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Reactions of atomic hydrogen with dichloromethane in a flow system

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ABSTRACT

Title of Thesis: Reactions of Atomic Hydrogen with Dichloromethane in a flow System.

Shun-Hsien Huang, Master of Science in Chemical Engineering, 1987.

Thesis Directed by : Dr. Joseph W. Bozzelli
Professor in Department of Chemical Engineering, Chemistry and Environmental Science.

The reaction kinetics of atomic hydrogen with dichloromethane were studied in a tubular flow reactor with 2.6 cm I.D. Pyrex tube at pressure of 2.1 to 2.7 torr absolute and room temperature . Hydrogen atoms were generated by a microwave discharge plasma. Atomic hydrogen concentration were measured by chemiluminescence titration with nitrogen dioxide. The concentrations of hydrogen atom ranged from $2.0 * 10^{14}$ to $5.0 * 10^{15}$ atoms per cm^3. Chlorocarbon reagent and products were monitored by online gas chromatography (FID).

Major products observed were hydrogen chloride and methane. The conversion of dichloromethane increases first to a maximum and then decreases with increasing concentration of dichloromethane.

A detailed reaction mechanism was developed incorporating QRRK activated complex theory and transition state theory. Sensitivity analysis on mechanism allows identification of the important rate constants. The results

of modeling mechanism are quite consistent with the experimental observation when the concentration ratio of dichloromethane to hydrogen atom is less than 0.15. This mechanism describes a path toward the formation of the major products.

Through computer modeling of the reaction scheme and comparison with experimental data, the room temperature rate constants of the primary steps were determined as follows.

$$H + CH_2Cl_2 \xrightarrow{k_1} HCl + CH_2Cl$$

$$k_1 = 3.63 * 10^9 \quad cm^3\ mole^{-1}\ s^{-1}$$

$$H + CH_2Cl_2 \xrightarrow{k_2} H_2 + CHCl_2$$

$$k_2 = 2.08 * 10^9 \quad cm^3\ mole^{-1}\ s^{-1}$$

APPROVAL SHEET

Title of Thesis: Reactions of Atomic Hydrogen with Dichloromethane in a Flow System

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REACTIONS OF ATOMIC HYDROGEN WITH DICHLOROMETHANE IN A FLOW SYSTEM

by

Shun-Hsien Huang

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I. INTRODUCTION

Chlorocarbons have been extensively used by industry either as intermediates for the production of end products, or as solvents. Due to the high volumetric rate of utilization of chlorocarbons, large amounts of chlorinated organic wastes are produced. The disposal of the chlorinated hydrocarbon wastes has generated much interest in recent years, since some chlorinated compounds are carcinogenic and disposal requires compliance with stringent environmental laws.

One popular disposal method that has been extensively used is landfill. This method, however, does not appear to provide a permanent solution to the problem in toxic waste disposal. Due to potential jeopardy of ground water by leaks from the toxic waste site , landfills are being phased out and remedially corrected. In the USA, many sites that were deemed to be safe by waste producers are now requiring remedies at great cost, with the originators of the wastes having to pick up the bill. New systems involving biological degradation, incineration and fixing in cement-type materials are gaining market acceptance <1>, even though they are expensive because they either destroy or render inmobile the toxic species.

Certain weaknesses are inherent in some treatment processes. For example, the biological treatment processes are inefficient when waste streams are highly variable in composition and concentration, or when solutions contain more than 1-5 percent of salts and/or other materials which can deplete part of the active culture. The efficiency of removing hazardous liquids and gases from waste streams by carbon adsorption is strongly dependent on pH , and disposal and regeneration of the carbon are always a problem.

Incineration seems to be a more effective way of managing the disposal of many wastes, such as combustible solids, semi-solids, sludges and concentrated liquid wastes. It reduces, if not eliminates, potential environmental risks and potentially converts wastes into recoverable energy. Comparing incineration to other disposal options, advantages may become evident in specific applications, especially as more wastes become regulated and added prohibitions and increasingly burdensome costs are placed on land disposal. However, incinerator seems to produce trace amounts of several undesirable but thermally stable combustion products. Partially oxygenated carbonchlorides (Dioxins) and chlorinated oxides are often formed in trace amount as end products which are often more toxic than the original starting waste materials. Therefore, air pollution control equipments are required, unless the waste being destroyed is a hydrocarbon which is uniform in composition. Thermal and catalytic destruction in a hydrogen rich atmosphere <2,3,4,5> have been shown to be promising alternatives to oxygen rich incineration for chlorocarbon compounds.

The incineration of halocarbons introduces a significant complication to combustion chemistry. The maintenance of flame stability and production of undesirable byproducts warrant research into the behavior of halocarbons in the presence of the important atoms and radicals found in flames, such as O, OH and H. It is also well known, for example, that addition of chlorinated or brominated methanes often serve as inhibitors in oxidation flames. Studies by Gaydon and Wolfhard <6> and by Arnold et. al. <7> have shown, on the other hand, that low pressure reactions of several chloro and bromo methanes in H/H_2 produce C_2^* and CH^* glow emission, with little presented in the way of mechanistic explanation.

This work examined global kinetic observations for low pressure reactions of atomic hydrogen with dilute concentrations of dichloromethane in a tubular flow discharge reactor and used a detailed mechanism to analyze the reaction system. Current study also involves Activated Complex Quantum Rice-Ramsperger-Kassel (QRRK) analysis on several important addition reations of hydrogen atom to radicals or an olefin, and an analysis of their importance to chain propagation steps in the reaction mechanism. This method has been proposed <8> as a less sophiscated but more easily used method for analyzing such addition reactions (combination to an activated complex). QRRK theory calculates probability of reaction vs. stabilization as function of pressure and temperature. Thus activated complex QRRK analysis permits evaluation of the reacting system over a wide range of temperatures and pressures. In present study, a mechanism is developed to describe the reagent conversion and product formation. It is hoped that this study will shed light on combustion reactions related to detoxification of hazardous wastes, especially in the incineration of halocarbons.

II. PREVIOUS STUDY

Reactions of atomic hydrogen with chloromethanes have been studied in the past, but little information is presented on dissociative mechanism of the adduct.

Chadwell and Titani <9> in 1933 investigated the reactions of methyl halides with hydrogen atoms which were produced in a Wood's discharge flow system, and identified the products of the reactions. Except for CH_3F, which was not found to react, this study gave values of the activation energy and proposed a general reaction, H. + RX <==> HX + R.. In the same year, Polanyi et al. <10> also made a report on the similar reactions, and noted that hydrogen halide was the only identified product. A direct measurement of the rate constant was not accessible, due to the limitation of the apparatus, but an estimation value of the activation energy was given in this report. Smyser and Smallwood (1933) <11>, however, obtained an unidentified solid product as well for the reaction H + CCl_4 in a Wood's discharge flow system with the pressure of about 0.7 torr.

Five years later, Vance and Baumann <12> reported Arrhenius parameters for reactions with CCl_4. This study used a Wood's tube in which a low-pressure stream of molecular hydrogen passes over metallic electrodes held at a relatively high voltages <25> to generate H atom and a calorimetric method to measure the H concentration. This report showed that the conditions which allowed complete conversion of H into HCl are a pressure of 0.8 torr 150-200 ^{o}C, and a CCl_4:H ratio of about 10:1. As it was well known, contamination from the electrodes and the limited pressure range are the major disadvantages of the Wood's tube.

In 1967, Some rather ill-defined results on H + CH_3F from combustion limit experiments by Parsamyan et al. <13> at about 900 K had appeared in the Russian literature. Later, a study of D + CH_3Br in a discharge flow system by Davies et al. <14> seemed to be a more direct approach to rate measurement at room and somewhat higher temperature, although there were complications due to secondary reactions. Hart et al. <15> have derived data on reactions of H atoms with CH_3F, CH_3Cl, and CH_3Br in a flame system by using a point source technique. None of the about works constituted a really direct access to the rate measurements.

Westenberg and deHaas (1975) <16> performed more direct rate measurements for reactions H + CH_3X (X= Br, Cl, F) with [H] >> [CH_3X] 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. Among these previous workers, however, little was done to fully investigate the reaction mechanism.

Studies by Gaydon and Wolfhard <6> in 1952 and by Arnold et. al. <7> in 1975 showed,that low pressure reactions of several chloro and bromo methanes in H/H_2 produce C_2^* and CH^* glow emission. Arnold (1975) concluded that these were probably due to the exothermic reaction $C + CX \dashrightarrow C_2 + X$ (X is halogen or hydrogen).

Clark and Tedder(1964) <17> examined the reactions with some halomethanes at pressure of 0.23 torr and room temperature and proposed a reaction sequence for these reactions This study concluded that the initial step is chlorine abstraction by a hydrogen atom. No absolute rate constants were reported and this study did not measure the concentrations of atomic hydrogen, but assumed them from bond energies and equilibrium calculations. This study probably does not have significant value.

The effect of halomethane on pre-mixed and diffusion flames was explored by Garner et al.<18> in 1956. They noted that brominated methane appears to be a more effective inhibitor than chlorinated methane. They also suggested that the main effect of the halomethane additives is to cause a reduction in the concentration of active free radicals in the flame boundary.

Only one mechanistic report by combourieu et al. <19> was found in the literature on the reaction of hydrogen atom with CH_2Cl_2. The H + CH_2Cl_2 rate constant was obtained and a mechanism was proposed to describe the production of CH_4, HCl, C_2H_2 and C_2H_4. They also suggested that the initial step is the chlorine abstraction by a hydrogen atom. The feasibility of CH_2Cl_2 acting as a flame inhibitor was recognized in this report. Several questions remain, however, regarding the reaction channels, the monitoring of the stable end products, and stoichiometry. For example, the dominate exit channel for the reaction H + $CHCl_2$ should be CH_2Cl + Cl according to the Bimolecular QRRK analysis. This previous studies have sometimes neglected such steps in considering halocarbon conversion mechanism.

Recently, Costes et al. <20> have utilized reactions of hydrogen atoms with CCl_4 showing the production of carbon atoms in a low pressure reactor. The initial reaction in these H-atom studies is thought to proceed by an initial slow chlorine abstraction by H-atom which is followed by subsequent fast chain branching and termination reactions resulting in a flame and the final products. A very recent study by Gould et al. <21> has also shown that Cl abstraction from $CDCl_3$ by H atom is more accessible than that of D abstraction. More recently, Jo and Bozzelli <22> have performed a mechanistic explanation on the reactions of H + $CHCl_3$ in a low pressure reactor at room temperature. In 1986, Jones and Ma <23> reported the rate constants for the reaction of H atom with methyl- and vinyl-halides at the pressure of 0.55 torr and room temperature.

Although some investigations of the reactions of H-atom with halomethanes have been implemented, they were rarely presented with mechanistic explanation. Considering H + halomethanes importance in flame inhibition, the incineration of halocarbons in the presence of H atoms, and the general study of atomic hydrogen reactions, it was strongly felt that an investigation on the kinetics and mechanism of the reactions of H + CH_2Cl_2 should be undertaken in detail.

Through UV-visible chemiluminescence from the reaction glow emission combined with gas chromatographic analysis of the stable end products, inferences were made. Moreover, the analysis of free radical reactions are of great importance in the field of flame inhibition and combustion research. Detailed kinetic models of these reactions are necessary to explain experimentally observed behavior. These models necessarily involve the estimation of the rate constant of related elementary reactions. The current study also focuses upon the use of Bimolecular Quantum-RRK theory <8, 24> to interprete the reaction channels. Bimolecular QRRK (Quantum Rice-Ramsperger-Kassel) analysis <Dean, 1985> is a simple method for calculating rate constants of addition and recombination reactions, based on unimolecular Quantum-RRK theory. Input parameters are readily derived, and rate constants and reaction branching can be predicted with remarkable accuracy. Such predictive power makes the method especially useful in developing mechanisms of elementary reactions. It is hoped that taken together these steps will adequately describe the experimental observations.

THEORY

A. Chemical Reactor Theory

Isothermal tubular flow reactors are commonly used for fundamental rate studies. When using steady-flow tubular reactor, one encounters the problem of relating axial distance along the reactor with residence time. In gas phase reactions, the experimental conditions are most frequently such that laminar flow occurs. The resulting parabolic velocity profile gives rise to a distribution of residence time for the reactive species such that those traveling near the wall stay in reactor longer and experience larger extent of reaction than those moving near the axis of the tube. Criteria for checking the validity of plug flow approximation are discussed in the following paragraph.

A rigorous analysis that is closely applicable to the present study is the report by Poirier and Carr. <27> They numerically solved the continuity equations for first- and second-oder chemical reactions, coupled with radial diffusion. For homogeneous first- and second-order reactions, they proposed that if D/kR^2, where D is the diffusion coefficient, k is the homogeneous rate constant, and R is the radius of reactor, is equal to or greater 0.5, plug flow assumption is probably satisfactory. Typical value of D/kR^2 for this study is calculated as follow.

The method of Fuller, Schettler and Giddings <26> was used to calculate the diffusion coefficient of the CH_2Cl_2 and H system, $D_{CH2Cl2-H}$. The value of $D_{CH2Cl2-H}$ is 227.4 cm^2/s. The homogeneous rate constant, k is 1.28 s^{-1} <19> for H + CH_2Cl_2 reaction. The radius of reactor, R is 1.3 cm. Typcial value of D/kR^2 obtained for this study is therefore 105 which is well above 0.5.

It is therefore assumed that ideal plug flow model is a good assumption for this work.

B. Hydrogen Atom Titration

Hydrogen atom concentrations are typically determined in flow discharge system by adding NO_2 and following the reaction H + NO_2 <==> OH + NO. <28> The reaction flame is whitish in color because of the combined effect of the various emissions. The radiating species in this case, HNO^*, emits primarily in the wavelength range of 686.5-698.5nm <29>. The intensity of the HNO emission could now be monitored by setting the spectrometer at 692.8nm. The reactions occuring are:

$$H + NO_2 \longrightarrow OH + NO \quad \text{(fast)} \qquad (A)$$

$$H + NO + M \longrightarrow HNO^* + M \quad \text{(slow)} \qquad (B)$$

$$HNO^* \longrightarrow HNO + h\nu \qquad (C)$$

where * denotes an excited molecule, and M is either another molecule or the wall, which removes some of HNO*'s excess energy, so it does not immediately dissociate. There are a fixed amount of hydrogen atoms present in the reaction, so if enough NO_2 is supplied to react with all H's, there should be no more H left over for reaction B. <6> At this point the emission would be just eliminated, there being no HNO* produced. The NO_2 flow is, therefore, increased to the point where the glow emission just disappears after its peak intensity, as indicated by a minimum in current on the picoammeter from the photomultiplier tube (PMT). Since NO_2 and H are in stoichiometric quantites at this point, the H atom concentration may be readily calculated from the NO_2 flow rate. The actual reaction scheme was, however, more complicated, owing to the secondary reactions of OH and recombination reactions of H. <28,30> For example,

(i) secondary reactions of OH:

$$OH \longrightarrow \text{Wall Loss}$$
$$OH + OH \longrightarrow H_2O + O$$
$$O + OH \longrightarrow O_2 + H$$
$$O + NO_2 \longrightarrow O_2 + NO$$
$$OH + H \longrightarrow H_2O$$

(ii) Recombination Reactions of H:

$$H + H + M \longrightarrow H_2 + M$$
$$H + H + \text{Wall} \longrightarrow H_2 + \text{Wall}$$

It has been shown that the activity of the surface in destroying OH increases in passing from excess [H] to excess [NO_2]. <30> The reactor wall was coated with phosphoric acid to reduce the wall effects. Studies by Mckenzie et al.

<30> suggested that the concentration of NO_2 required precisely to consume an H concentration can vary from about $1.1[H]_o$ to $1.5[H]_o$ depending on the activity of the surface. This ratio also depends on the type of reactor, coating used on the walls, and reaction times. Accordingly, a NO_2:H ratio of 1.25 was used in this study.

The NO_2 mixture used here came from a cylinder that was first flush several times with argon. evacuated to 19 torr torrand next filled to the extent of 285 torr with NO_2. Then it was pressurized to 1550 torr with argon. At a partial pressure of 252 torr, NO_2 exists in equilibrium with N_2O_4. In fact, it is equilibrium compositions that passed through the rotameter. The actual fraction of NO_2 and N_2O_4 changes with the total pressure as the pressure in cylinder decreases. In this study, equilibum constant, K_p, of NO_2-N_2O_4 system <31> is 86.2 torr and partial pressure of NO_2 and N_2O_4 in the cylinder is calculated as follows.

(i) first, at total pressure, 1550 torr

$$P(NO_2 + N_2O_4) = 252 \text{ torr}$$

for the system, $N_2O_4 \Longleftrightarrow 2\,NO_2$

$$K_p = \frac{(P(NO_2))^2}{P(N_2O_4)} = \frac{(P(NO_2))^2}{P(NO_2+N_2O_4) - P(NO_2)} = 86.2 \text{ torr}$$

Solving the above equation for $P(NO_2)$, we obtain

$P(NO_2) = 110$ torr

$P(N_2O_4) = P(NO_2+N_2O_4) - P(NO_2) = 252 - 110 = 142$ torr

The fraction of $P(NO_2+N_2O_4)$ to the total pressure is

$$F(NO_2+N_2O_4) = \frac{252}{1550} = 0.163$$

the fraction of P(Ar) to the total pressure is:

$F(Ar) = 1.0 - 0.163 = 0.837$

(ii) Next ,at total pressure, 1450 torr

$P(NO_2) = 106$ torr

$P(N_2O_4) = P(NO_2+N_2O_4) - P(NO_2) = 130$ torr

Assuming that fraction of $NO_2+N_2O_4$ to that of argon at 1450 torr is still same as that at 1550 torr, the above calculation is correct. In practice, as total pressure decreases the actual fraction of $NO_2+N_2O_4$ to that of argon increases. The ratio of N_2O_4 to NO_2 becomes larger at lower total pressure such that the fraction of $NO_2 + N_2O_4$ to that of argon increases. This is explained by the following calculation:

(a) At total pressure, 1550 torr $P(NO_2+N_2O_4) = 252$ torr the fraction of N_2O_4 to that of NO_2 is,

$$F(N_2O_4) = \frac{P(N_2O_4)}{P(N_2O_4 + NO_2)} = \frac{142}{252} = 0.562$$

$F(NO_2) = 1 - F(N_2O_4) = 1 - 0.562 = 0.438$

(b) At total pressure, 1450 torr, $P(NO_2+N_2O_4) = 236$ torr the fraction of N_2O_4 to that of NO_2 is,

$$F(N_2O_4) = \frac{P(N_2O_4)}{P(N_2O_4+NO_2)} = \frac{130}{236} = 0.051$$

$F(NO_2) = 1 - F(N_2O_4) = 1 - 0.551 = 0.449$

Comparing (a) with (b), the difference of $F(N_2O_4)$ is:

$F(N_2O_4) = 0.562 - 0.551 = 0.011$

Since every N_2O_4 dissociation gives $2NO_2$'s, change in $F(N_2O_4)$ thus represents the fraction of volume NO_2 gained. Increase in NO_2 is calculated as follows:

$P(NO_2+N_2O_4)$ * change in $F(N_2O_4)$ = 236 * 0.011 = 2.59 torr

Accordingly, $P(NO_2) = 106 + 2.59 = 109$ torr

and $P(NO_2+N_2O_4) = 236 + 2.59 = 239$ torr

The actual $P(NO_2+N_2O_4)$ can similarly be obtained at any pressure interested.

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

Outline: QRRK on Activated Complex calculate rate constant as functions of temperature and pressure. It shows the probability of reaction vs., stabilization as functions of temperature and pressure. Reference is the Dean's paper <8,24>.

Data Input: Semi-empirical estimation of A factors and Ea's value by using literature, reverse A's and Ea's from Thermo. Refer to Dean's paper <8>.

Assumption: The overall vibrations of a decomposing molecule can be represented by a single frequency ν, usually a geometric mean $<\nu>$ of the molecule's frequencies (Robinson and Holbrook, 1972). Next, each energy E is divided into $E/h<\nu>$ vibrational quanta. References are Forst <32> and Kassel <33>.

Application: atom or radical addition
to olefins
to acetylenes
to aromatics
and radical + radical
atom + radical
recombination
or reverse

Theory:

Kineticists recently have become increasingly concerned about the effect of pressure on the falloff behavior of dissociation-recombination reactions. Dean <24> has indicated that explicit attention must be paid to falloff effects for dissociation/recombination reactions at their high-pressure limit at high temperature. Qualitative reasons for the shift of falloff curves to higher pressure as the temperature is increased, can be found in the simplified Lindemann-Hinshelwood model: <34>

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^* + M \qquad (1)$$

$$A^* \xrightarrow{k_2} \text{products} \qquad (2)$$

Employing the steady-state assumption for the energized molecule A^*, we have

$$k_{uni} = \frac{1}{[A]} * \frac{d[\text{products}]}{dt} \qquad (3)$$

$$= \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

The high-pressure limit (k_{uni} not equal to f([M])) is characterized by $k_{-1}[M] >> k_2$. Since k_2 increases with temperature much faster than k_{-1}, higher pressures are required to maintain the inequality.

Dean(1985) <24> 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. The concepts and several of the terms of the equations are taken from unimolecular QRRK. Here, the method of Dean <8,24> is used to outline the basis for the calculations.

Development of the Working Equations

Consider the general case of recombination or addition to form an excited adduct A^*, followed by stabilization, redissociation to reactants, or chemically activated decomposition:

$$\begin{tikzcd} R + R' \arrow[r, shift left, "k_1"] & A^* \arrow[l, shift left, "k_{-1}(E)"] \arrow[r, "k_2"] \arrow[d, "bk_s[M]"] & \text{products} \\ & A & \end{tikzcd} \qquad (4)$$

Here R is a radical, R' is a radical (recombination) or unsaturated molecule (addition), A^* is the energized complex which can either dissociate or be collisionally stabilized, b is the collisional deactivation efficiency, and k_s is the collisional rate constant for stabilization. The collisional efficiency b was applied to modify the traditional, but incorrect, strong-collision assumption that collisional deexcitation rate constant, $k_{deexc} = k_s * [M]$, where k_s 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 energy 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 by master-equation methods, Troe (1977) fit most of the temperature dependence of b with the equation:

$$\frac{b}{1 - b^{1/2}} = \frac{-<\#E_{coll}>}{F(E) * kT} \qquad (5)$$

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 300-2,500 K for a series of reactions (Troe, 1977), F(E) = 1.15 was a median value. The value of b depends on the specific third-body molecule M through the value of $<\#E_{coll}>$. The dissociation rate constants k_{-1} and k_2 are written as explicit functions of energy. These energy dependencies are best treated via RRKM theory. <35> However, a simpler approach, quantum RRK theory (QRRK), is used here. The major advantage of QRRK is a substantial simplification of the input data required; one only needs to estimate a geometric mean specific frequency. Moreover, such a simplification still permits reasonable predictions of falloff curves. <35,36>

Applying the steady-state assumption to A^*, one can define two apparent rate constants, a stabilization rate constant k_{stab}

$$k_{stab} = \frac{d[A]/dt}{[R][R']} = k_1 \sum_{E_{crit}}^{\infty} \frac{bk_s[M] * f(E)}{bk_s[M] + k_{-1}(E) + k_2(E)} \quad (6)$$

and the rate constant k_{rxn} for formation of other dissociation products from A^*

$$k_{rxn} = \frac{d[products]/dt}{[R]\ [R']} = k_1 \sum_{E_{crit}}^{\infty} \frac{k_2 * f(E)}{bk_s[M] + k_{-1}(E) + k_2(E)} \quad (7)$$

where f(E) is the fraction of A^* at a specific energy E, the sums are in steps of $h\nu$ (ν = geometric mean frequency), and E_{crit} is the threshold energy for dissociation reactants. The chemical activation distribution function, f(E), can be expressed as <35>

$$f(E) = \frac{k_{-1}(E)K(E)}{\sum_{E_{crit}}^{\infty} k_{-1}(E)K(E)} \quad (8)$$

with

$$K(E) = a^n(1-a)^s \frac{(n + s - 1)!}{n!(s - 1)!} \quad (9)$$

where $a = \exp(-h\nu/kT)$, s = number of vibrational degrees of freedom, and $n = E/h\nu$, i.e., the number of quanta of energy. K(E) is the ratio of excitation to deexcitation rate constants for the quantum version of Kassel's theory using Hinshelwood's concept of excitation with many degree of freedom. <35> The energy dependent rate constants can be written as

$$k_i(E) = A_i \frac{n!(n - m_i + s - 1)!}{(n - m_i)!(n + s - 1)!} \tag{10}$$

where A_i is the high-pressure Arrhenius preexponential factor of reaction i, and m_i is the number of quanta ($E_i/h\nu$) corresponding to the energy threshold for reaction i.

