ABSTRACT

Title of Thesis: Thermal Decomposition of Dichloromethane/ 1,1,1-Trichloroethane Mixture in an Atmosphere of Hydrogen

Yang Soo Won, Master of Science in Environmental Science, 1988

Thesis Directed by Dr. J .W. Bozzelli

Thethermal decomposition of a dichloromethane/1,1,1-trichloroethane mixture diluted in hydrogen was conducted in tubular flow reactors at 1 atmosphere total pressure. The thermal degradation of each species was analyzed systematically over temperature ranges from 475 - 810 ^{o}C, residence times of 0.05 - 2.0 seconds and three different surface to volume ratio flow reactors.

It was found that the conversions of each species in the mixture were a function of both temperature and residence time. Complete decay occurs at about 810 ^{o}C for dichloromethane and around 570 ^{o}C for 1,1,1-trichloroethane at 1 second residence time. The major products observed were dichloroethylene, vinyl chloride, methyl chloride and dichloroethane at about 570 ^{o}C. Ethylene, methane, ethane, methyl chloride and HCl were the products at more complete conversions which occured near 810 ^{o}C and above. The hydrocarbon production increased approximately linearly with temperature. An increase in surface to volume ratio of the reactor tube was observed to accelerate the species

decomposition in hydrogen, but it had no effect on the distribution of major products.

This study demonstrated that selective formation of HCl can result from thermal reaction of dichloromethane/1,1,1-trichloroethane mixture and showed that synergistic effects of 1,1,1-trichloroethane decomposition accelerate the rate of dichloromethane decomposition. A detailed kinetic reaction mechanism was developed and used to model results obtained from the experimental reaction system. The detailed kinetic reaction mechanism was based on thermochemical principle and transition state theory.

Rate constants obtained for initially important decomposition of dichloromethane and 1,1,1-trichloroethane over the temperature range 475 to 810 ^{o}C are:

	A (1/s)	Ea (Kcal/mol)
CH_2Cl_2 ----> CH_2Cl + Cl	1.1E16	82.8
CH_3CCl_3 ----> CH_2CCl_2 + HCl	3.8E13	47.9
CH_3CCl_3 ----> CH_3CCl_2 + Cl	2.4E16	73.2

THERMAL DECOMPOSITION
OF DICHLOROMETHANE/1,1,1-TRICHLOROETHANE MIXTURE
IN AN ATMOSPHERE OF HYDROGEN

BY

YANG SOO WON

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

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I. INTRODUCTION

Controlled, high-temperature incineration has been identified as a desirable method for disposal of hazardous organic waste. This approach avoids many of the problems associated with storage of hazardous materials in landfills or impoundments[1]. Theoretically, incineration could result in the total conversion of hazardous organic compounds to innocuous thermodynamic end-products, such as carbon dioxide and water, and other simple compounds such as HCl which are easily scrubbed with existing pollution control equipment. In practice, total conversion to innocuous materials cannot be achieved without considerable expense, and for an incinerator of less than optimum design or operating conditions, the most thermally stable components in the waste feed may not be totally decomposed. Also of concern is the formation of stable toxic combustion products that are both stable and toxic.

Commercialized incineration at high temperature with excess oxygen has been made the chosen method[2], and is available, as there are a number of hazardous waste incineratores around the country . For chlorinated hydrocarbons, this technique may destroy all theinitial parent species, but reaction products are not all converted to carbon dioxide, as these combustion facilities are run in an oxygen-rich environment where is no stable and desirable

end adduct for chlorine. Chlorine oxide and Cl_2 are not acceptable end products for discharge to atmosphere, nor are they formed in a selective or quantitative manner for complete collection or neutralization. One preferred chloride product is hydrogen chloride, which can be quantitatively neutralized or collected. If an incinerator with excess oxygen operates under less than optimum conditions, the chlorine containing carbon products can usually be found as effluent which include partially decomposed and oxidized fragments of the initial chlorocarbon. These imcomplete combustion product can and often are more stable and more toxic than the parent compound[3,4]. The O-H bond in water is, however, stronger than the H-Cl bond, O_2-rich conditions therefore limit hydrogen availability. Another way of looking at the problem is that oxygen and Cl are both competing for the available fuel hydrogen and this is one reason that chlorocarbons serve as flame inhibitors. The C-Cl bond is the next strongest compared with other possible chlorinated products such as Cl-Cl, N-Cl or O-Cl bonds. Consequently, C-Cl may persist in a oxygen rich or hydrogen limited atmosphere[3]. This is one reason why emission of toxic chlorine-containing organic products persists through an oxygen-rich incineration, as carbon species are one of the more stable sinks for chlorine.

Instead of detoxifying chlorocarbons in an oxidizing

atmosphere, one alternative approach to incineration is detoxication of chlorinated hydrocarbon by reductive reactions using hydrogen[3,5,6,7], water vapor[3] or methane[8]. Methane reductive reaction process was developed and patented by S.W. Benson[9]. In this process, methane is added to chlorine containing compound and the mixture is heated in the absence of air to about 1000 ^{0}C. That converts all the chlorine into hydrochloric acid which can then combine with lye to form sodium chloride and hydrodechlorinated hydrocarbons which are usable fuel gas.

Chlorocarbons can also be detoxicated (destroyed) with a hydrogen reductive reaction. One desired and thermodynamically favorable product from a chlorocarbon process is HCl, providing there exists sufficient H_2 to achieve stoichiometric formation of HCl and other desired product-C_nH_m . One possible method to obtain quantitative formation of HCl as one of the desired and thermodynamically favoable products from chlorocarbon, might be straight forward thermal conversion of these compounds under a more reductive atmosphere of hydrogen. Other products expected are gaseous hydrocarbon and solid carbon. Also, the choice of pure hydrogen in research work is based on the conviction that leads to less complex chemical systems compared with cabnon based on other hydrogen source. It also provides a fundamental and more readily interpreted series of reactions.

The chlorocarbon conversion studies in hydrogen

reductive atmosphere which have be done so far, examined global kinetic information, such as kinetic parameters, reaction product distribution and overall mechanism, on pure chlorocarbon compounds. In this study, we performed the detailed experimental studies on the dichloromethane and 1,1,1-trichloroethane mixed system and developed a detailed reaction mechanism to describe the results.

The objectives of this work are ;

. examine the high temperature hydrodechlorination and thermal reactions of a CH_2Cl_2/CH_3CCl_3 mixture in a tubular flow system.

. characterize product distributions and synergistic effects of the mixed chlorocarbon reaction system.

.determine if complete and facile conversion to HClis achievable.

.enhance understanding of thermal reaction kineticsof chlorocarbons (C,H,Cl systems).

.formulate a detailed reaction mechanism based on fundamental thermochemical and kinetic principles for this system.

In the present study, Activated Complex Quantum RRK analysis is involved stable compounds and free radical species under going :

. addition

. beta scission

. recombination

these type reactions for evaluation of the reacting system over a wide range temperature and pressure. A detailed kinetic reaction mechanism was developed and used to model results obtained from the experimental reaction system.

II. Previous Studies

Remarkably little work has been done in the field on reaction studies of hydrogen with chlorinated hydrocarbon.

Relevant studies have been done throughly and systematically in the laboratories of NJIT, under the guidance of Dr. Bozzelli, since the initial work of Chuang (1982)[10].

Chuang studied the thermal decomposition of chloroform and 1,1,2-trichloroethane with hydrogen or water vapor, over temperature range of 550 to 1100 ^{o}C. Chang[11] in his work on the estimation of homogeneous and wall rate constants from laminar flow analysis has presented data on the reaction of hydrogen with 1,1,1-trichloroethane. The thermal reaction of chloroform and trichloroethylene with hydrogen was investigated by Mahmood[12] in 1985. Lee[13] investigated the thermal decomposition of 1,2-dichloroetane with hydrogen in 1986. Ritter[14] performed studies on the thermal decomposition of chlorobenzene in an atmosphere of hydrogen. More recently, the thermal reaction of hydrogen with methyl chloride and carbon tetrachloride at high temperature was examined by Tsao[15] (1987). The thermal decomposition of dichlorobenzene with hydrogen by Hung[16] was performed at atmospheric pressure, using tubular reactor and a hydrogen atmosphere.

The thermal decomposition of pure single chlorinated hydrocarbons both neat and in inert atmosphere has also been

studied. A number of reports were found on the thermal decomposition of pure dichloromethane and 1,1,1-trichloroethane.

A. DICHLOROMETHANE

Tsao<15> studied the thermal decomposition of dichloromethane with hydrogen over the temperature range of 700 to 950 ^{o}C, using almost same as our apparatus system. Activation energies of bulk and wall reaction on hydrogen reaction with dichloromethane are 50.0 Kcal/mole, 57.8 Kcal/mole A factors of $2.84 * 10^{10}$ and $2.65 * 10^{10}$ respectively were reported. The major products of reaction of dichloromethane in between 700 to 800 ^{o}C were methylchloride and methane. The minor products were ethylene, acethylene and HCl. Trace amounts of ethane, chloroethylene, 1,2-dichloroethylene, trichloroethylene, benzene were also observed. No chlorocarbons were found over 950 ^{o}C and one second residence time where the only products were methane, hydrogen chloride, acethylene, ethane and benzene.

Huang<17> studied the kinetics of the reaction of atomic hydrogen with dichloromethane in a flow system at pressure of 2.1 to 2.7 mm Hg absolute and room temperature. The major products observed were hydrogen chloride and methane. The extent conversion of dichloromethane increases first to a maximum and then decreases with incresing

concentration of dichloromethane. Through the modeling of the reaction scheme and comparsion with experimental data, the rate constants of the initial steps were determined as follows :

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

$k_1 = 3.63 * 10^9$ cm^3/mole sec.

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

$k_2 = 2.08 * 10^7$ cm^3/mole sec.

B. 1,1,1-TRICHLOROETHANE

Chang<18> who investigated the reactor modeling and and calculation of homogeneous bulk and wall rate constants from laminar flow reactor analysis on the reaction of hydrogen with 1,1,1-trichloroethane in the temperature range 555 to 681 ^oC. The activation energies of bulk and wall reaction were determined to be 25.3 Kcal/mol and 37.9 Kcal/mole respectively. The major products from the reaction were observed to be 1,1-dichloroethylene, chloroform, 1,1-dichloroethane, trichloroethylene, dichloromethane, 1,1,1,2-tetrachloroethane and HCl.

Barton and Onyon<5> (1950) studied 1,1,1-trichloroethane thermal decomposition in batch reactor in temperature range 635.7 to 707.0 ^oK and pressure range 10 to 120 mm Hg to give 1,1-dichloroethylene and HCl. They found that the decomposition rate in packed reactor was slower

than in empty reactor. They proposed the packed reactor has a larger surface to volume ratio so the recombination of some radicals to terminate the chain reactions occured at a faster rate and slowed the overall process. The initiation steps suggested by Barton and Onyon as follows :

$$CH_3CCl_3 \longrightarrow CH_2CCl_2 + HCl$$
$$CH_3CCl_3 \longrightarrow CH_3CCl_2 + Cl$$

Their results showed that the wall inhibited the decomposition reaction because the proposed "key" free radical CH_2CCl_3 was consumed faster at the wall. They reported that the first order rate constant for homogeneous unimolecular decomposition can be represented by 10 * EXP(-54,000/RT) sec.

Benson and Spokes<19> (1967), using the very low pressure technique, covered a high temperature range 890 to 1265 ^{o}K (so that the reactor was operated at gas flow rates from 10^{15} to 10^{16} molecules/sec. and most of the collisions made by reactant molecules were with wall rather than with other gas molecule) to estimate the homogeneous rate constant of the thermal decomposition of 1,1,1-trichloroethane at high pressure limit . The corresponding high pressure rate equation is $10^{13.8}\ e^{(-51,700/RT)}$ sec..

III. THEORY

The incineration of chlorocarbons is generally performed in an oxygen rich environment that contains excess O_2 and N_2[2], in addition to the C and Cl from the halocarbon, with relatively small amounts of available hydrogen from the limiting fuel operation. In considering products from incineration, the H-Cl bond is the strongest (thermodynamically) and has the lowest Gibbs free energyof formation per chlorine atom[3]. HCl is, therefore, the thermodynamically favored product for chlorine, providing there exists sufficient hydrogen for its stoichiometric formation. It is noted, however, that the O-H bond in water, specifically HO-H is stronger than the H-Cl bond, and the O_2-rich conditions limit hydrogen availability. The C-Cl bond is the next strongest compared with other possible chlorinated products such as Cl-Cl, N-Cl, or O-Cl bonds. Consequently, C-Cl may persist in a oxygen rich atmosphere. This suggests that the emission of toxic chlorine-containing organic products may persist through an oxygen-rich incineration, as it is one of the more stable sinks for the chlorine.

