH}_3$	16.9	89.4	89.8
$\text{C}_3\text{H}_8 \longrightarrow \text{C}_2\text{H}_5 + \text{CH}_3$	16.9	84.4	85.5
$\text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_3\text{H}_7 + \text{CH}_3$	17.0	84.7	85.9
$\text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$	16.9	80.2	81.9

Suggested Values: $A = 1 * 10^{17}$, $E_a = \Delta H - 1$

(Ref: Dean, A.M., J. Phys. Chem., 89, 4600, 1985)

(b) Complex fission (molecule elimination)

The molecular elimination reaction is one of the very important reaction channels in this study because it is a low energy barrier channel for HCl elimination. Consider the general reaction:



where # designates the activated complex located at the potential maximum.

The rate constant for decomposition of AB is given as follow.

$$k_{AB} = k_2 K_{AB}^\#$$

$$k_2 = k_b T/h$$

$$K_{AB}^\# = k_1/k_{-1}$$

$K_{AB}^\#$ is the equilibrium constant for formation of $[AB]^\#$ from AB.

where k_b = Boltzman constant

h = Planck constant

By expressing the equilibrium constant of $AB^\#$ in term of Gibbs free energy,

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# = -RT \ln K_{AB}^\#$$

$$K_{AB}^\# = e(-\Delta G^\#/RT) = e(-\Delta H^\#/RT + \Delta S^\#/R)$$

$$k_{AB} = (k_b T/h) * \text{EXP}(\Delta S_{AB}^\#/R) * \text{EXP}(-\Delta H_{AB}^\#/RT)$$

If the Arrhenius equation $A * \text{EXP}(-E_a/RT)$ for k_{AB} is expressed, it becomes

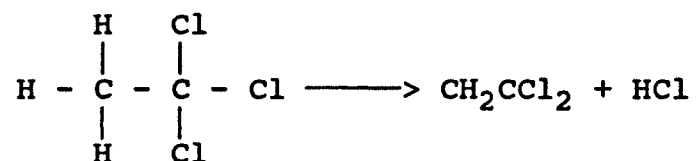
$$A = e k_b T_m/h * \text{EXP}(\Delta S_{AB}^\#/R), \quad E_a = \Delta H_{AB}^\# - RT_m$$

The $e k_b T_m/h$ will be in the range of $10^{13.72} \text{ sec}^{-1}$ for this experimental average temperature (700 °C). Benson^{<23>} noted that when the bond being broken becomes elongated and looser than AB, $\Delta S_{AB}^\# > 0$, and the A factors will be large. On the other hand, when the $[AB]^\#$ is more compact and stiffer than AB, $\Delta S_{AB}^\# < 0$, then the A factors will

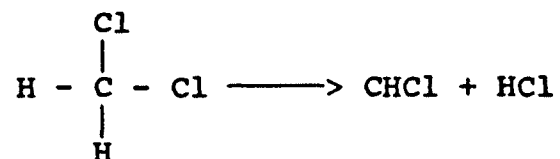
be small. Benson^{<23>} categorized these possibilities as "loose" and "tight" transition state complexes respectively.

However, the limited activation energies for the unimolecular elimination by four and three centered processes are available in literature and the range of these values are reasonably narrow within 10 - 20 Kcal range, usually $E_a = \Delta H_{rxn} + 40 (\pm 10)$

Unimolecular reactions can also take place in which more than one bond in a molecule is broken. While the complexity may varies, all proceed through the formation of cyclic transition state. An example, the most common seem to involve four atoms in a ring transition state and are frequently referred to as four-center reactions.



Cases are also found of three-center reaction



Second examples of rate constant determination for molecular elimination reactions follows:

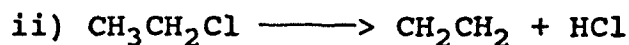
Case I) Four-center molecule elimination



$$A = \frac{ekT_m}{h} * \text{EXP}(\Delta S/R) * g$$

where g (degeneracy): each of 3 H's can react with 3 Cl's
(g = 3 * 3 = 9)

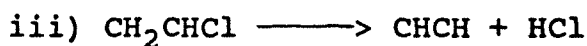
$$\Delta S = -4.0 \text{ (loss of a rotor)}$$



$$A = 10^{13.72} * \text{EXP}(-4/R) * 3 \text{ (1 rotor loss)}$$

$$E_a = \Delta H_r + 43$$

(Ref: Benson, S.W., "Thermochemical kinetics", 2nd Ed. 1976)

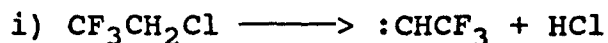


$$A = 10^{13.72} * 1 \text{ (no rotor loss and } g = 1)$$

$$E_a = \Delta H_r + 45$$

(Ref: Zabel, F., Int. J. Chem. Kinet., 9, 655, 1977)

Case II) Three-center molecule elimination



$$A = 10^{13.72} * 2 \text{ (} g = 2)$$

$$E_a = \Delta H_r$$

(Ref: Setser, D.W. and Lee, T., J. Phys. Chem., 89, 5799, 1985)



$$A = 10^{13.72} * 4 \text{ (} g = 4)$$

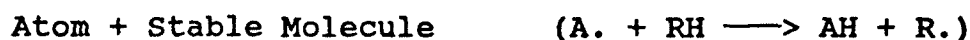
$$E_a = \Delta H_r + 7.5 \text{ (This work)}$$

3.3.2 Abstraction reactions

The E_a for an abstraction may be expected to correspond in some way to bond strength of the atom or radical being abstracted while the E_a of an addition reactions would

depend upon the delocalization of the electrons and the number of electron-withdrawing constituents (such as chlorine).

Examples of abstraction reactions follows:



Elementary reaction rate parameters for abstraction reaction are based on literature values and if literature data are not available on generic reaction A factors (comparison of the reaction to a similar reaction system, where the rate parameters are known) as seen in Table 3.3. If not available, similar reaction literature values can be chosen for A factor and E_a 's estimated from E_a versus ΔH_r plot (Evans-Polanyi) of similar reactions.

Table 3.3 Abstraction Reaction of H with Hydrocarbon

Reaction	g	log A	E_a	ΔH_r
$\text{H} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2$	4	14.1	11.0	0.9
$\text{H} + \text{C}_2\text{H}_6 \longrightarrow \text{CC.} + \text{H}_2$	6	14.1	9.7	-2.6
$\text{H} + \text{C}_3\text{H}_8 \longrightarrow \text{CCC.} + \text{H}_2$	6	14.1	9.7	-2.6
$\text{H} + \text{C}_3\text{H}_8 \longrightarrow \text{CC.C} + \text{H}_2$	2	13.8	7.7	-6.2
$\text{H} + \text{C}_4\text{H}_{10} \longrightarrow \text{CCCC.} + \text{H}_2$	6	14.1	9.7	-2.6
$\text{H} + \text{C}_4\text{H}_{10} \longrightarrow \text{CC.CC} + \text{H}_2$	4	14.1	7.7	-6.2

(Ref: Allara, D.L., & Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980. For A and E_a data, ΔH_r from Bozzelli group thermodynamic data base.)

As shown in Table 3.3 there is good relationship between E_a and ΔH_r . "Evans Polanyi" plot is good tool to estimate kinetic parameters of abstraction reaction, if the literature values are not available.

Bozzelli^{<24>} summarized kinetic parameter guide lines for types of reactions, as described in Table 3.4.

Table 3.4
Kinetic Parameter for Different Types of Reactions

Type of Reaction	A	E_a
Unimolecular	1.0E15 - 5.0E17	$\Delta H_r + (0-2)$
Disproportionation	3.0E11 - 5.0E12	0.0
Beta Scission	3.0E12 - 2.0E14	$\Delta H_r + (2-4)$
Combination	8.0E12 - 2.0E14	0.0
Intermolecular rearrangement	1.0E11- 1.0E14	$E_a = \Delta H_r + E_{abs} + RS$

3.4 Quantum Kassel Theory

Energized Complex/QRRK presented by Dean ^{<25>} and later modified by Ritter and Bozzelli^{<26>} for the formation of energized complex was used for modeling reactions involving atom and radical addition to an unsaturated bond and atom plus radical or radical plus radical combination reactions. The modified QRRK algorithm by Ritter and Bozzelli used Gamma function evaluations for the energy dependent term instead of factorials.

For condition of steady state: $(dAB^\ddagger/dt = 0)$

$$[AB]^\ddagger = k_1[A][B]/(k_{-1} + k_2 + k_{stab}) \quad (1)$$

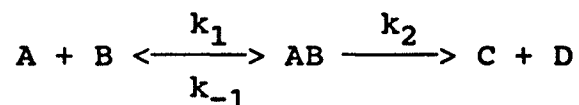
$$\frac{d([C]+[D])}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2 + k_{stab}} \quad (2)$$

$$\frac{d(AB^\circ)}{dt} = \frac{k_{stab} k_1 [A][B]}{k_{-1} + k_2 + k_{stab}} \quad (3)$$

Eq. (2) and (3) provides apparent reaction rate constants to provide C + D and stabilized adduct, AB° , by QRRK approach.

The k_1 and k_2 are functions of energy and are determined by expression given by Dean^{<25>}.

In contrast to the above QRRK approach the more conventional thermal equilibrium analysis will consider the reaction as:



For conditions of steady state

$$(AB)_{ss} = k_1 [A][B] / (k_{-1} + k_2) \quad (4)$$

$$\frac{d([C]+[D])}{dt} = \frac{k_1 k_2 [A][B]}{(k_{-1} + k_2)} = k_2 K_{eq} [A][B] \quad (5)$$

Eq. (5) in the limit $k_{-1} \gg k_2$ reduces to

$$\frac{d([C]+[D])}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1}} = k_2 K_{eq} [A][B] \quad (6)$$

where

$$K_{eq} = k_1/k_{-1} = [AB]/([A][B])$$

Eq. (3) and (6) demonstrates that substantial difference in the computed apparent rate constants for the formation of $C + D$, can arise depending upon whether one uses a QRRK or chemical thermal approach Ritter and Bozzelli^{<26>} showed that the two approaches become equivalent only at the high pressure limit, where all of the $[AB]^\ddagger$ is stabilized prior to reaction. Dean^{<25>} found that the pressure required for complete stabilization varies extensively energy with species and temperature.

The present study of $CH_2Cl_2/CH_4/O_2/Ar$ system was carried at temperature between 773 K and 1273 K and pressure of 1 atm. The Quantum Kassel treatment of energized complex formation and considerations of their stabilization, on forward and reverse reaction channels is a more accurate way to analyze the thermal reaction processes. Microreversibility for all reactions was also used in the mechanism such that equilibrium could be established for any reaction should the necessary conditions exist.

3.5 Computer Codes Used to Develop the Model

3.5.1 CHEMACT

CHEMACT^{<27>} is a computer code that performs the QRRK treatment of chemical activation reactions to estimate apparent bimolecular rate constants for various channels that can result in addition, recombination and insertion

reactions. Since the rate constants depend on both pressure and temperature of interest in the modeling calculation. (The resulting data expression is then valid over the temperature range fitted within CHEMACT.) In addition, the user must account for further reactions of the stabilized adducts, which are products of the chemical activation reaction in his model. The dissociation of stabilized adduct back to reactants is automatically included if the reactions are written reversibly, but, for completeness, dissociation to the other possible products must be explicitly.

General Input Data Requirements for CHEMACT:

i) Thermodynamic parameters:

Enthalpy (H_f), entropy (S_f) and heat capacities (C_p) as a function of temperature for reactants, adduct and products of the reaction system are important for accurate results.

ii) Molecular parameters describing the size, collisional energy transfer and energy levels of the adduct formed by the initial reaction are also needed. These include the mass, number of vibrational modes of the adducts, Lennard-Jones parameters and geometric mean vibrational frequency.

iii) The bath gas molecule collision diameter, well depth and average energy transferred per collision are needed.

iv) High pressure limit rate constants for adduct formation and various isomerization and dissociation product channels of the adduct are also needed.

3.5.2 DISSOC

Fall-off corrections for unimolecular decomposition reactions are made with the unimolecular Quantum RRK method^{<28>}. The DISSOC computer code^{<27>} analyzes unimolecular reaction with unimolecular QRRK analysis for the proper treatment of fall-off dependency and estimates apparent unimolecular dissociation rate constants for various dissociation or ionization channels. Since these rate constants depend on both pressure and temperature, it is important that the user include the appropriate expression for specific pressure of interest in the modeling calculation. The same input data with CHEMACT computer code is required to run DISSOC program.

3.5.3 THERM

Our thermo data is based upon the best currently available thermochemical data in literature. When experimentally based thermodynamic data were not available, the values were estimated using THERM computer code^{<29>}.

THERM is the computer code which can be used to estimate, edit, or enter thermodynamic property data for gas phase radicals and molecules using Benson's Group Additivity Method^{<23>}. All group contributions considered for a species are recorded and thermodynamic properties are generated in NASA polynomial format (for compatibility with CHEMKIN^{<30>} in addition to listings more convenient for thermodynamic, kinetic and equilibrium calculation.

3.5.4 CPFIT

CPFIT^{<27,28>} is a computer code that determine geometric mean frequency. It accepts input in the form of heat capacities versus temperature to 1000 K in addition to the number of vibrational modes and the number of internal rotors in the molecule. This code fits the heat capacity data in the above range to a five parameter harmonic oscillator model and extends the temperature range to 5000 K. An additional method of estimating the geometric mean frequency of a radical is to take the arithmetic mean of the frequency of the corresponding stable parent molecule (with one more H atom) and the frequency of the species with one less H atom than the radical of interest.

CHAPTR 4 EXPERIMENTAL METHOD

4.1 Experimental Apparatus

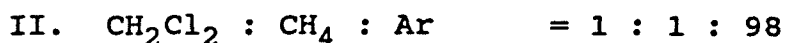
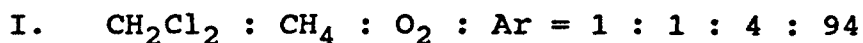
A diagram of the experimental apparatus is shown in Figure 4.1. The thermal reaction products of dichloromethane were analyzed by varying the temperature, residence time and reactant ratio set. The temperature range of 680 to 840 °C and residence time range of 0.3 to 2.0 seconds were studied in a high temperature tubular flow reactor which operated isothermally at 1 atm pressure in this study.

Argon, carrier gas, was passed through a saturation bubbler set held at 0 °C using ice bath. A second argon flow stream (after the bubbler) was used as make-up gas in order to achieve the desired mole fraction between reagents. Methane and/or oxygen were then added to the CH₂Cl₂/Ar flow as required. Before entering the reactor, the feed mixture could be transferred directly from the bubbler to the GC sampling valve via a by-pass line. This was necessary to determine the GC peak area that corresponded to the input initial concentration of the reagents without going through the high temperature reactor. The mixtures were preheated to about 150 °C to improve the reactor temperature control. A fraction (about 5%) of the reactor effluent gas passed through a heated line to the GC sampler and exhaust. All gas line to the analytical equipment were held at about 120 °C to limit condensation.

The fraction of product gas going to the GC, was passed through a glass tube which held packed glass wool to trap any carbon particles preventing contamination of the GC system. The bulk of the effluent was also passed through a glass tube packed with glass wool to trap carbon particles and/or soot, and then through a sodium bicarbonate (NaHCO_3) flask for partial neutralization before being released to the atmosphere via a fume hood.

Won and Bozzelli^{<31>}, Ritter et al.^{<29>}, and Siozopoulos^{<32>} demonstrated the effect of the reactor wall (surface to volume ratio) in the thermal reactions of CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CCl}_3$, $\text{C}_6\text{H}_5\text{Cl}$, and CHCl_3 respectively. They also demonstrated that relative product distribution did not change with reactor diameter at temperature between 500 °C to 1000 °C. They indicated that the conversion and product yields with 16.0 and 10.5 mm ID reactors were similar, but the 4.0 mm ID reactors showed higher conversions.

In this study, a quartz tube of 10.5 mm ID was chosen as the reactor for minimal effect of reactor wall and good control of the temperature profile and residence time. The thermal decomposition of the following four reactant ratio sets were studied to determine important chlorocarbon reaction pathways before initiating development of detailed reaction mechanism.



III. CH_2Cl_2 : O_2 : Ar = 1 : 4 : 95

IV. CH_2Cl_2 : Ar = 1 : 99

4.2 Temperature control and Measurement

A quartz reactor tube of 10.5mm i.d. was housed within a three zone electric tube furnace (Lindberg electric tube furnace) of 18 inches length equipped with three independent temperature controllers (Omega Engineering, Inc.) in order to adjust the operation condition nearly isothermally ($\pm 5^\circ\text{C}$). The actual temperature profile of the tubular reactor was obtained using type K thermocouple probe moved coaxially within the reactor. The temperature measurements were performed with a steady flow rate of Argon gas through the reactor tube. The temperature profiles with tight temperature control obtained as shown in Figure 4.2 were isothermal to within $\pm 5^\circ\text{C}$ for 12 inches (30.48 cm) that over 70% of the furnace length (central zone) for all temperature ranges of this study. Figure 4.3 shows isothermal temperature profiles at several temperatures.

4.3 Quantitative Analysis of Reaction Product

A HP 5890 on-line gas chromatograph with flame ionization detector was used to determine the concentration of the reaction products. The line between reactor exit and GC were heated to 120°C to limit condensation. The GC used

1.5 m long by 1/8" O.D. stainless steel tube packed with 1 % Alltech AT-1000 on graphpac GB as the column. Methane, carbon monoxide, and carbon dioxide from the reactor effluent stream were separated using 5 ft long by 1/8" O.D. stainless steel column packed with carbonsphere 80/100 mesh.

A six port gas sample valve with 1.0 ml volume loop was maintained at 170 °C and 1 atm pressure. Chromatogram peak integration was performed with a Varian 4270 integrator/plotter. A representative chromatogram is shown Figure 4.4, and table 4.1 with retention time and peak identification.

In order to increase the accuracy of quantitative analysis, a catalytic convertor, 5% ruthenium on alumina (30/40 mesh) catalyst, was used to reduce CO and CO₂ to CH₄ by reaction with H₂ (10 ml/min). CO and CO₂ were first separated in the carbonsphere packed column and resulted two different retention times of CH₄ product. Quantitative analysis of CO and CO₂ (after reduction to CH₄) was performed using the second flame ionization detector, a chromatogram is shown as Fig. 4.5.

Calibration of the flame ionization detector to obtain appropriate molar response factors was done by injecting a known quantity of the relevant compound such as CH₄, CH₃Cl, CHCl₃, C₂HCl₃ etc., then measuring the corresponding response area. The relative response factor was determined for compounds shown in Table 4.2. The

sensitivity of flame ionization detector corresponds to the number of carbons. We find that the response factors for C_1 compounds is similar, and the response factor of C_2 compounds are nearly twice the response of the C_1 compounds. The effect of chlorine in the relative response factor is small and can be neglected for this flame ionization detector. Analysis of larger or chlorohydrocarbon based on the experimentally verified relative response factors, the specific component peak area from each set of samples was converted to the equivalent number of moles of each compound.

4.4 Hydrochloric Acid Analysis

Quantitative analysis of HCl product was performed for reactions at each temperature and each residence time. The sample for HCl were collected independently from the GC sampling as illustrated as Figure 4.1. In the analysis, the effluent was bubbled through a two stage bubbler before exhaust to the fume hood. Each stage of bubbler contained 20ml of 0.005 M NaOH, plus three drops of phenolphthalien indicator. The gas passed through the two bubbler stages until the first stage solution reached the indicator end-point. The time required for this to occur was recorded. At this point the bubbling was stopped, and the aliquots were combined and then titrated to their end

point with standardized 0.01 M HCl. Several titrations were performed using buffer solution (pH 4.7) to discern if CO₂ was effecting the acidity. No significant effect was observed due to the relatively low levels and K_a of CO₂.

4.5 Qualitative Analysis of Reaction Products

We also employed GC/MS (Finnegan 4000 series) with a 50 m length, 0.22 mm ID methyl silicone stationary phase to check the GC identification .

Evacuated 25 ml stainless steel or Pyrex glass sampling cylinders were used to collect the reactor effluent gas. Injection of the samples into the GC/MS was made the use of a six port gas sampling valve. The samples were separated using a methyl silicone stationary phase capillary column with a tubing size of 0.22 mm ID x 50 m length.

4.6 Detailed Reaction Model Interpretation and Integration by CHEMKIN program

CHEMKIN is a package of FORTRAN programs which are designed to facilitate a chemist's interaction with the computer in modeling chemical kinetics. The CHEMKIN package^{<30>}, shown in Figure 4.6, is composed of four important species :

- (i) The INTERPRETER is a program which first reads the user's symbolic description of the reaction mechanism.
- (ii) The Thermodynamic Data Base has exactly the same format as that used by the NASA complex chemical equilibrium code by Gordon and McBride^{<33>}.
- (iii) The Linking File is ready by an initialization subroutine which is called from the user code, which contains all the current information on the element, species, and reaction mechanism.
- (iv) The Gas-Phase Subroutine Library, which are called to return information on the elements, species, reactions, equation of state, thermodynamic properties, chemical reduction rates, sensitivity parameters, derivatives of chemical production rates, and derivatives of thermodynamic properties.

Generally the input to these routines will be the state variables of the gas--pressure or density, temperature, and the species composition. All routine can be called with the species composition defined as mass fractions, mole fractions, or molar concentration.

Table 4.1
Average Retention Time of Products

Compound	Average Retention Time (min.)
CH ₄	1.32
CH ₃ CH	1.88
CH ₂ CH ₂	2.22
CH ₃ CH ₃	2.68
CH ₃ Cl	4.32
CH ₃ CCH ₃	6.97
CH ₂ CCl	7.02
C ₃ H ₆ & C ₃ H ₈	7.55
CH ₂ CHCl	9.02
CH ₃ CH ₂ Cl	10.20
CH ₂ Cl ₂	11.35
C ₂ Cl ₂	12.20
C ₄ H ₁₀	13.16
CH ₂ CCl ₂	13.90
CH ₃ CHCl ₂	14.10
CHClCHCl	15.35
CH ₂ ClCH ₂ Cl	15.81
CHCl ₃	17.09
CH ₃ CCl ₃	17.42
CCl ₄	17.90
CHClCCl ₂	19.60
CH ₂ ClCHCl ₂	20.00
C ₆ H ₆	20.86
CCl ₂ CCl ₂	28.30

* GC Operating conditions

Oven Temperature:

Initial Temperature: 45 °C (5 min.)

Increasing Rate: 15 °C/min.

Final Temperature: 220 °C

Injector Temperature: 170 °C

Detector Temperature: 270 °C

Carrier Gas Flow Rate: 17 cc/min.

(Helium supplied at 100 psi)

Column: 1.5m x 1/8" OD, 1% AT-1000 on Graphpac GB

Table 4.2
Relative Response Factor of Several Compounds

Compound	Relative Response Factor (RRF)
Methane	1.07
Acetylene	1.85
Ethylene	2.00
Ethane	2.15
Chloromethane	1.02
Propyne	3.33
Propene	3.45
Chloroethylene	1.93
Dichloromethane	1.00
1,1-Dichloroethylene	1.88
1,1,1-Trichloroethane	1.85
Chloroform	0.97
Tetrachlorocarbon	0.90
1,1,2-Trichloroethane	2.10