The values of the collisional stabilization rate constant (k_s) are computed by using Lennard-Jones collision rates <32>

$$k_s = 2.708 k_{Hs}(e/kT)^{1/3} \tag{11}$$

where k_{Hs} is the usual hard-sphere collision rate constant. Values for collision diameters and well depths were taken from Kee et al. <37>

Low- and High-Pressure Limits

The low-pressure and high-pressure limits for these channels may be derived from Eqs. 6 and 7. As pressure changes, the rate constants change because of the relative magnitudes of the 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. 6 to be

$$\lim_{[M]\dashrightarrow 0} k_{stab} = [M] * \sum_{E=E_{crit}}^{\infty} bk_s * \frac{k_1 * f(E)}{k_{-1}(E) + k_2(E)} \qquad (12)$$

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

Note the presence of $k_2(E)$ in Eq. 12. If chemically activated conversion of A^* is more rapid than decomposition back to reactants [$k_2(E) >> k_{-1}(E)$], then Eq. 12 shows that $k_{o,stab}$ will be dominated 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. 7 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. 7, the low-pressure limit for chemically activated pathway to products will be

$$\lim_{[M]\dashrightarrow 0} k_{rxn} = k_1 * \sum_{E=E_{crit}}^{\infty} \frac{k_2(E) * f(E)}{k_{-1}(E) + k_2(E)} \qquad (13)$$

and the high-pressure limit will be

$$\lim_{[M]\to\infty} k_{rxn} = \frac{1}{[M]} * \frac{k_1}{bk_s} * \sum_{E=E_{crit}}^{\infty} k_2(E) * f(E) \qquad (14)$$

with an inverse pressure dependence. While these results go against past intuition about low- and high-pressure limits, it is a natural consequence of physics when chemically activated reactions are recognized as possibilities. Accordingly, the same type of behavior will result from RRKM equations. 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.

The form of this method makes the problem and the results easier to apply and to understand. For example, low- and high-pressure limits for the rate constants are easily derived and interpreted. Some accuracy is sacrificed relative to the more complex methods, but the necessary input data for QRRK are at a reasonable level for the number of reactions needing analysis. All input parameters are properties of the radical or molecule that is the stabilized adduct: collision properties, vibrational frequencies, and high-pressure-limit rate constants for its unimolecular reactions. Such parameters often are available in the literature or can be estimated with good accuracy. For modeling combustion or pyrolysis, use of this method gives useful predictions of the effects of pressure on the rate constants.

D. Computer Aided Mechanism Modeling by CHEMKIN Program

CHEMKIN <49> is a general-purpose, problem-independent, transportable, FORTRAN chemical kinetics code package. CHEMKIN FORTRAN programs were designed to facilitate a chemist's interaction with the computer in modeling 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 1. <49> The INTERPRETER <49> of CHEMKIN program is a program which reads a symbolic description of a reaction mechanism, and then 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. <49> This file contains numerical information which describes the elements, species and reaction mechanism.

Input to the INTERPRETER <49> may be any number of reversible reactions, including those with arbitrary third bodies, photons or ionic species as reactants or products. Also, enhanced third body efficiencies may be specified for any of the species in three body reactions. The input to the INTERPRETER is in familiar chemical, not computational, notation.

A detailed instruction of the CHEMKIN programs is available from the SANDIA Laboratory <49>.

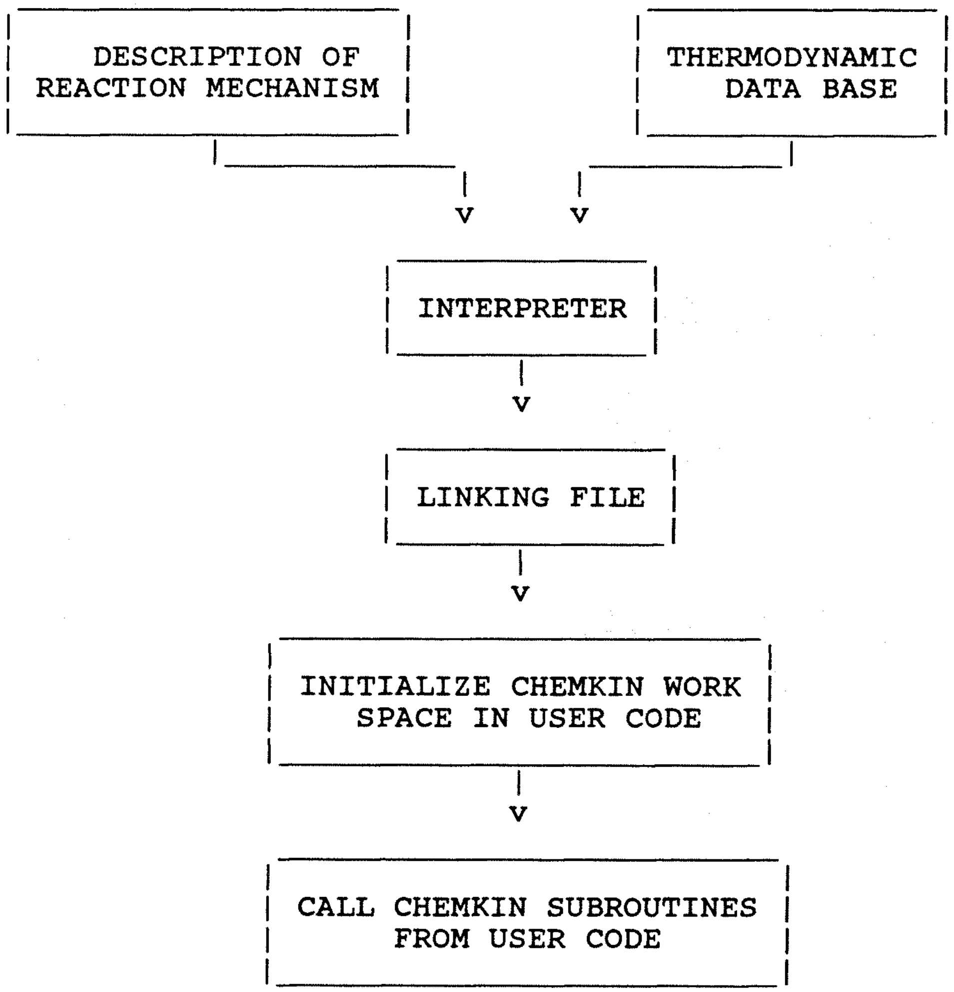


Figure 1. Structure of the CHEMKIN package

III. EXPERIMENTAL METHOD

A. EXPERIMENTAL APPARATUS:

A microwave discharge and a tubular flow reactor, operated at pressure of 2.1 to 2.7 torr absolute and room temperature was used for this study. A block diagram of the entire system is shown in Figure 2.

Very low flows of argon were passed through a saturator filled with the desired reagent(dichloromethane). The argon/dichloromethane vapor then entered the tubular flow reactor through an axially movable injector. The inlet position could be varied over 80 cm distance upstream of the spectrometer window. To improve mixing in the reaction zone, the inlet tube end was blocked off and six pinholes were pierced along the circumference of the tube at a distance of 1.5 cm above the tip. This forced the halomethane to flow outward first, for mixing, and then downward with the bulk of the flow. Dichloromethane flows were determined by the molar fraction of CH_2Cl_2 vapor in argon/CH_2Cl_2 mixture and the argon flow rate.

Hydrogen atoms were generated by passing a mixture of molecualr hydrogen and argon through a 2450 MHz electrodeless microwave discharge system. Typically the dilute mixture of 0.47% hydrogen and 99.26% argon, flowed through a 1" I.D. quartz tube placed in a microwave <38-40> to produce hydrogen atoms. The microwave resonant cavity and

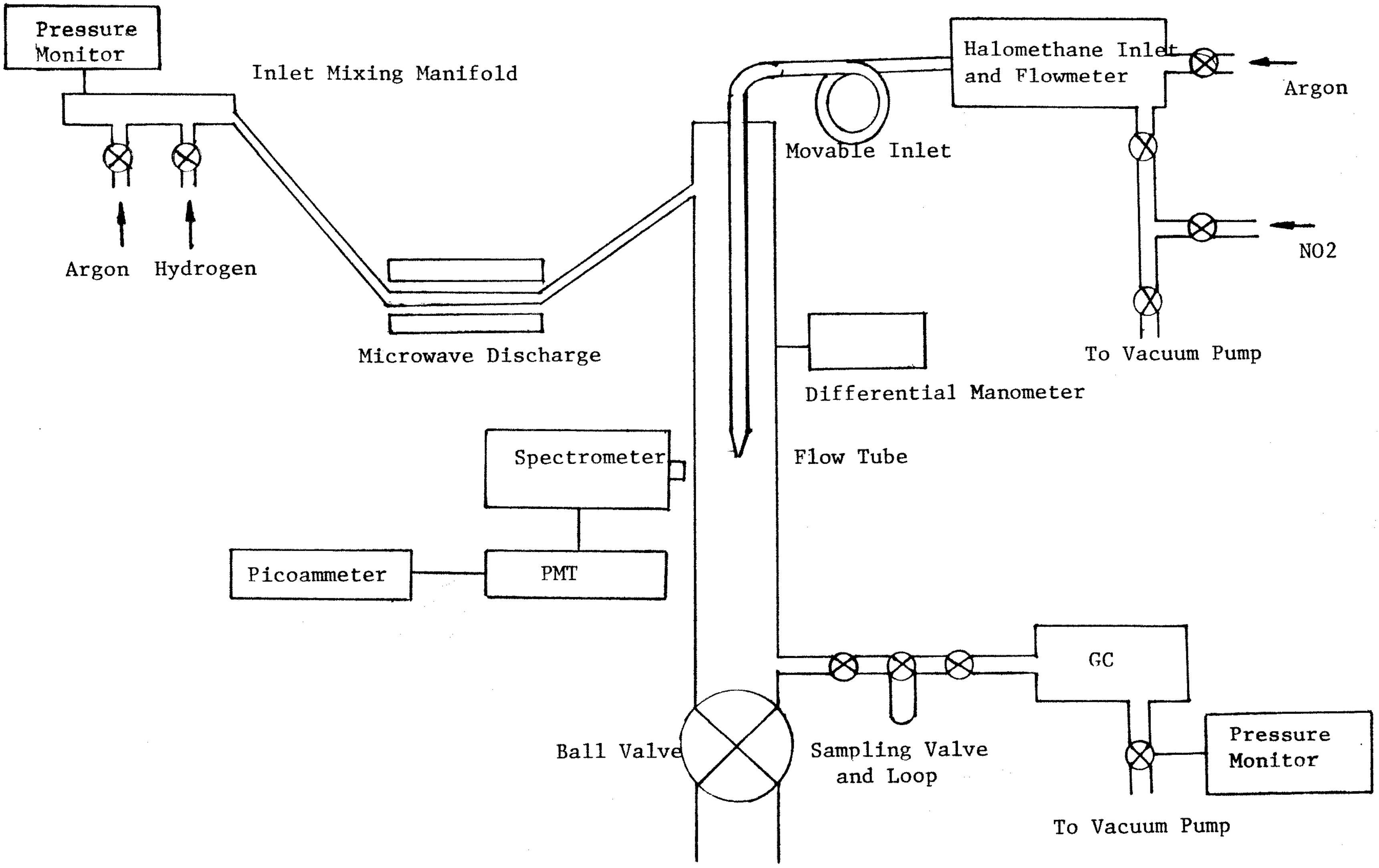


Figure 2. Experimental Setup.

waveguide are shown in Figure 3. The microwave power to plasma is controlled by using a 0-120 volt variac to adjust the input voltage to a transformer supplying the full wave rectified magnetron power supply. The discharge power could be varied approximately between 50 and 150 watts output power, and was normally operated at 50 watts.

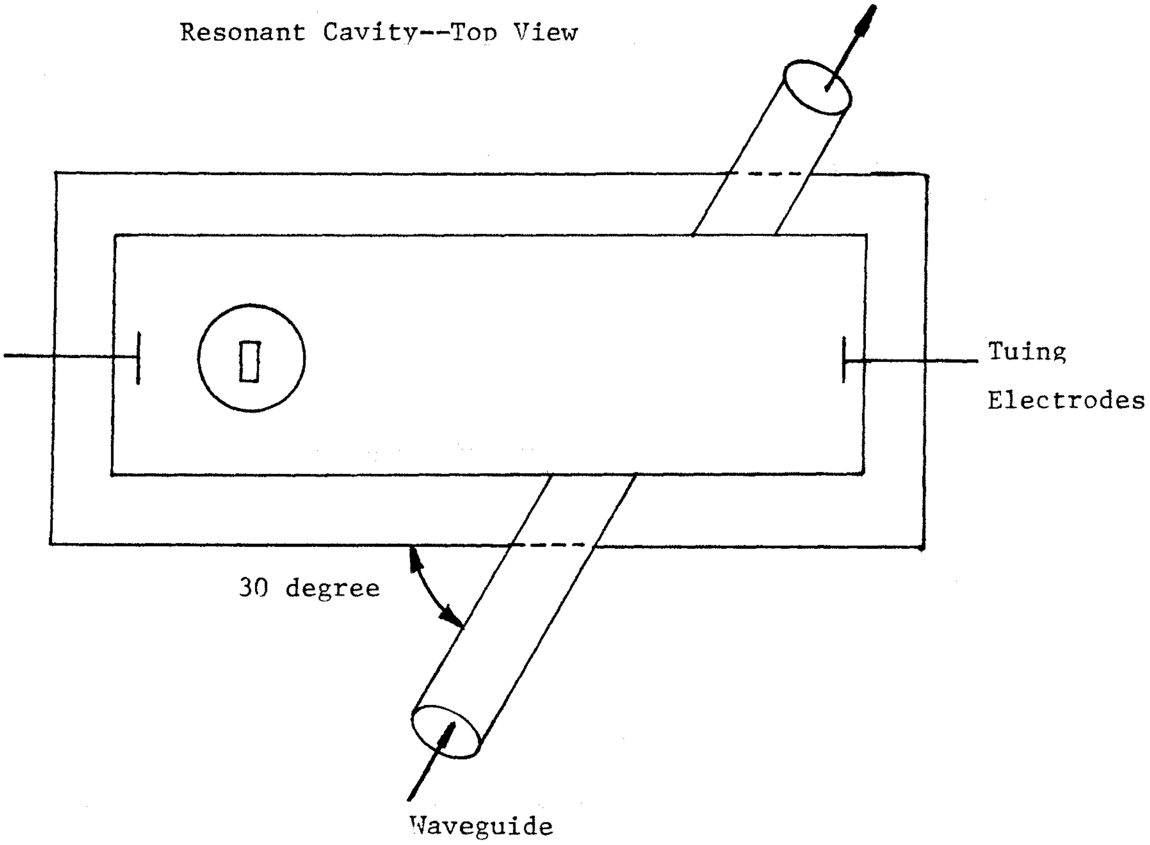
The hydrogen and argon mixture entered the reaction tube at 80 cm above the spectrometer window. The 2.54 cm quartz discharge tube and 26 mm I.D. Pyrex tubular reactor were coated with phosphoric acid to minimize the wall recombination effects. The concentration of atomic hydrogen was measured by NO_2 titration. An ultraviolet-visible spectrometer and photomultiplier tube with a high voltage power supply and picoammeter with DC output for chemiluminescent measurements were used.

Tubular flow reactor used for this study was a Pyrex tube with 2.6 cm I.D. and 1.1 meter length. This vacuum system allowed flow speed up to 12 m/sec in reactor.

Two Veeco TG-70 vacuum guages were used for pressure monitoring; one at the hydrogen-argon manifold and the other at the GC sampling system. An absolute argon pressure manometer partially filled with 0.8 Sp.gr. oil was positioned midway in the reactor-flow tube to measure pressure of the reaction system.

A ball valve which is located at 30 cm downstream of the spectrometer window was provided to regulate the flow, by throttling it, and to increase the reaction pressure in

Resonant Cavity--Top View



Resonant Cavity--Side View

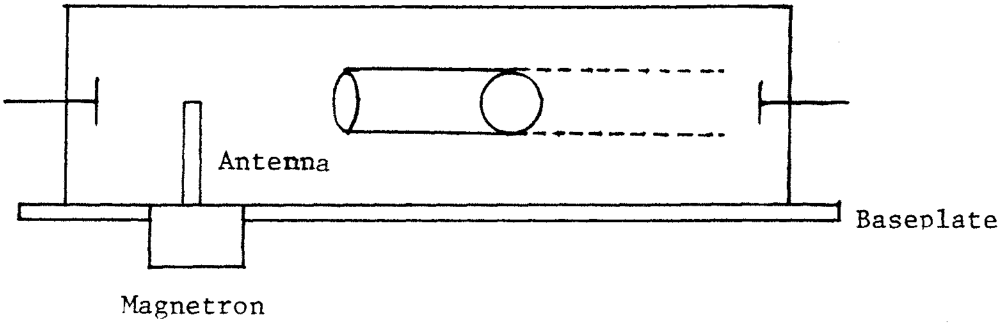


Fig. 3. Microwave Resonant Cavity and Waveguide

the flow tube for collecting sample. This ball valve was made of PVC plastic, and was connected to the reactor by a 1" I.D. tubing and elbows downstream of the reactor. To get a constant flame, not a flickering flame, HNO^* after glow a 35-liter stainless steel ballast was installed at the pump inlet to dampen the pulsations in flow stream caused by the pump. A calibrated differential pressure flow meter was used to measure the hydrogen flow, while the argon flow was measured by a calibrated rotameter.

The reactor effluent was monitored using an on-line gas chromatograph (Varian Aerograph Series 1200 GC) equipped with a Flame Ionization Detector (FID) and a cryofocussing concentrator - gas sampling valve assembly. A packing column with 10% silicone OV-101 on chrompack M, 6 feet long, and 1/8" I.D. stainless tube was used to achievethe necessary product separation. This column was maintained at 60°C when the halomethane used was dichloromethane. The column was routinely baked-out overnight at 130 °C (with the carrier gas flowing through it) before a set of runs. The detector was maintained at 200 °C.

The quantitative output of FID was measured by a Varian CDS III integrator coupled with a Hewlett Packard 7155B chart recorder. The reactor was flushed continuously with argon to prevent contamination from the environments, especially the oxygen, when the experiments were not being conducted.

The cryofocussing concentrator drew a fraction of the reactor gas through a stainless sampling loop by means of vacuum pump and liquid nitrogen. The bulk of the effluent, however, was exhausted to a fume hood.

The dichloromethane used was HPLC grade and purchased from Aldrich Chemical Company Inc. Gases used in these experiments were prepurified argon gas from MG Industries, prepurified hydrogen and nitrogen gas from AIRCO Inc.. Argon and hydrogen were purified gain in our system by passing through an activated copper catalyst oxygen removal bed (Chemalog R3-11 catalyst) and a molecular sieve trap for water removal, respectively.

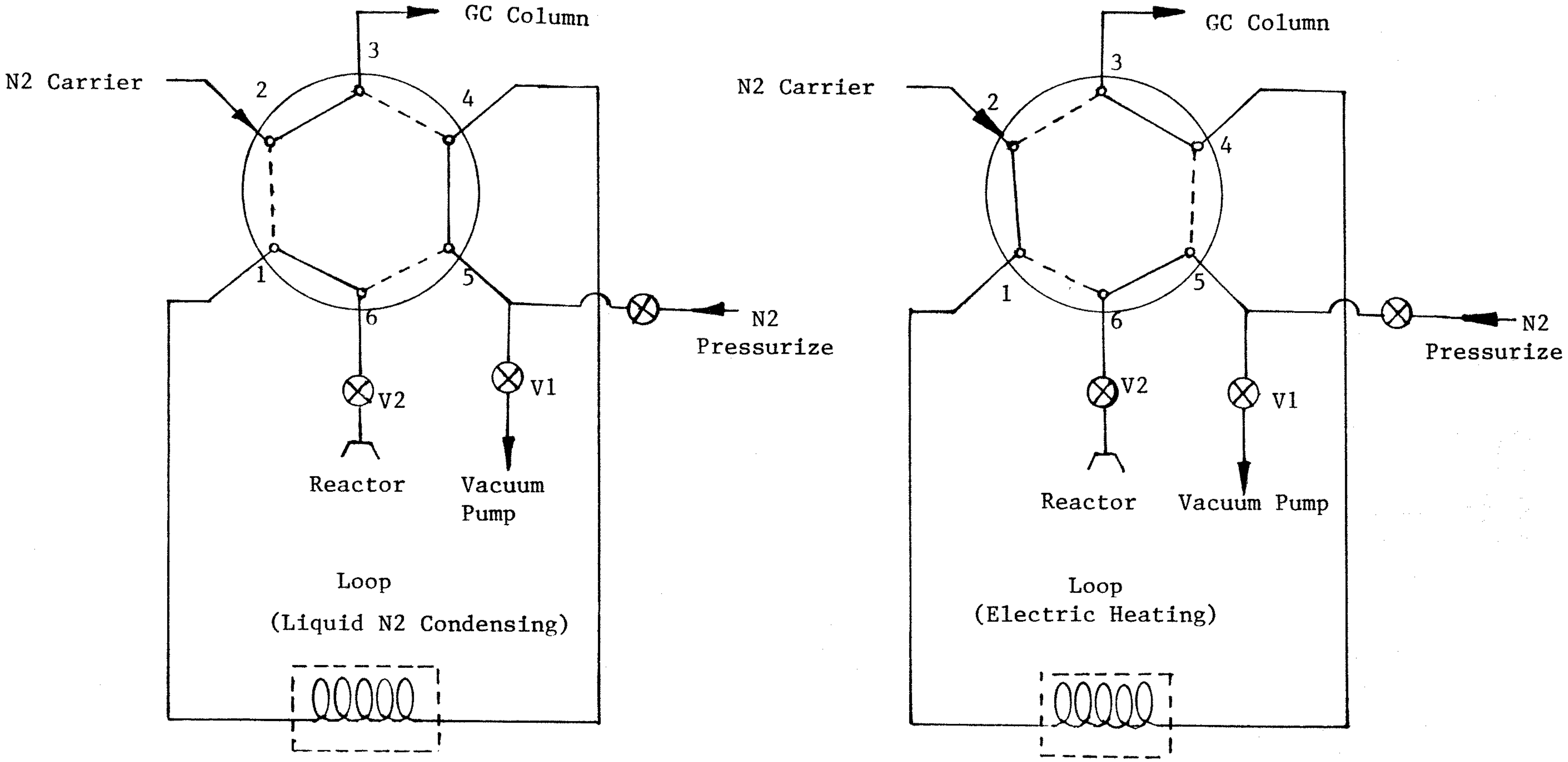
All materials for the gas handling and flow system were constructed from Pyrex, stainless steel, tygon connectors, or Teflon. All glass stopcock valves were greased with low volatility Apiezon type M grease.

B. Quantitative Analysis by Gas Chromatography:

Halocarbon analysis was introduced to the GC through a 4-way Rheodyne sample injection valve which is a Teflon rotary valve. This sample valve operates by rotation of a flat Kel-F, which is a kind of Teflon, rotor against a flat Teflon stator. All wetted parts are Teflon(TFE) or Kel-F(CTFE). Other structural parts are either Teflon, stainless steel or polypropylene except for the aluminum mounting flange. The valve are supplied with bore sizes of 0.8 mm or 1.5 mm. The tube connecting to the valve ports are of matching bore, and are terminated in 1/4-28 tube end fittings (flanged tubing type). An on-off valve was installed on the sample inlet line and the vacuum pump inlet line, respectively. They were positioned as close to the sample valve as possible to minimize dead volumes within the sampling system.

The vacuum pump used in the gas sampling section of the apparatus was a Welch Scientific Model 1400. Pump oil was routinly changed for proper maintenance of vacuum. With no sample flowing, this pump delivered a vacuum of below 1 millitorr at its inlet. Since the pressure in the reactor was normally around 2.68 torr, the pressure gradient of (2.68-0.001) torr, was the effective driving force pushing the sample through the loop. The sampling loop itself was a 36 cm long, 1/8" diameter stainless steel tubing, of which approximately 18 cm length was in a liquid nitrogen bath for sample collection. This corresponds to a volume of around 0.22 cm^3 in the entire loop.