In order to obtain quantitative formation of HCl from chlorocarbons, it might help to convert these chlorocarbons under a more reductive atmosphere of hydrogen. The chlorocarbon plus hydrogen system contains only carbon, hydrogen, and chlorine elements and is expected to lead to

formation of light hydrocarbons, carbon(s), and hydrogen chloride at the high temperatures where complete reaction occurs[3,7]. It also does not have wet HCl in the effluent and is, therefore, not nearly as corrosive as the system with water vapor present.

A. Trasition-State and Collision Theory

1. Transiton-State Theory

For many reactions and particularly elementary reactions the rate expression can be written as a product of a temperature dependent term and a composition term.

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

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

we have the following conceptual elementary scheme:

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

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

$$k_2 = \frac{kT}{h}$$

The observed rate of the forward reaction is then

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

$$= \frac{kT}{h} [AB^*]$$

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

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

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

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

the rate becomes

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

Theoretically both $\triangle S^*$ and $\triangle H^*$ vary very slowly with temperature. Hence, of the three terms that make up the rate

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

$$k_f \propto T\ EXP(-\triangle H_f^*/RT) \qquad (6)$$

$$k_r \propto T\ EXP(-\triangle H_r^*/RT)$$

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

2. Collision Theory

The collision rate of molecules in a gas can be found from the kinetic theory of gases. For the bimolecular collisions of like molecules A we have

$$Z_{AA} = d_A^2\ n_A^2 \cdot \frac{4\ kT}{M_A} = d_A^2\ \frac{N^2}{10^6} \cdot \frac{4\ kT}{M_A} \cdot C_A^2$$

where d = diameter of molecule, cm

M = mass of molecule, gm

N = Avogadro's number

C_A = concentration of A, mol/liter

n_A = number of molecules of A/cm^3

k = Boltzmann constant

For bimolecular collisions of unlike molecules in mixture of A and B kinetic theory gives

$$Z_{AB} = \left(\frac{d_A + d_B}{2}\right)^2 \cdot \frac{N^2}{10^6} \cdot 8\ kT\ \left(\frac{1}{M_A} + \frac{1}{M_B}\right) \cdot C_A \cdot C_B$$

If every colliion between reactant molecules results in the conversion of reactants into product, these expressions give the rate of bimolecular reaction. The actual rate is usually much lower than that predicted, and this indicates that only a small fraction of all collisions result in reaction. This suggests that only more energetic and violent collisions, or more specifically, only those collisions that involve energies in excess of a given minimum energy E lead to reaction. From the Maxwell distribution law of molecular energies the fraction of all bimolecular collisions that involve energies in excess of this minimum energy is given approximately by $e^{(-E/RT)}$, when $E >> RT$. Since we are only considering energetic collisions, this assumption is reasonable. Thus the rate of reaction is given by

$$-r_A = k\, C_A\, C_B = \left(\begin{array}{c}\text{collision}\\ \text{rate}\end{array}\right) \times \left(\begin{array}{c}\text{fraction of collisions invol-}\\ \text{ving energies in excess of E}\end{array}\right)$$

$$= Z_{AB} \frac{10^3}{N} e^{(-E/RT)}$$

$$= \left(\frac{d_A + d_B}{2}\right)^2 \frac{N}{10^3} \quad 8\, kT\left(\frac{1}{M_A} + \frac{1}{M_B}\right) e^{(-E/RT)}\, C_A\, C_B$$

A similar expression can be found for the bimolecular collisions between like molecules. For both, in fact for all bimolecular reaction, above equation shows that the temperature dependency of the rate constant is given by

$$k \propto T^{1/2}\, e^{(-E/RT)}$$

3. Comparison of Two Theories

It is interesting to note the difference in approach between the transition-state and collision theories. Consider A abd B colliding and forming an unstable intrmediate which then decomposes into product, or

$$A + B \text{ -------> } AB^{*} \text{ -------> } AB$$

collision theory views the rate to be governed by the number of energetic collisions between reactants. What happens to the unstable intermediate is of no concern. The theory simply assumes that this intermediate breaks down rapidly enough into products so as not to influence the rate of the overall process. Transition-state theory, on the other hand, views the reaction rate to be governed by the rate of decomposition of intermediate. The rate of formation of intermediate is assumed to be governed by collisions plus thermodynamics and it is present on equilibrium concentrations at all times. Thus collision theory views the first step to be slow and rate-controlling, whereas transition-state theory views the second step combined with the determination of complex concentration to be the rate controlling factors.

B. Tubular Flow Reactor Theory

The ideal tubular flow reactor is one in which there is no mixing in the direction of flow and complete mixing

perpendicular to the direction of flow (i.e. in the radial direction)[20,21]. In other words, all fluid elements of the fluid have the same reidence time in the reactor and there is no radial concentration gradient.

In our tubular flow reactor, radial mixing is due to molecular diffusion and axial mixing is due to fluid velocity gradients. Concentrations will vary along the length (axial) coordinate and to a smaller extent over the radial coordinate. These complication concerns the flow pattern which effects our kinetic interpretations. In turbulent flow, vortices and eddies produce mixing in the longitudinal direction. In the laminar flow, the parabolic velocity profile is formed across the tube. At low temperature and high pressure condition, the molecular diffusion process is relatively slow, so the annular elements of fluid flow through the reactor are only slightly mixed in the radial direction also. The fluid near the wall will have a longer residence time in the reactor than for ideal tubular flow performance, while the fluid near the center will have a short residence time. Our higher temperature conditions give a much higher diffusion rate and therefore a well mixed axial system.

To estimate the deviation of a tubular flow reactor with axial diffusion from the plug flow assumption, Reman[22] has used Danckwerts solution of a differential equation which describes a plug flow reactor following

first-order kinetics. He found that $D/vl < 0.1$ the reactor follows the plug flow assumption, and for $D/vl > 2.0$ the reactor behaves like a well-mixed one[23]. Here D is diffusion coefficient, v is mean velocity, l is reactor length. For our reactor, D/vl is always below 0.1 ($1.1 * 10^{-4} - 4.4 * 10^{-3}$). This would be sufficient for plug flow assumption to hold true if the Reynolds number were in the upper range of laminar flow when molecular diffusion effects in dispersion are negligible compared to the effect of the velocity[24]. This is, however, not true for our experiments ($N_{RE} = 5 - 600$).

A more rigorous analysis that is applicable to our system is the paper by Poirier and Carr[25]. They solved the continuity equations for a tubular flow reactor with radial diffusion first-order kinetics. They propose that if D/kR^2 (where R is the radius of reactor, k is homogeneous rate constant) is equal to or greater than 0.5, the plug flow approximation is satisfied. Our system has a D/kR^2 values from 10 to 170, so the plug flow model is a good approximation for our present reactor.

A comparison of the kinetic values found by plug flow analysis with values obtained by applying both the numerical and analytical solution of continuity equation for first order kinetics with laminar flow done by Chang and Bozzelli[18]. The comparison turns out to be favourable to the plug flow assumption for our experimental system.

C. Decoupling of the wall and Bulk Reaction Rate Constants

The decomposition of chlorinated hydrocarbons is not only a function of temperature and residence time but also of the radius of reactor. This means that, the reaction at wall in addition to the bulk reaction needs to be evaluated.

In order to simplify the formulation of governing equations for a reactor system in which both bulk and wall reactions are present, it is usually assumed that the two reactions are parallel and independent[21]. Hence, for the first order reaction of species A one can write:

A ------> Products

$$\text{Rate} = -\frac{d[A]}{dt} = k_b * [A] + k_w * [A] * [A_w]$$

$$= (k_b + k_w * [A_w]) * [A] \qquad (1)$$

$$k_{exp} = k_b + k_w * [A_w] \qquad (2)$$

Asuming a rapid radical diffusion, Aw can be written as[26]:

$$A_w = (S/V) \qquad (3)$$

where:

A_w = wall concentration

S/V = surface to volume ratio

= 2/R for a cylindrical reactor

From (2) and (3) one obtains:

$$K_{exp} = K_b + K_w * (2/R) \qquad (4)$$

In this equation k_b is the first order reaction rate constant for the bulk or homogeneous reaction and k_w is the rate constant for the wall or heterogeneous reaction. If one uses several reactors of different radius this equation allows kb and kw to be evaluated. The Arrhenius behavior of each rate constant can then be determined.

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

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

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

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

Calculation of the bimolecular rate constant involves the concept that the fate of the chemically activated adduct is determined by competition among the possible pathways; stabilization by collision, redissociation to reactants, or formation of new products dy dissociation or isomerization. References are the Dean's paper<27>.

1. Unimolecular QRRK Equation

Dean<27> (1985) has presented equations for bimolecular rate constants based on the Quantum-RRK or QRRK unimolecular reaction theory of Kassel (1928), which treats the storage of excess energy (relative to the ground

state) as quantized vibrational energy.

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

$$A + M \;\; \Longleftrightarrow \;\; A^* + M$$

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

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

The apparent k_{uni}:

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

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

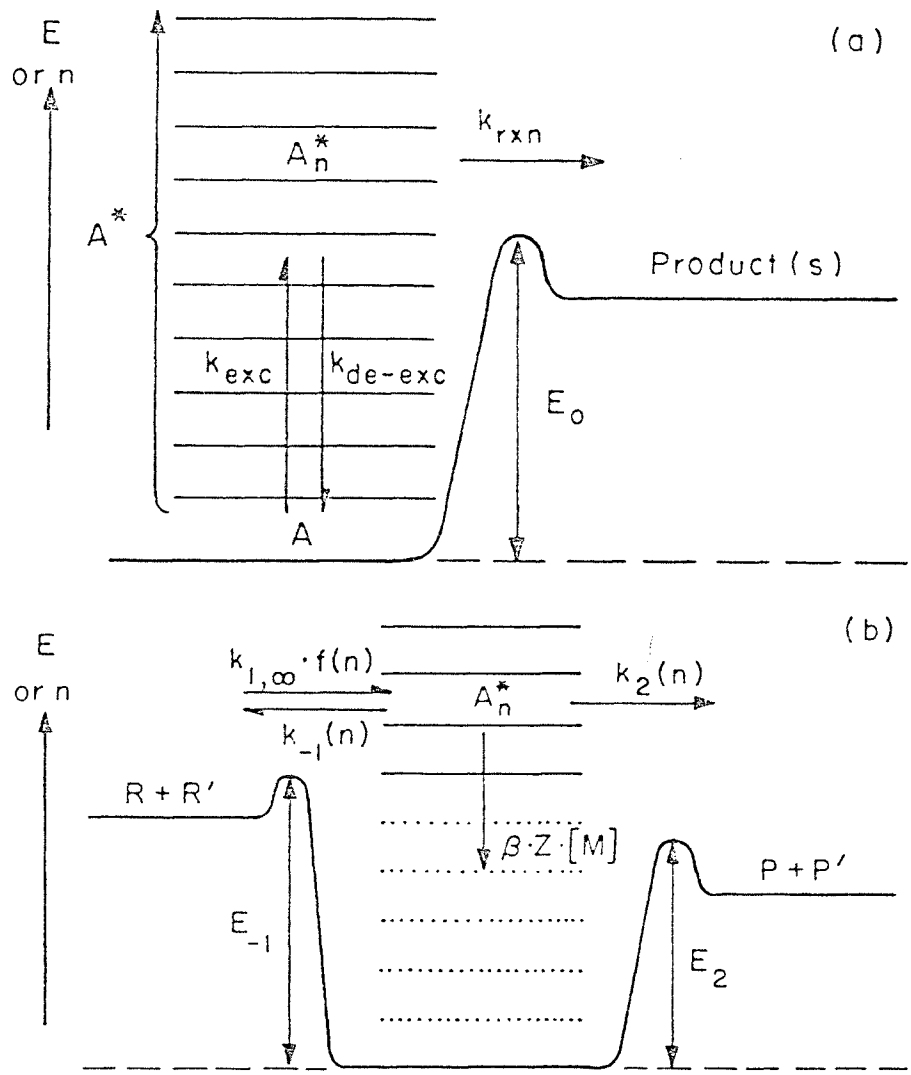

Figure 1. Energy diagrams for pressure-dependent reactions.

a. Unimolecular reaction
b. Bimolecular reaction with chemically activated pathway

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

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

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

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

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

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

where $a = e^{(-h\langle v\rangle/kT)}$.

In the present development, a collisional efficiency Beta has been applied to modify the traditional but incorrect strong-collision assumption that $k_{deexc} = Z\ [M]$, where Z is the collision frequency rate constant. The

strong-collision assumption implies that any collision between A^* and M would have to remove all the excess enrgy from A^*. Note that any species included as M would have to accommodate this energy content, regardless of its capacity for accepting the energy. Analyzing collisional energy transfer for master-equation methods, Troe (1977) fit most of the temperature dependence of Beta with the equation:

$$\frac{\text{Beta}}{1-(\text{Beta})^{1/2}} = \frac{-\langle \Delta E_{coll} \rangle}{F(E)\ k\ T} \qquad (5)$$

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

2. Bimolecular QRRK Equations

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

$$R + R' \underset{k_{-1}(E)}{\overset{k_1\ f(E,T)}{\Longleftrightarrow}} [RR']^* \xrightarrow[\text{Beta } k_s[M]]{k_2(E)} P + P'$$

$$[RR']^* \xrightarrow[\text{Beta } k_s[M]]{} A$$

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

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

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

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

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

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

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

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

3. Low- and High-Pressure Limits

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

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

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

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

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

give incorrect rate constants for "simple" addition.

