New Jersey Institute of Technology
Digital Commons @ NJIT

Theses
Electronic Theses and Dissertations

1-31-1990

Kinetic mechanism of the reactions of dichloromethane and chloroform with atomic hydrogen at low pressure and room temperature

Jia-Ling Linda Young
New Jersey Institute of Technology

Follow this and additional works at: https://digitalcommons.njit.edu/theses

Part of the Chemical Engineering Commons

Recommended Citation

Young, Jia-Ling Linda, "Kinetic mechanism of the reactions of dichloromethane and chloroform with atomic hydrogen at low pressure and room temperature" (1990). *Theses*. 1917.
https://digitalcommons.njit.edu/theses/1917

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Theses by an authorized administrator of Digital Commons @ NJIT. For more information, please contact digitalcommons@njit.edu.

Copyright Warning & Restrictions

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

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

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

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

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

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

KINETIC MECHANISM OF THE REACTIONS OF DICHLOROMETHANE AND CHLOROFORM WITH ATOMIC HYDROGEN AT LOW PRESSURE AND ROOM TEMPERATURE

BY

JIA-LING LINDA YOUNG

Thesis submitted to the faculty of the Graduate School of
the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering

1990

APPROVAL OF THESIS

Title of Thesis: Kinetic Mechanism Of The Reactions Of Dichloromethane And Chloroform With Atomic Hydrogen At Low Pressure And Low Temperature

Name of Candidate: Jia-Ling Linda Young
Master of Science in Chemical Engineering

Thesis and Abstract Approved by:

Jan 11 1990

Dr. Joseph W. Bozzelli
Professor
Department of Chemical Engineering,
Chemistry & Environment Science

Date

1/11/90

Dr. Richard S. Magee

Date

1/11/90

Dr. Dana E. Knox

Date

VITA

Name: Jia-Ling Linda Young

Present address:

Degree and date to be conferred: M.S. Ch.E., 1990

Date of birth:

Place of birth:

Secondary Education: Taipei First Girls' Senior High School
Taipei, Taiwan, R.O.C.

Collegiate institute	Date	Degree	Date of Degree
Chung Yuan Christian University	1982-1986	B.S.	July, 1986
New Jersey Institute of Technology	1987-1990	M.S.	Jan., 1990

Major: Chemical Engineering

ACKNOWLEDGEMENTS

I want to express my appreciation to Dr. Joseph W. Bozzelli for his advice and encouragement. I am deeply indebted to him for the opportunities which he made available to me.

My parents and my sister, they deserve my warmest gratitude for their love and inspiration without which I shall not achieve what I have done.

It is my pleasure to give thanks to Dr. Magee and Dr. Knox for their patience and constructive comments on this work, and all the members in the Combustion Group of NJIT.

ABSTRACT

Title of Thesis: Kinetic Mechanism Of The Reactions Of
Dichloromethane And Chloroform With Atomic
Hydrogen At Low Presure And Room Temperature

Jia-ling Linda Young, Master of Science in Chemical
Engineering, 1990

Thesis Directed by Dr. J. W. Bozzelli

The reaction mechanism of dichloromethane reaction (DCM) with atomic hydrogen in a flow reactor at room temperature (300 K) and low pressure (2.1 - 2.7 torr), argon bath gas, has been developed in this research to analyze the above reaction system. The important addition reactions of radicals (or atoms) to olefins and the radical/radical (atom/radical) combination reactions have been analyzed using the bimolecular version of the Quantum-Rice-Ramsperger-Kassel (QRRK) theory.

The detailed reaction mechanism satisfactorily fits the experimental data for the reagent (DCM) conversion from previous experimental over a initial ratio (atomic hydrogen to dichloromethane) range of 6.8 to 40. The initiation reactions are abstraction by atomic hydrogen on the dichloromethane. One channel is for hydrogen atom to abstract chlorine atom in DCM to form methyl chloride radical and HCl, the other is to abstract hydrogen atom in DCM to form hydrogen molecule and dichloromethane radical. After initiation, combination reactions, such as H+CH2Cl, H+CHCl2, CHCl2+CHCl2, CHCl2+CH2Cl, CHCl2+CH3, CH2Cl+CH2Cl, CH2Cl+CH3, and CH3+CH3 follow. The adducts formed are all treated as chemically activated complexes, with reaction from these complexes to products versus stabilization analyzed with QRRK theory. The major products are HCL and CH4, which agree with experiment.

The kinetic reaction mechanism is based on thermochemical principles and Transition State Theory. The rate constant obtained for the primary steps at 300 K are:

	k (cm^3 $mole^{-1}$ sec^{-1})
CH2Cl2 + H ----> CH2Cl + HCl	$2.41 * 10^9$
CH2Cl2 + H ----> CHCl2 + HCl	$2.17 * 10^7$

A second detailed mechanism was developed for the reaction of Chloroform with atomic hydrogen, argon bath gas, at room temperature (300 K) and low pressure (2.22 - 2.82 torr). The rate constants obtained for the initially important steps at 300 K are :

	k (cm3 mole-1 sec-1)
CHCl3 + H ----> CHCl2 + HCl	$3.72 * 10^{10}$
CHCl3 + H ----> CCl3 + H2	$2.52 * 10^8$

TABLE OF CONTENTS

LIST OF FIGURE AND TABLE

Figure Page

Table Page

I. INTRODUCTION

The reaction between hydrogen atoms and chloromethanes has received some kinetic attention, but not much. These reactions are now known to be important in the fuel rich stage of chlorocarbon combustion (incineration) and pyrolysis. It has been shown that a "Super Equilibrium" concentration of H atoms exists in these systems, due to very rapid reaction of Cl + H2 --> HCl + H, where H2 is pressent as a fuel or formed in hydrocarbon pyrolysis reactions <1,2>. The purpose of this research is to study the chemical kinetics of atomic hydrogen with dilute concentration of dichloromethane and chloroform in a tubular flow discharge reactor, at low pressure, room temperature. And used a detailed mechanism to analyze the reaction systems.

To develop detailed mechanisms, the Activated Complex Quantum Rice-Ramsperger-Kassel (QRRK) method <3> was utilized for

- Addition
- Beta scission
- Recombination

reactions. We evaluate these reactions under low pressure (0.76 - 10.0 torr) and low temperature (273 - 400 K) conditions. The Activated Complex Quantum RRK theory calculates probability of reaction versus stabilization as function of pressure and temperature. In the pressent study, mechanisms were developed to describe the experimentally observed reagents conversion and product formation.

These two overall reaction systems, H + CH_2Cl_2 and H + $CHCl_3$, can be considered as a model for hydro-dechlorination of chlorinated methanes, which is of interest as a method for detoxification of these chlorocompounds. The hydrogen atoms react with dichloromethane to form HCl and useful CH_4:

$$CH_2Cl_2 + H \Longleftrightarrow HCl + CH_2Cl \qquad (1)$$

$$CH_2Cl + H \Longleftrightarrow CH_3 + Cl \qquad (2)$$

$$Cl + H + M \Longleftrightarrow HCl + M \qquad (3)$$

$$CH_3 + H + M \Longleftrightarrow CH_4 + M \qquad (4)$$

Hydrogen atoms react with chloroform,

$$CHCl_3 + H \Longleftrightarrow CHCl_2 + HCl \qquad (5)$$

$$CHCl_2 + H \Longleftrightarrow CH_2Cl + Cl \qquad (6)$$

then reaction (2), (3), (4) follow to again form HCl and CH_4.

It have been shown in the previous experimental studies <4,5> that the primary stable-end products of these two reaction systems are CH_4 and HCl, the HCl can be readily scrubbed (neutralized) with caustic.

In the current study, the detailed mechanisms have been developed and compared with the experimental data. Rate constants (at 300 K) for the primary reactions were obtained:

CH2Cl2 + H <===> HCl + CH2Cl

$k = 2.41 * 10^9 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$

CH2Cl2 + H <===> H2 + CHCl2

$k = 2.17 * 10^7 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$

CHCl3 + H <===> HCl + CHCl2

$k = 3.72 * 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$

CHCl3 + H <===> H2 + CCl3

$k = 2.52 * 10^8 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$

II. PREVIOUS STUDY

A surprisingly small number of reactions of atomic hydrogen with halomethanes have been studied in the past five decades, and very little detailed mechanistic information is available on these reaction systems.

In 1933, Chadwell and Titani<6> investigated the reactions of methyl halides with hydrogen atoms, which were produced in a Wood's discharge flow system. They identified the products of the reactions and generated some data for the heat of reactions and proposed a general reaction process: H. + RX <===> HX + R.. The heat of reactions were reported as followed,

Reaction	Heat of Reaction(Kg cal/g mole)
H + CH3F <===> HF + CH3	30
H + CH3Cl <===> HCl + CH3	30
H + CH3Br <===> HBr + CH3	28
H + CH3I <===> HI + CH3	27

Polanyi et. al. <7> made a report on the similar reactions in the same year, and only identified hydrogen halide products. Due to the limitations of their apparatus, there was no direct measurement of the rate constant, but Polanyi and his co-woirkers were able to make an estimate of the activation energy, as for reaction H + CCl4 <===> HCl+ CCl3, the activation energy was estimated to be less than 2.8 Kcal.

Vance and Baumann <8> in 1938 studied the reaction of hydrogen atom with CCl_4 at torr pressure and reported a formula for rate constant k (as a function of temperature),

$k = SZe^{-A/RT}$ where $Z = 3.1 * 10^{13} / T$

S = Steric Factor

A = Activation Energy

in Vance and Baumann's experiment, they indicated that the complete conversion of H into HCl occurred at 0.8 torr, 150-200 oC, with a CCl_4:H ratio of about 10:1 and five minutes reaction time. Where the Steric Factor is 0.007 the Activation Energy is 3.45 Kcal/mole and Arrhenius A factor is $2.2 * 10^{11}$.

Clark and Tedder <9> in 1964 examined the reactions of hydrogen atom with some halomethanes, at pressure of 0.23 torr and room temperature, and proposed a reaction sequence for these reactions. They considered the initial step in the reaction system is chlorine abstraction by hydrogen atoms. But in this study, they didn't measure the concentration of hydrogen atoms and there was no absolute rate constant reported.

Gaydon and Wolfhard <10> were the first to report flame- like emission when atomic hydrogen reacted with several halocarbons in 1952. They have characterized the emitting species as $C_2^{\#}$ and $CH^{\#}$. In 1975, Arnold, Kimbell, and Snelling <11> observed C_2 visible and infrared emissions in the reactions of atomic hydrogen with halomethanes, supporting the identification of Gaydon and Wolfhard. Arnold et. al. concluded that these were probably due to the exothermic reaction $C + CX \longrightarrow C_2 + X$ (where X is halogen or hydrogen). We can obtain some important information as to the existance of intermediates from the various emission observed. This is helpful as we first formulate the reaction mechanism. The disadventage to their studies is that neither the concentrations, stoichiometry, nor the stable end-products were precisely.

One mechanistic report was published in 1973, Combourieu et. al. <12> introduced a mechanism of the reaction of hydrogen atom with dichloromethane. The rate constant of $H + CH_2Cl_2$ was obtained and a mechanism was proposed to describe the production of CH_4, HCl, C_2H_2, and C_2H_4. They assumed that the initial step is the chlorine abstraction by a hydrogen atom. The feasibility of CH_2Cl_2 acting as a flame inhibitor was also recognized in this report. We feel that we can improve this mechanism of Combouriu, by treating the combination reactions with the bimolecular QRRK analysis <13> and adding a number of reaction channels which are easily accessable to the initially formed chemically energized adduct. An example of these for the combourien mechanism is $H + CH_2Cl \longrightarrow CH_2Cl_2^{\#} \longrightarrow CH_3 + Cl$.

Westenberg and deHaas (1975)<14> performed more direct rate measurment for reactions H + CH3X (X = Br, Cl, F) with [H] >> [CH3X] at the temperature range of 298-996 K. This study presented that as methyl halides were added in excess amount, there was always a sharply accelerating decay in the H signal with distance, namely, with complete removal of H atom in a short distance.

In 1979, Costes et. al. <15> showed that carbon atoms can be produced by the reaction of hydrogen atoms with CCl4 in a low pressure reactor. It was also proposed that the initial reaction in these H-atom with halocarbons is an initial slow chlorine abstraction by hydrogen atom which is followed by subsequent fast chain branching and termination reactions resulting in a flame and the final products.

Gould et. al. <16> have recently studied the reaction of hydrogen atoms (generated by photolysis of HBr or HI) with CDCl3. They showed that Cl abstraction from CDCl3 by H atom is more accessible than that of D abstraction. They reported a ratio of Cl abstraction is 7.2 times larger than that of D abstraction, as normalized to equal numbers of Cl and D atoms.

Jo and Bozzelli <4> have studied the reaction of H + CHCl3 in a flow reactor, at low pressure (2.22-2.82 torr) and room temperature. They have proposed a mechanism for the secondary reactions that almost all chloroform consumed went toward the production of methane. The kinetics were computer simulated by solving the simultaneous first-order differential equations. Runge-Kutta method and Rosenbrock method were used for integration and optimization of the system. In this study, the rate constant (at 298 K) for the primary reaction is obtained,

$$H + CHCl3 \longrightarrow HCl + CHCl2$$

$$k = 2.53 * 10^{10} (cm^3/mole\ sec)$$

Huang and Bozzelli <5> (1987) studied the kinetics of atomic hydrogen with dichloromethane in a flow reactor at pressure of 2.1 to 2.7 torr and room temperature. A detailed mechanism was developed to fit the experimental data, yet the results of that model is not fully satisfactory as comparing with the experimental data. The rate constants used in Huang's model (298 K) for the initial steps were

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

$$k = 3.63 * 10^9 cm^3/mole\ sec$$

$$H + CH2Cl2 \longrightarrow H2 + CHCl2$$

$$k = 2.08 * 10^7 cm^3/mole\ sec$$

The current study may be considered as a follow-up study of the previous research of S.H. Huang and W.K. Jo on their reaction mechanism model. The model necessarily involves the estimation of the rate constants for relevent elementary reactions. We also focus upon the use of Bimolecular Quantum-RRK theory <13> to interpret the reaction channels. Hopefully, this study may contribute a little to the field of flame inhibition and combustion research.

III. THEORY

A. Transiton-State Theory

For many kinds of reactions, especially for elementary reactions, their rate constants may be expressed as a product of a temperature dependent term and a composition term.

A more detailed explanation of how the reactants transform into products is given by the Trasition-State Theory. The reactants combining to form unstable intermediates called activated complexes which then decompose spontaneously into products. The Transition-State Theory assumes that an equilibrium exists between the concentration of reactants and activated complex at all times and that the rate of decomposition of complex is the same for all reactions which is given by **kT/h** ,where **k** is the Boltzmann constant and **h** is the Planck constant. Thus for the forward elementary reaction of a reversible reaction,

$$A + B \underset{k_r}{\overset{k_f}{\Longleftrightarrow}} AB \qquad (1)$$

we have the following conceptual elementary scheme:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^* \xrightarrow{k_2} AB \qquad (2)$$

$$K^* = \frac{k_1}{k_{-1}} = \frac{[AB^*]}{[A][B]}$$

$$k_2 = \frac{\mathbf{k}T}{\mathbf{h}}$$

The observed rate of the forward reaction is then

$$r_{AB,forward} = (\text{conc. of activated complex}) \times (\text{rate of decomposition activated complex})$$

$$= \frac{\mathbf{k}T}{\mathbf{h}} [AB^*]$$

$$= \frac{\mathbf{k}T}{\mathbf{h}} K^* C_A C_B \qquad (3)$$

By expressing the equilibrium constant of activated complex in terms of the standard free energy,

$$\triangle G^* = \triangle H^* - T\triangle S^* = -RT \ln K^* \qquad (4)$$

$$K^* = EXP(-\triangle G^*/RT) = EXP(-\triangle H^*/RT + \triangle S^*/R)$$

the rate becomes

$$r_{AB,foward} = \frac{\mathbf{k}T}{\mathbf{h}} EXP(\triangle S^*/R)\ EXP(-\triangle H^*/RT)\ C_A\ C_B \qquad (5)$$

Theoretically both $\triangle S^*$ and $\triangle H^*$ vary very slowly with temperature. Hence, of the three terms that make up the rate constant in Eq. 5, the middle one, $EXP(\triangle S^*/R)$, is so much less temperature-senstive than the other two terms that we may take it to be constant. So for the forward reaction, and similarly for the reverse reaction of Eq. 1, we have approximately

$$k_f \quad T\ \mathrm{EXP}(-\Delta H_f^*/RT) \qquad (6)$$

$$k_r \quad T\ \mathrm{EXP}(-\Delta H_r^*/RT)$$

where $\Delta H_f^* - \Delta H_r^* = \Delta H_{RXN}$

Transition-state theory views the reaction rate to be governed by the rate of decomposition of intermediate. The rate of formation of intermediate is assumed to be governed by collisions plus thermodynamics and it is present on equilibrium concentrations at all times. That is, Transition-state theory considers the second step combined with the determination of complex concentration to be the rate controlling factors.

B. Prediction of Rate Constants for Radical Addition and Recombination Reactions by Bimolecular QRRK Theory

The decomposition of a radical or molecule has a unimolecular, pressure-independent rate constant in the limit of high pressure, but as pressure is reduced the rate constant eventually falls off or decreases with pressure. In the low-pressure limit, it becomes directly proportional to the pressure. Rationalizing and qualifying these effects, first accomplished in the 1920's <17>, again has become an active area in kinetics research.

Radical combination or radical-molecule addition to an unsaturated molecule would seem to be simply the reverse of decompositon, having the same decay behavior by microscopic reversibility. This is true for the specific reaction channel that leads to formation of the collisionally stabilized adduct. The reason is that the adduct species has an energy distribution where is in thermal equilibrium with surrounding gas molecules, just as for a species that is thermally decomposing.

It is very important to note but not well recognized that additional products can be formed from combination and addition reactions by this chemical activated pathway. The initially formed adduct has a chemical energy distribution, different from a thermal energy distribution because the thermal energies of the reactants are augmented by the chemical energy released by making the new bond. This chemical energy is initially the same as the energy barrier for dissociation of the collisionally stabilized adduct to the original adducts. If the energy in the chemical activation energy distribution extends above the barrier for another dissociation (or isomerization reaction pathway) of the adduct, then that reaction pathway can also occur.

Calculation of the bimolecular rate constant involves the concept that the fate of the chemically activated adduct is determined by competition among the possible pathways; stabilization by collision, redissociation to reactants, or formation of new products dy dissociation or isomerization. References are the Dean's paper.<18>

1. Unimolecular QRRK Equation

Dean (1985) <18> has presented equations for bimolecular rate constants based on the Quantum-RRK or QRRK unimolecular reaction theory of Kassel (1928), which treats the storage of excess energy (relative to the ground state) as quantized vibrational energy.

In the simplest form of the theory, the assumption is made that the vibrations of the decomposing molecule can be represented by a single frequency <v>, usually a geometric mean <v> of the molecule's frequencies. Next, energy E initially activated of the complex and each barrier to reaction path relative to the ground state of the stabilized molecule is divided into E/h<v> vibrational quanta. For the total energy variable E, the symbol n is used; and for number of quanta to the energy barrier to reaction Eo, the quantized energy is m quanta; quantum level and the rate processes are illustrated in Figure 1-a. A very general scheme for unimolecular reaction is as follows:

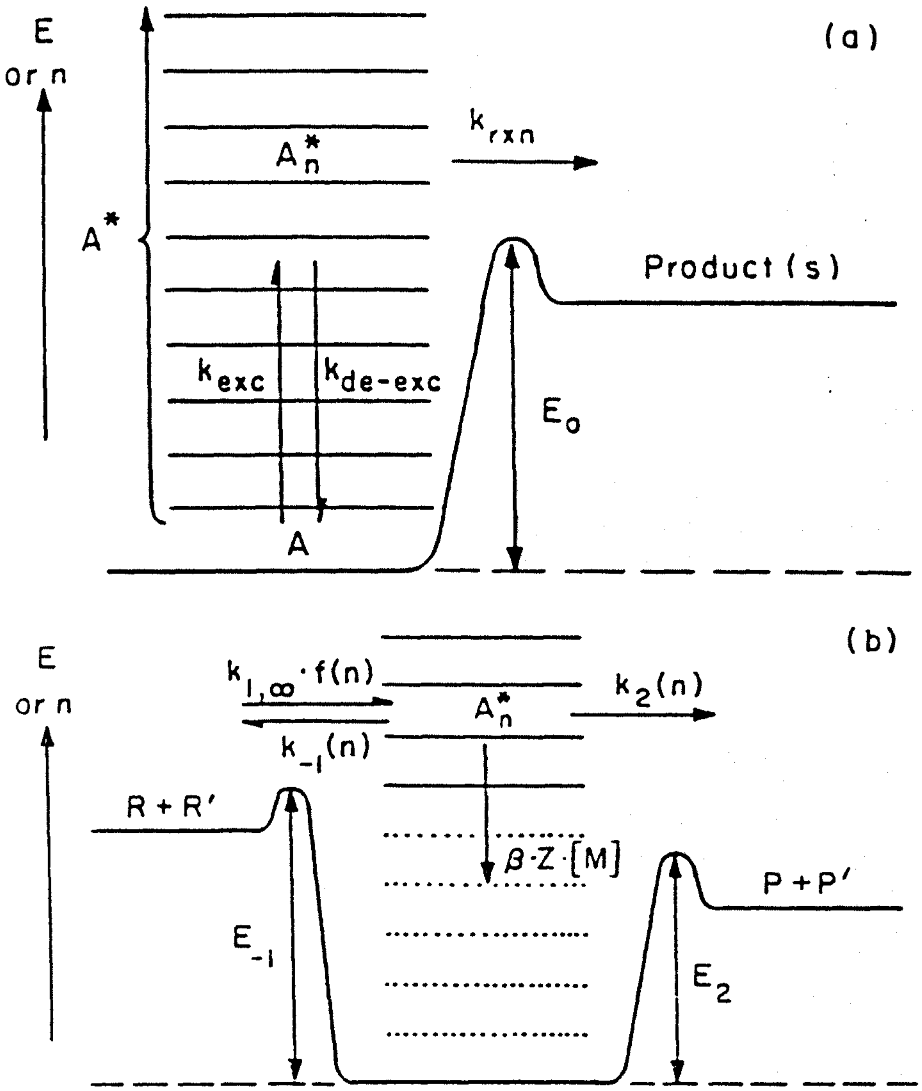


Figure 1. Energy diagrams for pressure-dependent reactions.

a. Unimolecular reaction

b. Bimolecular reaction with chemically activated pathway

$$A + M \Longleftrightarrow A^{*} + M$$

$$A^{*} \longrightarrow \text{Products}$$

Here M stands for the third body and only serves to raise the reacting molecule to its energized state A^{*} by collisional activation.

The apparent k_{uni}:

$$k_{uni} = \frac{1}{[\ A\ ]} \frac{d\ [\text{Products}]}{dt} \qquad (1)$$

is then evaluated by a sum over all energies, assuming pseudo-steady state for each energy level of A* and collisional excitation or deexcitation with rate constants k_{exc} and k_{deexc}:

$$k_{uni} = \frac{1}{[A]} \ k_{rxn}(E)\ [A^{*}(E)]$$

$$= \ k_{rxn}(E) \ \frac{k_{deexc}[M]\ K(E,T)}{k_{deexc}[M] + k_{rxn}(E)} \qquad (2)$$

where K(E,T) is the thermal-energy distribution function (k_{exc}/k_{deexc}). Kassel assumed that if a molecule were excited to an energy E, then $k_{rxn}(E)$ would be proportional to the probability that one of the s oscillators could have energy Eo or greater (sufficient energy to cause reaction); that is, m or more of the n total quanta. The proportionality constant was shown to be A , the Arrhenius preexponential factor for dissociation of A in the high presure limit, so the energy-dependent rate constant is:

$$k_{rxn}(E) = A \frac{n!\ (n-m+s-1)!}{(n-m)!\ (n+s-1)!} \qquad (3)$$

Likewise, he derived the quantized thermal energy distribution K(E,T) to be:

$$K(E,T) = a^n\ (1-a)^s \frac{(n+s-1)!}{n!\ (s-1)!} \qquad (4)$$

where $a = e^{(-h<v>/kT)}$.

In the present development, a collisional efficiency Beta has been applied to modify the traditional but incorrect strong-collision assumption that $k_{deexc} = Z\ [M]$, where Z is the collision frequency rate constant. The strong-collision assumption implies that any collision between A^* and M would have to remove all the excess enrgy from A^*. Note that any species included as M would have to accommodate this energy content, regardless of its capacity for accepting the energy. Analyzing collisional energy transfer for master-equation methods, Troe (1977) fit most of the temperature dependence of Beta with the equation:

$$\frac{\text{Beta}}{1-(\text{Beta})^{1/2}} = \frac{-<\triangle E_{coll}>}{F(E)\ k\ T} \qquad (5)$$

where $< E_{coll}>$ is the average amount of energy transferred per collision and F(E) is a factor, weakly dependent on energy,that is related to the number of excited states. Over the temperature range of 300-2500 ^{o}K for a series of reactions (Troe, 1977); F(E) = 1.15 was observed as a median value. The value of Beta depends on the specific third-body molecule M through the value of $<\triangle E_{coll}>$.

2. Bimolecular QRRK Equations

The bimolecular QRRK equations follow (Dean, 1985) from unimolecular QRRK and the defintion of the chemical activation distribution function. Consider recombination or addition to occur via the sequence:

$$\begin{tikzcd} R + R' \arrow[r, shift left, "k_1 \quad f(E,T)"] & {[RR']^*} \arrow[l, shift left, "k_{-1}(E)"] \arrow[r, dashed, "k_2(E)"] \arrow[d, dotted, "\text{Beta } k_s{[M]}"] & P + P' \\ & A & \end{tikzcd}$$

Here R is a radical, R' is a radical (recombination) or unsaturated molecule (addition), A^* is the energized complex which can either disoociate or be collisionally stabilized, Beta is the collisional deactivation efficiency, and ks is the collisional rate constant for stabilization. k_1 is the high-pressure-limit rate constant for forming adduct and f(E,T) is the energy distribution for chemical activation:

$$f(E,T) = \frac{k_{-1}(E)\ K(E,T)}{k_{-1}(E)\ K(E,T)} \qquad (6)$$

where K(E,T) is the QRRK thermal distribution from Eq. 4. Rate constants $k_{-1}(E)$ and $k_2(E)$ are calculated from the QRRK equation for $k_{rxn}(E)$ (Eq.3) using $m_{-1}(E_{-1}/h<v>)$ and $m_2(E_2/h<v>)$,respectively. A typical energy diagram for these reactions is shown in Figure 1-b.

To obtain the bimolecular rate constant for a particular product channel, a pseudosteady-state analysis is made as before. The rate constant for forming the addition/stabilization product [RR'] from R + R' is:

$$k_{stab} = \frac{d[RR']/dt}{[R][R']} = \text{Beta}\ k_s[M]\ \frac{k_1\ \ f(E,T)}{\text{Beta}\ k_s[M] + k_{-1}(E) + k_2(E)} \qquad (7)$$

and, for forming the addition/decomposition product P + P':

$$k_{dec} = \frac{d[Prod]/dt}{[R][R']} = k_2(E)\ \frac{k_1\ \ f(E,T)}{\text{Beta}\ k_s[M] + k_{-1}(E) + k_2(E)} \qquad (8)$$

If more decomposition channels are available, the $k_{rxn}(E)$ for each channel is added in the denominator of Eqs.7 and 8, and an equation in the form of Eq.8 is written for each additional channel, substituting the respective $k_{rxn}(E)$ for $k_2(E)$ as the multiplier term.

3. Low- and High-Pressure Limits

The low-pressure and high-pressure limits for these channels may be derived from Eqs. 7 and 8. As pressure changes, the rate constants change because of the relative magnitutes of terms in the denominator, $Bk_s[M]$ vs. $k_{-1}(E)$ and $k_2(E)$.

The low-pressure limit for addition/stabilization (or recombination) is derived from Eq.7 to be

$$\lim_{M \to 0} k_{stab} = [M] \text{ Beta } k_s \frac{k_1 \; f(E,T)}{k_{-1}(E) + k_2(E)} \qquad (9)$$

sometimes written as [M]*ko (as a termolecular reaction), and the high-pressure limit reduces properly to k_1 . At a given temperature, the falloff curve for stabilization can be plotted as log(kstab) vs. log(P) or log(M).

Note the presence of $k_2(E)$ in Eq.9. If chemically activated conversion of $[RR']^*$ is more rapid than decomposition to reactants [$k_2(E) >> k_{-1}(E)$], then Eq.9 shows that ko_{stab} will be divided by $k_2(E)$ rather than by $k_{-1}(E)$. thus, ignoring the chemically activated pathway could give incorrect rate constants for "simple" addition.