Operations of the 4-way Rheodyne sample injection valve were shown in Figure 4. The sampling valve was switched to sampling position and the valve v2, at the sample inlet end, was closed. Meanwhile, the valve v1, at the vacuum pump end, was opened to evacuate the loop until the pressure gauge showed its lowest value -- below 1 millitorr. Before products were sampled, a liquid nitrogen dewar was placed under the loop. This step allowed to cool down the loop accessible to the liquid nitrogen temperature.



(a) Sample Loading

(b) Sample Injection

Figure 4. Operation of Sample Injection Valve

Exactly after thirty seconds, the valve v2 was opened and allowed the sample to flow through the system for three minutes. As the sample flowed through the loop, the condensibles would collect and remain in the loop trap, but gases like hydrogen and argon would pass through it. To save experimental time, the sampling time was appropriately varied with flow rate of gases passing through the system. After the proper sampling time, the valves v1 and v2 were closed simultaneously, and the liquid nitrogen dewar was removed. Then the system was pressurized with nitrogen gas to improve the injection of samples to the GC column. The pressurization was done by opening and closing the nitrogen valve in one second. Then, electric heating tape was slipped around the loop and heating started. The voltage heating the loop was fixed at 40 volts AC.

After heating was done for exactly 3 minutes, the sample collected was injected to GC. A stop watch was used to insure consistency in sample collection time. About three minutes later, the sampling valve was switched back to sampling position and the valve v1 was reopened to evacuate the system for next collection.

C. Titration of Hydrogen Atoms:

The spectrometer used to monitor chemiluminescence for titration of hydrogen atoms was a Mckee Pedersen 0.47 meter spectrometer fitted with a Jarrell Ash grating blazed at 350 nm, and containing 1300 lines per millimeter. This spectrometer was coupled with a side-on type photomultiplier tube (PMT), a Model R928 by Hammamatsu. The signals from the PMT were input to a high voltage power supply (MODEL 228 by Pacific Photometric Instruments) and then to a Keithley 480 high-speed Picoammeter which showed the current intensity in digital output. The spectrometer was capable of 0.01 nm resolution, and allowed scaning rates of 2 to 10 nm per minutes. The spectrometer was calibrated using mercury and sodium vapor lamps on the standard lines of 253.7 nm, 366.3 nm, and 589.6 nm for sodium <41>.

A black cloth was wound around the entire flow reactor to limit outside (room) light. The PMT used in this study, a Hammamatsu R928, had a spectral range of 200-800nm, the slit at the spectrometer was controlled to a desired value -- usually less than 5000 microns. Higher slit widths gave higher PMT current but lower resolution. Often a compromise had to be struck between these two parameters when deciding upon a slitwidth. Care was taken, however, to prevent opening the slitwidth to such an extent that the PMT current was greater than 1 microampere, at which level the PMT could be damaged. For especially strong glow emission the bias to the PMT, normally at 1 KV, could be reduced to decrease the PMT current. With this knowledge the slit was adjusted to the least opening, 4800 microns in this study that gave proper intensity of picoammeter in the whole range desired. Setting the flow across the titration range was then repeated at a desired flow rate to obtain an idea of the magnitude of the emission intensities. Since the intensity of output is directly related to the current in the picoammeter, this current was read directly off the picoammeter, by choosing the required ampere range. This allowed for meaningful comparison of all intensities on one scale.

The hydrogen atom concentration in the reactor flame was measured by chemiluminescence titration with nitrogen dioxide. The NO_2-Argon mixture (16% of NO_2 and 84% of Argon) was made up in a 35 liter stainless cylinder to a pressure of 30 psia. The NO_2-Argon mixture entered the halomethane system manifold after its flow was monitored on a calibrated rotameter. The flow was controlled by a needle valve installed on the line between the rotameter pressure and the manifold. The mixture entered the reactor through injection tube, same as dichloromethane which was now closed off.

Before the microwave discharge was turned on, care was taken to ensure that the discharge coolant fan was running and the discharge cavity was not overheated. The discharge radiation observed was purple. The variac adjusting the voltage to the microwave was first set at 100 volts to start the plasma and after 30 seconds set at 90 volts for all experiments. The atomic hydrogen produced by the discharge was allowed to react with the impurities absorbed on the walls of the reactor and thus clean the reactor. Then a dilute mixture of NO_2 in argon (about 16% NO_2 by volume) was allowed to take the path normally taken by chloromethane. The chemiluminescence from the resulting HNO^* emission was monitored.

The emission dissipated by the reaction of hydrogen atoms with NO_2 was scanned in the range 300-800 nm. As noted earlier, a large band was found in the region of 686.65-698.5 nm. <29> , and the largest signal in this range determined our titration wavelength. The NO_2-Argon mixture was then varied for observation of the intensities of HNO^* at various flow of NO_2-Argon mixture. The effect of this parameter on the intensity of emission of HNO^* at 692.8 nm was monitored. The titration itself was performed by observing the digital signal resulting from the picoammeter current, as a function of the NO_2 flow (cm^3/s).

Before any readings were taken, the system was conditioned by running for about one hour to get consistent results in the spectroscopic analysis of the reaction. To focus the light from the reaction flame into the spectrometer, aluminum foil was wrapped around reaction tube at the level of spectrometer window.

IV. RESULTS AND DISCUSSION

A. Experimental Results

The reaction kinetics of atomic hydrogen with dichloromethane was studied in a tubular flow reactor at pressure of 2.1 to 2.7 torr absolute and room temperature. Although there were active chemical fragments in the reactor such as, free radicals and other components that were emitting radiation, they were consumed or stabilized presumably by wall loss before entering the sampling tube. The gas chromatograph was used to analyze only the stable chlorocarbon products and reactants. The major products observed are hydrogen chloride, methane, and hydrogen.

Data were first obtained for eight different CH_2Cl_2 concentrations at a fixed hydrogen flow. The experiments were then repeated for two different reaction time by changing the effective reactor length. Different hydrogen flow rates were also tried.

The experiments were repeated with and without the microwave discharge for determining the conversion of the dichloromethane, through the formula:

$$\text{conv.} = 1 - \frac{\text{Area under } CH_2Cl_2 \text{ peak in sample with rxn.}}{\text{Area under } CH_2Cl_2 \text{ peak in sample without rxn.}}$$

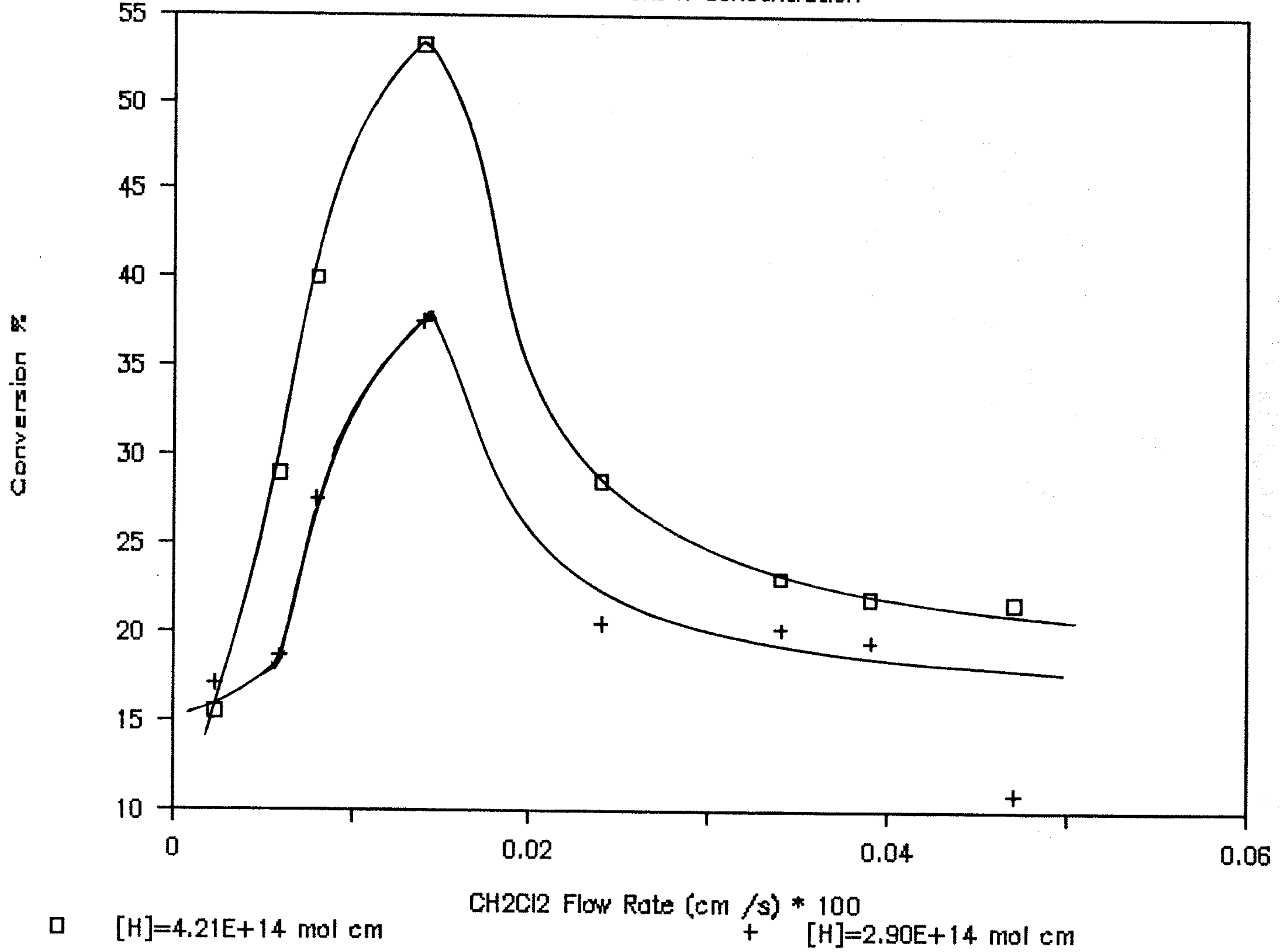
This technique was considered more accurate than that involved the measurement of the area of CH_2Cl_2 as a fraction of the total area under the various peaks in the reaction samples. It was felt, however, that there was scope for error in the collection efficiency of the trap of all products, specifically methane. The boiling points(BP) and melting points(MP) at atmospheric pressure <41> of the selected components are listed below. In particalar, the boiling point of methane will be considerably lowered at the pressure of 2.7 torr absolute and might not be completely condensed at the temperature of liquid nitrogen. This could give error in the products collection at low pressure.

COMPONENTS	MP ^oC	BP ^oC
N_2	-209.86	-195.8
CH_4	-182.0	-164.0
CH_2Cl_2	-95.1	40.0
CH_3Cl	-97.1	-24.2
HCl	-114.8	-84.9
C_2H_4	-169.0	-103.7
C_2H_2	-80.8	-84.0
C_2H_6	-183.3	-88.6

Plots of CH_2Cl_2 flow rate vs. CH_2Cl_2 total conversion at two different initial hydrogen atom concentrations are demonstrated in Figures 5. The conversion of CH_2Cl_2 increases to a maximum and then decreases as the concentration of CH_2Cl_2 increases. This indicates that the conversion of CH_2Cl_2 is increased at low reagent

Fig. 5 H + CH2Cl2 Experimental Results

at Two Different H Concentration



conceantration as the flow rate is increased; however, at higher CH_2Cl_2 concentration, conversion is limited by the hydrogen atom concentration. Figure 5 also illustrates that maximum conversion was different at two different H inital concentrations. This means that higher maximum conversion of CH_2Cl_2 can be obtained at higher initial H concentration.

The flow rates of H_2 and argon to the microwave discharge system were set at a constant value through one whole experimental series of CH_2Cl_2 flow. Providing that the dissociation efficiency of this H atom generation system was unchanged for the same input components, the initial $[H]_o$ obtained should be constant. Therefore, the H atom concentration becomes the limiting factor for the reaction at higher CH_2Cl_2 concentrations. This effect could be explained as follows. The higher was the CH_2Cl_2 concentration, the more quenching of excited radicals, H, occured before reaction happened. For example,

$$H + H + M \text{ ----> } H_2 + M$$

and $$H + H + CH_2Cl_2 \text{ -----> } H_2 + CH_2Cl_2$$

Dichloromethane is a more efficient collider than argon, because it contains more vibrational modes, while argon can only remove energy by increasing its translational energy. Besides, the initial Cl abstaction of CH_2Cl_2 by H atom is an exothermic reaction and its heat of reaction, delta H, at 298 K is:

Fig. 6 H-CH2CL2 Experimental Results

at [H]o =4.21*E14 molecule/cc

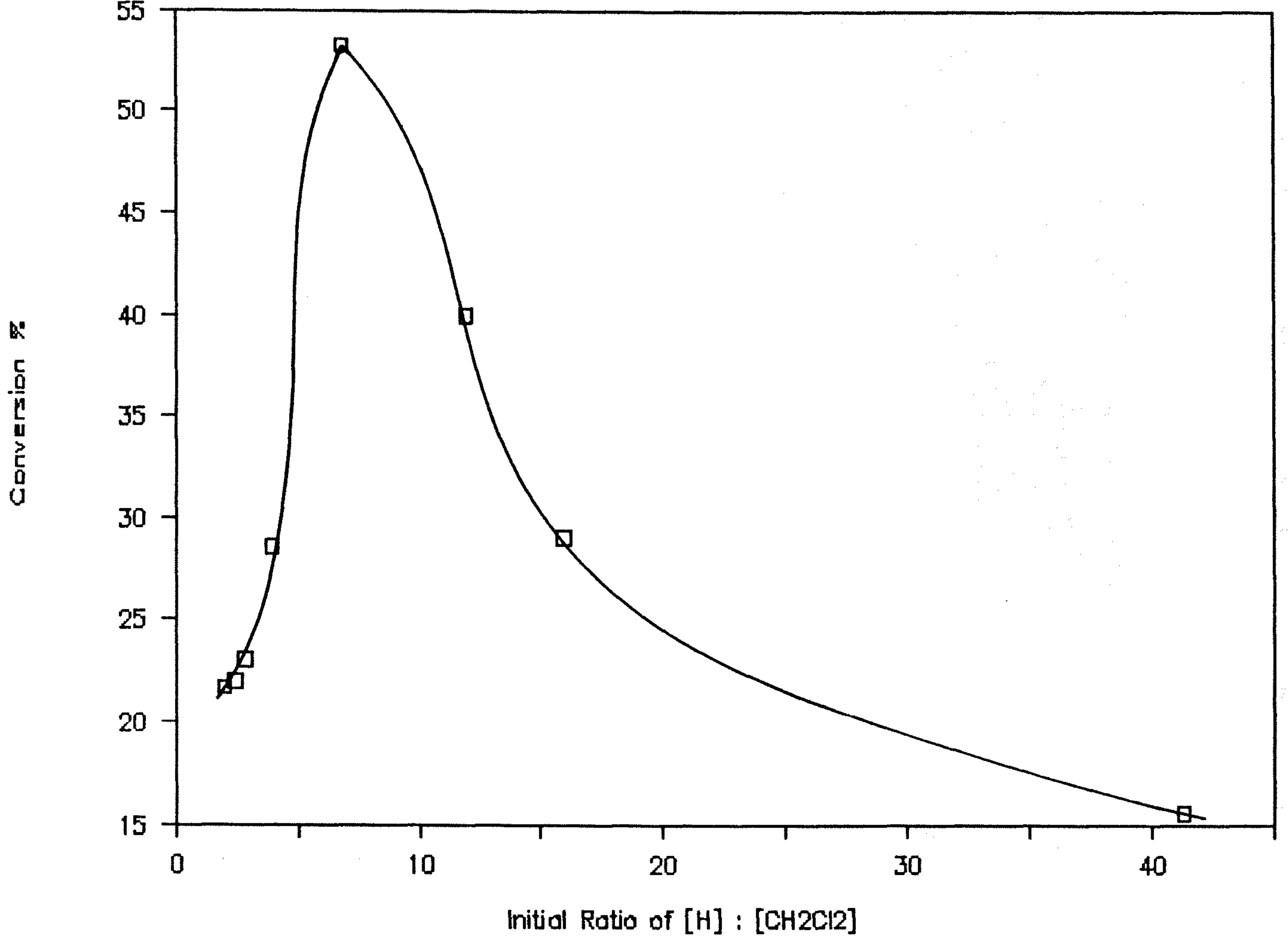
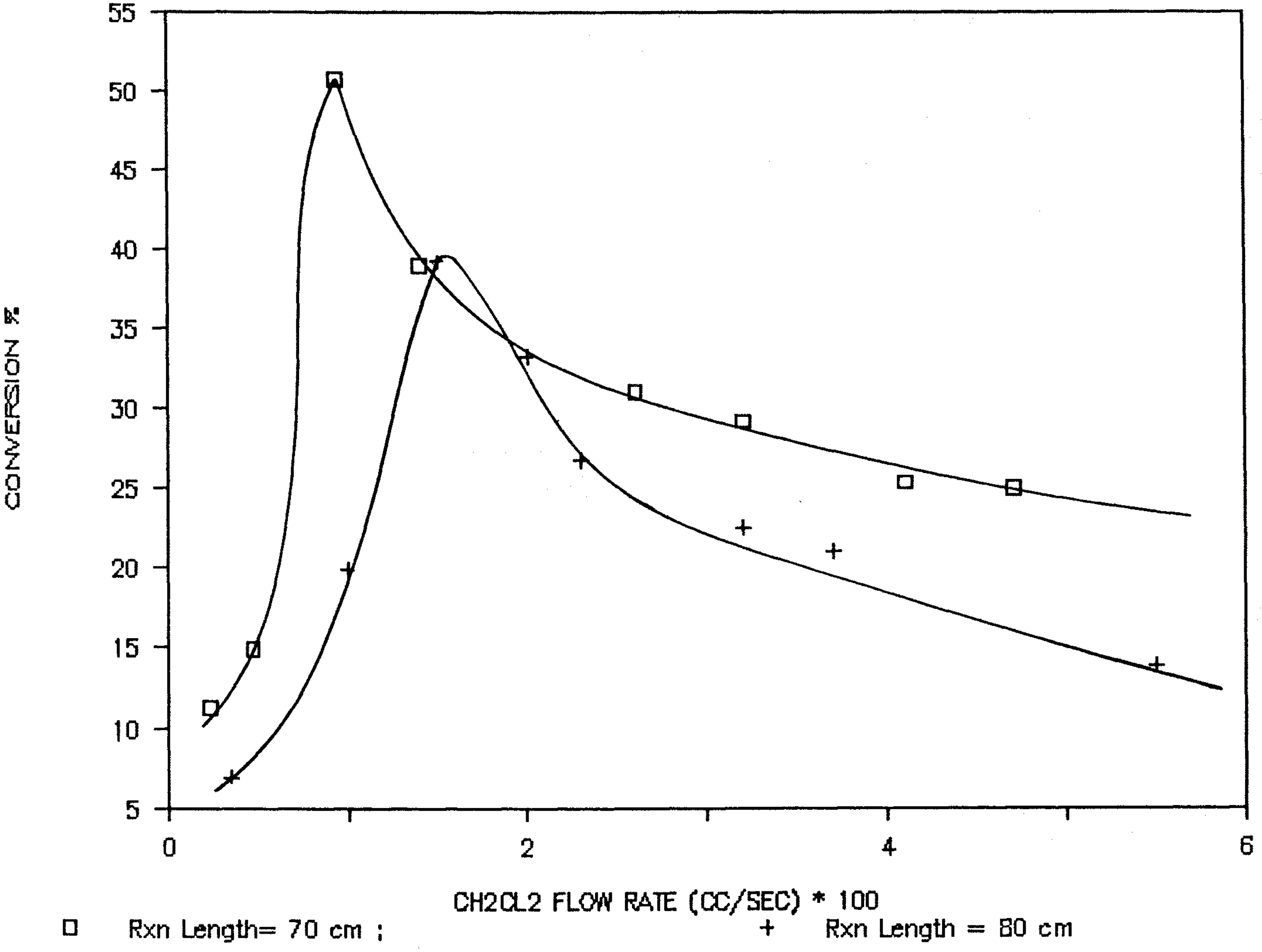


Fig. 7 H–CH2CL2 Experimental Results

at Two Different Reaction Length



$$CH_2Cl_2 + H = HCl + CH_2Cl$$

$$\text{delta } H = Hf_{HCl} + Hf_{CH2Cl} - Hf_{CH2Cl2} - Hf_H$$

$$= (-22.06) + (31.1) - (-22.8) - (52.1)$$

$$= -20.26 \text{ (kcal/mole)}.$$

It can be thought that the reaction of atomic hydrogen with dichloromethane at lower reagent concentration, was accelerated by the dissipated heat of the primary reaction due to less quenching. This acceleration step was suppressed by the quenching effect at higher input concentrations. A more straight-forward way to elucidate the effect of [H] on dichloromethane conversion is to plot the ratio $H:CH_2Cl_2$ vs. conversion. Figure 6 shows that the falloff phenomena happens as the ratio $H:CH_2Cl_2$ is greater than about seven.

The effects of effective reactor length on the total conversion of dichloromethane are illustrated in Figure 7. The maximum conversion obtained is lower at the longer reactor length. This could be a consequence of more radical recombination back to the reagent and hydrogen. For example,

$$Cl + CH_2Cl \text{ ----> } CH_2Cl_2^* \text{ ----> } CH_2Cl_2$$

or $$H + H + M \text{ ----> } H_2 + M.$$

The knowledge of exact concentration of atomic H is required for analyzing the reaction kinetics. The NO_2 titration technique was used to measure the initial hydrogen atom concentrations. The compositions calculated from the pressure measurements were corrected for the N_2O_4 <---> $2NO_2$ equilibrium as previous work <42> using a value of K_p = 86.2 torr <31> . The initial H concentrations, $[H]_o$, were determined by adding increasing concentrations of NO_2 such that $[NO_2]_o < [H]_o$, and measuring the intensity of the HNO^* emission produced. Two typical titration curves are depicted in Figures 8. As the figure shows, the relative intensity of the HNO^* emission rose up to a maximum before decreasing steeply. A tangent was drawn at the point of the maximum negative slope and extrapolated to the X axis to determine the NO_2 flow rate that corresponded to the end point of the titration. There is only a little increase in the titration end point, as the inlet flow of molecular hydrogen is increased slightly.

The flow tube and discharge tube were coated with phosphoric acid to inhibit the surface destruction of atoms and radicals. Kleindienst and Finlayson <28> have indicated that if the intensity of emission from HNO^* upon addition of NO through the movable inlet remained constant as the inlet was moved upstream from the detection point, there was not vital wall effect in the reactor. No significant decay of atomic hydrogen on the walls of the flow tube or movable inlet occurred, as shown in the Figure 9. Although there is about 10 % deviation of the titration end points between two reactor lengths, it is within acceptable experimental error.