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

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

and the high-pressure limit will be

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

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

IV. EXPERIMENTAL METHOD

A diagram of the experimental system is shown in Figure 2. A high temperature tubular flow reactor, operated isothermally and atmospheric pressure was used for this study. The tubular flow reactor was made of quartz, which was maintained at a constant temperature by a three - zone oven, each zone controlled separately.

Hydrogen gas, which acted both as reagent and carrier, was passed through separate parallel sets of two saturation bubblers to pick up dichloromethane and 1,1,1-trichloroethane, both kept at 0 ^{o}C using an ice bath. Before entering the reactor, the hydrogen, dichloromethane and 1,1,1-trichloroethane were preheated to limit cooling at the reactor entrance. Quartz reactor tubes of 4 mm, 10.5 mm and 16 mm were housed within a three zone Lindberg electric tube furnance. The reactor effluent was monitored using an on - line gas chromatograph (GC) equipped with Flame Ionization Detector. The lines between reactor exit and GC analysis were heated to 65 ^{o}C to limit condensation.

Whenthe inlet switching valves were properly selected, the mixture (CH_2Cl_2 and CH_3CCl_3) vapor would be transferrd directly from the bubbler to GC sample inlet via a reactor by-pass line. This was necessary to determine the GC peak area which corresponded to the input concentration of mixture. The reactor effluent gas passed through heated

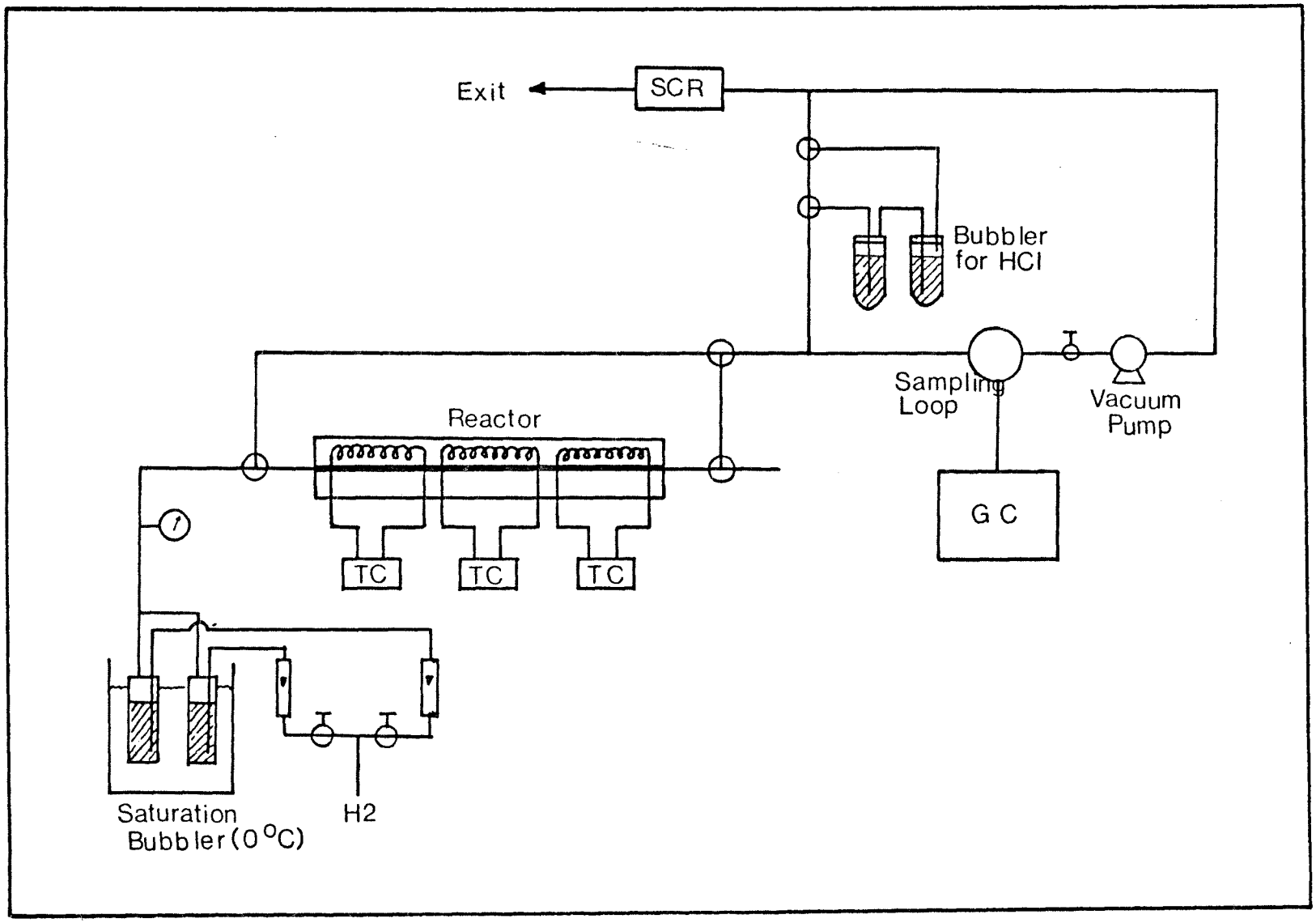

Figure 2. EXPERIMENTAL SET UP

transfer line to the GC sampler and exhaust.

In this study, three different reactor diameters were studied measured 0.4, 1.05 and 1.6 cm as required to vary reactor surface to volume ratio (S/V). This ratio allows one to decouple apparent wall and bulk phase decomposition rates using a plug flow assumption based upon the work of Kaufman[26] for pseudo-first order reaction system.

Outlet gases from the reactor were passed to the GC through a glass tube, loosely packed with glass wool to trap any carbon particles preventing contamination of the GC sampling system. The bulk of the effluent, however, was passed through a sodium - bicabonate flask before being release to the atmosphere via a fume hood.

A. Temperature Control and Measurement

This study was carried out with isothermal reaction at the desired temperature using a three zone furnace equipped with three independent temperature controllers (Burling Instrument Co. Chatham, NJ).

The actual temperature profile of the tubular reactor was obtained using type K thermocouple which could be moved coaxially within reactor from one end to the other. The temperature measurements were performed with steady flow rate of Argon gas through reactor. Temperature profiles obtainedas shown in Figure 3 were isothermal to within $\pm$ 3 ^{o}C for 70 % of reactor length.

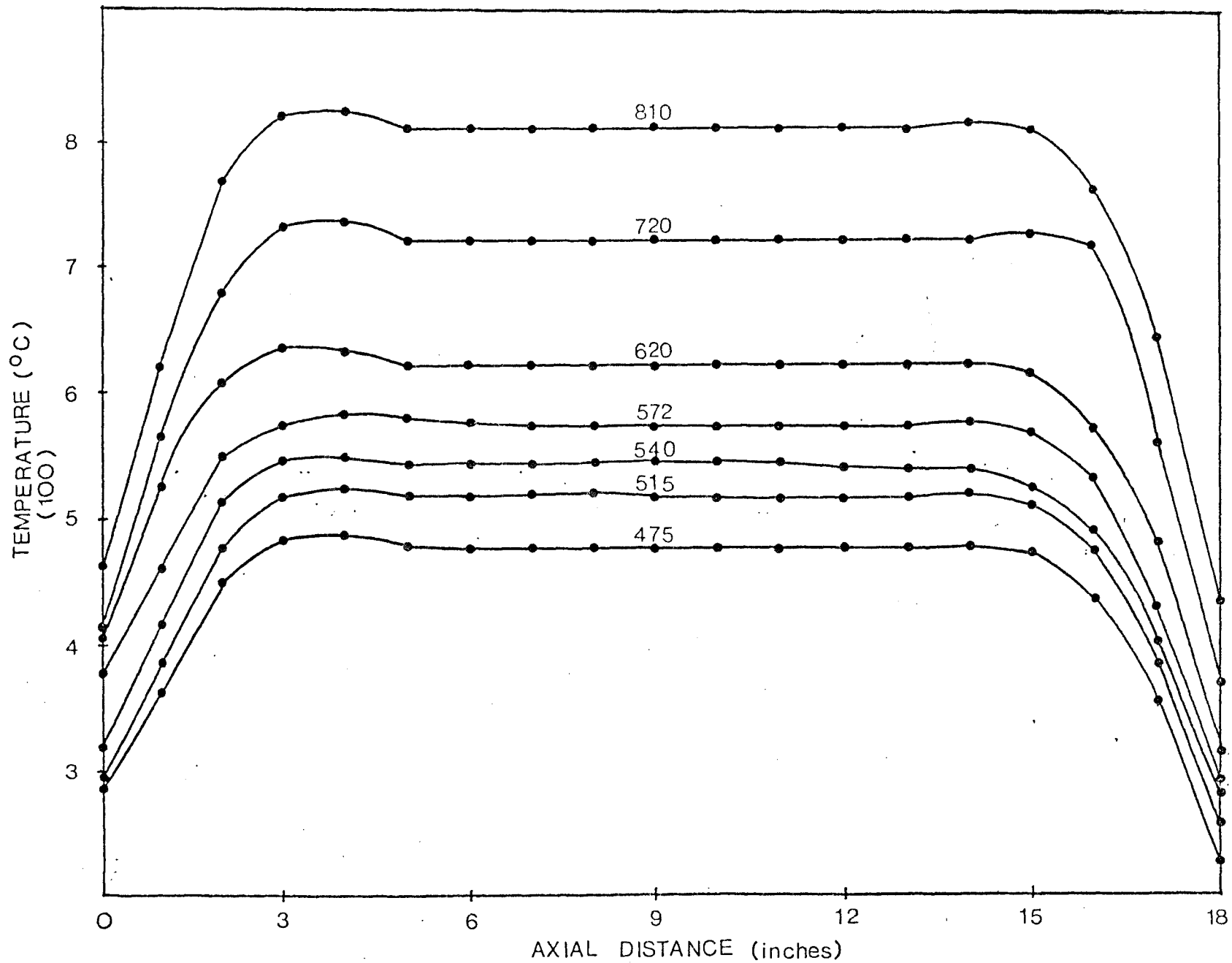

Figure 3. Reactor Temperature Profile (axial)

As illustrated in APPENDIX 2, an energy balance calculation based upon the experimental results and a detailed reaction mechanism is performed. The heat of reaction in this system can change at most 1.5 ^{o}C which is less than 50 % of our temperature control error bounds and is insignificant. The reaction condition can be, therefore, controlled by temperature controllers and considered accurate. Thus, the actual temperature profile of the tubular reactor with reaction is occurring indeed that of Figure 3.

B. Quantitative Analysis of Reaction Products

A Varian 3700 on-line gas chromatograph with flame ionization detector was used to determine the concentration of the reaction products. The lines between reactor exit and GC analysis were heated to 65 ^{o}C to limit condensation. The GC used a 1.5 m long by 1/8 inch o.d. stainless steel column packed with 1 % Alltech AT-1000 on graphpac GB as the column.

A six port gas sample valve (Valco Instrument Co.) with a 1.0 ml volume loop was maintained at 170 ^{o}C and 1 atm pressure. The integration of the chromatogram was performed with Varian 4270 integrator using an attenuation of 2 and a chart speed of 0.5 cm/min. A representative chromatogram is shown Figure4 and Table 1 with retention times and peak identification.