* corrected area = measured area / RRF

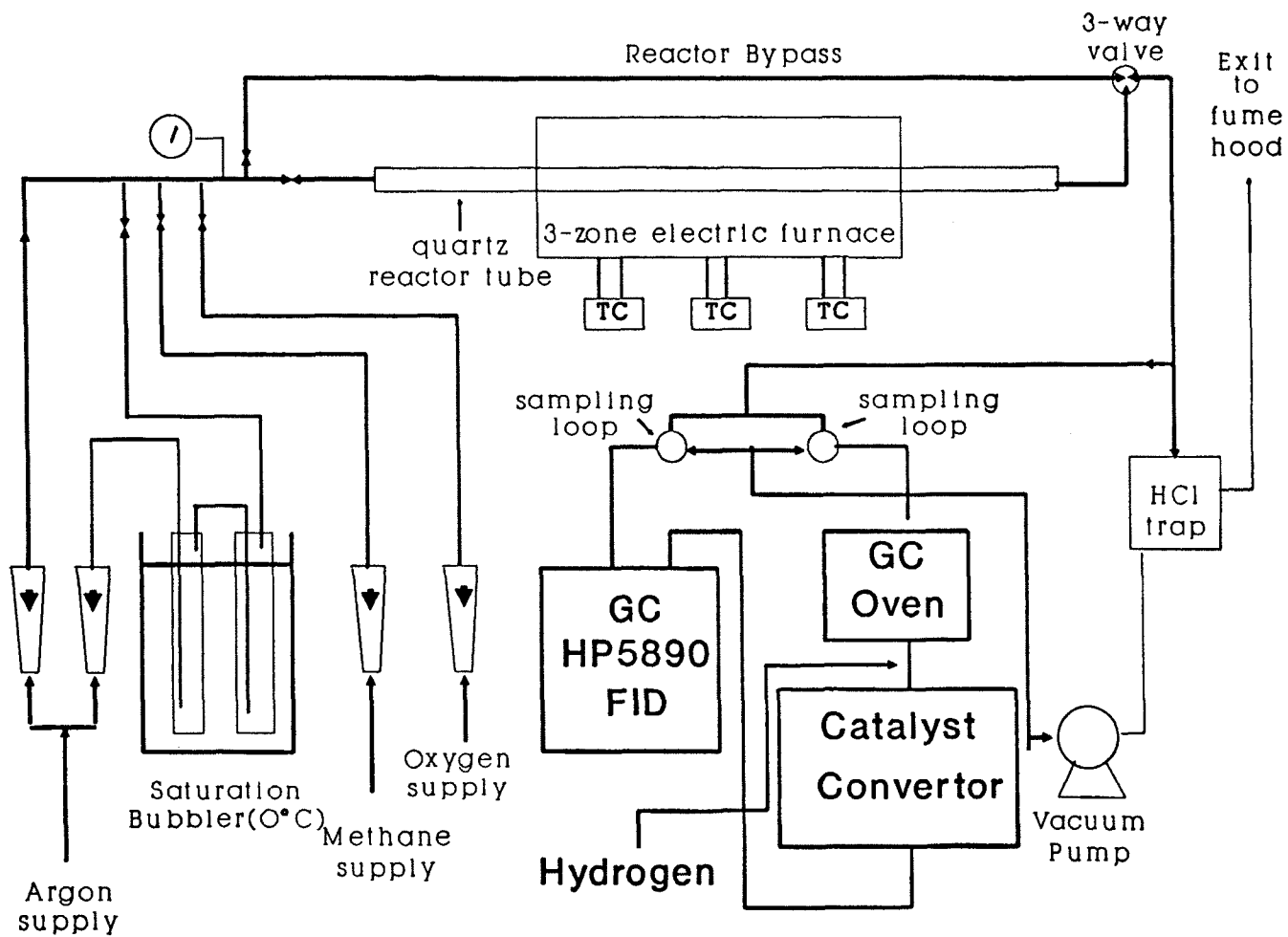


Figure 4.1 Experimental system

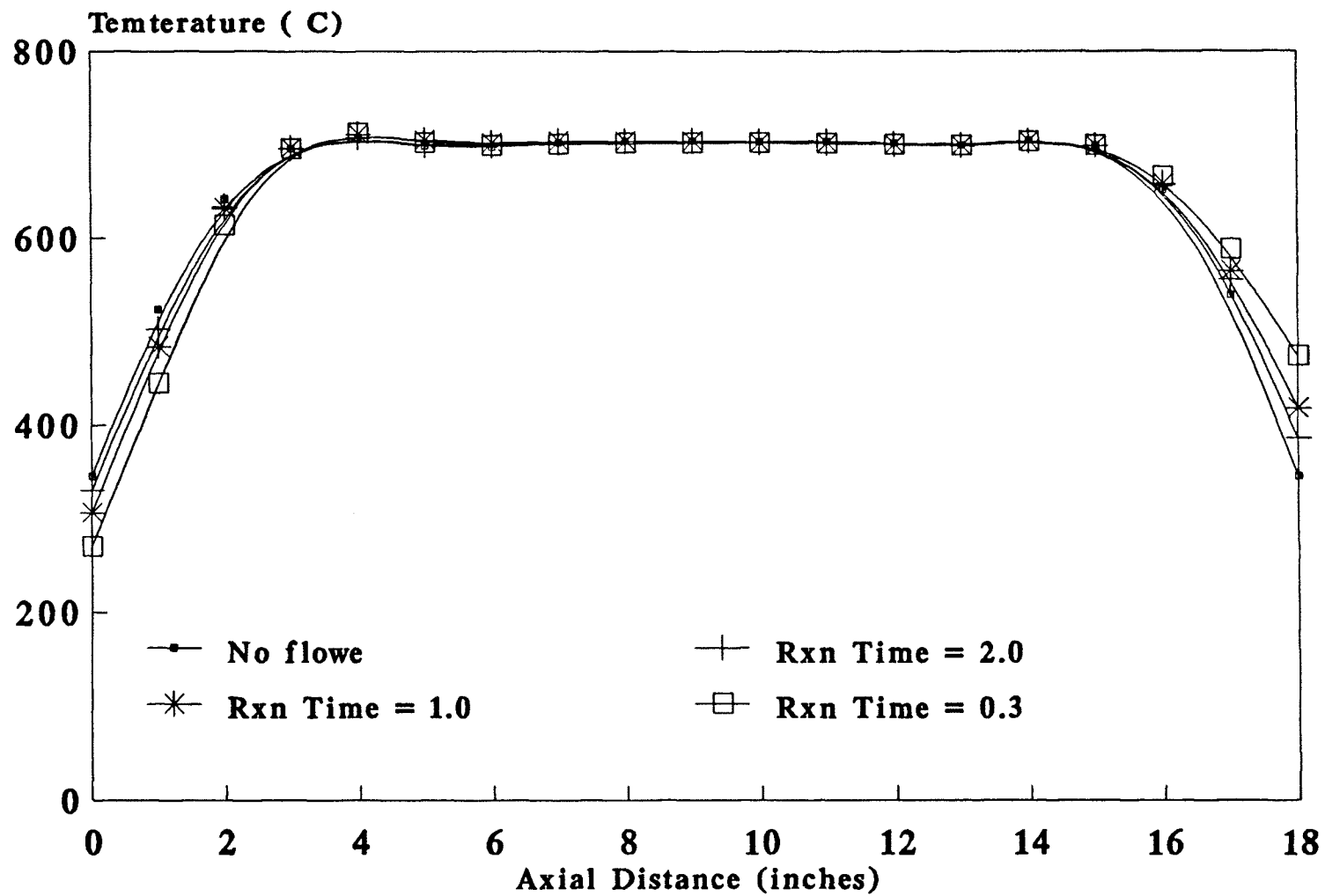


Fig 4.2 Reactor Temperature Profiles with Tight Control

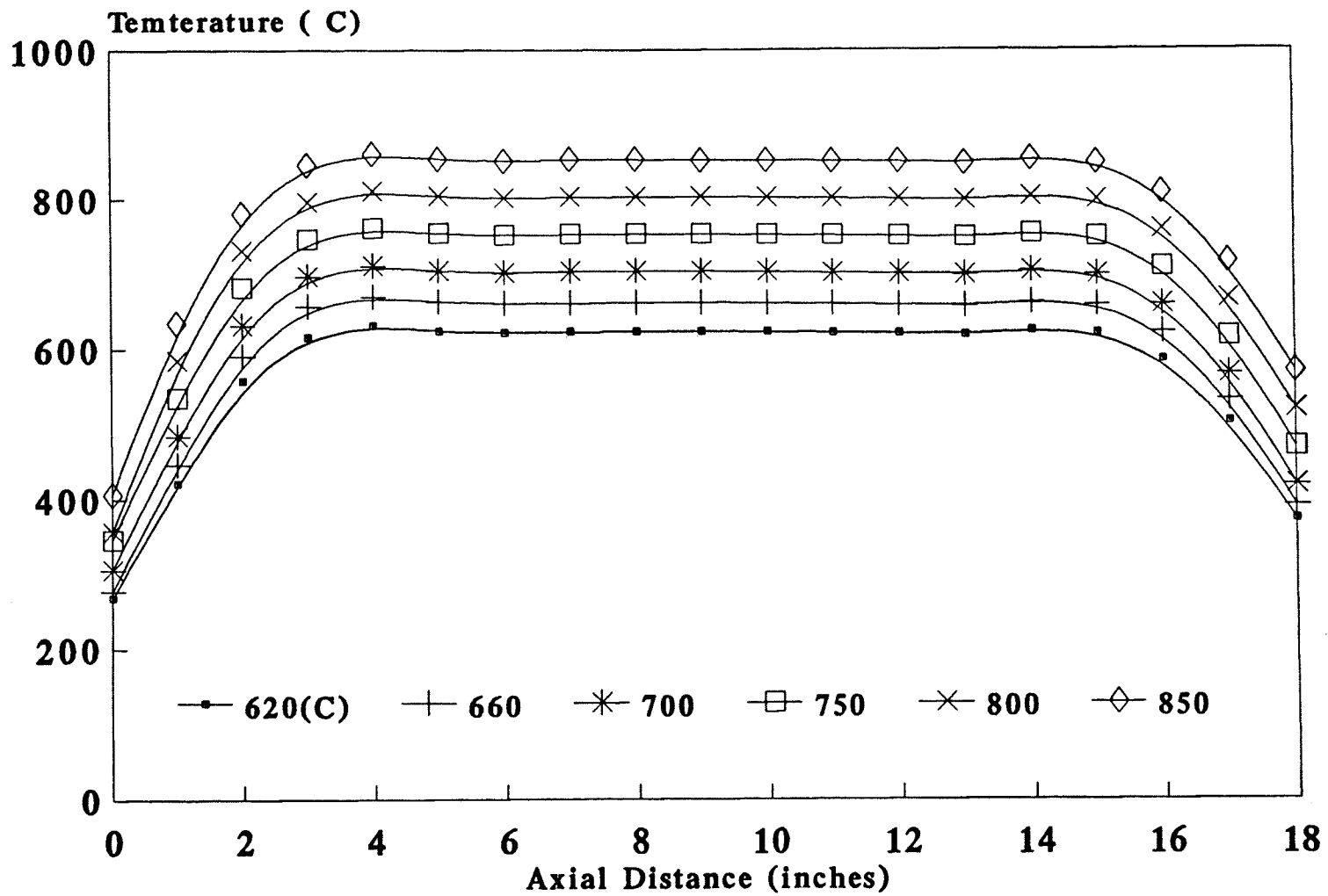


Fig 4.3 Reactor Temperature Profiles with Tight Control

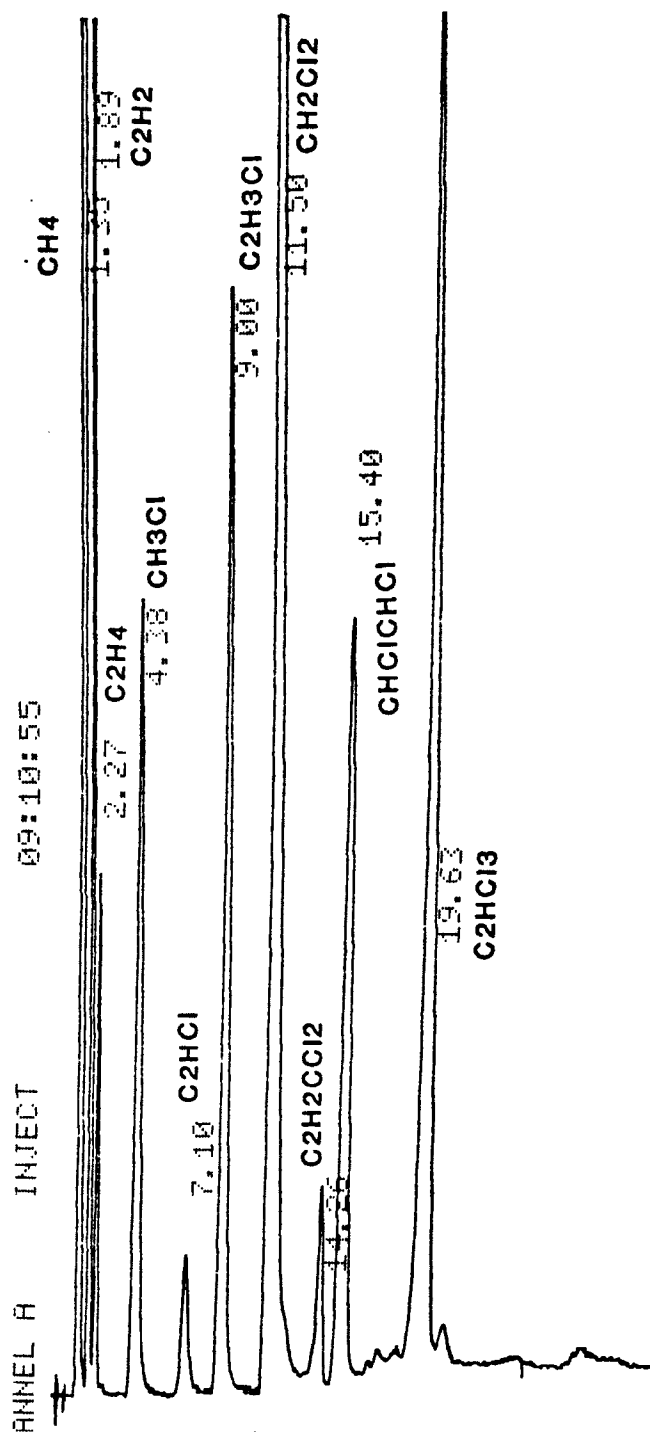


Figure 4.4
Sample Chromatogram CH₂Cl₂/CH₄/O₂/Ar Decomposition

Column: 1.5m x 1/8" o.d. 1% AT-1000 on Graphpac GB
 Detector: FID 270 °C
 Temperature: 45 °C (5min), 15 °C/min to 220 °C
 Carrier Gas: Helium supplied at 100 psig
 * Reaction conditions: CH₂Cl₂:CH₄:O₂:Ar = 1:1:4:94
 1 second under 780 °C

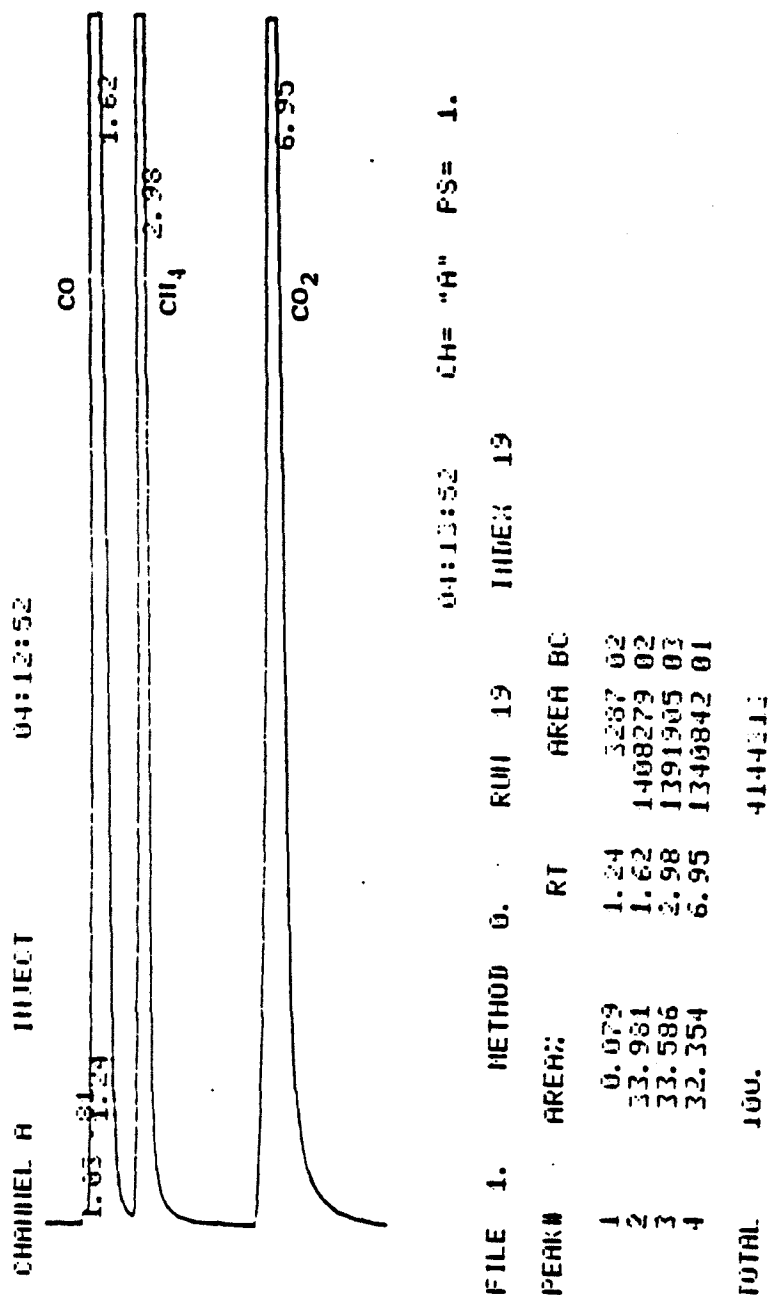


Figure 4.5
Sample Chromatogram $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ Decomposition

Column: 5ft x 1/8"o.d. Carbosphere 80/100 mesh
 Detector: 270 °C
 Temperature: 70 °C
 Carrier Gas: 34 ml/min
 Standard Gas Conc.(%) $\text{CO}:\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:1:97$

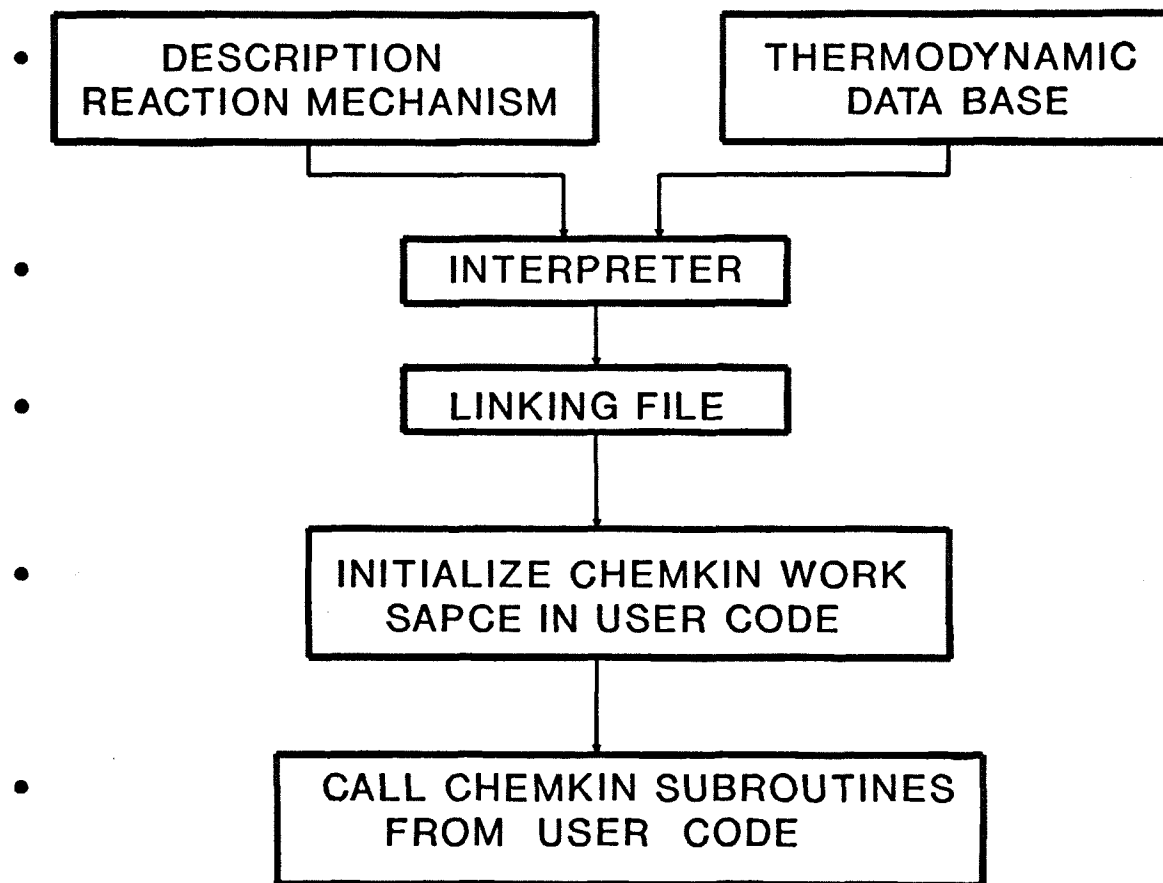


Figure 4.6 Structure of The CHEMKIN Package

CHAPTER 5
RESULT AND DISCUSSION

Thermal decomposition of dichloromethane mixtures in absence and presence of added methane and/or oxygen and in a argon bath gas was carried out at 1 atm total pressure in a tubular reactor. Table 5.1 shows reaction condition which were studied to investigate the important dichloromethane reaction pathways before initiating development of the detail reaction mechanism.

Table 5.1 Experimental condition

	Reactant Mole fraction (%)	Temperature Range (°C)
I.	CH ₂ Cl ₂ : CH ₄ : O ₂ : Ar = 1:1:4:94	680 — 840
II.	CH ₂ Cl ₂ : CH ₄ : Ar = 1:1:98	680 — 820
III.	CH ₂ Cl ₂ : O ₂ : Ar = 1:4:95	680 — 840
IV.	CH ₂ Cl ₂ : Ar = 1:99	680 — 840

5.1 Experimental Results

5.1.1 Reagent Conversion

Experimental results on decomposition of dichloromethane are shown in Figures 5.1-1, 5.1-2, 5.1-3 and 5.1-4, which show the normalized concentration (C/Co) as a function of reaction time and temperature in the four reaction environments. Figure 5.2-1 and 5.2-2 compares dichloro

methane decay as a function of temperature at 1.0 second reaction time, and as a function of reaction time at 760 °C respectively in the four different reactants ratio sets.

O₂ has a positive effect on the decomposition of dichloromethane in this study, the same result was observed by Ho^{<17>}. The accelerated decomposition of dichloromethane, when O₂ is added, results in part, from the bimolecular reaction of O₂ with CH₂Cl₂ to HO₂ + CHCl₂ products. This reaction occurs in parallel with the unimolecular dissociation of dichloromethane under initiation conditions.

The slowest dichloromethane decay occurs in the presence of CH₄ and absence of O₂. The atoms and radicals which are produced from CH₂Cl₂ unimolecular dissociation react with CH₄, (instead of reaction with CH₂Cl₂), which was added to serve as a fuel (hydrogen) source for HCl production. When O₂ was added to the CH₂Cl₂ + CH₄ reaction system, CH₄ decay also accelerated. The comparison of CH₄ decay in different reaction environments are shown in Figure 5.3-1 and 5.3-2. This implies that the oxygen catalyzed hydro-pyrolysis occurs, which is also observed in chloroform reaction systems^{<8>}.

The experimental data on decomposition of DCM, as shown in Figure 5.4-1, 5.4-2, 5.4-3, and 5.4-4, exhibit good linearity for pseudo first-order rate equations. The

first-order decay plots do not pass the zero point possibly due to error in residence time measurements. This error is mainly due to the non-uniformity of reactor temperature at the inlet and outlet (temperature up and down respectively). The global rate constants, k , for decomposition of CH_2Cl_2 are tabulated in Table 5.2. The A factors and Activation Energies were obtained from Arrhenius plots shown in Figure 5.5.

Table 5.2
Rate Constants for $\text{CH}_2\text{Cl}_2 + \text{CH}_4$ and/or O_2 P = 1 atm

Reaction Environments	I	II	III	IV
Temp (K)	Rate Constant (k)			
993		0.13		0.12
1013	0.27	0.40	0.17	0.29
1033	0.63	1.37	0.38	0.59
1053	1.27	3.33	0.66	1.50
1073	2.70		1.31	3.12
1093	4.07		1.95	
Ea	75.84	114.68	67.85	86.92
A	6.74E15	1.56E24	6.46E13	1.21E18

k : Rate Constant (1/sec.), for CH_2Cl_2 decrease

A : Frequency Factor (1/sec.)

Ea: Activation Energy (Kcal/mole)

I, II, III, IV : Reactant ratio sets, see Table 5.1

5.1.2 Product Distribution and Material Balance for Each Reaction Environments

In this study all of the products except HCl and CO, CO₂ (under the added oxygen conditions) are below 10% [C/(CH₂Cl₂)₀] levels.

Table 5.3 presents the product distribution in four different reaction environments at temperature 760 °C and 1.0 second reaction time. The concentration of all chlorinated compounds are below 10%.

a. Product Distribution in CH₂Cl₂/CH₄/O₂/Ar

Figure 5.6 illustrates the distributions for the major products C₂HCl₃, CHClCHCl, C₂H₃Cl, CH₃Cl, C₂H₂, CO and CO₂ as a function of temperature at 1.0 second reaction time. The minor products are C₂HCl, CH₂CCl₂, C₂H₄, CHCl₃ and benzene. Formation of chlorinated carbons species (CHClCHCl, C₂HCl₃, CH₃Cl and C₂H₃Cl etc.) increased with increasing temperature, with the maximum levels appearing near 780 °C (for 1.0 residence time). The formation of C₂H₂ increases when chlorinated carbons and CH₄ decrease. C₂H₂ starts to decrease at about 820 °C. The major product CO rises as the temperature increases to around 740 °C where reagents and chlorinated products decrease.

Benzene formation is observed above 800 °C. Benzene can be formed from smaller, nonaromatic hydrocarbons (C₂H₂, C₂H₄, C₃H₄, and C₃H₆ etc.), but the mechanism for its formation is not a part of this study. To form an

aromatic ring from smaller aliphatic species, there must be molecular-weight growth, cyclization, and aromatization reactions. It is beyond the scope of the present study, introduce the mechanism of benzene formation.

Figure 5.7 presents the product distribution as a function of reaction time at 760 °C.

b. Product Distribution in CH₂Cl₂/CH₄/Ar

Figures 5.8 and 5.9 show the observed product distributions as functions of temperature at 1.0 second residence time, and as functions of reaction time at 760 °C respectively. The major products are CH₃Cl, CHClCHCl, C₂HCl₃, and C₂H₂. The minor products are C₂H₄, C₂H₃Cl, C₂HCl, CH₂CCl₂, CHCl₃, and benzene. The product distribution for the CH₂Cl₂/CH₄/Ar reaction is qualitatively similar to the CH₂Cl₂/CH₄/O₂/Ar reaction.

The production of benzene of these conditions is more stable and two times higher than that at CH₂Cl₂/CH₄/O₂/Ar reaction system. Higher levels of C₂H₂ and C₂H₄ are also produced.

c. Product Distribution in the CH₂Cl₂/O₂/Ar Reaction system

The main products over wide range of temperatures are C₂HCl₃, CHClCHCl, CH₃Cl, CO, and CO₂ as presented in Figure 5.10 as a function of temperature at 1.0 second reaction time. The minor products are CH₂CCl₂, C₂HCl, with

trace amounts of C_2Cl_4 . Oxygen has a significant effect on the decomposition of parent CH_2Cl_2 . More than 99% conversion of parent CH_2Cl_2 is observed at 800 °C at 1.0 second reaction time. Same results has obtained in the previous study.

Figure 5.11 shows the products distribution as a function of reaction time at 760°C.

d. Product Distribution in CH_2Cl_2/Ar Reaction System

The decay of CH_2Cl_2 , along with the formation and decay of stable intermediate products, at 1.0 second residence time as a function temperature are illustrated in Figure 5.12. In this reaction system, we can exclude the effects of oxygen and methane. The major products are still are C_2HCl_3 , CH_3Cl , and $CHClCHCl$.

The product distribution as a function of reaction time at temperature 760°C is shown in Figure 5.13.

e. Material Balance

The material balance gives us important information about high molecular weight compounds, soot and oxy-chlorinateds which are not quantitatively detected. The carbon material balances for the present study are listed in Table 5.4, 5.5, 5.6, and 5.7.

The oxygen containing reaction system ($CH_2Cl_2/CH_4/O_2/Ar$ and $CH_2Cl_2/O_2/Ar$) shows relatively good

material balance over wide temperature range 680°C - 840°C at 1.0 residence time. Comparing with model prediction, the CO concentration of experiment are much higher than that of model prediction.

In the reaction environments of an absence of oxygen (CH₂Cl₂/CH₄/Ar and CH₂Cl₂/Ar), Table 5.6 and Table 5.7 show that the material balances indicate a loss at temperatures above 780°C. In the experiments at temperature above 780°C, we found brown soot in the post-reactor zone and filter before the exhaust to the hood. This implies that the formation of high molecular species and soot is occurring at higher temperature in the absence of oxygen. When added oxygen, the overall CH₂Cl₂ breakdown process is enhanced and soot formation is not observed.

5.1.3 Comparison of Main Product Distribution in Four Different Reaction Environments

Figure 5.14 to Figure 5.20 compare the formation of intermediate stable products as a function of temperature at 1.0 second residence time and as a function of reaction time at temperature 760 °C for the different reaction systems.

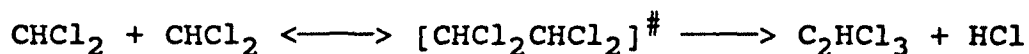
a. C₂HCl₃ Products Distributions

The formation of C₂HCl₃ in the CH₂Cl₂/Ar reaction system, is higher than that in any other system. When O₂ (4%) is added into the CH₂Cl₂/Ar system, (reaction environment

III), O_2 increases the rate of C_2HCl_3 formation and also increases the rate of C_2HCl_3 decomposition. Figure 5.14 shows that C_2HCl_3 is more stable in the absence of O_2 .

C_2HCl_3 is formed from the combination of $CHCl_2 + CHCl_2$ radicals. When CH_4 is presented, (reaction environment I, II), the concentration of C_2HCl_3 is relatively low; owing to CH_3 and H radicals which will compete with $CHCl_2$ to collide with $CHCl_2$.

The C_2HCl_3 formation pathway can be described below:



b. CH_3Cl Product Distribution

In the $CH_2Cl_2/O_2/Ar$ reaction system, the concentration of CH_3Cl is relatively low. Considering "stoichiometric concepts", the concentration of O_2 is in excess, that is more O_2 is present than is needed to convert all carbon to CO_2 and H to H_2O or HCl . This O_2 will increase the oxidation of chlorinated hydrocarbon.

The formation pathways for CH_3Cl can be described as below:

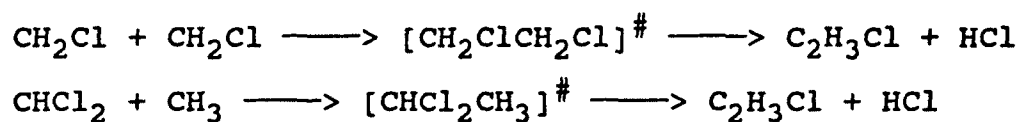


Figure 5.15-1 and 5.15-2 show that, in the CH_4 reaction systems, (reaction environment I, II), the concentration of CH_3Cl is relatively high, above all the other experiment where there was O_2 present.

c. C₂H₃Cl product distribution

Figures 5.16-1 and 5.16-2 show that significant levels of C₂H₃Cl were observed in the presence of CH₄. Formation of C₂H₃Cl increases with increasing temperature to the maximum near 800 °C and drops in CH₂Cl₂/CH₄/O₂/Ar and CH₂Cl₂/CH₄/Ar cases. Formation of C₂H₃Cl in both reaction systems shows similar trends. However, C₂H₃Cl in CH₂Cl₂/CH₄/O₂/Ar drops more quickly than that in CH₂Cl₂/CH₄/Ar as the temperature increases above 780 °C. This implies that bimolecular reaction of hydrophilic radicals (OH, O and HO₂) and O₂ is responsible for acceleration of the C₂H₃Cl decay.

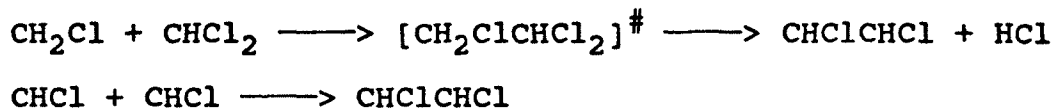
The formation pathways for C₂H₃Cl can be described as below:



d. CHClCHCl product distribution

Figure 5.17-1 and 5.17-2 show that O₂ has significant effect on the formation of CHClCHCl. The concentration of CHClCHCl in presence of CH₄ is relatively low. The reason is that CH₂Cl, CHCl₂ and CHCl, which are produced from the parent compound CH₂Cl₂, react with CH₄, and other H containing species formed from reactions of CH₄. This limits CHClCHCl formation.

The formation pathways for CHClCHCl are shown below:



e. C_2H_2 Product Distribution

In the absence of O_2 , C_2H_2 is a relatively stable product. Figure 5.18-1 and 5.18-2 shows that in $\text{CH}_2\text{Cl}_2/\text{O}_2/\text{Ar}$ reaction system, the concentration of C_2H_2 is relatively low. The excess O_2 accelerates C_2H_2 oxidation. In the presence CH_4 and absence of O_2 , the concentration of C_2H_2 is high.

f. CO and CO_2 Product Distribution

Figures 5.19, 5.20 show that the formation of CO and CO_2 are increasing sharply when temperature increases above 740°C . The formation CO in the $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ system is different from that in the $\text{CH}_2\text{Cl}_2/\text{O}_2/\text{Ar}$ system, but the ultimate concentration of CO in both system is almost the identical. In both reaction systems, the concentration of O_2 is high enough to react with CH_2Cl_2 and/or CH_4 to stoichiometrically form CO.

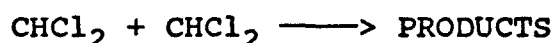
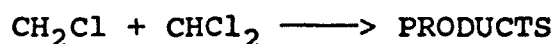
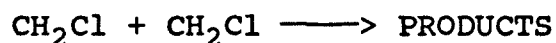
5.2 Model Prediction

5.2.1 Development of Kinetic Mechanism

The detail kinetic reaction mechanism was starting point was that developed by Ho et al.^{<35>} for the $\text{CH}_2\text{Cl}_2/\text{O}_2/\text{H}_2$ system. Ho's kinetic mechanism consists 167 elementary reactions, and 63 species. I did not have sufficient description of CH_3 radical reactions. We modified Ho's

kinetic mechanism by adding several reaction for CH_3 radical and its derivative reactions. This kinetic mechanism, consisting of 94 species and 382 elementary reactions, is shown in Table 5.8 together with the rate parameters for the forward reaction paths. The kinetic parameters used for CH_2Cl_2 mechanism were obtained from the literature where appropriate. For some of the proposed elementary reactions in the mechanism, kinetic data do not exist. We estimated kinetic parameters by using Thermochemical Kinetic methods of Benson^{<23>}, and by comparison of the reaction to a similar system of which the rate parameters are well known. Quantum RRK calculation, as described in section 3.4, were used to estimate apparent rate parameters for addition, combination and dissociation reactions. In all cases, rate parameters are consistent with the thermodynamic database shown as Table 5.9.

Figure 5.21, 5.22, 5.23, 5.24, 5.25 present the energy level diagram for



The input rate parameters used in the QRRK calculations and results from the calculation are summarized in APPENDIX A.

The CHEMKIN computer program package, as described in section 4.6, was used in interpreting and integrating the detailed reaction mechanism. This computer work was executed on the Digital Equipment Corporation (DEC) VAX/VMS V5.5 computer of NJIT.

5.2.2 Comparison of Prediction with Experimental Data

The detailed reaction mechanism, as shown in Table 5.8, was developed to describe the systems of reactions studied. For model prediction, the initial step, $\text{CH}_2\text{Cl}_2 = \text{CH}_2\text{Cl} + \text{Cl}$, was studied to determine the rate constants of the initiation reaction of CH_2Cl_2 .

Figure 5.26 compares model predictions with experimental data for CH_2Cl_2 decay in the $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ reaction system. As seen from Figure 5.26, model predictions for the net rates of CH_2Cl_2 decay are slower than those for experimental results. Figure 5.27 present the major products distribution of the model prediction. Figure 5.28 shows the comparison of prediction with experiment of major products (CH_3Cl and C_2HCl_3), model results match the experimental data at the temperatures below 780 °C. As the temperature increases above 780 °C, the model overpredicts the product levels.

Work on improvement of the model is ongoing and will (I hope) be reported in my Ph.D. thesis.