It is well known that error could be incurred in

Fig. 8: Hydrogen Atom Titration Curves

at Two Different H2 Flow Rate

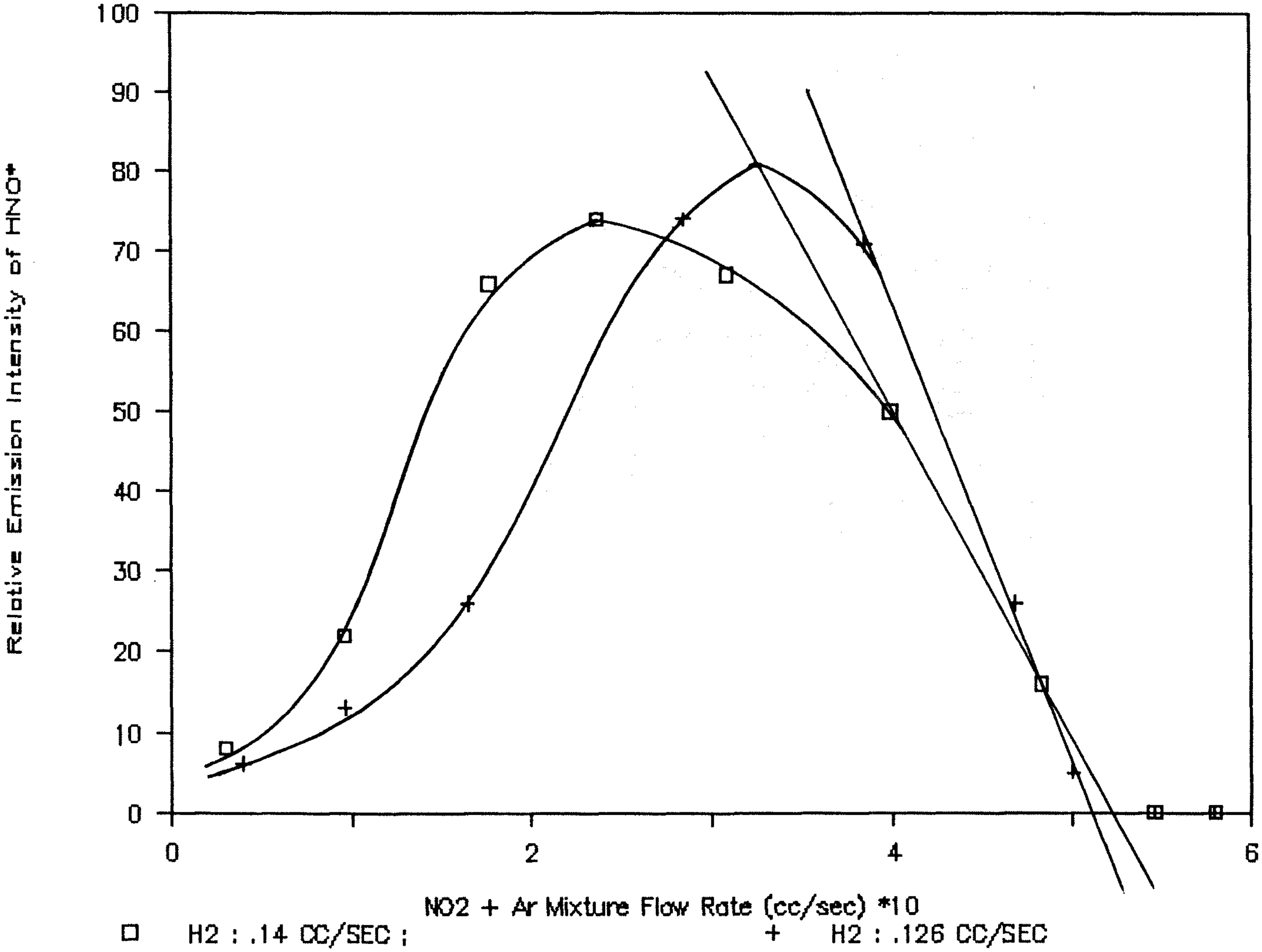
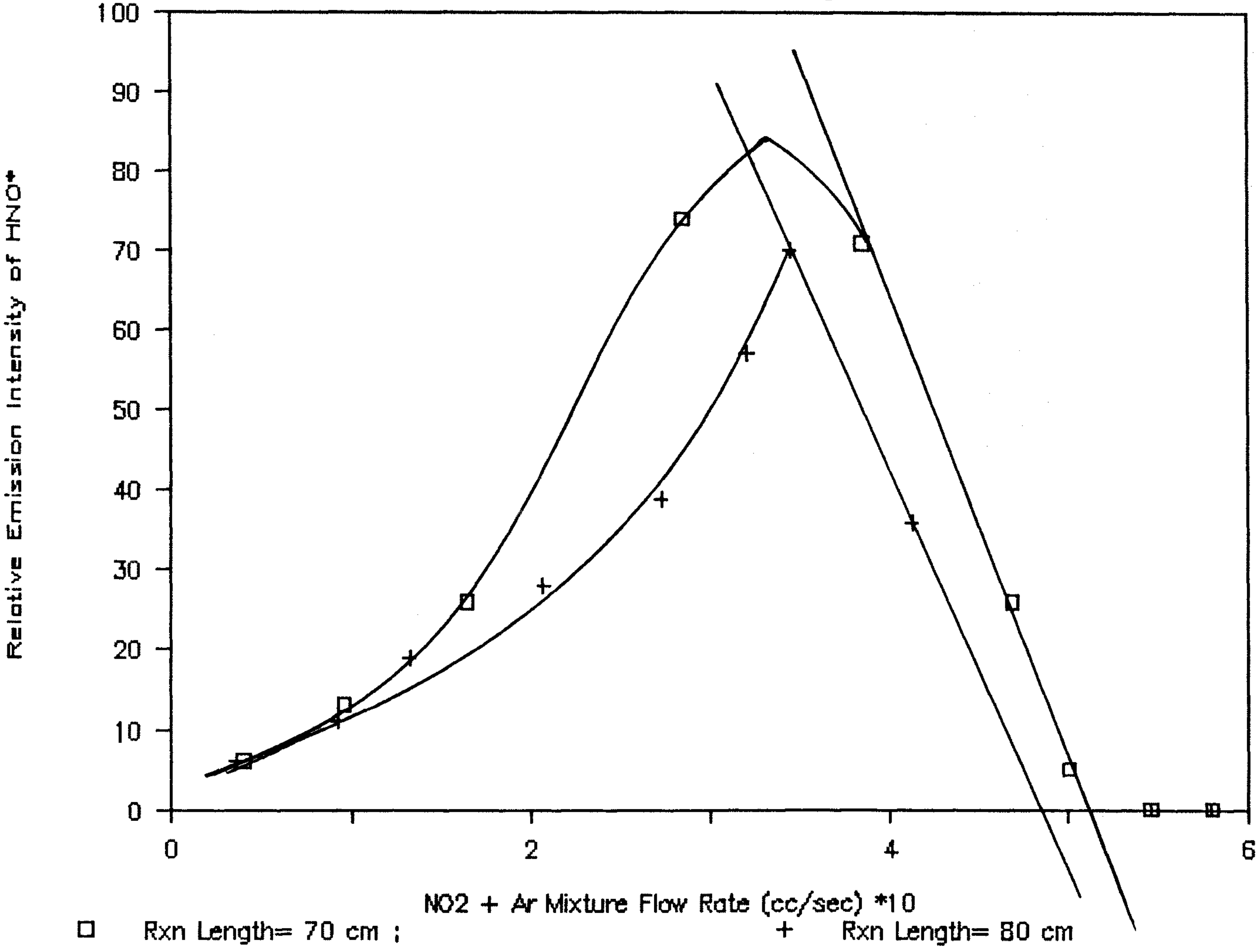


Fig. 9: Hydrogen Atom Titration Curves

at Two Different Reaction Length



drawing tangent to empirical best fit curve. Thus, any deduction from empirical results derived from tangent construction should be carefully made.

The calculations of the hydrogen atom concentration from the experimental data were shown in Appendix 3.

B. REACTION MECHANISM

The mechanism was set up, by determining the initial step first. In addition to relatively slower abstraction reactions, the major reagent, H atom, will add to a radical or an olefin forming an energized complex. This complex can then collisionally stabilize (pressure dependent), unimolecularly decompose back to reactants, or decompose to lower energy reaction products. The QRRK calculations were used to predict the rate constant and also to classify the appropriate exit channels. Many reaction rate constants such as abstraction reactions were obtained from the literature.

The initial reaction in chloromethanes is a slow abstraction of Cl or H from the chlorocarbon to produce chloromethyl radical and HCl or H_2.

$$H + CH_2Cl_2 \Longleftrightarrow HCl + CH_2Cl$$

$$H + CH_2Cl_2 \Longleftrightarrow H_2 + CHCl_2$$

The Cl abstraction process of CH_2Cl_2 by H has been studied previously <19> at pressure near 1 torr and 298-460 K temperature range, and the activation energy was determined as 6.1 kcal/mole. Reports by Gould et al.<21> have shown that the probabilities of Cl abstraction is 2.6 that of D abstraction, if normalized to equal numbers of Cl and D atoms, in the reactions of H + $CDCl_3$. Thus Cl abstraction is most likely the predominant initial step, with H abstraction included in the mechanism as a possible step.

The chloromethyl radical, CH_2Cl, can then react with H_2 to form a Cl_xmethane and regenerate an H or Cl atom, again a relatively slow abstraction reaction at 298 K:

$$H_2 + CH_2Cl \Longleftrightarrow CH_3Cl + H$$

H atom concentrations are, however, similar to H_2 in this system and can add to the chloromethyl radicals forming an activated complex. This is indicated in Fig. 10. The energized CH_3Cl^* complex can then be stabilized, dissociated to reagents, or reacted to lower energy Cl + CH_3 products.

$$H + CH_2Cl \Longleftrightarrow CH_3Cl^* \Longleftrightarrow CH_3Cl$$
$$H + CH_2Cl \Longleftrightarrow CH_3Cl^* \Longleftrightarrow CH_3 + Cl$$

Fig. 11 illustrates that the low energy exit channel to Cl + CH_3 dominates in this reaction sequence, 298 K to pressure above 10 atm. and argon bath gas as determined by QRRK analysis. The Cl atom will then react with H_2 or a chloromethane to form HCl and a H or a Cl_xmethyl radical, respectively.

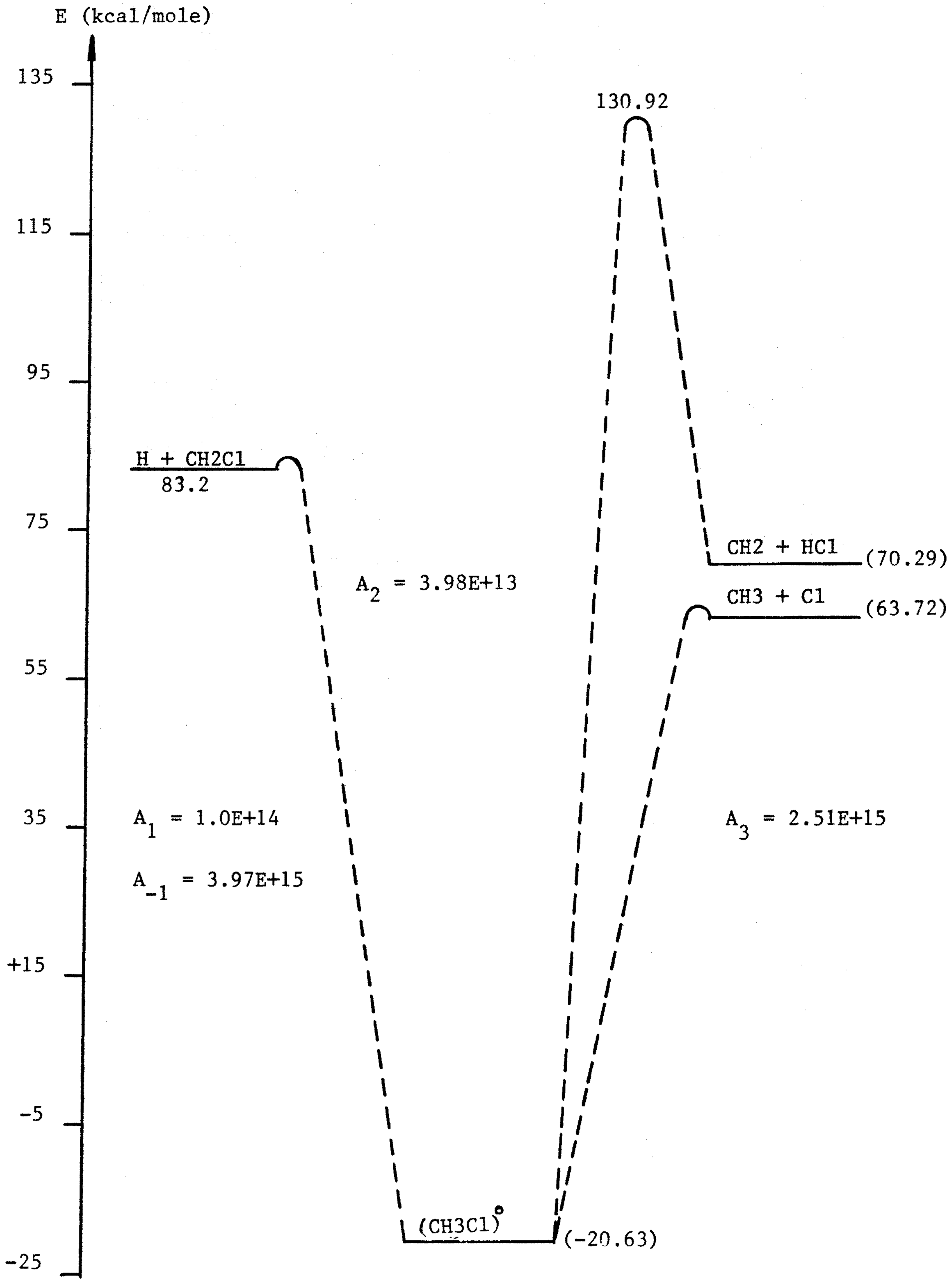
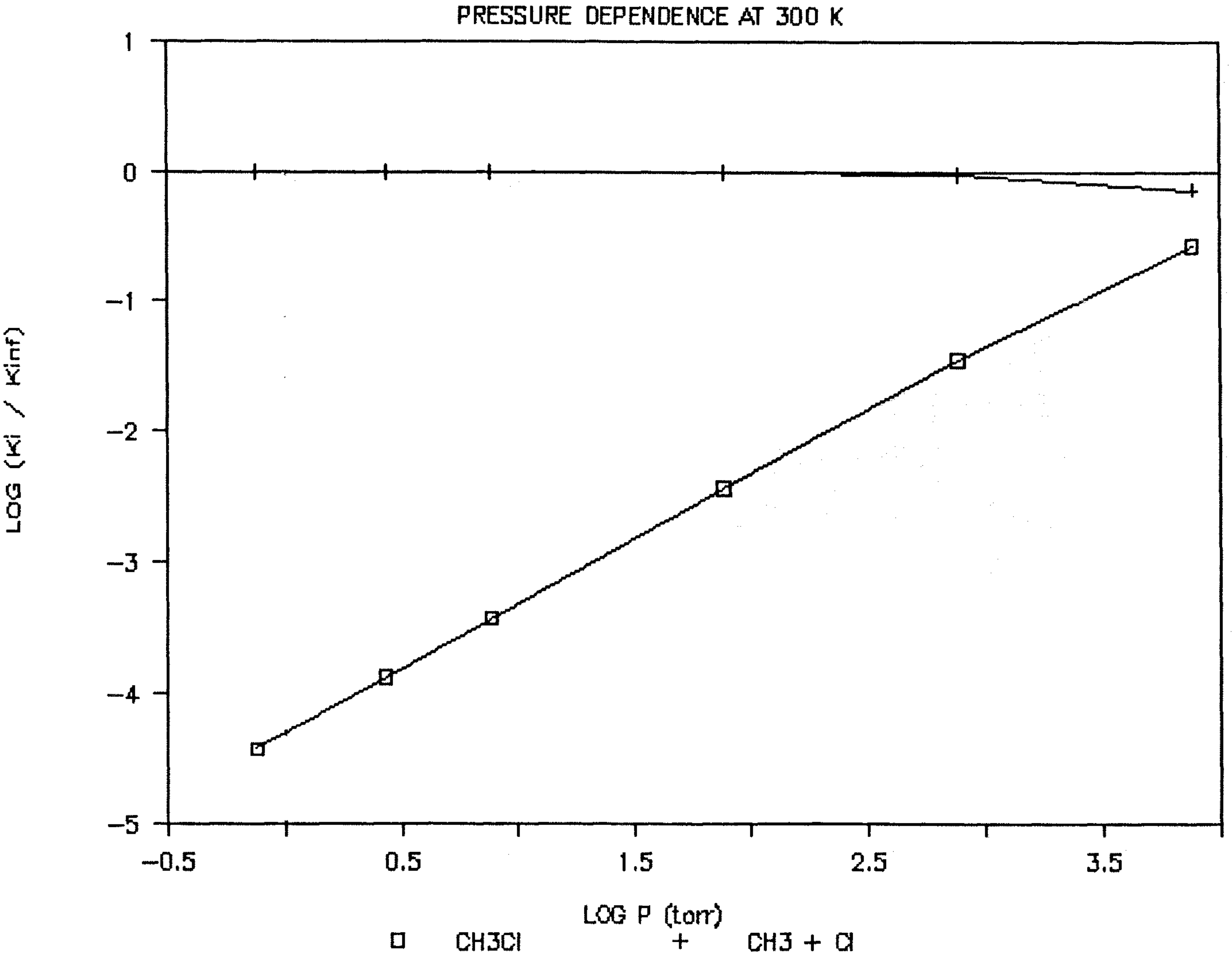


Figure 10. Energy diagram for H + CH2Cl

Fig. 11: H + CH2Cl <=> Products



$Cl + H_2 \Longleftrightarrow HCl + H$

$Cl + CH_2Cl_2 \Longleftrightarrow HCl + CHCl_2$

The reactions of halogen atom with hydrogen molecules have been studied for nearly a century and have played a central role in the history of chemical kinetics. Despite the intense effort to understand these elementary systems, there remained a number of significant problems. Miller and Gordon <43> 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 $Cl + H_2$ are used in this study. The rate constant of reaction $Cl + CH_2Cl_2$ is 3.9*10E+11 $cm^3 mole^{-1} s^{-1}$ at room temperature which was reported by Clyne and Walker <44>.

The Cl_xmethyl radicals can again react with H_2 or H as mentioned above.

$CH_3 + H_2 \Longleftrightarrow CH_4 + H$

$CH_3 + H \Longleftrightarrow CH_4$

$CHCl_2 + H_2 \Longleftrightarrow CH_2Cl_2 + H$

$CHCl_2 + H_2 \Longleftrightarrow CH_3Cl + Cl$

$CHCl_2 + H_2 \Longleftrightarrow CH_2Cl + HCl$

$CHCl_2 + H \Longleftrightarrow CH_2Cl_2$

$CHCl_2 + H \Longleftrightarrow CH_2Cl + Cl$

$CHCl_2 + H \Longleftrightarrow CHCl + HCl$

An energy diagram for H atom addition to $CHCl_2$ is shown in Fig. 12. Here the low energy exit channel to CH_2Cl + Cl controls this reaction sequence up to pressures of 10 atm. in argon, 298 K as demonstrated in Fig. 13. The QRRK calculations also show that formation of :CHCl + HCl is orders of magnitudes less due to a lower Arrhenius preexponential factor, A, and higher exit barrier. This is in apparant contradiction to results reported by Chang et. al. <45>; but it is not known if they considered the Cl atom dissociation channel.

The wall recombination steps which may compete with H abstraction from dichloromethane by Cl atom are:

Cl + Cl(wall) ----> Cl_2;
H + H(wall) ----> H_2.

It was indicated previously <19> that wall recombination of Cl atoms may not be negligible in comparison with H abstraction, if an uncoated or imperfectedly coated wall was used.

Another heterogeneous wall effect might manipulate the reaction mechanism are as follows.

H + Cl(wall) ----> HCl
H(wall) + Cl ----> HCl

Since the discharge tube and tubular reactor were coated with phosphoric acid, these heterogeneous reactions were considered to be insignificant.

A termolecular reaction scheme was proposed to acount for the recombination steps in this mechanism.

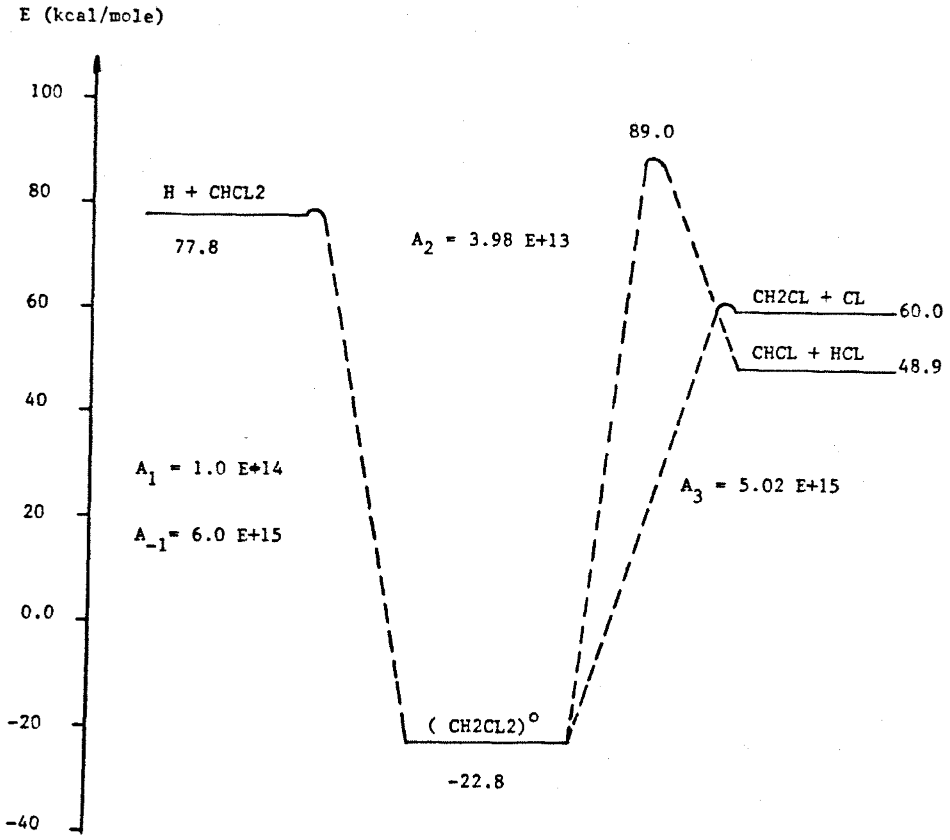
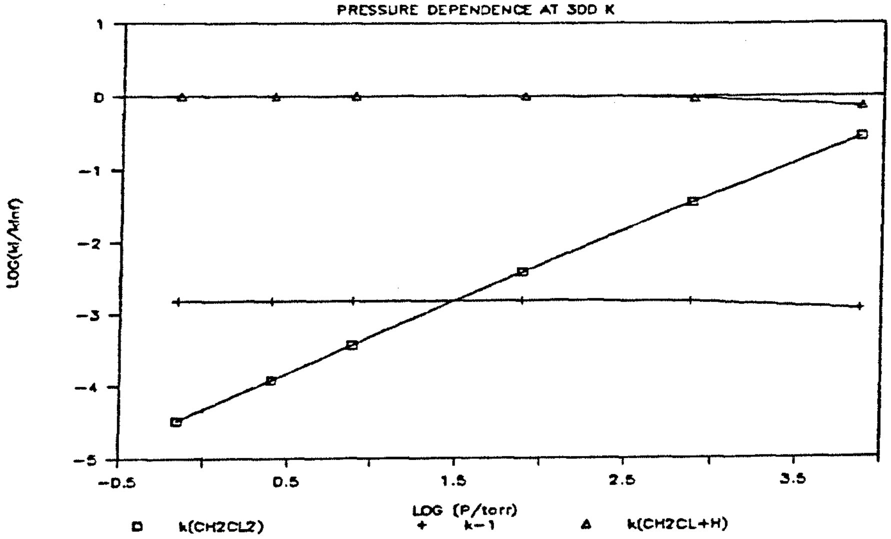


Figure 12 Energy diagram for H + CHCL2

FIGURE 13 H + CHCL2 ⇌ PRODUCTS



$H + H + M \Longleftrightarrow H_2 + M$, where M is a third body.

$H + Cl + M \Longleftrightarrow HCl + M$

$Cl + Cl + M \Longleftrightarrow Cl_2 + M$

The rate constants for these homogeneous termolecular reactions were quoted from CRC tabulation of rate constant by Kerr and Moss <46>.

No visible flame was observed in this study. Flames were observed previouly <47> for CCl_4 and $CHCl_3$ reactions with hydrogen atom when concentrations were both $10^{14}/cm^3$ or higher, with carbon formation occuring on the injector tip and reactor wall adjacent to the flame area. When concentration of the chlorocarbon was lowered, (0.2 to 0.01 that of H.) no flame was observed. In the present research, no attention was paid to the flame formation because measurement of the flame temperature was not made. Carbon formation was not monitored under present experimental conditions.

Once the methane was formed, it might react with the Cl atom by the reaction:

$Cl + CH_4 \Longleftrightarrow CH_3 + HCl$

which was studied previously <48>, and its rate constant is known to be $7.5 * 10^{10}$ $cm^3/(mole*s)$ at 298 K. This step competes with reactions of $Cl + H_2$ in the excess H_2 and reactions of $Cl + CH_2Cl_2$ and is relatively insignificant. Nevertheless, this step was still put into the computer modeling mechanism.

The mechanism accessible to the formation of the major products, hydrogen chloride and methane, has been explored. The other possible reactions which may be helpful to elucidate the complex character of the H + CH_2Cl_2 reaction are listed below. Their rate constants were calculated by the Energized Complex Quantum-RRK theory.