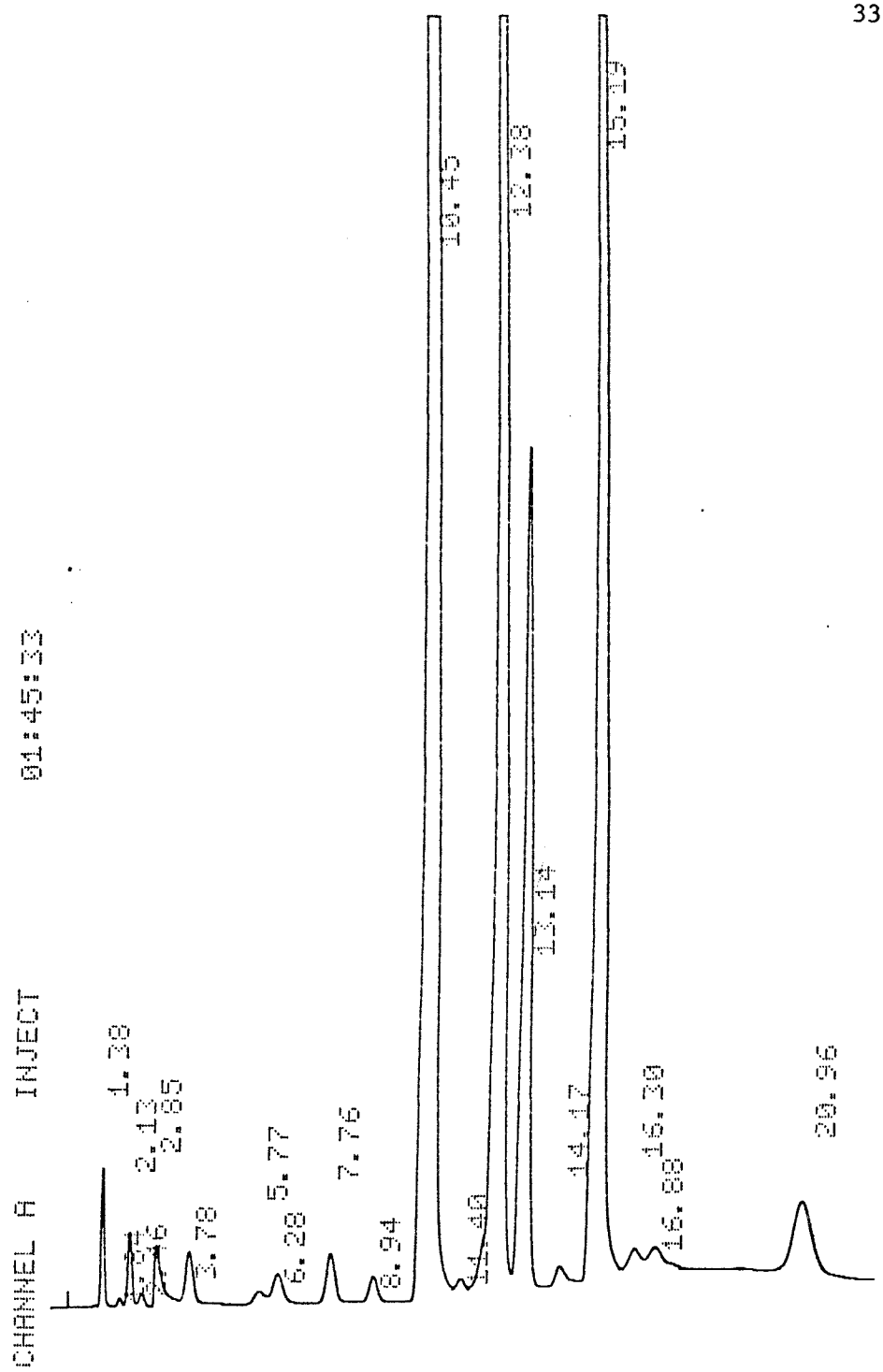

Figure 4-a. Sample Chromatogram $CH_2Cl_2/CH_3CCl_3/H_2$ Decomposition

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Column: 1.5m x 1/8" ID 1%-AT 1000 on Graphpac GB
Detector: 270°C (FID)
Temperature: 45°C(5 min) : 15°C/min to 200°C(final)
Carrier Gas: He supplied at 100 psig

*Reaction Conditions: 1 sec. under 515°C

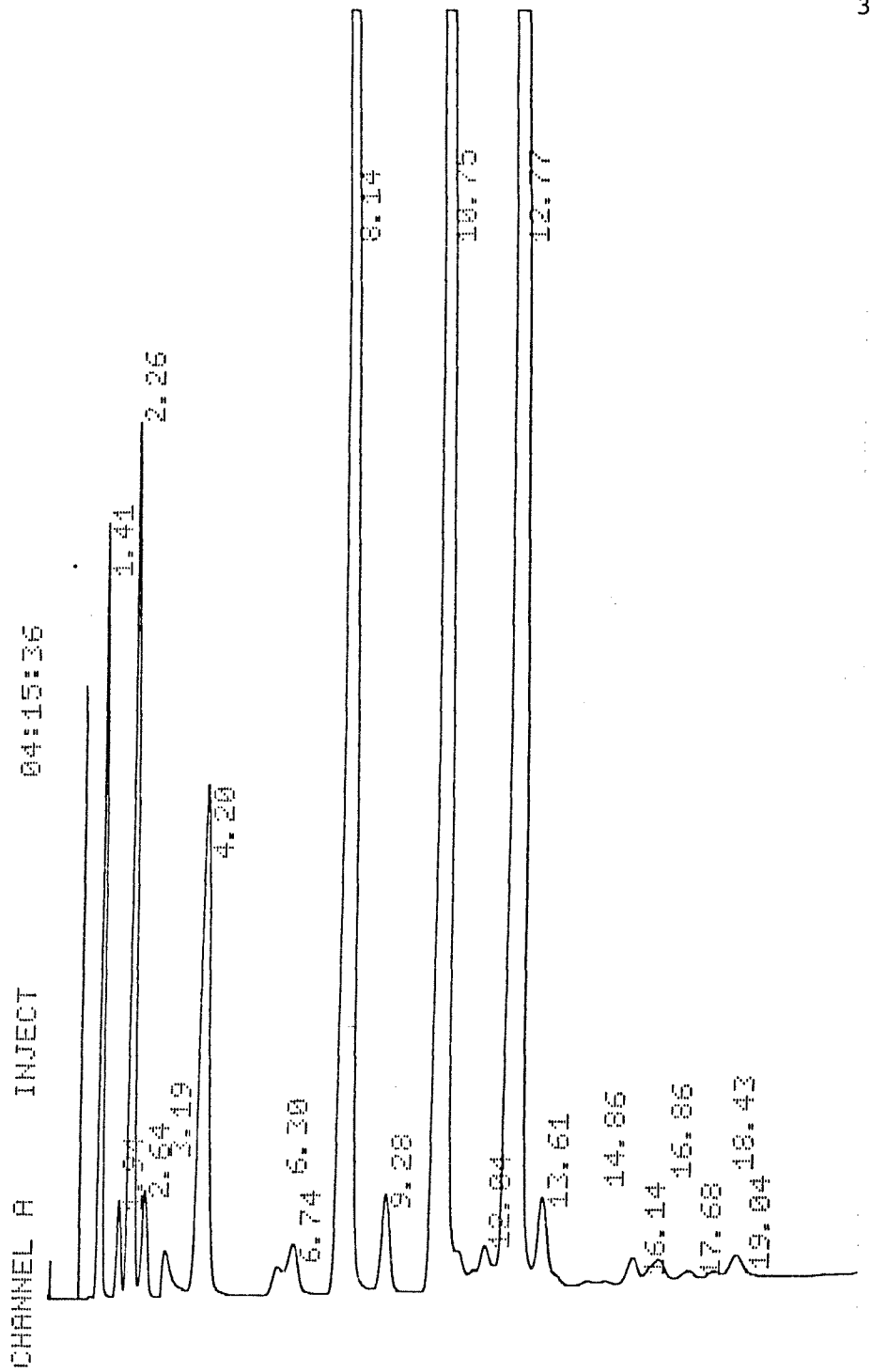

Figure 4-b. Sample Chromatogram $CH_2Cl_2/CH_3CCl_3/H_2$ Decomposition

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*Reaction Conditions: 0.3 sec. under 720°C

Table 1

Average Retention Time of Products

Compound	Average Retention Time (min.)
CH_4	1.40
CHCH	1.85
CH_2CH_2	2.20
CH_3CH_3	2.70
CHCCl	3.19
CH_3Cl	4.00
$CHCCH_3$	5.77
C_3H_6 & C_3H_8	6.28
CH_2CHCl	7.76
CH_3CH_2Cl	8.94
CH_2Cl_2	10.45
C_4H_{10}	11.40
CH_2CCl_2	12.38
CH_3CHCl_2	13.14
CHClCHCl	14.17
CH_3CCl_3	15.20
$CHClCCl_2$	16.88
C_6H_6	17.60
$CH_2ClCHCl_2$	20.95

Table 2

Relative Response Factor of Several Compounds

Compound	Relative Response Factor (RRF)
Methane	1.07
Acethylene	2.28
Ethylene	2.00
Ethane	1.96
Propyne	3.38
Propene	3.47
propane	3.42
Butane	4.31
Dichloromethane	1.00
1,1,1-Trichloroethane	1.85
1,1-Dichloroethylene	2.10
Chloroform	0.98
Tetrachlorocarbon	1.18
1,1,2-Trichloroethane	2.10

* corrected area = measured area x RRF

Calibration of the flame ionization detector to obtain appropriate molar response factor was done by injecting a known quantity of the relevant compound such as CH_4, C_2H_6, CH_2CCl_2, CH_3CCl_3 etc., then measuring the corresponding response area. The relative response factor has been determined for such compounds as shown in Table2. The respose factor for C_1 compounds are close to each other, and the response factor of C_2 compounds are near twice th response of C_1 compounds. These results agree with the general principle of flame ionization detector which is well known as a carbon counter<28>. Thus, the effect of chlorine in the relative response factor can be neglected for this flame ionization detector and the relative response factors being considered as corresponding to the number of carbon in the molecule were found accurate. Based on the experimentally verified relative response factors, the specific component peak area from each set of samples was converted to the equivalent of moles of each component.

C. Hydrochloric Acid Analysis

Quantitative analysis of HCl product was performed for reactions in each diameter reactor and each residence time. The samples for HCl analysis were collected independent from GC sampling as illustrated as Figure 2. In this analysis, the effluent was bubbled through a two stage bubbler before being exhausted to hood. Each stages contained 15 ml of

standardized 0.01 M NaOH. The gas was passed through the two stage bubbler until the first stage solution reached its phenolphthalein end point. The time required for this to occur was recorded. At this point the bubbling was stopped, the aliquots were combined, and titrated to their end point with standardized 0.01 M HCl.

The HCl produced by reaction was easily calculated; Since the concentration and molar flow rate of chlorine as dichloromethane and 1,1,1 - trichloroethane mixture was known, an estimate of the amount of organic chlorine which remained unaccounted for was available. As we shall show evidence was found that organic chlorine compounds were produced which, for one reason or another, did not lend themselves to GC analysis under the condition of this study.

V. RESULTS and DISCUSSION

The experimental conditions of the reaction of dichloromthane/1,1,1-trichloroethane mixture with hydrogen are listed below:

.Reactants Ratio (CH_2Cl_2 : CH_3CCl_3 : H_2)	:	1 : 1 : 24.6
.Reactor Temperature (^oC)	:	475, 515, 540, 572, 620, 720, 810
.Effective Reactor Length	:	30.5 cm
.Reactor Diameter (cm)	:	0.40, 1.05, 1.60
.Residence Time Range (sec.)	:	0.05 - 0.7 (i.d. = 0.40) 0.2 - 2.0 (i.d. = 1.05) 0.5 - 2.0 (i.d. = 1.60)
.Operating Pressure	:	1 atm.

Seven temperatures ranging from 475 to 810 ^oC were studied within the 1.05 cm i.d. reactor, and each temperature has 7 residence time points from 0.2 to 2.0 sec. When using the 0.4 cm and 1.6 cm i.d. reactor, five temperatures ranging from 540 to 810 ^oC were studied. Average residence times within 0.4 cm i.d. ranged from 0.05 sec. to 0.7 sec. and within 1.6 cm i.d. did from 0.5 sec. to 2.0 sec.. Constant molar ratio CH_2Cl_2:CH_3CCl_3:H_2 of 1:1:24.6 was maintained through the experiment.

A. Reaction of Dichloromethane/1,1,1-trichloroethane Mixture with Hydrogen

Experimental results on decomposition of

dichloromethane(CH_2Cl_2) and 1,1,1-trichloroethane(CH_3CCl_3), are in Figure 5, shows the normalized each compound concentration (C / Co) for each chlorocarbon reagent as a function of the average residence time for several temperatures studied and each different i.d. reactor.

The dichloromethane and 1,1,1-trichloroethane concentration consistently decrease with increasing reaction time for all temperature shown; and for a constant residence times increases in temperature result in lower reactant concentrations.

It is observed that dissociation of the CH_3CCl_3 is favored over that of CH_2Cl_2, since the dissociation activation energy of the CH_3CCl_3 is only 47.6 cal/mol for products CH_2CCl_2+HCl<29> and the bond dissociation energy of CH_3CCl_2-Cl is lower than that of CH_2Cl-Cl [BE (CH_3CCl_2-Cl) = 73.2 Kcal/mol as opposed to BE (CH_2Cl-Cl) = 82.8 Kcal/mol]. Dissociation of the C-Cl bonds are favored compared with 10 Kcal/mol stronger C-H bond<30,31>.

Conversion of CH_3CCl_3 was 85 %, while that of CH_2Cl_2 was only 16 % in 0.5 sec. reaction time, 540 ^oC and 1.05 cm i.d. reaction conditions. Complete decay (99%) of parent compounds took place at about 810 ^oC for CH_2Cl_2 and around 570 ^oC for CH_3CCl_3 in 1 sec. residence time of 1.05 i.d.cm reactor. This indicates that CH_2Cl_2 is more stable than CH_3CCl_3 under our conditions.