Table 5.3
Products Distribution in Varied Reaction Environments

Temperature = 760 °C

Reaction Time = 1.0 second

Species	Reaction Environments			
	I	II	III	IV
CH ₄	44.76%	47.75%		
C ₂ H ₂	XX	**	X	**
C ₂ H ₄	**		XX	*
CH ₃ Cl	XXX	XX	XXX	XXX
C ₂ HCl	**	**	**	**
C ₂ H ₃ Cl	XXX	**	XX	**
CH ₂ Cl ₂	26.93%	20.0%	35.41%	31.23%
CH ₂ CCl ₂	**	*	*	**
CHClCHCl	XXX	XXXX	XXXX	XXXX
C ₂ HCl ₃	XXX	XXXX	XXX	XXX
CHCl ₃			*	*
CO	XXXX	XXXX		
CO ₂	XX	XXX		

I. CH₂Cl₂ : CH₄ : O₂ : Ar = 1 : 1 : 4 : 94
 II. CH₂Cl₂ : CH₄ : Ar = 1 : 1 : 98
 III. CH₂Cl₂ : O₂ : Ar = 1 : 4 : 95
 IV. CH₂Cl₂ : Ar = 1 : 99

* < 0.1 < ** < 0.3 < X < 0.5
 0.5 < XX < 1.0 < XXX < 0.3 < XXXX

Percent = Carbon Mole / (CH₄ + CH₂Cl₂)_o

Table 5.4 Material Balance for 100 moles Carbon
in $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{O}_2/\text{Ar}$

$$\text{CH}_2\text{Cl}_2 : \text{CH}_4 : \text{O}_2 : \text{Ar} = 1 : 1 : 4 : 94$$

Reaction Time = 1.0 second

Species	Reaction Temperature ($^{\circ}\text{C}$)								
	680	700	720	740	760	780	800	820	840
CH_4	49.13	49.00	48.92	46.47	45.21	41.45	35.54	29.82	21.53
C_2H_2	0.01	0.03	0.09	0.19	0.52	1.27	2.74	3.92	3.91
C_2H_4	0.02	0.04	0.07	0.12	0.21	0.37	0.51	0.56	0.03
CH_3Cl	0.15	0.21	0.49	0.73	1.55	2.29	2.38	1.49	0.0
C_2HCl	0.0	0.0	0.0	0.0	0.16	0.25	0.41	0.23	0.0
$\text{C}_2\text{H}_3\text{Cl}$	0.11	0.18	0.40	0.69	1.23	1.73	1.66	0.82	0.0
CH_2Cl_2	47.70	46.53	44.41	37.38	26.67	14.46	3.44	0.52	0.11
C_2HCCl_2	0.0	0.0	0.0	0.0	0.12	0.25	0.59	0.65	0.0
CHCl_3	0.12	0.45	0.51	0.76	1.26	1.63	1.36	0.48	0.0
C_2HCl_3	0.23	0.51	1.08	1.64	2.79	3.34	2.20	0.70	0.0
C_6H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.05	0.04	0.0
CO	0.78	0.95	2.00	3.91	8.76	15.95	29.16	41.69	75.10
CO_2	0.0	0.05	0.09	0.19	0.69	1.50	2.36	4.31	11.59
Total	98.37	97.98	98.57	92.84	90.42	86.11	83.76	85.73	108.76

Table 5.5 Material Balance for 100 moles Carbon
in $\text{CH}_2\text{Cl}_2/\text{CH}_4/\text{Ar}$

$\text{CH}_2\text{Cl}_2 : \text{CH}_4 : \text{Ar} = 1 : 1 : 98$

Reaction Time = 1.0 sec

Species	Reaction Temperature ($^{\circ}\text{C}$)								
	680	700	720	740	760	780	800	820	840
CH_4	49.80	50.10	49.79	48.29	47.73	45.78	44.14	39.24	37.31
C_2H_2	0.0	0.02	0.04	0.11	0.30	0.75	1.86	3.27	5.27
C_2H_4	0.06	0.11	0.20	0.33	0.52	0.79	1.17	1.45	1.79
CH_3Cl	0.34	0.44	0.73	1.28	2.24	3.31	4.28	4.29	4.10
C_2HCl	0.0	0.0	0.0	0.0	0.13	0.24	0.40	0.64	0.84
$\text{C}_2\text{H}_3\text{Cl}$	0.07	0.12	0.24	0.46	0.88	1.28	1.59	1.37	0.75
CH_2Cl_2	47.35	47.69	42.97	40.94	35.41	25.82	14.03	7.55	3.13
C_2Cl_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.82	1.31
CH_2CCl_2	0.0	0.0	0.0	0.58	0.97	1.36	2.19	2.75	3.57
CHClCHCl	0.34	0.56	1.03	1.77	2.78	3.66	4.23	3.93	2.77
C_2HCl_3	0.12	0.24	0.50	0.85	1.63	2.33	2.64	2.29	1.52
CHCl_3	0.0	0.0	0.0	0.0	0.06	0.18	0.15	0.22	0.13
C_6H_6	0.0	0.0	0.0	0.0	0.0	0.04	0.11	0.02	0.03
Total	98.10	99.31	96.41	94.09	91.84	84.68	74.91	65.55	59.67

Table 5.6 Material Balance for 100 moles Carbon
in $\text{CH}_2\text{Cl}_2/\text{O}_2/\text{Ar}$

$\text{CH}_2\text{Cl}_2 : \text{O}_2 : \text{Ar} = 1 : 4 : 95$

Reaction Time = 1.0 second

Species	Reaction Temperature ($^{\circ}\text{C}$)							
	680	700	720	740	760	780	800	820
C_2H_2	0.0	0.0	0.04	0.11	0.35	0.85	0.37	0.04
C_2H_4	0.03	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_3Cl	0.16	0.32	0.61	1.08	1.79	0.0	0.0	0.0
C_2HCl	0.0	0.0	0.0	0.16	0.43	0.0	0.0	0.0
$\text{C}_2\text{H}_3\text{Cl}$	0.0	0.0	0.0	0.14	0.26	0.0	0.0	0.0
CH_2Cl_2	93.33	91.44	89.08	69.81	39.55	3.42	0.22	0.0
CH_2CCl_2	0.0	0.0	0.0	0.33	0.18	0.0	0.0	0.0
CHClCHCl	0.55	2.02	2.49	4.03	7.22	0.0	0.0	0.0
C_2HCl_3	0.54	1.40	3.20	5.47	9.75	1.53	0.0	0.0
CO	1.16	2.04	4.52	9.25	22.26	67.99	75.40	77.18
CO_2	0.0	0.0	0.40	0.50	2.12	8.47	9.33	14.40
C_2Cl_4	0.0	0.0	0.0	0.0	0.0	0.0	0.48	0.0
Total	95.78	97.23	100.00	90.90	83.95	82.28	85.34	91.63

Table 5.7 Material Balance for 100 moles Carbon
in $\text{CH}_2\text{Cl}_2/\text{Ar}$

$\text{CH}_2\text{Cl}_2 : \text{Ar} = 1 : 99$

Reaction Time = 1.0 sec

Species	Reaction Temperature ($^{\circ}\text{C}$)								
	680	700	720	740	760	780	800	820	840
C_2H_2	0.0	0.0	0.0	0.10	0.23	0.53	1.34	2.43	3.43
C_2H_4	0.0	0.0	0.0	0.46	0.23	0.67	0.94	0.03	0.0
CH_3Cl	0.51	0.78	1.33	2.24	3.64	4.13	1.82	0.0	0.0
C_2HCl	0.0	0.0	0.0	0.0	0.23	0.52	1.71	4.71	5.70
$\text{C}_2\text{H}_3\text{Cl}$	0.0	0.13	0.23	0.40	0.59	0.76	0.76	0.19	0.0
C_2Cl_2	0.0	0.0	0.0	0.0	0.0	0.0	0.80	0.99	0.82
CH_2Cl_2	94.49	93.93	87.32	77.92	62.47	33.94	5.71	0.0	0.0
CH_2CCL_2	0.0	0.0	0.0	0.08	0.21	0.19	0.42	0.46	0.32
CHClCHCl	0.77	1.47	2.71	4.66	7.63	10.10	9.76	2.97	0.57
C_2HCl_3	0.38	0.71	1.43	2.87	5.33	8.06	8.73	6.52	4.18
Total	96.15	97.08	93.04	88.36	80.55	58.59	31.72	19.72	18.87

Fig 5.1-1 Experimental Result
Decay of CH₂Cl₂ vs Time/Temp

Ar:O₂:CH₄:CH₂Cl₂=94:4:1:1

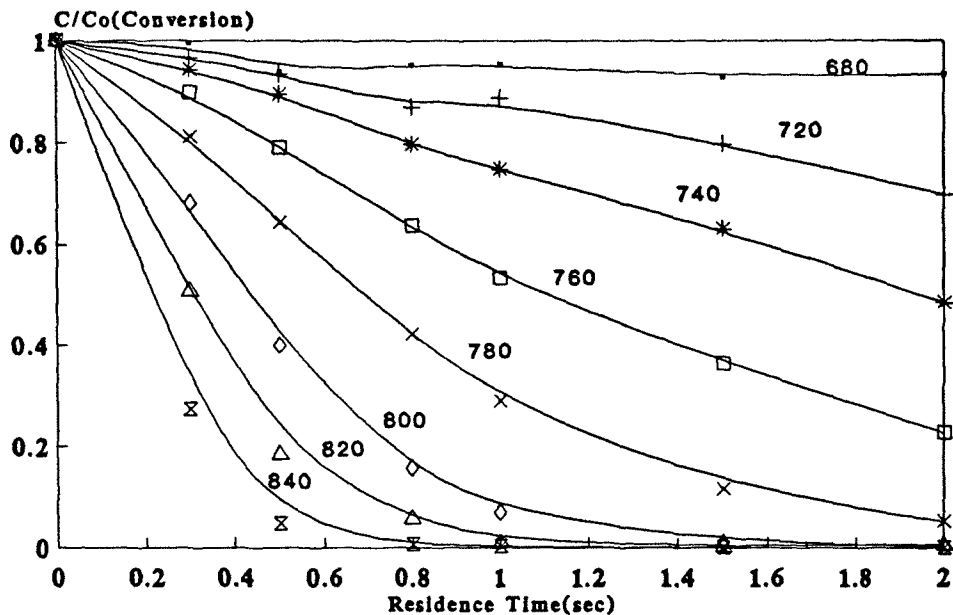


Fig 5.1-2 Experimental Result
Decay of CH₂Cl₂ vs Time/Temp

Ar:CH₄:CH₂Cl₂=98:1:1

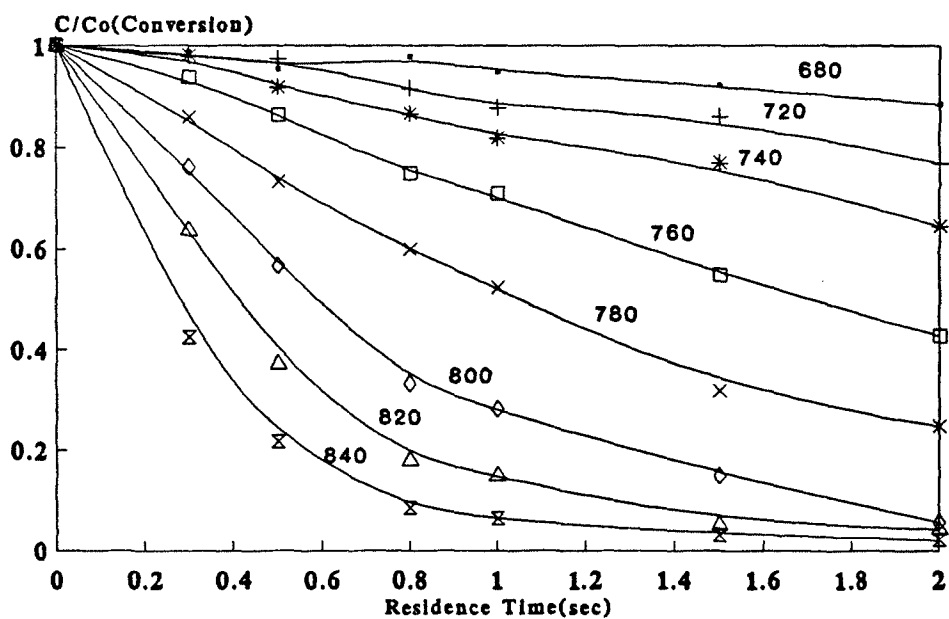


Fig 5.1-3 Experimental Result
Decay of CH₂Cl₂ vs Time/Temp

Ar:O₂:CH₂Cl₂=95:4:1

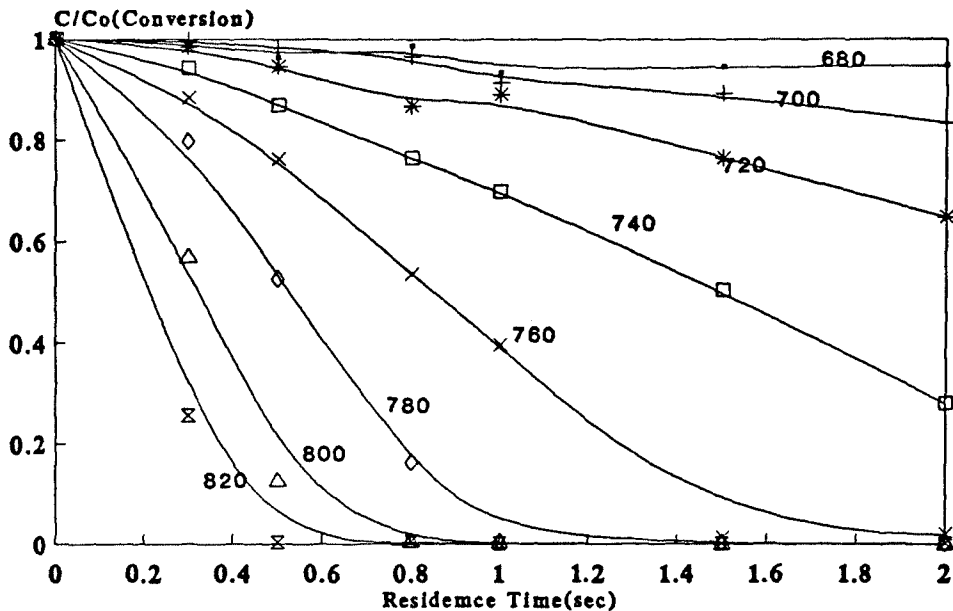


Fig 5.1-4 Experimental Result
Decay of CH₂Cl₂ vs Time/Temp

Ar:CH₂Cl₂=99:1

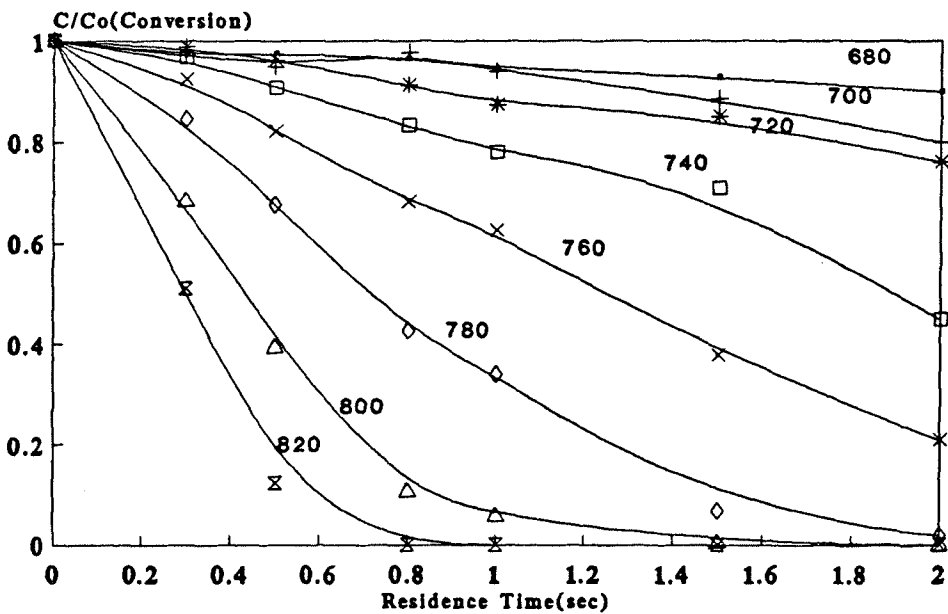


Fig 5.2-1 Decay of DCM vs Temperature
in Different Reaction Environments

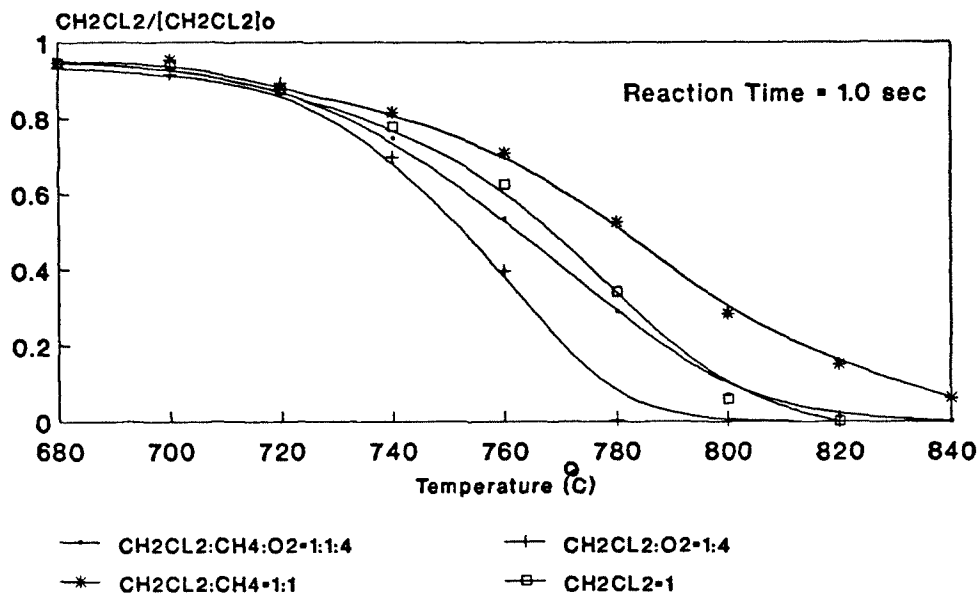


Fig 5.2-2 Decay of DCM vs Time
in Different Reaction Environments

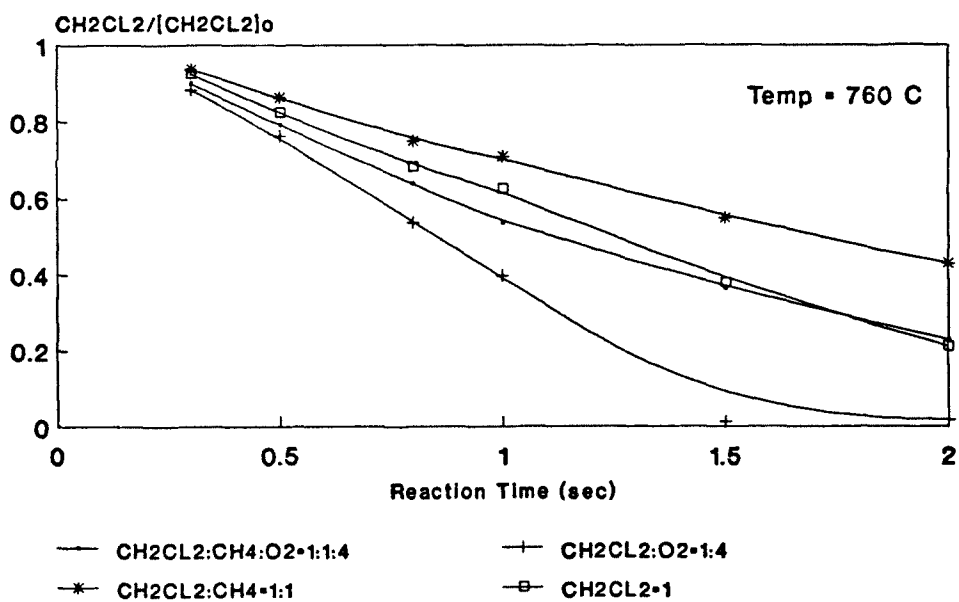


Fig 5.3-1 Decay of CH₄ vs Temperature
in Different Reaction Environments

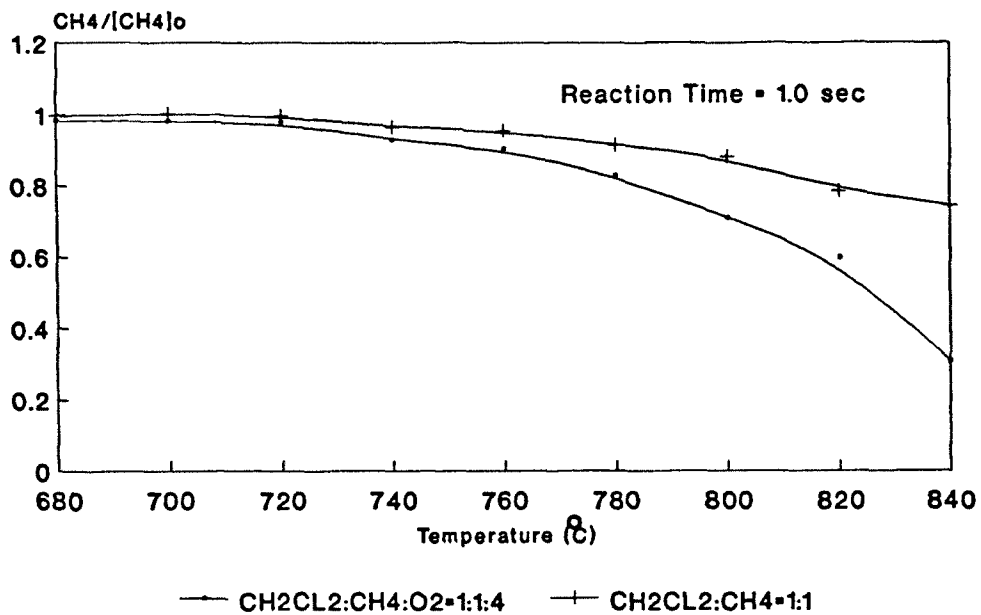


Fig 5.3-2 Decay of CH₄ vs Time
in Different Reaction Environments

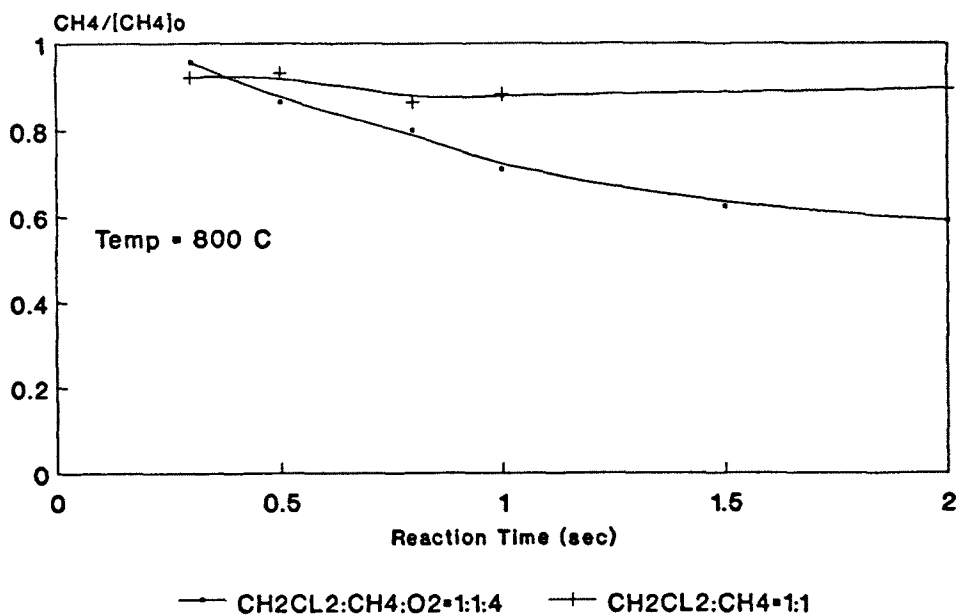


Fig 5.4-1 First Order Decay Plot
DCM vs Time/Temp

Ar:O₂:CH₄:CH₂Cl₂=94:4:1:1

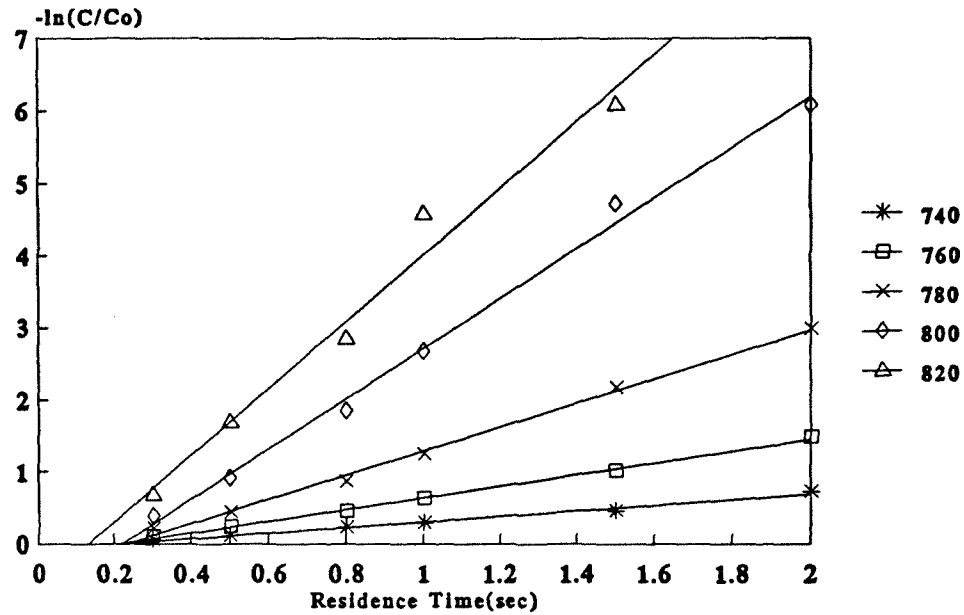


Fig 5.4-2 First Order Decay Plot
DCM vs Time/Temp

Ar:CH₄:CH₂Cl₂=98:1:1

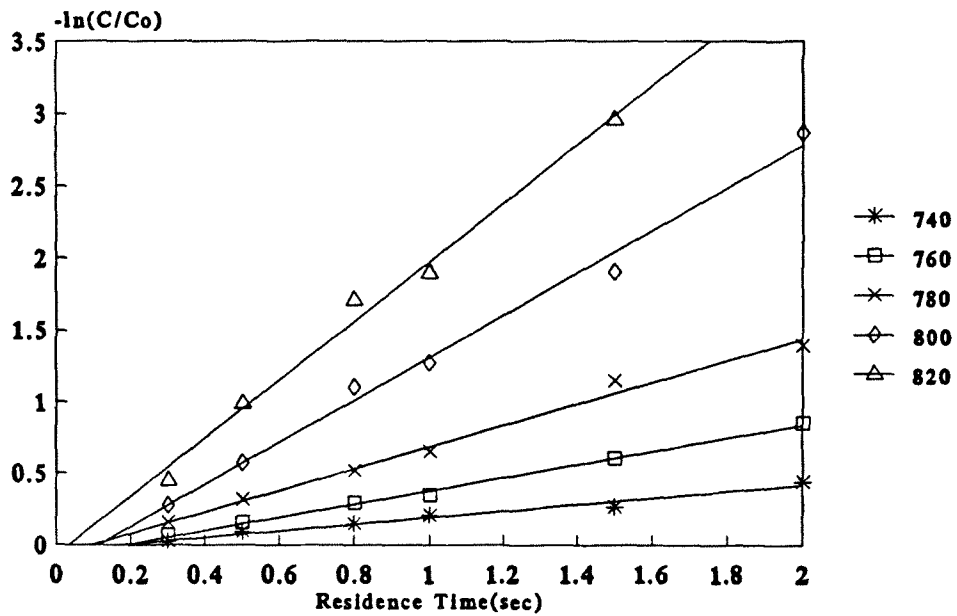


Fig 5.4-3 First Order Decay Plot
DCM vs Time/Temp

Ar:O₂:CH₂Cl₂=95:4:1

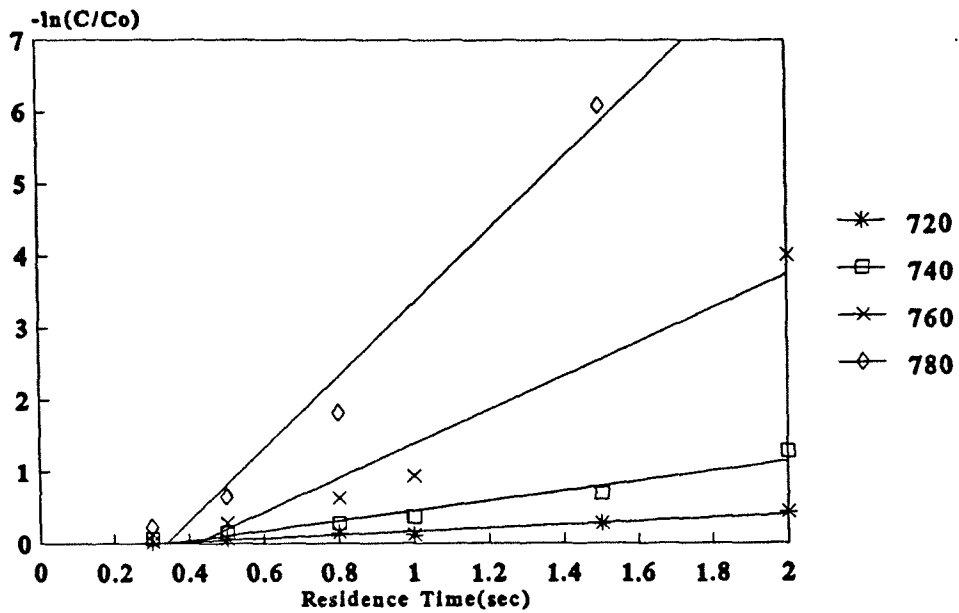
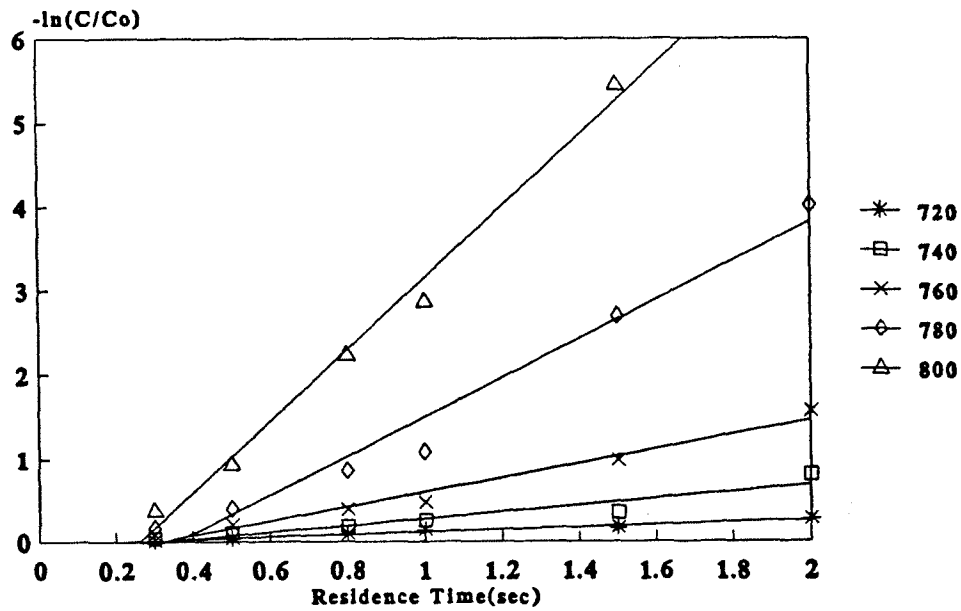
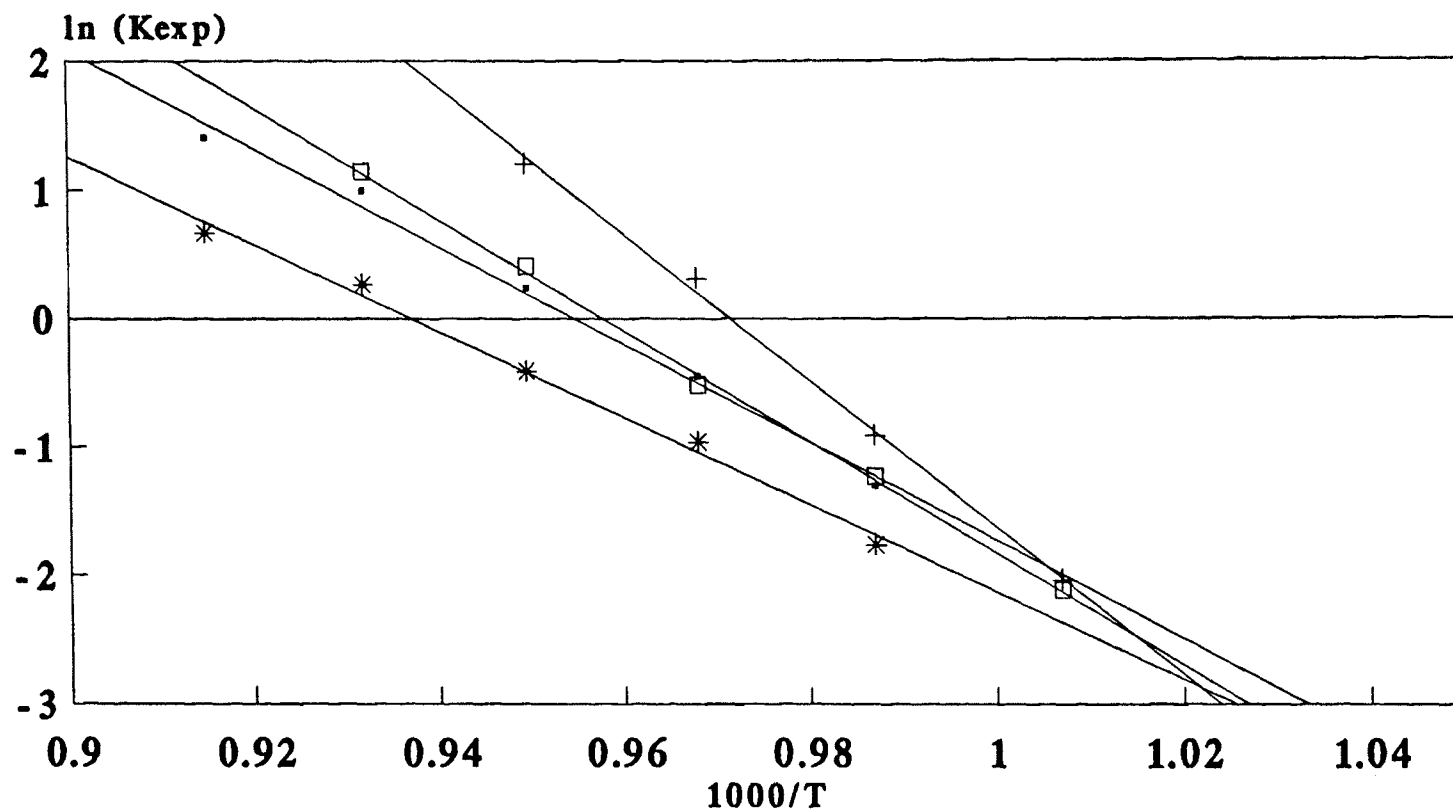