Similar analysis of Eq.8 implies that chemically activated decomposition has a falloff curve that is the opposite of addition/stabilization, with a rate constant that is pressure-independent at low pressure and inversely proportional to pressure at high pressure. From Eq.8, the low-pressure limit for the chemically activated pathway to P and P' will be

$$\lim_{M \to 0} k_{dec} = k_1 \frac{k_2(E)\ f(E,T)}{k_{-1}(E) + k_2(E)} \qquad (10)$$

and the high-pressure limit will be

$$\lim_{M \to 0} k_{dec} = \frac{1}{[M]} \frac{k_1}{\text{Beta}\ k_s} k_2(E)\ f(E,T) \qquad (11)$$

with an inverse pressure dependence. While this result goes against past tuiotion about low- and high- pressure limits, it is a natural consequence of physics when chemically activated reaction are recognized as possibilities. One consequence is that a reaction of the form A + B ---> C + D with a rate constant measured to be pressure-independent may be proceeding via addition

C. Computer Aided Mechanism Modelling by CHEMKIN Program

CHEMKIN <19> program is a general-purpose, problem-independent, transportable chemical kinetics code package, which is written by FORTRAN. This package was designed to facilitate a chemist's interaction with the computer in modelling chemical kinetics. Using the CHEMKIN package requires the manipulation of a number of programs, subroutines and data files.

The general structure of the CHEMKIN package is shown in Figure 2. The Interpreter of CHEMKIN program is a program whichh reads a symbolic description of a reaction mechanism, and thenb extracts the needed thermodynamic data for each species involved from the Thermodynamic Data Base. The primary output from the Interpreter is a binary file which is called the Linking file. This file contains numerical information which describes the elements, species and reaction mechanism.

Input to the Interpreter may be any number of reversible reactions, including those with arbitrary third bodies, photons or ionic species as reactants or products. And enhanced third body efficiencies may also be specified for any of the species in three body reactions. The input to the Interpreter is in familiar chemical, not so much computational, notation.

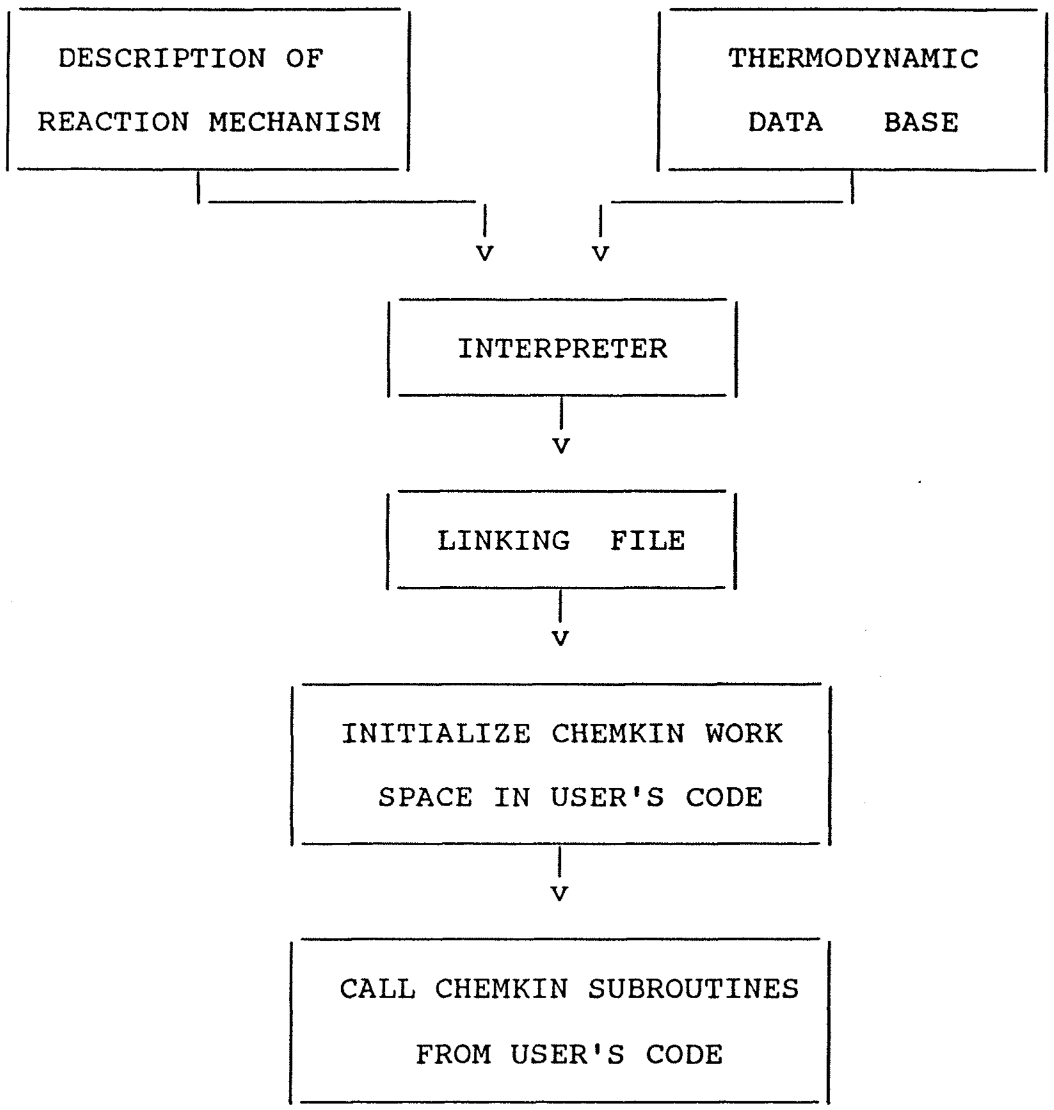


Figure 2. Structure of the CHEMKIN package

IV. RESULTS AND DISCUSSION

A. Detailed Kinetics Mechanism and Modeling

The Reaction mechanism was constructed by determining the initial reaction and then considering plausible reactions of the products from the initial reaction. Thus process continued until the mechanism incorporated all the plausible and likely important reactions leading to the observed stable products; and accounted properly for all the important intermediate species.

1. Reaction of Atomic Hydrogen with Dichloromethane

The possible initial reactions in the reaction system for the reaction of H atom with dichloromethane is a slow abstraction of Cl or H from dichloromethane to produce chloromehtyl radical and HCl or H2,

$$H + CH_2Cl_2 \Longleftrightarrow HCL + CH_2Cl \qquad (1)$$

$$H + CH_2Cl_2 \Longleftrightarrow H_2 + CHCl_2 \qquad (2)$$

The abstraction of Cl from CH2Cl2 by H atom has been studied previously <12> at pressure near 1 torr and 298-460 oK temperature range, the activated energy was determined as 6.1 Kcal. Gould et. al. <16> have reported that the probabilities of Cl abstraction is 2.6 times larger than that of D abstraction (if normalized to equal numbers of Cl and D atom), in the reaction of H + CDCl3. That is the Cl abstraction is likely to be the predominant initial step.

The chloromethyl radical, can then react with H2 and H (which are present in relatively high concentration in the system),

H2 + CH2Cl <===> CH3Cl + H (3)
H + CH2Cl <===> [CH3Cl]# <===> CH3 + Cl (4)
H + CH2Cl <===> [CH3Cl]# <===> CH3Cl (5)

Reaction (4) and (5), have been discussed in the previous section as analyzed by Quantum-RRK. Thus, two important radicals, Cl and CH3, are generated. And by reaction (3), H atoms are regenerated.

The other initial carbon centered radical CHCl2, can also react with H2 and H,

CHCl2 + H2 <===> CH2Cl2 + H (6)
CHCl2 + H <===> [CH2Cl2]# <===> CH2Cl2 (7)
CHCl2 + H <===> CH2Cl + Cl (8)

where reaction (6) is the reverse of reaction (2). The reaction (7) and reaction (8) have been analyzed by QRRK method in the previous section.

As Cl atoms are generated, they will react with H2 or dichloromethane to form HCl and a H atom or a dichloromethyl radical, respectively.

Cl + H2 <===> HCl + H (9)
Cl + CH2Cl2 <===> HCl + CHCl2 (10)

The reaction of halogen atom with hydrogen molecules bave been studied for nearly a century and have played a contral role in the history of chemical kinetics. Miller and Gordon <22> concluded that the ratio of the forward to the reverse rate constant is indeed equal to the equilibrium constant. Therefore, Miller and Gordon's rate constant for reaction Cl + H2 are used in this study.

The reaction of Cl with CH2Cl2 is found to be a very important reaction in this mechanism. Clyne and Walker <23> have reported a Cl + CH2Cl2 rate constant of 3.9*10E+11 cm^3 $mole^{-1}$ s^{-1} at room temperature.

CH3 also can react with H2, H and dichloromethane,

CH3 + H2 <===> CH4 + H (11)
CH3 + H <===> CH4 (12)
CH3 + CH2Cl2 <===> CH4 + CHCl2 (13)
CH3 + CH2Cl2 <===> CH3Cl +CH2Cl (14)

For CH3, there are also important combination reactions with CH2Cl, CHCl2 and CH3 itself.

CH3 + CH2Cl <===> [CH3CH2Cl]# <===> C2H5Cl (15)
CH3 + CH2Cl <===> [CH3CH2Cl]# <===> C2H4 + HCl (16)
CH3 + CH2Cl <===> [CH3CH2Cl]# <===> C2H5 + Cl (17)

CH3 + CHCl2 <===> [CH3CHCl2]# <===> CH3CHCl2 (18)
CH3 + CHCl2 <===> [CH3CHCl2]# <===> CH3CHCl + Cl (19)
CH3 + CHCl2 <===> [CH3CHCl2]# <===> CH2CHCl + HCl(20)

CH3 + CH3 <===> [C2H6]# <===> C2H6 (21)

These reactins all have been calculated by QRRK method (are shown in APPENDIX 1). The two chlorocarbon radicals, CH2CL and CHCL2, may react with themselves and also with each other,

CH2Cl+CH2Cl<===>[CH2ClCH2Cl]#<===> CH2ClCH2Cl (22)
CH2Cl+CH2Cl<===>[CH2ClCH2Cl]#<===>CH2ClCHCl+Cl(23)
CH2Cl+CH2Cl<===>[CH2ClCH2Cl]#<===>CH2CHCl+HCl (24)

CH2Cl+CHCl2<===>[CH2ClCHCl2]#<===>CH2ClCHCl2 (25)
CH2Cl+CHCl2<===>[CH2ClCHCl2]#<===>CH2ClCHCl+Cl(26)
CH2Cl+CHCl2<===>[CH2ClCHCl2]#<===>CHClCHCl+HCl(27)

CHCl2+CHCl2<===>[CHCl2CHCl2]#<===>CHCl2CHCl2 (28)
CHCl2+CHCl2<===>[CHCl2CHCl2]#<===>CHCl2CHCl+Cl(29)
CHCl2+CHCl2<===>[CHCl2CHCl2]#<===>CHClCCl2+HCl(30)

The wall recombination steps which may compete with H abstraction from dichloromethane by CL atom are,

Cl + Cl (wall) ---> Cl2
H + H (wall) ---> H2

The wall recombination of Cl atoms may not be negligible , if an uncoated or imperfectedly coated wall was used. <12>

Other heterogeneous wall recombination reaction which effect the mechanism are:

$H + Cl\ (wall) \longrightarrow HCl$

$H\ (wall) + Cl \longrightarrow HCl$

Since the discharge tube and tubular reactor in the experiment were coated with phosphoric acid, and then conditioned under vacoom (2 torr) with H atoms CA = $1 * 10^{14}$ /cm^3 for 6 hours. These heterogeneous reaction were consider to be insignificant.

A termolecular reaction scheme was proposed to account for the recombination steps in this mechanism,

$H + H + M \longrightarrow H_2 + M$ (M is a third body) (31)

$H + Cl + M \longrightarrow HCl + M$ (32)

$Cl + Cl + M \longrightarrow Cl_2 + M$ (33)

The rate constants of these termolecular reactions were taken from Kerr and Moss <24> at appropriate pressure.

No visible flame was reported in the experiment. Carbon formation was not monitored under the experimental conditions <15>.

The methane was formed, it may react with the CL atom,

$Cl + CH_4 \Longleftrightarrow CH_3 + HCl$ (34)

This reaction competes with reaction of $Cl + H_2$ in the excess H_2 and reaction of $Cl + CH_2Cl_2$. It is relatively insignificant, because of the larger concentration of H and CH_2Cl_2.

The Cl atoms, besides to react with dichloromethane, will also undergo combination, addition and abstraction reactions as follow:

Cl + CH2Cl <===> CH2Cl2 (35)

Cl + CHCl2 <===> [CHCl3]# <===> CHCl3 (36)

Cl + CHCl2 <===> [CHCl3]# <===> CCl2 + HCl (37)

Cl + CH3 <===> CH3Cl (38)

Cl + C2H4 <===> C2H4Cl (39)

Cl + CH3Cl <===> HCl + CH2Cl (40)

Cl + C2H4Cl2 <===> HCl + C2H3Cl2 (41)

Cl + C2H5Cl <===> HCl + C2H4Cl (42)

These reaction were analyzed by Quantum-RRK method. For the abstraction reactions, mostly can be found in the "CRC Handbook of Bimolecular and Termolecular Gas Reactions" by Kerr and Moss <24>.

The other possible reactions which may be helpful to elucidate the complex charactor of the H + CH2Cl2 reaction system are listed below, (their rate constant were calculated by QRRK method)

H+C2H2Cl2<===>[C2H3Cl2]#<===>C2H3Cl + Cl (43)

H+C2H2Cl2<===>[C2H3Cl2]#<===>C2H3Cl2 (44)

H+C2H2Cl3<===>[C2H3Cl3]#<===>C2H3Cl2 + Cl (45)

H+C2H2Cl3<===>[C2H3Cl3]#<===>C2H3Cl3 (46)

H+C2H2Cl3<===>[C2H3Cl3]#<===>C2H2Cl2 + HCl(47)

H+C2H3Cl2<===>[C2H4Cl2]#<===>C2H4Cl + Cl (48)

H+C2H3Cl2<===>[C2H4Cl2]#<===>C2H4Cl2 (49)

H+C2H3Cl2<===>[C2H4Cl2]#<===>C2H3Cl + HCl (50)

H+C2H4Cl<===>[C2H5Cl]#<===>C2H5 + Cl (51)

H+C2H4Cl<===>[C2H5Cl]#<===>C2H5Cl (52)

H+C2H4Cl<===>[C2H5Cl]#<===>C2H4 + HCl (53)

H+C2H3Cl<===>[C2H4Cl]#<===>C2H4 + Cl (54)

H+C2H3Cl<===>[C2H4Cl]#<===>C2H4Cl (55)

Table 1 lists all the reactions considered in the overall reaction mechanism and the rate constants. APPENDIX 1 lists the estimations of rate constant of radical recombination/addition reactions by QRRK theory. This mechanism describes a reasonable path toward to the formation of the major products.

2. Reaction of Atomic Hydrogen with Chloroform

The initial step of the reaction system, which is similar to that in CH2Cl2 mechanism, is an abstraction reaction of CL or H atom from chloroform to produce chloromethyl radical and HCl or H2,

H + CHCl3 <===> HCl + CHCl2 (1)

H + CHCl3 <===> H2 + CCl3 (2)

Gould et. al. <16> show that the ratio of Cl abstraction is 7.2 times larger than that of H abstraction.

Two chloromethyl radicals may react with H2 and H,

H2 + CHCl2 <===> CH2Cl2 + H (3)
H + CHCl2 <===> [CH2Cl2]# <===> CH2Cl2 (4)
H + CHCl2 <===> [CH2Cl2]# <===> CH2Cl + Cl (5)
H2 + CCl3 <===> CHCl3 + H (6)
H + CCl3 <===> [CHCl3]# <===> CHCl3 (7)
H + CCl3 <===> [CHCl3]# <===> CHCl2 + Cl(8)
H + CCl3 <===> [CHCl3]# <===> CCl2 + HCl(9)

Reaction (3), (4) and (5) have been discussed in the CH2Cl2 mechanism. Reaction (6) is endothermic by 14 Kcal/mole, therefore, not significant at room temperature. A QRRK calculation has been done for reaction (7) to reaction (8) to show that CHCl2 + Cl is the predominant reaction (APPENDIX 1, Table 16).

The HCl formed may react with the hydrogen atoms

H +HCl <===> H2 + Cl (10)

Watson and Clyne, et. al. <25,23> have shown the occurrence of the following reaction;

Cl + CHCl3 <===> CCl3 + HCl (11)

When the concentration of CHCl2, CH2Cl and CCl3 rises, they will react with one another, or themselves. The possible reactions between CHCl2 and CH2Cl have been described in the H + CH2Cl2 reaction system, here we concentrate on the additional reactions with CCl3 only,

CCl3 + CHCl2 <===> [CHCl2CCl3]# <===> C2HCl5 (12)
CCl3 + CHCl2 <===> [CCl3CHCl2]# <===> C2Cl4+HCl (13)

CCl3 + CHCl2 <===> [CCl3CHCl2]# <===> C2Cl4+HCl (13)

CCl3 + CHCl2 <===> [CCl3CHCl2]# <===> C2HCl4+Cl (14)

CCl3 + CH2Cl <===> [CH2ClCCl3]# <===> C2H2Cl4 (15)

CCl3 + CH2Cl <===> [CH2ClCCl3]# <===> C2HCl3+HCl(16)

CCl3 + CH2Cl <===> [CH2ClCCl3]# <===> C2H2Cl3+Cl(17)

Analysis by QRRK theory shows that in reaction (12) to reaction (14), stabilization represents the major fraction of collisions. As the pressure is increased, the C2Cl4 + HCl and the C2HCl4 + Cl reaction become even less important (APPENDIX 1, Table 17). For reaction (15) - reaction (17), the predominant reaction is HCl + C2HCl3 as analyzed by QRRK (APPENDIX 1, Table 19).

For the CCl3 + CCl3 combination reaction; since it is not easy to generate CCl3 (most H + CHCl3 goes to CHCl2 + HCl), the concentration of CCl3 is relatively low, i.e. the probability for a CCl3 to meet another CCl3 is very low. And it shows in the experimental results that there is no trace of C2Cl6 in the end product, but we include this reaction in the mechanism for completeness.

The hydrogen atom can then react with some important radicals and olefins generated by the above chloromethyl cobination reactions.

Reactions of H+CH2Cl, H+C2H3Cl, H+C2H2Cl2, H+C2H3Cl2, H+C2H4Cl and H+C2H2Cl3, have previously been discussed in the CH2Cl2 mechanism.

Please refer to the CH_2Cl_2 discussion for the combination and abstraction reaction with Cl.

The unique (non CH_2Cl_2) part of the H+$CHCl_3$ system , are the CCl_3 reactions and the formation of carbon at room temperature. We have to consider the steps by which carbon may be generated.

As CCl_2 generated by H+CCl_3, reaction (8), it may undergo the reactions,

$$H + CCl_2 \Longleftrightarrow CCl + HCl \qquad (18)$$

$$H + CCl \Longleftrightarrow C + HCl \qquad (19)$$

Though these two reactions the formation of the carbon atoms as observed in Costes et. al. and in our studies on the tip of the movable injection tube can be explained.

Since CH_2Cl_2 is formed in $CHCl_3$ reaction system, the other reactions listed in CH_2Cl_2 reaction system can be also taken, i.e. CH_2Cl_2 system can be considered as a sub-system to this $CHCl_3$ reaction system.

B. QRRK Calculations :

The decomposition and stabilization of the energized redical or molecule complexes was modeled by using the Quantum RRK calculation <3,13>. The details of the bimolecular QRRK method and its application to a number of chemically activated reaction system have been previously discussed in the theory section.

Energized complex/ QRRK theory, which was presented by Westmoreland and Dean <3> is used for modeling of radical addition and combination reactions. And this method has been modified by Ritter and Bozzelli <1> to use gamma function instead of factorials. The QRRK computer code was need to determine the energy dependant rate constants for all chemicals. The program incorporates QRRK theory to calculate rate constant as a function of temperature and pressure. It is important in determination of the accurate rate constant needed for input to the mechanism and in the choice of the important reaction paths.

A QRRK analysis of the chemically activated system, using generic estimates or literature values for high pressure rate constants and species thermodynamic properties for the enthalpies of reaction, yields thermodynamically and kinetically plausible apparent rate constants are shown in Figure 3, 4, 5 and 6. The results from the calculations input rate parameters used in these calculations are summarized in Appendix 1 Table 1 to 20. The calculation were performed for each of six pressure between 0.76 torr and 10 torr (since the current study is under low presure, and we focus on temperature 300 K, which is the temperature condition of the experiments.)

1. QRRK Calculation for Reaction H + CH2Cl

For the reaction of hydrogen atom with Dichloromethane, one of the initial steps is for the hydrogen atom to abstract the chlorine atom from DCM molecule. Thus, the methyl chloride radical, and HCl are formed. The methyl Chlorine radical will then react with the other hydrogen atoms to form other products. Under this circumstant we therefore consider the H + CH2CL reaction as the first combination reaction in the system,

$$\begin{tikzcd}
\text{H + CH2Cl} \arrow[r, shift left, "1"] & {[\text{CH3Cl}]^{\#}} \arrow[l, shift left, "-1"] \arrow[r, "2"] \arrow[dr, "3"] \arrow[d, dotted, "Ks"] & \text{CH2 + HCl (70.29)} \\
\text{(81.20)} & \text{CH3Cl} & \text{CH3 + Cl (64.02)} \\
 & \text{(-19.59)} &
\end{tikzcd}$$

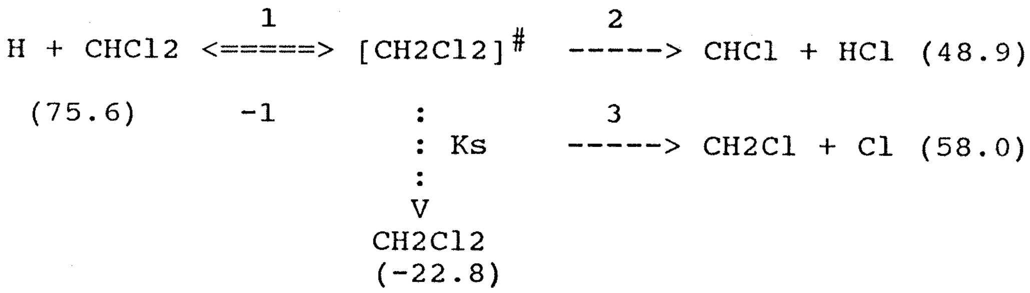
The hydrogen and CH2Cl, first form a energized complexe (# denotes energized). The energized complex can further decomposes as shown in reaction (2) and (3), be stabilized or return to initial reactants. The reaction (2) does not likely to occur due to the thermo limitations (the high energy barrier can not be overcomed under our experimental conditions), as it is endothermicily. The reactants to lower energy as reaction (3) is the thermodynamically favorable channel relative to the initial energy of the reaction.

The calculation results, pressure dependent rate constants and an energy diagram for H atom and CH2Cl radical combination are shown in Figure 3.

The QRRK calculations for presure range of 0.76 to 10 torr and at 298 oK show that the CH3 + Cl channel is the dominant channel. Under low pressure the stabilization reaction cannot compete with the other channels (k-1 and k2) but it becomes more important as the pressure raised).

2. QRRK Calculation for Reaction CHCl2 + H

For the reaction of atomic hydrogen with chloroform, the initial step is for the hydrogen atom to abstract the chlorine atom from the choroform molecule, forming HCl and CHCl2. The CHCl2 will undergoing a series of addition or combination reactions. Reaction with hydrogen atoms may be considered as most probable because [H] >> [CHCl2], i.e. the concentraction of H is higher than the other radicals.



Although the products from reaction (2) are at a lower energy level, the energy barrier (Ea) is very high and it is very difficult to see H + CHCL2 goes to HCl + CHCl.

Figure 4 shows that CH2Cl + Cl is the dominant channel over pressure range of 0.76 to 10 torr and it also shwqws that the stabilization reaction is more likely to occur than the k-1 reaction in the pressure range > 10 torr.

3. QRRK Calculation for Reaction CHCl2 + CH2Cl

Another important reaction in the reaction systems is CH2Cl + CHCl2. For reaction of hydrogen atom with Dichloromethane, CHCl2 is generated when the dichloromethane molecule loses one hydrogen atom by abstraction with atomic hydrogen (H + CH2Cl2 --> CHCl2 + H2). This is considered as a second initial step in the H + dichloromethane reaction system. And for H + Choroform reaction system, it is generated by H + CHCl2 --> Cl + CH2Cl.

$$\begin{tikzcd}
\mathrm{CH_2Cl+CHCl_2} \arrow[r, shift left, "1"] & {[\mathrm{CH_2ClCHCl_2}]^{\#}} \arrow[l, shift left, "-1"] \arrow[r, "2"] \arrow[dr, "3"'] \arrow[d, dotted, "K_s"] & \mathrm{CH_2ClCHCl+Cl}\ (40.39) \\
(52.60) & {\mathrm{CH_2ClCHCl_2}\ (-35.4)} & \mathrm{CHClCHCl+HCl}\ (-21.31)
\end{tikzcd}$$

Where the energized complex can further decompose to products as shown by reacction (2) and (3). The energy diagram is illustrated in Figure 5. It must be noted that reaction (3) corresponds to the composite behavior of four-center 1,2 and three- center 1, 1 (or 2, 2) HCl elimination processes, because the CH2ClCCl: (or :CHCHCl2) formed in the latter case rapidly isomerize to CHClCHCl. Both 1, 2 and 1, 1 (or 2, 2) HCl elimination process are expected to have similar A factors <20> and a slightly lower activated energy for 1, 2 HCl elimination process <21>.

4. QRRK Calculation for Reaction H + C2H3Cl

H + C2H3Cl is an important additional reaction in these two system. C2H4, which is the one of the important stable end products can be generated, through this reaction.

$$\begin{tikzcd}
\mathrm{H + C_2H_3Cl} \arrow[r, shift left, "1"] & {[\mathrm{C_2H_4Cl}]^{\#}} \arrow[l, shift left, "-1"] \arrow[r, "2"] \arrow[d, dotted, "K_s"] & \mathrm{C_2H_4 + Cl}\ (41.44) \\
(60.5) & {\mathrm{C_2H_4Cl}\ (17.51)} &
\end{tikzcd}$$

The energy diagram for these reactions is illustrated in Figure 6-a and the calculation results for pressure dependant are show in Figure 6-b. We can see that the beta scission reaction is the dominant exit channel. And it is more likely to become stabilized than to dissociate back to the reactants (pressure of 1.26 torr). The C2H4Cl complex contains relatively higher energy resulting from formation of a new chemical bond, Prior to stabilization it may unimolecularly isomerize. And the results of the addition may form two kinds of energized complex [CH3CHCl]* or [CH2CH2Cl]*. For the former one, if undergoing beta siccision, it will shift the H atom spontaneously and then release the Cl atom.