The large excess of hydrogen allowed simplification to

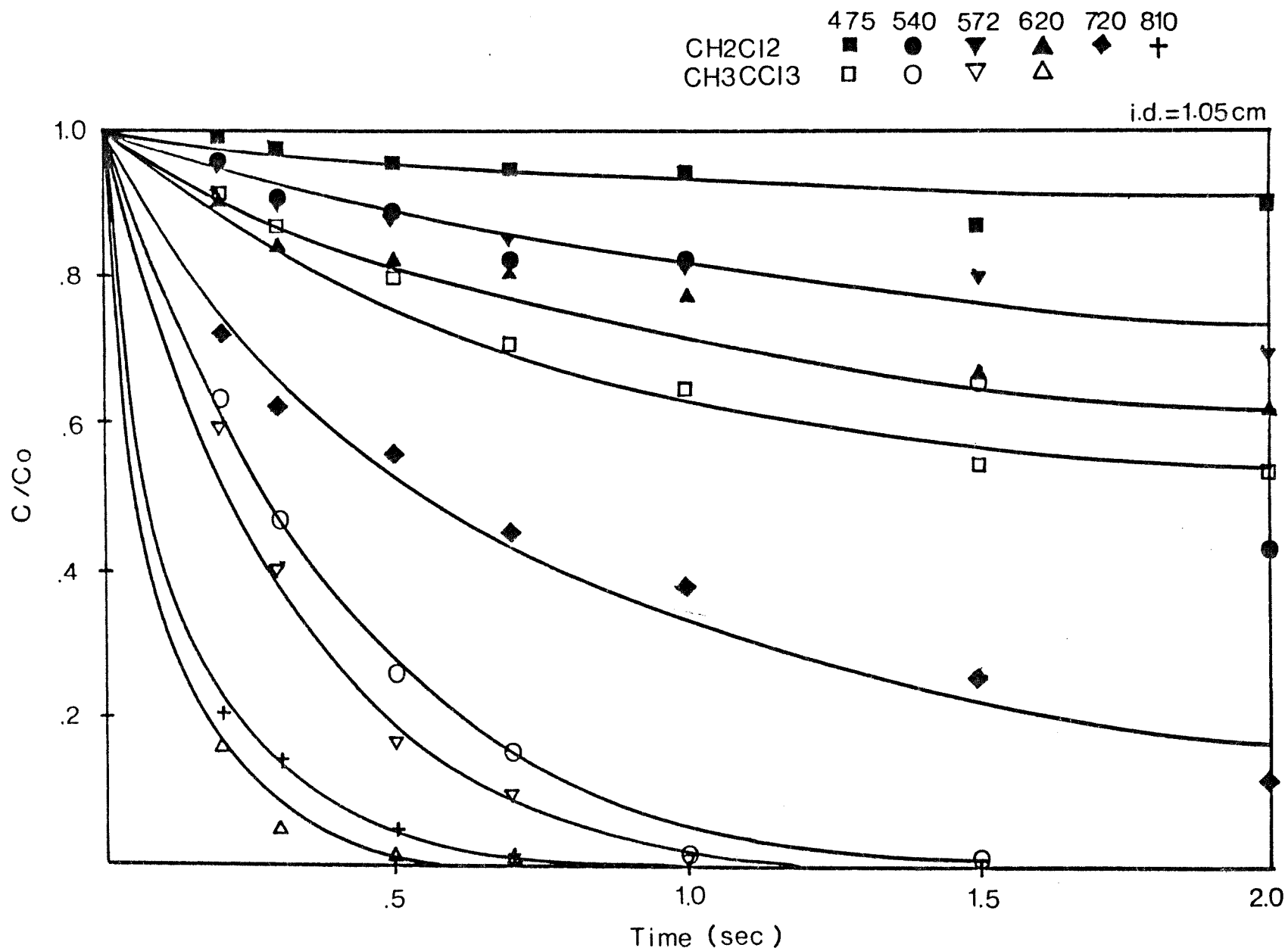


Figure 5 Decay of CH_2Cl_2 and CH_3CCl_3 vs Time

pseudo-1st order kinetics for each reactants of mixture. Integrated rate equation plots for the each conversion of CH_2Cl_2 and CH_3CCl_3 in mixture reaction to fit the first order rate equation are shown in Figure 6 and 7. A 1st order rate plot for decay of CH_3CCL_3 shows excellent linearity for all temperature but similar CH_2Cl_2 plots are not linear from the lower temperature mixed reagent experiments. This implies that there is a strong interaction of decay products from CH_3CCl_3 which react with parent CH_2Cl_2.

It is seen that for different values of temperature and diameter, the data fit the integrated first order rate equation well for each reagent. Decomposition was most rapid with the 4mm i.d. and slowest with the 16mm i.d. reactor as shown in Figure 8. This trend is expected since observed reagent loss may be the result of two reaction paths, both contributing under our conditions. The homogeneous reaction occurs in the bulk of the gas mixture and a heterogeneous reaction occurs on the surface of the flow tube wall. Clearly the relative importance of the wall reaction is greater when the surface to volume (S/V) ratio or relative extent of the wall surface is greater. The activation energies and Arrhenius frequency factor for each reagent in the mixture are found from Arrhenius plot such as Figure 9 and 10. The equations for each compounds and diameters in mixture reaction are listed below:

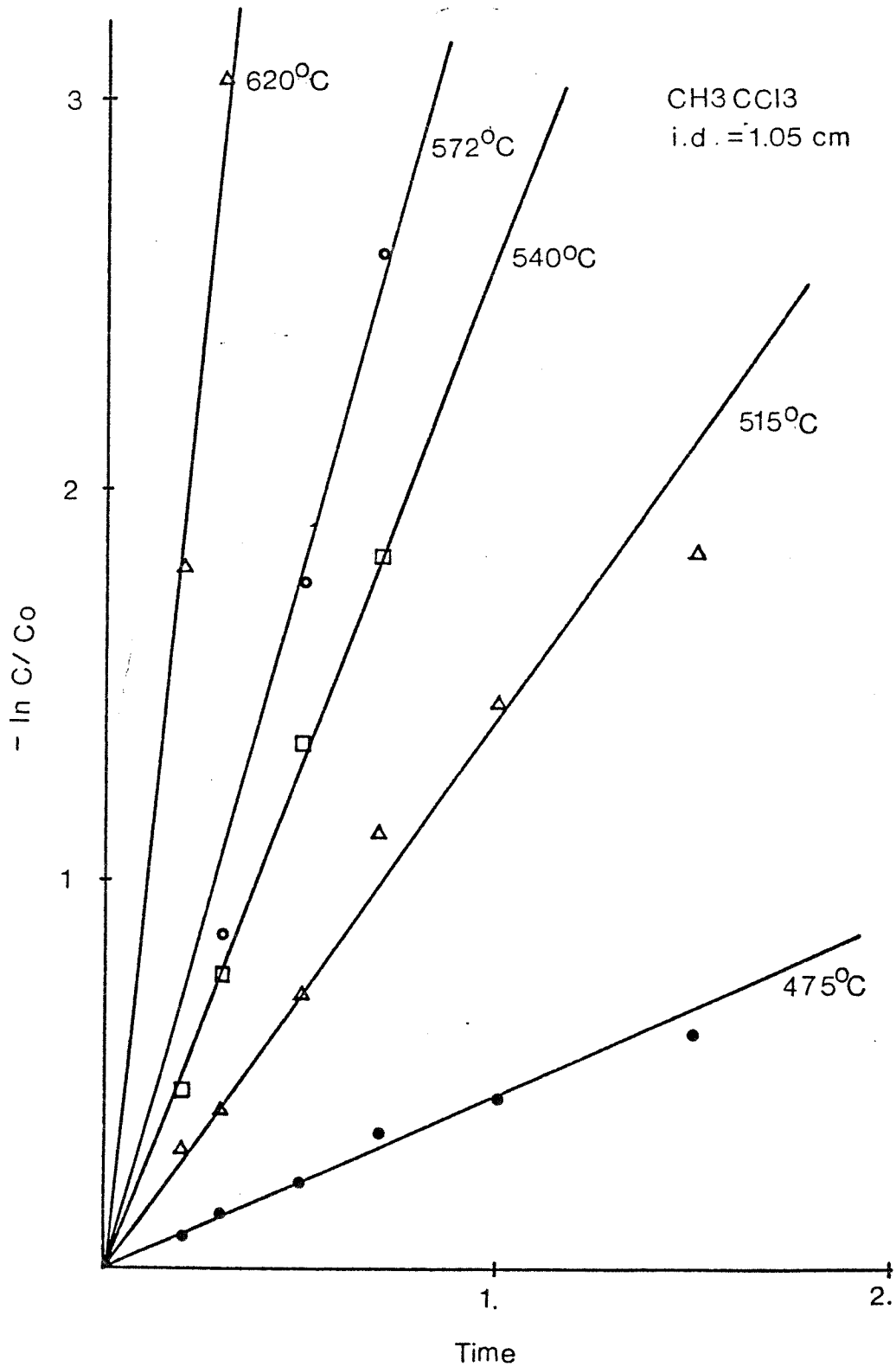


Figure 6. 1st-order Kinetics Fit of CH_3CCl_3 Decomposition

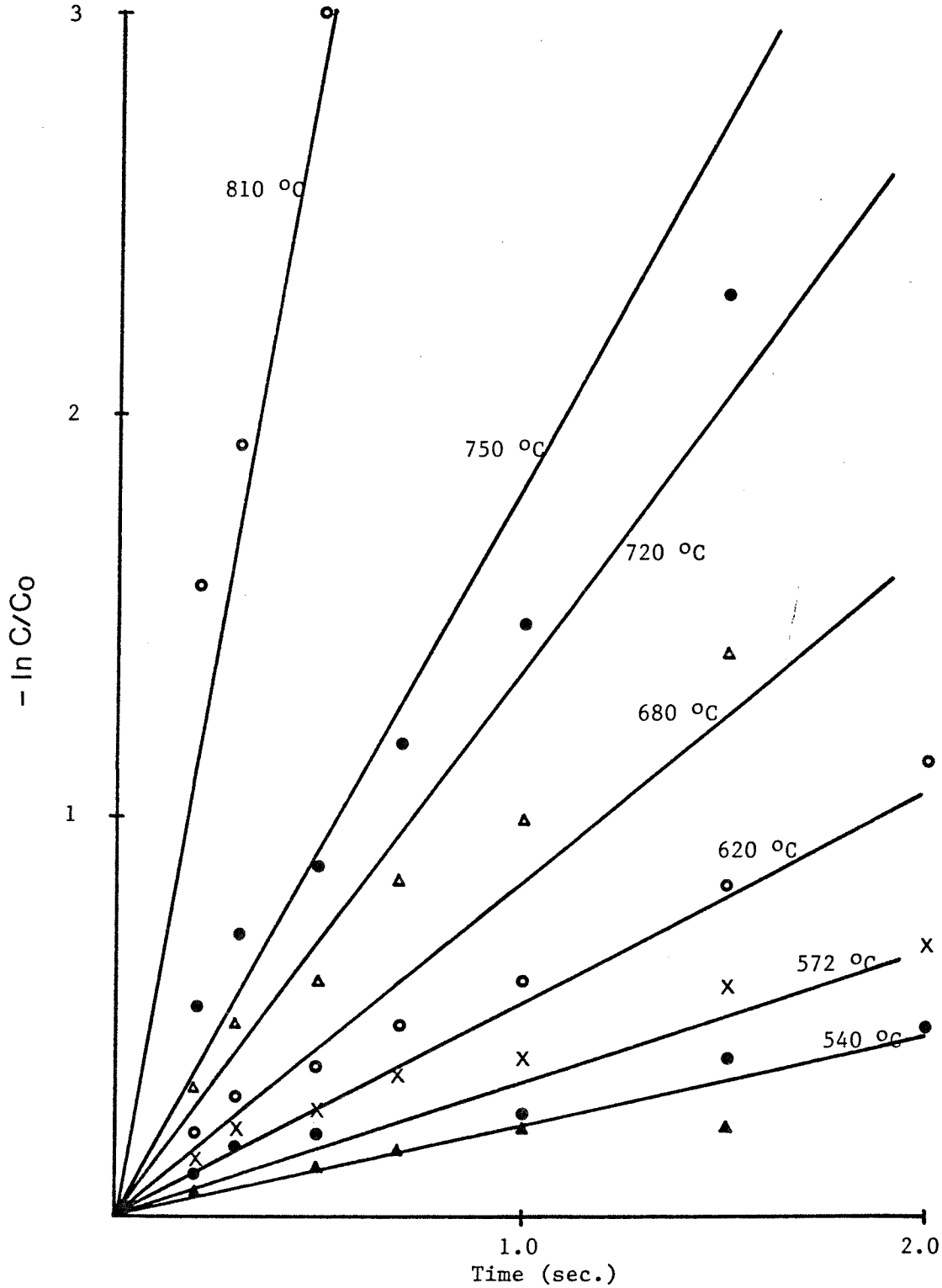


Figure 7. 1st Order Kinetics Fit of CH_2Cl_2 Decomposition

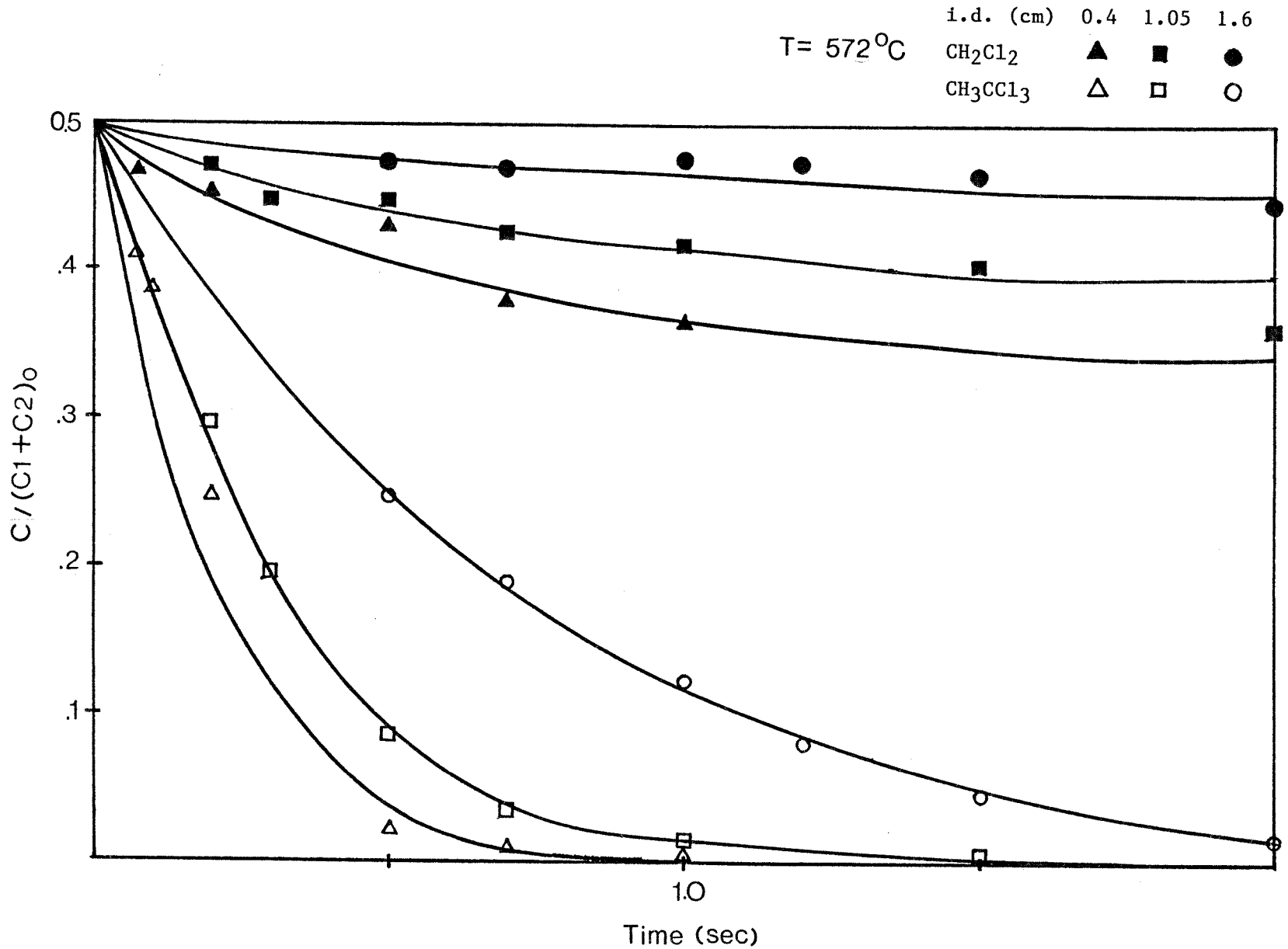


Figure 8. Reagent Decay vs Reaction Time: Comparison of Different Tube Diameters

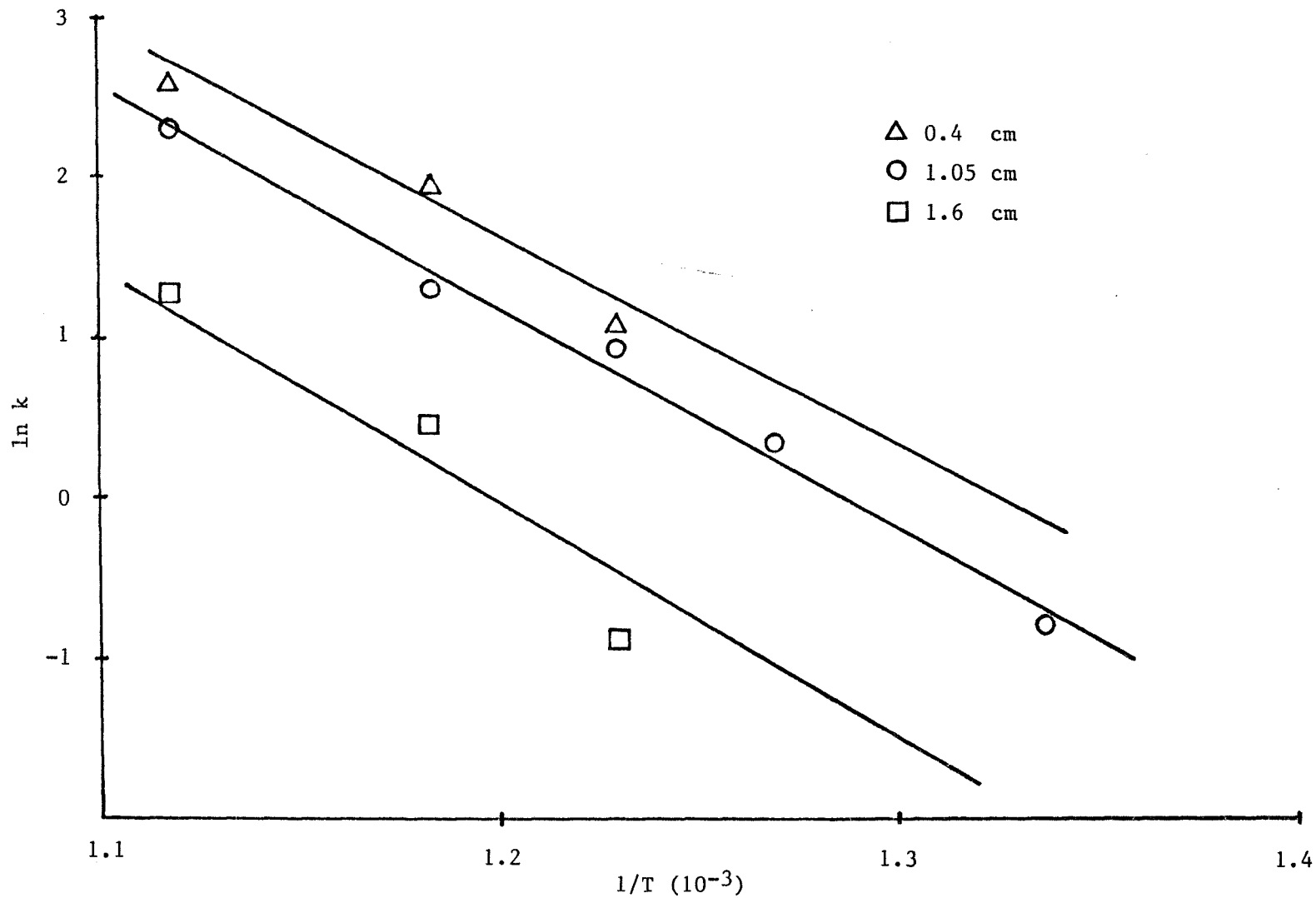


Figure 9. Arrhenius Behavior of k_{exp} for CH_3CCl_3

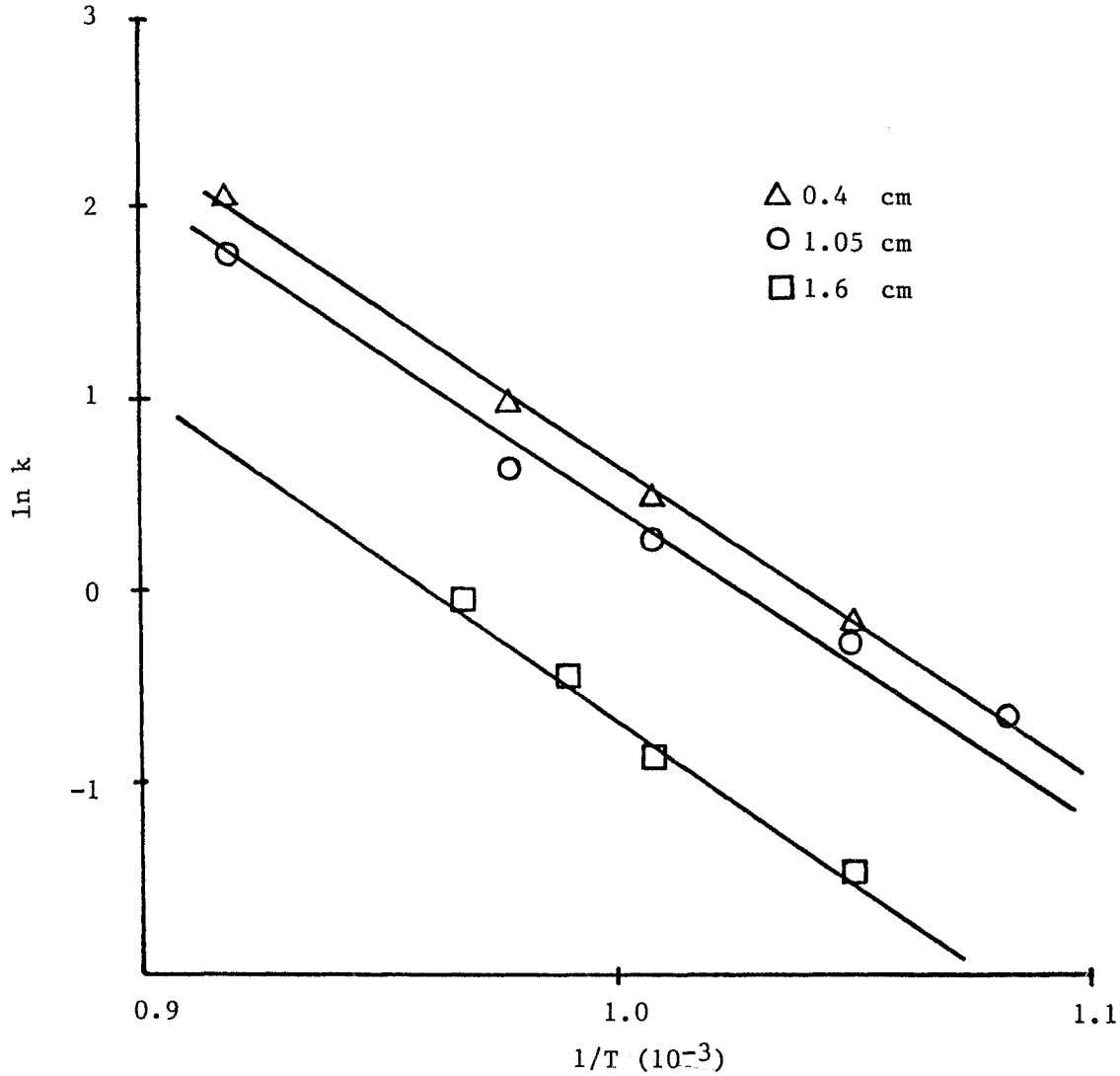


Figure 10. Arrhenius Behavior of k_{exp} for CH_2Cl_2

CH_2Cl_2

for 0.40 cm $k = 6.27 * 10^{16} \; e^{(-31,800/RT)}$ (1/sec.)

for 1.05 cm $k = 6.03 * 10^{16} \; e^{(-32,500/RT)}$ (1/sec.)

for 1.60 cm $k = 2.56 * 10^{16} \; e^{(-33,900/RT)}$ (1/sec.)

CH_3CCl_3

for 0.40 cm $k = 2.50 * 10^{17} \; e^{(-26,100/RT)}$ (1/sec.)

for 1.05 cm $k = 5.80 * 10^{17} \; e^{(-27,400/RT)}$ (1/sec.)

for 1.60 cm $k = 2.50 * 10^{17} \; e^{(-28,800/RT)}$ (1/sec.)

This is done by plotting k against 2/R, where R is the radius of reactor in centimeter. The slope is k_w and the intercept is k_b. Activation energies for the wall and homogeneous rate constants as well as for global rate constants are found by Arrhenius plots as shown in Figure 11 and 12. The values found for all the parameters are discussed and are listed .