Fig 5.4-4 First Order Decay Plot
DCM vs Time/Temp

Ar:CH₂Cl₂=99:1





- $\text{CH}_2\text{CL}_2:\text{CH}_4:\text{O}_2=1:1:4$
- *— $\text{CH}_2\text{CL}_2:\text{CH}_4=1:1$
- +— $\text{CH}_2\text{CL}_2:\text{O}_2=1:4$
- $\text{CH}_2\text{CL}_2=1$

Fig 5.5 Arrhenius Behavior of K_{exp} for CH_2CL_2 in Different Reaction Environments

Fig 5.6 Product Distribution vs Temp
in CH₂CL₂/CH₄/O₂/Ar

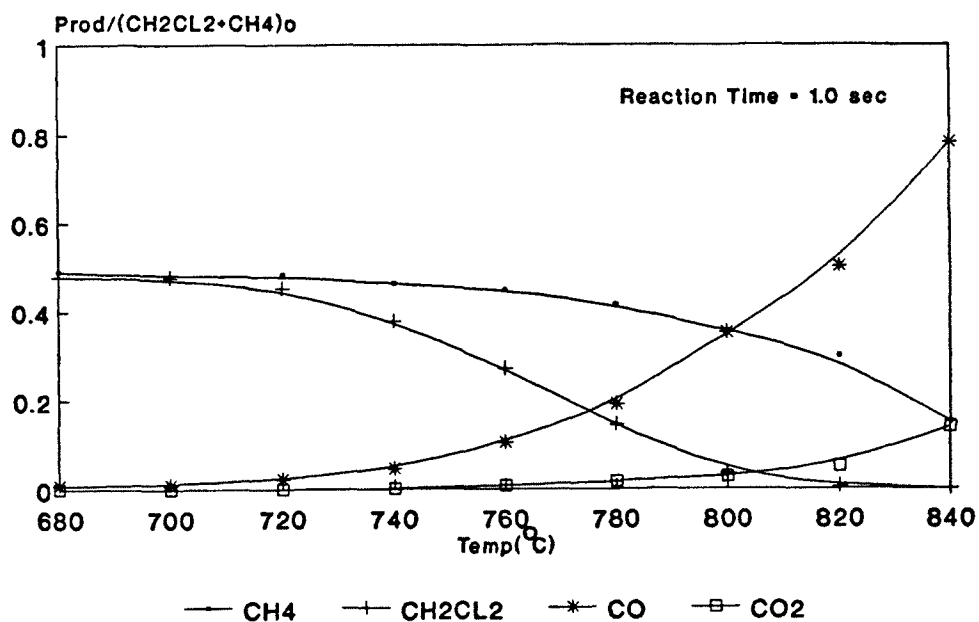
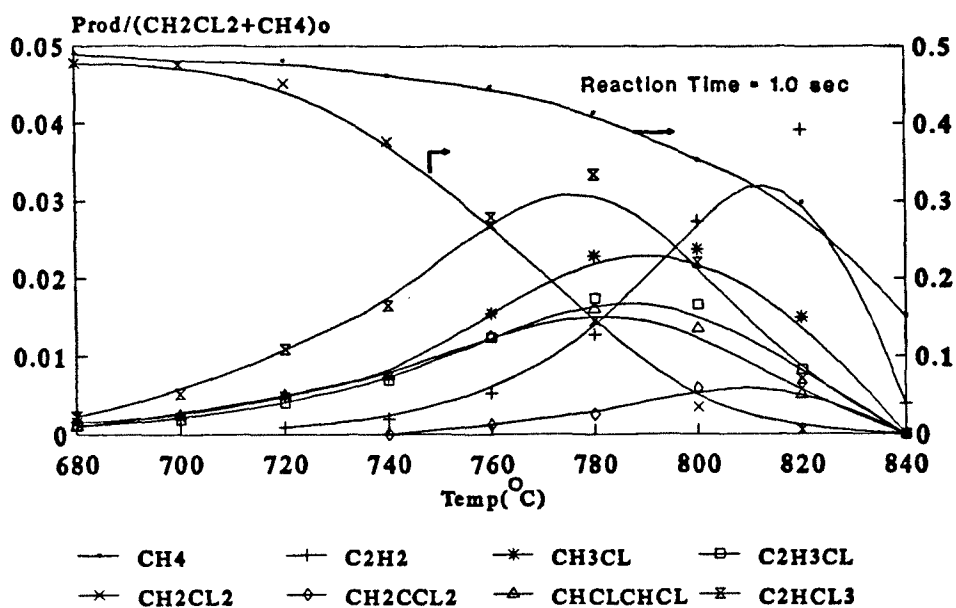


Fig 5.7 Product Distribution vs Time
in CH₂CL₂/CH₄/O₂/Ar

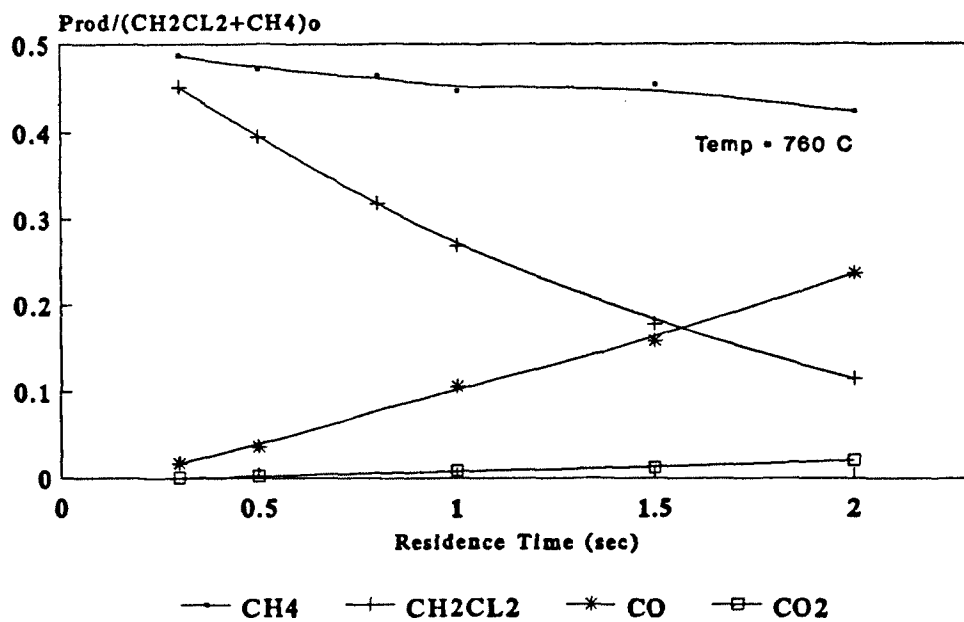
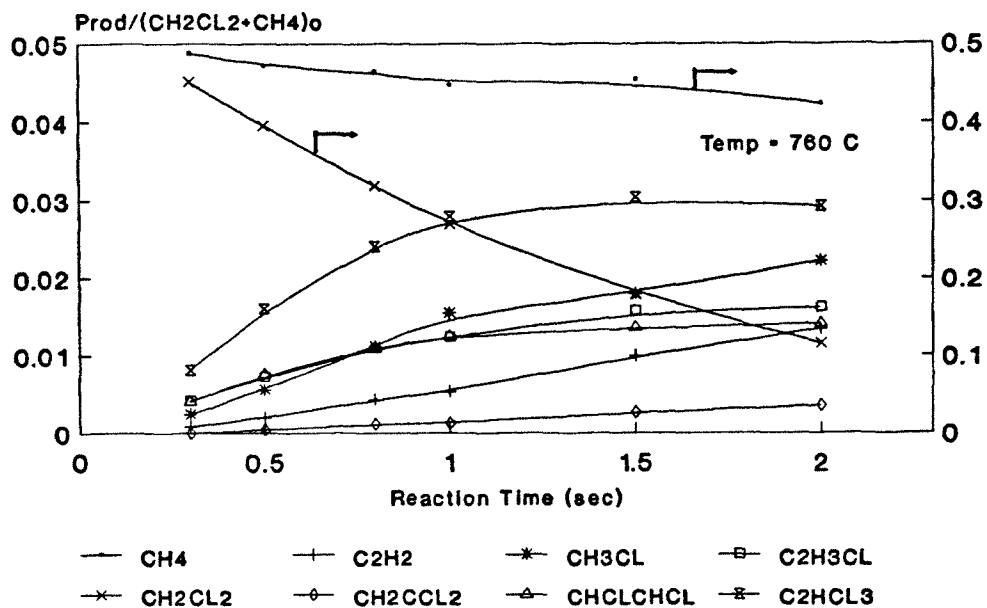


Fig 5.8 Product Distribution vs Temp
in CH₂CL₂/CH₄/Ar

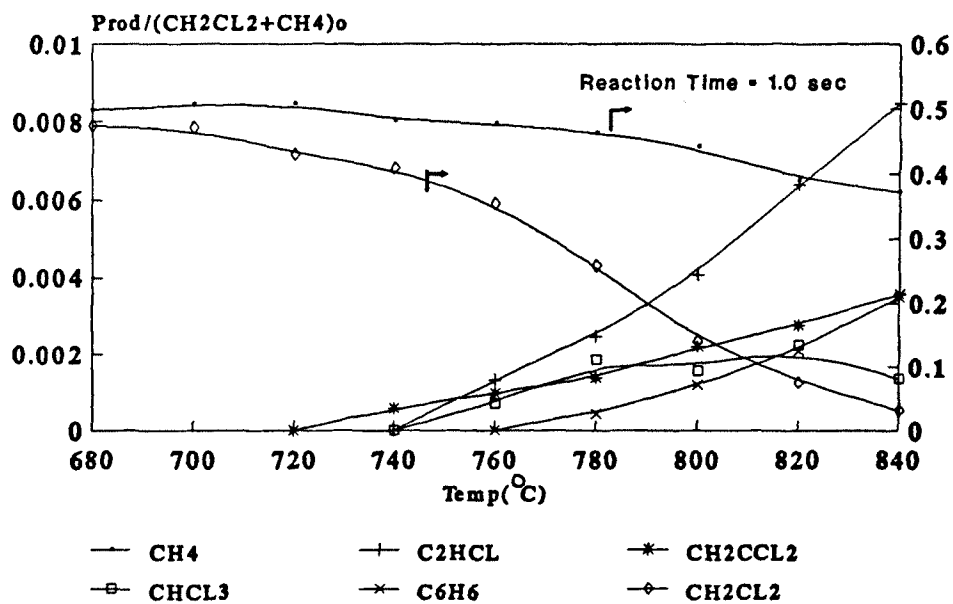
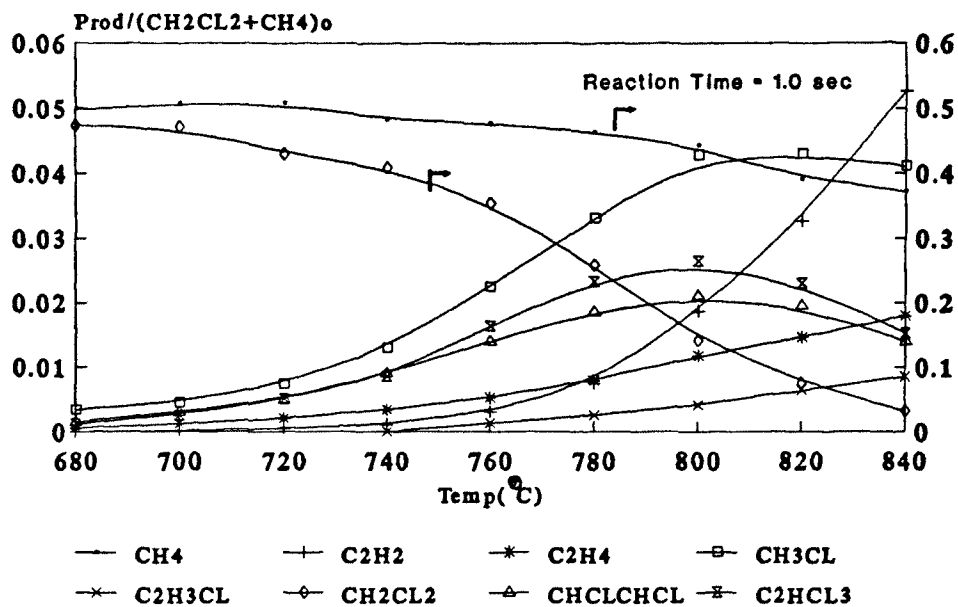


Fig 5.9 Product Distribution vs Time
in CH₂CL₂/CH₄/Ar

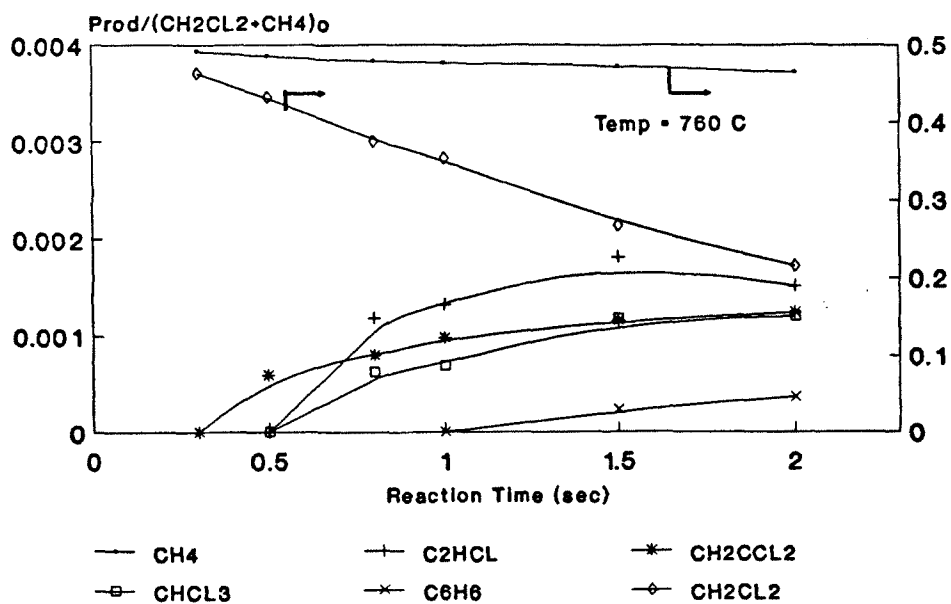
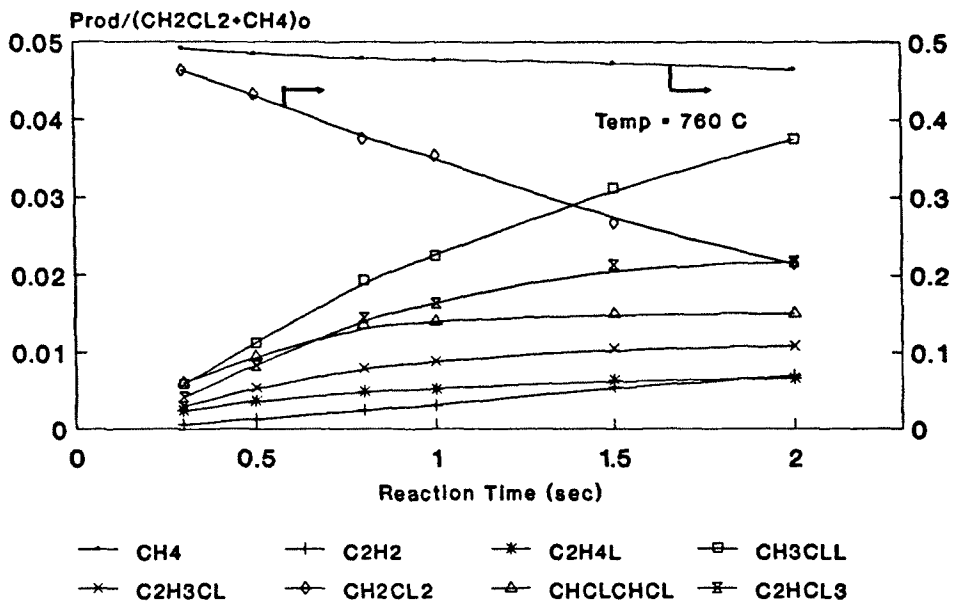


Fig 5.10 Product Distribution vs Temp
in CH₂CL₂/O₂/Ar

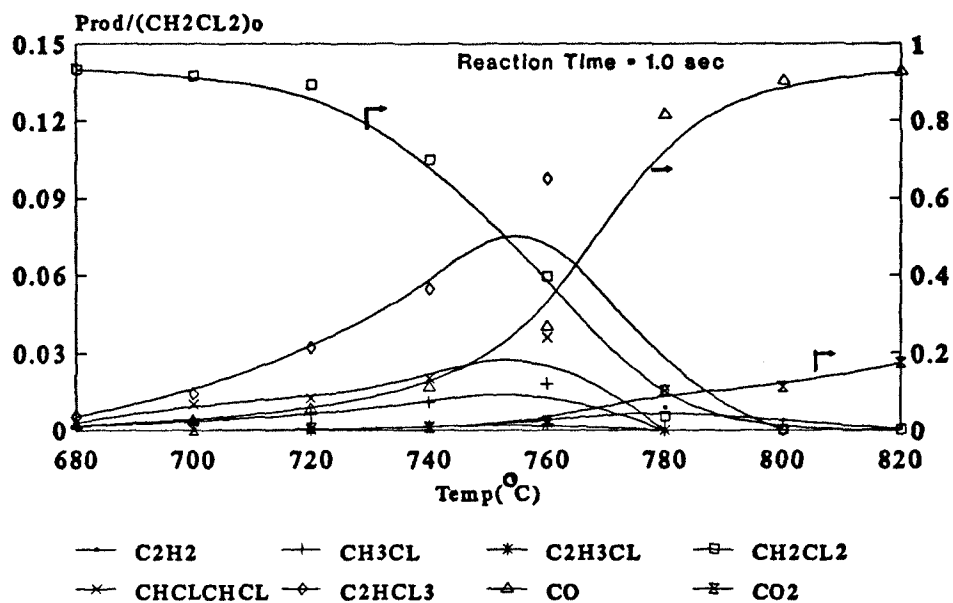


Fig 5.11 Product Distribution vs Time
in CH₂CL₂/O₂/Ar

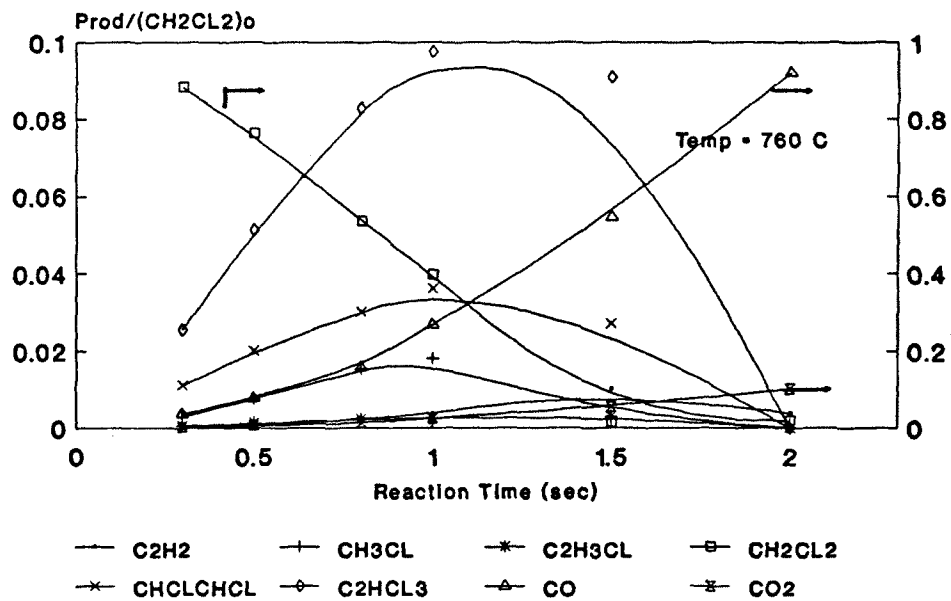


Fig 5.12 Product Distribution vs Temp
in CH₂CL₂/Ar

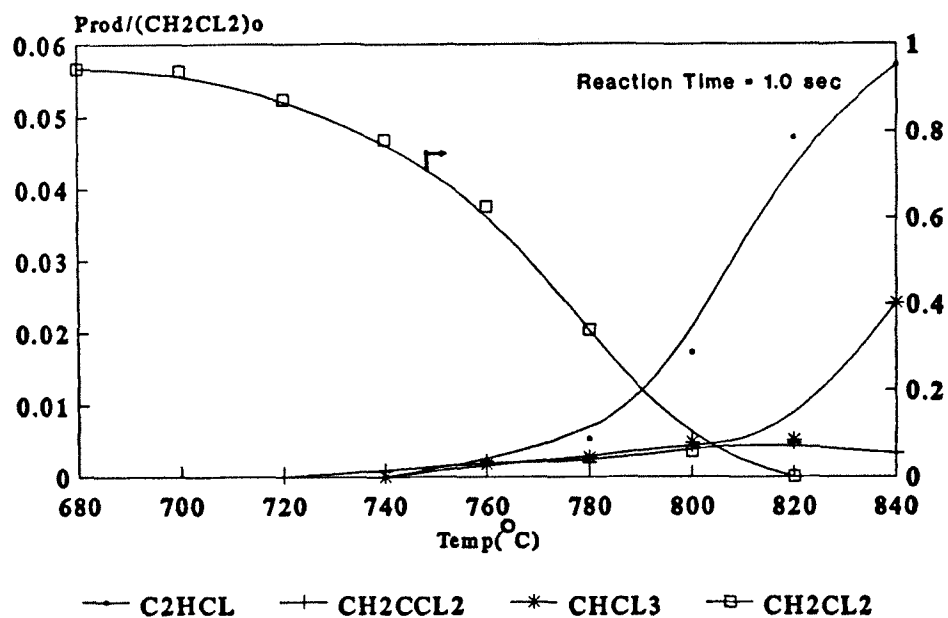
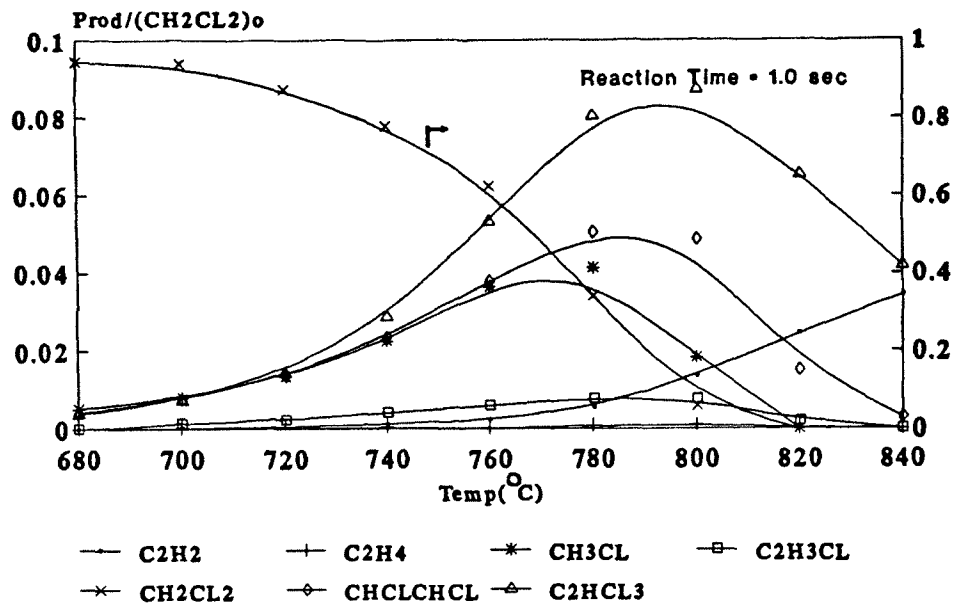


Fig 5.13 Product Distribution vs Time
in CH₂CL₂/Ar

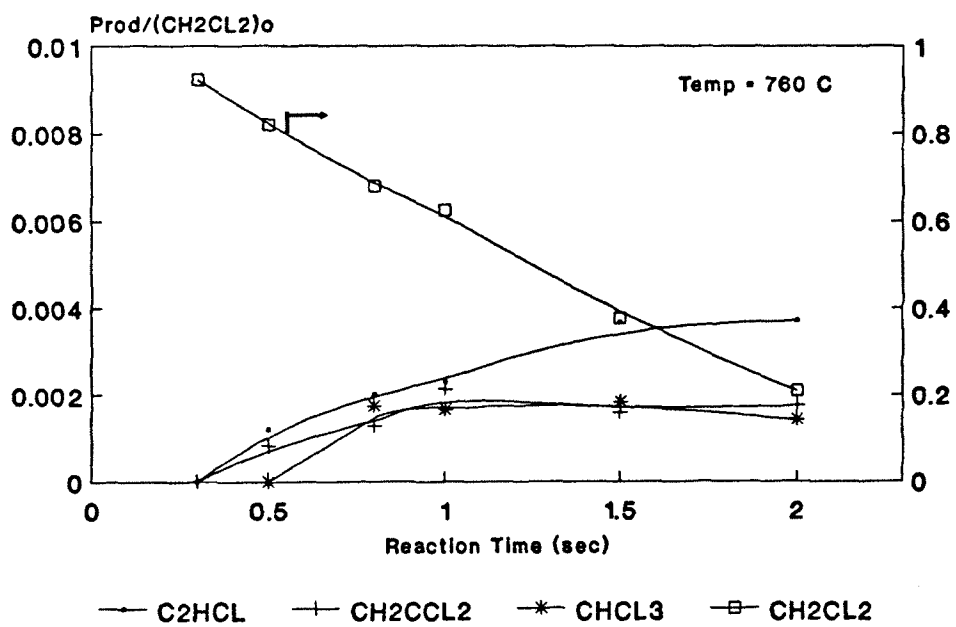
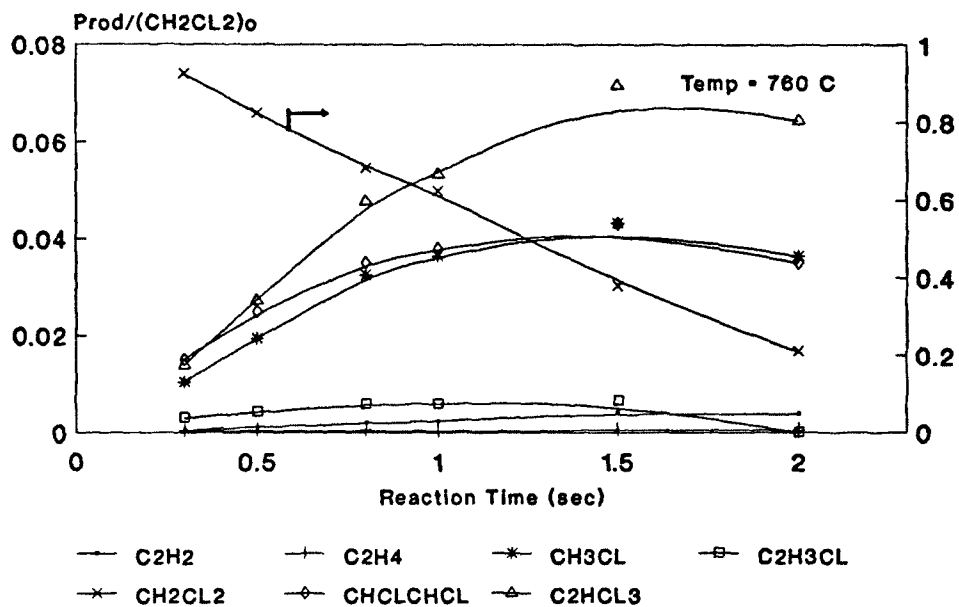


Fig 5.14-1 C₂HCL₃ Formed Distribution vs Temp.
in Different Reaction Environments

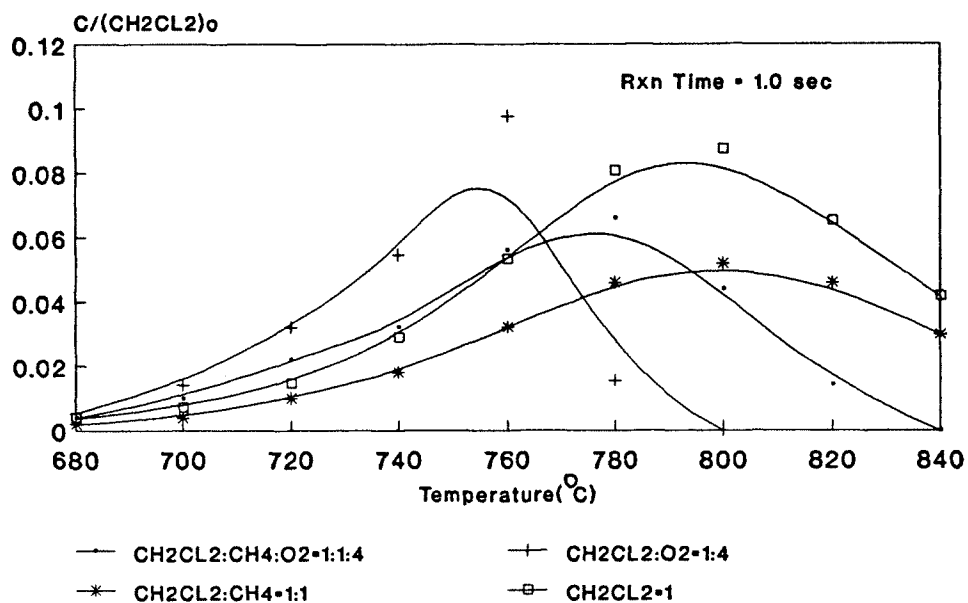


Fig 5.14-2 C₂HCL₃ Formed Distribution vs Time.
in Different Reaction Environments