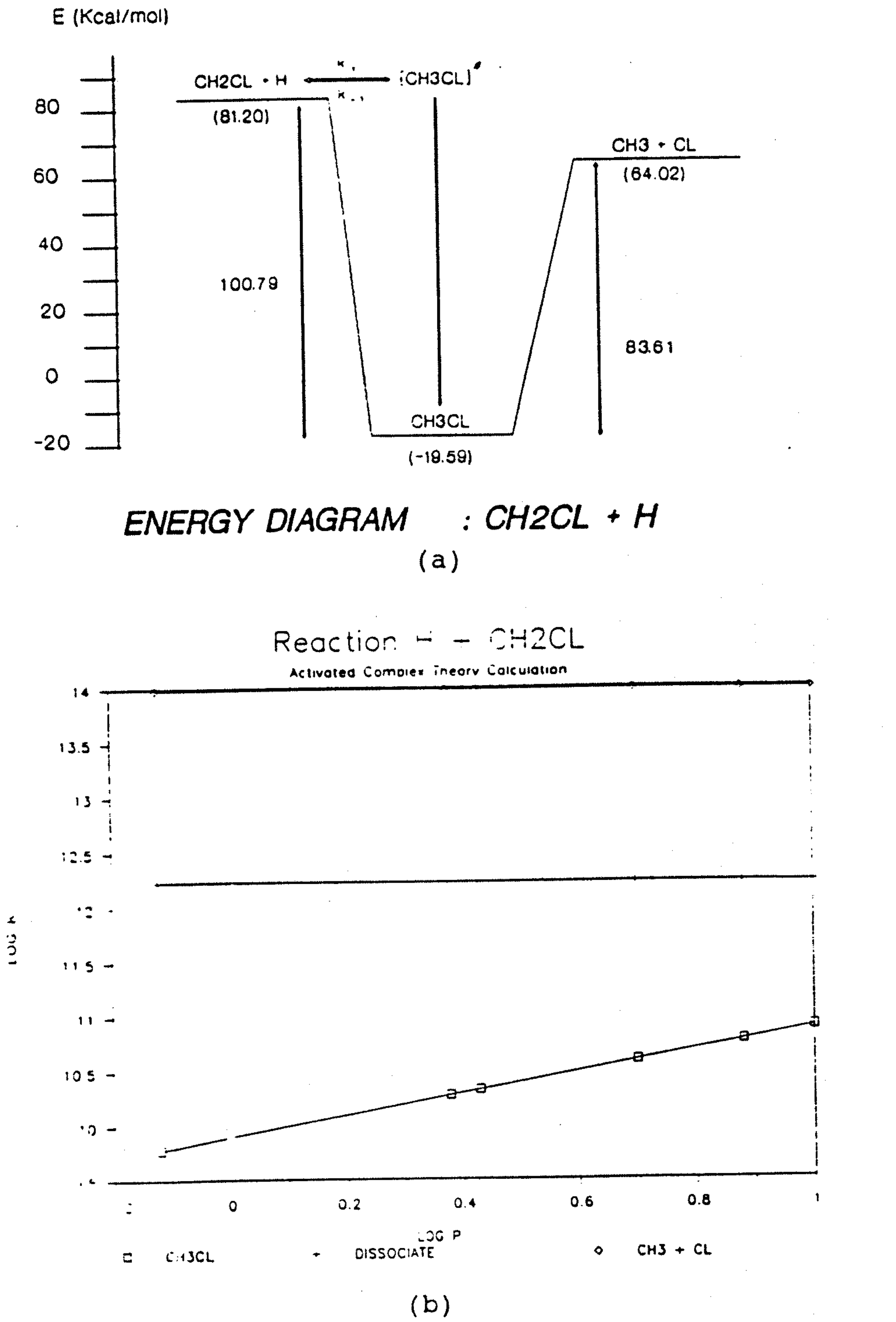
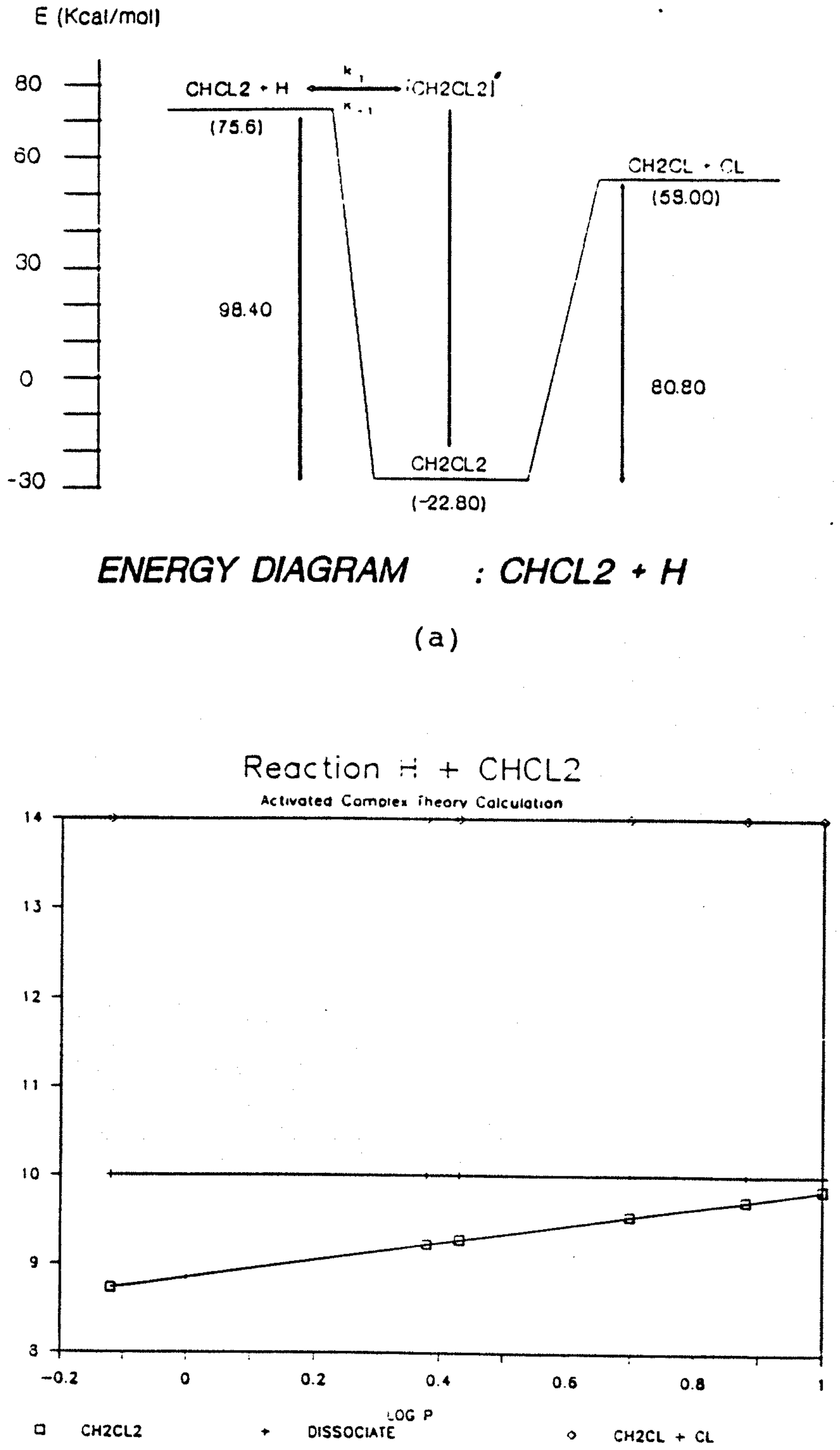


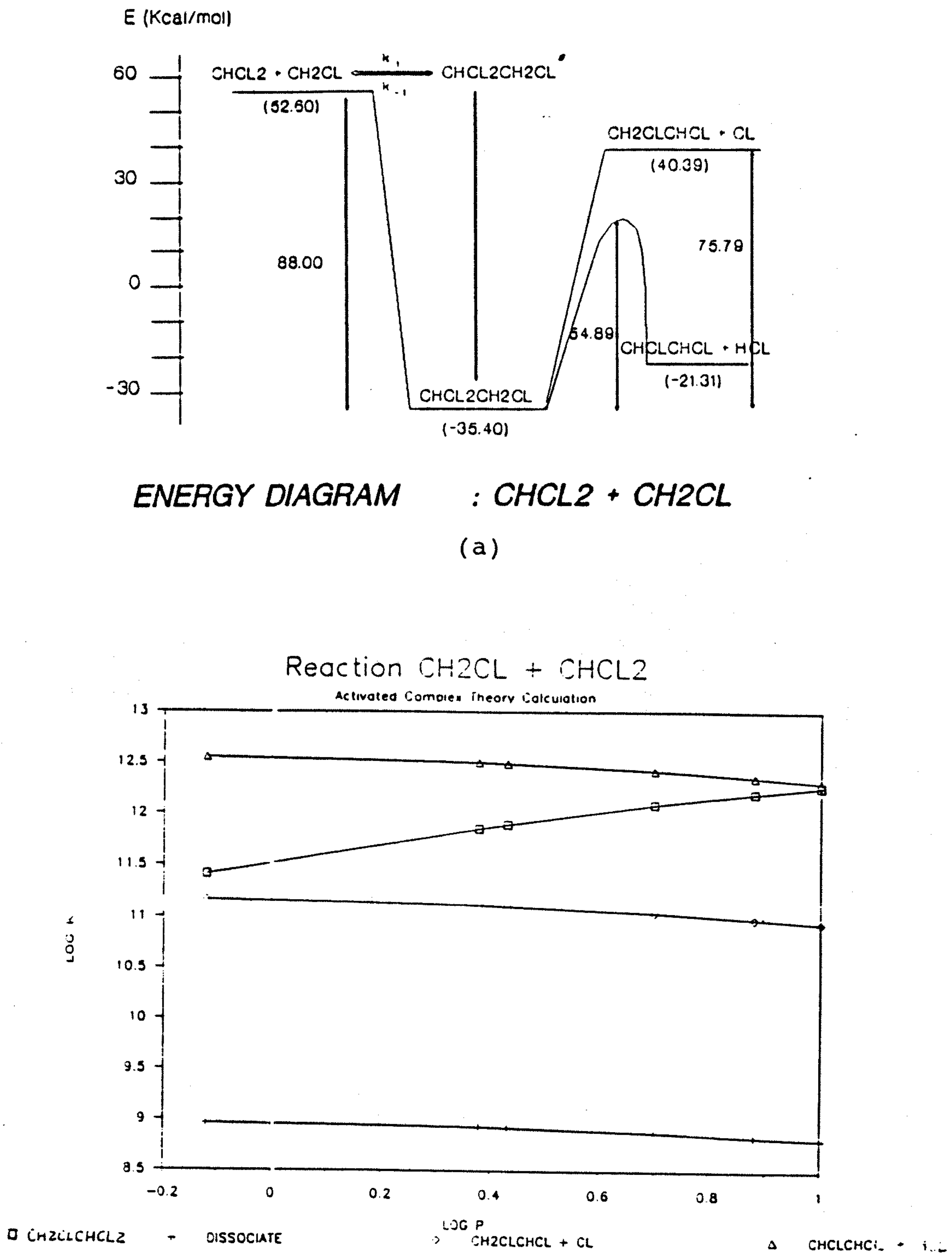
Figure 3. Energy Diagram (a) and CHEMACT Results (b) for Reaction H + CH2CL <==> Product



(a)

(b)

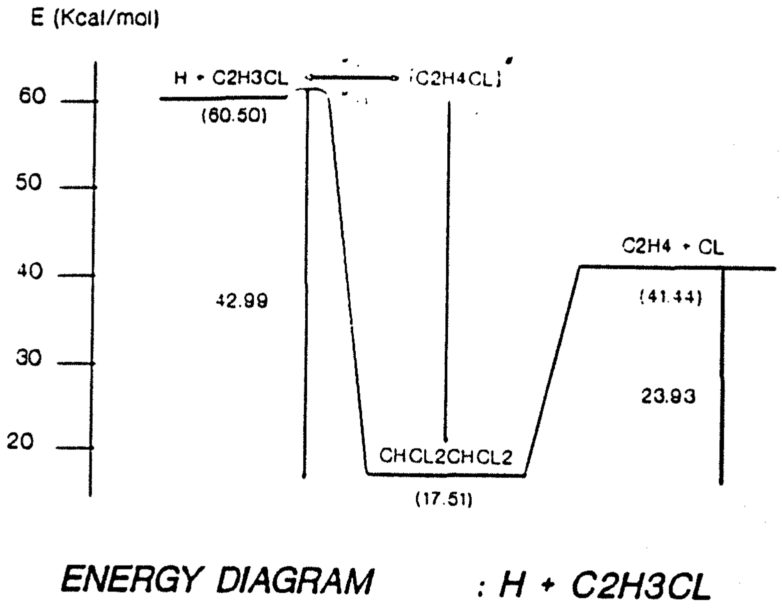
Figure 4. Energy Diagram (a) and CHEMACT Results (b) for Reaction H + CHCL2 <==> Product



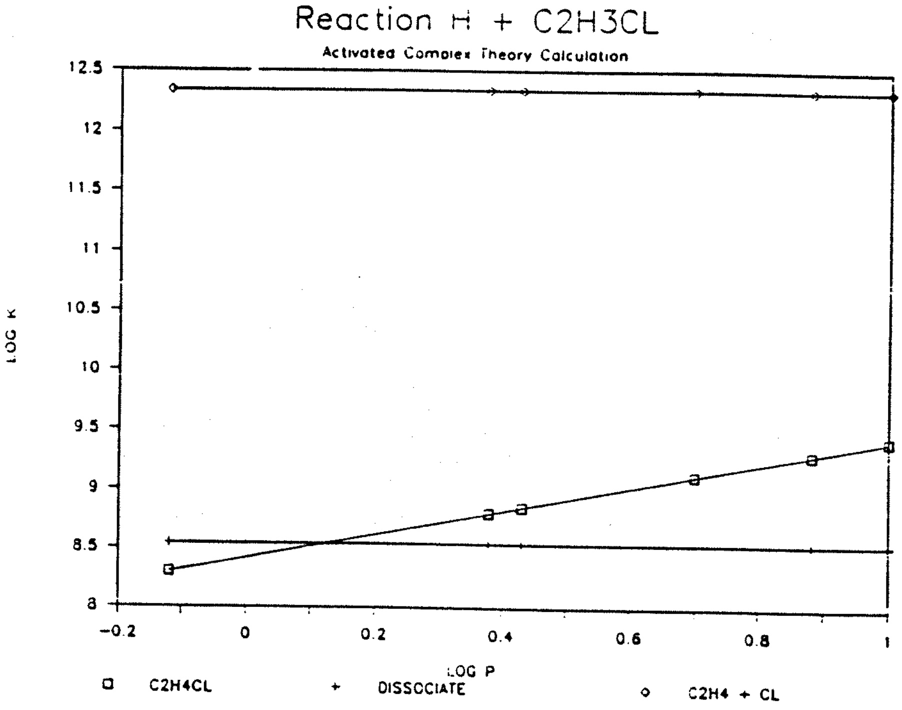
(a)

(b)

Figure 5. Energy Diagram (a) and CHEMACT Results (b) for Reaction CH2CL + CHCL2 <==> Product



(a)



(b)

Figure 6. Energy Diagram (a) and CHEMACT Results (b) for Reaction H + C2H3CL

C. Mechanism Modeling by CHEMKIN Program

The input data requirement to run the CHEMKIN program included:

* Detailed reaction mechanism (mass balance).

* Mole fraction of gases present in the reaction system.

* Pressure and temperature of the reaction system.

* Time increment at which the concentration of species present in the system need to be reported.

* A thermodynamic data base for all species in the reaction mechanism.

A thermodynamic data base for species eith C/H/Cl elements is developed at NJIT and used for modeling of the kinetic scheme of reaction system investigated. For those species that thermodynamic information were not available in the data base, thermodynamic data was generated utilizing JANAFIT program. This program requires heat capacities in the temperature rang of interest, as input. Heat of formation and entropies, as well as heat capacities, were calculated by group additivity method of Benson <20> when not available in literature.

This computer work was executed at Digital VAX/VMS 11/785 computer of NJIT.

The detailed mechanism for the two reactions are shown in Table 1 (H + CH2CL2) and Table 2 (H + CHCL3). The modeling results are found reasonably fit the experimental results, which are shown in figure 7, 8, 9 (H + DCM) and figure 10, 11 (H + chloroform).

Table 1. Detailed Mechanism For Reaction Of Atoimc Hydrogen With Dichloromethane

REACTIONS	A	Temp exp	Ea(cal/mol)	source
1.H+CH2CL2=HCL+CH2CL	7.0E13	0.0	6165.	a
2.H+CH2CL2=H2+CHCL2	9.9E13	0.0	9200.	b
3.H+CH2CL=CH3+CL	9.80E13	0.0	-1.65	QRRK 1
4.H+CHCL2=CH2CL+CL	1.00E14	0.0	-0.058	QRRK 2
5.CH3+CH2CL=C2H5CL	1.10E11	0.0	-1000.	QRRK 6
6.CH3+CH2CL=C2H4+HCL	2.0E13	0.0	22.1	QRRk 6
7.CH3+CHCL2=CH3CHCL2	1.50E11	0.0	-1260.	QRRK 7
8.CH3+CHCL2=HCL+C2H3CL	1.97E13	0.0	47.9	QRRK 7
9.CH3+CHCL2=CL+C2H4CL	1.90E12	0.0	764.	QRRK 7
10.CH2CL+CH2CL=C2H4CL2	1.07E11	0.0	-1180.	QRRK 3
11.CH2CL+CH2CL=C2H4CL+CL	5.95E11	0.0	1030.	QRRK 3
12.CH2CL+CH2CL=C2H3CL+HCL	4.32E12	0.0	201.	QRRK 3
13.H+C2H3CL=C2H4+CL	8.0E12	0.0	3300.	QRRK 8
14.H+C2H3CL=C2H4CL	4.32E08	0.0	2300.	QRRK 8
15.CHCL2+CH2CL=C2H3CL3	9.14E10	0.0	-1260.	QRRK 4
16.CHCL2+CH2CL=C2H3CL2+CL	8.95E11	0.0	1160.	QRRK 4
17.CHCL2+CH2CL=C2H2CL2+HCL	4.28E12	0.0	198.	QRRK 4
18.H+C2H2CL2=C2H3CL+CL	8.0E12	0.0	4000.	QRRK 10
19.CHCL2+CHCL2=C2H2CL4	4.48E09	0.0	-1610.	QRRK 5
20.CHCL2+CHCL2=C2H2CL3+CL	9.38E10	0.0	1690.	QRRK 5
21.CHCL2+CHCL2=C2HCL3+HCL	1.24E12	0.0	67.5	QRRK 5
22.H+C2H2CL3=C2H3CL3	7.38E11	0.0	-1350.	QRRK 13
23.H+C2H2CL3=C2H3CL2+CL	3.30E13	0.0	618.	QRRK 13
24.H+C2H2CL3=C2H2CL2+HCL	8.11E13	0.0	-0.034	QRRK 13
25.H+C2H3CL2=C2H4CL2	1.07E11	0.0	-1180.	QRRK 11
26.H+C2H3CL2=C2H4CL+CL	5.95E11	0.0	1030.	QRRK 11
27.H+C2H3CL2=C2H3CL+HCL	4.32E12	0.0	201.	QRRK 11
28.H+C2H4CL=C2H5CL	7.94E11	0.0	-951.	QRRK 9
29.H+C2H4CL=C2H4+HCL	5.08E13	0.0	66.9	QRRK 9
30.H+H+M=H2+M	2.5E17	0.0	0.	14
AR / 0.007 /				
H2 / 0.005 /				
31.H+CL+M=HCL+M	1.40E18	0.0	0.	14
AR / 0.04 /				
H2 / 0.025 /				
32.H2+CL=HCL+H	1.2E13	0.0	4300.	14
33.CH3+H+M=CH4+M	5.85E17	0.0	-797.	o
34.H+CH3CL=HCL+CH3	3.72E13	0.0	9300.	q
35.H+CCL2=CHCL2	8.61E13	0.0	-291.	r
36.CL+CH2CL2=HCL+CHCL2	1.00E14	0.0	3000.	s
37.CL+CH2CL=CH2CL2	6.59E10	0.0	-1240.	r
38.CL+CH3CL=HCL+CH2CL	5.76E13	0.0	3400.	s
39.CL+CHCL2=CHCL3	1.28E11	0.0	-1550.	QRRK 15
40.CL+CHCL2=CCL2+HCL	1.80E12	0.0	-432.	QRRK 15
41.CL+CH4+M=HCL+CH3+M	2.63E13	0.0	3900.	14
42.CL+CL+M=CL2+M	1.6E15	0.0	-1200.	14
AR / 0.3 /				
H2 / 0.2 /				
43.CL2+H=HCL+CL	8.31E13	0.0	1200.	14
44.H2+CH3=CH4+H	5.01E11	0.0	9900.	v
45.H2+CH2CL=H+CH3CL	2.08E12	0.0	11840.	b

46.H+CH2CL=CH3CL	4.34E09	0.0	-947.	QRRK 1
47.H+C2H2CL2=C2H3CL2	9.73E07	0.0	2720.	QRRK 10
48.H+C2H4=C2H3+H2	1.82E13	0.0	12000.	x
49.H+C2H3=H2+C2H2	4.00E13	0.0	3.62	r
50.H+C2H3=C2H4	3.47E10	0.0	-1020.	r
51.CH3+CH3=C2H6	1.88E13	0.0	-107.	r
52.H+C2H3CL=HCL+C2H3	1.00E13	0.0	9500.	w
53.CH3+CH2CL2=CH4+CHCL2	6.8E10	0.0	7200.	y
54.CH3+CH2CL2=CH3CL+CH2CL	1.4E11	0.0	4900.	z
55.CL+C2H6=HCL+C2H5	9.12E13	0.0	1000.	1
56.H+C2H5=C2H6	5.18E12	0.0	-994.	QRRK 20
57.H2+C2H5=C2H6+H	3.24E11	0.0	11300.	3
58.CL+CH3+M=CH3CL+M	3.11E18	0.0	-868.	o
59.CL+C2H4=C2H4CL	4.23E11	0.0	6950.	r
60.H+C2H4=C2H5	3.08E12	0.0	1770.	r
61.CL+C2H4CL2=HCL+C2H3CL2	6.31E13	0.0	3100.	4
62.CL+C2H5CL=HCL+C2H4CL	4.57E13	0.0	1500.	5
63.CL+C2H4CL=HCL+C2H3CL	1.86E13	0.0	1290.	QRRK 14
64.CL+C2H4CL=C2H4CL2	3.55E12	0.0	-469.	QRRK 14

Table 2. Detailed Mechanism For Reaction Of Atomic Hydrogen With Chloroform

REACTIONS	A	Temp exp	Ea(cal/mol)	source
1.H+CHCL3=HCL+CHCL2	1.11E14	0.0	4800.	p
2.H+CHCL3=H2+CCL3	4.1E13	0.0	7200.	b
3.H2+CL=H+HCL	1.2E13	0.0	4300.	o
4.CHCL3=CCL2+HCL	2.37E13	0.0	67900.	7
5.CL+CHCL3=CCL3+HCL	2.0E13	0.0	2800.	13
6.H+CCL3=CHCL2+CL	9.95E13	0.0	0.312	QRRK 16
7.H+CCL3=CCL2+HCL	4.85E11	0.0	-58.6	QRRK 16
8.H+CCL3=CHCL3	2.30E8	0.0	-1110.	QRRK 16
9.H+CHCL2=CH2CL+CL	1.0E14	0.0	0.0577	QRRK 2
10.H+CHCL2=CH2CL2	3.42E8	0.0	-1020.	QRRK 2
11.CCL3+CCL3=C2CL6	1.97E12	0.0	-93.5	QRRK 18
12.CCL3+CCL3=C2CL5+CL	1.93E13	0.0	6040.	QRRK 18
13.CCL3+CHCL2=C2HCL5	7.71E11	0.0	-497.	QRRK 17
14.CCL3+CHCL2=C2CL4+HCL	4.0E12	0.0	2130.	QrrK 17
15.CCL3+CHCL2=C2HCL4+CL	1.76E13	0.0	3230.	QRRK 17
16.CCL3+CH2CL=C2H2CL4	2.29E10	0.0	-1610.	QRRK 19
17.CCL3+CH2CL=C2HCL3+HCL	6.58E12	0.0	61.9	QRRK 19
18.CCL3+CH2CL=C2H2CL3+CL	5.22E11	0.0	1620.	QRRK 19
19.CH2CL+CH2CL=C2H4CL2	1.07E11	0.0	-1180.	QRRK 3
20.CH2CL+CH2CL=C2H4CL+CL	5.95E11	0.0	1030.	QRRK 3
21.CH2CL+CH2CL=C2H3CL+HCL	4.32E12	0.0	210.	QRRK 3
22.H+C2H3CL=C2H4+CL	8.0E12	0.0	3300.	QRRK 8
23.H+C2H3CL=C2H4CL	4.32E8	0.0	2300.	QRRK 8
24.CHCL2+CH2CL=C2H3CL3	9.14E10	0.0	-1260.	QRRK 4
25.CHCL2+CH2CL=C2H3CL2+CL	8.95E11	0.0	1160.	QRRK 4
26.CHCL2+CH2CL=C2H2CL2+HC	4.28E12	0.0	198.	QRRK 4
27.H+C2H2CL2=C2H3CL+CL	8.0E12	0.0	4000.	QRRK 10
28.H+C2H2CL2=C2H3CL2	9.73E7	0.0	2720.	QRRK 10
29.CHCL2+CHCL2=C2H2CL4	4.48E09	0.0	-1610.	QRRK 5
30.CHCL2+CHCL2=C2H2CL3+CL	9.38E10	0.0	1690.	QRRK 5
31.CHCL2+CHCL2=C2HCL3+HCL	1.24E12	0.0	67.5	QRRK 5
32.H+C2H2CL3=C2H3CL3	7.38E11	0.0	-1350.	QRRK 13
33.H+C2H2CL3=C2H3CL2+CL	3.30E13	0.0	618.	QRRK 13
34.H+C2H2CL3=C2H2CL2+HCL	8.11E13	0.0	-0.0335	QRRK 13
35.H+C2H3CL2=C2H4CL2	9.55E11	0.0	-1250.	QRRK 11
36.H+C2H3CL2=C2H4CL+CL	1.36E13	0.0	620.	QRRK 11
37.H+C2H3CL2=C2H3CL+HCL	9.6E13	0.0	57.2	QRRK 11
38.H+C2H4CL=C2H5CL	7.94E11	0.0	-951.	QRRK 9
39.H+C2H4CL=C2H5+CL	5.08E12	0.0	66.9	QRRK 9
40.H+C2H4CL=C2H4+HCL	9.92E13	0.0	12.2	QRRK 9
41.H+H+M=H2+M	2.5E17	0.0	0.	14
AR / 0.007 /				
H2 / 0.005 /				
42.H+CL+M=HCL+M	1.40E18	0.0	0.	14
AR / 0.04 /				
H2 / 0.025 /				
43.H+CH3+M=CH4+M	5.87E17	0.0	-797.	o
44.H+CH3CL=HCL+CH3	3.72E13	0.0	9300.	q

45.H+CCL2=CHCL2	8.61E13	0.0	-291.	r
46.CL+CH2CL2=HCL+CHCL2	2.69E13	0.0	3000.	s
47.CL+CH2CL=CH2CL2	6.59E10	0.0	-1240.	r
48.CL+CH3CL=HCL+CH2CL	5.76E13	0.0	3400.	s
49.CL+CHCL2=CHCL3	1.28E11	0.0	-1550.	QRRK 15
50.CL+CHCL2=CCL2+HCL	1.80E12	0.0	-432.	QRRK 15
51.CL+CH4=CH3+HCL	2.63E13	0.0	3900.	14
52.CL+CL+M=CL2+M	1.6E15	0.0	-1200.	14
AR / 0.3 /				
H2 / 0.2 /				
53.CL2+H=HCL+CL	8.31E13	0.0	1200.	14
54.H2+CH3=CH4+H	5.01E11	0.0	9900.	v
55.H2+CH2CL=H+CH3CL	2.08E12	0.0	11840.	b
56.H+C2H3=H2+C2H2	4.00E13	0.0	3.62	r
57.H+C2H3=C2H4	3.47E10	0.0	-1020.	r
58.H+CH2CL=CH3+CL	9.8E13	0.0	-1.65	QRRK 1
59.H+CH2CL=CH3CL	4.34E9	0.0	-947.	QRRK 1
61.CH3+CH3=C2H6	1.88E13	0.0	-107.	r
62.CH3+CH2CL=C2H5CL	1.1E11	0.0	-1000.	QRRK 6
63.CH3+CH2CL=C2H5+CL	1.48E11	0.0	396.	QRRK 6
64.CH3+CH2CL=C2H4+HCL	2.00E13	0.0	22.1	QRRK 6
65.CL+C2H6=HCL+C2H5	9.12E13	0.0	1000.	1
66.H+C2H5=C2H6	5.18E12	0.0	-994.	QRRK 20
67.H+C2H5=CH3+CH3	1.97E14	0.0	136.	QRRK 20
68.H2+C2H5=C2H6+H	3.24E11	0.0	11300.	3
69.CL+CH3+M=CH3CL+M	3.11E18	0.0	-868.	o
70.CL+C2H4=C2H4CL	4.23E11	0.0	6950.	r
71.H+C2H4=C2H5	3.08E12	0.0	1770.	r
72.CL+C2H4CL2=HCL+C2H3CL2	6.31E13	0.0	3100.	4
73.CL+C2H5CL=HCL+C2H4CL	4.57E13	0.0	1500.	5
74.CH3+CHCL2=C2H4CL2	1.5E11	0.0	-1260.	QRRK 7
75.CH3+CHCL2=C2H4CL+CL	1.90E12	0.0	764.0	QRRK 7
76.CH3+CHCL2=C2H3CL+HCL	1.97E13	0.0	47.9	QRRK 7
77.CH3+CHCL3=CH4+CCL3	1.90E10	0.0	5800.	12
78.H+CH2CL2=HCL+CH2CL	4.5E13	0.0	5900.	a
79.H+CH2CL2=H2+CHCL2	9.9E13	0.0	9200.	b

SOURCE

<a> A factor is from Kerr, J.A. and Moss, S.J., "Handbook of Bimolecular and Termolecular Gas Reaction", Vol. I, CRC press Inc., 1981.
Ea is modified by this work.

<b> A factors for reaction of CHCl2+H2 and CH2Cl+H2 taken from linear extrapolation between H2+CH3 log A = 11.7, (Kerr), and H2+CCl3 log A = 12.72, (Kerr), thus $A_{CHCl2+H2}$ = 3.67E12 and $A_{CH2Cl+H2}$ = 2.08E12. A factors for reverse reactions are taken from thermodynamics.
Ea is from Evans-Polanyi Plot, in APPENDIX 2, Figure 1.

<c> CHEMACT 1, in APPENDIX 1, Table 1.

<d> CHEMACT 2, in APPENDIX 1, Table 2.

<e> CHEMACT 6, in APPENDIX 1, Table 6.

<f> CHEMACT 7, in APPENDIX 1, Table 7.

<g> CHEMACT 3, in APPENDIX 1, Table 3.

<h> CHEMACT 8, in APPENDIX 1, Table 8.

<i> CHEMACT 4, in APPENDIX 1, Table 4.

<j> CHEMACT 10, in APPENDIX 1, Table 10.

<k> CHEMACT 5, in APPENDIX 1, Table 5.

<l> CHEMACT 13, in APPENDIX 1, Table 13.

<m> CHEMACT 11, in APPENDIX 1, Table 11.

<n> CHEMACT 9, in APPENDIX 1, Table 9.

<o> Barat, R.B. and Bozzelli, J.W., "Reaction of Atomic Hydrogen with Vinyl Chloride", to be submitted to J. Phys. Chem. (1988).