$CH_3 + CH_2Cl \Longleftrightarrow C_2H_4 + HCl$

$CH_3 + Cl \Longleftrightarrow CH_3Cl$

$Cl + CH_2Cl \Longleftrightarrow CH_2Cl_2$

$Cl + CHCl_2 \Longleftrightarrow CHCl_3$

$CHCl_2 + CH_2Cl \Longleftrightarrow C_2H_2Cl_2 + HCl$

$H + C_2H_2Cl_2 \Longleftrightarrow C_2H_3Cl + Cl$

$CHCl_2 + CHCl_2 \Longleftrightarrow C_2H_2Cl_3 + Cl$

$H + C_2H_2Cl_3 \Longleftrightarrow C_2H_3Cl_2 + Cl$

$H + C_2H_2Cl_3 \Longleftrightarrow C_2H_2Cl_2 + HCl$

$H + C_2H_3Cl_2 \Longleftrightarrow C_2H_3Cl + HCl$

$CH_2Cl + CH_2Cl \Longleftrightarrow C_2H_3Cl + HCl$

$H + C_2H_3Cl \Longleftrightarrow C_2H_4 + Cl$

These steps indicate the recombination reactions among the minor radicals and their subsequent reactions. An example of these reactions analyzed by QRRK method is H atom addition to vinyl chloride, forming an energized chloroethyl radical, which can decompose by a low energy exit channel to Cl atom and C_2H_4. An energy diagram for H atom addition to vinyl chloride is shown in Fig. 14.

Here the Cl product channel dominates up to 10 atm. in argon, 298 K as illustrated in Fig. 15. Previous studies <23> have sometimes neglected such steps in considering halocarbon conversion mechanisms.

Appendix IV lists all the reactions considered in the overall reaction mechanism and the rate constants. Appendix IV lists the estimations of rate constants of radical recombination/ addition reactions by QRRK theory. This mechanism describes a reasonable path toward to the formation of the major products. The computer modeling of these reactions is currently being explored.

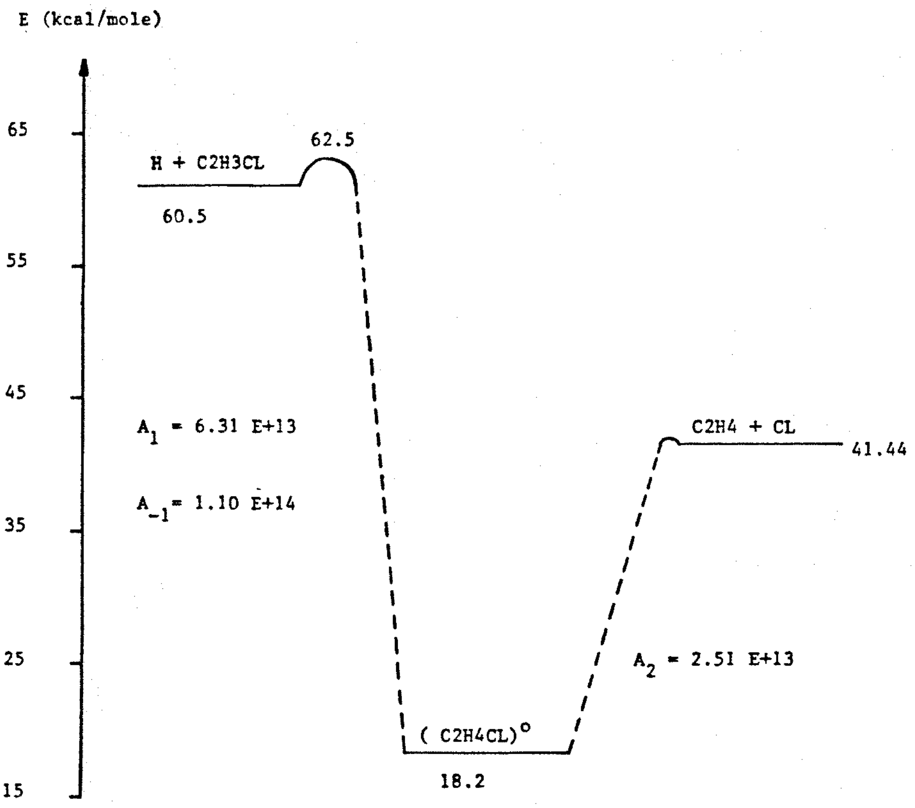
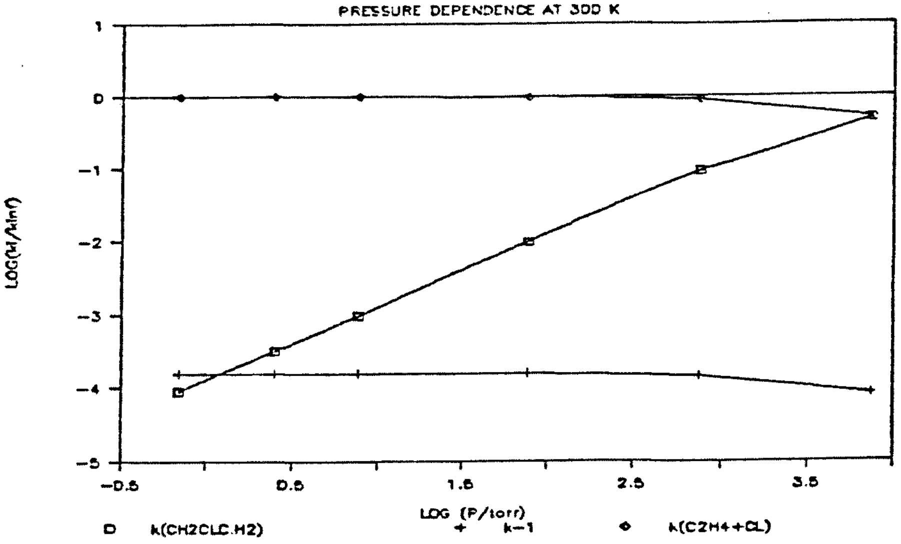


Figure 14 Energy diagram for H + C2H3CL

FIGURE 15 H + C2H3CL ⇌ PRODUCTS



C. Mechanism Modeling by CHEMKIN Program

CHEMKIN Fortran programs <49> were employed to model chemical kinetics. The modeling process requires that the chemist formulate an applicable reaction mechanism with rate constants, formulate and solve an appropriate system of governing equations <the Gas-Phase Subroutine Library>. Once the mechanism and governing equations are defined, CHEMKIN provides a means to describe symbolically the reaction mechanism and a means to describe computationally an arbitrary system of governing equations. This computer work was executed at Digital VAX/VMS model 11/785 computer of N.J.I.T..

Modeling results were constantly compared to the experimental data. Applications of sensitivity analysis <50> to the results of this initial mechanism would then indicate which specific reactions warrant further attention. The message from the sensitivity analysis indicates that the following reaction channels are the important reactions for this systems.

1. $H + CH_2Cl_2 \quad <--> \quad HCl + CH_2Cl$
2. $Cl + CH_2Cl_2 \quad <--> \quad HCl + CHCl_2$
3. $H + CH_2Cl \quad <--> \quad CH_3 + Cl$
4. $H + CHCl_2 \quad <--> \quad CH_2Cl + Cl$
5. $H + HCl \quad <--> \quad H_2 + Cl$
6. $H + CH_3 \quad <--> \quad CH_4$
7. $H + H + M \quad <--> \quad H_2 + M$

8\. $H + Cl + M \longleftrightarrow HCl + M$

9\. $CH_3 + CH_2Cl \longleftrightarrow C_2H_4 + HCl$

10\. $Cl + CH_3 \longleftrightarrow CH_3Cl$

Plot of product concentration calculated through activated complex and QRRK theory, normalized to initial CH_2Cl_2 concentration, of the modeling results vs. residence time are illustrated in Figure 16. Concentrations of HCl formed are initially larger than those of CH_4 as the figure shown. This trend coincides with the stoichiometric reaction equation:

$$4H + CH_2Cl_2 \longrightarrow CH_4 + 2HCl$$

Major products predicted by the model are hydrogen chloride, methane and hydrogen. A trace amount of C_2H_4, CH_3Cl and other chlorinated compound are presented in the product distribution of the modeling mechanism. These predicted major products are quite in agreement with the experimentally observed data.

Figure 17 demonstrates the comparison of observed and predicted falloff curves for reaction: $H + CH_2Cl_2$ at $[H]_o = 4.21 * 10^{14}$ molecules/cm^3. The model results agree with the experimental data based on the overall conversion of CH_2Cl_2, when the concentration of atomic hydrogen is greater than about 6.5 that of dichloromethane. The computer modeling of the reaction mechanism is still being continued. This mechanism describes a suitable path toward the formation of

Figure 16.

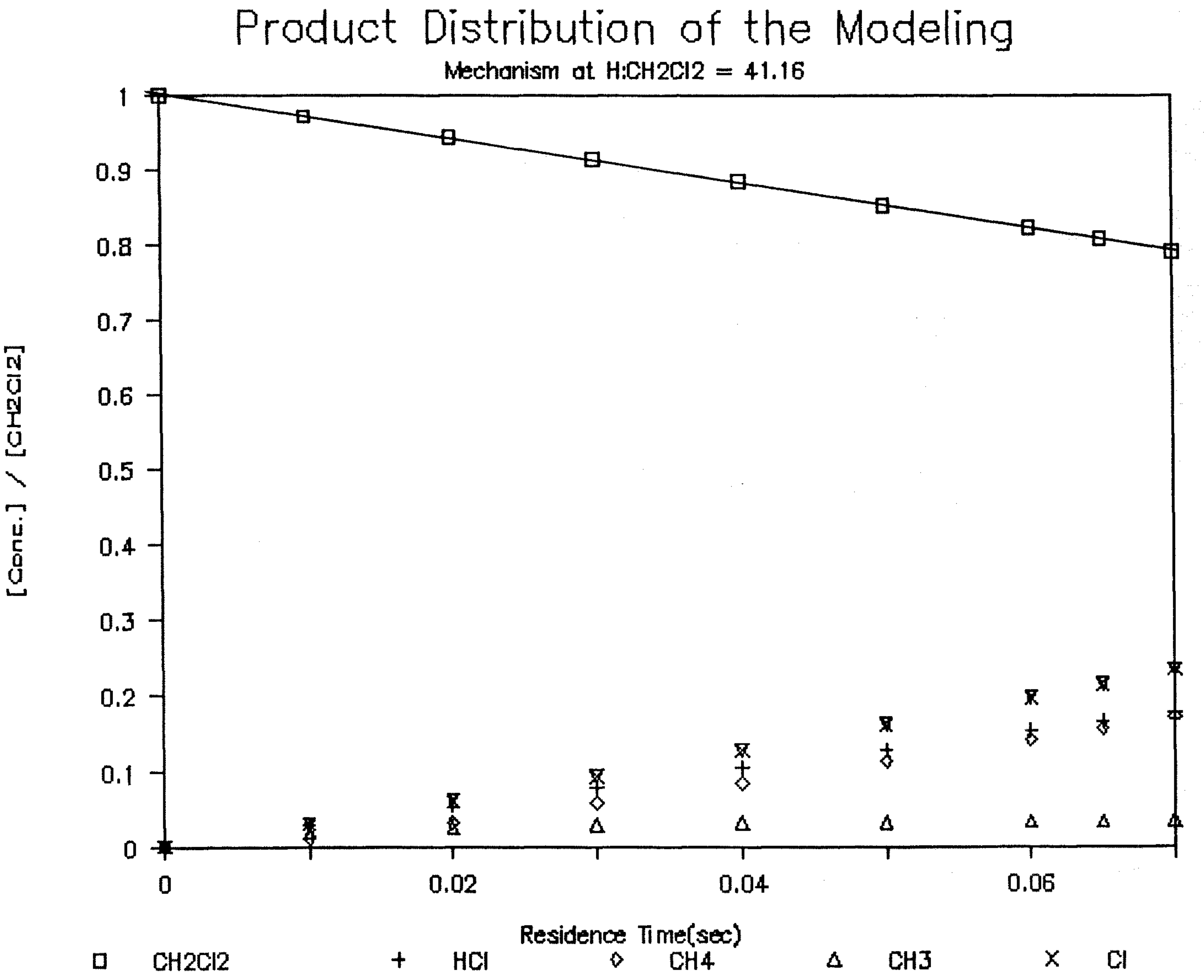
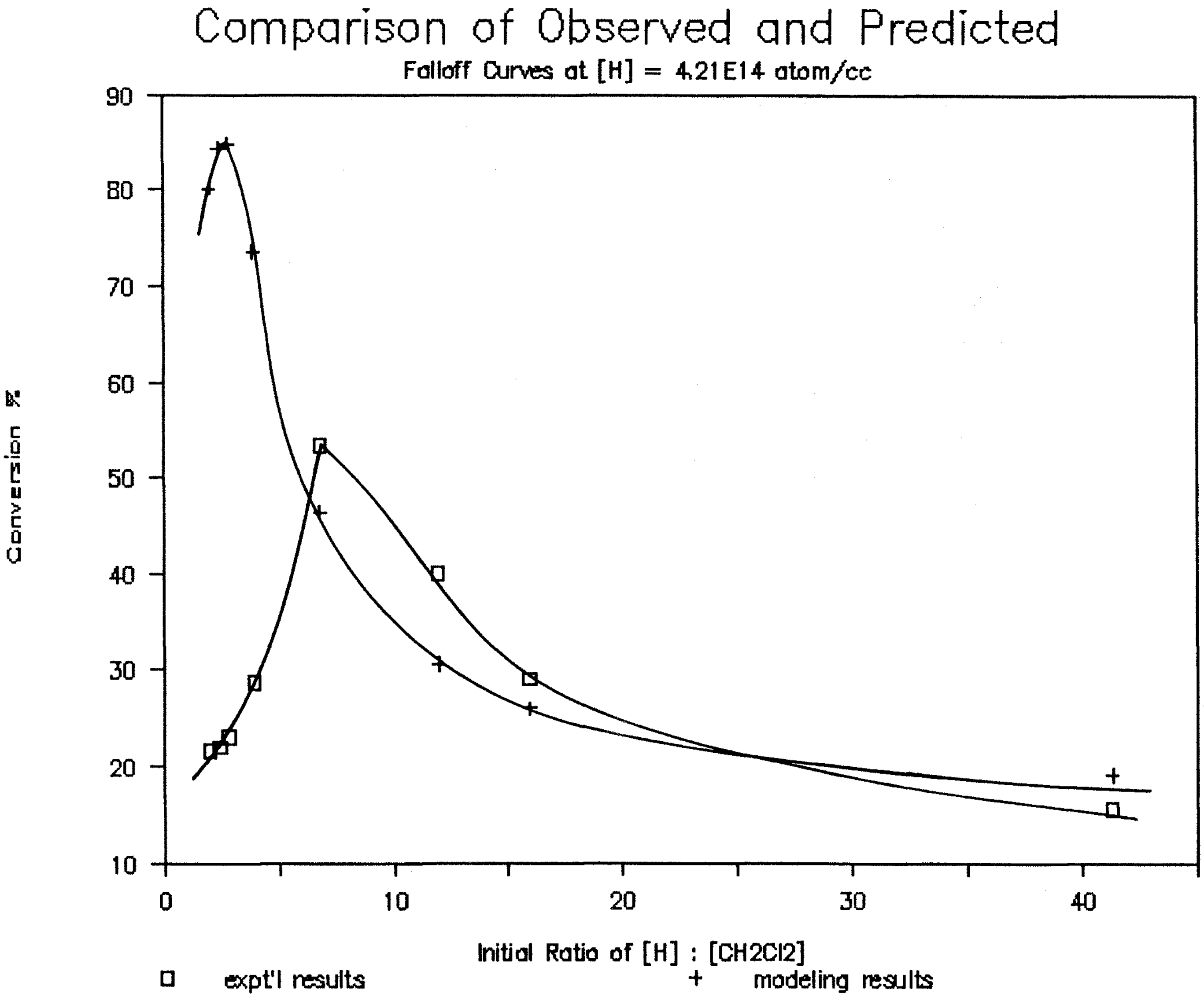

Product Distribution of the Modeling
Mechanism at H:CH2Cl2 = 41.16
[Conc.] / [CH2Cl2]
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.02
0.04
0.06
Residence Time(sec)
□ CH2Cl2
+ HCl
◇ CH4
△ CH3
× Cl

Figure 17.


Comparison of Observed and Predicted
Falloff Curves at [H] = 4.21E14 atom/cc
90
80
70
60
50
40
30
20
10
Conversion %
0
10
20
30
40
Initial Ratio of [H] : [CH2Cl2]
□ expt'l results
+ modeling results

the principal products.

Through this computer modeling of the reaction scheme and comparison with experimental data, the room temperature rate constants of the primary steps were established as follows.

$$H + CH_2Cl_2 \xrightarrow{k_1} HCl + CHCl_2$$

$$k_1 = 3.63 * 10^9 \ cm^3 \ mole^{-1} \ s^{-1}$$

$$H + CH_2Cl_2 \xrightarrow{k_2} H_2 + CHCl_2$$

$$k_2 = 2.08 * 10^7 \ cm^3 \ mole^{-1} \ s^{-1}$$

The k_1 value which was calculated by the pseudo-first-order kinetic analysis was used as an initial input value to the modeling mechanism. A typical k_1 value from the pseudo-first-order assumption is $5.7 * 10^9$ cm^3 $mole^{-1}$ s^{-1}. By comparing the experimental results with the predicted data, the k_1 value was obtained as shown above.

VI. CONCLUSION

The reaction kinetics of atomic hydrogen with dichloromethane were studied in a discharge tubular flow reactor with 2.6 cm I.D. at pressure of 2.1 to 2.7 torr absolute and room temperature. Hydrogen atoms were generated by a microwave discharge plasma. Atomic hydrogen concentrations were measured by chemiluminescence titration with nitrogen dioxide. Chlorocarbon reactant and products were monitored by online gas chromatography (FID).

The major products observed were hydrogen chloride, hydrogen and methane. The conversion of dichloromethane increases first to a maximum and then decreases as inlet concentration of dichloromethane increases. This is believed to be partially due to the quenching effects of dichloromethane on atomic hydrogen.

There is scope for impovement in the products collection efficiency of the sampling loop. The amount of products trapped can be increased by modification of the collection loop and flow through measurements.

A detailed reaction mechanism was developed by incorporating activated complex and Quantum RRK theory. Sensitivity analysis on the reaction mechanism was performed to identify the important reaction channels and to improve the fit of the mechanism on experimental observation. The model results are consistent with the observed major products and CH_2Cl_2 concentration when the concentration of atomic hydrogen is greater than 6.5 that of dichloromethane concentration. This mechanism indicates a reasonable path toward the formation of the major products. The computer modeling of these reactions is still being pursued. Through this computer modeling of the reaction scheme and comparison with experimental data, the rate constants of the initial steps were determined as follows.

$$H + CH_2Cl_2 \xrightarrow{k_1} HCl + CHCl_2$$

$$k_1 = 3.63 * 10^9 \quad cm^3\ mole^{-1}\ s^{-1}$$

$$H + CH_2Cl_2 \xrightarrow{k_2} H_2 + CHCl_2$$

$$k_2 = 2.08 * 10^7 \quad cm^3\ mole^{-1}\ s^{-1}$$

This study provides a mechanistic explanation of chloromethane and atomic hydrogen reactions. Since a study of the reactions of halomethanes with hydrogen atoms can provide needed kinetic data in the incineration of halocarbons, it is hoped that the present work will make future studies on similar reactions simpler and yet more fruitful.

APPENDIX I: REACTION MECHANISM

REACTIONS CONSIDERED	PRE EXP	TEMP EXP	ACT ENG
1. H+CH2Cl2=HCl+CH2Cl	0.108D+15	0.00000E+00	6100.0
2. H+CH2Cl2=H2+CHCl2	0.216D+14	0.00000E+00	8700.0
3. H+CH2Cl=CH3+Cl	0.990D+14	0.00000E+00	-1.7400
4. H+CHCl2=CH2Cl+Cl	0.999D+14	0.00000E+00	-0.5070
5. CH3+CH3=C2H6	0.123D+14	0.00000E+00	-343.00
6. CH3+CH2Cl=C2H5Cl	0.109D+12	0.00000E+00	-1150.0
7. CH3+CH2Cl=C2H5+Cl	0.206D+12	0.00000E+00	700.00
8. CH3+CH2Cl=C2H4+HCl	0.124D+14	0.00000E+00	45.400
9. CH2Cl+CH2Cl=C2H4Cl2	0.122D+11	0.00000E+00	-1490.0
10. CH2Cl+CH2Cl=C2H4Cl+Cl	0.213D+12	0.00000E+00	1140.0
11. CH2Cl+CH2Cl=C2H3Cl+HCl	0.123D+13	0.00000E+00	92.000
12. H+C2H3Cl=C2H4+Cl	0.158D+14	0.00000E+00	2800.0
13. CHCl2+CH2Cl=C2H3Cl3	0.765D+10	0.00000E+00	-1630.0
14. CHCl2+CH2Cl=C2H3Cl2+Cl	0.609D+12	0.00000E+00	1180.0
15. CHCl2+CH2Cl=C2H2Cl2+HCl	0.975D+13	0.000000E+00	-2.790
16. H+C2H2Cl2=C2H3Cl+Cl	0.223D+14	0.00000E+00	1500.0
17. CHCl2+CHCl2=C2H2Cl4	0.473D+10	0.00000E+00	-1700.0
18. CHCl2+CHCl2=C2H2Cl3+Cl	0.486D+11	0.00000E+00	2040.0
19. CHCl2+CHCl2=C2HCl3+HCl	0.443D+12	0.00000E+00	279.00
20. H+C2H2Cl3=C2H3Cl3	0.865D+11	0.00000E+00	-1590.0
21. H+C2H2Cl3=C2H3Cl2+Cl	0.160D+14	0.00000E+00	937.00
22. H+C2H2Cl3=C2H2Cl2+HCl	0.175D+15	0.00000E+00	-16.200
23. H+C2H3Cl2=C2H4Cl2	0.205D+13	0.00000E+00	-1510.0
24. H+C2H3Cl2=C2H4Cl+Cl	0.603D+14	0.00000E+00	951.00

```
25. H+C2H3Cl2=C2H3Cl+HCl    0.278D+15     0.00000E+00   40.300

26. H+C2H4Cl=C2H5Cl         0.785D+12     0.00000E+00  -1150.0

27. H+C2H4Cl=C2H4+HCl       0.218D+15     0.00000E+00   21.600

28. H+C2H5=C2H6             0.124D+13     0.00000E+00  -1170.0

29. H+C2H5=CH3+CH3          0.270D+15     0.00000E+00   29.300

30. H+H+M=H2+M              0.100D+17     0.00000E+00   0.0000
       AR / 0.05 /
       CH2Cl2 / 25 /

31. H+Cl+M=HCl+M            0.140D+19     0.00000E+00   0.0000
       AR / 0.05 /

32. H+HCl=H2+Cl             0.109D+14     0.00000E+00   3500.0

33. H+CH3=CH4               0.100D+15     0.00000E+00   0.0000

34. H+CH3Cl=HCl+CH3         0.372D+14     0.00000E+00   9300.0

35. H+CCl2=CHCl2            0.861D+14     0.00000E+00  -291.00

36. Cl+CH2Cl2=HCl+CHCl2     0.503D+14     0.00000E+00   2875.0

37. Cl+CH2Cl=CH2Cl2         0.808D+11     0.00000E+00  -1270.0

38. Cl+CH3Cl=HCl+CH2Cl      0.128D+14     50.00000E+00  3546.0

39. Cl+CH3=CH3Cl            0.100D+13     0.00000E+00   0.0000

40. Cl+CHCl2=CHCl3          0.148D+11     0.00000E+00  -1570.0

41. Cl+CHCl2=CCl2+HCl       0.142D+13     0.00000E+00  -76.200

42. Cl+CH4=HCl+CH3          0.306D+14     0.00000E+00   3556.0

43. Cl+Cl+M=Cl2+M           0.251D+15     0.00000E+00  -1800.0
       AR / 0.05 /
       CH2Cl2 / 25 /

44. CCl2+CCl2=C2Cl4         0.600D+14     0.00000E+00  -351.00

45. Cl2+H=HCl+Cl            0.457D+13     0.00000E+00   1400.0

46. H2+CH3=CH4+H            0.158D+13     0.00000E+00   11300.

47. H2+C2H5=H+C2H6          0.398D+13     0.00000E+00   14000.

48. H2+CH2Cl=H+CH3Cl        0.100D+14     0.00000E+00   7370.0
```

49.	H+CH2Cl=CH3Cl	0.113D+10	0.00000E+00	-737.00
50.	H+C2H3Cl=C2H4Cl	0.495D+09	0.00000E+00	2060.0
51.	H+C2H2Cl2=C2H3Cl2	0.964D+10	0.00000E+00	654.00
52.	H+C2H4=C2H3+H2	0.182D+14	0.00000E+00	6600.0
53.	H+C2H3=H2+C2H2	0.400D+14	0.00000E+00	4.7600
54.	H+C2H3=C2H4	0.455D+11	0.00000E+00	-1050.0

APPENDIX II: EXPERIMENTAL DATA

Experimental 1 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl2 Initial Conc. (molecules/cm^3)	Exp't Conversion %
$2.3 * 10^{-3}$	$1.05 * 10^{13}$	23.5
$4.7 * 10^{-3}$	$2.14 * 10^{13}$	27.3
$9.4 * 10^{-3}$	$4.31 * 10^{13}$	48.7
$1.4 * 10^{-2}$	$6.35 * 10^{13}$	33.9
$3.2 * 10^{-2}$	$1.45 * 10^{14}$	26.8
$4.1 * 10^{-2}$	$1.86 * 10^{14}$	26.4
$4.7 * 10^{-2}$	$2.14 * 10^{14}$	25.9

Initial H Atom Concentration = $4.13 * 10^{14}$ molecules/cm^3

Initial H_2 Concetration = $6.39 * 10^{14}$ molecules/cm^3
(Input to Discharge System)

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

Dissociation Efficiency = 32.3 %

Residence Time = 0.069 sec.