CH_2Cl_2

$k_b = 3.24 * 10^{15} \; e^{(-35,600/RT)}$ (1/sec.)

$k_w = 9.49 * 10^{10} \; e^{(-24,500/RT)}$ (cm/sec.)

CH_3CCl_3

$k_b = 6.40 * 10^{8} \; e^{(-32,000/RT)}$ (1/sec.)

$k_w = 1.24 * 10^{7} \; e^{(-27,600/RT)}$ (cm/sec.)

As can be seen in Figure 11 and 12, there is poor linear regression relationship for determining of bulk and wall reaction rate constant comparing with each pure

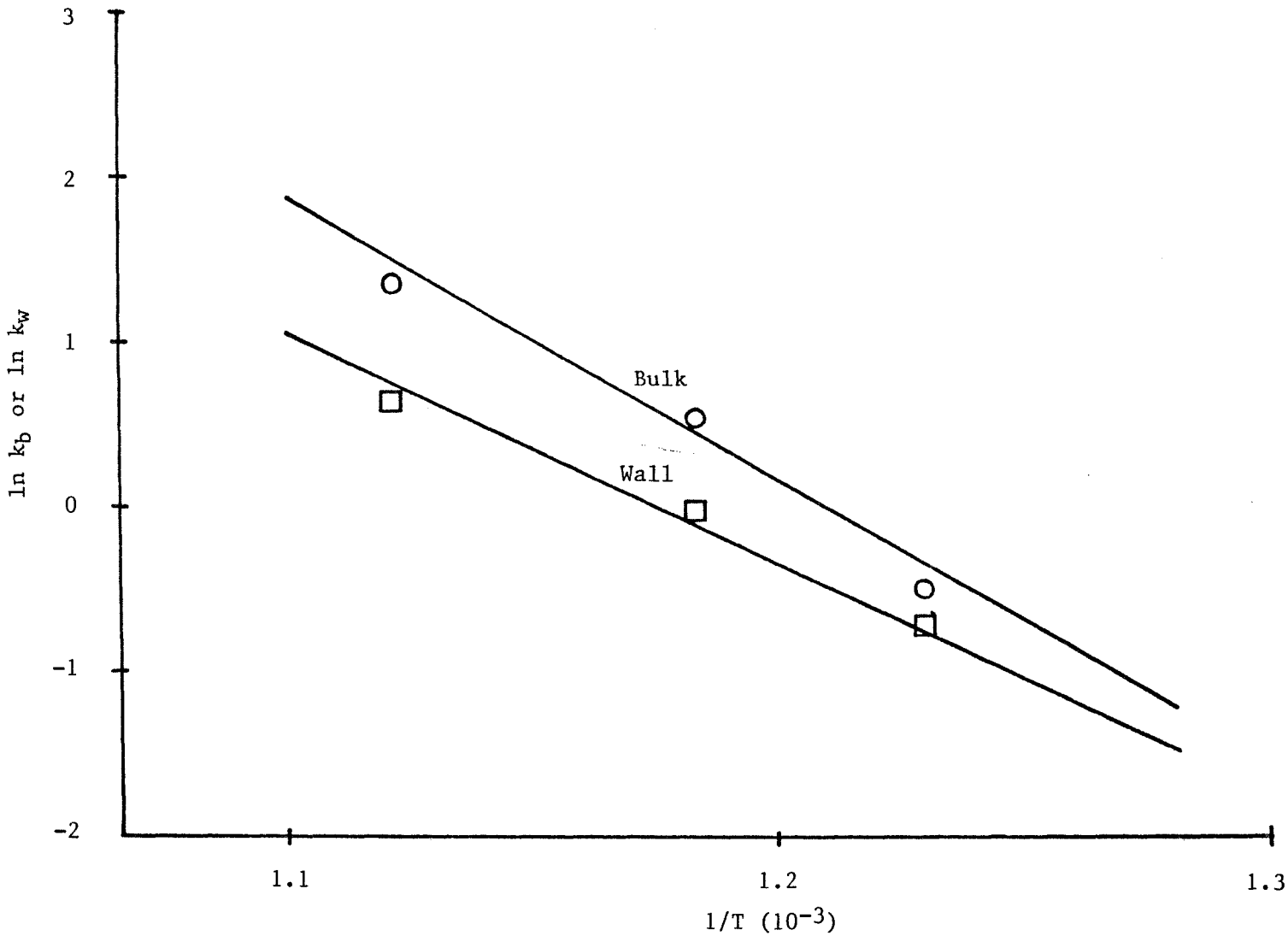


Figure 11. Arrhenius Behavior of k_b and k_w for CH_3CCl_3

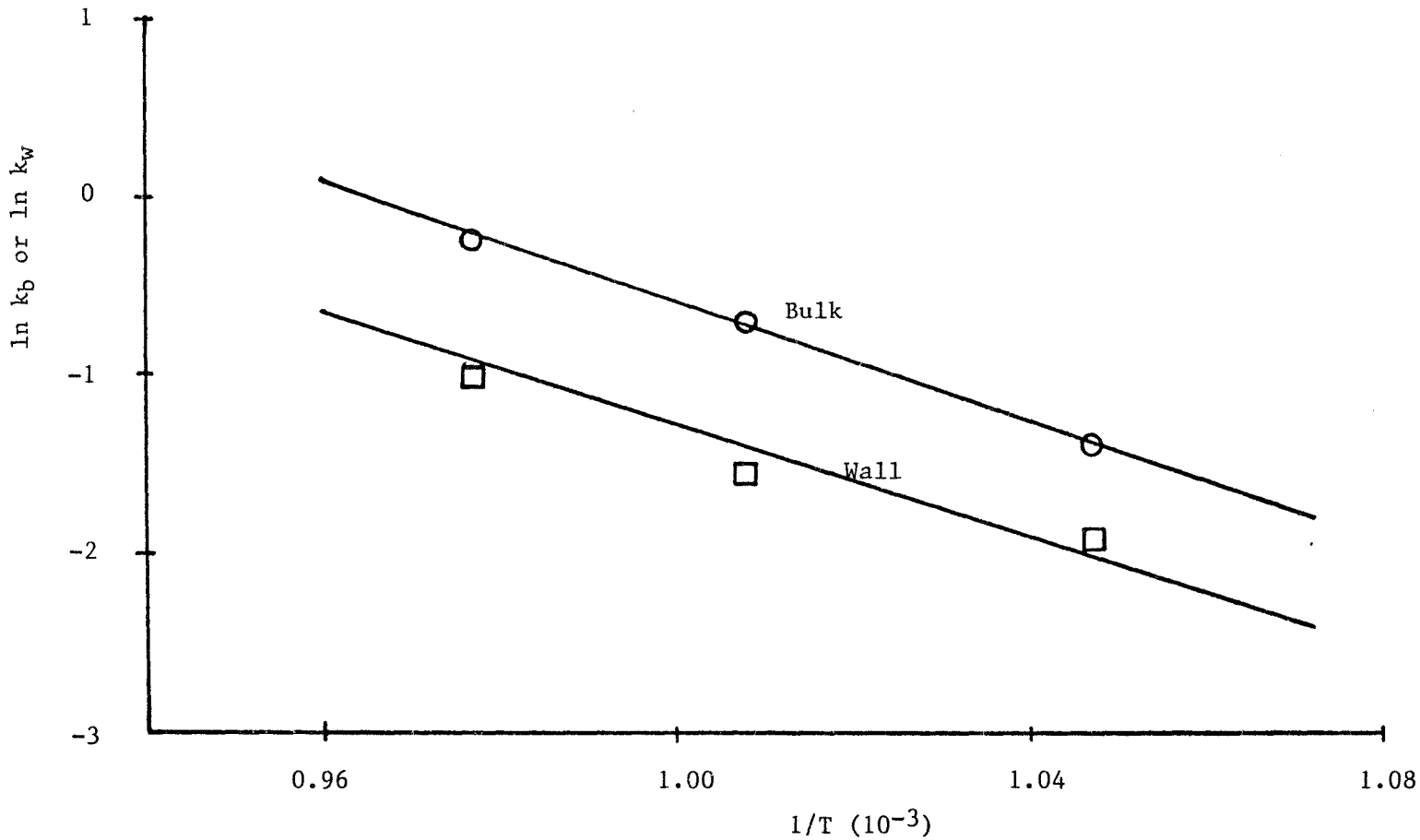


Figure 12. Arrhenius Behavior of k_b and k_w for CH_2Cl_2

compound reactions[11,15] because of synergistic effects of mixture reaction which will be discussed in next sections and reaction accelleration or self catalysis at higher temperatures due to reactions of chlorine radical.

B. Reagent Conversion and Product Distribution

Appreciable conversions (50%) of dichloromethane and 1,1,1-trichloroethane were observed at reaction temperature above 720 ^{o}C and 515 ^{o}C for the respective reagents at 0.5 sec. residence time as shown in Figure 5. Figure 5 shows that the conversion of each reagent consistently increases with increasing temperature and mean residence time. The major product distributions are shown in Figure 13 and 14 for varying temperature and reaction conditions. 1,1-dichloroethylene (CH_2CCl_2), 1,1-dichloroethane (CH_3CHCl_2), vinyl chloride (CH_2CHCl), methyl chloride (CH_3Cl) and HCl were the major product at 570 ^{o}C, where up to 95 % conversion of CH_3CCl_3 and 13 % conversion of CH_2Cl_2 were observed as shown in Figure 5 and 13. Minor products at this temperature of methane, ethylene and ethane (whereas these are major products at temperatures above 720 ^{o}C). Monochloroethane (CH_3CH_2Cl) and 1,1,2-trichloroethane ($CHCl_2CH_2Cl$) are also found at this temperature; As shown in semi-quantitative product distribution Table 6 and 7 the trace quantities of trichloroethylene (CCl_2CHCl), 1,2-dichloroethylene (CHClCHCl) and C_3 hydrocarbon were also