<p> A factor for reaction of H+CHCl3 taken from extrapolation between H+CH2Cl2, A = 7.0E13, (Kerr), and H+CH3Cl, A = 3.7E13, (Kerr), thus $A_{H+CHCl3}$ = 1.1E14.
Ea is from Evans-Polanyi Plot.

<q> Westenberg, A.A. and deHaas, N., J. Chem. Phys., 62,

3321 (1975).

<r> QRRK calculation. (see input data list in APPENDIX 1)

<s> A factor is taken from Kerr.
Ea is gained from Evans-Polanyi plot, in APPENDIX 2., figure 1.

<t> CHEMACT 15, in APPENDEX 1, Table 15.

<u> Pritchard, H.O., Pyke, J.B. and Trotman-Dickenson, A.F., J. Amer. Chem. Soc., 77, 2629 (1955).

<v> Whittle, E. and Steacie, E.W.R., J. Chem. Phys.,21,993 (1953).

<w> Barat, R.B. and Bozzelli, J.W., Poster presented at 2nd International Conference on Chemical Kinetics, Gaithersburg, MD, 1989.

<x> A factor from Voevodsky, V.V. and Kondratiev, V.N., Progress in Reaction Kinetics, Pergamon 3.
Ea is from Evans-Polanyi Plot.

<y> Ridge, M.J. and Steacie, E.W.R., Can. J. Chem.,33,396 (1955).

<z> Won, Y.S. and Bozzelli, J.W., "Gas Phase Reaction of Dichloromethane/1,1,1-Trichloroethane Mixture with Hydrogen in a Tubular Flow", The Eastern Section of the Combustion Institute, 1988 Technical Meeting.

<1> Knox, J.H., Chem. Ind. (London), 1631 (1955).

<2> Chemact 20, in APPENDIX 1, table 20.

<3> Boddy, P.J. and Steacie, E.W.R., Can. J. Chem.., 39, 13 (1961).

<4> Cillien, C., Goldfinger, P., Huybrechts, G., Trans. Faraday Soc., 63, 1631 (1967).

<5> Pritchard, H.O., Pyke, J.B. and Trontman-Dickenson, A.F., J. Am. Chem., 77, 2629 (1955).

<6> Chemact 14, in APPENDEX 1, Table 14.

<7> Dissoc 1, APPENDIX 1. (the input data list is in APPENDIX 1)

<8> Chemact 16, in APPENDEX 1, Table 16.

<9> Chemact 18, in APPENDEX 1, Table 18.

<10> Chemact 17, in APPENDEX 1, Table 17.

<11> Chemact 19, in APPENDEX 1, Table 19.

<12> Raal, F.A. and Steacie, E.W.R., J. Chem. Phys., 20, 578, 1952.

<13> Clyne, M.A.A. and Walker, R.F., J. Chem. Soc., Faraday Trans. 1, 69,1547, 1973.

(14) From Kerr, J.A. and Moss, S.J., "Handbook of Bimolecular and Termolecular Gas Reaction", Vol. I & II, CRC press Inc., 1981.

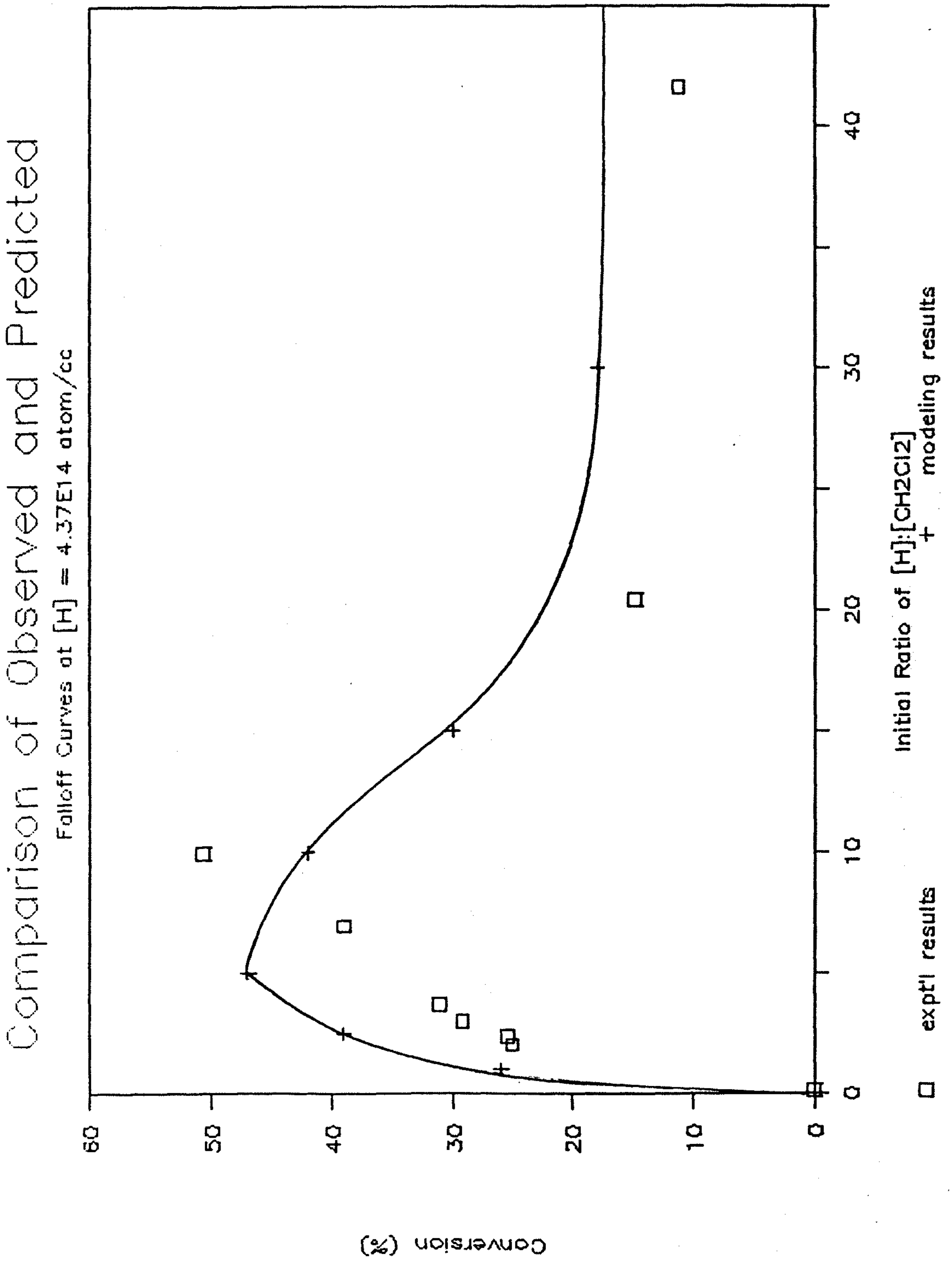


Figure 7. Modeling Result for Atomic Hydrogen with DCM, [H] = 4.37E14 atom/cc

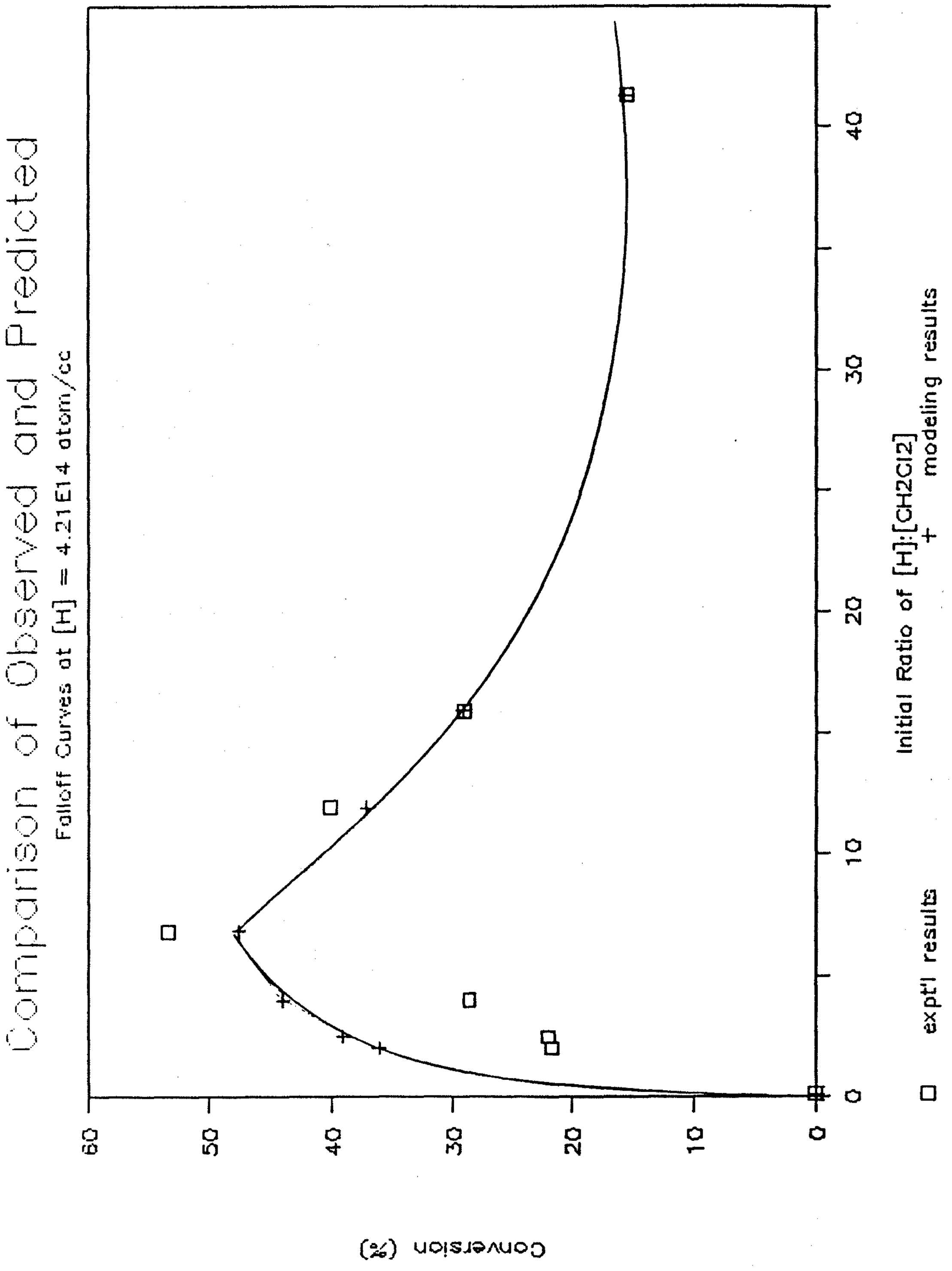


Figure 8. Modeling Result for Atomic Hydrogen with DCM
[H] = 4.21E14 atom/cc

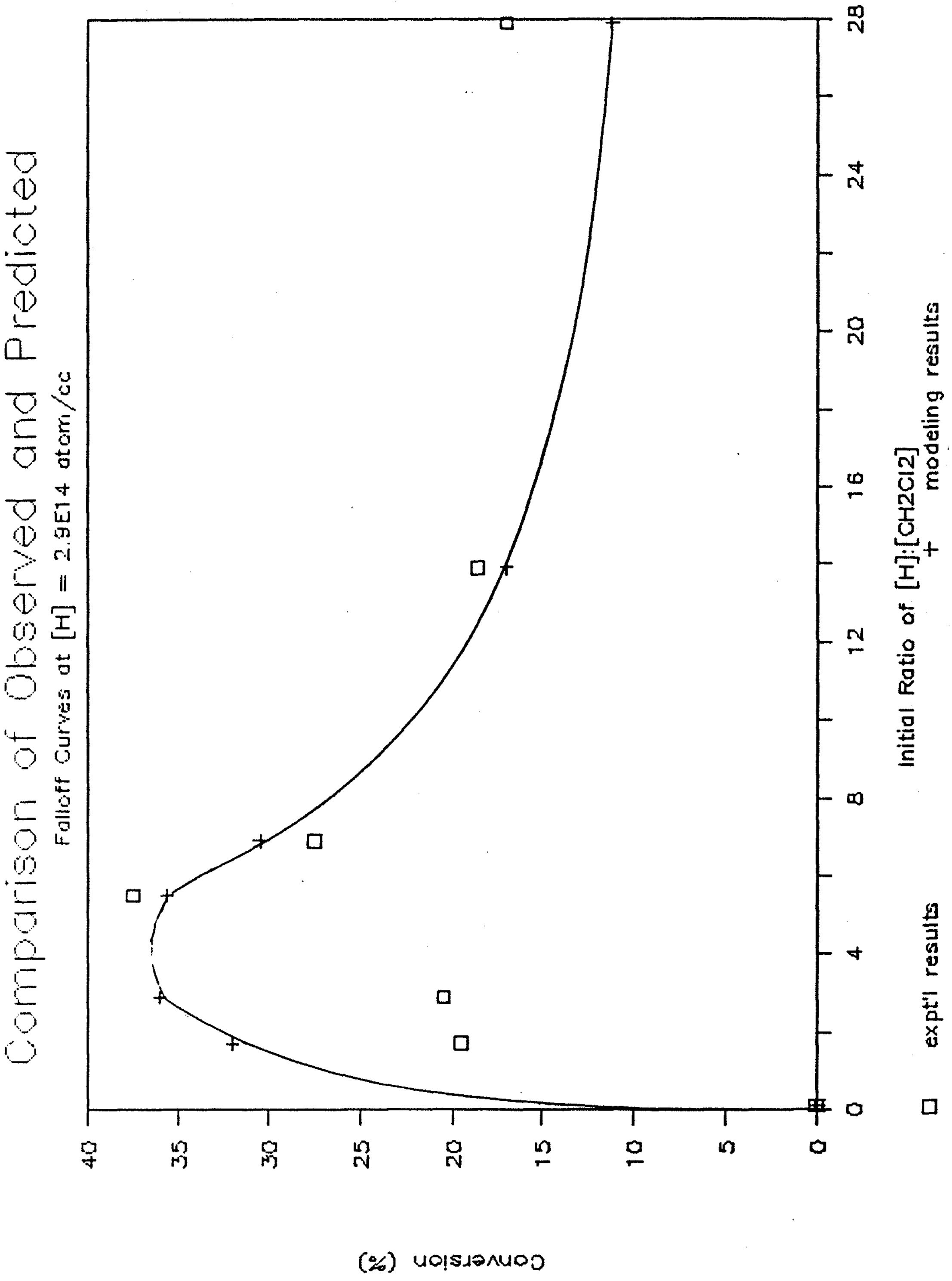


Figure 9. Modeling Result for Atomic Hydrogen with DCM
[H] = 2.9E14 atom/cc

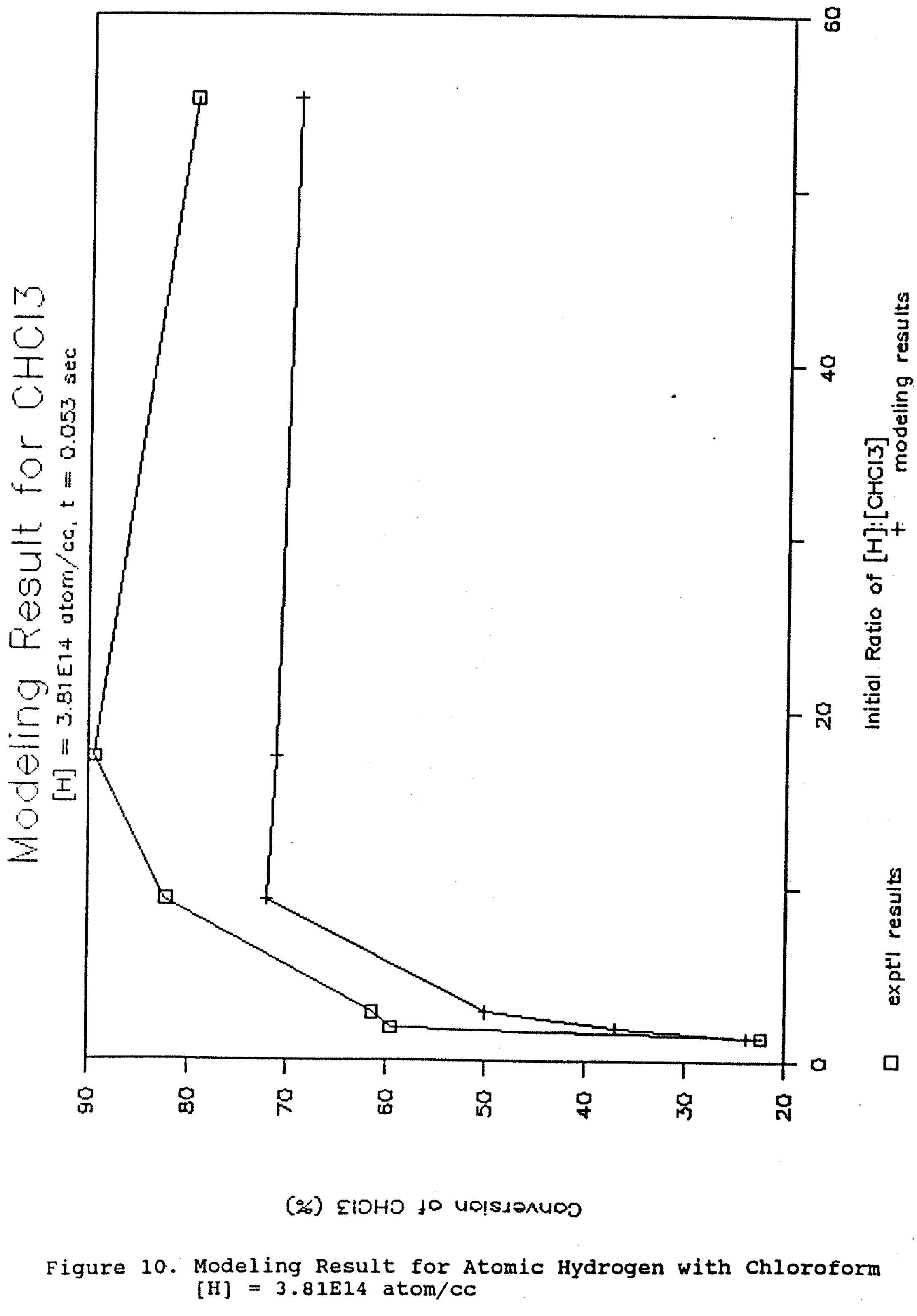


Figure 10. Modeling Result for Atomic Hydrogen with Chloroform
[H] = 3.81E14 atom/cc

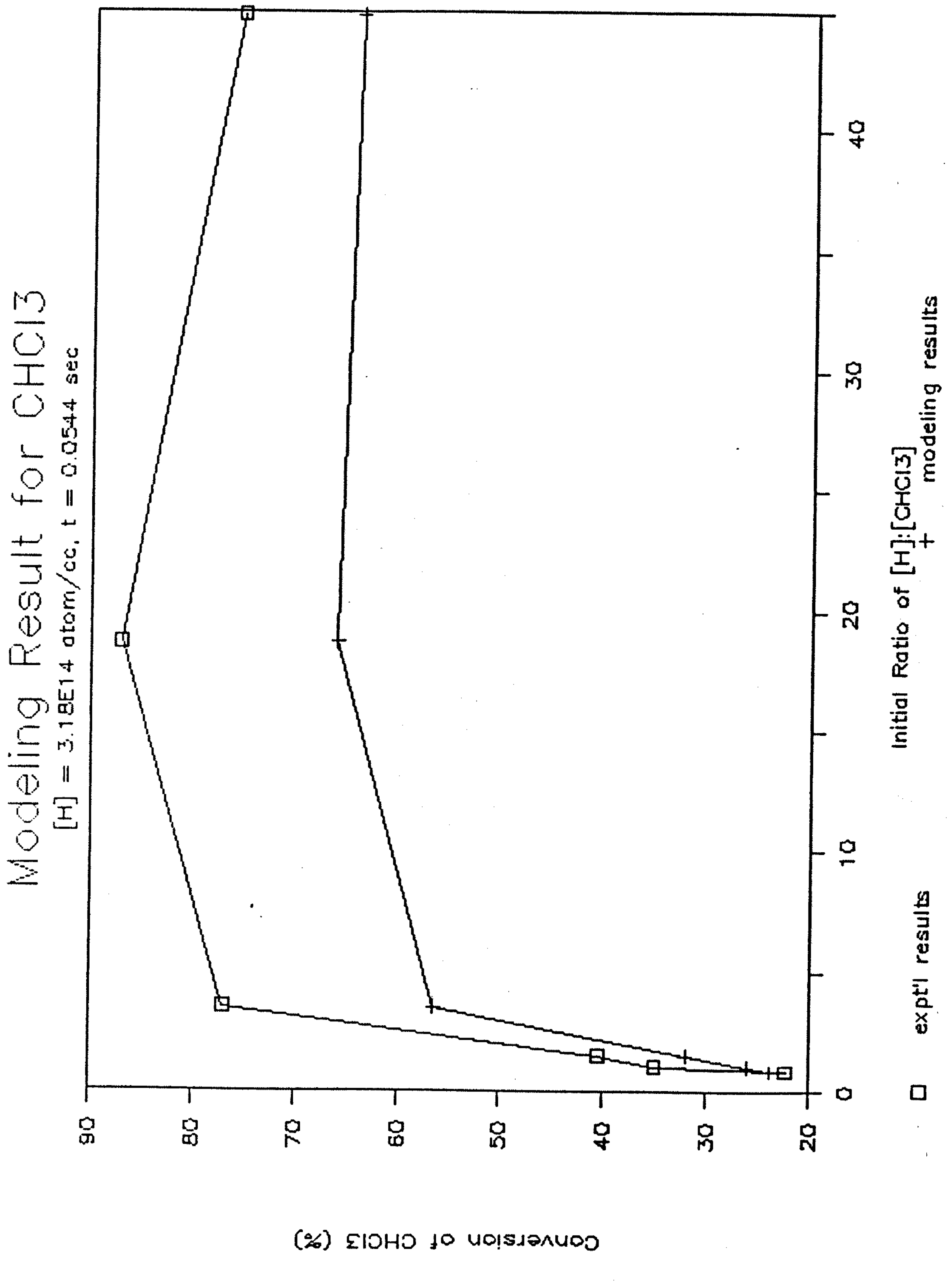


Figure 11. Modeling Result for Atomic Hydrogen with Chloroform
[H] = 3.18E14 atom/cc

V. CONCLUSION

Detailed mechanisms were developed for the reaction of atomic hydrogen with dichloromethane and with chloroform. The two reaction systems were under low pressure (2.1-2.7 torr for dichloromethane, 2.22-2.82 torr for chloroform system) and at room temperature (298 K).

The unimolecular and bimolecular versions of Quantum RRK theory were used to develop kinetic mechanisms for the reaction of atomic hydrogen with dichloromethane and with chloroform. Sensitivity <19> analysis on these reaction mechanism was performed to identify the important reaction channels and to improve the fit of the mechanism on experimental observation.

The model results for the reaction of hydrogen atom with dichloromethane, gives a satisfactory fit for the conversion of dichloromethane with the experimental data. The fit is very good over a range of initial H/CH_2Cl_2 ratio above 6.8. This mechanism also indicated an acceptable path toward the formation of the major products, CH_4 and HCl. Through the computer modeling of the reaction scheme and comparison with the experimental data, the rate constants of the initial reactions are,

	A(1/s)	Ea(Kcal/mol)
$H + CH_2Cl_2 \Longleftrightarrow HCl + CH_2Cl$	7.0E13	6.165
$H + CH_2Cl_2 \Longleftrightarrow H_2 + CHCl_2$	9.9E13	9.2

The reaction of atomic hydrogen with chloroform is more complicated than the first one since the formation of carbon and emission from excited $C2^{\#}$ been reported in previous experimental research. The model results of this mechanism also give a reasonable fit for the conversion of chloroform vs. CHCl3 flow rate.

The rate constants obtained by this model for the initial important reaction steps are:

	A(1/s)	Ea(Kcal/mol)
H + CHCl3 <===> HCl + CHCl2	1.1E14	4.8
H + CHCl3 <===> H2 + CCl3	4.1E13	7.2

The detailed mechanism of these reactions provide important imformation for understanding of the chemistry of these species in incineration and in pyrolysis atmospheres. It is hoped that the present study will make the future studies in kinetic modeling for all reactions with chlorocarbons more fruitful.

VI. REFERENCES

<1> Ritter, E.R., Bozzelli, J.W. and Deam, A.M., J. Phys. Chem., Feb., 1990.

<2> Ho, W. and Bozzelli, J.W., submitted to Int'l Combustion Institute Meeting, 1990.

<3> Westmoreland, P.R., Howard, J.B., Longwell, J.B. and Deam, A.M., AICHE J., Vol. 32, No. 12, December, 1986.

<4> Jo, W., Master thesis, NJIT, 1985.

<5> Huang, S., Master thesis, NJIT, 1987.

<6> Chadwell and Titani, J. Amer. Chem. Soc., 55, pp 1363, 1933.

<7> Cremer, Curry, and Polanyi, Z. Physik Chem. B., 23, pp 445, 1933.

<8> Vance J.E. and Baumann, W.C., J. Chem. Phys., 6, pp 811 1938.

<9> Clark D.T. and Tedder, H.M., Trans. Faraday Soc., 62, pp 393-414, 1966.

<10> Gaydon, A.G. and Wolfhard H.G., Proc. R. Soc. London, A 213, pp 366, 1952.

<11> Arnold, S.J., Kimbell, G.H. and Snelling, D.R., Can. J. Chem., 53, pp 2491, 1975.

<12> Combourieu, J., LeBrad G. and Paty, C., 14th Int'l symposium on Combustion, pp 485-492, 1973.

<13> Deam, A.M., J. of Phys. Chem., 89, 4600, 1985.

<14> Westenberg A.A. and deHaas N., J. Chem. Phys., 62, 8,

15 April, 1975.

<15> Costes, M., Dorthe G. and Destriau, M., Chem. Phys. Letter, 61, 3, pp 588-592, March, 1979.

<16> Gould P.C. and Oldershaw, G.A., Inter. J. of Chem. Kinetics, 14, pp 1105-1112, 1982.

<17> Kassel, L.S., J. Phys. Chem., 32, pp 1065, 1982.

<18> Kee, R.J., Miller, J.A. and Jefferson, T.H., "CHEMKIN: A General-purpose, Problem-independent, Transportable, Fortran Chemical Kinetics Code Package.", SANDIA Lab., ReportSAND 80-8003, Livermore, CA, 1980.

<19> Kramer, M.A., Kee, R.J. and Rabitz, H., "CHEMSEN: A Computer Code for Sensitivity Analysis of Elementary Chemical Reaction Products", SANDIA Lab., Report 82-8230, 1982.

<20> Benson, S.W., Thermochemical Kinetics, 2nd Ed., Wiley, NY., 1976.

<21> Setser, D.W. and Lee, T., Amer. Chem. Soc., 89, pp 5799, 1985.

<22> Miller, J.C. and Gordon, R.H., J. Chem. Phys., 75, 11, December, 1981.

<23> Clyne, M.A.A. and Walker, R.F., J. Chem. Soc. Faraday Trans. I, 1547, 69, 1973.

<24> Kerr, J.A. and Moss, S.J., "CRC Handbook of Bimolecular and Termolecular Gas Reactions", Volume I & II, Florida, CRC Press, 1981.

<25> Watson, R.T., J. Phys. Chem. Ref. Data 6, 871, 1977.

APPENDIX

1. Input Parameters to Chemical Activation (QRRK) and Dissociation Reactions

2. Evans-Polanyi Plot for Abstraction Reactions

3. Experimental data used in modeling

1. Input Parameters to Chemical Activation (QRRK)

And

Dissociation Reactions

TABLE 1-a

$$\mathrm{H + CH2CL} \underset{-1}{\overset{1}{<\!\!==\!\!=\!\!>}} \mathrm{[CH3CL]\#}$$

$$\mathrm{{-}{-}{-}{-}{>}\ CH3 + CL\ (2)}$$

$$\mathrm{{-}{-}{-}{-}{>}\ CH3CL\ (Stab.)}$$

k	A	Ea	source
1	1.00E14	0.0	a
-1	8.92E15	100.2	b
2	1.28E15	83.0	c

$\langle V \rangle = 1575\ \mathrm{cm}^{-1}$ d

Lennard-Jones Parameters: e

Sigma = 4.18 A^{o} e/k = 350.0 ^{o}K

a. A factor is based on H + CCC., log A = 14.0,
H + CC.C, log A = 14.0,
Ref: Allara, D. L. and Shaw, R., Journal of Physical Chemistry, Ref. Data, 9, 523, 1980.

b. Calculated from thermodynamics and reverse A.

c. A factor is based on CH3 + CH3, log A=13.4
Estimated, for CH3+CL, log A=13.4.
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 523, 1980.

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

e. Activated complex L-J parameters are estimated using ctitical property data tabulated in Reid, Prausnitz and Sherwood(The Properties of Gases and Liquids, 3rd ed.)