Experimental 2 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl3 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 H_2 Concentration = $5.6 * 10^{14}$ molecules/cm^3
(Input to Discharge System)

Initial Argon Concentration = $8.39 * 10^{16}$ molecules/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 %
$2.34 * 10^{-3}$	$1.04 * 10^{13}$	17.1
$4.67 * 10^{-3}$	$2.08 * 10^{13}$	18.6
$9.44 * 10^{-3}$	$4.20 * 10^{13}$	27.5
$1.19 * 10^{-2}$	$5.30 * 10^{13}$	37.5
$2.24 * 10^{-2}$	$9.97 * 10^{13}$	20.5
$2.78 * 10^{-2}$	$1.23 * 10^{14}$	20.2
$3.37 * 10^{-2}$	$1.66 * 10^{14}$	19.5
$5.02 * 10^{-2}$	$2.23 * 10^{14}$	10.9

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

Initial H_2 Concentration = $6.22 * 10^{14}$ molecules/cm^3
(Input to Discharge System)

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

Dissociation Efficiency = 23.3 %

Residence Time = 0.077 sec.

Experimental 4 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl2 Initial Conc. ($molecules/cm^3$)	Exp't Conversion %
$3.5 * 10^{-3}$	$1.57 * 10^{13}$	6.9
$1.0 * 10^{-2}$	$4.46 * 10^{13}$	20.0
$1.5 * 10^{-2}$	$6.85 * 10^{13}$	39.2
$2.0 * 10^{-2}$	$8.84 * 10^{13}$	33.3
$2.3 * 10^{-2}$	$1.04 * 10^{14}$	26.8
$3.2 * 10^{-2}$	$1.41 * 10^{14}$	22.5
$3.7 * 10^{-2}$	$1.66 * 10^{14}$	21.1
$5.5 * 10^{-2}$	$2.43 * 10^{14}$	14.0

Initial H Concentration = $3.61 * 10^{14}$ molecules/cm^3

Initial H_2 Concentration = $6.22 * 10^{14}$ molecules/cm^3
(Input to Discharge System)

Initial Argon Concentration = $8.39 * 10^{14}$ molecules/cm^3

Dissociation Efficiency = 29.0 %

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

Initial H_2 Concetration = $6.39 * 10^{14}$ molecules/cm^3
(Input to Discharge System)

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

Dissociation Efficiency = 8.62 %

Residence Time = 0.069 sec.

Experimental 6 :

CH2Cl2 Flow Rate (cm^3/s)	CH2Cl2 Initial Conc. ($molecules/cm^3$)	Exp't Conversion %
$4.7 * 10^{-3}$	$2.15 * 10^{13}$	20.4
$1.0 * 10^{-2}$	$4.77 * 10^{13}$	38.5
$1.7 * 10^{-2}$	$7.94 * 10^{13}$	21.8
$2.6 * 10^{-2}$	$1.18 * 10^{14}$	18.9
$3.3 * 10^{-2}$	$1.50 * 10^{14}$	18.0
$4.0 * 10^{-2}$	$1.82 * 10^{14}$	17.7
$4.8 * 10^{-2}$	$2.18 * 10^{14}$	16.2
$5.7 * 10^{-2}$	$2.61 * 10^{14}$	14.9

Initial H Atom Concentration = $3.78 * 10^{14}$ molecules/cm^3

Initial H_2 Concetration = $6.39 * 10^{14}$ molecules/cm^3
(Input to Discharge System)

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

Dissociation Efficiency = 29.61 %

Residence Time = 0.069 sec.

APPENDIX III. CALCULATION OF HYDROGEN ATOM AND DICHLOROMETHANE CONCENTRATION

Total Flow Rate, F_{total} (at 1 Atm.) $= F_{Ar} + F_{H2} + F_{CH2Cl2}$

$= 18.87 + 0.14 +$ (relatively small)

$= 19.01 \quad cm^3/s$

Pressure of The Reactor $= 3.8 * \frac{0.959}{13.6} * 10$

$= 2.68$ torr

Tatal Flow at 2.68 torr $= 19.01 * \frac{760}{2.68}$

$= 5391 \quad cm^3/s$

Molecules of Total Inlet Flow Rate

$$= \frac{19.01}{82.06 * 298} * 6.02 * 10^{23} = 4.68 * 10^{20} \text{ molecules/s}$$

$$N_T = \frac{\text{\# molecules}}{cm^3} = \frac{4.68 * 10^{20} \text{ molecules/s}}{5391 \quad cm^3/s}$$

$$= 8.68 * 10^{16} \text{ molecules/cm}^3$$

Inlet Fraction of $[H]_o$

$$= \frac{(NO_2 \text{ flow}) * (\text{correction factor for } N_2O_4 <=> 2NO_2)}{(\text{total flow rate}) * (\text{correction factor for } NO_2 \text{ 2nd rxn.})}$$

$$= \frac{0.485 * (0.073 + 0.08 * 2)}{19.01 * 1.25}$$

$$= 4.75 * 10^{-3}$$

$$[H]_o = (4.75 * 10^{-3}) * (8.68 * 10^{16})$$

$$= 4.12 * 10^{14} \text{ molecules/cm}^3$$

$$\text{Fraction of } H_2 = \frac{F_{H2}}{F_{total}} = \frac{0.14 \ \text{cm}^3/\text{s}}{19.01 \ \text{cm}^3/\text{s}} = 7.36 * 10^{-3}$$

$$N_{H2} = (7.36 * 10^{-3}) * (8.68 * 10^{16})$$

$$= 6.39 * 10^{14} \ \text{molecules/cm}^3$$

$$\% \text{ Dissociation} = \frac{\text{atom H}}{\text{molecules } H_2 * 2}$$

$$= \frac{4.12 * 10^{14}}{6.39 * 10^{14} * 2} = 32.3 \ \%$$

Residence Time, t, at 70 cm distance

$$t = \frac{V}{F} = \frac{5.31 \ \text{cm}^2 * 70 \ \text{cm}}{5391 \ \text{cm}^3/\text{sec.}} = 0.069 \text{ sec.}$$

CH_2CL_2 Inlet Flow Rate = (carrier gas, Ar, flow rate) * (vapor pressure ratio of CH_2Cl_2 to Ar)

$$= F_{Ar} * \frac{P_{CH2Cl2}}{P_{Ar}}$$

Vapor pressure of CH_2Cl_2 at 25°C is calculated as follows:

$$\text{Antoine Equation, } \log P = A - \frac{B}{t+C}$$

where P is pressure (torr), t is temperature (°C) and A,B and C are constants for a specific gas <51>.

For CH_2Cl_2, A = 7.4092, B = 1325.9, C = 252.6. <51>

$$\log P = 7.4092 - \frac{1325.9}{25 + 252.6} = 2.6329$$

vapor pressure of CH_2Cl_2 at 25°C = 429 torr

$$\frac{P_{CH2Cl2}}{P_{Ar}} = \frac{429/760}{(14.7 + 2)/14.7} = 0.497$$

The flow rate of CH_2Cl_2 can thus be represented as:

$$F_{CH2Cl2} = F_{Ar} * 0.479$$

APPENDIX IV. CALCULATION OF RATE CONSTANTS BY QRRK THEORY

ISOMACT INPUT FILE ---- REACTION: H + C2H2Cl2

```
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 + CHClCHCl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
CH2ClCHCl           CH2CHCl + Cl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
736.2,                 15,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N     E (CAL)
                              2.22E+13,    0.,   1500,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
 97.96,                         5.5,           433.0,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,         800.0,

A(M-CC-S)       E (KCAL)
 1.2E+13,        42.9,          K-1
 2.51E+13,       25.9,          K2
 0.0,            0.0,           K3
 0.0,            0.0,           K4
 0.0,            0.0,           K-4
 0.0,            0.0,           K5
 0.0,            0.0,           K6

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

NUMBER OF TEMPERATURES  T1    T2    T3    T4    T5    T6(K)
6,                     273., 300., 350., 400., 450., 500.,

NUMBER OF PRESSURES  P1     P2     P3     P4     P5     P6(TORR)
6,                 0.76,   2.7,   7.6,   76.,   760.,   7600.,
```

```
ARRHENIUS  PARAMETERS  FOR  APPARENT  RATE  CONTANTS  FOR
   P = 2.70E+00  TORR

H + CHClCHCl   =   CH2ClCHCl         T   273.  K  TO   500.  K

         A =   5.43E+09      E = -1.33E+02  CAL

   T            K EXP          K CALC          PERCENT ERROR
   273.         6.37E+09       6.93E+09          -8.0
   300.         6.88E+09       6.78E+09           1.5
   350.         7.20E+09       6.57E+09           9.7
   400.         6.93E+09       6.41E+09           8.1
   450.         6.33E+09       6.29E+09           0.5
   500.         5.57E+09       6.20E+09         -10.1

H + CHClCHCl   =   CH2CHCl + Cl      T   273.  K  TO   500.  K

         A =   2.23E+13      E =   1.50E+03  CAL

   T            K EXP          K CALC          PERCENT ERROR
   273.         1.39E+12       1.39E+12           0.0
   300.         1.79E+12       1.79E+12           0.0
   350.         2.56E+12       2.56E+12           0.0
   400.         3.36E+12       3.36E+12           0.0
   450.         4.14E+12       4.14E+12           0.0
   500.         4.90E+12       4.90E+12           0.0

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

H + CHClCHCl   =   CH2ClCHCl         T   273.  K  TO   500.  K

         A =   2.05E+12      E =   4.85E+02  CAL

   T            K EXP          K CALC          PERCENT ERROR
   273.         7.79E+11       8.38E+11          -7.1
   300.         9.18E+11       9.08E+11           1.1
   350.         1.11E+12       1.02E+12           8.5
   400.         1.20E+12       1.11E+12           7.5
   450.         1.20E+12       1.19E+12           0.7
   500.         1.14E+12       1.26E+12          -9.4

H + CHClCHCl   =   CH2CHCl + Cl      T   273.  K  TO   500.  K

         A =   3.30E+13      E =   2.16E+03  CAL

   T            K EXP          K CALC          PERCENT ERROR
   273.         6.19E+11       6.14E+11           0.9
   300.         8.75E+11       8.78E+11          -0.4
   350.         1.46E+12       1.47E+12          -0.9
   400.         2.17E+12       2.17E+12          -0.3
   450.         2.95E+12       2.94E+12           0.3
   500.         3.77E+12       3.74E+12           0.5
```

```
ISOMACT INPUT FILE ---- H + C2H2Cl3
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 + CHCl2CHCl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
 CHCl2CH2Cl          CHClCH2Cl + Cl      CHClCHCl + HCl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
 699.95,                18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                              1.84E+14,    0.,   0.,

COLLISION COMPLEX MASS(A.U.)  DIAMETER(A)   WELL DEPTH(K)
 133.4,                         6.15,          463.5,

THIRD BODY
AR MASS(A.U.) DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
  39.95,       3.54,         93.3,             800.0,

A(M-CC-S)       E (KCAL)
 6.0E+15,        92.0,         K-1
 6.0E+15,        71.7,         K2
 1.26E+14,       50.0,         K3
 0.0,            0.0,          K4
 0.0,            0.0,          K-4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES T1    T2    T3    T4    T5    T6(K)
6,                    273., 300., 350., 400., 450., 500.,.

NUMBER OF PRESSURES  P1   P2    P3    P4    P5    P6 (TORR)
6,                 0.76, 2.7,  7.6,   76., 760.,  7600.,
```

```
ARRHENIUS  PARAMETERS  FOR  APPARENT  RATE  CONTANTS  FOR
   P = 2.70E+00 TORR

H + CHCl2CHCl   =   CHCl2CH2Cl          T  273.  K TO  500.  K

         A =  8.65E+10      E = -1.59E+03  CAL

    T          K EXP          K CALC         PERCENT  ERROR
    273.      1.48E+12       1.61E+12          -7.6
    300.      1.25E+12       1.24E+12           1.4
    350.      9.22E+11       8.45E+11           9.2
    400.      6.84E+11       6.35E+11           7.7
    450.      5.12E+11       5.09E+11           0.5
    500.      3.85E+11       4.26E+11          -9.7

H + CHCl2CHCl   =   CHClCH2Cl + Cl      T  273.  K TO  500.  K

         A =  1.60E+13      E =  9.37E+02  CAL

    T          K EXP          K CALC         PERCENT  ERROR
    273.      3.04E+12       2.84E+12           7.0
    300.      3.28E+12       3.32E+12          -1.2
    350.      3.86E+12       4.16E+12          -7.2
    400.      4.62E+12       4.92E+12          -6.0
    450.      5.59E+12       5.61E+12          -0.3
    500.      6.77E+12       6.23E+12           8.8

H + CHCl2CHCl   =   CHClCHCl + HCl      T  273.  K TO  500.  K

         A =  1.75E+14      E = -1.62E+01  CAL

    T          K EXP          K CALC         PERCENT  ERROR
    273.      1.79E+14       1.80E+14          -0.2
    300.      1.79E+14       1.79E+14           0.0
    350.      1.79E+14       1.79E+14           0.3
    400.      1.79E+14       1.78E+14           0.3
    450.      1.78E+14       1.78E+14           0.0
    500.      1.77E+14       1.77E+14          -0.4
```

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

H + CHCl2CHCl   =  CHCl2CH2Cl        T  273. K TO  500. K

        A =  3.33E+13     E = -7.60E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.     1.27E+14      1.35E+14          -5.8
    300.     1.20E+14      1.19E+14           0.8
    350.     1.06E+14      9.93E+13           6.9
    400.     9.21E+13      8.66E+13           6.3
    450.     7.85E+13      7.79E+13           0.7
    500.     6.59E+13      7.16E+13          -8.0

H + CHCl2CHCl   =  CHClCH2Cl + Cl    T  273. K TO  500. K

        A =  2.74E+13     E =  1.85E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.     9.80E+11      9.00E+11           8.8
    300.     1.20E+12      1.22E+12          -2.0
    350.     1.74E+12      1.91E+12          -8.8
    400.     2.48E+12      2.66E+12          -6.8
    450.     3.45E+12      3.45E+12           0.1
    500.     4.68E+12      4.24E+12           0.1

H + CHCl2CHCl   =  CHClCHCl + HCl    T  273. K TO  500. K

        A =  2.64E+14     E =  8.52E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.     5.58E+13      5.48E+13           1.7
    300.     6.27E+13      6.32E+13          -0.7
    350.     7.61E+13      7.75E+13          -1.8
    400.     8.94E+13      9.03E+13          -1.0
    450.     1.02E+14      1.02E+14           0.3
    500.     1.13E+14      1.12E+14           1.4
```

```
ISOMACT INPUT FILE ---- REACTION: H + C2H3
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                H2 + C2H2

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
 1586,                  12,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                             4.0E+13,     0.,   0.0,

COLLISION COMPLEX MASS(A.U.) DIAMETER(A)  WELL DEPTH(K)
   28.06,                     4.163,        224.7,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
  39.95,       3.54,         93.3,              800.0,

A(M-CC-S)       E (KCAL)
 1.7E+15,        109.4,        K-1
 1.1E+14,        81.0,         K2
 0.0,            0.0,          K3
 0.0,            0.0,          K4
 0.0,            0.0,          K-4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

DELTAHFOR A* === B* (KCAL/MOL) XLAM(COLLISION COEFFICIENT)
 0.,                                0.,

NUMBER OF TEMPERATURES T1     T2     T3     T4     T5     T6(K)
6,                     273., 300., 350., 400., 450., 500.,

NUMBER OF PRESSURES P1     P2     P3     P4    P5      P6(TORR)
6,                 0.76,  2.7,   7.6,   76., 760., 7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + C2H3  =  C2H4              T  273. K TO  500. K

         A =  4.55E+10     E = -1.05E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       3.05E+11       3.18E+11          -3.9
    300.       2.69E+11       2.67E+11           0.7
    350.       2.17E+11       2.07E+11           4.5
    400.       1.78E+11       1.71E+11           3.9
    450.       1.48E+11       1.48E+11           0.3
    500.       1.25E+11       1.32E+11          -5.1

H + C2H3  =  H2 +C2H2          T  273. K TO  500. K

         A =  4.00E+13     E =  4.76E+00 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       3.96E+13       3.96E+13           0.0
    300.       3.97E+13       3.97E+13           0.0
    350.       3.97E+13       3.97E+13           0.0
    400.       3.98E+13       3.98E+13           0.0
    450.       3.98E+13       3.98E+13           0.0
    500.       3.98E+13       3.98E+13           0.0

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

H + C2H3  =  C2H4              T  273. K TO  500. K

         A =  1.23E+13     E = -4.49E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       2.74E+13       2.81E+13          -2.7
    300.       2.62E+13       2.61E+13           0.4
    350.       2.42E+13       2.34E+13           3.1
    400.       2.22E+13       2.16E+13           2.8
    450.       2.04E+13       2.03E+13           0.3
    500.       1.86E+13       1.93E+13          -3.7

H + C2H3  =  H2 +C2H2          T  273. K TO  500. K

         A =  3.94E+13     E =  6.25E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       1.26E+13       1.25E+13           1.4
    300.       1.38E+13       1.38E+13          -0.3
    350.       1.58E+13       1.60E+13          -1.5
    400.       1.77E+13       1.80E+13          -1.2
    450.       1.96E+13       1.96E+13           0.0
    500.       2.14E+13       2.10E+13           1.7
```

```
ISOMACT INPUT FILE ---- REACTION: H  + C2H3Cl
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 + C2H3Cl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H4Cl              C2H4 + Cl

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)
                             6.31E+13,    0.,   2.0,

COLLISION COMPLEX MASS(A.U.)    DIAMETER(A)   WELL DEPTH(K)
64.51,                          5.3,           322.0,

THIRD BODY
AR  MASS (A.U.) DIAMETER(A) WELL DEPTH(K) ENERGY TRANS(CAL)
    39.95,      3.54,       93.3,         800.0,

A(M-CC-S)       E (KCAL)
1.10E+14,       44.3,         K-1
2.51E+13,       23.24,        K2
0.0,            0.0,          K3
0.0,            0.0,          K4
0.0,            0.0,          K-4
0.0,            0.0,          K5
0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES T1    T2    T3    T4    T5    T6(K)
6,                    273., 300., 350., 400., 450., 500.,

NUMBER OF PRESSURES P1     P2    P3     P4    P5    P6(TORR)
6,                0.76, 2.7,  7.6,     76.,  760.,   7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + C2H3Cl   =   C2H4Cl             T  273. K TO  500. K

         A =  3.41E+09      E =  8.63E+02 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       6.62E+08       6.94E+08         -4.7
     300.       8.08E+08       8.01E+08          0.8
     350.       1.04E+09       9.85E+08          5.5
     400.       1.21E+09       1.15E+09          4.8
     450.       1.30E+09       1.30E+09          0.4
     500.       1.34E+09       1.43E+09         -6.1

H + C2H3Cl   =   C2H4 + Cl          T  273. K TO  500. K

         A =  6.31E+13      E =  2.00E+03 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       1.58E+12       1.58E+12          0.0
     300.       2.20E+12       2.20E+12          0.0
     350.       3.56E+12       3.56E+12          0.0
     400.       5.09E+12       5.09E+12          0.0
     450.       6.74E+12       6.74E+12          0.0
     500.       8.42E+12       8.42E+12          0.0

K-1(T) COMPLEX A DISSOC  T  273. K TO  500. K

         A =  7.64E+10      E =  3.20E+03 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       2.36E+08       2.09E+08         13.2
     300.       3.49E+08       3.55E+08         -1.7
     350.       6.64E+08       7.65E+08        -13.1
     400.       1.20E+09       1.36E+09        -11.5
     450.       2.11E+09       2.13E+09         -0.9
     500.       3.59E+09       3.04E+09         17.9
```

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

H + C2H3Cl   =   C2H4Cl              T  273. K TO  500. K

          A =  9.92E+11      E =  9.42E+02 CAL

     T          K EXP            K CALC          PERCENT ERROR
     273.       1.67E+11         1.75E+11          -4.7
     300.       2.06E+11         2.04E+11           0.8
     350.       2.70E+11         2.56E+11           5.5
     400.       3.18E+11         3.03E+11           4.8
     450.       3.48E+11         3.46E+11           0.4
     500.       3.61E+11         3.85E+11          -6.1

H + C2H3Cl   =   C2H4 + Cl           T  273. K TO  500. K

          A =  6.55E+13      E =  2.08E+03 CAL

     T          K EXP            K CALC          PERCENT ERROR
     273.       1.41E+12         1.41E+12           0.0
     300.       2.00E+12         2.00E+12           0.0
     350.       3.29E+12         3.29E+12           0.0
     400.       4.78E+12         4.78E+12           0.0
     450.       6.39E+12         6.39E+12           0.0
     500.       8.06E+12         8.06E+12           0.0

K-1(T) COMPLEX A DISSOC  T  273. K TO  500. K

          A =  8.11E+10      E =  3.29E+03 CAL

     T          K EXP            K CALC          PERCENT ERROR
     273.       2.12E+08         1.87E+08          13.3
     300.       3.17E+08         3.23E+08          -1.8
     350.       6.18E+08         7.12E+08         -13.1
     400.       1.14E+09         1.29E+09         -11.5
     450.       2.02E+09         2.04E+09          -0.8
     500.       3.47E+09         2.95E+09          17.9
```

ISOMACT INPUT FILE ---- REACTION: H + C2H3Cl2

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 + CH2ClCHCl

 A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
 C2H4Cl2             C2H4Cl + Cl         C2H3Cl + HCl

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

 FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
 797.2,                 18,

 HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                              2.98E+14,    0.0,  0.,

 COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
  98.96,                          5.57,          432.,

 THIRD BODY
 AR MASS (A.U.) DIAMETER(A) WELL DEPTH(K) ENERGY TRANS(CAL)
    39.95,      3.54,       93.3,         813.0,

 A(M-CC-S)       E (KCAL)
  1.2E+16,        94.5,         K-1
  5.02E+15,       78.1,         K2
  3.98E+13,       58.0,         K3
  0.0,            0.0,          K4
  0.0,            0.0,          K-4
  0.0,            0.0,          K5
  0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES T1      T2     T3    T4    T5     T6(K)
 6,                    273.   300.,  350., 400., 450.,  500.,

 NUMBER OF PRESSURES P1    P2    P3    P4    P5     P6 (TORR)
 6,                0.76, 2.7,  7.6,   76.,  760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + CH2ClCHCl  =  C2H4Cl2           T  273. K TO  500. K

        A =  2.05E+12     E = -1.51E+03 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       3.03E+13       3.29E+13          -8.1
    300.       2.60E+13       2.57E+13           1.4
    350.       1.96E+13       1.79E+13           9.8
    400.       1.48E+13       1.36E+13           8.4
    450.       1.11E+13       1.10E+13           0.6
    500.       8.36E+12       9.34E+12         -10.4

H + CH2ClCHCl  =  C2H4Cl + Cl       T  273. K TO  500. K

        A =  6.03E+13     E =  9.51E+02 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       1.12E+13       1.05E+13           6.8
    300.       1.21E+13       1.22E+13          -1.2
    350.       1.43E+13       1.54E+13          -7.0
    400.       1.72E+13       1.82E+13          -5.8
    450.       2.08E+13       2.08E+13          -0.2
    500.       2.51E+13       2.32E+13           8.5