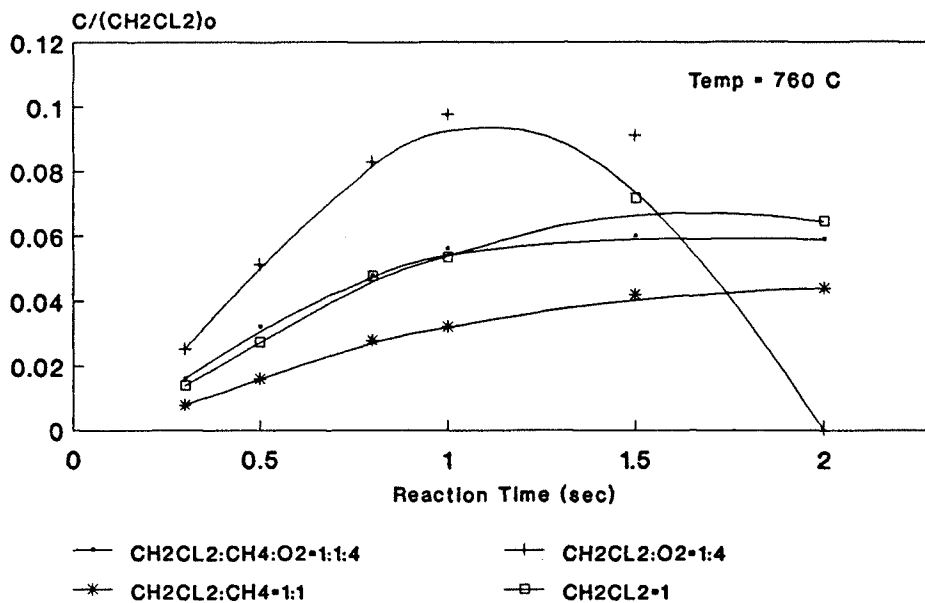


Fig 5.15-1 CH₃CL Formed Distribution vs Temp.
in Different Reaction Environments

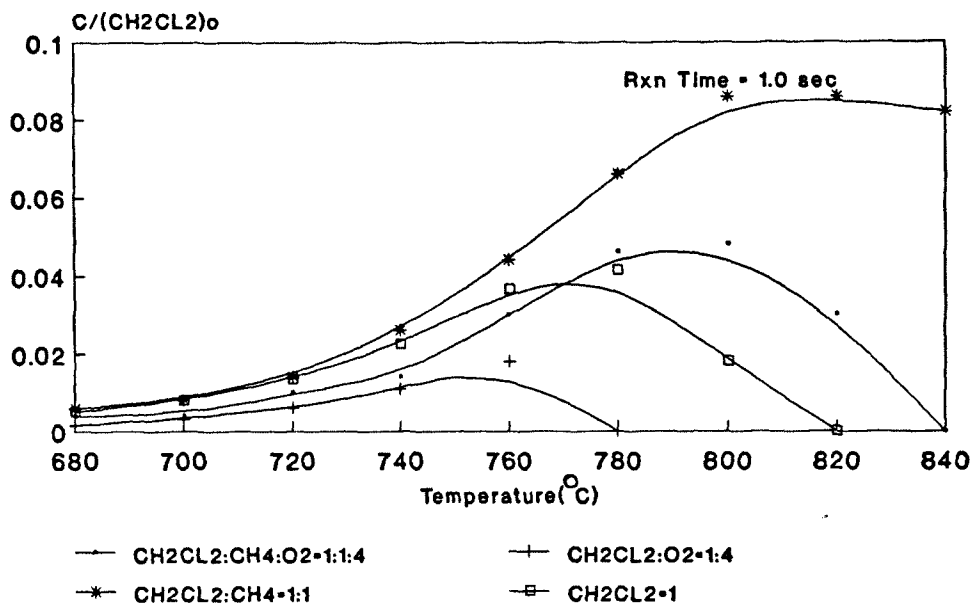


Fig 5.15-2 CH₃CL Formed Distribution vs Time.
in Different Reaction Environments

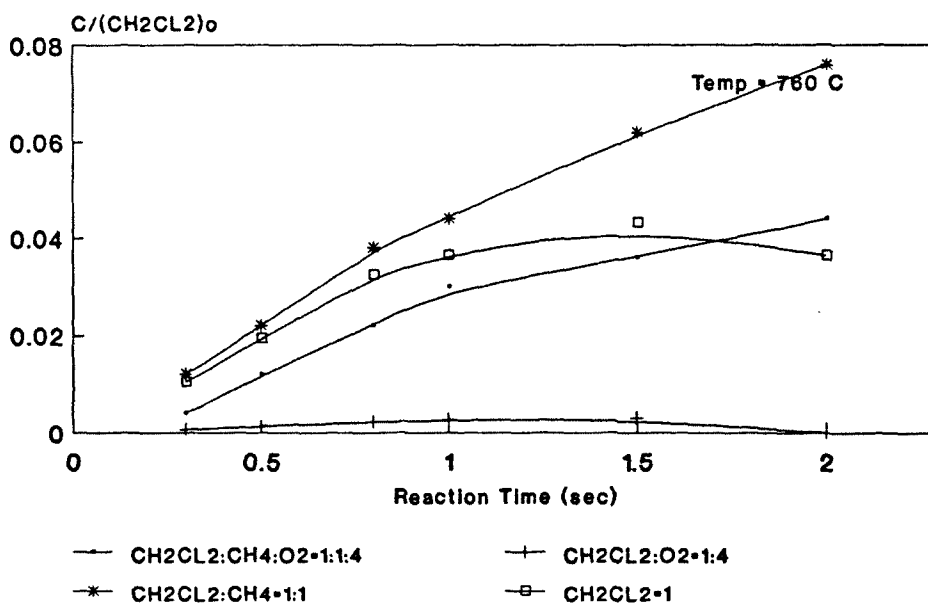


Fig 5.16-1 C₂H₃CL Formed Distribution vs Temp.
in Different Reaction Environments

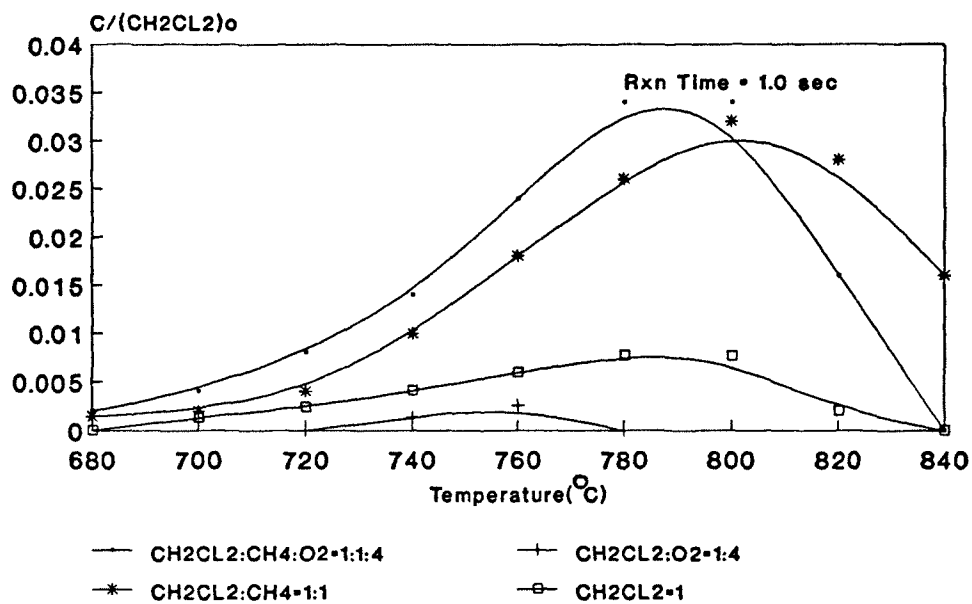


Fig 5.16-2 C₂H₃CL Formed Distribution vs Time.
in Different Reaction Environments

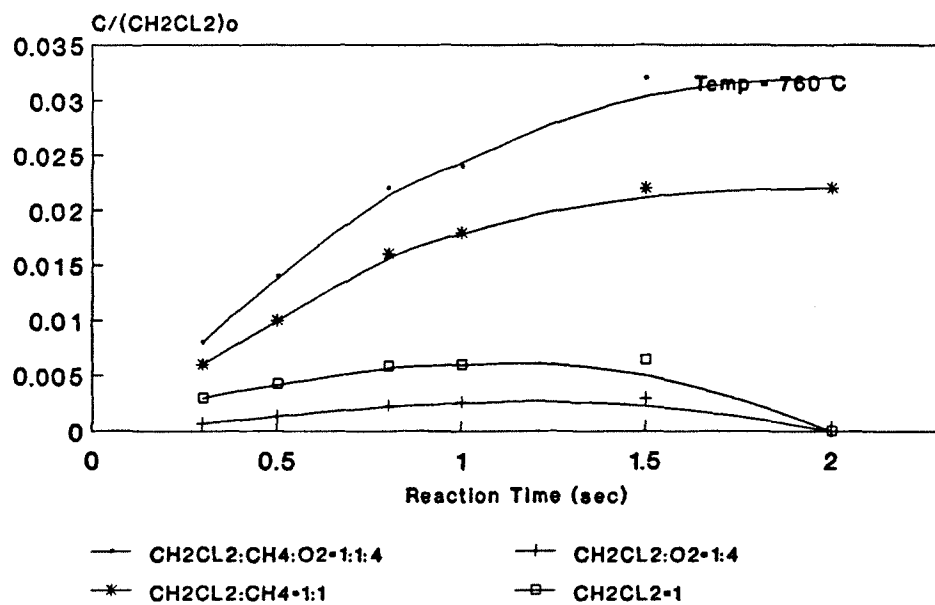


Fig 5.17-1 CHCLCHCL Formed Distribution vs Temp.
in Different Reaction Environments

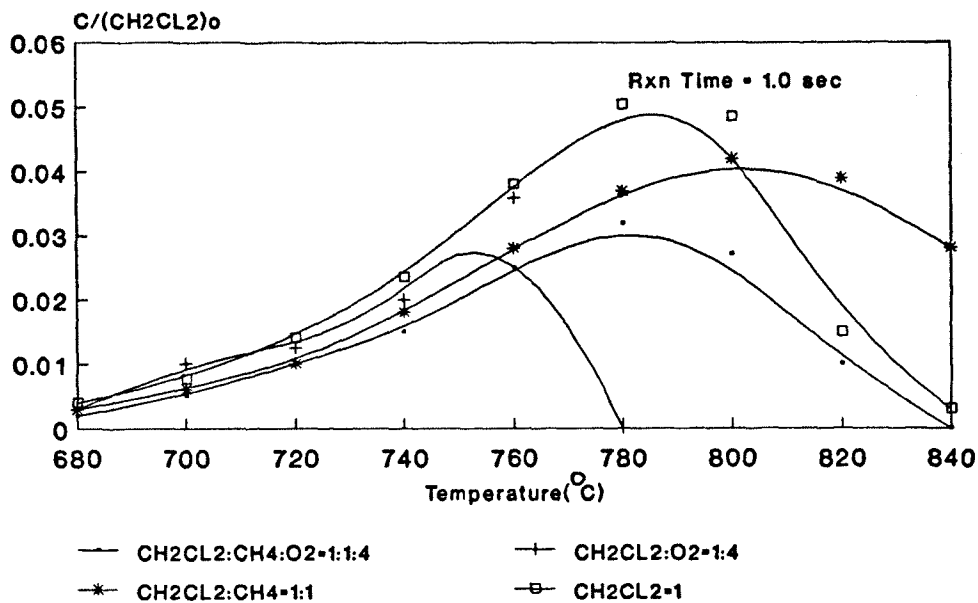


Fig 5.17-2 CHCLCHCL Formed Distribution vs Time.
in Different Reaction Environments

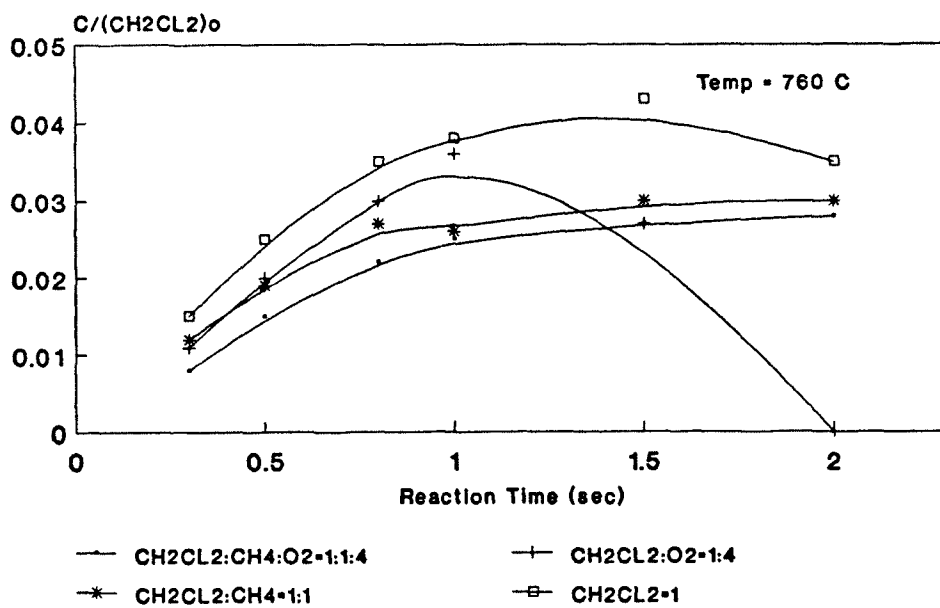


Fig 5.18-1 C₂H₂ Formed Distribution vs Temp.
in Different Reaction Environments

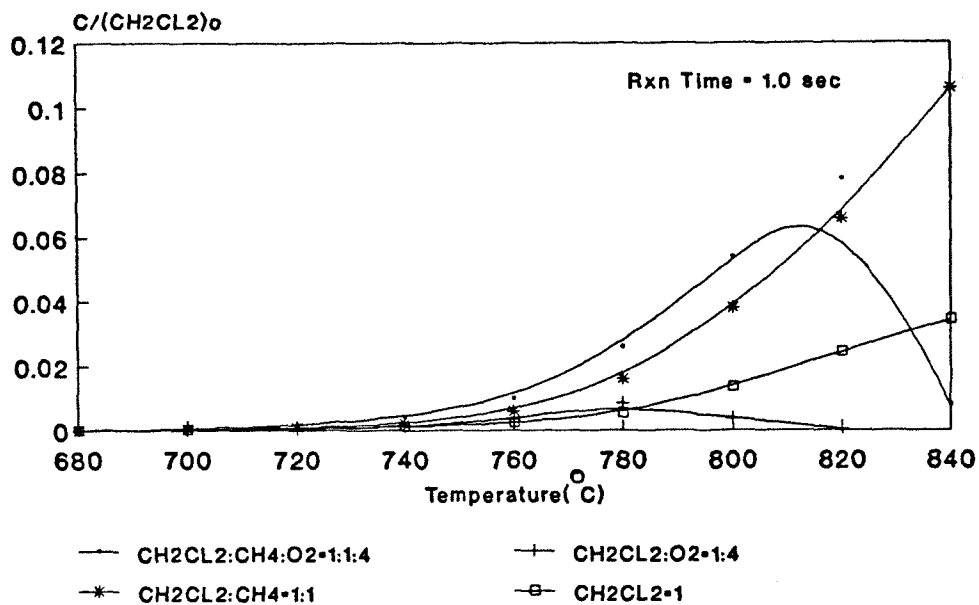


Fig 5.18-2 C₂H₂ Formed Distribution vs Time.
in Different Reaction Environments

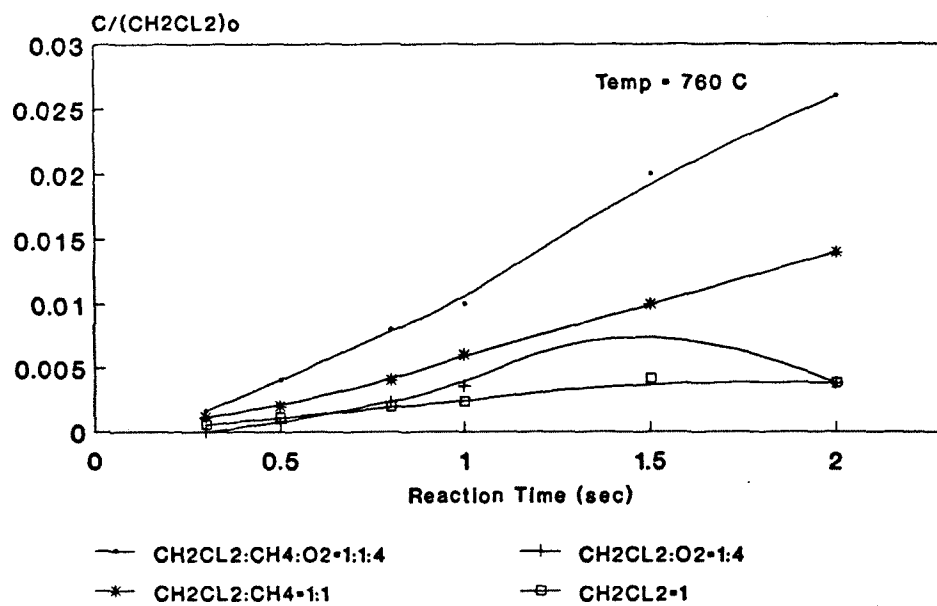


Fig 5.19-1 CO Formed Distribution vs Temp.
in Different Reaction Environments

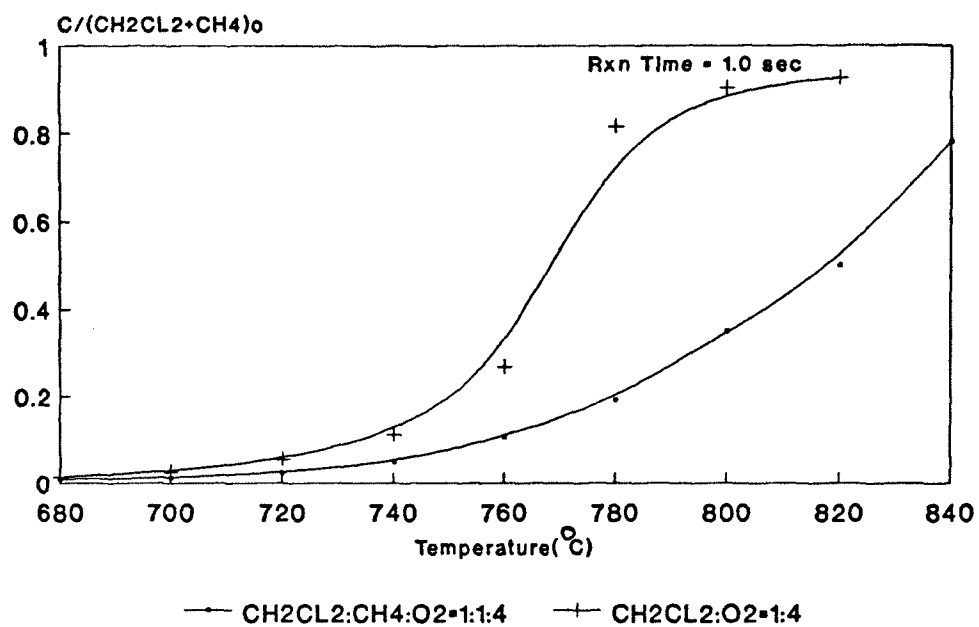


Fig 5.19-2 CO Formed Distribution vs Time.
in Different Reaction Environments

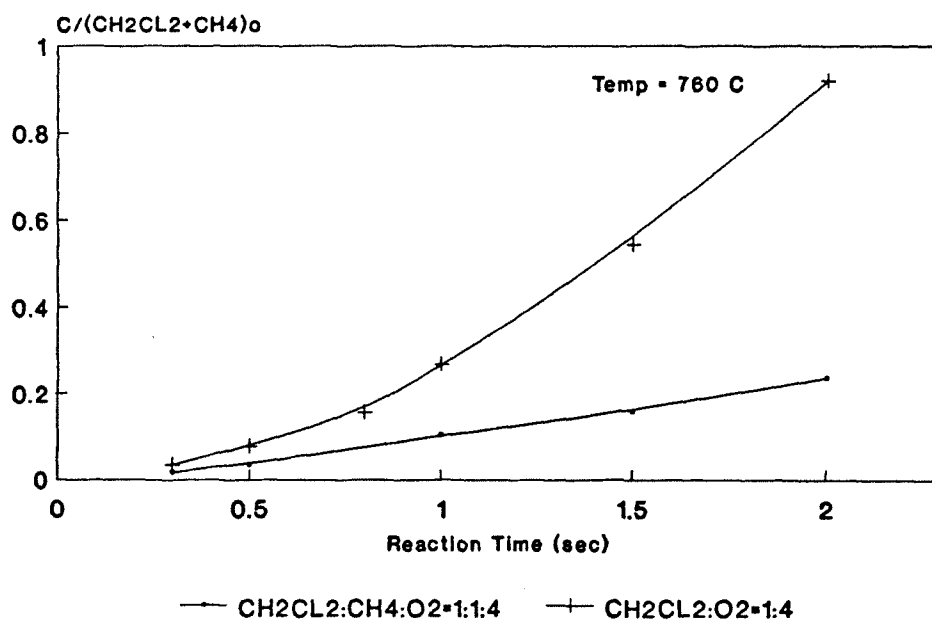


Fig 5.20-1 CO₂ Formed Distribution vs Temp.
in Different Reaction Environments

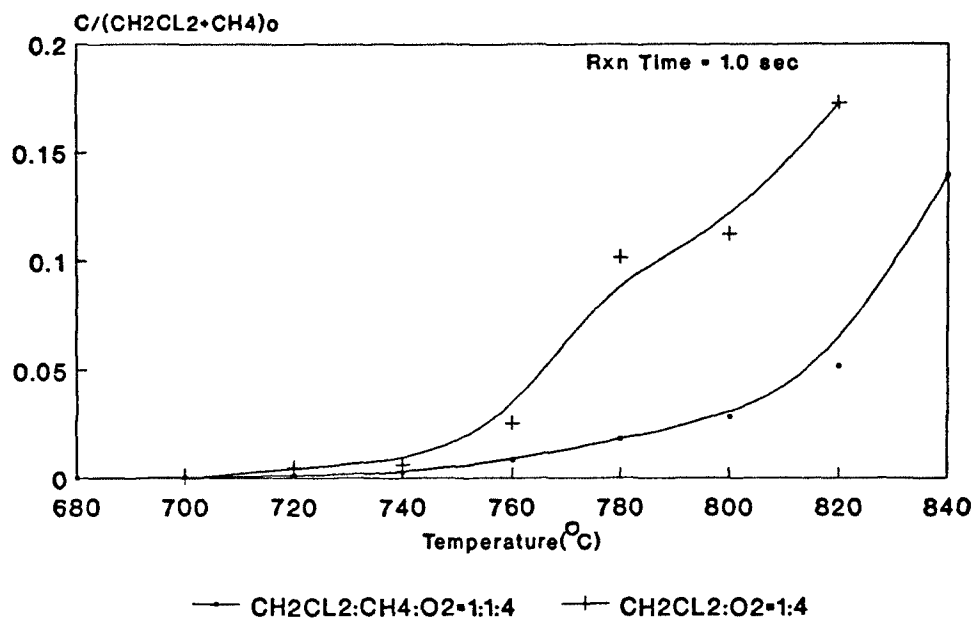
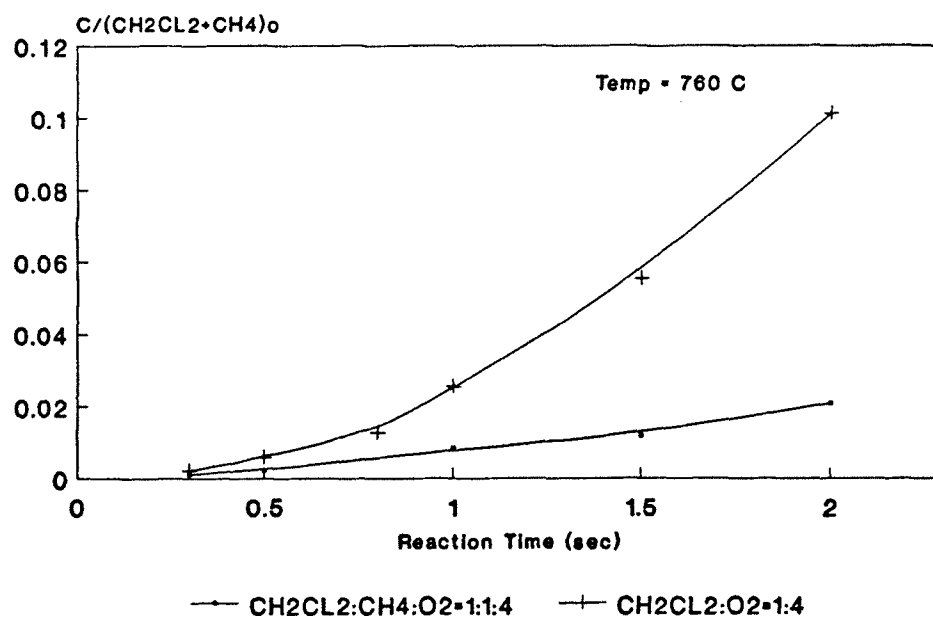