TABLE 1-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CH2CL = CH3CL	1.22E+09	-948.
2.69		4.34E+09	-947.
7.6		1.22E+10	-947.
0.76	H+CH2CL = CH3+CL	9.8E+13	-1.78
2.69		9.8E+13	-1.65
7.6		9.8E+13	-1.33

Bath Gas: Ar
Temperature: 300 K

TABLE 2-a

$$\mathrm{H + CHCL2} \underset{-1}{\overset{1}{\Longleftrightarrow}} [\mathrm{CH2CL2}]\#$$

$\longrightarrow$ CH2CL + CL (2)
$\longrightarrow$ CH2CL2 (Stab.)

k	A	Ea	source
1	1.00E14	0.0	a
-1	6.02E15	100.0	b
2	2.09E16	80.6	c

<V> = 1116 cm^{-1} d

Lennard-Jones Parameters: e

Sigma = 4.77 A^{o} e/k = 420.3^{o}K

a. A factor is based on H+CC.C, log A=14.0
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

b. Calculated from thermodynamics and reverse A.

c. A factor is based on CH3+CH3, log A=13.4
CH3+C2H5, log A=13.3
CH3+1-C3H7, log A=13.3
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, pp 528, 1980.

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

e. Activated complex L-J parameters are estimated using critical property data tabulated in Reid, Prausnitz and Sherwood(The Properties of Gases and Liquids, 3rd. ed.)

TABLE 2-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CHCL2 = CH2CL2	9.63E+07	-1020.0
2.69		3.42E+08	-1020.0
7.6		9.63E+08	-1020.0
0.76	H+CHCL2 = CH2Cl+CL	1.0E+14	-0.07
2.69		1.0E+14	-0.058
7.6		1.0E+14	-0.027

Bath Gas: Ar
Temperature: 300 K

TABLE 3-a

$$CH_2CL + CH_2CL \underset{-1}{\overset{1}{\Longleftrightarrow}} [CH_2CLCH_2CL]\#$$

$$\longrightarrow CH_2CLCH_2 + CL \quad (2)$$
$$\longrightarrow C_2H_3CL + HCL \quad (3)$$
$$\longrightarrow CH_2CLCH_2CL \ (\text{stab.})$$

k	A	Ea	source
1	3.98E12	0.0	a
-1	5.04E17	88.6	b
2	5.0E15	76.8	c
3	3.98E13	58.0	d

$<V> = 797.2\ cm^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 5.1166 A^{o} e/k = 471.2 ^{o}K

a. A factor is based on 1-C_3H_7 + 1-C_3H_7, log A=12.6
Ref: Allara, D. L. and Shaw, R., Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

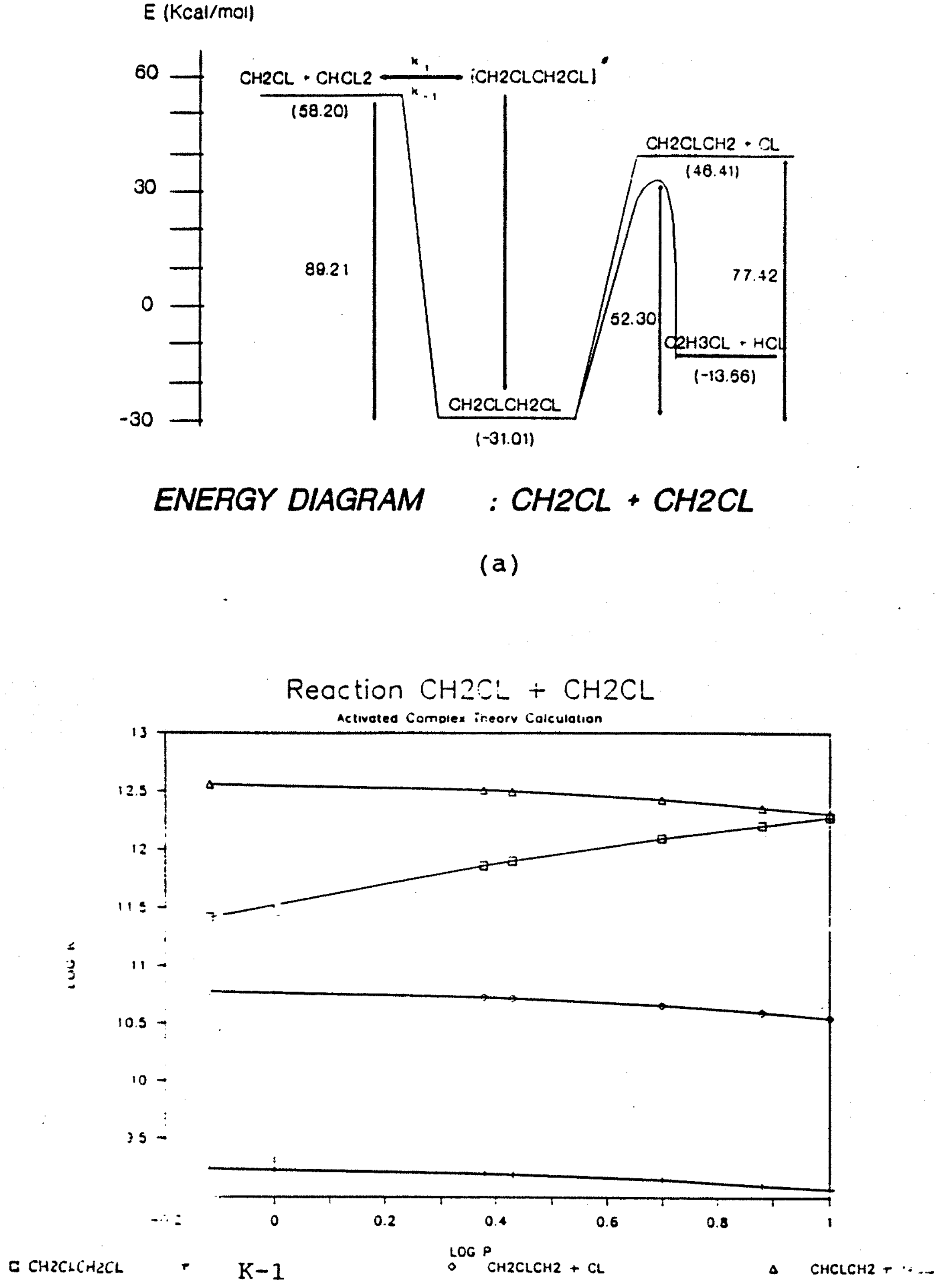
b. Calculated from thermodynamics and reverse A.

c. A-2 based on CH_3 + C_3H_7, log A= 13.3
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

d. Weissman and Benson, I. J. of Chem. Kinetics, Vol. 16, 1984.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



(a)

(b)

Figure 1 Energy Diagram (a) and CHEMACT Results (b) for Reaction CH2CL + CH2CL

TABLE 3-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CH2CL+CH2CL = CH2CLCH2CL	2.85E+10	-1320.
2.69		1.11E+11	-1170.
7.6		3.47E+11	-915.
0.76	CH2CL+CH2CL = CH2CH2CL+CL	2.74E+11	892.
2.69		3.17E+11	1060.
7.6		3.94E+11	1360.
0.76	CH2CL+CH2CL = CH2CHCL+HCL	4.02E+12	57.3
2.69		4.51E+12	218.
7.6		5.26E+12	490.

Bath Gas: Ar
Temperature: 300 K

TABLE 4-a

$$\text{CH2CL + CHCL2} \underset{-1}{\overset{1}{\Longleftrightarrow}} \text{[CH2CLCHCL2]\#}$$

$$\begin{aligned} &\longrightarrow \text{CH2CLCHCL + CL (2)} \\ &\longrightarrow \text{CHCLCHCL + HCL (3)} \\ &\longrightarrow \text{CH2CLCHCL2 (Stab.)} \end{aligned}$$

k	A	Ea	source
1	3.97E12	0.0	a
-1	5.28E17	89.6	b
2	3.69E15	75.1	c
3	1.92E13	54.9	d

<V> = 678.7 cm^{-1} e

Lennard-Jones Parameters: f

Sigma=5.72A^{o} e/k=498.9^{o}K

a. A factor is based on C2H5+CCC., logA=12.9
C2H5+CC.C,logA=12.9
Estimated, CH2CL + CHCL2, A = 1/2 * $10^{12.9}$.
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

b. Calculated from thermodynamics and reverse A.

c. For CH3 + C2H5, log A= 13.3
Estimated, A_{-3}=1/2 * $10^{13.3}$
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

d. A=$10^{13.55}$ * $10^{-(4/4.6)}$ * 4 = 1.92E13
Ea = del H + 40.8
Ref: Bamford, D. H. and Tipper, C.F., Comprehensive Chemical Kinetics, Vol. 5, 1972.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.

TABLE 4-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CH2CL+CHCL2 = CH2CLCHCL2	2.31E+10	-1420.0
2.69		9.14E+10	-1260.0
7.6		2.94E+11	-998.0
0.76	CH2CL+CHCL2=CH2CLCHCL+CL	7.69E+11	986.0
2.69		8.95E+11	1160.0
7.6		1.13E+12	1130.0
0.76	CH2CL+CHCL2=CHCLCHCL+HCL	3.76E+12	32.6
76.0		4.28E+12	198.0
760.0		5.11E+12	482.0

Bath Gas: Ar
Temperature: 300 K

TABLE 5-a

$$\text{CHCL2 + CHCL2} \underset{-1}{\overset{1}{\Longleftrightarrow}} \text{[CHCL2CHCL2]\#}$$

$$\longrightarrow \text{CHCL2CHCL + CL (2)}$$
$$\longrightarrow \text{CHCLCCL2 + HCL (3)}$$
$$\longrightarrow \text{CHCL2CHCL2 (Stab.)}$$

k	A	Ea	source
1	1.18E12	0.0	a
-1	8.29E17	84.2	b
2	2.0E16	74.0	c
3	2.0E14	53.7	d

$<V> = 578.0\ cm^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 5.91 A^{o} e/k = 525.9 ^{o}K

a. A factor is based on CCC. + CCC., log A= 12.6
CC.C + CC.C, log A= 12.5
Estimate, for CHCL2 + CHCL2, A = 1/3 * $10^{12.55}$
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

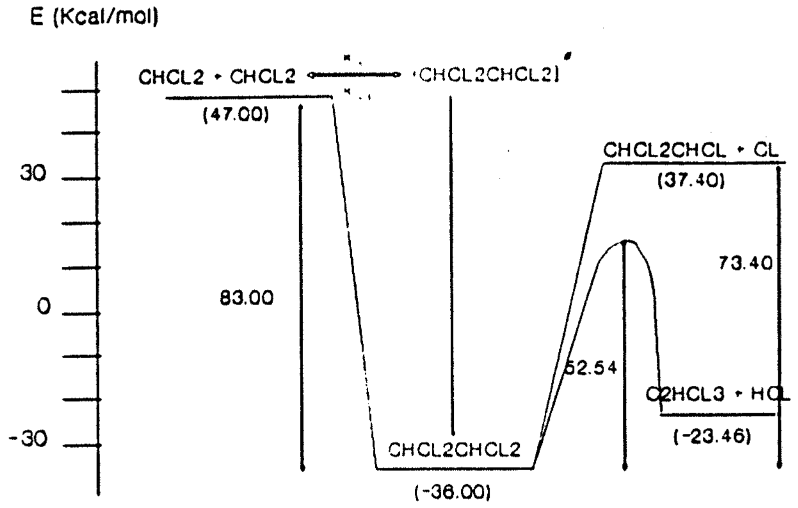
b. Calculated from thermodynamics and reverse A.

c. A factor is based on C2HCL5 = C2HCL4 + CL, log A=16.2
Estimated, C2H2CL4 = C2H2CL3 + CL, A= 2 * 10^{16}
Calculated from thermo and reverse A.
Ref: Weissman and Benson, I. J. of Chem. Kinetics, Vol. 14, 1287-1304, 1982.

d. Estimated, A=2.0E14

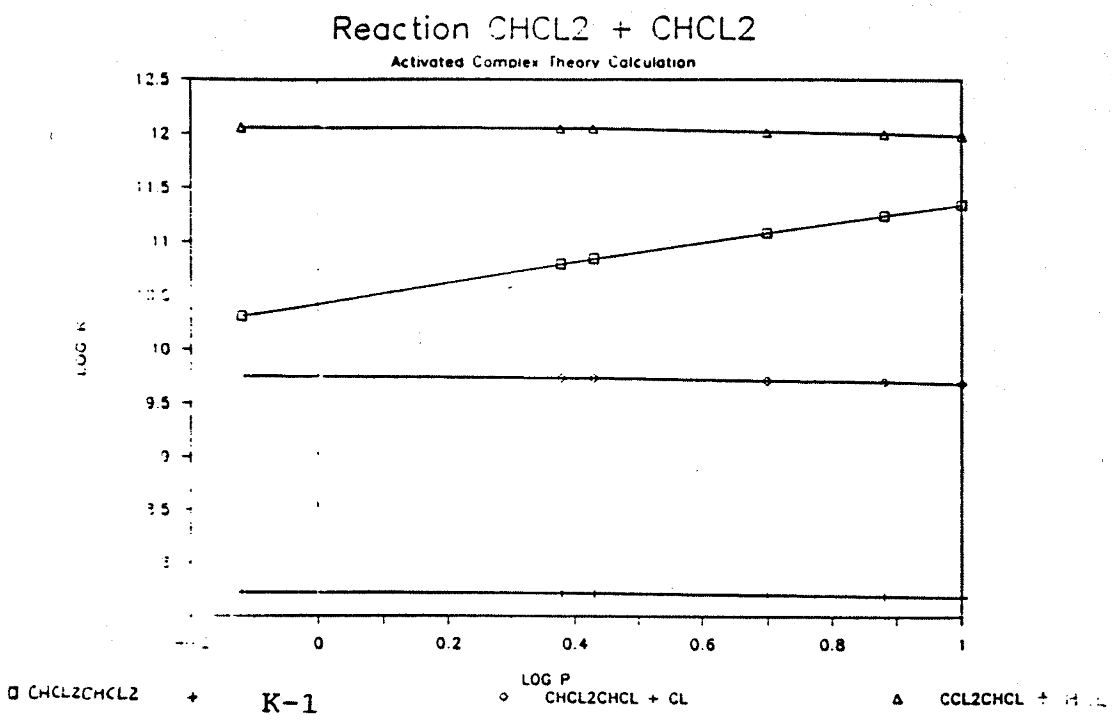
e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



ENERGY DIAGRAM : CHCL2 + CHCL2

(a)



(b)

Figure 2 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CHCL2 + CHCL2 <==> Product

TABLE 5-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CHCL2+CHCL2 = CHCL2CHCL2	1.21E+09	-1670.0
2.69		4.48E+09	-1610.0
7.6		1.39E+10	-1490.0
0.76	CHCL2+CHCL2=CHCL2CHCl+CL	8.89E+10	1640.
2.69		9.38E+10	1690.
7.6		1.05E+11	1810.
0.76	CHCL2+CHCL2=CHCLCCL2+HCL	1.46E+11	376.
2.69		1.48E+11	396.
7.6		1.53E+11	445.

Bath Gas: Ar
Temperature: 300 K

TABLE 6-a

$$CH_3 + CH_2CL \underset{-1}{\overset{1}{\Longleftrightarrow}} [CH_3CH_2CL]\#$$

$$\longrightarrow C_2H_4 + HCL \quad (2)$$

$$\longrightarrow C_2H_5 + CL \quad (3)$$

$$\longrightarrow C_2H_5CL \quad (\text{stab.})$$

k	A	Ea	source
1	2.0E13	0.0	a
-1	2.63E17	91.3	b
2	2.73E15	83.4	c
3	3.24E13	56.6	d

$\langle V \rangle = 1265.3\ cm^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 4.898 A^o e/k = 300.0 ^oK

---

a. A factor is based on CH3 + CH3, log A= 13.4
Estimated, for CH3 + CHCL, A = 2/3 * $10^{13.4}$
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

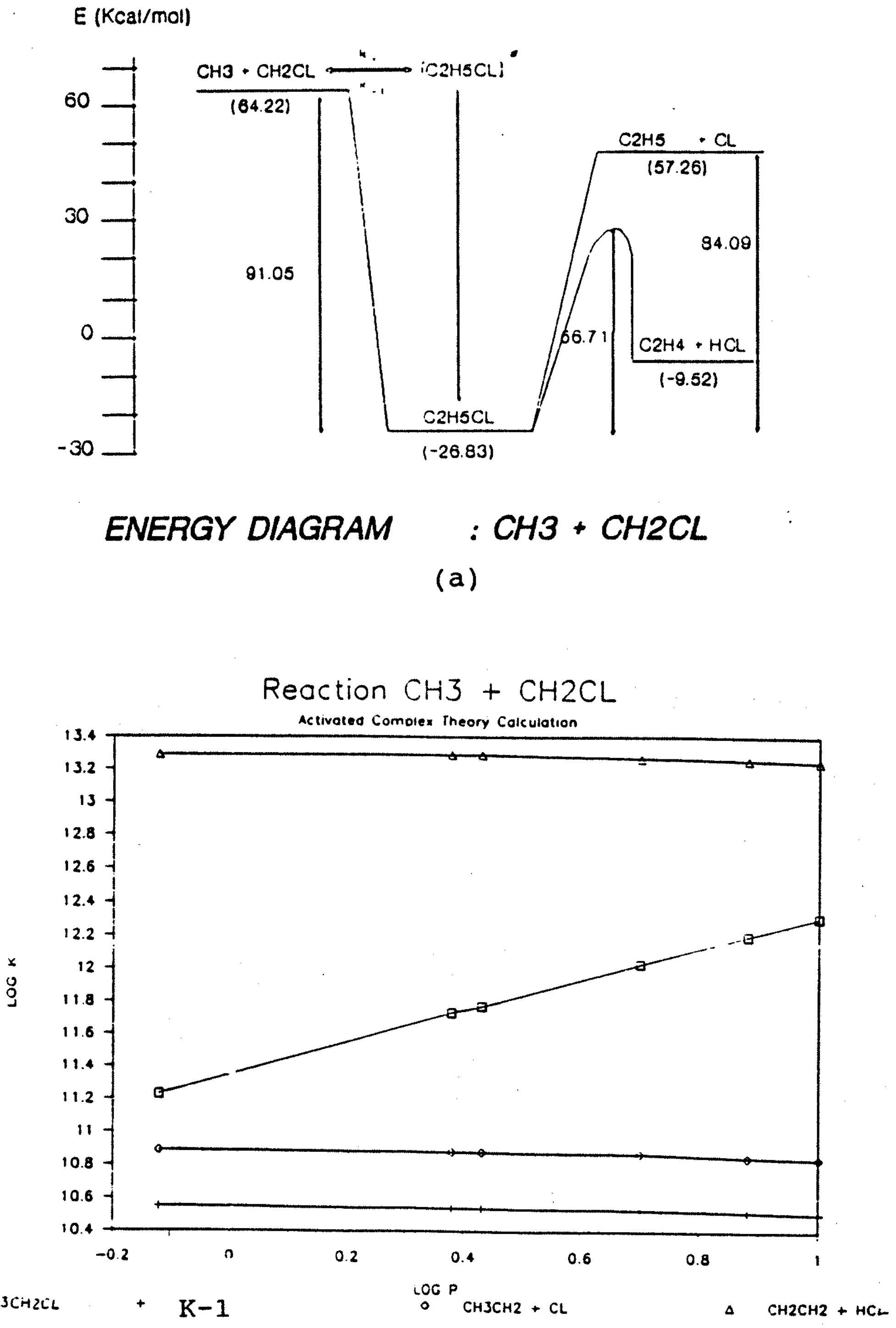
b. Calculated from thermo and reverse A.

c. For H + C2H5, log A= 13.6, CH3 + C2H5, log A = 13.3
Estimate $A_{-2} = 10^{13.4}$
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

d. Ea = del H + 39.4
Ref: Benson, S.W., " Thermochemical Kinetics", 2nd, Ed. 1976.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



(a)

(b)

Figure 3 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CH3 + CH2CL

TABLE 6-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CH3+CH2CL = CH3CH2CL	3.06E+10	-1020.
2.69		1.10E+11	-1000.
7.60		3.15E+11	-959.
0.76	CH3+CH2CL = CH3CH2+CL	1.46E+11	376.
2.69		1.48E+11	396.
7.60		1.53E+11	445.
0.76	CH3+CH2CL = C2H4+HCL	1.98E+13	3.16
2.69		2.0E+13	22.1
7.60		3.15E+13	959.

Bath Gas: Ar
Temperature: 300 K

TABLE 7-a

$$CH_3 + CHCL_2 \underset{-1}{\overset{1}{\Longleftrightarrow}} [CH_3CHCL_2]\#$$

$\longrightarrow CH_3CHCL + CL$ (2)
$\longrightarrow CH_2CHCL + HCL$ (3)
$\longrightarrow CH_3CHCL_2$ (stab.)

k	A	Ea	source
1	2.0E13	0.0	a
-1	2.63E17	91.3	b
2	3.92E15	76.2	c
3	3.92E13	55.4	d

$<V> = 797.2\ CM^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 5.12 A^{o} e/k = 471.2 ^{o}K

a. A factor is based on CH3 + CCC. log A=13.3
Estimate CH3 + CHCL2, A = 2.0E13
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

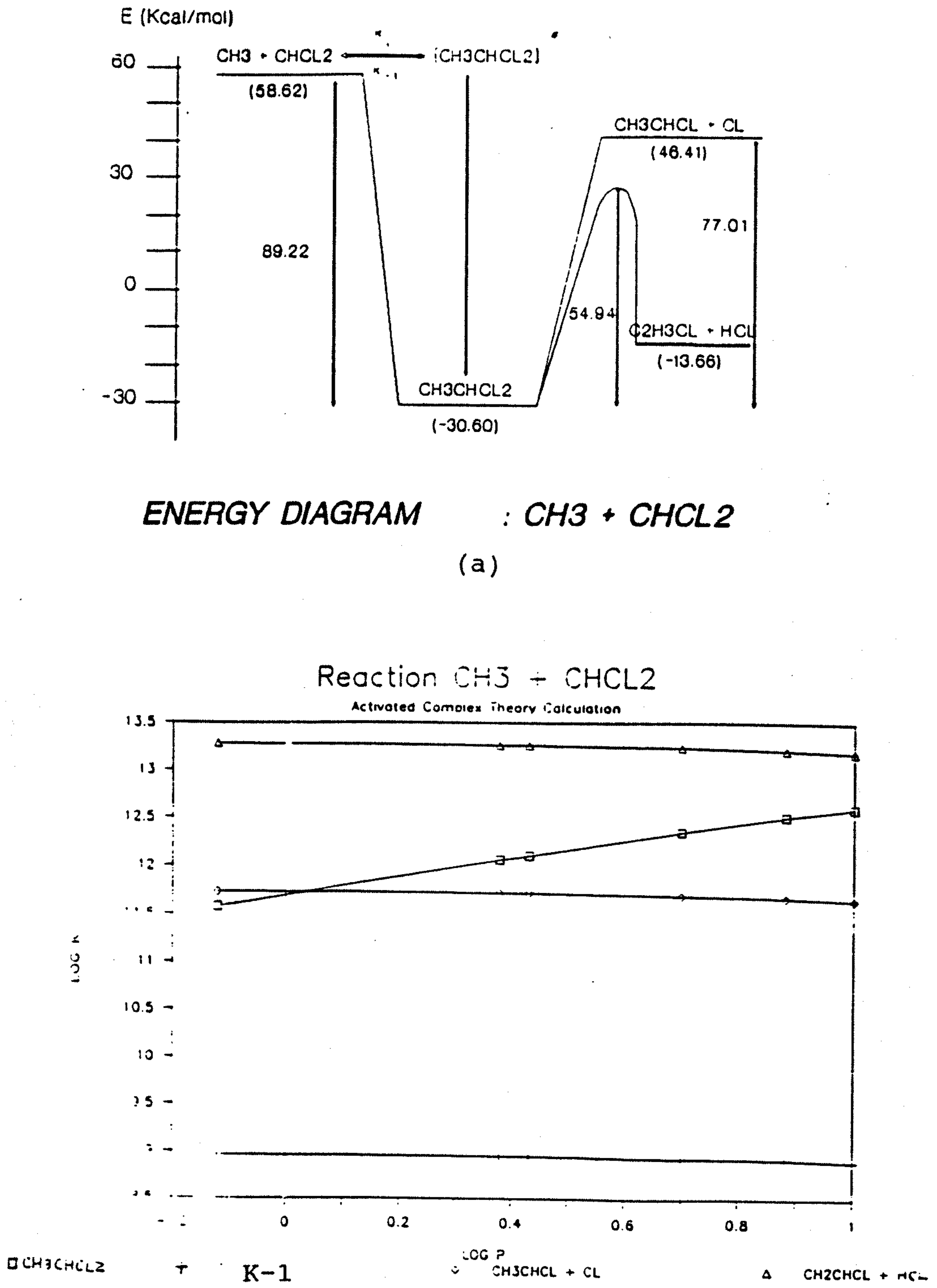
b. Calculated from thermo and reverse A.

c. For CH3 + C2H5, log A= 13.3
Estimated, $A_{-3}=1/2 * 10^{13.3}$
Ref: Allara, D. L. and Shaw, R. The Journal of Physical Chemistry, Ref. Data, Vol. 9, 1980.

d. For CLCH2CH2Cl = C2H3Cl + HCL, log A=13.6
Ref: Weissman and Benson, I. J. of Chem. Kinetics, Vol. 16, 1984.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



(a)

(b)

Figure 4 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CH3 + CHCL2

TABLE 7-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	$CHCL2+CH3 = CH3CHCL2$	4.1E+10	-1310.0
2.69		1.5E+11	-1260.0
7.6		4.51E+11	-1160.0
0.76	$CHCL2+CH3 = CH3CHCL+CL$	1.81E+12	711.0
2.69		1.90E+12	764.0
7.6		2.08E+12	880.0
0.76	$CHCL2+CH3 = CH2CHCL+HCL$	1.90E+13	-2.05
2.69		1.97E+13	47.9
7.6		2.13E+13	158.0

Bath Gas: Ar
Temperature: 300 K

TABLE 8-a

$$H + C_2H_3CL \underset{-1}{\overset{1}{\Longleftrightarrow}} [C_2H_4CL]^{\#}$$

$$\longrightarrow C_2H_4 + CL \ (2)$$

$$\longrightarrow C_2H_4CL \ (\text{stab.})$$

k	A	Ea	source
1	8.0E12	3.3	a
-1	7.7E12	45.1	b
2	2.51E13	23.24	c

$\langle V \rangle = 1265.3\ cm^{-1}$ d

Lennard-Jones Parameters: e

Sigma = 5.30 A^{o} e/k = 322.0 ^{o}K

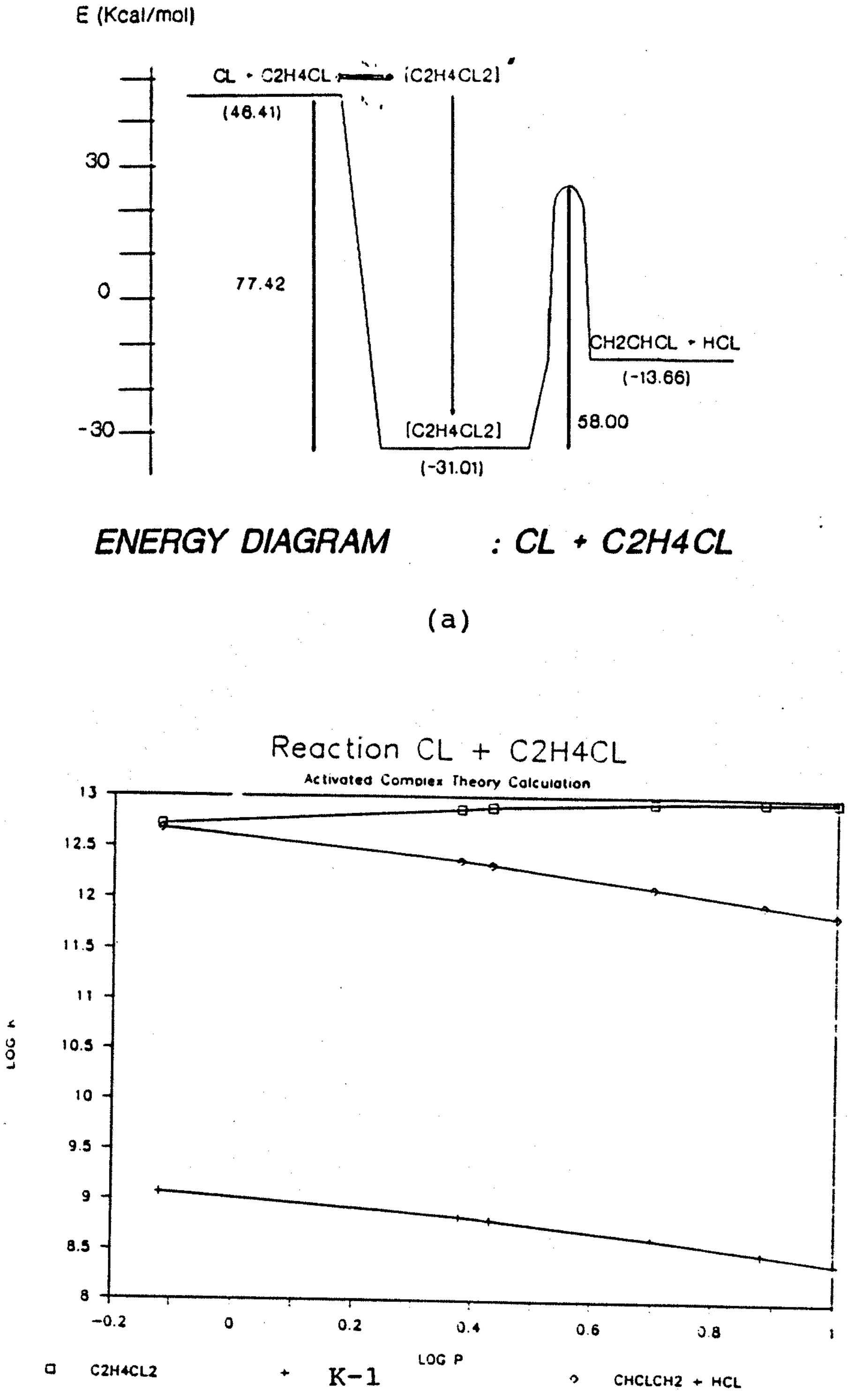
a. A factor and Ea is taken as that for H + CH3CHCH2, Ref: Dean, A.M., J. Phys. Chem., 89, pp 4600, 1985.

b. Calculated from thermodynamics and reverse A.

c. A-2 factor is based on CH3 + CH3CH2, A=2.0E+13, A2 calculated using thermodynamics and A-2. Ref: Dean, A.M., J. Phys. Chem., 89, pp 4600, 1985.