H + CH2ClCHCl  =  C2H3Cl + HCl      T  273. K TO  500. K

        A =  2.78E+14     E =  4.03E+01 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       2.57E+14       2.58E+14          -0.6
    300.       2.60E+14       2.60E+14           0.0
    350.       2.64E+14       2.62E+14           0.7
    400.       2.66E+14       2.64E+14           0.7
    450.       2.66E+14       2.66E+14           0.1
    500.       2.64E+14       2.67E+14          -0.9
```

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

H + CH2ClCHCl  =  C2H4Cl2          T  273. K TO  500. K

        A =  2.34E+14     E = -1.22E+02 CAL

    T          K EXP         K CALC        PERCENT ERROR
    273.       2.89E+14      2.92E+14        -1.3
    300.       2.87E+14      2.87E+14         0.1
    350.       2.83E+14      2.78E+14         1.5
    400.       2.77E+14      2.72E+14         1.6
    450.       2.69E+14      2.68E+14         0.4
    500.       2.59E+14      2.64E+14        -2.1

H + CH2ClCHCl  =  C2H4Cl + Cl      T  273. K TO  500. K

        A =  5.73E+13     E =  2.76E+03 CAL

    T          K EXP         K CALC        PERCENT ERROR
    273.       4.13E+11      3.51E+11        17.6
    300.       5.37E+11      5.55E+11        -3.3
    350.       9.00E+11      1.08E+12       -16.4
    400.       1.53E+12      1.77E+12       -13.3
    450.       2.60E+12      2.60E+12        -0.1
    500.       4.31E+12      3.55E+12        21.4

H + CH2ClCHCl  =  C2H3Cl + HCl     T  273. K TO  500. K

        A =  1.62E+14     E =  1.61E+03 CAL

    T          K EXP         K CALC        PERCENT ERROR
    273.       8.97E+12      8.29E+12         8.2
    300.       1.07E+13      1.08E+13        -1.6
    350.       1.46E+13      1.59E+13        -8.4
    400.       1.98E+13      2.13E+13        -6.7
    450.       2.66E+13      2.67E+13        -0.1
    500.       3.51E+13      3.19E+13        10.0
```

ISOMACT INPUT FILE ---- H + C2H4

```
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                H2 +C2H3

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
1458,                  15,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N     E (CAL)
                             2.0E+14,      0.,   6.3,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
29.00,                         4.303,         220.2,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,           800.0,

A(M-CC-S)       E (KCAL)
 3.0E+12,        39.9,         K-1
 1.5E+14,        39.94,        K2
 0.0,            0.0,          K3
 0.0,            0.0,          K4
 0.0,            0.0,          K-4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES T1    T2    T3    T4     T5    T6(K)
6,                    273., 300., 350., 400.,  450., 500.,

NUMBER OF PRESSURES P1    P2    P3    P4    P5    P6 (TORR)
6,                0.76,  2.7,  7.6,   76., 760.  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + C2H4   =   C2H5                 T  273. K TO  500. K

        A =  8.01E+12      E = -1.01E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       4.88E+13       5.17E+13         -5.7
    300.       4.41E+13       4.37E+13          0.8
    350.       3.66E+13       3.43E+13          6.7
    400.       3.03E+13       2.86E+13          6.1
    450.       2.50E+13       2.48E+13          0.8
    500.       2.04E+13       2.22E+13         -7.8

H + C2H4   =  H2 +C2H3              T  273. K TO  500. K

        A =  2.16E+14      E =  2.15E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       1.46E+14       1.46E+14          0.3
    300.       1.51E+14       1.51E+14         -0.1
    350.       1.58E+14       1.59E+14         -0.3
    400.       1.65E+14       1.65E+14         -0.2
    450.       1.70E+14       1.70E+14          0.0
    500.       1.75E+14       1.74E+14          0.3

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

H + C2H4   =   C2H5                 T  273. K TO  500. K

        A =  1.82E+14      E = -4.20E+01 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       1.96E+14       1.97E+14         -0.6
    300.       1.95E+14       1.95E+14          0.0
    350.       1.95E+14       1.93E+14          0.7
    400.       1.93E+14       1.92E+14          0.8
    450.       1.91E+14       1.91E+14          0.2
    500.       1.88E+14       1.90E+14         -1.0

H + C2H4   =  H2 +C2H3              T  273. K TO  500. K

        A =  5.85E+13      E =  1.87E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       2.14E+12       1.88E+12         13.8
    300.       2.51E+12       2.56E+12         -1.9
    350.       3.46E+12       4.00E+12        -13.6
    400.       4.93E+12       5.60E+12        -11.9
    450.       7.21E+12       7.27E+12         -0.7
    500.       1.06E+13       8.95E+12         18.5
```

ISOMACT INPUT FILE ---- H + C2H4Cl

```
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 + C2H4Cl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
 C2H5Cl              C2H5 + Cl           C2H4 + HCl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
 1265.3,                18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                              2.16E+14,    0.,   0.,

COLLISION COMPLEX MASS(A.U.)  DIAMETER(A)   WELL DEPTH(K)
 64.515,                       5.4,           322,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
   39.95,       3.54,         93.3,              800.0,

A(M-CC-S)       E (KCAL)
 6.0E+15,        97.03,        K-1
 2.51E+13,       83.82,        K2
 3.16E+13,       57.2,         K3
 0.0,            0.0,          K4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES T1    T2    T3     T4    T5    T6(K)
6,                    273., 300., 350.,  400., 450., 500.,

NUMBER OF PRESSURES  P1   P2    P3    P4     P5    P6(TORR)
6,                 0.76, 2.7,  7.6,   76.,  760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + C2H4Cl  =  C2H5Cl            T  273. K TO  500. K

         A =  7.85E+11     E = -1.15E+03 CAL

    T         K EXP          K CALC         PERCENT ERROR
    273.      6.19E+12       6.52E+12          -5.1
    300.      5.44E+12       5.39E+12           0.8
    350.      4.34E+12       4.09E+12           6.0
    400.      3.50E+12       3.33E+12           5.2
    450.      2.85E+12       2.84E+12           0.5
    500.      2.33E+12       2.49E+12          -6.7

H + C2H4Cl  =  C2H5 + Cl         T  273. K TO  500. K

         A =  9.73E+10     E =  4.16E+02 CAL

    T         K EXP          K CALC         PERCENT ERROR
    273.      4.73E+10       4.52E+10           4.7
    300.      4.82E+10       4.84E+10          -0.4
    350.      5.08E+10       5.35E+10          -5.0
    400.      5.48E+10       5.76E+10          -4.9
    450.      6.06E+10       6.11E+10          -0.8
    500.      6.85E+10       6.40E+10           7.0

H + C2H4Cl  =  C2H4 + HCl        T  273. K TO  500. K

         A =  2.18E+14     E =  2.16E+01 CAL

    T         K EXP          K CALC         PERCENT ERROR
    273.      2.10E+14       2.10E+14           0.0
    300.      2.11E+14       2.11E+14           0.0
    350.      2.12E+14       2.12E+14           0.0
    400.      2.12E+14       2.12E+14           0.0
    450.      2.13E+14       2.13E+14           0.0
    500.      2.14E+14       2.14E+14           0.0
```

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

H + C2H4Cl   =  C2H5Cl            T  273. K TO  500. K

         A =  1.34E+14      E = -2.07E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       1.93E+14       1.96E+14         -1.7
    300.       1.90E+14       1.89E+14          0.2
    350.       1.84E+14       1.80E+14          1.9
    400.       1.77E+14       1.74E+14          1.9
    450.       1.69E+14       1.69E+14          0.3
    500.       1.61E+14       1.65E+14         -2.5

H + C2H4Cl   =  C2H5 + Cl         T  273. K TO  500. K

         A =  7.98E+10      E =  1.52E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       5.29E+09       4.80E+09         10.3
    300.       6.10E+09       6.18E+09         -1.3
    350.       7.98E+09       8.91E+09        -10.4
    400.       1.06E+10       1.17E+10         -9.3
    450.       1.44E+10       1.45E+10         -0.9
    500.       1.96E+10       1.72E+10         14.1

H + C2H4Cl   =  C2H4 + HCl        T  273. K TO  500. K

         A =  1.46E+14      E =  1.02E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       2.33E+13       2.23E+13          4.2
    300.       2.63E+13       2.64E+13         -0.7
    350.       3.23E+13       3.38E+13         -4.4
    400.       3.90E+13       4.05E+13         -3.7
    450.       4.67E+13       4.67E+13         -0.2
    500.       5.52E+13       5.24E+13          5.3
```

```
ISOMACT INPUT FILE ---- REACTION: H + C2H5
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 + C2H5

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
 C2H6                CH3 +CH3

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
 1458,                  18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                              2.66E+14,    0.,   0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
 30.07,                          4.9,           235,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
  39.95,       3.54,         93.3,             800.0,

A(M-CC-S)       E (KCAL)
 1.8E+16,        100.54,       K-1
 1.0E+17,        88.9,         K2
 0.0,            0.0,          K3
 0.0,            0.0,          K4
 0.0,            0.0,          K-4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES T1    T2    T3     T4    T5     T6(K)
6,                    273., 300., 350.,  400., 450.,   500.,

NUMBER OF PRESSURES  P1    P2     P3     P4      P5     P6 (TORR)
6,                 0.76, 2.7,  7.6,    76.,    760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + C2H5  =  C2H6               T  273. K TO  500. K

         A =  1.24E+12      E = -1.17E+03 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       1.01E+13       1.07E+13          -5.6
    300.       8.87E+12       8.80E+12           0.8
    350.       7.09E+12       6.65E+12           6.6
    400.       5.71E+12       5.39E+12           6.0
    450.       4.61E+12       4.58E+12           0.7
    500.       3.71E+12       4.02E+12          -7.7

H + C2H5  =  CH3 +CH3           T  273. K TO  500. K

         A =  2.70E+14      E =  2.93E+01 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       2.56E+14       2.56E+14           0.0
    300.       2.57E+14       2.57E+14           0.0
    350.       2.59E+14       2.59E+14           0.0
    400.       2.60E+14       2.60E+14           0.0
    450.       2.61E+14       2.61E+14           0.0
    500.       2.62E+14       2.62E+14           0.0

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

H + C2H5  =  C2H6               T  273. K TO  500. K

         A =  1.72E+14      E = -2.01E+02 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       2.44E+14       2.49E+14          -1.9
    300.       2.41E+14       2.40E+14           0.1
    350.       2.34E+14       2.29E+14           2.2
    400.       2.26E+14       2.21E+14           2.3
    450.       2.16E+14       2.15E+14           0.5
    500.       2.04E+14       2.10E+14          -3.0

H + C2H5  =  CH3 +CH3           T  273. K TO  500. K

         A =  1.94E+14      E =  1.21E+03 CAL

    T          K EXP          K CALC          PERCENT ERROR
    273.       2.22E+13       2.08E+13           6.4
    300.       2.52E+13       2.55E+13          -1.0
    350.       3.18E+13       3.40E+13          -6.7
    400.       3.99E+13       4.23E+13          -5.8
    450.       5.00E+13       5.01E+13          -0.3
    500.       6.22E+13       5.74E+13           8.4
```

```
ISOMACT INPUT FILE ---- REACTION: H + CCl3
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 + CCl3

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
CHCl3               CCl2 + HCl          CHCl2 + Cl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
1265,                  9,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N      E (CAL)
                              6.0E+13,   0.0,    1000.,

COLLISION COMPLEX MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)
 119.5,                         5.389,        340.2,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,             813.0,

A(M-CC-S)       E (KCAL)
 1.0E+15,        96.21,       K-1
 4.0E+13,        69.0,        K2
 1.3E+16,        79.8,        K3
 0.0,            0.0,         K4
 0.0,            0.0,         K-4
 0.0,            0.0,         K5
 0.0,            0.0,         K6

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

NUMBER OF TEMPERATURES  T1     T2     T3     T4     T5    T6(K)
6,                     273., 300.,  350., 400., 450., 500.,

NUMBER OFPRESSURES  P1     P2     P3    P4    P5     P6(TORR)
6,                 0.76,  2.7,   7.6,   76.,  760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + CCl3   =   CHCl3               T  273. K TO  500. K

         A =   2.98E+08      E = -1.11E+02 CAL

    T          K EXP            K CALC           PERCENT ERROR
    273.       3.49E+08        3.66E+08           -4.5
    300.       3.62E+08        3.59E+08            0.8
    350.       3.67E+08        3.49E+08            5.1
    400.       3.58E+08        3.42E+08            4.4
    450.       3.38E+08        3.37E+08            0.4
    500.       3.14E+08        3.33E+08           -5.8

H + CCl3   =   CCl2 + HCl          T  273. K TO  500. K

         A =   1.65E+12      E =   9.53E+02 CAL

    T          K EXP            K CALC           PERCENT ERROR
    273.       2.83E+11        2.84E+11           -0.6
    300.       3.33E+11        3.33E+11            0.0
    350.       4.21E+11        4.19E+11            0.6
    400.       5.00E+11        4.97E+11            0.6
    450.       5.68E+11        5.68E+11            0.1
    500.       6.26E+11        6.32E+11           -0.8

H + CCl3   =   CHCl2 + Cl          T  273. K TO  500. K

         A =   5.83E+13      E =   1.00E+03 CAL

    T          K EXP            K CALC           PERCENT ERROR
    273.       9.21E+12        9.21E+12            0.0
    300.       1.09E+13        1.09E+13            0.0
    350.       1.38E+13        1.38E+13            0.0
    400.       1.65E+13        1.66E+13            0.0
    450.       1.90E+13        1.90E+13            0.0
    500.       2.13E+13        2.13E+13            0.0
```

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

H + CCl3  =  CHCl3             T  273. K TO  500. K

        A =  8.40E+10     E = -1.04E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       9.73E+10       1.02E+11          -4.5
    300.       1.01E+11       1.00E+11           0.8
    350.       1.03E+11       9.76E+10           5.2
    400.       1.00E+11       9.58E+10           4.4
    450.       9.48E+10       9.44E+10           0.4
    500.       8.80E+10       9.33E+10          -5.8

H + CCl3  =  CCl2 + HCl        T  273. K TO  500. K

        A =  1.65E+12     E =  9.61E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       2.80E+11       2.82E+11          -0.6
    300.       3.30E+11       3.30E+11           0.0
    350.       4.18E+11       4.16E+11           0.6
    400.       4.97E+11       4.94E+11           0.6
    450.       5.66E+11       5.65E+11           0.1
    500.       6.24E+11       6.29E+11          -0.8

H + CCl3  =  CHCl2 + Cl        T  273. K TO  500. K

        A =  5.86E+13     E =  1.01E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       9.12E+12       9.12E+12           0.0
    300.       1.08E+13       1.08E+13           0.0
    350.       1.37E+13       1.37E+13           0.0
    400.       1.65E+13       1.65E+13           0.0
    450.       1.89E+13       1.89E+13           0.0
    500.       2.12E+13       2.12E+13           0.0
```

```
ISOMACT INPUT FILE ---- H + CHCl2
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 + CHCl2

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
CH2Cl2              CHCl + HCl           CH2Cl + H

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
1116.27,               9,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)     N     E (KCAL)
                              1.0E+14,      0.,    0.5,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
 84.93,                         4.898,         356.3,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,             800.0,

A(M-CC-S)       E (KCAL)
 6.0E+15,        101.1,        K-1
 3.98E+13,       111.74,       K2
 5.02E+15,       82.8,         K3
 0.0,            0.0,          K4
 0.0,            0.0,          K-4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES  T1    T2    T3    T4    T5    T6(K)
6,                     273., 300., 350., 400., 450., 500.,

NUMBER OF PRESSURES   P1    P2    P3    P4     P5     P6(TORR)
6,                  0.76,  2.7,  7.6,  76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + CHCl2  =  CH2Cl2           T  273. K TO  500. K

         A =  1.81E+09      E = -6.68E+02 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       5.89E+09      6.19E+09         -4.9
     300.       5.59E+09      5.54E+09          0.9
     350.       4.99E+09      4.72E+09          5.7
     400.       4.40E+09      4.19E+09          4.9
     450.       3.83E+09      3.82E+09          0.4
     500.       3.32E+09      3.54E+09         -6.4

H + CHCl2  =  CHCl + HCl       T  273. K TO  500. K

         A =  4.78E+10      E =  1.33E+04 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       1.16E+00      1.16E+00          0.0
     300.       1.05E+01      1.05E+01          0.0
     350.       2.51E+02      2.51E+02          0.0
     400.       2.72E+03      2.72E+03          0.0
     450.       1.74E+04      1.74E+04          0.0
     500.       7.65E+04      7.65E+04          0.0

H + CHCl2  =  CH2Cl + H        T  273. K TO  500. K

         A =  9.98E+13      E =  4.99E+02 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       3.98E+13      3.98E+13          0.0
     300.       4.32E+13      4.32E+13          0.0
     350.       4.87E+13      4.87E+13          0.0
     400.       5.33E+13      5.33E+13          0.0
     450.       5.71E+13      5.71E+13          0.0
     500.       6.04E+13      6.04E+13          0.0

K-1(T) COMPLEX A DISSOC  T  273. K TO  500. K

         A =  2.68E+11      E =  1.42E+03 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       2.12E+10      1.94E+10          9.3
     300.       2.42E+10      2.46E+10         -1.3
     350.       3.13E+10      3.46E+10         -9.5
     400.       4.10E+10      4.46E+10         -8.2
     450.       5.42E+10      5.45E+10         -0.5
     500.       7.17E+10      6.39E+10         12.2
```

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

H + CHCl2  =  CH2Cl2           T  273. K TO  500. K

         A =  5.15E+11     E = -6.39E+02 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       1.59E+12      1.67E+12        -4.9
     300.       1.52E+12      1.51E+12         0.9
     350.       1.37E+12      1.29E+12         5.7
     400.       1.21E+12      1.15E+12         4.9
     450.       1.06E+12      1.05E+12         0.4
     500.       9.18E+11      9.81E+11        -6.4

H + CHCl2  =  CHCl + HCl       T  273. K TO  500. K

         A =  4.79E+10     E =  1.33E+04 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       1.15E+00      1.15E+00         0.0
     300.       1.04E+01      1.04E+01         0.0
     350.       2.50E+02      2.50E+02         0.0
     400.       2.71E+03      2.71E+03         0.0
     450.       1.73E+04      1.73E+04         0.0
     500.       7.63E+04      7.63E+04         0.0

H + CHCl2  =  CH2Cl + H       T  273. K TO  500. K

         A =  1.01E+14     E =  5.30E+02 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       3.82E+13      3.82E+13         0.0
     300.       4.17E+13      4.17E+13         0.0
     350.       4.73E+13      4.73E+13         0.0
     400.       5.21E+13      5.21E+13         0.0
     450.       5.61E+13      5.61E+13         0.0
     500.       5.95E+13      5.95E+13         0.0

K-1(T) COMPLEX A DISSOC  T  273. K TO  500. K

         A =  2.74E+11     E =  1.46E+03 CAL

     T          K EXP         K CALC        PERCENT ERROR
     273.       2.04E+10      1.87E+10         9.3
     300.       2.34E+10      2.38E+10        -1.4
     350.       3.05E+10      3.37E+10        -9.5
     400.       4.02E+10      4.38E+10        -8.2
     450.       5.34E+10      5.37E+10        -0.5
     500.       7.09E+10      6.32E+10        12.2
```

ISOMACT INPUT FILE ---- REACTION: CHCl2 + CHCl2

```
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)
CHCl2 + CHCl2

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H2Cl4             CHCl2CHCl + Cl      C2HCl3 + HCl

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

FREQ (FREQUENCY)(HZ)    NS (WAVENUMBERS)
578.23,                 18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N     E (CAL)
                             3.62E+11,     0.0,  0.0,

COLLISION COMPLEX MASS(A.U.)    DIAMETER(A)    WELL DEPTH(K)
 167.86                          6.5,            500,

THIRD BODY
AR MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)   ENERGY TRANS(CAL)
   39.95,        3.54,          93.3,               800.0,

A(M-CC-S)        E (KCAL)
 2.51E+17,        86.6,          K-1
 3.16E+15,        74.6,          K2
 5.0E+13,         53.74,         K3
 0.0,             0.0,           K4
 0.0,             0.0,           K-4
 0.0,             0.0,           K5
 0.0,             0.0,           K6

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

NUMBER OF TEMPERATURE    T1     T2     T3     T4     T5     T6(K)
6,                      273.,  300.,  350.,  400.,  450.,  500.,

NUMBER OF PRESSURE    P1     P2     P3     P4     P5     P6(TORR)
6,                  0.76,  2.7,   7.6,   76.,  760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

CHCl2 + CHCl2  =  C2H2Cl4          T  273. K TO  500. K

         A =  4.73E+09      E = -1.70E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       9.72E+10       1.08E+11         -9.8
    300.       8.29E+10       8.14E+10          1.8
    350.       6.08E+10       5.42E+10         12.1
    400.       4.40E+10       4.00E+10         10.2
    450.       3.17E+10       3.15E+10          0.6
    500.       2.28E+10       2.61E+10        -12.4

CHCl2 + CHCl2  =  CHCl2CHCl + Cl    T  273. K TO  500. K

         A =  4.86E+10      E =  2.04E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       1.23E+09       1.12E+09          9.7
    300.       1.54E+09       1.58E+09         -2.1
    350.       2.32E+09       2.57E+09         -9.6
    400.       3.44E+09       3.71E+09         -7.5
    450.       4.94E+09       4.94E+09          0.1
    500.       6.91E+09       6.21E+09         11.3

CHCl2 + CHCl2  =  C2HCl3 + HCl      T  273. K TO  500. K

         A =  4.43E+11      E =  2.79E+02 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       2.64E+11       2.65E+11         -0.6
    300.       2.78E+11       2.78E+11          0.0
    350.       2.99E+11       2.97E+11          0.7
    400.       3.14E+11       3.12E+11          0.7
    450.       3.25E+11       3.25E+11          0.2
    500.       3.32E+11       3.35E+11         -1.0
```

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

CHCl2 + CHCl2   =  C2H2Cl4           T  273. K TO  500. K

        A =  3.19E+11      E = -6.69E+01 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       3.58E+11       3.61E+11         -0.8
    300.       3.57E+11       3.57E+11          0.0
    350.       3.55E+11       3.51E+11          0.9
    400.       3.51E+11       3.47E+11          1.0
    450.       3.45E+11       3.44E+11          0.3
    500.       3.37E+11       3.41E+11         -1.3

CHCl2 + CHCl2   =  CHCl2CHCl + Cl    T  273. K TO  500. K

        A =  4.84E+10      E =  4.33E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       2.03E+07       1.64E+07         23.8
    300.       3.21E+07       3.37E+07         -4.8
    350.       7.53E+07       9.52E+07        -20.8
    400.       1.74E+08       2.07E+08        -16.3
    450.       3.82E+08       3.80E+08          0.4
    500.       7.88E+08       6.17E+08         27.7

CHCl2 + CHCl2   =  C2HCl3 + HCl      T  273. K TO  500. K

        A =  1.97E+11      E =  2.21E+03 CAL

    T          K EXP          K CALC         PERCENT ERROR
    273.       3.72E+09       3.34E+09         11.4
    300.       4.71E+09       4.82E+09         -2.2
    350.       7.27E+09       8.19E+09        -11.2
    400.       1.11E+10       1.22E+10         -9.0
    450.       1.66E+10       1.66E+10         -0.1
    500.       2.42E+10       2.13E+10         13.7
```