Fig 5.20-2 CO₂ Formed Distribution vs Time.
in Different Reaction Environments



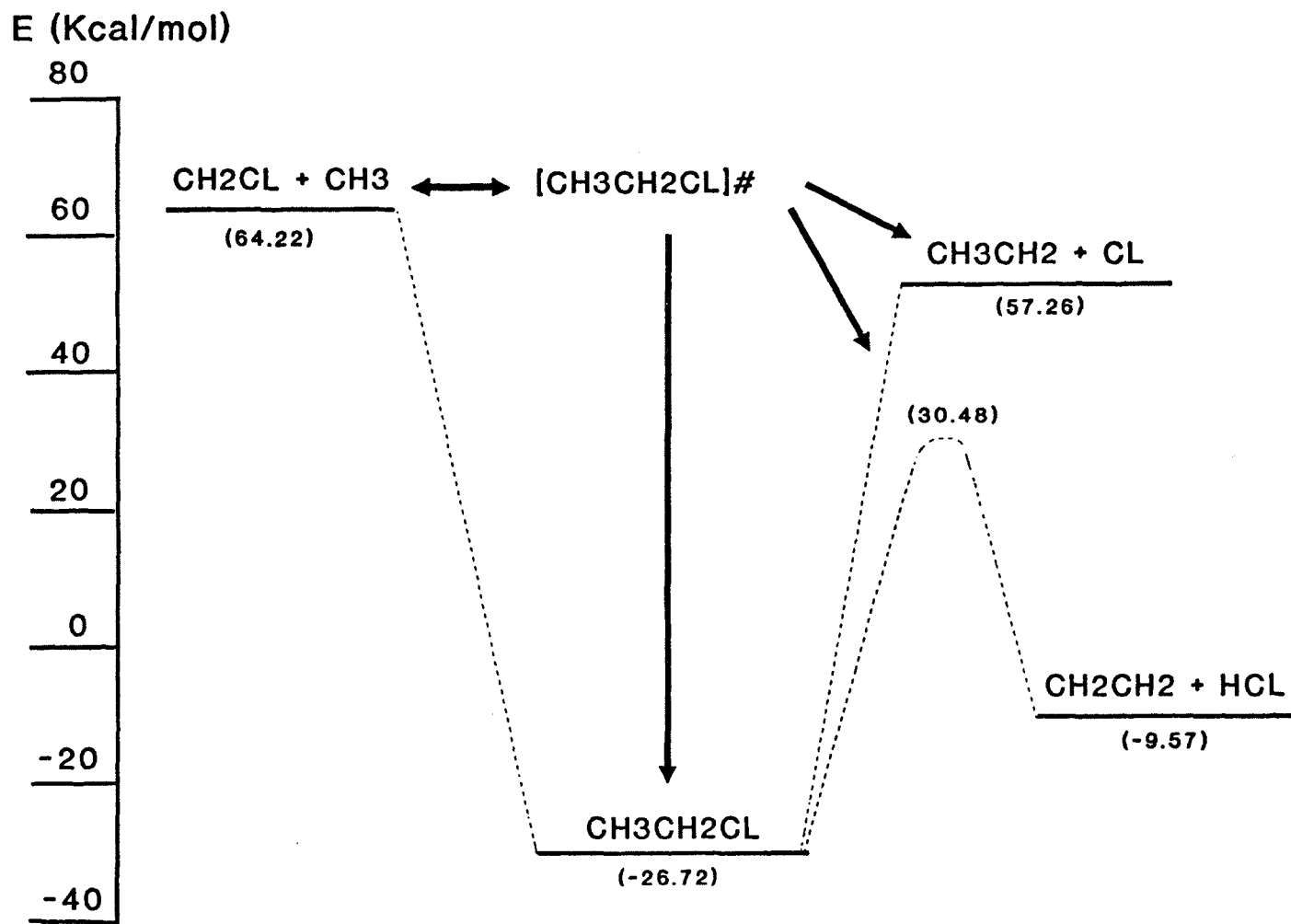


Fig 5.21 Potential Energy Diagram for $\text{CH}_3 + \text{CH}_2\text{Cl}$

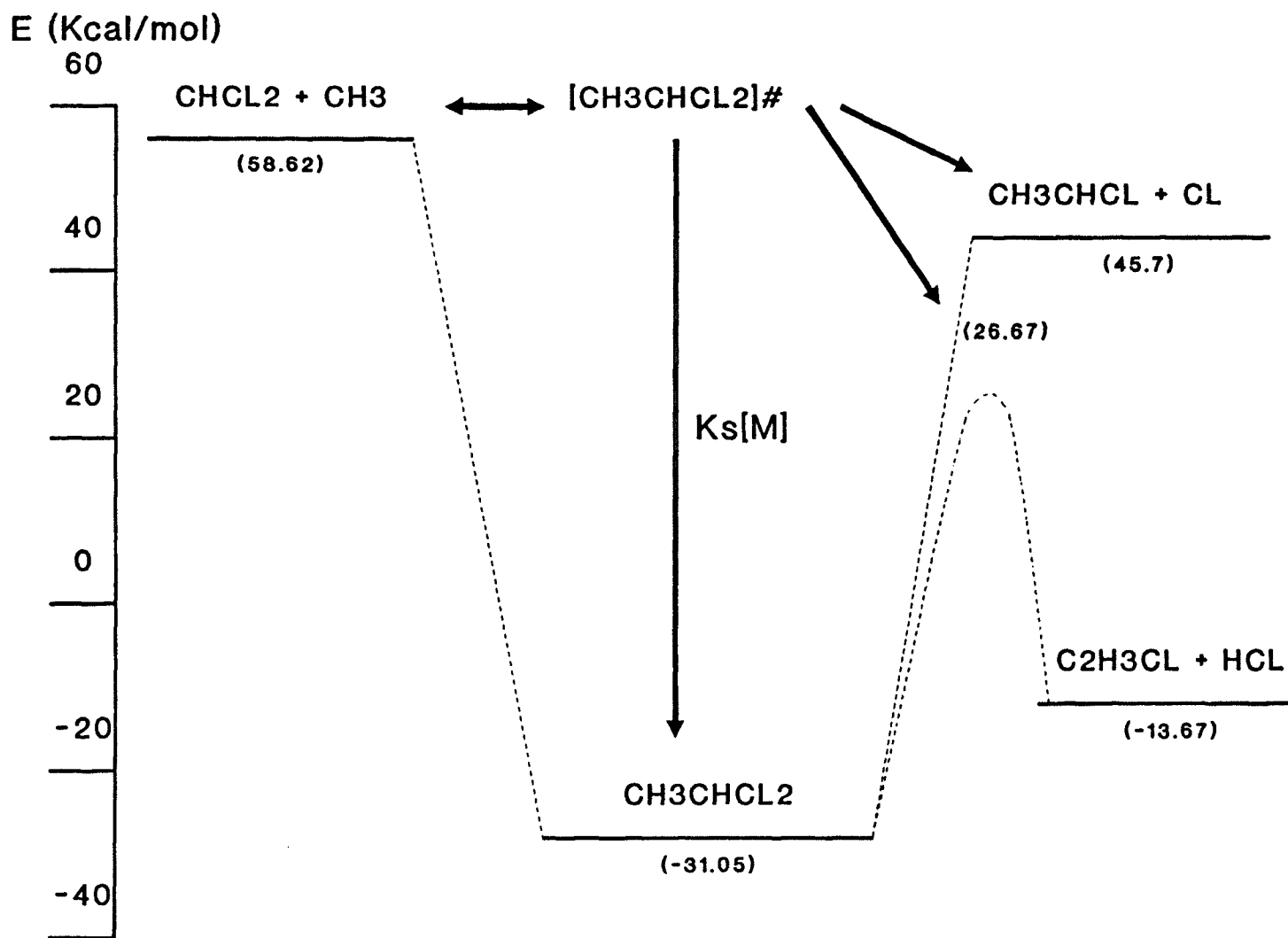


Figure 5.22 Potential Energy Diagram for CH₂Cl₂ + CH₃

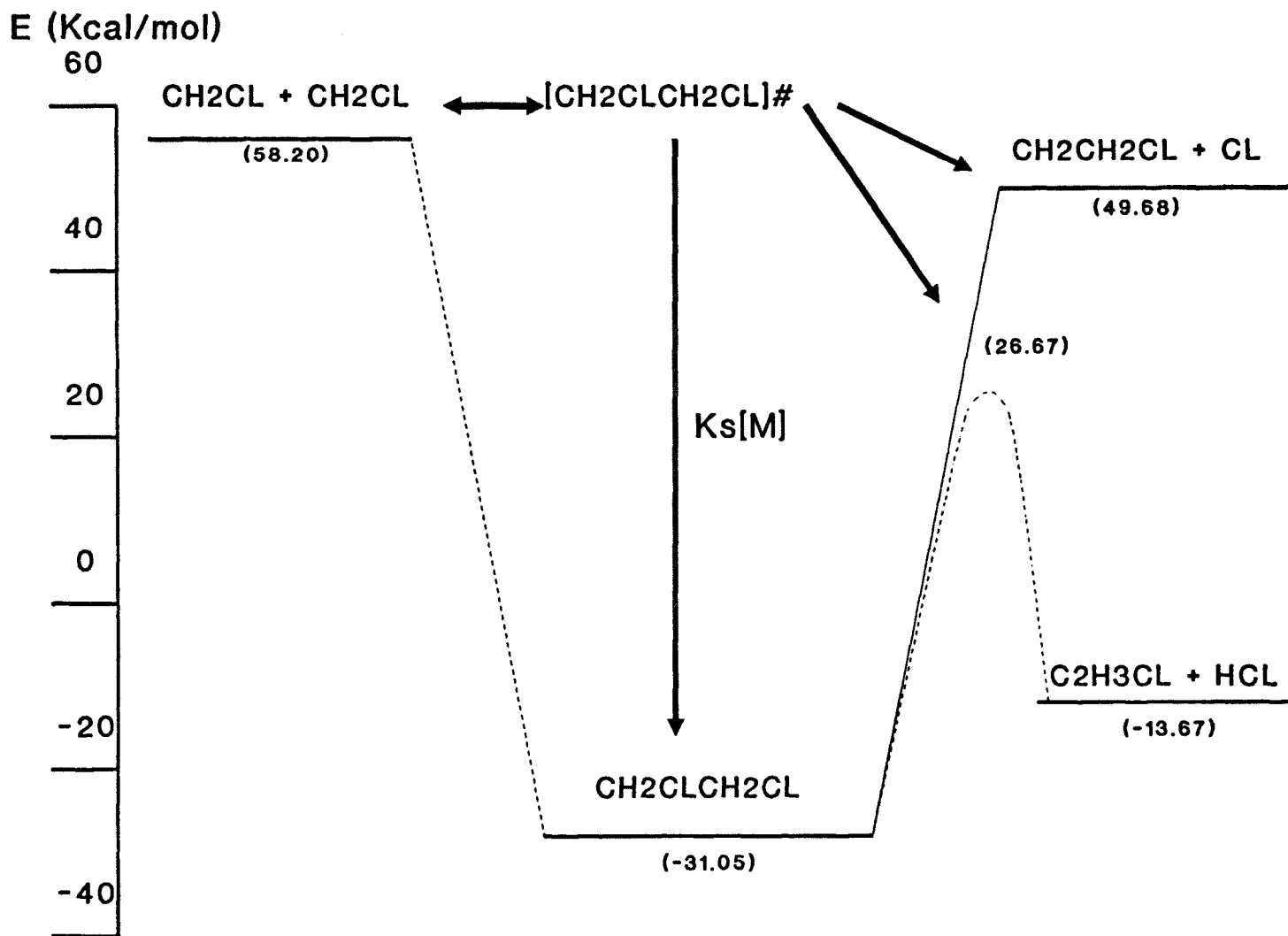


Fig 5.23 Potential Energy Diagram for CH₂CL + CH₂CL

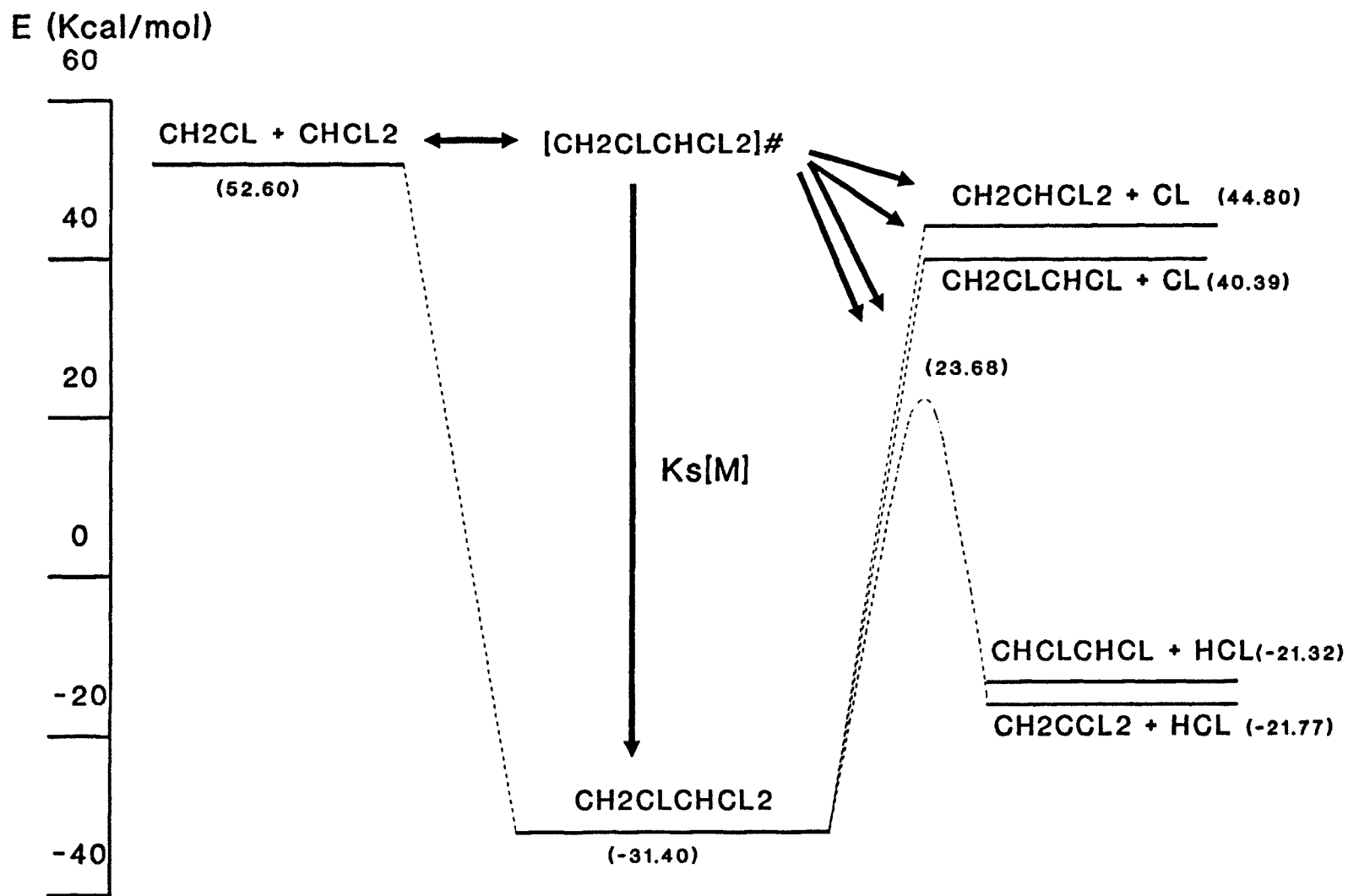


Fig 5.24 Potential Energy Diagram for $\text{CH}_2\text{CL} + \text{CHCL}_2$

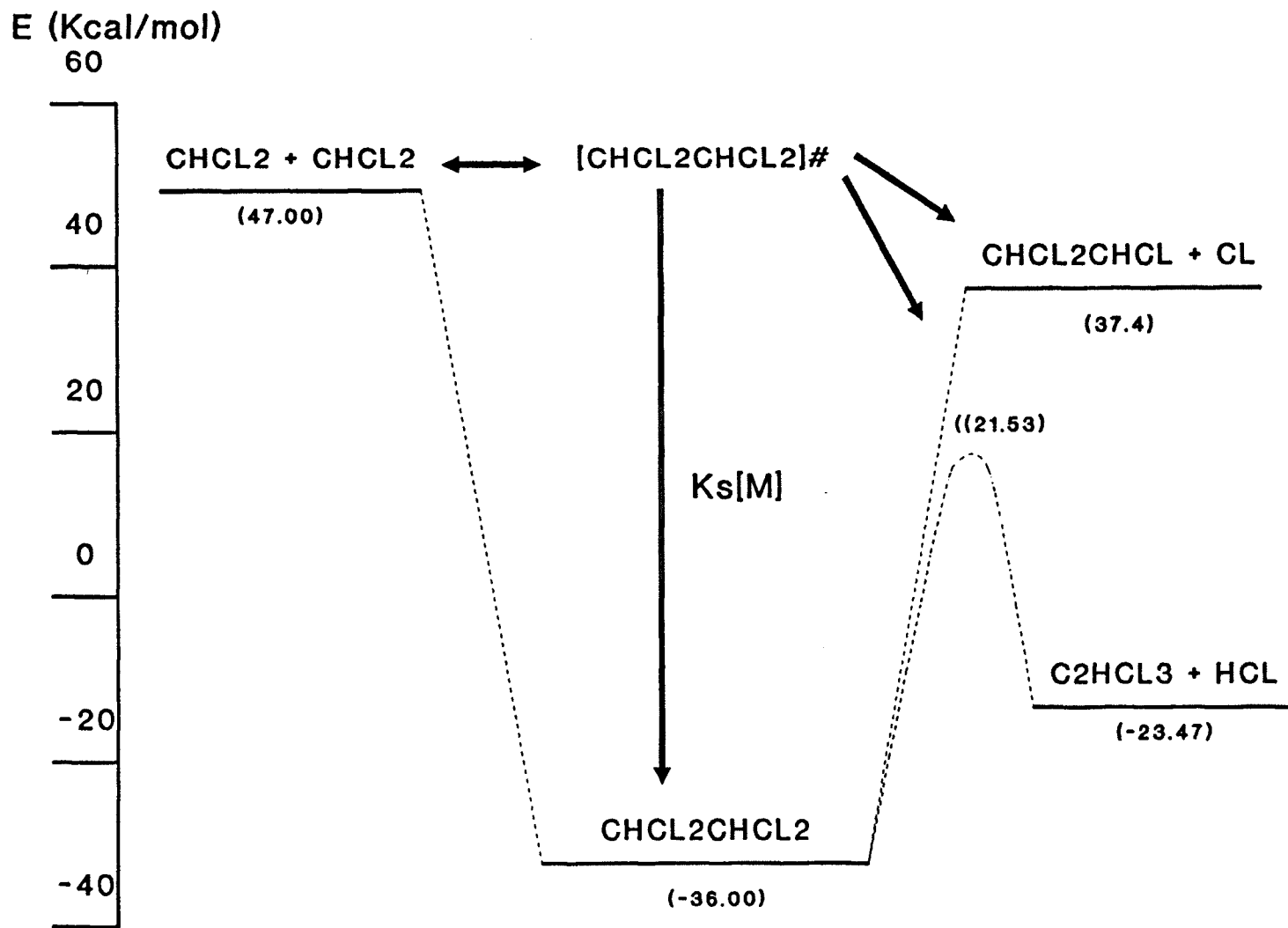
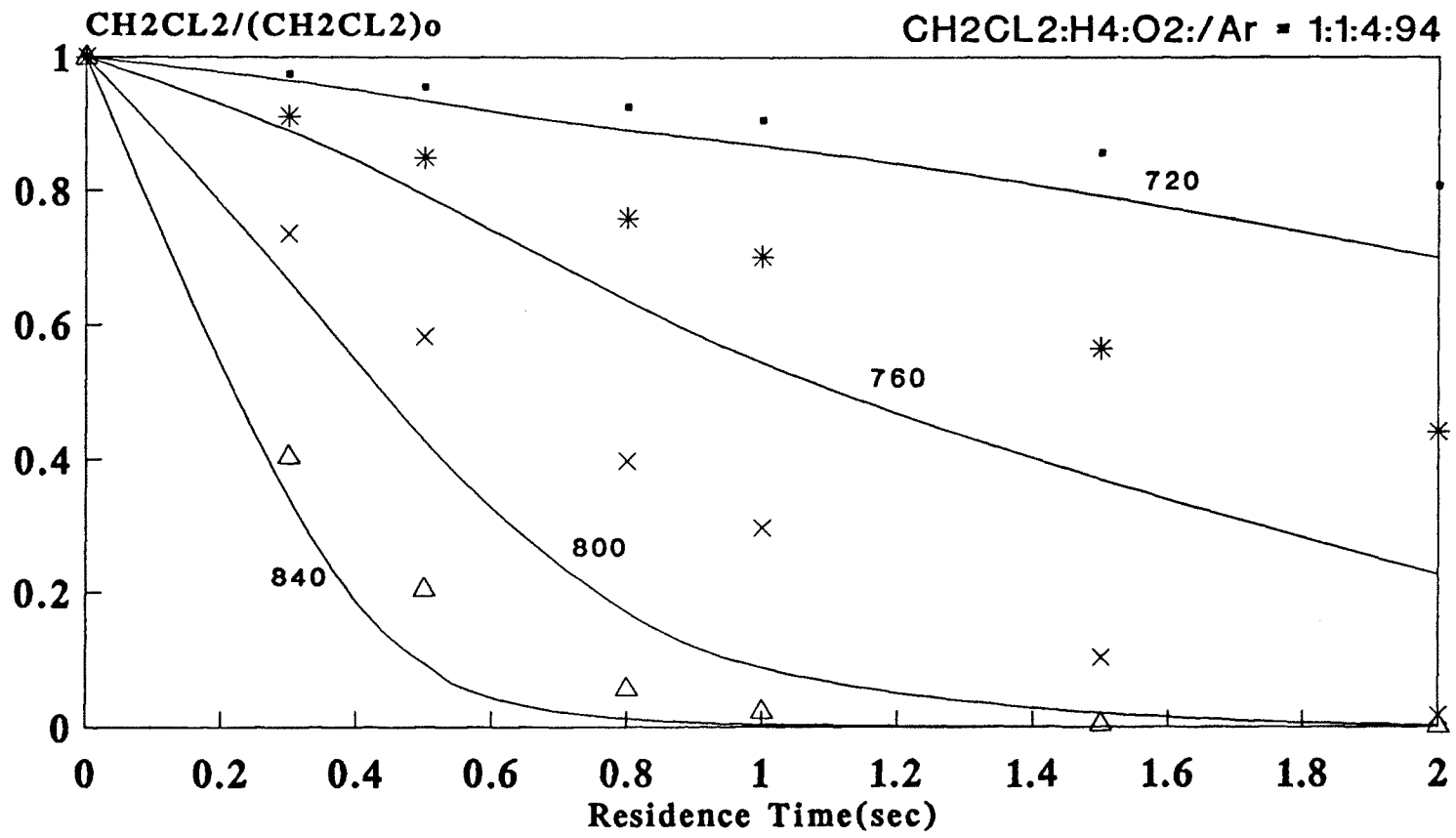


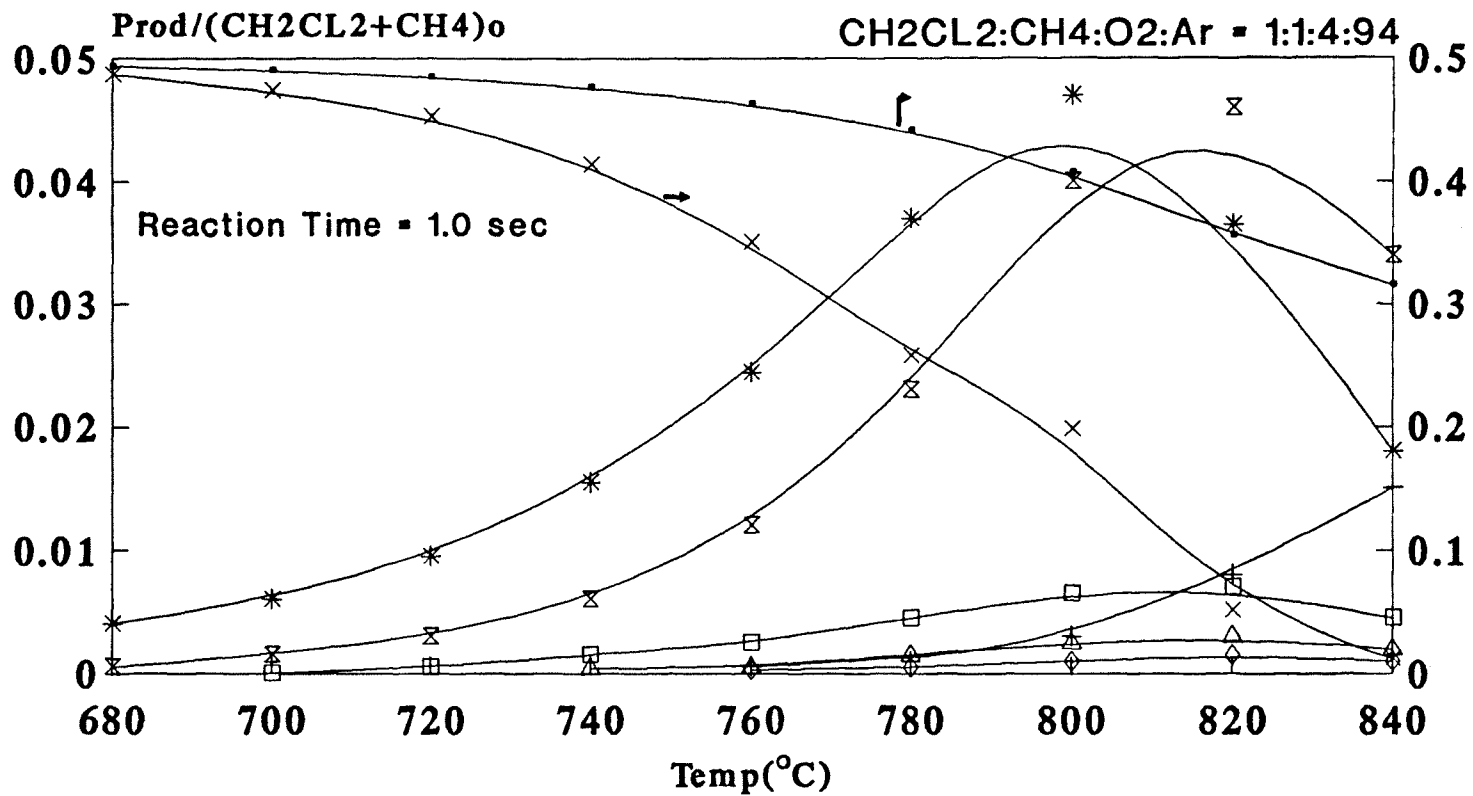
Fig 5.25 Potential Energy Diagram for CHCL₂ + CHCL₂



Point: Model Prediction

· 720 * 760 × 800 △ 840

**Fig 5.26 Comparison of Prediction with Experiment
 Decay of CH₂CL₂ vs Time/Temp**



—•— CH₄ —+— C₂H₂ —*— CH₃CL —□— C₂H₃CL
 —×— CH₂CL₂ —◇— CH₂CCL₂ —△— CHCLCHCL —⊗— C₂HCL₃

Fig 5.27 Model Prediction
Product Distribution vs Temp

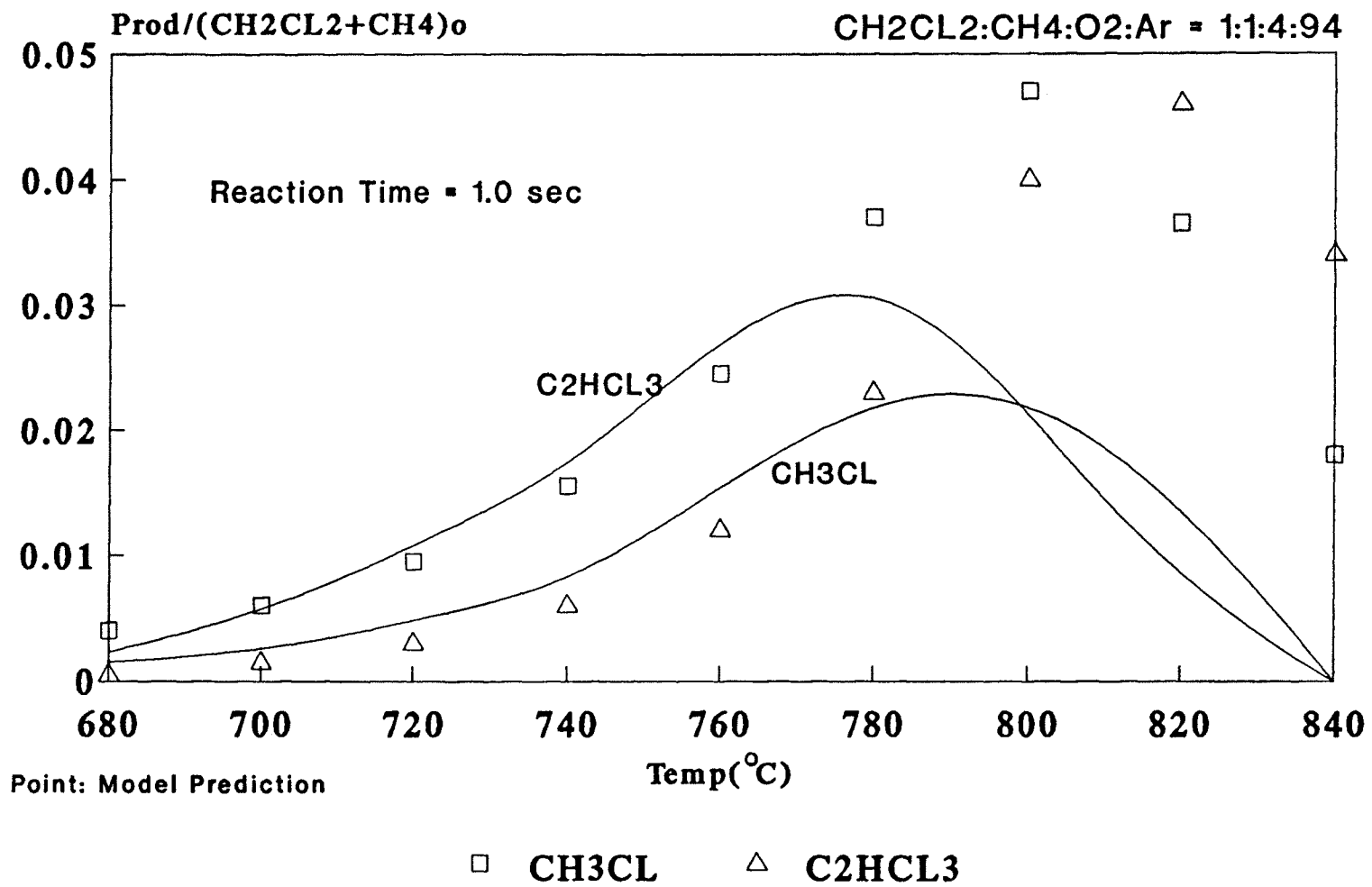


Fig 5.28 Comparison of Prediction with Experiment

TABLE 5.8 Detailed Mechanism for CH₂Cl₂/CH₄/O₂/Ar Reaction System

No.	REACTION	A	n	Ea	sources
1.	CH ₂ Cl ₂ = CHCl + HCl	1.44E37	-7.60	86.2	1
2.	CH ₂ Cl ₂ = CH ₂ Cl + Cl	7.41E40	-8.02	84.34	1
3.	CH ₂ Cl ₂ + HO ₂ = CHCl ₂ + H ₂ O ₂	6.00E10	0.00	15.3	2
4.	CH ₂ Cl ₂ + O ₂ = CHCl ₂ + HO ₂	1.34E13	0.00	50.3	2
5.	CH ₂ Cl ₂ + OH = CHCl ₂ + H ₂ O	2.57E12	0.00	2.2	3
6.	CH ₂ Cl ₂ + O = CHCl ₂ + OH	6.00E12	0.00	5.8	5
7.	CH ₂ Cl ₂ + H = CH ₂ Cl + HCl	7.00E13	0.00	7.3	3
8.	CH ₂ Cl ₂ + Cl = CHCl ₂ + HCl	5.00E13	0.00	2.9	3
9.	CH ₂ Cl ₂ + Cl = CH ₂ Cl + Cl ₂	1.00E14	0.00	21.4	3
10.	CH ₂ Cl ₂ + CH ₃ = CH ₄ + CHCl ₂	6.76E10	0.00	7.2	3
11.	CH ₂ Cl ₂ + CH ₃ = CH ₃ Cl + CH ₂ Cl	1.40E11	0.00	4.9	3
12.	CH ₃ Cl = CH ₃ + Cl	1.26E37	-6.91	90.54	1
13.	CH ₃ Cl = CH ₂ S + HCl	8.52E27	-5.13	109.64	1
14.	CH ₃ Cl + O ₂ = CH ₂ Cl + HO ₂	2.00E13	0.00	52.7	2
15.	CH ₃ Cl + H = CH ₃ + HCl	1.00E14	0.00	7.62	3
16.	CH ₃ Cl + Cl = CH ₂ Cl + HCl	3.20E13	0.00	3.1	4
17.	CH ₃ Cl + Cl = CH ₃ + Cl ₂	1.00E14	0.00	25.0	3
18.	CH ₃ Cl + CH ₃ = CH ₄ + CH ₂ Cl	3.30E11	0.00	9.4	3
19.	CH ₃ Cl + O = CH ₂ Cl + OH	2.00E13	0.00	7.8	5
20.	CH ₃ Cl + OH = CH ₂ Cl + H ₂ O	1.32E12	0.00	2.3	3
21.	CH ₃ Cl + HO ₂ = CH ₂ Cl + H ₂ O ₂	9.00E10	0.00	8.5	2
22.	CHCl ₃ = CHCl ₂ + Cl	5.70E12	0.00	67.7	2
23.	CHCl ₃ = CCl ₂ + HCl	5.20E12	0.00	51.5	2
24.	CHCl ₃ + OH = H ₂ O + CCl ₃	3.30E12	0.00	2.3	6
25.	CHCl ₃ + O ₂ = HO ₂ + CCl ₃	1.00E13	0.00	47.2	2
26.	CHCl ₃ + HO ₂ = H ₂ O ₂ + CCl ₃	4.50E10	0.00	14.2	2
27.	CHCl ₃ + H = HCl + CHCl ₂	3.60E12	0.00	6.2	2
28.	CHCl ₃ + O = OH + CCl ₃	3.00E12	0.00	4.9	5
29.	CHCl ₃ + CH ₃ = CH ₄ + CCl ₃	1.90E10	0.00	5.8	3
30.	CHCl ₃ + CH ₃ = CH ₃ Cl + CHCl ₂	2.40E13	0.00	12.0	3
31.	CHCl ₃ + Cl = HCl + CCl ₃	1.60E13	0.00	3.3	7
32.	CH ₂ Cl + CH ₂ Cl = C ₂ H ₄ Cl ₂	2.61E11	0.00	-5.18	QRRK
33.	CH ₂ Cl + CH ₂ Cl = CH ₂ ClCH ₂ + Cl	2.49E13	0.00	5.93	QRRK
34.	CH ₂ Cl + CH ₂ Cl = C ₂ H ₃ Cl + HCl	3.21E12	0.00	2.13	QRRK
35.	CH ₂ Cl + O ₂ = CH ₂ ClOO	2.73E33	-7.50	4.4	1
36.	CH ₂ Cl + O ₂ = CH ₂ O + ClO	1.91E14	-1.27	3.81	1
37.	CH ₂ Cl + O ₂ = CHClO + OH	4.00E13	0.00	34.0	1
38.	CH ₂ Cl + O = CH ₂ O + Cl	5.59E13	-0.13	0.71	QRRK
39.	CH ₂ Cl + O = CH ₂ CLO	1.29E15	-1.98	1.1	QRRK
40.	CH ₂ Cl + OH = CH ₂ O + HCl	1.24E22	-2.72	3.86	QRRK
41.	CH ₂ Cl + OH = CH ₃ O + Cl	2.00E12	0.29	3.27	QRRK
42.	CH ₂ Cl + CH ₂ O = CH ₃ Cl + CHO	2.00E11	0.00	6.0	3,8
43.	CH ₂ Cl + H ₂ = CH ₃ Cl + H	3.90E12	0.00	14.05	3
44.	CH ₂ Cl + CHCl ₂ = CH ₂ ClCHCl ₂	4.05E10	0.00	-7.49	QRRK
45.	CH ₂ Cl + CHCl ₂ = CH ₂ CCl ₂ + HCl	3.20E11	0.00	-1.21	QRRK
46.	CH ₂ Cl + CHCl ₂ = CHClCHCl + HCl	6.28E11	0.00	-1.59	QRRK

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
47.	$\text{CH}_2\text{Cl} + \text{CH}_3 = \text{C}_2\text{H}_5\text{Cl}$	1.09E12	0.00	-4.38	QRRK
48.	$\text{CH}_2\text{Cl} + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{HCl}$	6.30E12	0.00	1.68	QRRK
49.	$\text{CH}_2\text{Cl} + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{Cl}$	1.52E13	0.00	5.78	QRRK
50.	$\text{CH}_2\text{Cl} + \text{H} = \text{CH}_2\text{Cl}$	3.04E25	-4.47	3.49	1
51.	$\text{CH}_2\text{Cl} + \text{H} = \text{CH}_2\text{S} + \text{HCl}$	9.48E04	1.91	2.6	1
52.	$\text{CH}_2\text{Cl} + \text{H} = \text{CH}_3 + \text{Cl}$	5.12E14	-0.22	0.31	1
53.	$\text{CH}_2\text{Cl} + \text{ClO} = \text{CH}_2\text{ClO} + \text{Cl}$	4.15E12	0.07	1.11	1
54.	$\text{CH}_2\text{Cl} + \text{ClO} = \text{CHClO} + \text{HCl}$	4.13E19	-2.22	2.36	1
55.	$\text{CH}_2\text{Cl} + \text{HO}_2 = \text{CH}_2\text{ClO} + \text{OH}$	1.00E13	0.00	0.0	9,10
56.	$\text{CHCl}_2 + \text{OH} = \text{CHCl}_2\text{OH}$	4.06E09	0.00	-6.2	2
57.	$\text{CHCl}_2 + \text{OH} = \text{CHClO} + \text{HCl}$	4.29E12	0.00	-1.6	2
58.	$\text{CHCl}_2 + \text{OH} = \text{CHClOH} + \text{Cl}$	1.44E13	0.00	2.0	2
59.	$\text{CHCl}_2 + \text{O}_2 = \text{CHCl}_2\text{OO}$	4.66E07	0.00	-12.2	2
60.	$\text{CHCl}_2 + \text{O}_2 = \text{CHCl}_2\text{O} + \text{O}$	9.89E11	0.00	45.2	2
61.	$\text{CHCl}_2 + \text{O}_2 = \text{CHClOOCl}$	4.29E04	0.00	3.2	2
62.	$\text{CHCl}_2 + \text{O}_2 = \text{CHClO} + \text{ClO}$	7.00E09	0.00	6.4	2
63.	$\text{CHCl}_2 + \text{O} = \text{CHCl}_2\text{O}$	5.79E07	0.00	-3.3	2
64.	$\text{CHCl}_2 + \text{O} = \text{CHClO} + \text{Cl}$	1.56E13	0.00	0.0	2
65.	$\text{CHCl}_2 + \text{CH}_3 = \text{CH}_3\text{CHCl}_2$	1.21E11	0.00	-7.0	QRRK
66.	$\text{CHCl}_2 + \text{CH}_3 = \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	4.41E12	0.00	0.3	QRRK
67.	$\text{CHCl}_2 + \text{CH}_3 = \text{CH}_3\text{CHCl} + \text{Cl}$	3.61E13	0.00	3.66	QRRK
68.	$\text{CHCl}_2 + \text{HO}_2 = \text{CHCl}_2\text{OOH}$	1.86E08	0.00	-9.1	2
69.	$\text{CHCl}_2 + \text{HO}_2 = \text{CHCl}_2\text{O} + \text{OH}$	6.58E12	0.00	-0.3	2
70.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{H}_2\text{Cl}_4$	3.22E10	0.00	-8.5	QRRK
71.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}$	1.73E13	0.00	2.1	QRRK
72.	$\text{CHCl}_2 + \text{CHCl}_2 = \text{C}_2\text{HCl}_3 + \text{HCl}$	2.55E11	0.00	-0.9	QRRK
73.	$\text{CHCl}_2 + \text{H}_2 = \text{CH}_2\text{Cl}_2 + \text{H}$	4.63E12	0.00	15.29	3
74.	$\text{CHCl}_2 + \text{H} = \text{CH}_2\text{Cl}_2$	4.81E26	-4.82	3.81	1
75.	$\text{CHCl}_2 + \text{H} = \text{CH}_2\text{Cl} + \text{Cl}$	1.25E14	-0.03	0.57	1
76.	$\text{CHCl} + \text{OH} = \text{CHClOH}$	2.25E09	0.00	-3.56	QRRK
77.	$\text{CHCl} + \text{OH} = \text{CHClO} + \text{H}$	1.98E13	0.00	0.0	QRRK
78.	$\text{CHCl} + \text{OH} = \text{CH}_2\text{ClO}$	8.53E05	0.00	-2.05	QRRK
79.	$\text{CHCl} + \text{OH} = \text{CH}_2\text{O} + \text{Cl}$	1.33E12	0.00	1.05	QRRK
80.	$\text{CHCl} + \text{O}_2 = \text{CHClOO}$	9.46E07	0.00	-8.08	QRRK
81.	$\text{CHCl} + \text{O}_2 = \text{CHClO} + \text{O}$	5.50E11	0.00	-0.98	QRRK
82.	$\text{CHCl} + \text{CH}_3 = \text{CH}_3\text{CHCl}$	9.67E09	0.00	-5.2	QRRK
83.	$\text{CHCl} + \text{CH}_3 = \text{C}_2\text{H}_3\text{Cl} + \text{H}$	9.95E12	0.00	-0.26	QRRK
84.	$\text{CHCl} + \text{CH}_3 = \text{CH}_2\text{ClCH}_2$	1.32E09	0.00	-3.93	QRRK
85.	$\text{CHCl} + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{Cl}$	9.96E12	0.00	0.54	QRRK
86.	$\text{CHCl} + \text{O} = \text{CHClO}$	5.40E08	0.00	-3.4	QRRK
87.	$\text{CHCl} + \text{O} = \text{CHO} + \text{Cl}$	1.98E13	0.00	-0.01	QRRK
88.	$\text{CHCl} + \text{CHCl} = \text{CHClCHCl}$	8.78E08	0.00	-5.3	QRRK
89.	$\text{CHCl} + \text{CHCl} = \text{CHCHCl} + \text{Cl}$	2.73E12	0.00	0.55	QRRK
90.	$\text{CHCl} + \text{CHCl} = \text{C}_2\text{HCl} + \text{HCl}$	1.48E12	0.00	-0.42	QRRK
91.	$\text{C}_2\text{H}_5\text{Cl} = \text{C}_2\text{H}_4 + \text{HCl}$	7.81E19	-2.00	60.66	1
92.	$\text{C}_2\text{H}_5\text{Cl} = \text{C}_2\text{H}_5 + \text{Cl}$	2.35E43	-8.50	96.98	1
93.	$\text{C}_2\text{H}_5\text{Cl} + \text{H} = \text{HCl} + \text{C}_2\text{H}_5$	1.00E14	0.00	7.9	3