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

e. Activated complex L-J parameters are estimated using ctitical property data tabulated in Reid, Prausnitz and Sherwood(The Properties of Gases and Liquids, 3rd ed.)



(a)

(b)

Figure 5 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CL + C2H4CL

TABLE 8-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	$C_2H_3CL+H = C_2H_4CL$	1.22E+08	2300.
2.69		4.32E+08	2300.
7.60		1.22E+09	2300.
0.76	$C_2H_3CL+H = C_2H_4+CL$	8.00E+12	3300.
2.69		8.00E+12	3300.
7.60		8.00E+12	3300.

Bath Gas: Ar
Temperature: 300 K

TABLE 9-a

$$\mathrm{H + CH3CHCL} \underset{-1}{\overset{1}{\Longleftrightarrow}} \mathrm{[CH3CH2CL]\#}$$

$$\longrightarrow \mathrm{C2H5 + CL}\ (2)$$
$$\longrightarrow \mathrm{C2H4 + HCL}(3)$$
$$\longrightarrow \mathrm{C2H5CL}\ (\mathrm{stab})$$

k	A	Ea	source
1	1.00E13	2.5	a
-1	2.79E14	95.1	b
2	1.80E15	82.8	c
3	2.00E13	56.6	d

$\langle V \rangle = 1265.3\ \mathrm{cm}^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 4.898 A^{o} e/k = 300.0 ^{o}K

a. From R.B. Barat and J.W. Bozzelli, J. Phys. Chem., to be submitted.

b. Calculated from thermodynamics and reverse A.

c. A-2 factor is based on CH3+C2H5, log A=13.3
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

d. Ea = del H + 39.4
Ref: Benson, S.W., "Thermochemical Kinetics", 2nd Ed., 1976.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.

TABLE 9-b

APPARENT REACTION RATE CONSTANTS PREDICTED
USING BIMOLECULAR QRRK ANALYSIS
(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	$H+C_2H_4CL = C_2H_5CL$	7.71E+10	-1010.
2.69		2.77E+11	-995.
7.6		7.94E+11	-951.
0.76	$H+C_2H_4CL = C_2H_5+CL$	1.05E+12	264.
2.69		1.07E+12	284.
7.6		1.10E+12	331.
0.76	$H+C_2H_4CL = C_2H_4+HCL$	4.92E+13	3.82
2.69		4.97E+13	22.6
7.6		5.08E+13	66.9

Bath Gas: Ar
Temperature: 300 K

TABLE 10-a

$$\mathrm{CHCLCHCL + H \underset{-1}{\overset{1}{\Longleftrightarrow}} [CH2CLCHCL]\#}$$

$$\mathrm{\longrightarrow C2H3CL + CL\ (2)}$$

$$\mathrm{\longrightarrow CH2CLCHCL(stab)}$$

k	A	Ea	source
1	8.00E12	4.0	a
-1	4.36E12	44.46	b
2	1.95E14	22.9	c

<V> = 736.2 cm^{-1} d

Lennard-Jones Parameters: e

Sigma = 5.50 A^{o} e/k = 433.0 ^{o}K

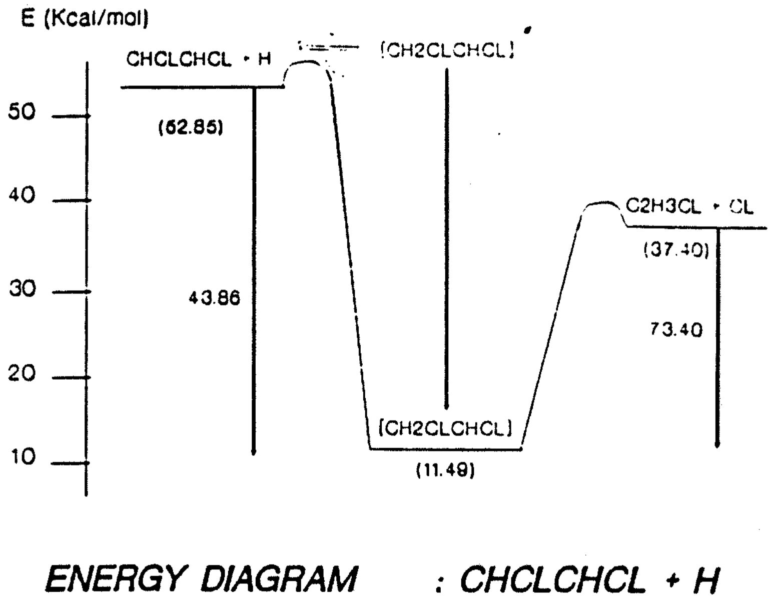
a. A factor is based on H+CH3CHCH2, A = 8.0E13
Ref: Kerr, J.A. and Moss, S.J., "Hand book of Bimolecular and Termolecular Gas Reaction Vol.II, CRC Press Inc., 1981.

b. Calculated from thermodynamics and reverse A.

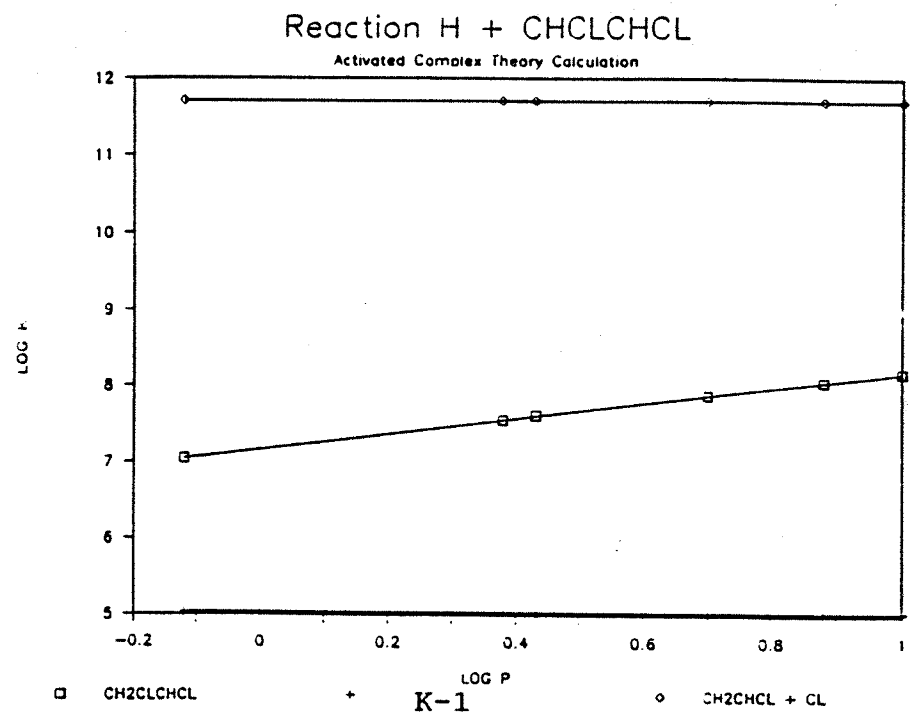
c. Based upon (del S) CH2CH2 + CL, with A = 1.8E13, take A_{-2} = 1.8E13, Calculated from thermo and reverse A.
Ref: Kerr, J.A. and Moss, S.J., "Hand book of Bimolecular and Termolecular Gas Reaction Vol.II, CRC Press Inc., 1981.

d. See note (d) of Table 1-a.

e. See note (e) of Table 1-a.



(a)



(b)

Figure 6 . Energy Diagram (a) and CHEMACT Results (b) for Reaction H + CHCLCHCL

TABLE 10-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CHCLCHCL = CH2CLCHCL	2.74E+07	2720.
2.69		9,73E+07	2720.
7.6		2.74E+08	2720.
0.76	H+CHCLCHCL = C2H3CL+CL	8.0E+12	4000.
2.69		8.0E+12	4000.
7.6		8.0E+13	4000.

Bath Gas: Ar
Temperature: 300 K

TABLE 11-a

$$\mathrm{CH2CLCHCL + H} \underset{-1}{\overset{1}{<===>}} [\mathrm{CH2CLCH2CL}]\#$$

---> CH2CLCH2 + CL (2)
---> CH2CHCL + HCL (3)
---> CH2CLCH2CL (stab)

k	A	Ea	source
1	1.0E14	0.0	a
-1	4.05E15	94.6	b
2	5.0E15	76.8	c
3	3.98E13	58.0	d

$\langle V \rangle = 797.20\ \mathrm{cm}^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 5.12 A^{o} e/k = 471.2 ^{o}K

a. A factor is based on
CCC.+H, log A=14., CC.C+H, log A=14.,
Estimated, for CH2CLCHCL+H, A = 1.0E14.
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

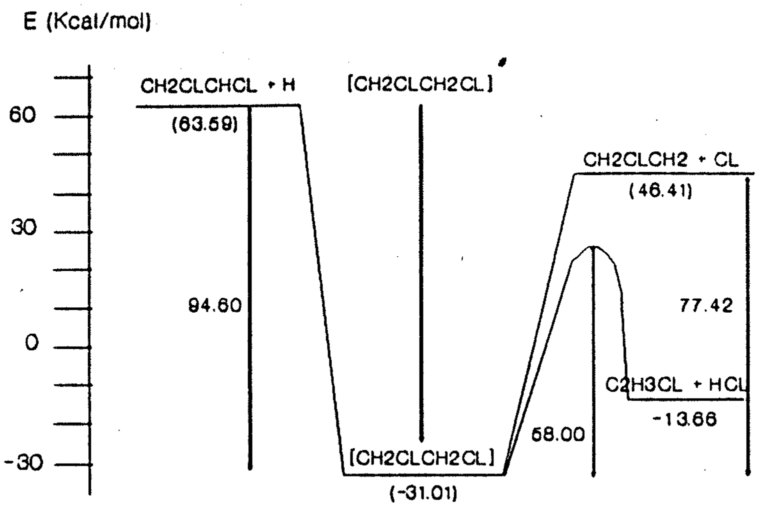
b. Calculated from thermodynamics and reverse A.

c. A-2 factor is based on CH3+C3H7, A= 2E+13
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

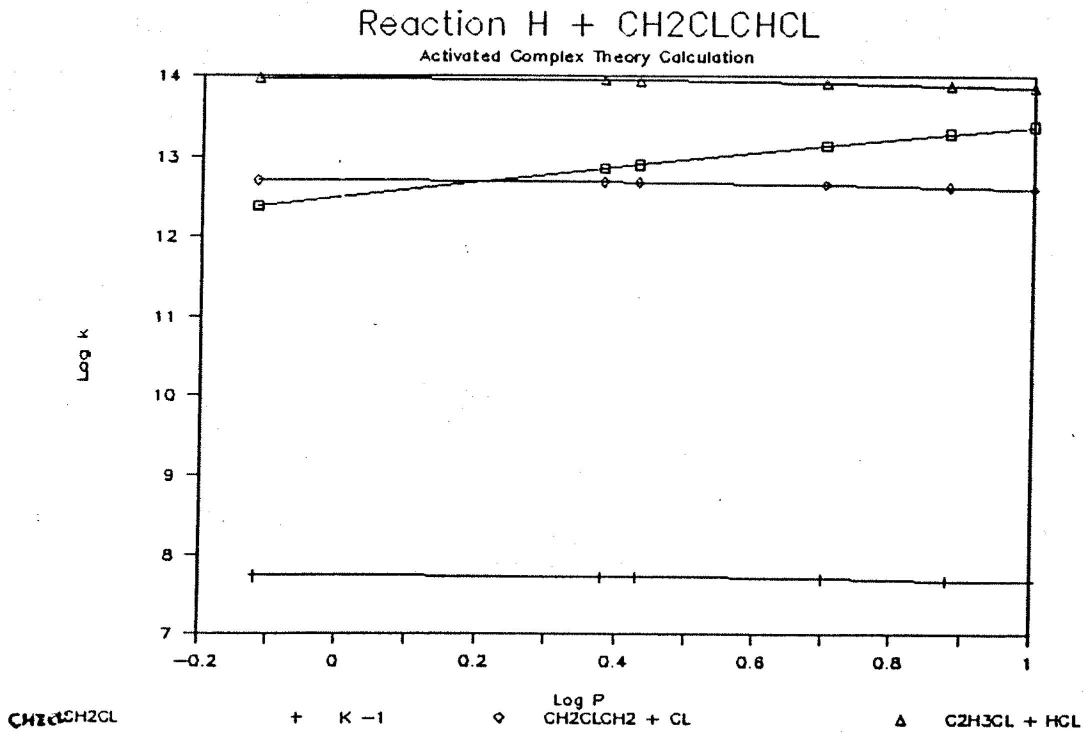
d. Ref: From Weissman and Benson, I. J. of Chem. Kinetics, Vol. 16, pp 307, 1984.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



ENERGY DIAGRAM (a) *: CH2CLCHCL + H*



(b)

Figure 7 . Energy Diagram (a) and CHEMACT Result (b) for Reaction H + CH2CLCHCL <==> Product

TABLE 11-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CH2CLCHCL = CH2CLCH2CL	2.76E+10	-1330.0
2.69		1.07E+11	-1180.0
7.6		3.37E+12	-927.0
0.76	H+CH2CLCHCL = CH2ClCH2+CL	5.15E+11	864.0
2.69		5.95E+11	1030.0
7.6		7.42E+11	1330.0
0.76	H+CH2CLCHCL=CHCLCHCL+HCL	3.86E+12	42.1
2.69		4.32E+12	201.
7.6		5.05E+12	472.

Bath Gas: Ar
Temperature: 300 K

TABLE 12-a

$$\mathrm{CHCLCCL2 + H} \underset{-1}{\overset{1}{\Longleftarrow\!\!\Longrightarrow}} \mathrm{[CH2CLCCL2]\#}$$

$$\longrightarrow \mathrm{CH2CCL2 + CL}\ (2)$$

$$\longrightarrow \mathrm{CH2CLCCL2}\ (\mathrm{stab})$$

k	A	Ea	source
1	8.0E12	2.1	a
-1	7.47E12	44.65	b
2	1.04E14	22.7	c

$\langle V \rangle = 666.62\ \mathrm{cm}^{-1}$ d

Lennard-Jones Parameters: e

Sigma = 5.6 A^{o} e/k = 510.0 ^{o}K

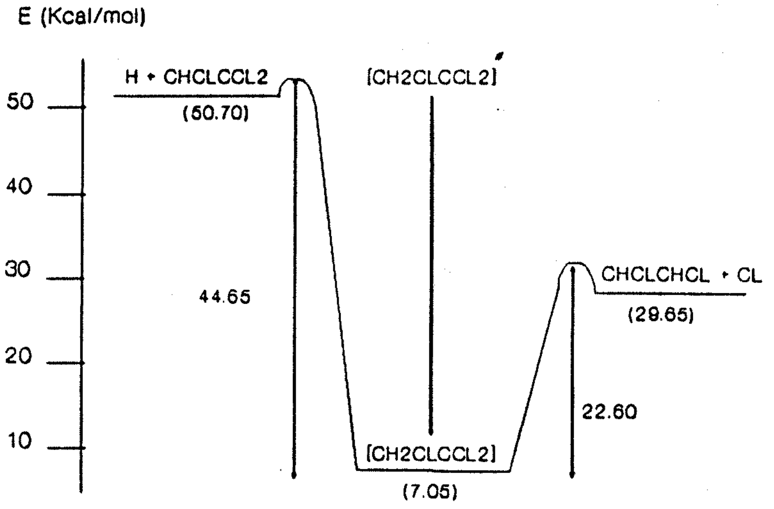
a. A factor is based on H+C=CC, log A= 12.9, Ea=1.2,
H+C=CCC, log A= 12.9, Ea=2.9,
Estimate, log A = 12.9, Ea = 2.1.
Ref: Dean, A. M., J. Phys. Chem., 89, 4600, 1985.

b. Calculated from thermodynamics and reverse A.

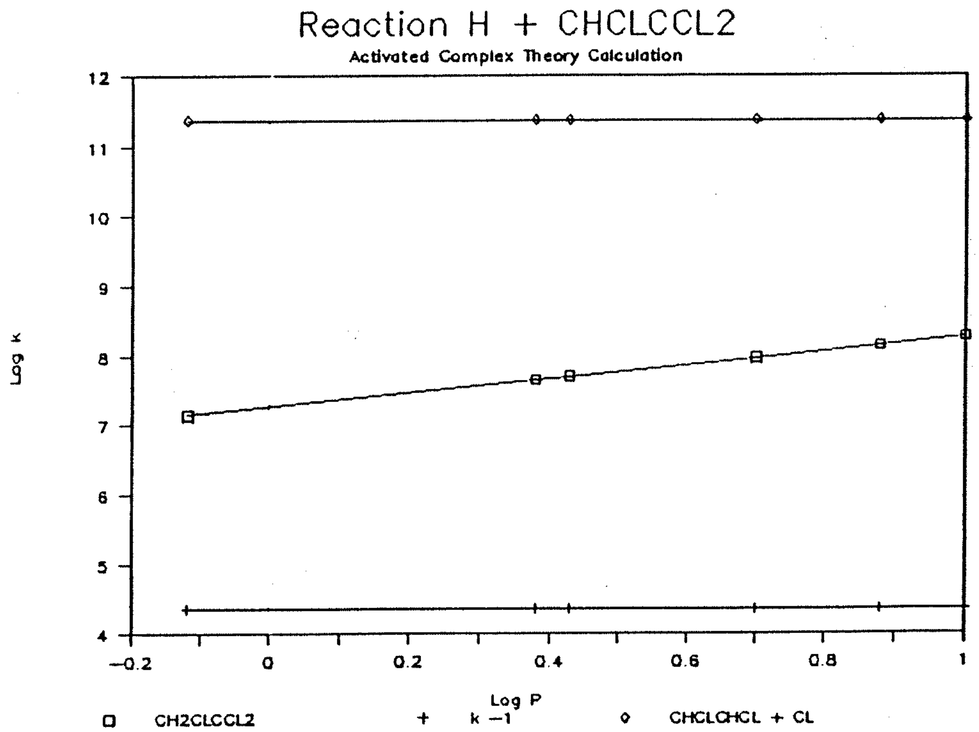
c. A-2 factor is based on CL+C2H4=CH2CH2CL,
take A_{-2}=1.8E13,
A2 calculated from thermo and reverse A.
Ref: Kerr, J. A. and Moss, S. J., "Hand book of Bimolecular and Termolecular Gas Reaction Vol.II, CRC Press Inc., 1981.

d. See note (d) of Table 1-a.

e. See note (e) of Table 1-a.



ENERGY DIAGRAM (a) : H + CHCLCCL2



(b)

Figure 8 . Energy Diagram (a) and CHEMACT Result (b) for Reaction H + CHCLCL2 <==> Product

TABLE 12-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CHCLCCL2 = CH2CLCCL2	4.87E+07	755.
2.69		1.54E+08	755.
7.6		1.73E+08	755.
0.76	H+CHCLCCL2 = CH2CCL2+CL	8.00E+12	2100.
2.69		8.00E+12	2100.
7.6		8.00E+12	2100.

Bath Gas: Ar
Temperature: 300 K

TABLE 13-a

$$\mathrm{CHCL2CHCL + H} \underset{-1}{\overset{1}{<===>}} \mathrm{[CHCL2CH2CL]^{*}}$$

---> CHCLCH2CL + CL (2)
---> CHCLCHCL + HCL (3)
---> CH2CLCHCL2 (stab)

k	A	Ea	source
1	1.00E14	0.0	a
-1	3.28E15	96.0	b
2	3.69E15	75.1	c
3	1.92E13	54.9	d

$\langle V \rangle$ = 699.90 cm^{-1} e

Lennard-Jones Parameters: f

Sigma = 5.720 A^{o} e/k = 498.9 ^{o}K

---

a. A factor is based on H+1-C3H7, log A= 14.0
H+2-C3H7, log A= 14.0
Estimate CHCL2CHCL+H, log A = 14.0.
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

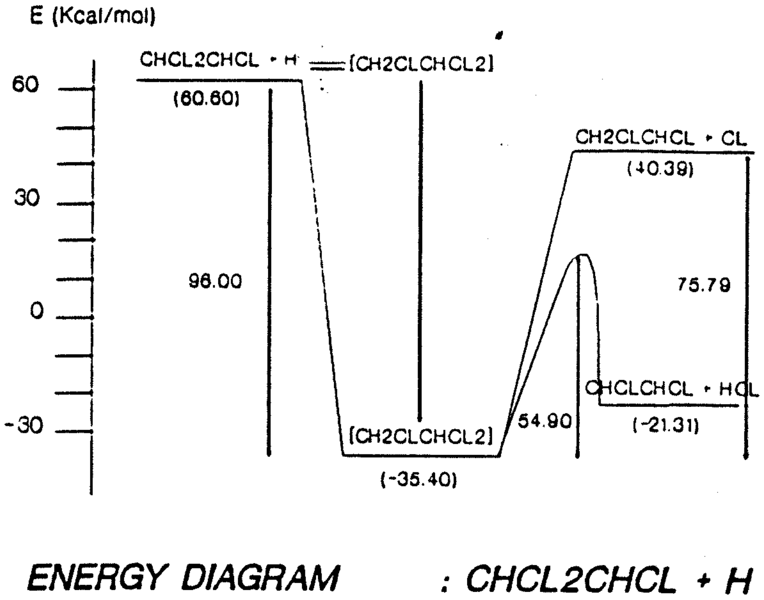
b. Calculated from thermo and reverse A.

c. From CH3+C2H5, log A= 13.3,
take log A_{-2} = 1/2 * 13.3
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

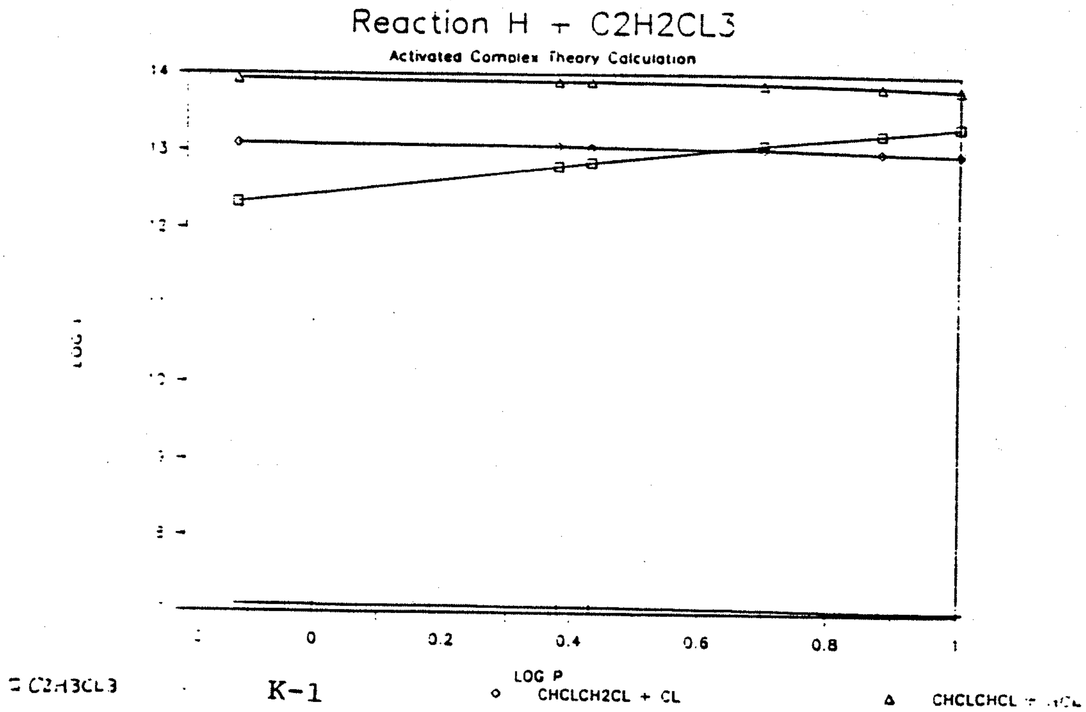
d. A = $10^{13.55} * 10^{(-4/4.6)} * 4 = 1.92 * 10^{13}$
Ea = del H + 40.8.
Ref: Bamford, D.H. and Tipper, C.F. comprehensive Chemical Kinetics, 5, 1972.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



(a)



(b)

Figure 9 . Energy Diagram (a) and CHEMACT Results (b) for Reaction H + C2H2CL3

TABLE 13-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CHCL2CHCl = C2H4CL2	1.99E+11	-1400.0
2.69		7.38E+11	-1350.0
7.6		2.25E+12	-1220.0
0.76	H+CHCL2CHCL=CH2CLCHCL+CL	3.13E+13	557.0
2.69		3.30E+13	618.0
7.6		3.68E+13	752.0
0.76	H+CHCL2CHCL=CHCLCHCL+CL	7.74E+13	-59.50
76.0		8.11E+13	-0.034
760.0		8.9E+13	129.0

Bath Gas: Ar
Temperature: 300 K

TABLE 14-a

$$\mathrm{CL + CH_2ClCH_2} \underset{-1}{\overset{1}{<===>}} \mathrm{[CH_2ClCH_2Cl]\#}$$

$$\mathrm{---->\ C_2H_3CL + HCL(2)}$$

$$\mathrm{---->\ C_2H_4CL_2\ (stab.)}$$

k	A	Ea	source
1	1.0E13	0.0	a
-1	2.5E15	76.8	b
2	3.98E13	58.0	c

$\langle V \rangle = 797.0\ \mathrm{cm^{-1}}$ d

Lennard-Jones Parameters: e

Sigma = 5.12 A^{o} e/k = 471.2 ^{o}K

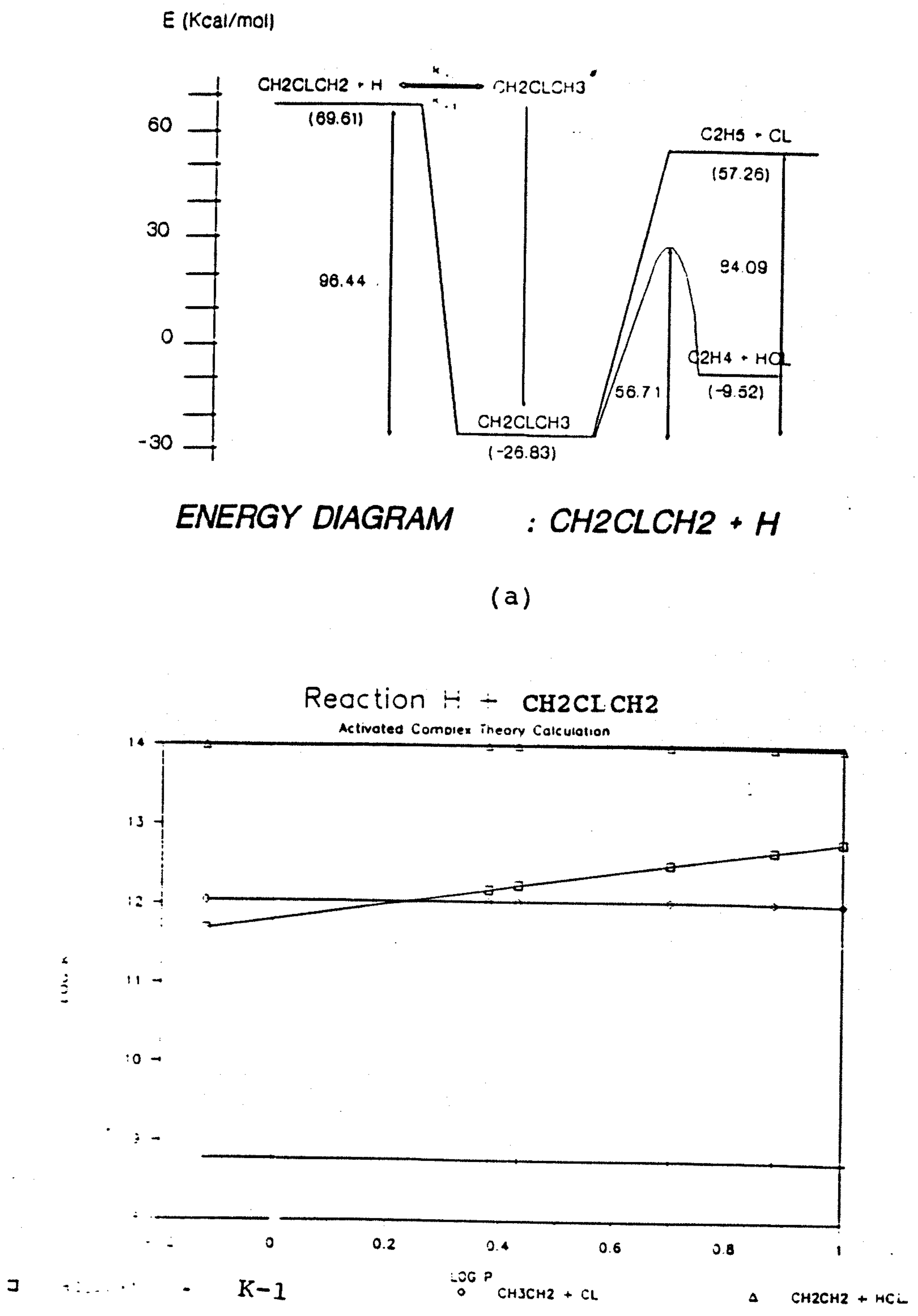
a. A factor is based on CH3 + CH3CH2, log A = 13.3, and we estimated $A_1 = 1/2 * 10^{13.3}$. Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

b. Calculated from thermodynamics and reverse A.

c. From Weissman and Benson, I. J. Chem. Kinetics, Vol. 16, 1984.