ISOMACT INPUT FILE ---- REACTION: CHCl2 + CH2Cl

```
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)
CHCl2 + CH2Cl

A* (RECOMBINATION)   P2 (1ST A* DECOMP)   P3 (2ND A* DECOMP)
CHCl2CH2Cl           CHClCH2Cl + Cl       CHClCHCl + HCl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
699.95,                18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N      E (CAL)
                             1.0E+13,      0.,    0.,

COLLISION COMPLEX MASS(A.U.)    DIAMETER(A)    WELL DEPTH(K)
 133.4,                          6.15,           463.5,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
   39.95,       3.54,        93.3,               800.0,

A(M-CC-S)        E (KCAL)
 1.33E+18,        88.2,         K-1
 6.0E+15,         71.7,         K2
 1.26E+14,        50.0,         K3
 0.0,             0.0,          K4
 0.0,             0.0,          K-4
 0.0,             0.0,          K5
 0.0,             0.0,          K6

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

NUMBER OF TEMPERATURES   T1     T2     T3     T4     T5     T6(K)
6,                      273., 300.,  350.,  400.,  450.,  500.,

NUMBER OF PRESSURES   P1     P2     P3     P4     P5     P6(TORR)
6,                  0.76,  2.7,   7.6,   76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

CHCl2 + CH2Cl  =  CHCl2CH2Cl        T  273. K TO  500. K

         A =  7.65E+09      E = -1.63E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       1.42E+11       1.54E+11          -8.0
     300.       1.19E+11       1.18E+11           1.5
     350.       8.73E+10       7.96E+10           9.6
     400.       6.43E+10       5.94E+10           8.1
     450.       4.76E+10       4.73E+10           0.5
     500.       3.55E+10       3.94E+10         -10.1

CHCl2 + CH2Cl  =  CHClCH2Cl + Cl    T  273. K TO  500. K

         A =  6.09E+11      E =  1.18E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       7.52E+10       6.92E+10           8.6
     300.       8.29E+10       8.42E+10          -1.6
     350.       1.02E+11       1.12E+11          -8.7
     400.       1.28E+11       1.38E+11          -7.2
     450.       1.62E+11       1.63E+11          -0.3
     500.       2.06E+11       1.86E+11          10.7

CHCl2 + CH2Cl  =  CHClCHCl + HCl    T  273. K TO  500. K

         A =  9.75E+12      E = -2.79E+00 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       9.78E+12       9.80E+12          -0.2
     300.       9.80E+12       9.80E+12           0.0
     350.       9.81E+12       9.79E+12           0.2
     400.       9.81E+12       9.78E+12           0.2
     450.       9.79E+12       9.78E+12           0.0
     500.       9.75E+12       9.78E+12          -0.3
```

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

CHCl2 + CH2Cl   =  CHCl2CH2Cl         T  273. K TO  500. K

         A =  2.85E+12      E = -5.87E+02 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       7.97E+12       8.39E+12          -5.0
     300.       7.66E+12       7.62E+12           0.6
     350.       7.01E+12       6.62E+12           5.9
     400.       6.28E+12       5.95E+12           5.6
     450.       5.53E+12       5.49E+12           0.8
     500.       4.77E+12       5.14E+12          -7.1

CHCl2 + CH2Cl   =  CHClCH2Cl + Cl     T  273. K TO  500. K

         A =  1.18E+12      E =  2.38E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       1.64E+10       1.47E+10          11.8
     300.       2.12E+10       2.18E+10          -2.7
     350.       3.41E+10       3.85E+10         -11.5
     400.       5.40E+10       5.91E+10          -8.7
     450.       8.27E+10       8.25E+10           0.3
     500.       1.22E+11       1.08E+11          13.4

CHCl2 + CH2Cl   =  CHClCHCl + HCl     T  273. K TO  500. K

         A =  1.52E+13      E =  1.11E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       2.01E+12       1.95E+12           3.2
     300.       2.32E+12       2.34E+12          -1.0
     350.       2.96E+12       3.06E+12          -3.3
     400.       3.66E+12       3.74E+12          -2.1
     450.       4.39E+12       4.37E+12           0.4
     500.       5.10E+12       4.95E+12           3.0
```

ISOMACT INPUT FILE ---- REACTION: CH2Cl +CH2Cl

```
RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION)
USING QRRK

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

R (REACTANTS)
CH2Cl + CH2Cl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H4Cl2             C2H4Cl + Cl         C2H3Cl + HCl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
797.2,                 18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                             1.24E+12,   0.0,   0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
  98.96,                         5.57,          432.,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,             800.0,

A(M-CC-S)       E (KCAL)
 1.58E+17,       91.2,          K-1
 5.02E+15,       78.1,          K2
 3.98E+13,       58.0,          K3
 0.0,            0.0,           K4
 0.0,            0.0,           K-4
 0.0,            0.0,           K5
 0.0,            0.0,           K6

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

NUMBER OF TEMPERATURES    T1    T2    T3    T4    T5    T6(K)
6,                      273., 300.,  350., 400., 450., 500.,

NUMBER OF PRESSURES   P1     P2     P3     P4     P5     P6(TORR)
6,                  0.76,  2.7,    7.6,   76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

CH2Cl + CH2Cl  =  C2H4Cl2           T  273. K TO  500. K

         A =  1.22E+10     E = -1.49E+03 CAL

     T          K EXP          K CALC          PERENT ERROR
     273.       1.76E+11       1.92E+11          -8.3
     300.       1.52E+11       1.50E+11           1.4
     350.       1.15E+11       1.05E+11          10.0
     400.       8.69E+10       8.00E+10           8.6
     450.       6.54E+10       6.49E+10           0.7
     500.       4.91E+10       5.49E+10          -0.7

CH2Cl + CH2Cl  =  C2H4Cl + Cl       T  273. K TO  500. K

         A =  2.13E+11     E =  1.14E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       2.79E+10       2.59E+10           7.9
     300.       3.09E+10       3.13E+10          -1.4
     350.       3.79E+10       4.12E+10          -8.0
     400.       4.72E+10       5.06E+10          -6.6
     450.       5.92E+10       5.93E+10          -0.2
     500.       7.40E+10       6.74E+10           9.8

CH2Cl + CH2Cl  =  C2H3Cl + HCl      T  273. K TO  500. K

         A =  1.23E+12     E =  9.20E+01 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       1.04E+12       1.04E+12          -0.5
     300.       1.06E+12       1.06E+12           0.0
     350.       1.09E+12       1.08E+12           0.6
     400.       1.11E+12       1.10E+12           0.6
     450.       1.11E+12       1.11E+12           0.1
     500.       1.12E+12       1.12E+12          -0.8
```

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

CH2Cl + CH2Cl   =  C2H4Cl2           T  273. K TO  500. K

          A =  1.04E+12     E = -9.04E+01 CAL

     T         K EXP          K CALC         PERCENT ERROR
     273.      1.21E+12       1.23E+12         -1.0
     300.      1.21E+12       1.21E+12          0.0
     350.      1.19E+12       1.18E+12          1.1
     400.      1.18E+12       1.16E+12          1.2
     450.      1.15E+12       1.15E+12          0.3
     500.      1.12E+12       1.14E+12         -1.6

CH2Cl + CH2Cl   =  C2H4Cl + Cl       T  273. K TO  500. K

          A =  1.77E+11     E =  3.06E+03 CAL

     T         K EXP          K CALC         PERCENT ERROR
     273.      7.59E+08       6.33E+08         20.0
     300.      1.01E+09       1.05E+09         -3.6
     350.      1.79E+09       2.18E+09        -18.3
     400.      3.22E+09       3.78E+09        -14.8
     450.      5.79E+09       5.80E+09         -0.1
     500.      1.02E+10       8.16E+09         24.5

CH2Cl + CH2Cl   =  C2H3Cl + HCl      T  273. K TO  500. K

          A =  5.63E+11     E =  1.71E+03 CAL

     T         K EXP          K CALC         PERCENT ERROR
     273.      2.63E+10       2.41E+10          9.2
     300.      3.15E+10       3.20E+10         -1.7
     350.      4.37E+10       4.82E+10         -9.2
     400.      6.06E+10       6.55E+10         -7.6
     450.      8.31E+10       8.32E+10         -0.2
     500.      1.12E+11       1.01E+11         11.3
```

```
ISOMACT INPUT FILE ---- REACTION: CH3 + CH2Cl
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 + CH2Cl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
C2H5Cl              C2H5 + Cl           C2H4 + HCl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
1265.3,                18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N      E (CAL)
                             1.23E+13,     0.,    0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
  64.515,                        5.4,           322,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
   39.95,        3.54,         93.3,             800.0,

A(M-CC-S)        E (KCAL)
 1.00E+17,        91.64,        K-1
 3.0E+15,         83.82,        K2
 3.16E+13,        57.2,         K3
 0.0,             0.0,          K4
 0.0,             0.0,          K-4
 0.0,             0.0,          K5
 0.0,             0.0,          K6

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

NUMBER OF TEMPERATURES    T1    T2    T3    T4    T5    T6(K)
6,                      273., 300., 350., 400., 450., 500.,

NUMBER OF PRESSURES   P1     P2     P3     P4     P5     P6(TORR)
6,                  0.76,  2.7,   7.6,   76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

CH3 + CH2Cl   =   C2H5Cl             T   273. K TO   500. K

          A =   1.09E+11      E = -1.15E+03 CAL

     T           K EXP           K CALC          PERCENT ERROR
     273.        8.55E+11        9.04E+11          -5.5
     300.        7.53E+11        7.47E+11           0.9
     350.        6.04E+11        5.67E+11           6.4
     400.        4.88E+11        4.61E+11           5.7
     450.        3.95E+11        3.93E+11           0.6
     500.        3.21E+11        3.46E+11          -7.2

CH3 + CH2Cl   =   C2H5 + Cl          T   273. K TO   500. K

          A =   2.06E+11      E =  7.00E+02 CAL

     T           K EXP           K CALC          PERCENT ERROR
     273.        6.11E+10        5.68E+10           7.5
     300.        6.33E+10        6.38E+10          -0.8
     350.        6.95E+10        7.55E+10          -7.9
     400.        7.93E+10        8.56E+10          -7.4
     450.        9.35E+10        9.44E+10          -0.9
     500.        1.13E+11        1.02E+11          10.8

CH3 + CH2Cl   =   C2H4 + HCl         T   273. K TO   500. K

          A =   1.24E+13      E =  4.54E+01 CAL

     T           K EXP           K CALC          PERCENT ERROR
     273.        1.14E+13        1.14E+13          -0.1
     300.        1.15E+13        1.15E+13           0.0
     350.        1.16E+13        1.16E+13           0.1
     400.        1.17E+13        1.17E+13           0.1
     450.        1.18E+13        1.18E+13           0.0
     500.        1.18E+13        1.18E+13          -0.2
```

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

CH3 + CH2Cl   =   C2H5Cl            T   273. K TO   500. K

          A =   9.84E+12      E = -1.01E+02 CAL

     T           K EXP          K CALC          PERCENT ERROR
     273.        1.17E+13       1.18E+13          -0.9
     300.        1.17E+13       1.17E+13           0.1
     350.        1.15E+13       1.14E+13           1.0
     400.        1.13E+13       1.12E+13           1.1
     450.        1.10E+13       1.10E+13           0.2
     500.        1.07E+13       1.09E+13          -1.4

CH3 + CH2Cl   =   C2H5 + Cl         T   273. K TO   500. K

          A =   1.28E+11      E =   2.11E+03 CAL

     T           K EXP          K CALC          PERCENT ERROR
     273.        3.05E+09       2.62E+09          16.7
     300.        3.63E+09       3.71E+09          -2.1
     350.        5.18E+09       6.16E+09         -16.0
     400.        7.72E+09       9.00E+09         -14.2
     450.        1.19E+10       1.21E+10          -1.2
     500.        1.88E+10       1.53E+10          22.9

CH3 + CH2Cl   =   C2H4 + HCl        T   273. K TO   500. K

          A =   4.73E+12      E =   1.19E+03 CAL

     T           K EXP          K CALC          PERCENT ERROR
     273.        5.58E+11       5.27E+11           5.8
     300.        6.36E+11       6.42E+11          -0.9
     350.        8.02E+11       8.54E+11          -6.1
     400.        1.00E+12       1.06E+12          -5.3
     450.        1.24E+12       1.25E+12          -0.4
     500.        1.54E+12       1.43E+12           7.7
```

```
ISOMACT INPUT FILE ---- REACTION: CH3 + CH3
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)
1458,                  18,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                             2.51E+13,    0.,   0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
   30.07,                         4.9,            235,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
   39.95,       3.54,         93.3,             800.0,

A(M-CC-S)       E (KCAL)
 1.0E+17,        88.8,          K-1
 1.8E+16,        98.2,          K2
 0.0,            0.0,           K3
 0.0,            0.0,           K4
 0.0,            0.0,           K-4
 0.0,            0.0,           K5
 0.0,            0.0,           K6

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

NUMBER OF TEMPERATURES    T1    T2    T3    T4    T5    T6(K)
6,                      273., 300.,  350., 400., 450., 500.,

NUMBER OF PRESSURES   P1     P2    P3    P4    P5    P6(TORR)
6,                  0.76,  2.7,  7.6,   76.,  760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

CH3 + CH3   =   C2H6                T  273. K TO  500. K

         A =  1.23E+13      E = -3.43E+02 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       2.24E+13       2.32E+13          -3.6
     300.       2.20E+13       2.19E+13           0.2
     350.       2.10E+13       2.02E+13           4.1
     400.       1.98E+13       1.90E+13           4.3
     450.       1.83E+13       1.81E+13           0.9
     500.       1.65E+13       1.74E+13          -5.5

CH3 + CH3   =   C2H5 + H            T  273. K TO  500. K

         A =  4.59E+12      E =  1.25E+04 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       4.22E+02       4.22E+02           0.0
     300.       3.38E+03       3.38E+03           0.0
     350.       6.81E+04       6.81E+04           0.0
     400.       6.48E+05       6.48E+05           0.0
     450.       3.74E+06       3.74E+06           0.0
     500.       1.52E+07       1.52E+07           0.0

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

CH3 + CH3   =   C2H6                T  273. K TO  500. K

         A =  2.49E+13      E = -4.46E+00 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       2.51E+13       2.51E+13          -0.1
     300.       2.51E+13       2.51E+13           0.0
     350.       2.51E+13       2.51E+13           0.1
     400.       2.51E+13       2.50E+13           0.1
     450.       2.50E+13       2.50E+13           0.0
     500.       2.50E+13       2.50E+13          -0.1

CH3 + CH3   =   C2H5 + H            T  273. K TO  500. K

         A =  3.30E+12      E =  1.37E+04 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       3.66E+01       3.44E+01           6.4
     300.       3.31E+02       3.34E+02          -1.0
     350.       8.35E+03       8.95E+03          -6.7
     400.       9.93E+04       1.05E+05          -5.8
     450.       7.15E+05       7.17E+05          -0.3
     500.       3.60E+06       3.33E+06           8.4
```

```
ISOMACT INPUT FILE ---- REACTION: H + CH2Cl
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 + CH2Cl

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
CH3Cl               CH2 + HCl           CH3 + Cl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
1575,                  9,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N      E (CAL)
                             1.0E+14,   0.0,     0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
  50.49,                         4.18,           350.,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)    ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,             813.0,

A(M-CC-S)       E (KCAL)
 8.97E+15,       103.8          K-1
 3.98E+13,       130.9,         K2
 2.5E+15,        84.6,          K3
 0.0,            0.0,           K4
 0.0,            0.0,           K-4
 0.0,            0.0,           K5
 0.0,            0.0,           K6

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

NUMBER OF TEMPERATURES   T1     T2     T3     T4     T5     T6(K)
6,                      273., 300., 350., 400., 450.,    500.,

NUMBER OF PRESSURES   P1     P2     P3     P4     P5     P6(TORR)
6,                  0.76,  2.7,   7.6,   76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

H + CH2Cl  =  CH3Cl              T  273. K TO  500. K

          A =  2.24E+09     E = -1.05E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       1.49E+10       1.55E+10          -3.8
     300.       1.31E+10       1.30E+10           0.7
     350.       1.06E+10       1.01E+10           4.4
     400.       8.70E+09       8.38E+09           3.7
     450.       7.26E+09       7.24E+09           0.3
     500.       6.12E+09       6.44E+09          -4.9

H + CH2Cl  =  CH2 + HCl          T  273. K TO  500. K

          A =  9.06E+10     E =  2.70E+04 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       2.04E-11       2.04E-11           0.3
     300.       1.81E-09       1.81E-09           0.0
     350.       1.18E-06       1.18E-06          -0.3
     400.       1.52E-04       1.52E-04          -0.3
     450.       6.66E-03       6.67E-03          -0.1
     500.       1.38E-01       1.37E-01           0.4

H + CH2Cl  =  CH3 + Cl           T  273. K TO  500. K

          A =  9.90E+13     E = -1.74E+00 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       9.93E+13       9.93E+13           0.0
     300.       9.93E+13       9.93E+13           0.0
     350.       9.92E+13       9.92E+13           0.0
     400.       9.92E+13       9.92E+13           0.0
     450.       9.92E+13       9.92E+13           0.0
     500.       9.91E+13       9.91E+13           0.0
```

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

H + CH2Cl  =  CH3Cl              T  273. K TO  500. K

         A =  6.37E+11      E = -1.02E+03 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       4.03E+12       4.19E+12         -3.8
     300.       3.56E+12       3.53E+12          0.7
     350.       2.89E+12       2.77E+12          4.4
     400.       2.39E+12       2.30E+12          3.7
     450.       2.00E+12       2.00E+12          0.3
     500.       1.69E+12       1.78E+12         -4.9

H + CH2Cl  =  CH2 + HCl          T  273. K TO  500. K

         A =  9.06E+10      E =  2.70E+04 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       2.04E-11       2.03E-11          0.3
     300.       1.81E-09       1.81E-09          0.0
     350.       1.17E-06       1.18E-06         -0.3
     400.       1.52E-04       1.52E-04         -0.3
     450.       6.66E-03       6.66E-03         -0.1
     500.       1.38E-01       1.37E-01          0.4

H + CH2Cl  =  CH3 + Cl           T  273. K TO  500. K

         A =  1.00E+14      E =  2.68E+01 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       9.53E+13       9.53E+13          0.0
     300.       9.57E+13       9.57E+13          0.0
     350.       9.64E+13       9.64E+13          0.0
     400.       9.69E+13       9.68E+13          0.0
     450.       9.72E+13       9.72E+13          0.0
     500.       9.74E+13       9.75E+13          0.0
```

ISOMACT INPUT FILE ---- REACTION: Cl + CH2Cl

```
RECOMBINATION AND DECOMPOSITION (WITH ISOMERIZATION)
USING QRRK

            P2      P3        P5
            \       /         |
             \K2   /K3        |
         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              CHCl + HCl           CHCl2 + H

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
1116.27,               9,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)    N     E (CAL)
                             9.56E+12,     0.,   0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
  84.93,                         4.898,         356.3,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,              800.0,

A(M-CC-S)       E (KCAL)
 5.02E+15,       82.8,          K-1
 3.98E+13,       111.74,        K2
 6.0E+15,        100.6,         K3
 0.0,            0.0,           K4
 0.0,            0.0,           K-4
 0.0,            0.0,           K5
 0.0,            0.0,           K6

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

NUMBER OF TEMPERATURES    T1     T2     T3     T4     T5     T6(K)
6,                       273.,  300.,  350.,  400.,  450.,   500.,

NUMBER OF PRESSURES    P1     P2     P3     P4     P5     P6(TORR)
6,                   0.76,  2.7,   7.6,   76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

Cl + CH2Cl   =   CH2Cl2              T  273. K TO  500. K

          A =   8.08E+10     E = -1.27E+03 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       7.87E+11       8.43E+11          -6.6
     300.       6.90E+11       6.83E+11           1.0
     350.       5.43E+11       5.03E+11           7.9
     400.       4.28E+11       4.00E+11           7.0
     450.       3.37E+11       3.35E+11           0.7
     500.       2.65E+11       2.91E+11          -8.8

Cl + CH2Cl   =   CHCl + HCl          T  273. K TO  500. K

          A =   7.49E+10     E =  2.87E+04 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       7.55E-13       7.55E-13           0.0
     300.       8.86E-11       8.86E-11           0.0
     350.       8.66E-08       8.65E-08           0.0
     400.       1.51E-05       1.51E-05           0.0
     450.       8.38E-04       8.38E-04           0.0
     500.       2.08E-02       2.08E-02           0.0

Cl + CH2Cl   =   CHCl2 + H          T  273. K TO  500. K

          A =   1.14E+13     E =  1.91E+04 CAL

     T          K EXP          K CALC          PERCENT ERROR
     273.       5.32E-03       5.32E-03           0.0
     300.       1.27E-01       1.27E-01           0.0
     350.       1.25E+01       1.25E+01           0.0
     400.       3.92E+02       3.92E+02           0.0
     450.       5.70E+03       5.70E+03           0.0
     500.       4.85E+04       4.85E+04           0.0
```

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

Cl + CH2Cl   =   CH2Cl2             T  273. K TO  500. K

         A =   6.53E+12      E = -1.96E+02 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       9.16E+12       9.37E+12         -2.2
     300.       9.08E+12       9.07E+12          0.1
     350.       8.87E+12       8.65E+12          2.5
     400.       8.57E+12       8.35E+12          2.6
     450.       8.17E+12       8.13E+12          0.5
     500.       7.68E+12       7.95E+12         -3.4

Cl + CH2Cl   =   CHCl + HCl         T  273. K TO  500. K

         A =   7.51E+10      E =  2.87E+04 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       7.49E-13       7.49E-13          0.0
     300.       8.80E-11       8.80E-11          0.0
     350.       8.61E-08       8.60E-08          0.0
     400.       1.50E-05       1.50E-05          0.0
     450.       8.35E-04       8.35E-04          0.0
     500.       2.07E-02       2.07E-02          0.0

Cl + CH2Cl   =   CHCl2 + H         T  273. K TO  500. K

         A =   1.16E+13      E =  1.92E+04 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       5.13E-03       5.13E-03          0.0
     300.       1.24E-01       1.24E-01          0.0
     350.       1.22E+01       1.22E+01          0.0
     400.       3.84E+02       3.84E+02          0.0
     450.       5.61E+03       5.61E+03          0.0
     500.       4.79E+04       4.79E+04          0.0
```

```
ISOMACT INPUT FILE ---- REACTION: Cl + CHCl2
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 +CHCl2

A* (RECOMBINATION)  P2 (1ST A* DECOMP)  P3 (2ND A* DECOMP)
CHCl3               CCl2 + HCl

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

FREQ (FREQUENCY)(HZ)   NS (WAVENUMBERS)
709.38,                9,

HIGH PRESSURE RATE CONSTANT: A (M-CC-S)   N     E (CAL)
                             2.00E+12,    0.,   0.,

COLLISION COMPLEX MASS(A.U.)   DIAMETER(A)   WELL DEPTH(K)
  119.38,                        5.389,         340.2,

THIRD BODY
AR MASS(A.U.)  DIAMETER(A)  WELL DEPTH(K)  ENERGY TRANS(CAL)
    39.95,       3.54,         93.3,              800.0,

A(M-CC-S)       E (KCAL)
 2.51E+15,       78.8,         K-1
 3.98E+13,       69.0,         K2
 0.0,            0.0,          K3
 0.0,            0.0,          K4
 0.0,            0.0,          K-4
 0.0,            0.0,          K5
 0.0,            0.0,          K6

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

NUMBER OF TEMPERATURES  T1    T2    T3    T4    T5    T6(K)
6,                     273., 300., 350., 400., 450., 500.,

NUMBER OF PRESSURES  P1     P2     P3     P4     P5     P6(TORR)
6,                 0.76,  2.7,   7.6,   76.,   760.,  7600.,
```

```
ARRHENIUS PARAMETERS FOR APPARENT RATE CONTANTS FOR
   P = 2.70E+00 TORR

Cl + CHCl2  =  CHCl3             T  273. K TO  500. K

         A =  1.48E+10      E = -1.57E+03 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       2.43E+11       2.65E+11         -8.4
     300.       2.08E+11       2.05E+11          1.5
     350.       1.55E+11       1.41E+11         10.1
     400.       1.15E+11       1.06E+11          8.6
     450.       8.57E+10       8.52E+10          0.6
     500.       6.39E+10       7.15E+10        -10.6

Cl + CHCl2  =  CCl2 + HCl        T  273. K TO  500. K

         A =  1.44E+12      E = -7.62E+01 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       1.63E+12       1.66E+12         -1.8
     300.       1.64E+12       1.64E+12          0.2
     350.       1.64E+12       1.61E+12          2.1
     400.       1.62E+12       1.58E+12          1.9
     450.       1.57E+12       1.57E+12          0.3
     500.       1.51E+12       1.55E+12         -2.6

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

Cl +CHCl2  =  CHCl3              T  273. K TO  500. K

         A =  1.46E+12      E = -1.64E+02 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       1.94E+12       1.98E+12         -1.9
     300.       1.93E+12       1.93E+12          0.1
     350.       1.89E+12       1.85E+12          2.2
     400.       1.84E+12       1.80E+12          2.3
     450.       1.77E+12       1.76E+12          0.5
     500.       1.67E+12       1.73E+12         -3.0

Cl +CHCl2  =  CCl2 + HCl         T  273. K TO  500. K

         A =  1.10E+12      E =  1.71E+03 CAL

     T          K EXP          K CALC         PERCENT ERROR
     273.       5.08E+10       4.74E+10          7.2
     300.       6.18E+10       6.30E+10         -1.8
     350.       8.78E+10       9.47E+10         -7.3
     400.       1.22E+11       1.29E+11         -5.2
     450.       1.64E+11       1.63E+11          0.5
     500.       2.13E+11       1.98E+11          7.6
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