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
94.	$C_2H_5Cl + Cl = HCl + CH_3CHCl$	3.55E13	0.00	1.5	3
95.	$C_2H_5Cl + Cl = HCl + CH_2ClCH_2$	1.12E13	0.00	1.5	3
96.	$CH_3CHCl_2 = C_2H_3Cl + HCl$	2.94E21	-2.37	59.46	1
97.	$CH_3CHCl_2 = CH_3CHCl + Cl$	3.17E42	-8.10	92.67	1
98.	$CH_3CHCl_2 + H = CH_3CHCl + HCl$	2.00E13	0.00	5.9	11
99.	$CH_3CHCl_2 + OH = CHCl_2CH_2 + H_2O$	1.92E11	0.00	0.1	12
100.	$CH_3CHCl_2 + O = CHCl_2CH_2 + OH$	3.00E12	0.00	4.8	5
101.	$CH_3CHCl_2 + O_2 = CHCl_2CH_2 + HO_2$	1.30E13	0.00	51.0	2
102.	$C_2H_4Cl_2 = C_2H_3Cl + HCl$	6.40E10	0.00	47.0	13
103.	$C_2H_3Cl_3 = CHClCHCl + HCl$	1.39E20	-2.03	60.45	1
104.	$C_2H_3Cl_3 = CH_2CCl_2 + HCl$	3.13E19	-2.02	60.33	1
105.	$C_2H_2Cl_4 = C_2H_3Cl + HCl$	8.62E21	-2.57	51.87	1
106.	$C_2H_3Cl + H = CH_2ClCH_2$	1.81E25	-4.37	5.98	14
107.	$C_2H_3Cl + H = C_2H_4 + Cl$	1.34E13	0.00	3.32	14
108.	$C_2H_3Cl + H = C_2H_3 + HCl$	1.00E13	0.00	6.5	15
109.	$C_2H_3Cl = C_2H_2 + HCl$	1.62E28	-4.29	75.78	1
110.	$C_2H_3Cl = C_2H_3 + Cl$	1.71E38	-7.13	96.37	1
111.	$C_2H_3Cl + OH = CHCHCl + H_2O$	1.20E13	0.0	4.0	16
112.	$C_2H_3Cl + OH = CH_2CCl + H_2O$	6.00E12	0.0	4.0	16
113.	$C_2H_3Cl + OH = CH_2CHOH + Cl$	1.44E22	-2.7	5.21	14
114.	$C_2H_3Cl + OH = CH_3 + CHClO$	3.13E07	0.91	9.39	14
115.	$C_2H_3Cl + OH = CH_3CHO + Cl$	3.91E13	-0.98	10.37	14
116.	$C_2H_3Cl + O = CH_2CHClO$	2.65E32	-7.14	5.96	14
117.	$C_2H_3Cl + O = CH_2 + CHClO$	5.01E12	-0.23	1.65	14
118.	$C_2H_3Cl + O = CHCHCl + OH$	2.00E12	0.0	5.2	2
119.	$C_2H_3Cl + O_2 = CHCHCl + HO_2$	1.40E13	0.0	57.4	2
120.	$C_2H_3Cl + O_2 = CH_2CCl + HO_2$	1.10E13	0.0	56.0	2
121.	$C_2H_3Cl + CH_3 = C_2H_3 + CH_3Cl$	2.70E11	0.0	9.8	2
122.	$C_2H_3Cl + Cl = CHCHCl + HCl$	5.00E13	0.0	7.0	17
123.	$CH_2CCl_2 = C_2HCl + HCl$	1.45E14	0.00	69.22	1
124.	$CH_2CCl_2 + H = C_2H_3Cl + Cl$	7.21E12	0.00	7.51	1
125.	$CHClCHCl = C_2HCl + HCl$	7.26E13	0.00	69.09	1
126.	$CHClCHCl + H = C_2H_3Cl + Cl$	3.44E13	-0.03	5.89	1
127.	$C_2HCl_3 = CHClCCl + Cl$	3.20E14	0.00	82.8	2
128.	$C_2HCl_3 = CHCCl_2 + Cl$	1.40E14	0.00	82.6	2
129.	$C_2HCl_3 = C_2Cl_2 + HCl$	2.70E13	0.00	73.3	2
130.	$C_2HCl_3 + H = CH_2ClCCl_2$	1.51E23	-4.18	7.52	1
131.	$C_2HCl_3 + H = C_2H_2Cl_3$	2.87E22	-4.09	1.08	1
132.	$C_2HCl_3 + H = CH_2CCl_2 + Cl$	1.45E13	-0.01	5.83	1
133.	$C_2HCl_3 + H = CHClCHCl + Cl$	7.37E12	-0.01	9.22	1
134.	$C_2HCl_3 + OH = C_2Cl_3 + H_2O$	3.00E12	0.0	5.8	2
135.	$C_2HCl_3 + O = C_2Cl_3 + OH$	3.10E12	0.0	7.0	2
136.	$C_2HCl_3 + O_2 = C_2Cl_3 + HO_2$	2.30E12	0.0	61.9	2
137.	$C_2HCl_3 + H = CHClCCl + HCl$	3.60E12	0.0	9.2	2
138.	$C_2HCl_3 + CH_3 = CHClCCl + CH_3Cl$	5.00E12	0.0	13.8	2
139.	$C_2HCl_3 + Cl = C_2Cl_3 + HCl$	1.70E13	0.0	7.0	2
140.	$C_2HCl + H = HCl + C_2H$	1.00E13	0.00	17.03	18

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
141.	$C_2HCl + H = C_2H_2 + Cl$	2.00E13	0.00	2.1	19
142.	$C_2HCl + OH = CH_2Cl + CO$	2.40E-3	4.00	-2.0	14
143.	$C_2HCl + O = CHCl + CO$	5.10E06	2.00	1.9	14
144.	$C_2HCl + O = CHCO + Cl$	5.10E06	2.00	1.9	14
145.	$CH_4 = CH_3 + H$	7.43E13	0.00	101.0	1
146.	$CH_4 + H = CH_3 + H_2$	2.20E04	3.00	8.74	20
147.	$CH_4 + Cl = CH_3 + HCl$	3.09E13	0.00	3.6	20
148.	$CH_4 + O_2 = CH_3 + HO_2$	7.90E13	0.00	56.0	20
149.	$CH_4 + O = CH_3 + OH$	1.02E09	1.5	8.6	20
150.	$CH_4 + OH = CH_3 + H_2O$	1.60E06	2.10	2.5	21
151.	$CH_4 + HO_2 = CH_3 + H_2O_2$	1.81E11	0.00	18.6	22
152.	$CH_4 + CH_3O = CH_3 + CH_3OH$	1.57E11	0.00	8.84	22
153.	$CH_3 + C_2H_5 = CH_4 + C_2H_4$	5.50E11	0.00	0.0	1
154.	$CH_3 + H = CH_2 + H_2$	9.00E13	0.00	15.1	20
155.	$CH_3 + O_2 = CH_2O + OH$	3.04E10	0.00	11.7	14
156.	$CH_3 + O_2 = CH_3O + O$	2.05E19	-1.57	29.22	20
157.	$CH_3 + O_2 = CH_3OO$	2.58E33	-7.18	5.3	23
158.	$CH_3 + OH = CH_3OH$	1.12E41	-8.44	11.8	23
159.	$CH_3 + OH = CH_3O + H$	1.54E19	-1.74	7.6	23
160.	$CH_3 + OH = CH_2O + H + H$	5.30E12	0.00	0.0	24
161.	$CH_3 + OH = CH_2 + H_2O$	7.50E06	2.0	5.0	20
162.	$CH_3 + O = CH_2O + H$	8.94E14	-0.03	0.0	23
163.	$CH_3 + O = CH_3O$	6.76E15	-2.14	0.6	23
164.	$CH_3 + HO_2 = CH_3O + OH$	2.00E13	0.0	0.0	9
165.	$CH_3 + ClO = CH_3O + Cl$	3.33E11	0.46	0.03	1
166.	$CH_3 + ClO = CH_2O + HCl$	3.47E18	-1.80	2.07	1
167.	$CH_2S + M = CH_2 + M$	1.00E13	0.00	0.0	25
168.	$CH_2S + O_2 = CO + H_2O$	2.41E11	0.00	0.0	25
169.	$CH_2S + CH_4 = C_2H_5 + H$	9.43E12	-0.13	6.62	1
170.	$CH_2S + CH_4 = CH_3 + CH_3$	3.45E22	-2.48	7.46	1
171.	$CH_2S + CH_4 = C_2H_6$	5.78E46	-10.31	12.83	1
172.	$CH_2S + CH_3Cl = C_2H_5Cl$	7.85E31	-6.15	5.83	1
173.	$CH_2S + CH_3Cl = C_2H_4 + HCl$	1.60E18	-1.47	2.71	1
174.	$CH_2S + CH_3Cl = C_2H_5 + Cl$	3.09E07	1.70	0.52	1
175.	$CH_2S + H_2 = CH_4$	3.82E25	-4.47	3.77	1
176.	$CH_2S + H_2 = CH_3 + H$	1.27E14	-0.08	0.13	1
177.	$CH_2 + CH_4 = CH_3 + CH_3$	1.82E05	0.00	0.0	1
178.	$CH_2 + CH_3Cl = CH_3 + CH_2Cl$	9.10E04	0.00	0.0	1
179.	$CH_2 + H = CH + H_2$	1.00E18	-1.56	0.0	20
180.	$CH_2 + OH = CH + H_2O$	1.13E07	2.00	3.0	20
181.	$CH_2 + OH = CH_2O + H$	2.50E13	0.00	0.0	20
182.	$CH_2 + CO_2 = CH_2O + CO$	1.10E11	0.00	1.0	20
183.	$CH_2 + O = CO + 2H$	5.00E13	0.00	0.0	20
184.	$CH_2 + O = CO + H_2$	3.00E13	0.00	0.0	20
185.	$CH_2 + O_2 = CO_2 + 2H$	1.60E12	0.00	1.0	20
186.	$CH_2 + O_2 = CH_2O + O$	5.00E13	0.00	9.0	20
187.	$CH_2 + O_2 = CO_2 + H_2$	6.90E11	0.00	0.5	20

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
188.	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{H}_2\text{O}$	1.90E10	0.00	-1.0	20
189.	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	8.60E10	0.00	-0.5	20
190.	$\text{CH}_2 + \text{O}_2 = \text{CHO} + \text{OH}$	4.30E11	0.00	-0.5	20
191.	$\text{CH}_2 + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H}_2$	4.00E13	0.00	0.0	20
192.	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_5 + \text{H}$	3.64E16	0.00	89.5	1
193.	$\text{C}_2\text{H}_6 = \text{CH}_3 + \text{CH}_3$	2.03E14	0.00	92.3	1
194.	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$	2.29E17	0.00	67.64	39
195.	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	5.75E11	0.00	11.6	3
196.	$\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$	6.61E13	0.00	9.7	3
197.	$\text{C}_2\text{H}_6 + \text{Cl} = \text{C}_2\text{H}_5 + \text{HCl}$	4.64E13	0.00	0.17	26
198.	$\text{C}_2\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{OH}$	3.00E07	2.00	5.1	21
199.	$\text{C}_2\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	6.30E06	2.00	0.6	21
200.	$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	4.04E13	0.00	50.9	22
201.	$\text{C}_2\text{H}_6 + \text{HO}_2 = \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2$	6.00E12	0.00	19.3	21
202.	$\text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H}$	1.83E39	-7.75	52.82	27
203.	$\text{C}_2\text{H}_5 + \text{H} = \text{CH}_3 + \text{CH}_3$	5.10E14	0.00	2.85	1
204.	$\text{C}_2\text{H}_5 + \text{O} = \text{CH}_2\text{O} + \text{CH}_3$	1.61E13	0.00	0.0	22
205.	$\text{C}_2\text{H}_5 + \text{O} = \text{C}_2\text{H}_4 + \text{OH}$	5.00E13	0.00	0.0	9
206.	$\text{C}_2\text{H}_5 + \text{O} = \text{CH}_3\text{CHO} + \text{H}$	5.00E13	0.00	0.0	28
207.	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$	8.89E28	-5.43	9.92	14
208.	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_5\text{OO}$	1.65E55	-13.49	15.03	14
209.	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_5\text{O} + \text{O}$	3.24E14	-0.65	28.63	14
210.	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{CH}_2\text{CH}_2\text{OOH}$	1.02E50	-12.40	15.46	14
211.	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CHO} + \text{OH}$	5.89E12	-0.77	9.36	14
212.	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_3 + \text{C}_2\text{H}_6$	1.68E13	0.00	22.16	39
213.	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	1.40E12	0.00	0.0	22
214.	$\text{C}_2\text{H}_5 + \text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	2.41E13	0.00	0.0	22
215.	$\text{C}_2\text{H}_5 + \text{Cl}_2 = \text{C}_2\text{H}_5\text{Cl} + \text{Cl}$	7.58E12	0.00	-0.24	29
216.	$\text{C}_2\text{H}_5 + \text{HO}_2 = \text{C}_2\text{H}_4 + \text{H}_2\text{O}_2$	3.01E11	0.00	0.0	22
217.	$\text{C}_2\text{H}_5 + \text{CH}_2\text{O} = \text{C}_2\text{H}_6 + \text{CHO}$	4.93E10	2.81	5.86	22
218.	$\text{C}_2\text{H}_4 = \text{C}_2\text{H}_3 + \text{H}$	2.82E15	0.00	108.0	27
219.	$\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$	8.52E43	-8.32	121.24	21
220.	$\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	1.45E13	0.00	4.18	16
221.	$\text{C}_2\text{H}_4 + \text{OH} = \text{CH}_3 + \text{CH}_2\text{O}$	1.00E13	0.00	0.0	24
222.	$\text{C}_2\text{H}_4 + \text{CH}_3 = \text{CH}_4 + \text{C}_2\text{H}_3$	0.36	4.00	11.11	27
223.	$\text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2$	4.22E13	0.00	57.62	22
224.	$\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	1.50E14	0.00	10.2	21
225.	$\text{C}_2\text{H}_4 + \text{Cl} = \text{C}_2\text{H}_3 + \text{HCl}$	2.39E13	0.00	2.6	4
226.	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_3 + \text{CHO}$	1.33E08	1.55	0.4	22
227.	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_2\text{O} + \text{CH}_2$	2.50E13	0.00	5.0	30
228.	$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_5 + \text{H}$	1.02E13	0.00	68.15	22
229.	$\text{C}_2\text{H}_4 + \text{AR} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{AR}$	2.60E17	0.00	79.29	21
230.	$\text{C}_2\text{H}_4 + \text{HO}_2 = \text{CH}_3\text{CHO} + \text{OH}$	6.03E09	0.00	15.8	22
231.	$\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H}$	6.24E29	-5.29	46.5	27
232.	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	9.64E13	0.00	0.0	22
233.	$\text{C}_2\text{H}_3 + \text{OH} = \text{C}_2\text{H}_2 + \text{H}_2\text{O}$	3.01E13	0.00	0.0	22
234.	$\text{C}_2\text{H}_3 + \text{H}_2\text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$	1.21E10	0.00	-0.59	22

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
235.	$C_2H_3 + CH_2O = C_2H_4 + CHO$	5.42E03	2.81	5.68	22
236.	$C_2H_3 + O_2 = C_2H_3OO$	2.26E38	-8.10	8.45	31
237.	$C_2H_3 + O_2 = CH_2CHO + O$	9.86E14	-0.59	5.03	31
238.	$C_2H_3 + O_2 = CH_2OCHO$	3.01E28	-6.24	7.31	31
239.	$C_2H_3 + O_2 = CHOCHO + H$	1.47E23	-3.83	6.24	31
240.	$C_2H_3 + O_2 = CHO + CH_2O$	5.64E27	-4.73	8.48	31
241.	$C_2H_3 + O_2 = C_2H_2 + HO_2$	5.04E23	-3.61	8.04	31
242.	$C_2H_3 + Cl_2 = C_2H_3Cl + Cl$	5.25E12	0.00	-0.48	29
243.	$C_2H_2 = C_2H + H$	1.16E13	0.00	124.0	27
244.	$C_2H_2 + Cl = C_2H + HCl$	1.58E14	0.00	26.9	4
245.	$C_2H_2 + O_2 = C_2H + HO_2$	1.20E13	0.00	74.5	22
246.	$C_2H_2 + O_2 = CHO + CHO$	1.20E11	0.00	44.5	14
247.	$C_2H_2 + O = CO + CH_2$	7.94E13	0.00	15.0	2
248.	$C_2H_2 + O = CH_2CO$	1.70E11	0.00	0.0	2
249.	$C_2H_2 + O = CHCO + H$	3.50E04	2.70	1.4	32
250.	$C_2H_2 + OH = C_2H + H_2O$	1.45E04	2.68	12.04	22
251.	$C_2H_2 + OH = CH_2CO + H$	3.20E11	0.00	0.20	33
252.	$C_2H_2 + HO_2 = CH_2CO + OH$	6.02E09	0.00	7.98	22
253.	$C_2H_2 = H_2C_2$	3.98E13	0.00	52.6	34
254.	$H_2C_2 + O_2 = CH_2 + CO_2$	5.00E12	0.00	0.0	34
255.	$H_2C_2 + O_2 = CH_2O + CO$	5.00E12	0.00	0.0	34
256.	$C_2H + O_2 = CO + CHO$	5.00E13	0.00	1.5	21
257.	$C_2H + O = CH + CO$	1.00E13	0.00	0.0	21
258.	$C_2H + H_2 = C_2H_2 + H$	3.50E12	0.00	2.1	21
259.	$C_2H + CH_4 = C_2H_2 + CH_3$	1.20E13	0.00	0.0	23
260.	$C_2H + C_2H_4 = C_2H_2 + C_2H_3$	1.20E13	0.00	0.0	23
261.	$CH_3CHO = CH_3 + CHO$	3.80E15	0.00	39.5	39
262.	$CH_3CHO + OH = CH_3CO + H_2O$	3.40E12	0.00	-0.6	35
263.	$CH_3CHO + O = CH_3CO + OH$	5.00E12	0.00	1.8	21
264.	$CH_3CHO + HO_2 = CH_3CO + H_2O_2$	1.50E11	0.00	9.0	23
265.	$CH_3CHO + O_2 = CH_3CO + HO_2$	1.00E13	0.00	38.9	23
266.	$CH_3CHO + CH_3 = CH_3CO + CH_4$	8.50E10	0.00	6.0	21
267.	$CHCO + H = CH_2S + CO$	3.00E13	0.00	0.0	21
268.	$CH_2CO = CH_2 + CO$	3.00E14	0.00	35.7	39
269.	$CH_2CO + O = CH_2 + CO_2$	1.74E12	0.00	1.35	20
270.	$CH_2CO + H = CH_3 + CO$	3.40E13	0.00	1.9	14
271.	$CH_2CO + O = CHCO + OH$	1.00E12	0.00	8.0	20
272.	$CH_2CO + O = CH_2O + CO$	1.70E12	0.00	1.4	2
273.	$CH_2CO + OH = CHCO + H_2O$	7.50E12	0.00	2.0	20
274.	$CH_2CO + OH = CH_2O + CHO$	1.00E13	0.00	0.0	28
275.	$CH_3O + O_2 = CH_2O + HO_2$	1.00E13	0.00	7.16	21
276.	$CH_3O + M = CH_2O + H + M$	1.96E14	0.00	25.07	39
277.	$CH_3O + CO = CO_2 + CH_3$	1.57E13	0.00	11.8	2
278.	$CH_3O + HO_2 = CH_2O + H_2O_2$	3.01E11	0.00	0.0	2
279.	$CH_3O + CH_3 = CH_4 + CH_2O$	2.41E13	0.00	0.0	22
280.	$CH_3O + O = OH + CH_2O$	6.03E12	0.00	0.0	2
281.	$CH_3O + OH = H_2O + CH_2O$	1.81E13	0.00	0.0	2

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
282.	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	1.99E13	0.00	0.0	2
283.	$\text{CH}_3\text{O} + \text{CH}_2 = \text{CH}_3 + \text{CH}_2\text{O}$	1.81E10	0.00	0.0	2
284.	$\text{CH}_3\text{O} + \text{C}_2\text{H}_5 = \text{C}_2\text{H}_6 + \text{CH}_2\text{O}$	2.41E13	0.00	0.0	2
285.	$\text{CH}_3\text{O} + \text{ClO} = \text{HOCl} + \text{CH}_2\text{O}$	2.41E13	0.00	0.0	2
286.	$\text{CH}_3\text{O} + \text{Cl} = \text{HCl} + \text{CH}_2\text{O}$	4.00E14	0.00	0.0	2
287.	$\text{CH}_2\text{O} = \text{CO} + \text{H}_2$	4.52E15	0.00	35.29	39
288.	$\text{CH}_2\text{O} + \text{ClO} = \text{CHO} + \text{HOCl}$	6.03E11	0.00	4.2	26
289.	$\text{CH}_2\text{O} + \text{CH}_3 = \text{CH}_4 + \text{CHO}$	1.00E11	0.00	6.0	21
290.	$\text{CH}_2\text{O} + \text{O} = \text{CHO} + \text{OH}$	3.50E13	0.00	3.5	21
291.	$\text{CH}_2\text{O} + \text{OH} = \text{CHO} + \text{H}_2\text{O}$	3.00E13	0.00	1.19	21
292.	$\text{CH}_2\text{O} + \text{HO}_2 = \text{CHO} + \text{H}_2\text{O}_2$	1.00E12	0.00	8.0	2
293.	$\text{CH}_2\text{O} + \text{Cl} = \text{CHO} + \text{HCl}$	4.40E13	0.00	0.0	35
294.	$\text{CH}_2\text{O} = \text{CHO} + \text{H}$	1.00E12	0.00	75.7	21
295.	$\text{CH}_2\text{O} + \text{O}_2 = \text{CHO} + \text{HO}_2$	2.00E13	0.00	38.9	23
296.	$\text{CH}_2\text{O} + \text{H} = \text{CHO} + \text{H}_2$	2.50E13	0.00	3.99	21
297.	$\text{CHO} = \text{H} + \text{CO}$	2.50E14	0.00	13.3	21
298.	$\text{CHO} + \text{H} = \text{CO} + \text{H}_2$	2.00E14	0.00	0.0	21
299.	$\text{CHO} + \text{O}_2 = \text{CO} + \text{HO}_2$	3.00E13	0.00	0.0	21
300.	$\text{CHO} + \text{O} = \text{CO} + \text{OH}$	3.00E13	0.00	0.0	21
301.	$\text{CHO} + \text{O} = \text{H} + \text{CO}_2$	3.01E13	0.00	0.0	21
302.	$\text{CHO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	5.00E13	0.00	0.0	21
303.	$\text{CHO} + \text{CH}_3 = \text{CH}_4 + \text{CO}$	1.00E12	0.00	0.0	2
304.	$\text{CHO} + \text{HO}_2 = \text{CO} + \text{H}_2\text{O}_2$	5.00E12	0.00	0.0	2
305.	$\text{CHO} + \text{Cl} = \text{CO} + \text{HCl}$	1.50E13	0.00	0.0	2
306.	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	4.40E06	1.50	-0.7	21
307.	$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$	1.50E14	0.00	23.5	21
308.	$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	2.50E13	0.00	47.6	21
309.	$\text{CO} + \text{O} = \text{CO}_2$	5.90E15	0.00	4.1	21
310.	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	2.20E14	0.00	16.8	36
311.	$\text{H} + \text{O}_2 = \text{HO}_2$	7.00E17	-0.8	0.0	21
312.	$\text{O} + \text{H}_2 = \text{H} + \text{OH}$	1.08E04	2.8	5.92	21
313.	$\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$	1.50E10	1.14	17.24	22
314.	$\text{H} + \text{H}_2\text{O} = \text{H}_2 + \text{OH}$	4.60E08	1.6	18.56	21
315.	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	7.50E23	-2.6	0.0	21
316.	$\text{O}_2 + \text{M} = \text{O} + \text{O} + \text{M}$	1.20E14	0.00	107.55	20
317.	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	2.29E14	0.00	3.9	3
318.	$\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$	1.50E14	0.00	1.0	21
319.	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	2.50E13	0.00	0.69	21
320.	$\text{O} + \text{HO}_2 = \text{OH} + \text{O}_2$	2.30E13	0.00	0.0	21
321.	$\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$	2.00E13	0.00	0.0	21
322.	$\text{OH} + \text{H}_2\text{O}_2 = \text{HO}_2 + \text{H}_2\text{O}$	7.00E12	0.00	1.4	21
323.	$\text{O} + \text{H}_2\text{O}_2 = \text{HO}_2 + \text{OH}$	2.80E13	0.00	6.4	21
324.	$\text{H} + \text{H}_2\text{O}_2 = \text{OH} + \text{H}_2\text{O}$	1.00E13	0.00	3.6	21
325.	$\text{H} + \text{H}_2\text{O}_2 = \text{H}_2 + \text{HO}_2$	4.82E13	0.00	7.95	21
326.	$\text{O}_2 + \text{H}_2\text{O}_2 = \text{HO}_2 + \text{HO}_2$	5.42E13	0.00	39.74	21
327.	$\text{H}_2\text{O}_2 = \text{OH} + \text{OH}$	1.20E17	0.00	45.2	21
328.	$\text{O} + \text{HCl} = \text{OH} + \text{Cl}$	6.03E12	0.00	6.6	26

Table 5.8 (Cont'd)

No.	REACTION	A	n	Ea	sources
329.	$\text{OH} + \text{HCl} = \text{Cl} + \text{H}_2\text{O}$	2.45E12	0.00	1.1	3
330.	$\text{Cl} + \text{Cl} = \text{Cl}_2$	2.34E14	0.00	-1.8	3
331.	$\text{H} + \text{Cl} = \text{HCl}$	1.00E17	0.00	0.0	37
332.	$\text{H} + \text{H} = \text{H}_2$	1.00E18	0.00	0.0	37
333.	$\text{H} + \text{HCl} = \text{H}_2 + \text{Cl}$	2.30E13	0.00	3.5	3
334.	$\text{Cl} + \text{HO}_2 = \text{HCl} + \text{O}_2$	1.08E13	0.00	0.1	26
335.	$\text{Cl} + \text{HO}_2 = \text{ClO} + \text{OH}$	2.47E13	0.00	0.89	26
336.	$\text{ClO} + \text{CO} = \text{Cl} + \text{CO}_2$	6.03E11	0.00	7.35	26
337.	$\text{ClO} + \text{CH}_3 = \text{CH}_3\text{Cl} + \text{O}$	6.00E12	0.00	4.0	2
338.	$\text{HOCl} = \text{Cl} + \text{OH}$	1.76E20	-3.01	56.72	1
339.	$\text{HOCl} = \text{H} + \text{ClO}$	8.12E14	-2.09	93.69	1
340.	$\text{CHClO} + \text{H} = \text{CHO} + \text{HCl}$	8.33E13	0.00	7.4	1
341.	$\text{CHClO} + \text{H} = \text{CH}_2\text{O} + \text{Cl}$	6.99E14	-0.58	6.36	1
342.	$\text{CHClO} = \text{CHO} + \text{Cl}$	8.86E29	-5.15	92.92	1
343.	$\text{CHClO} = \text{CO} + \text{HCl}$	1.10E30	-5.19	92.96	1
344.	$\text{CHClO} + \text{OH} = \text{CClO} + \text{H}_2\text{O}$	7.50E12	0.00	1.2	2
345.	$\text{CHClO} + \text{O} = \text{CClO} + \text{OH}$	8.80E12	0.00	3.5	2
346.	$\text{CHClO} + \text{O}_2 = \text{CClO} + \text{HO}_2$	4.50E12	0.00	41.8	2
347.	$\text{CHClO} + \text{Cl} = \text{CClO} + \text{HCl}$	1.25E13	0.00	0.5	2
348.	$\text{CHClO} + \text{CH}_3 = \text{CClO} + \text{CH}_4$	2.50E10	0.00	6.0	2
349.	$\text{CHClO} + \text{CH}_3 = \text{CHO} + \text{CH}_3\text{Cl}$	1.50E13	0.00	8.8	2
350.	$\text{CHClO} + \text{ClO} = \text{CClO} + \text{HOCl}$	3.00E11	0.00	7.0	26
351.	$\text{CH}_2\text{ClO} = \text{CHClO} + \text{H}$	1.83E27	-5.13	21.17	1
352.	$\text{CH}_2\text{ClO} = \text{CH}_2\text{O} + \text{Cl}$	4.53E31	-6.41	22.56	1
353.	$\text{H}_2\text{O}_2 + \text{Cl} = \text{HCl} + \text{HO}_2$	6.62E12	0.00	1.95	26
354.	$\text{H} + \text{HOCl} = \text{HCl} + \text{OH}$	9.55E13	0.00	7.62	2
355.	$\text{Cl} + \text{HOCl} = \text{Cl}_2 + \text{OH}$	1.81E12	0.00	0.26	26
356.	$\text{Cl} + \text{HOCl} = \text{HCl} + \text{ClO}$	7.28E12	0.00	0.1	26
357.	$\text{O} + \text{HOCl} = \text{OH} + \text{ClO}$	6.03E12	0.00	4.37	26
358.	$\text{ClO} + \text{Cl} = \text{O} + \text{Cl}_2$	1.05E12	0.00	9.2	26
359.	$\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl}$	8.59E13	0.00	1.17	38
360.	$\text{ClO} + \text{CH}_4 = \text{CH}_3 + \text{HOCl}$	6.03E11	0.00	15.0	39
361.	$\text{ClO} + \text{CH}_3\text{Cl} = \text{CH}_2\text{Cl} + \text{HOCl}$	3.03E11	0.00	10.7	2
362.	$\text{ClO} + \text{H}_2 = \text{HOCl} + \text{H}$	6.03E11	0.00	14.1	2
363.	$\text{CClO} = \text{CO} + \text{Cl}$	1.30E14	0.00	8.0	2
364.	$\text{CClO} + \text{OH} = \text{CO} + \text{HOCl}$	3.30E12	0.00	0.0	2
365.	$\text{CClO} + \text{O}_2 = \text{CO}_2 + \text{ClO}$	1.00E13	0.00	0.0	2
366.	$\text{CClO} + \text{H} = \text{CO} + \text{HCl}$	3.50E16	-0.79	5.0	40
367.	$\text{CClO} + \text{Cl} = \text{CO} + \text{Cl}_2$	1.50E19	-2.17	1.5	38
368.	$\text{COCl}_2 = \text{CClO} + \text{Cl}$	1.20E16	0.00	75.5	2
369.	$\text{COCl}_2 + \text{OH} = \text{CClO} + \text{HOCl}$	1.00E13	0.00	15.0	2
370.	$\text{COCl}_2 + \text{O} = \text{CClO} + \text{ClO}$	2.00E13	0.00	17.0	2
371.	$\text{COCl}_2 + \text{H} = \text{CClO} + \text{HCl}$	5.00E13	0.00	6.3	2
372.	$\text{COCl}_2 + \text{Cl} = \text{CClO} + \text{Cl}_2$	3.20E14	0.00	23.5	2
373.	$\text{COCl}_2 + \text{CH}_3 = \text{CClO} + \text{CH}_3\text{Cl}$	1.90E13	0.00	12.9	2
374.	$\text{CCl}_2 + \text{O}_2 = \text{COCl}_2 + \text{O}$	5.78E10	0.00	4.1	2
375.	$\text{CCl}_3 + \text{CH}_3 = \text{C}_2\text{H}_3\text{Cl}_3$	9.54E46	-10.66	11.74	2

Table 5.8 (Cont'd)

376.	$\text{CCl}_3 + \text{CH}_3 = \text{CH}_2\text{CCl}_2 + \text{HCl}$	1.62E30	-5.33	8.64	2
377.	$\text{CCl}_3 + \text{CH}_3 = \text{CH}_3\text{CCl}_2 + \text{Cl}$	3.98E22	-2.63	7.09	2
378.	$\text{CCl}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_2\text{Cl}_4$	4.01E45	-10.15	10.67	2
379.	$\text{CCl}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{HCl}_3 + \text{HCl}$	4.74E30	-5.08	8.81	2
380.	$\text{CCl}_3 + \text{CH}_2\text{Cl} = \text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}$	5.90E23	-2.84	8.96	2
381.	$\text{C}_2\text{Cl}_3 + \text{O}_2 = \text{CCl}_2\text{O} + \text{CClO}$	1.21E12	0.0	-0.8	41
382.	$\text{C}_2\text{Cl}_3 + \text{CH}_4 = \text{C}_2\text{HCl}_3 + \text{CH}_3$	6.26E10	0.0	10.0	2

@ Unit of A factor are cc/(mol sec.) for bimolecular reactions
and 1/sec for unimolecular reactions.