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

e. Activated complex L-J parameters are estimated using crtitical property data tabulated in Reid, Prausnitz and Sherwood (The Properties of Gases and Liquids, 3rd ed).



(a)

(b)

Figure 10. Energy Diagram (a) and CHEMACT Results (b) for Reaction H + CH2CLCH2

TABLE 14-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	C2H4CL+CL = C2H4CL2	1.16E+12	-889.
2.69		3.55E+12	-469.
7.60		6.19E+12	-226.
0.76	C2H4CL+CL = C2H3CL+HCL	1.68E+13	747.
2.69		1.86E+13	1290.
7.60		1.44E+13	1640.

Bath Gas: Ar
Temperature: 300 K

TABLE 15-a

$$\mathrm{CL} + \mathrm{CHCL2} \underset{-1}{\overset{1}{\Longleftrightarrow}} [\mathrm{CHCL3}]^*$$

$$\begin{aligned} &\longrightarrow \mathrm{CCL2} + \mathrm{HCL}\ (2) \\ &\longrightarrow \mathrm{CHCL3}\ (\mathrm{stab}) \end{aligned}$$

k	A	Ea	source
1	2.0E13	0.0	a
-1	2.52E16	74.6	b
2	2.37E13	67.1	c

$\langle V \rangle = 880.00\ CM^{-1}$ d

Lennard-Jones Parameters: e

Sigma = 5.390 A^{O} e/k = 340.2 ^{O}K

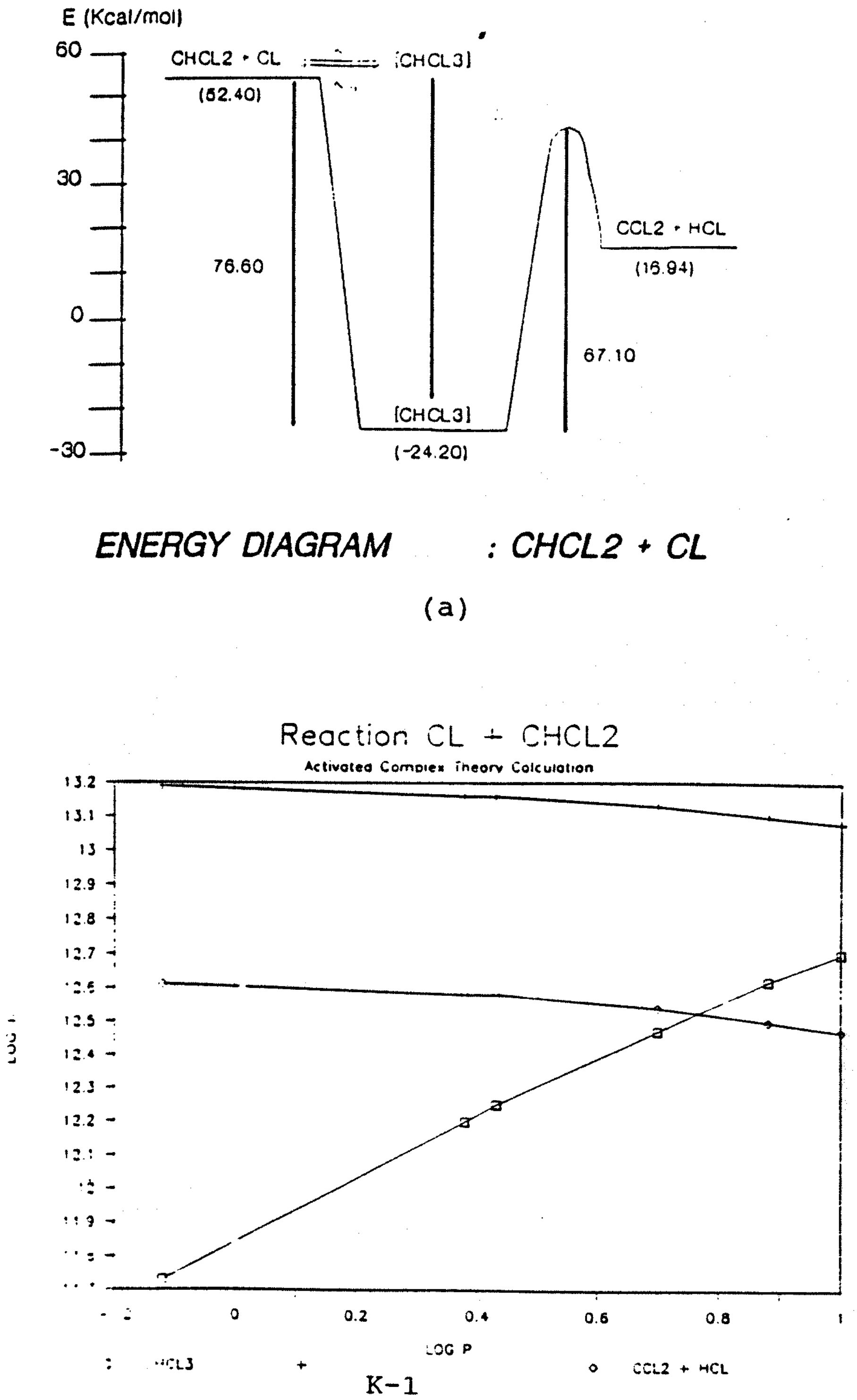
a. A factor is based on CH3+C2H5, log A=13.3,
CH3+CCC., log A=13.3,
CH3+CC.C, log A=13.2,
Estimate CL+CHCL2, A = $2.0*10^{13}$
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

b. Calculated from thermo and reverse A.

c. Mechanism of thermal reactions of CHCl3 and CCl4 in H2.

d. See note (d) of Table 1-a.

e. See note (e) of Table 1-a.



(a)

K-1

(b)

Figure 11 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CL + CHCL2

TABLE 15-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CL+CHCL2 = CHCL3	3.47E+10	-1620.0
2.69		1.28E+11	-1550.0
7.6		3.81E+11	-1410.0
0.76	CL+CHCL2 = CCL2+HCL	1.72E+12	-506.
2.69		1.8E+12	-432.
7.6		1.97E+12	-280.

Bath Gas: Ar
Temperature: 300 K

TABLE 16-a

$$\mathrm{H + CCL3} \underset{-1}{\overset{1}{<\!===\!>}} \mathrm{[CHCL3]^{*}}$$

$$\begin{aligned} &\text{--->}\ \mathrm{CHCL2 + CL}\ (2) \\ &\text{--->}\ \mathrm{CCL2 + HCL}\ (3) \\ &\text{--->}\ \mathrm{CHCL3}\ \text{(stab)} \end{aligned}$$

k	A	Ea	source
1	1.0E14	0.0	a
-1	1.75E15	94.7	b
2	2.52E16	74.6	c
3	2.37E13	67.1	d

$<V> = 880.0\ cm^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 5.390 A^{o} e/k = 340.2 ^{o}K

---

a. A factor is based on H + CCC., log A = 14.
H + CC.C, log A = 14., H + CH3, log A = 14.3
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

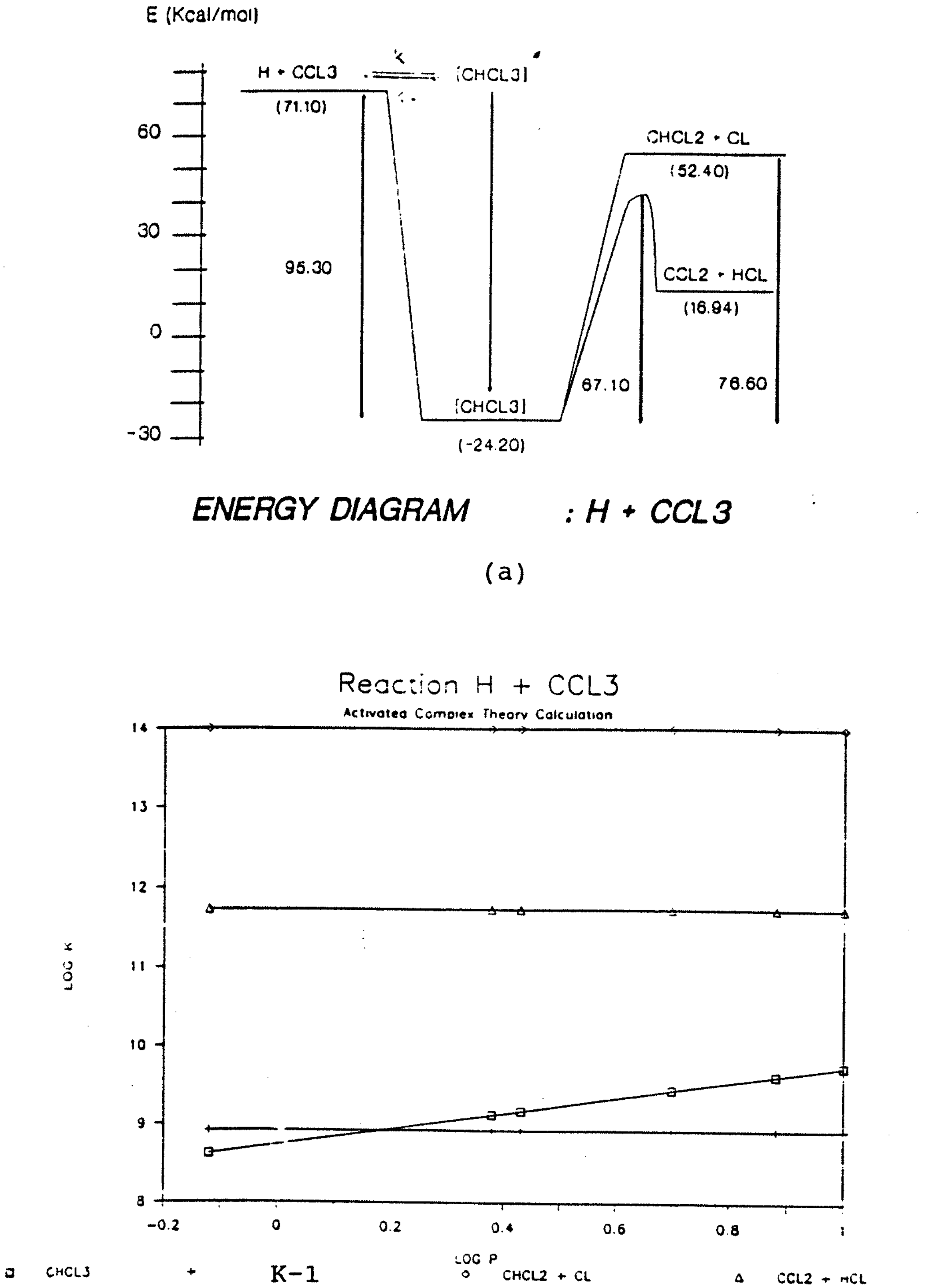
b. Calculated from thermo and reverse A.

c. A-2 factor is based on CH3+CC.C, log A=13.2
CH3+CCC., log A=13.3, Estimated A_{-2}=2E13, A2 calculated from thermodynamic and A-2.
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

d. See note (c) of Table 15-a.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



(a)

(b)

Figure 12 . Energy Diagram (a) and CHEMACT Results (b) for Reaction H + CCL3

TABLE 16-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+CCL3 = CHCL3	6.48E+07	-1110.0
2.69		2.30E+08	-1110.0
7.60		6.48E+08	-1110.0
0.76	H+CCL3 = CHCL2+CL	9.95E+13	0.3030
2.69		9.95E+13	0.3130
7.60		9.95E+13	0.3380
0.76	H+CCL3 = CCL2+HCL	4.85E+11	-58.70
2.69		4.85E+11	-58.60
7.60		4.85E+11	-58.60

Bath Gas: Ar
Temperature: 300 K

TABLE 17-a

$$\mathrm{CHCL2 + CCL3} \underset{-1}{\overset{1}{\Longleftrightarrow}} [\mathrm{CHCL2CCL3}]^*$$

$$\begin{aligned} &\longrightarrow \mathrm{CHCL2CCL2 + CL}\ (2) \\ &\longrightarrow \mathrm{CCL4 + HCL}\ (3) \\ &\longrightarrow \mathrm{CHCL2CCL3}\ (\mathrm{stab}) \end{aligned}$$

k	A	Ea	source
1	2.00E13	0.0	a
-1	6.91E17	76.5	b
2	1.58E16	68.1	c
3	1.26E14	59.7	d

$<V> = 470.0\ \mathrm{cm}^{-1}$ e

Lennard-Jones Parameters: f

Sigma = 6.37 A^{o} e/k = 548.9 ^{o}K

---

a. A factor is based on CH3+CH3, log A= 13.4
CH3+C2H5, log A= 13.3, CH3+CCC., log A= 13.3
take $A_1 = 2 * 10^{13}$
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

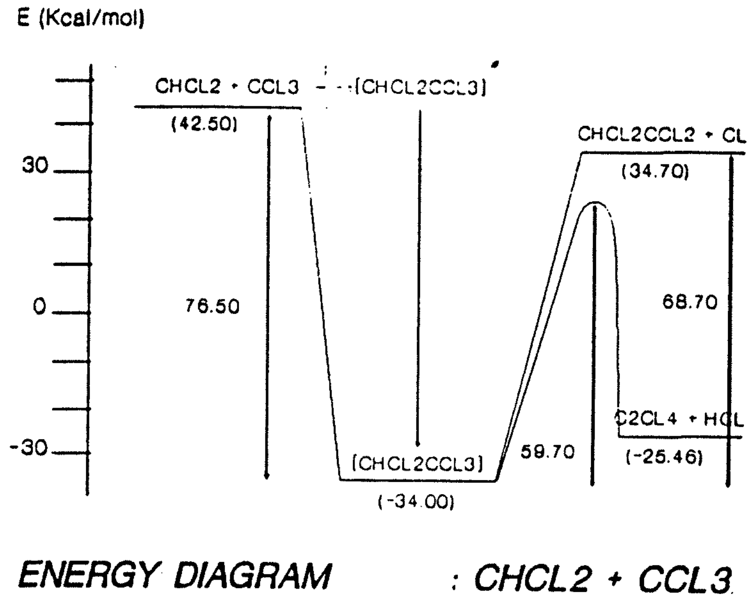
b. Calculated from thermo and reverse A.

c. From Benson and Weissman, I. J. of Chem. Kinetics, Vol 14, 1287-1304, 1982.

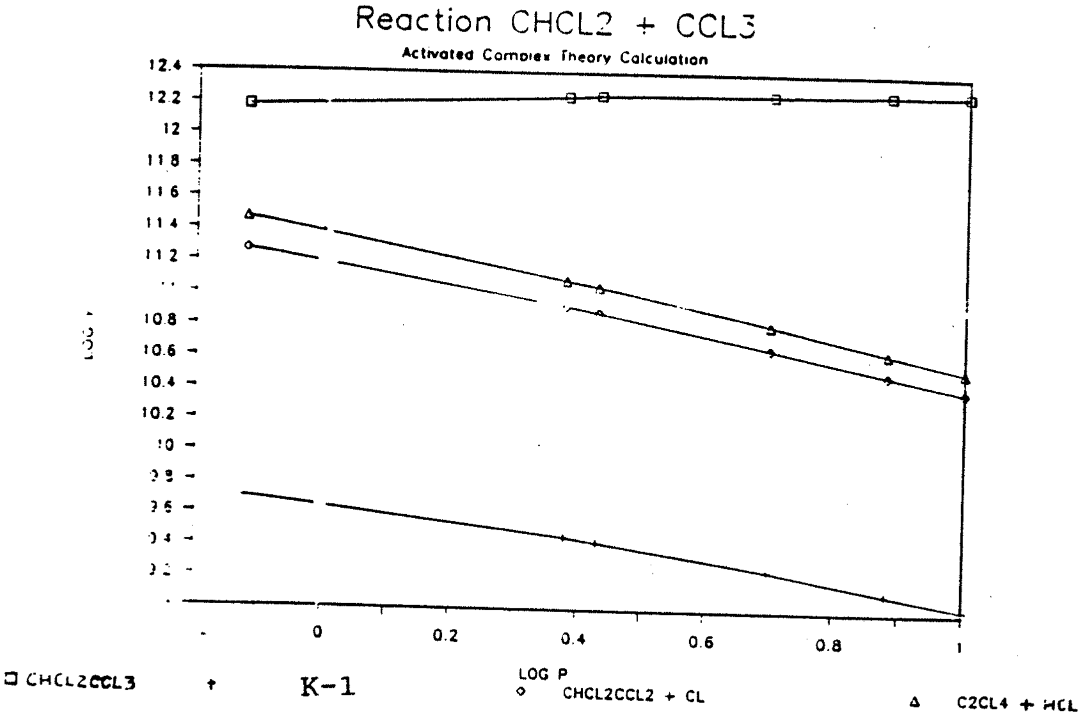
d. From Benson and Weissman, I. J. of Chem. Kinetics, Vol 14, 1982.

e. See note (d) of Table 1-a.

f. See note (e) of Table 1-a.



(a)



(b)

Figure 13. Energy Diagram (a) and CHEMACT Results (b) for Reaction CHCL2 + CCL3 <==> Product

TABLE 17-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CHCL2+CCL3 = C2HCL5	2.93E+11	-963.0
2.69		7.71E+11	-497.0
7.60		1.24E+12	-254.0
0.76	CHCL2+CCL3 = C2HCL4+CL	1.08E+13	2420.0
2.69		1.76E+12	3230.0
7.60		1.97E+12	3800.0
0.76	CHCL2+CCL3 = C2CL4+HCL	3.19E+12	1420.0
2.69		4.0E+12	2130.0
7.60		3.49E+12	2580.0

Bath Gas: Ar
Temperature: 300 K

TABLE 18-a

$$\mathrm{CCL3 + CCL3} \underset{-1}{\overset{1}{<===>}} [\mathrm{C2CL6}]^*$$

$$\mathrm{---> C2CL5 + CL\ (2)}$$
$$\mathrm{---> C2CL6\ (stab)}$$

k	A	Ea	source
1	2.32E12	0.0	a
-1	6.31E17	71.2	b
2	1.2E16	69.9	c

<V> = 400.0 CM^{-1} d

Lennard-Jones Parameters: e

Sigma = 6.52 A^{o} e/k = 690.51 ^{o}K

---

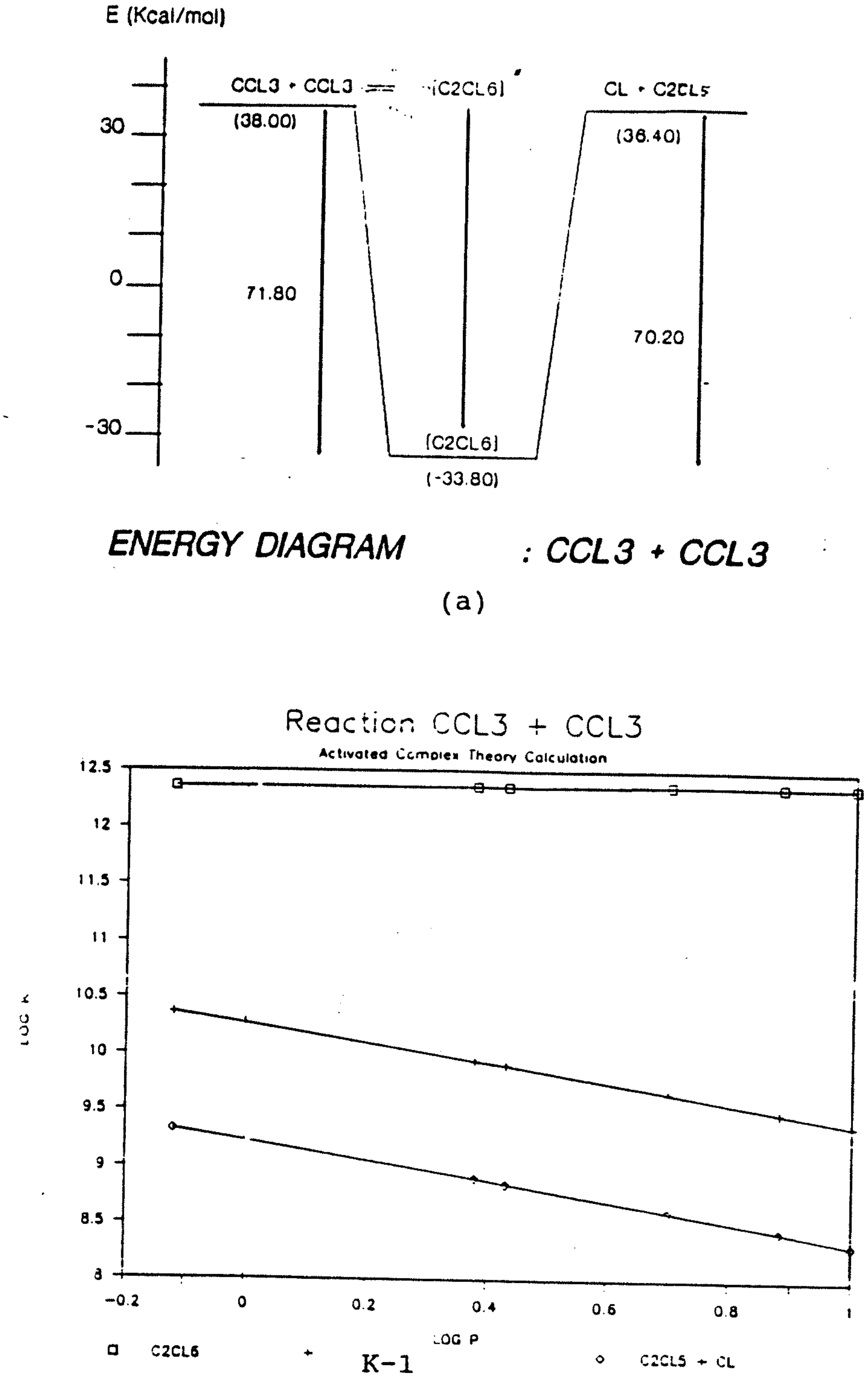
d. From Benson and Weissman, I. J. of Chem. Kinetics, Vol 14, 1982.

b. Calculated from thermo and reverse A.

c. From Benson and Weissman, I. J. of Chem. Kinetics, Vol 14, 1982.

d. See note (d) of Table 1-a.

e. See note (e) of Table 1-a.



(a)

(b)

Figure 14 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CCL3 + CCL3

TABLE 18-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CCL3+CCL3 = C2CL6	1.64E+12	-198.
2.69		1.97E+12	-93.5
7.60		2.14E+12	-46.3
0.76	CHCL2+CH2CL = C2H3CL2+CL	1.77E+13	5370.0
2.69		1.92E+13	6070.0
7.60		1.66E+13	6540.0

Bath Gas: Ar
Temperature: 300 K

TABLE 19-a

$$\text{CH2CL + CCL3} \underset{-1}{\overset{1}{<===>}} [\text{CH2CLCCL3}]^{*}$$

---> CH2CLCCL2 + CL(2)
---> C2HCL3 + HCL (3)
---> CH2CLCCL3 (stab)

k	A	Ea	source
1	6.31E12	0.0	a
-1	4.85E17	84.7	b
2	2.00E16	74.0	c
3	2.00E14	53.7	d

<V> = 579.2 cm^{-1} e

Lennard-Jones Parameters: f

Sigma = 6.13 A^{o} e/k = 523.9 ^{o}K

---

a. A factor is based on 2-C4H9 + C3H7, logA = 12.8
CC.C + CC.C, logA = 12.5
estimate for CH2CL+CCL3, A = 6.31E12
Ref: Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 1980.

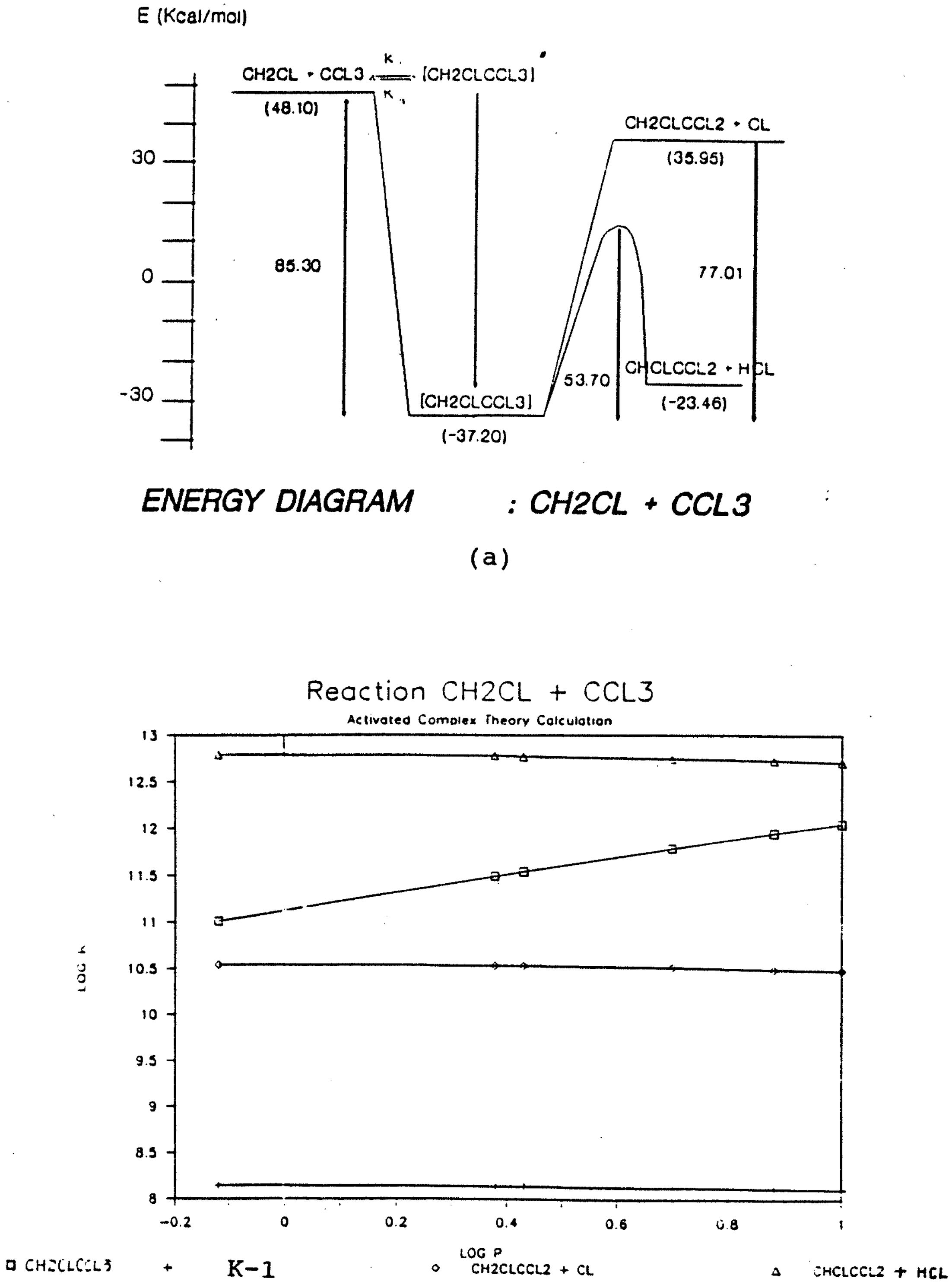
b. Calculated from thermo and reverse A.

c. A factor is based on, for C2HCL5 = C2HCL4 + CL, logA = 16.2, estimate A = 2E16.
Ref: S. W. Benson and M. Weissman, I. J. of Chem. Kinetics, Vol 14, 1982.

d. A factor is based on C2HCL5= HCL+C2CL4, log A=14.1
Estimated A= 2.0E+14, Ea= del H+ 40
Ref: S. W. Benson and M. Weissman, I. J. of Chem. Kinetics, Vol 14, 1982.

e. See note (d) of Table I-1.

f. See note (e) of Table I-1.



(a)

(b)

Figure 15 . Energy Diagram (a) and CHEMACT Results (b) for Reaction CH2CL + CCL3 <==> Product

TABLE 19-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	CH2CL+CCL3 = CH2CLCCL3	6.19E+09	-1660.0
2.69		2.29E+10	-1610.0
7.60		7.05E+10	-1490.0
0.76	CH2CL+CCL3 = CH2CLCCL2+CL	4.97E+11	1570.0
2.69		5.22E+11	1620.0
7.60		5.84E+11	1740.0
0.76	CH2CL+CCL3 = C2HCL3+HCL	6.27E+12	9.7
2.69		6.58E+12	61.9
7.60		7.28E+12	179.0

Bath Gas: Ar
Temperature: 300 K

TABLE 20-a

$$\mathrm{H + CH3CH2} \underset{-1}{\overset{1}{\Longleftrightarrow}} \mathrm{[CH3CH2]\#}$$

$$\longrightarrow \mathrm{CH3 + CH3}\ (2)$$
$$\longrightarrow \mathrm{C2H6}\ (\mathrm{stab})$$

k	A	Ea	source
1	1.85E14	0.0	a
-1	1.26E16	98.0	b
2	7.94E16	90.3	c

<V> = 1509.0 cm^{-1} d

Lennard-Jones Parameters: e

Sigma = 4.342 A^{o} e/k = 246.8 ^{o}K

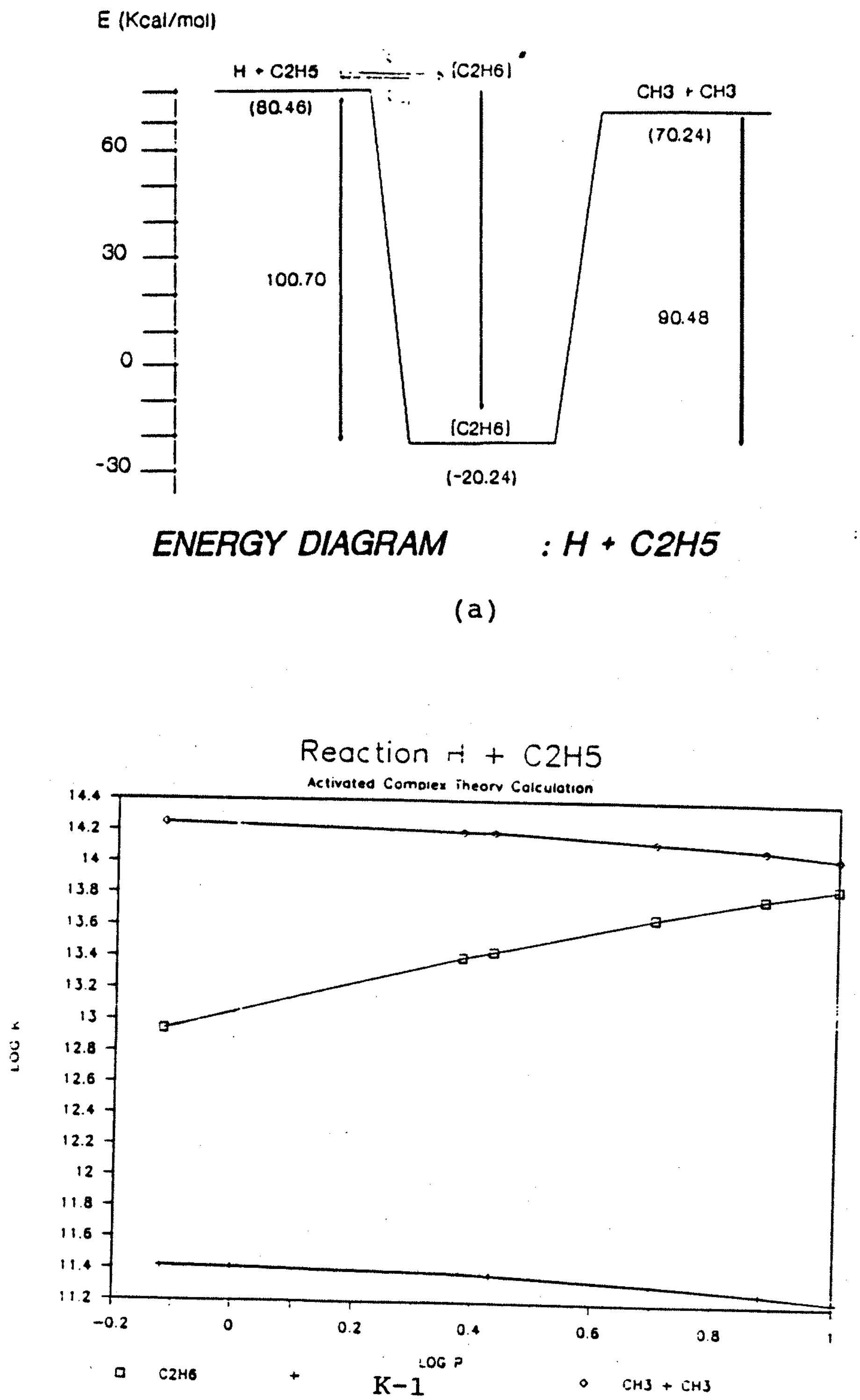
a. A factor is based on C2H6=H+C2H5, log A=16.1 calculate from the reverse A.
Ref: Dean, A.M., J. Phys. Chem., 89, 4600, 1985.

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

c. A factor is based on C2H6=2CH3, log A=16.9
Ref: Dean, A.M., J. Phys. Chem., 89, 4600, 1985.

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

e. Activated complex L-J parameters are estimated using critical property data tabulated in Reid, Prausnitz and Sherwood(The Properties of Gases and Liquids, 3rd. ed.)



(b)

Figure 16 . Energy Diagram (a) and CHEMACT Results (b) for Reaction H + C2H5

TABLE 20-a

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

(At Pressure of 0.76, 2.69, 7.6 torr)

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
0.76	H+C2H5 = C2H6	1.42E+12	-1083.
2.69		5.18E+12	-994.
7.6		1.51E+13	-830.
0.76	H+C2H5 = CH3+CH3	1.89E+14	41.6
2.69		1.97E+14	136.
7.6		2.10E+14	316.

Bath Gas: Ar
Temperature: 300 K

TABLE 21

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK

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

```
R (REACTANTS)
H + C2H3

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H4                C2H2 + H2

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


FREQ.(FREQUENCY)(HZ)   NS (WAVENUMBERS)
1586.0,                12,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N      E (KCAL)
                             4.0E+13,    0.0,    0.0,

COLLISION COMPLEX MASS(A.U.)   DIAMETER (A)   WELL DEPTH (CAL)
28.06,                           4.16,          224.7,

THIRD BODY
AR           MASS (A.U.)  DIAMETER (A)  WELL DEPTH (CAL)  ENERGY TRANS (CAL)
             40.0,          3.33,       136.5,            630.0,

A(M-CC-S)      E (K CAL)
1.7E+15,     109.4,          K-1

1.10E+14,    116.0,          K2

0.,            0.,           K3

0.,            0.,           K4

0.,            0.,           K-4

0.,            0.,           K5

0.,            0.,           K6

DELTA H FOR A* === B* (KCAL/MOL)   XLAM (COLLISION COEFF)
0.0,                               0.,

NUMBER OF TEMPERATURES    T1      T2      T3      T4      T5      T6 (K)
6,                       273.,   300.,   325.,   350.,   400.,   450.,

NUMBER OF PRESSURES       P1      P2      P3      P4      P5      P6 (TORR)
6,                       0.76,   2.4,    2.7,    5.0,    7.6,    10.0,
```

TABLE 22

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK

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


R (REACTANTS)
H + C2H4

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H5

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


FREQ.(FREQUENCY)(HZ)   NS (WAVENUMBERS)
1522.0,                15,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N      E (KCAL)
                               1.38E+13,  0.0,    0.0,

COLLISION COMPLEX MASS(A.U.)   DIAMETER (A)   WELL DEPTH (CAL)
29.,                           4.30,          220.2,

THIRD BODY
AR           MASS (A.U.)  DIAMETER (A)  WELL DEPTH (CAL)  ENERGY TRANS (CAL)
             40.0,         3.542,        93.3,            630.0,

A(M-CC-S)        E (K CAL)
1.95E+14,        22.23,        K-1

0.,               0.,          K2

0.,               0.,          K3

0.,               0.,          K4

0.,               0.,          K-4

0.,               0.,          K5

0.,               0.,          K6

DELTA H FOR A* === B* (KCAL/MOL)    XLAM (COLLISION COEFF)
0.0,                                0.,

NUMBER OF TEMPERATURES    T1      T2      T3      T4      T5      T6 (K)
6,                       273.,   300.,   325.,   350.,   400.,   450.,

NUMBER OF PRESSURES       P1      P2      P3      P4      P5      P6 (TORR)
2,                       2.4,    2.7,
```

TABLE 23

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK

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

R (REACTANTS)
CL + CH2CL

A* (RECOMBINATION)	P2 (1ST A* DECOMP)	P3 (2ND A* DECOMP)
CH2CL2		

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

FREQ.(FREQUENCY)(HZ)	NS (WAVENUMBERS)
1116.3,	9,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)	N	E (KCAL)
4.0E+13,	0.0,	0.0,

COLLISION COMPLEX MASS(A.U.)	DIAMETER (A)	WELL DEPTH (CAL)
84.,	4.77,	420.3,

THIRD BODY	MASS (A.U.)	DIAMETER (A)	WELL DEPTH (CAL)	ENERGY TRANS (CAL)
AR	40.0,	3.542,	93.3,	630.0,

A(M-CC-S)	E (K CAL)	
2.09E+16,	80.6,	K-1
0.,	0.,	K2
0.,	0.,	K3
0.,	0.,	K4
0.,	0.,	K-4
0.,	0.,	K5
0.,	0.,	K6

DELTA H FOR A* --- B* (KCAL/MOL)	XLAM (COLLISION COEFF)
0.0,	0.,

NUMBER OF TEMPERATURES	T1	T2	T3	T4	T5	T6 (K)
6,	273.,	300.,	325.,	350.,	400.,	450.,

NUMBER OF PRESSURES	P1	P2	P3	P4	P5	P6 (TORR)
2,	2.4,	2.7,				

TABLE 24

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK

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

```
R (REACTANTS)
CH3 + CH3

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H6            -   C2H5 + H

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


FREQ.(FREQUENCY)(HZ)   NS (WAVENUMBERS)
1509.0,                18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N       E (KCAL)
                               2.72E+13,   0.0,     0.43,

COLLISION COMPLEX MASS(A.U.)   DIAMETER (A)   WELL DEPTH (CAL)
30.,                           4.342,         246.8,

THIRD BODY
AR            MASS (A.U.)  DIAMETER (A)  WELL DEPTH (CAL)  ENERGY TRANS (CAL)
              40.0,          3.542,        93.3,           630.0,

A(M-CC-S)       E (K CAL)
7.94E+16,      90.3,          K-1

1.26E+16,       98.0,          K2

0.,             0.,           K3

0.,             0.,           K4

0.,             0.,           K-4

0.,             0.,           K5

0.,             0.,           K6

DELTA H FOR A* === B* (KCAL/MOL)    XLAM (COLLISION COEFF)
0.0,                                0.,

NUMBER OF TEMPERATURES    T1      T2      T3      T4      T5      T6 (K)
6,                       273.,   300.,   325.,   350.,   400.,   450.,

NUMBER OF PRESSURES       P1      P2      P3      P4      P5      P6 (TORR)
2,                       2.4,    2.7,
```

TABLE 25

RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION) USING QRRK

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


R (REACTANTS)
CL + C2H4

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H4CL

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


FREQ.(FREQUENCY)(HZ)    NS (WAVENUMBERS)
1265.3,                 15,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N      E (KCAL)
                               1.8E+13,   0.0,    0.0,

COLLISION COMPLEX MASS(A.U.)    DIAMETER (A)    WELL DEPTH (CAL)
63.52,                          5.3,            322.0,

THIRD BODY
AR            MASS (A.U.)  DIAMETER (A)  WELL DEPTH (CAL)  ENERGY TRANS (CAL)
              40.0,          3.542,        93.3,           630.0,

A(M-CC-S)        E (K CAL)
1.95E+14,      22.9,          K-1

0.,              0.,          K2

0.,              0.,          K3

0.,              0.,          K4

0.,              0.,          K-4

0.,              0.,          K5

0.,              0.,          K6

DELTA H FOR A* === B* (KCAL/MOL)     XLAM (COLLISION COEFF)
0.0,                                 0.,

NUMBER OF TEMPERATURES     T1       T2       T3       T4       T5       T6 (K)
6,                        273.,    300.,    325.,    350.,    400.,    450.,

NUMBER OF PRESSURES        P1       P2       P3       P4       P5       P6 (TORR)
2,                        2.4,     2.7,
```

TABLE 26

```
CHCL3 DISSOCIATION
****DISSOCIATING SPECIES****
CHCL3
****PRODUCT CHANNEL 1 (LOWEST ENERGY)****
CCL2 + HCL
****PRODUCT CHANNEL 2 ****
CHCL2 + CL
****PRODUCT CHANNEL 3 ****

***GEOMETRIC MEAN FREQUENCY;    # OF OSCILLATORS (S)*****
       880.0,                        9,
***COLLISION COMPLEX MASS;     DIAMETER;     WELL DEPTH*****
         119.5,                5.39,            340.2
***THIRD BODY (COLLISION PARTNER)*****
AR
***THIRD BODY MASS;   DIAMETER;   WELL DEPTH;    ENERGY TRANSFERRED******
         40.0,         3.542,      93.3,                630.0
****COLLISION COEFFICIENT****
           0.0
****CHANNEL 1:  HIGH PRESSURE A FACTOR;  EA(KCAL/MOL)*****
                   2.37E+13,               67.1
****CHANNEL 2:  HIGH PRESSURE A FACTOR;  EA(KCAL/MOL)*****
                   2.52E+16,               74.6
****CHANNEL 3:  HIGH PRESSURE A FACTOR;  EA(KCAL/MOL)*****
                      0.0,                  0.0

NUMBER OF TEMPERATURES   T1      T2      T3      T4      T5      T6 (K)
6,                       273.,   300.,   325.,   350.,   375.,   400.,

NUMBER OF PRESSURES      P1      P2      P3      P4      P5      P6 (TORR)
6,                       0.76,   2.4,    2.7,    5.0,    7.6,   10.0,

Tdist (FOR DISTRIBUTION Ki(E) vs. E AT THIS TEMP (K))
300.,

Pdist (FOR DISTRIBUTION Ki(E) vs. E AT THIS PRESS (TORR))
2.7,

OUTPUT OPTION (-1,0,1,2,3,4,5,6, or 7)
-1,
NOTE:   OUTPUT OPTION
   -1  -  DISTRIBUTION ONLY FOR Tdist and Pdist
    0  -  ALL DISTRIBUTIONS
    1  -  DISTRIBUTION AT Tdist AND ALL PRESSURES
    2  -  DISTRIBUTION AT Pdist AND ALL TEMPERATURES
    3  -  CHANNEL SUMMARY ONLY: ALL TEMP & PRESSURES
    4  -  CHANNEL SUMMARY ONLY FOR Tdist & Pdist ONLY
    5  -  CHANNEL SUMMARY FOR Tdist AND ALL PRESSURES
    6  -  CHANNEL SUMMARY FOR Pdist AND ALL TEMPERATURES
    7  -  SUPPRESS ALL DISTRIBUTIONS AND CHANNEL SUMMARIES
```

2. Evans-Polanyi Plot for Abstraction Reactions

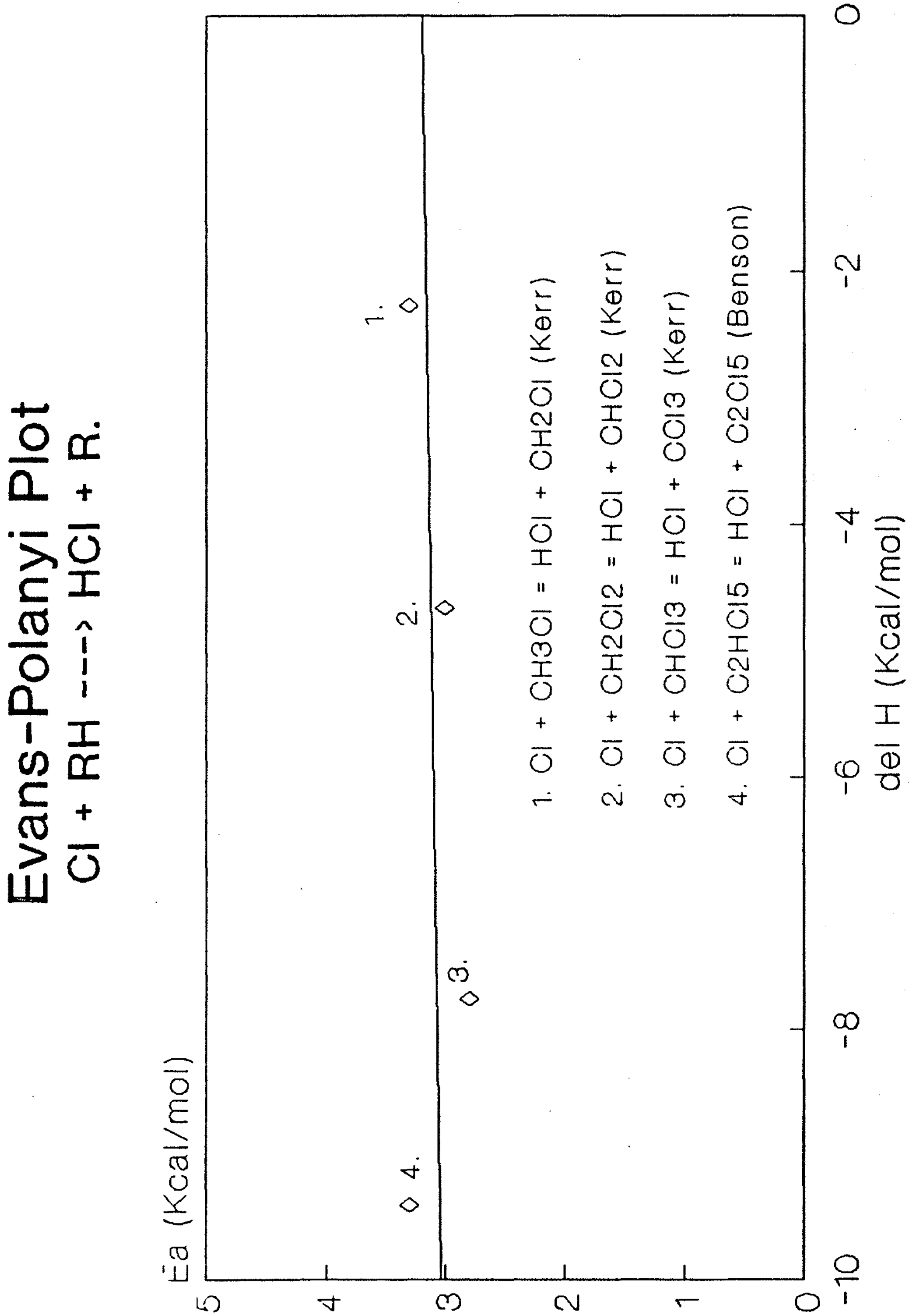
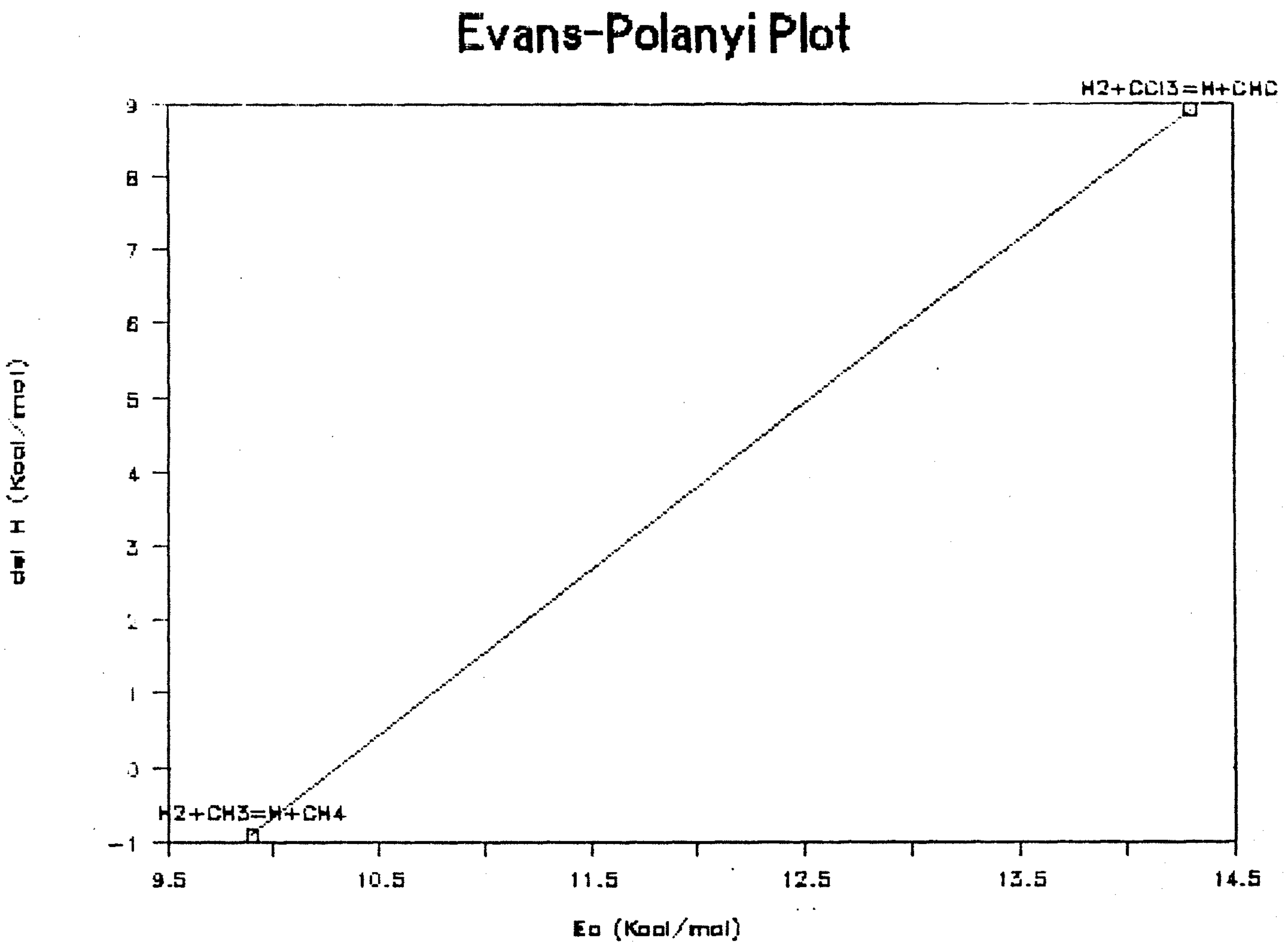


Figure 1. Evans-Polanyi Plot for Cl. + RH ---> HCl + RH .



	Ea (Kcal/mol)	log A	Reference
1. H2 + CCl3 = H + CHCl3	14.3	12.72	Kerr
2. H2 + CH3 = H + CH4	9.9	11.7	Kerr

Figure 2. Evans-Polanyi Plot for H2 + R. ---> H. + R

2. Experimental Data Used in Modeling

A. Atomic Hydrogen with Dichloromethane (2.69 torr, 300 K)

Experimental 2 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl2 Initial Conc. ($molecules/cm^3$)	Exp't Conversion %
$2.3 * 10^{-3}$	$1.02 * 10^{13}$	15.5
$5.9 * 10^{-3}$	$2.65 * 10^{13}$	29.0
$8.0 * 10^{-3}$	$3.54 * 10^{13}$	40.0
$1.4 * 10^{-2}$	$6.19 * 10^{13}$	53.3
$2.4 * 10^{-2}$	$1.08 * 10^{14}$	28.6
$3.4 * 10^{-2}$	$1.50 * 10^{14}$	23.1
$3.9 * 10^{-2}$	$1.72 * 10^{14}$	22.0
$4.7 * 10^{-2}$	$2.08 * 10^{14}$	21.7

Initial H Concentration = $4.21 * 10^{14}$ molecules/cm^3

Initial H2 Concentration = $5.6 * 10^{14}$ molecule/cm^3

Initial Argon Concentration = $8.39 * 10^{16}$ molecule/cm^3

Dissociation Efficiency = 37.6 %

Residence Time = 0.067 sec.

Experimental 3 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl2 Initial Conc. ($molecules/cm^3$)	Exp't Conversion %
$2.3 * 10^{-3}$	$1.04 * 10^{13}$	17.1
$4.7 * 10^{-3}$	$2.08 * 10^{13}$	18.6
$9.4 * 10^{-3}$	$4.20 * 10^{13}$	27.5
$1.2 * 10^{-2}$	$5.30 * 10^{13}$	37.5
$2.2 * 10^{-2}$	$9.97 * 10^{13}$	20.5
$2.8 * 10^{-2}$	$1.23 * 10^{14}$	20.2
$3.4 * 10^{-2}$	$1.66 * 10^{14}$	19.5
$5.0 * 10^{-2}$	$2.23 * 10^{14}$	10.9

Initial H Concentration = $2.90 * 10^{14}$ molecules/cm^3

Initial H2 Concentration = $6.22 * 10^{14}$ molecule/cm^3

Initial Argon Concentration = $8.39 * 10^{16}$ molecule/cm^3

Dissociation Efficiency = 23.3 %

Residence Time = 0.077 sec.

Experimental 5 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl2 Initial Conc. ($molecules/cm^3$)	Exp't Conversion %
$2.3 * 10^{-3}$	$1.05 * 10^{13}$	11.3
$4.7 * 10^{-3}$	$2.14 * 10^{13}$	14.9
$9.4 * 10^{-3}$	$4.31 * 10^{13}$	50.7
$1.4 * 10^{-2}$	$6.35 * 10^{13}$	39.0
$2.6 * 10^{-2}$	$1.18 * 10^{14}$	31.1
$3.2 * 10^{-2}$	$1.45 * 10^{14}$	29.2
$4.1 * 10^{-2}$	$1.86 * 10^{14}$	25.4
$4.7 * 10^{-2}$	$2.14 * 10^{14}$	25.0

Initial H Concentration = $4.37 * 10^{14}$ molecules/cm^3

Initial H2 Concentration = $6.39 * 10^{14}$ molecule/cm^3

Initial Argon Concentration = $8.62 * 10^{16}$ molecule/cm^3

Dissociation Efficiency = 34.2 %

Residence Time = 0.069 sec.

B. Atomic Hydrogen with Chloroform (300 K)

Experimental 1 :

CHCl3 Flow Rate (cm^3/s)	CHCl3 Initial Conc. (molecules/cm^3)	Exp't Conversion %
$1.7 * 10^{-3}$	$7.09 * 10^{12}$	75.6
$4.0 * 10^{-3}$	$1.70 * 10^{13}$	87.0
$6.8 * 10^{-3}$	$2.84 * 10^{13}$	93.5
$2.1 * 10^{-2}$	$9.03 * 10^{13}$	77.1
$3.3 * 10^{-2}$	$1.40 * 10^{14}$	56.7
$5.1 * 10^{-2}$	$2.13 * 10^{14}$	40.4
$7.3 * 10^{-2}$	$3.07 * 10^{14}$	35.1
$9.0 * 10^{-2}$	$3.78 * 10^{14}$	22.4

Initial H Concentration = $3.18 * 10^{14}$ molecules/cm^3

Initial H2 Concentration = $5.88 * 10^{14}$ molecule/cm^3

Initial Argon Concentration = $7.94 * 10^{16}$ molecule/cm^3

Dissociation Efficiency = 27.04 %

Residence Time = 0.0544 sec.

Pressure = 2.47 torr

Experimental 5 :

CHCl3 Flow Rate (cm^3/s)	CHCl3 Initial Conc. ($molecules/cm^3$)	Exp't Conversion %
$1.7 * 10^{-3}$	$6.91 * 10^{12}$	79.6
$4.1 * 10^{-3}$	$1.66 * 10^{13}$	86.7
$5.4 * 10^{-3}$	$2.19 * 10^{13}$	89.4
$1.0 * 10^{-2}$	$4.12 * 10^{13}$	82.2
$3.4 * 10^{-2}$	$1.38 * 10^{14}$	61.4
$5.1 * 10^{-2}$	$2.07 * 10^{14}$	59.5
$7.0 * 10^{-2}$	$2.87 * 10^{14}$	26.7
$9.2 * 10^{-2}$	$3.74 * 10^{14}$	13.85

Initial H Concentration = $3.81 * 10^{14}$ $molecules/cm^3$

Initial H2 Concentration = $5.73 * 10^{14}$ $molecule/cm^3$

Initial Argon Concentration = $7.71 * 10^{16}$ $molecule/cm^3$

Dissociation Efficiency = 33.24 %

Residence Time = 0.053 sec.

Pressure = 2.4 torr