\$ Unit of Ea is Kcal/mol

High pressure limit value

* Apparent rate constants by DISSOC computer code analysis
Pressure dependent: rate expression given for 760 torr
Temperature range: 773 - 1273 K

DISSOC: apparent rate constant by DISSOC computer code analysis

QRRK: apparent rate constant by CHEMACT computer code analysis

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TABLE 5.9 THERMOCHEMICAL DATABASE

SPECIES	Hf(298)	S(298)	Cp						COMMENTS
			300	500	800	1000	1500	2000	
AR	0.00	36.98	4.97	4.97	4.97	4.97	4.97	4.97	JANAF
C	170.88	38.31	4.98	4.97	4.97	4.97	4.97	5.01	JANAF
CL	28.90	39.50	5.20	5.40	5.35	5.30	5.24	3.40	BSN
H2	0.00	31.21	6.90	6.99	7.10	7.21	7.72	8.17	JANAF
H	52.10	27.36	4.97	4.97	4.97	4.97	4.97	4.97	JANAF
CH	142.00	43.72	6.97	7.03	7.40	7.78	8.74	9.36	JANAF
HCL	-22.07	44.64	6.96	6.99	7.29	7.56	8.10	8.40	SWS
CL2	0.00	53.30	8.10	8.59	8.91	8.99	9.10	9.16	BSN
CH2	92.35	46.32	8.28	8.99	10.15	10.88	12.22	13.00	JANAF
CH2S	101.44	44.15	8.28	8.99	10.15	10.88	12.22	13.00	
CH3	35.12	46.38	9.26	10.81	12.90	14.09	16.26	17.56	JANAF
CH4	-17.90	44.48	8.51	11.10	15.00	17.20	20.61	22.61	JANAF
C2H	132.00	49.58	8.88	10.22	11.54	12.16	13.32	14.11	Field87
H2C2	94.80	50.80	10.63	12.98	15.34	16.42	18.20		Field87
C2H2	54.19	50.80	10.63	12.98	15.31	16.29	18.31	19.57	JANAF
C2H3	70.40	56.20	10.89	13.87	17.16	18.73	21.34	23.20	MG
C2H4	12.54	52.39	10.28	14.91	20.03	22.45	26.21	28.35	JANAF
C2H5	28.36	57.90	12.26	17.13	22.85	25.74	30.54	33.31	BLP
C2H6	-20.24	54.85	12.58	18.68	25.80	29.33	34.91	38.37	JANAF
CHCL	71.00	56.17	8.80	10.13	12.11	13.22	14.78	14.96	LKL
CH2CL	29.10	59.60	9.32	11.14	14.10	15.83	18.31	18.93	ROUX
CH3CL	-19.59	56.01	9.77	13.20	17.02	18.87	21.80	23.40	RDG
CCL2	38.98	48.94	11.09	12.52	13.61	14.09	15.41	15.84	LKL
CCL3	19.00	71.01	15.25	17.53	18.89	19.14	19.56	19.69	BSN
CCL4	-22.90	74.20	19.91	22.96	24.67	24.95	25.51	25.80	SWS
CHCL2	23.50	67.40	13.11	14.68	16.83	17.98	19.80	21.20	ROUX
CH2CL2	-22.80	64.59	12.26	15.88	19.36	20.81	22.90	24.00	SWS
CHCL3	-24.20	70.66	15.77	19.31	21.96	22.82	24.21	24.60	SWS
C2HCL	60.00	58.10	13.17	15.18	16.88	17.55	18.80	19.55	EST
C2H3CL	8.40	63.09	12.33	17.73	22.47	24.26	26.88	28.80	SWS
CH2CCL2	0.30	69.25	15.81	20.56	24.68	26.19	28.21	29.60	SWS
CHCLCHCL	0.75	69.25	15.81	20.56	24.68	26.19	28.21	29.60	PNK
CHCHCL	61.83	64.46	11.39	16.35	21.23	23.38	26.87	28.80	EST
CHCCL2	58.20	68.88	17.52	22.16	25.74	26.90	28.60	29.85	EST
CH2CCL	60.40	64.46	11.39	16.35	21.23	23.38	26.87	28.80	EST
CHCLCCL	58.63	70.65	17.52	22.16	25.74	26.90	28.60	29.85	EST
C2HCL2	58.20	68.88	17.52	22.16	25.74	26.90	28.60	29.85	EST
C2HCL3	-1.40	77.63	19.22	23.75	26.80	27.60	28.98	30.10	SWS
CH2CLCH2	20.78	68.50	14.01	20.09	25.88	28.37	33.44	34.21	EST
CH3CHCL	16.80	67.31	14.10	19.79	25.42	27.99	32.50	34.70	ROUX
CH3CCL2	13.40	73.60	17.28	22.86	28.09	30.18	33.09	35.01	EST
CCL3CH2	11.90	82.90	20.21	25.68	30.14	31.77	34.50	36.10	EST
CHCL2CH2	15.90	74.30	17.35	22.95	28.03	30.29	33.07	34.55	EST
CH2CLCHCL	11.49	75.80	16.81	22.56	27.67	29.75	33.21	34.50	EST

TABLE 5.9 (Cont'd)

SPECIES	HF(298)	S(298)	Cp						COMMENTS
			300	500	800	1000	1500	2000	
CH2CLCCL2	7.05	83.20	20.21	25.68	30.14	31.77	34.50	36.10	EST
C2H2CL3	8.50	83.10	20.21	25.68	30.14	31.77	34.50	36.10	
C2H5CL	-26.72	66.03	15.06	21.67	28.43	31.47	36.27	39.17	JANAF
CH3CHCL2	-31.05	72.89	18.29	24.81	30.87	33.44	37.80	40.16	PNK
C2H4CL2	-31.01	73.78	18.99	24.74	30.32	33.06	38.79	40.77	PNK
CH2CLCH2CL	-31.01	73.78	18.99	24.74	30.32	33.06	38.79	40.77	
CH3CCL3	-34.60	78.60	22.52	28.45	33.70	35.73	38.91	41.60	BSN
C2H3CL3	-30.90	78.60	22.52	28.45	33.70	35.73	38.91	41.60	
C2H2CL4	-37.20	86.01	25.23	31.32	36.05	37.59	39.82	41.10	
C2CL3	56.50	79.03	20.99	25.21	28.09	28.80	29.70	30.55	B686
C2CL2	50.10	65.00	15.71	17.48	18.86	19.32	20.05	20.38	JANAF
CH2CLCHCL2	-36.10	81.50	21.01	27.67	33.26	35.36	38.91	41.10	SWS
CLO	24.20	54.10	7.50	8.21	8.69	8.81	9.00	9.10	BSN
CLOO	23.00	63.00	11.60	12.71	14.01	14.66	15.70	16.46	BSN
CL2O	19.71	63.66	11.19	12.55	13.34	13.51	13.74	13.85	SND
CLO2	25.00	61.50	9.99	11.72	12.97	13.32	13.80	13.86	BSN
HOCL	-17.80	56.50	8.91	10.08	11.13	11.58	12.40	12.80	BSN
CCLO	-4.00	63.50	10.80	11.70	12.50	12.90	13.40	13.70	BSN
CCL2O	-52.60	67.80	13.81	16.26	17.97	18.45	19.21	19.50	BSN
COCL2	-52.60	67.80	13.81	16.26	17.97	18.45	19.21	19.50	BSN
CHCLO	-39.30	61.80	11.12	13.55	15.70	16.58	18.11	18.80	BSN
O	59.55	38.47	5.23	5.08	5.01	5.01	4.98	4.98	JANAF
O2	0.0	49.01	7.02	7.44	8.04	8.35	8.73	9.04	JANAF
OH	9.49	43.88	7.16	7.05	7.15	7.33	7.87	8.27	JANAF
H2O	-57.80	45.10	8.02	8.41	9.24	9.85	11.23	12.20	BSN
HO2	3.50	54.73	8.37	9.48	10.78	11.43	12.47	13.23	JANAF
H2O2	-32.53	55.66	10.42	12.35	14.30	15.21	16.85	17.88	JANAF
CO	-26.42	47.21	6.96	7.13	7.61	7.94	8.41	8.67	JANAF
CHO	10.40	53.66	8.27	9.27	10.73	11.51	12.55	13.15	EST
CO2	-94.05	51.07	8.90	10.65	12.30	12.97	13.93	14.45	JANAF
CH2O	-25.96	52.26	8.45	10.49	13.34	14.86	16.95	18.14	PNK
CH3O	3.96	54.70	9.02	12.10	16.33	18.41	21.51	23.26	JWB91
CH2CO	-12.40	57.79	12.43	15.67	18.79	20.24	22.44	25.55	SND
CH3CO	-5.40	63.75	12.41	16.35	20.91	23.09	26.19	28.07	BCT
CH3OH	-48.00	57.30	10.50	14.29	19.03	21.44	25.01	27.25	BCT
CH3OO	4.70	62.83	13.29	17.20	21.79	24.47	27.49	29.25	JWB91
CH2OOH	11.90	65.84	16.39	20.40	23.87	25.47	27.50	28.36	JWB91
CH3CHO	-39.18	63.13	13.22	18.16	24.17	27.17	30.60	34.20	JWB91
C2H5O	-4.24	64.50	14.01	20.40	27.24	30.87	36.45		THERM
C2H5OO	-4.70	73.75	18.07	25.59	33.40	36.89	42.03	45.03	THERM
CH2CH2OOH	7.24	79.77	19.56	27.40	35.06	38.28	42.81		THERM
C2H3OO	29.23	71.61	16.43	21.12	26.60	29.42			THERM
CH2CHO	3.90	63.71	13.73	17.81	21.84	23.87	27.11	28.16	JWB91
CH2OCHO	-23.00	71.32	14.70	19.96	25.85	28.62	32.58		JB86
CHCL2OH	-53.00	73.15	15.89	20.27	23.96	25.29	27.70	29.22	THERM

TABLE 5.9 (Cont'd)

SPECIES	HF(298)	S(298)	Cp						COMMENTS
			300	500	800	1000	1500	2000	
CHCHO	-50.60	65.42	14.90	19.64	24.28	25.80			BURCAT
CHCLOH	-1.26	65.43	13.79	17.27	19.69	20.70	22.60	24.80	EST
CH2CLOO	-1.90	73.11	15.84	18.98	22.92	24.57	27.10	28.40	RSG1
CHCL2D	-1.04	70.55	14.42	18.15	21.24	22.32	23.62	24.44	THERM
CHCL2OO	-5.00	78.71	18.69	23.25	26.82	28.38	29.64	30.44	THERM
CHCL2OOH	-37.60	81.33	20.69	26.35	30.46	31.98	34.12	35.47	THERM
CHCLOOCL	5.80	87.75	18.69	23.25	26.82	28.38	29.64	30.44	EST
CHCLOO	46.64	75.15	15.06	17.36	19.91	20.77	22.41	22.72	EST
CCL2OH	-14.50	69.95	16.99	20.37	22.28	22.69	23.85	24.58	THERM
CHCO	21.00	60.00	12.20	15.30	17.67	18.46	19.88	21.17	THERM
CH2CHCLO	38.20	75.21	16.73	20.43	27.25	29.20			THERM
CH2CHOH	-26.24	64.71	13.60	18.14	23.74	26.33	30.50	33.40	THERM
CH2CLO	2.16	63.27	11.22	15.05	18.65	20.33	22.40	23.70	
CH2CLOO	3.50	73.11	15.84	17.98	22.92	24.57	27.10	28.40	
CH2OOCL	10.00	78.60	17.50	22.10	27.10	28.80	31.70	33.30	
CH2OH	-5.90	59.61	9.72	12.58	15.99	17.60	19.80	21.00	

Units: Hf, Kcal/mol; S and Cp, cal/(mol °K)

References for Thermodynamic Properties

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CHAPTER 6 CONCLUSION

Kinetic measurements on the thermal decomposition of dichloromethane in oxidative and pyrolytic reaction environments and argon bath gas was carried out in a tubular flow reactor. The experiments were studied at 1 atmosphere total pressure with residence times of 0.3 - 2.0 seconds in the temperature range 680 - 840 °C.

Dichloromethane decay and product distributions were varied in the presence and presence of added O₂ and/or CH₄. The slowest decay of dichloromethane occurs when added CH₄ but absence of O₂. The concentration of all products, (except HCl, CO, and CO₂ in presence of oxygen), are below 10%. The chlorinated products, such C₂HCl₃, CH₃Cl, and CHClCHCl, in the pyrolytic reaction were more stable than in the oxidative reaction. When oxygen is present, the concentration of chlorinated products decrease more quickly at the temperature above 780 °C than when no oxygen is present. The carbon mass balance in the CH₂Cl₂/Ar reaction environment was less than 60% at the temperature above 780 °C, and even less than 20% when the temperature above 820 °C. This likely implies that the formation of high molecular species and soot is occurring at higher temperature in the absence of oxygen.

The overall (global) rate constants of CH₂Cl₂ decay were determined by using an Arrhenius plot. The activation energy (E_a) and frequency factor (A) were obtained

and put in the Arrhenius equation. The following overall rate equations were found to fit the reaction system studied.

- I. $\text{CH}_2\text{Cl}_2 : \text{CH}_4 : \text{O}_2 : \text{Ar} = 1 : 1 : 4 : 94$
 $k = 6.74 \times 10^{15} \times \text{EXP}(-75.84/\text{RT}) \quad (1/\text{sec})$
- II. $\text{CH}_2\text{Cl}_2 : \text{O}_2 : \text{Ar} = 1 : 4 : 95$
 $k = 1.56 \times 10^{24} \times \text{EXP}(-114.68/\text{RT}) \quad (1/\text{sec})$
- III. $\text{CH}_2\text{Cl}_2 : \text{CH}_4 : \text{Ar} = 1 : 1 : 98$
 $k = 6.46 \times 10^{13} \times \text{EXP}(-67.85/\text{RT}) \quad (1/\text{sec})$
- IV. $\text{CH}_2\text{Cl}_2 : \text{Ar} = 1 : 99$
 $k = 1.21 \times 10^{18} \times \text{EXP}(-86.92/\text{RT}) \quad (1/\text{sec})$

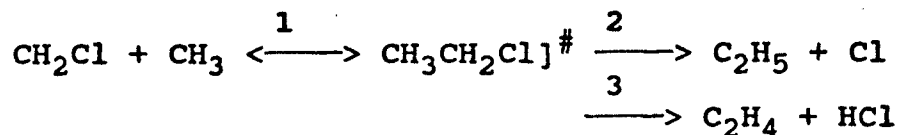
A detailed kinetic reaction mechanism was according to the detailed mechanism for $\text{CH}_2\text{Cl}_2/\text{O}_2/\text{H}_2$ reaction system, and modified to describe the products formation and reactant decay. The mechanism, consisting of 94 species and 382 elementary reactions, is based on thermochemical principles and Transition State Theory. The reaction steps involve stable compounds and free radical species with the addition and recombination reactions all analyzed by Chemical activation Quantum RRK theory. Unimolecular dissociations and isomerization were analyzed by unimolecular QRRK analysis.

The model prediction results for reactant decay are slower than experimental results and major products (CH_3Cl and C_2HCl_3) distribution below 780°C match the experimen-

tal results well. The improvement of reaction mechanism is on going.

APPENDIX

**GISOQRRK INPUT DATA
and CALCULATION RESULTS**

A.1 CH₂Cl + CH₃

k	A	Ea	Source
1	2.00E13	0.0	a
-1	1.43E17	88.92	b
2	1.96E15	81.98	c
3	2.28E13	60.19	d
$\langle v \rangle = 1265.30 \text{ cm}^{-1}$			e
LJ PARAMETERS:			f
$\sigma = 4.898 \text{ \AA}$		$\epsilon/k = 300.00 \text{ K}$	

a. A₁ taken as that for CC.+C. (A=2.0E13, Ref: A-S)
Ea = 0.0

b. Reverse reaction (k₋₁) from thermodynamics

c. A₂ taken as that for CC.+ C. (A=2.0E13, Ref:A-S)
and microscopic reversibly Ea = $\Delta H - RT$

d. Transition State Theory; loss of a rotor and degeneracy
A₃ = 10^{13.72} * 10^(-4/4.6) * 3
Ea = $\Delta H + (43)$
(Ea Ref: Weissman, M & Benson, S.W., IJCK,
16, 941,1984)

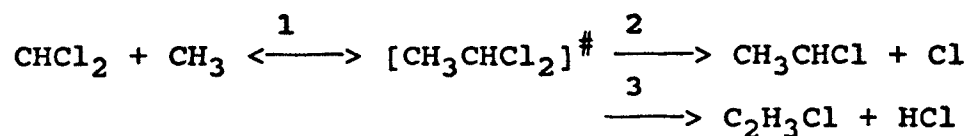
e. Shimanouchi, T., Table of Molecular Vibration Frequencies Consolidated Vol.I. Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39

f. Calculated from critical properties for CH₃CH₂Cl
(Ref:RPS)

CALCULATED APPARENT FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CH ₃ CH ₂ Cl	1.09E12	-4.38
		C ₂ H ₅ + Cl	1.51E13	5.78
		C ₂ H ₄ + HCl	6.28E12	1.68

Temperature Range: 773 K - 1273 K

A.2 CHCl₂ + CH₃

k	A	Ea	Source
1	1.58E13	0.0	a
-1	1.80E17	87.67	b
2	5.54E15	74.75	c
3	4.56E13	60.38	d
$\langle v \rangle = 1076.59 \text{ cm}^{-1}$			e
LJ PARAMETERS:			f
$\sigma = 5.103 \text{ \AA}$		$\epsilon/k = 415.31 \text{ K}$	

a. A₁ taken as that for 2-CCC. + C. (A=1.58E13, Ref: A-S)
Ea = 0.0

b. Reverse reaction (k₋₁) from thermodynamics

c. A₂ taken as that for 2-CCC.+ C. (A=1.58E13, Ref: A-S)
and microscopic reversibility Ea = ΔH - RT

d. Transition State Theory; loss of a rotor and degeneracy
A₃ = 10^{13.72} * 10^(-4/4.6) * 6 Ea = ΔH + (41)
(Ea Ref: Weissman, M. & Benson, S.W., IJCK, 16, 941, 1984)

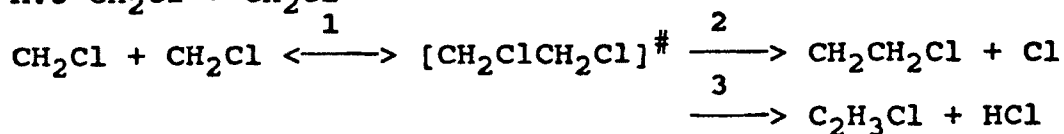
e. From "CPFIT" program and Cp data

f. Calculated from critical properties for CH₃CHCl₂
(Ref:RPS)

CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CH ₃ CHCl ₂	1.86E11	-6.35
		CH ₃ CHCl + Cl	2.98E13	3.40
		C ₂ H ₃ Cl + HCl	3.73E12	0.58

Temperature Range: 773 K - 1273 K

A.3 CH₂Cl + CH₂Cl

k	A	Ea	Source
1	8.00E12	0.0	a
-1	4.38E17	87.21	b
2	8.15E15	78.69	c
3	3.03E13	60.34	d
$\langle v \rangle = 797.20 \text{ cm}^{-1}$			e
LJ PARAMETERS:			f
$\sigma = 5.116 \text{ \AA}$		$\epsilon/k = 445.49 \text{ K}$	

a. A₁ taken as 2 * that for CC. + CC. (A=3.98E12, Ref: A-S) Ea = 0.0

b. Reverse reaction (k₋₁) from thermodynamics

c. A₂ taken as that for 1-CCC.+ C. (A=2.0E13, Ref: A-S) and microscopic reversibility Ea = $\Delta H - RT$

d. Transition State Theory : loss of a rotor and degeneracy A₃ = 10^{13.72} * 10^(-4/4.6) * 4 Ea = $\Delta H + (43)$ (Ea Ref: Weissman, M. & Benson, S.W., IJCK, 16, 941, 1984)

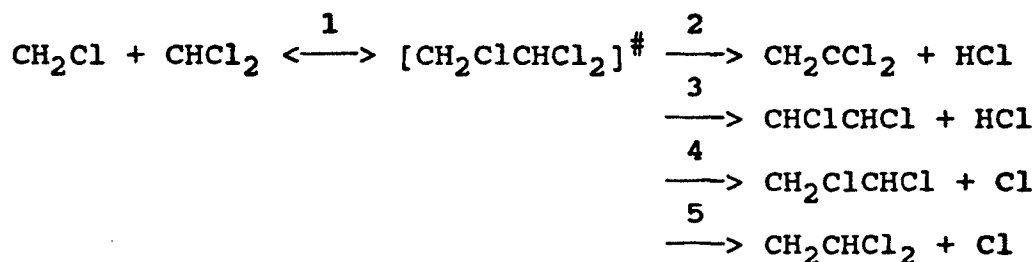
e. Shimanouchi, T., Table of Molecular Vibration Frequencies Consolidated Vol.I. Natl. Stand. Ref. Data Ser.(U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39

f. Calculated from critical properties for CH₂ClCH₂Cl (Ref:RPS)

CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CH ₂ ClCH ₂ Cl	7.16E11	-2.74
		CH ₂ CH ₂ Cl + Cl	1.73E13	9.13
		C ₂ H ₃ Cl + HCl	1.83E12	5.31

Temperature Range: 773 K - 1273 K

A.4 CH₂Cl + CHCl₂

k	A	Ea	Source
1	7.94E12	0.0	a
-1	9.11E17	82.00	b
2	7.59E12	52.95	c
3	3.03E13	53.08	d
4	4.17E15	69.79	e
5	1.97E15	74.20	f

$$\langle v \rangle = 916.443 \text{ cm}^{-1} \quad \text{g}$$

LJ PARAMETERS: h

$$\sigma = 5.397 \text{ \AA} \quad \epsilon/k = 478.04 \text{ K}$$

a. A₁ taken as that for CC. + 2-CCC. (A=7.94E12, Ref: A-S)
Ea = 0.0

b. Reverse reaction (k₋₁) from thermodynamics

c. Transition State Theory : loss of a rotor and degeneracy
A₂ = 10^{13.72} * 10^(-4/4.6) * 1 Ea = ΔH + (43)
(Ea Ref: Weissman, M. & Benson, S.W., IJCK, 16, 941, 1984)

d. Transition State Theory : loss of a rotor and degeneracy
A₃ = 10^{13.72} * 10^(-4/4.6) * 4 Ea = ΔH + (43)
(Ea Ref: Weissman, M. & Benson, S.W., IJCK, 16, 941, 1984)

e. A₄ taken as that for CC. + 2-CCC. (A=7.94E12, Ref: A&S) and microscopic reversibility Ea = ΔH - RT

f. A₅ taken as that for CCCC. + C. (A=1.58E13, Re: A&S) and microscopic reversibility Ea = ΔH - RT

g. From "CPFIT" program and Cp data

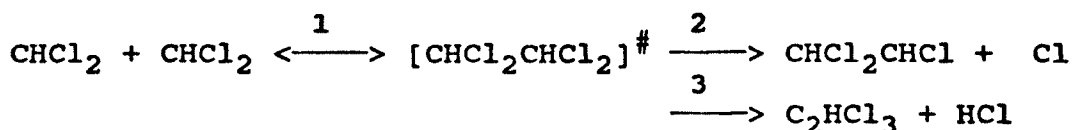
h. Calculated from critical properties for CH₂ClCHCl₂

(Ref:RPS)

CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CH ₂ ClCHCl ₂	4.05E10	-7.49
		CH ₂ CHCl ₂ + HCl	2.28E11	-1.28
		CHClCHCl + HCl	8.85E11	-1.27
		CH ₂ ClCHCl + Cl	2.73E12	1.43
		CH ₂ CHCl ₂ + Cl	6.33E11	2.74

 Temperature Range: 773 K - 1273 K

A.5 CHCl₂ CHCl₂

k	A	Ea	Source
1	1.18E12	0.0	a
-1	8.29E17	84.20	b
2	2.37E16	71.40	c
3	2.83E13	58.50	d
$\langle v \rangle = 578.20 \text{ cm}^{-1}$			e
LJ PARAMETERS:			f
$\sigma = 5.91 \text{ \AA}$		$\epsilon/k = 525.9 \text{ K}$	

a. A₁ taken as 1/3 that for CC.C + CC.C(A=3.00E12,
Ref: A-S) Ea = 0.0

b. Reverse reaction (k₋₁) from thermodynamics

c. A₋₂ taken as that for 2-C₅H₁₁ + CH₃ (A=1.58E13,
Ref: A-S) and microscopic reversibility Ea = ΔH - RT

d. Transition State Theory; loss of a rotor and degeneracy
A₃ = 10^{13.72} * 10^(-4/4.6) * 4 Ea = ΔH + (43)
(Ea Ref: Weissman, M. & Benson, S.W., IJCK,
16, 941, 1984)

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

f. Calculated from critical properties for CH₂ClCH₂Cl
(Ref:RPS)

CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

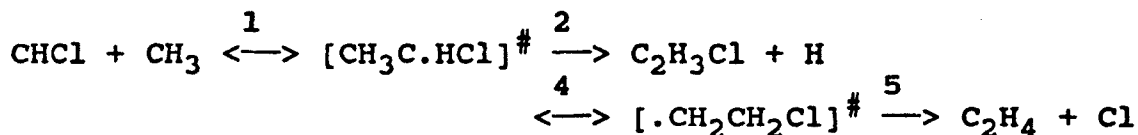
Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CHCl ₂ CHCl ₂	3.22E10	-8.50
		CHCl ₂ CHCl + Cl	1.73E13	2.10
		C ₂ HCl ₃ + HCl	2.55E11	-0.90

Temperature Range: 773 K - 1273 K

i. Calculated from critical properties (estimated by using Lydersen method) for CH_2ClOH (Ref: RPS)
CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CHClOH	2.25E09	-3.56
		CHClO + H	1.98E13	0.0
		CH ₂ ClO	8.53E05	-2.05
		CH ₂ O + Cl	1.33E12	1.05

Temperature Range: 773 K - 1273 K

A.7 CHCl + CH₃

k	A	Ea	Source
1	2.00E13	0.0	a
-1	6.40E15	87.48	b
2	1.60E13	38.81	c
4	2.27E13	40.68	d
-4	1.24E13	36.78	e
5	1.07E13	18.67	f
$\langle v \rangle = 1197.20 \text{ cm}^{-1}$			g
LJ PARAMETERS:			h
$\sigma = 4.777 \text{ \AA}$		$\epsilon/k = 351.26 \text{ K}$	

- a. A₁ taken as that for CC. + C. (A=2.0E13, A-S)
Ea = 0.0
- b. Reverse reaction (k₋₁) from thermodynamics
- c. A₋₂ taken as 1/3 that for C=C + H (A=4.0E14 Ref: A-S)
and microscopic reversibility
Ea = 5.8 (Estimate from C₂CL₄ + H & C₂H₄ + H)
- d. Transition State Theory; loss of a rotor and degeneracy
A₄ = 10^{13.72} * 10^(-4/4.6) * 3
Ea = RS + Δ Hr + Eabs = 27.7 + 3.98 + 9
- e. Reverse reaction (k₋₄) from thermodynamics
- f. A₋₅ taken as that for C₂H₄ + Cl (A=1.6E13, Ea=0.0
Ref: Kerr, J.A., & Moss, S.J., "Handbook of
Bimolecular and Thermolecular Gas Reaction",
Vol. I & II, CRC Press Inc. 1981)
and microscopic reversibility
- g. From "CPFIT" program and Cp data
- i. Calculated from critical properties (estimated by using
Lydersen method) for CH₃CHCL (Ref: RPS)

CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CH ₃ CHCl	9.67E09	-5.2
		C ₂ H ₃ Cl + H	9.95E12	-0.026
		CH ₂ CH ₂ Cl	1.32E09	-3.93
		C ₂ H ₄ + Cl	9.96E12	0.054

Temperature Range: 773 K - 1273 K

A.8 CHCl + O



k	A	Ea	Source
1	2.00E13	0.0	a
-1	2.92E15	168.00	b
2	9.33E15	76.86	c
$\langle v \rangle = 1158.07 \text{ cm}^{-1}$			d
LJ PARAMETERS:			e
$\sigma = 4.664 \text{ \AA}$		$\epsilon/k = 415.10 \text{ K}$	

- a. A_1 taken as that for CC. + C. (A=2.0E13, Ref: A-S)
Ea = 0.0
- b. Reverse reaction (k_{-1}) from thermodynamics
- c. A_{-2} taken as that for CC. + C. (A=2.0E13, Ref: A-S)
Ea = 0.0 and microscopic reversibility
- d. From "CPFIT" program and Cp data
- e. Calculated from critical properties (estimated by using Lydersen method) for CHClOH (Ref: RPS)

CALCULATED PARAMETER FORWARD REACTION RATE CONSTANTS

Bath Gas	P (torr)	Product Channel	A (cc/mole s)	Ea (Kcal/mole)
Ar	760	CHClO	5.40E08	-3.41
		CHO + Cl	1.98E13	-0.015

Temperature Range: 773 K - 1273 K

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