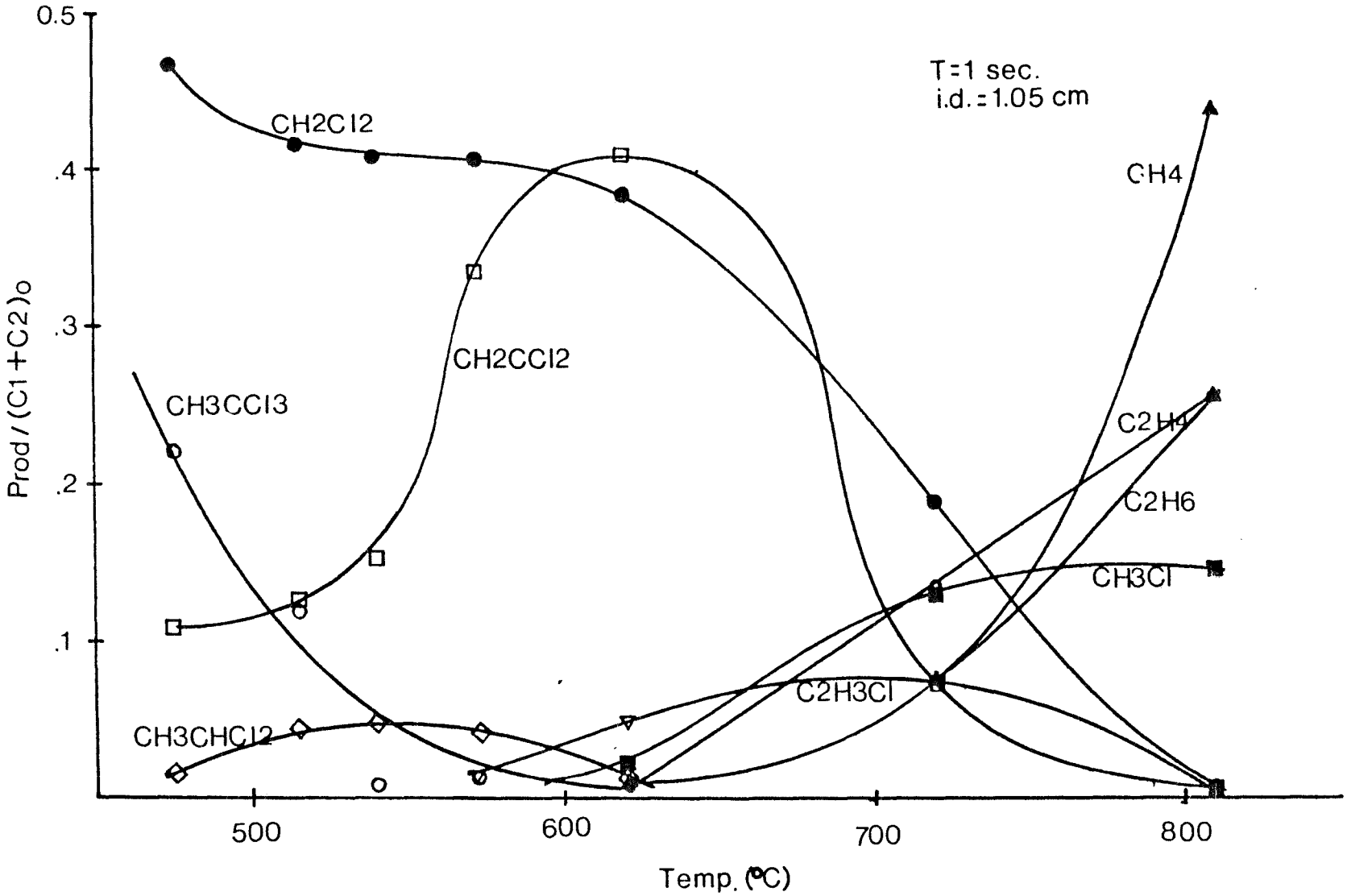


Figure 13. Product Distribution vs Temp. in CH2Cl2/CH3CCl3/H2

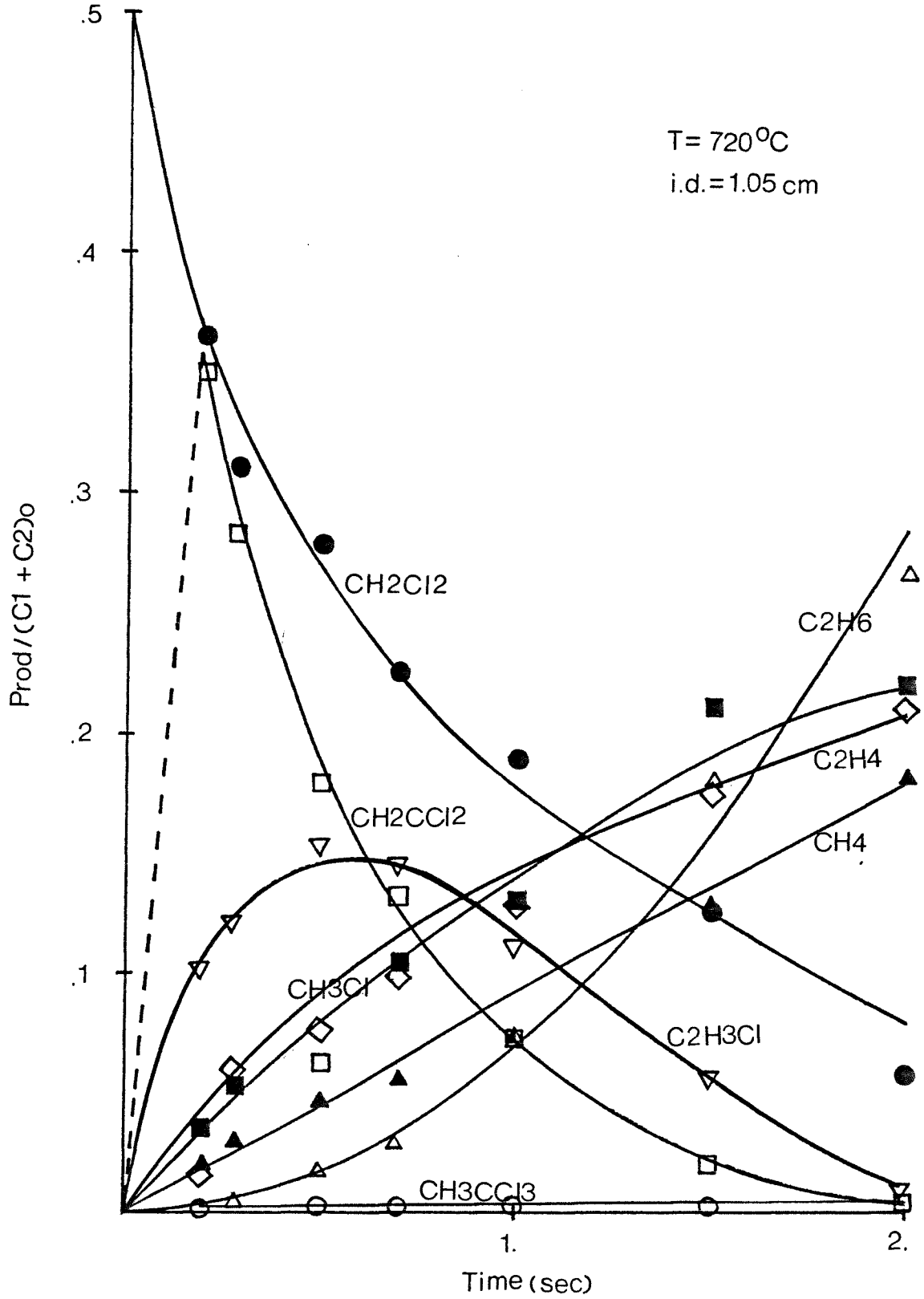


Figure 14. Product Distribution vs Time in $CH_2Cl_2/CH_3CCl_3/H_2$

observed at temperatures below 720 ^{o}C . As illustrated in Figure 15, formation of non-chlorinated hydrocarbon is shown to increase with increasing temperature. The number of chlorine containing hydrocarbon products decreases with increasing temperature and residence time and HCl formation increases as shown in the chlorine material balance Table3. The number and quantity of chlorinated hydrocarbon products drops quickly at about 720 ^{o}C, where only CH_3Cl was observed at 810 ^{o}C and 1 sec. reaction conditions. This indicates that CH_3Cl is the most stable chlorocarbon in this reactig system. It is consistent with the bond strengths C-Cl bonds on chlorocarbons which increases with decreasing chlorination.

The conversion of CH_2Cl_2 increases slowly or reaches an apparent steady state value of about 13 % at temperature below 515 and 620 ^{o}C as illustrated in Figure 13. However, conversion for CH_2Cl_2 rises quickly as the temperature increase from 620 ^{o}C where CH_3Cl and CH_4 as the C_1 products rapidly increase. This occurs because CH_2Cl_2 by itself does not react to significant degree below 620 ^{o}C but radicals which are produced from CH_3CCl_3 can attack the CH_2Cl_2. However, as the temperature increases from about 620 ^{o}C, CH_2Cl_2 decomposition reaction sets in. Formation of CH_3Cl and CH_4 increases proportionally to decrease in CH_2Cl_2 from 620 to 720 ^{o}C and further reaction of these species will be discussed with CH_3CCl_3 by-product reaction.

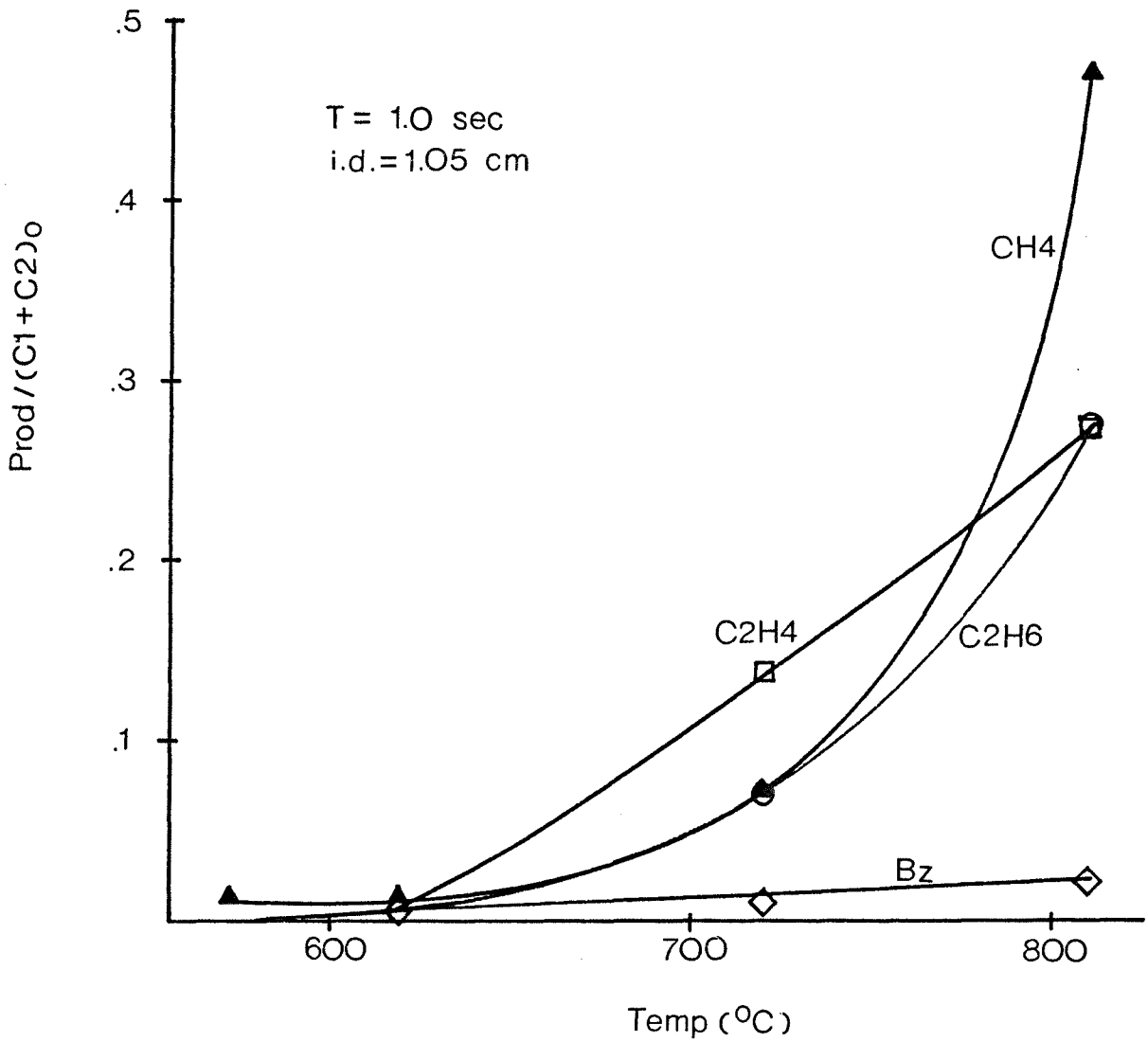


Figure 15. Dechlorinated Hydrocarbon Product Distribution versus Temperature

Table 3

Material Balance for 100 Moles Chlorine

CH_2Cl_2 : CH_3CCl_3 : H_2 = 1 : 1 : 24.6

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

Species (%)	Temperature (^oC)				
	475	572	620	720	810
CHCCl	ND	0.28	0.12	1.0	2.3
CH_3Cl	0.12	0.84	1.1	6.3	3.8
CH_2CHCl	0.03	0.75	1.92	4.8	ND
CH_3CH_2Cl	ND	0.15	0.15	0.5	ND
CH_2Cl_2	35.7	33.4	30.9	16.2	0.4
CH_2CCl_2	8.8	27.0	33.0	8.1	0.2
CH_3CHCl_2	ND	3.7	1.0	0.3	ND
CHClCHCl	0.12	0.12	0.1	ND	ND
CH_3CCl_3	38.9	0.3	0.1	0.54	0.5
$CHClCCl_2$	ND	0.1	0.1	ND	ND
$CHCl_2CH_2Cl$	0.3	0.5	0.2	1.4	ND
HCl	12.5	35.6	37.5	56.7	92.7
Total	98.3	102.7	106.5	95.8	99.9

Table 4

Material Balance for 100 Moles Carbon

CH_2Cl_2 : CH_3CCl_3 : H_2 = 1 : 1 : 24.6

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

Species (%)	Temperature (^oC) 475	572	620	720	810
CH_4	0.1	0.5	1.0	4.7	29.4
CHCH	ND	0.15	0.5	0.8	ND
CH_2CH_2	ND	0.3	0.2	19.2	28.4
CH_3CH_3	ND	0.15	0.2	9.5	28.4
CHCCl	ND	0.2	0.3	1.5	3.8
CH_3Cl	0.2	1.4	1.8	10.5	6.3
$CHCCH_3$	ND	0.3	0.2	0.3	ND
C_3H_6 & C_3H_8	ND	0.3	0.4	1.3	0.15
CH_2CHCl	0.1	2.5	6.5	16.0	ND
CH_3CH_2Cl	ND	0.5	0.5	1.6	ND
CH_2Cl_2	31.2	27.8	25.7	13.5	0.3
CH_2CCl_2	14.6	45.0	55.0	9.8	ND
CH_3CHCl_2	ND	6.1	1.6	0.5	ND
CHClCHCl	0.2	0.2	0.15	ND	ND
CH_3CCl_3	43.2	0.3	0.1	0.2	0.3
$CHClCCl_2$	ND	0.1	0.1	ND	ND
C_6H_6	ND	ND	0.1	1.4	2.6
$CHCl_2CH_2CL$	0.3	0.5	0.2	1.5	ND
Total	89.9	86.3	94.5	92.4	99.75

Formation of CH_2CCl_2 as one of major product from CH_3CCl_3 increases with increasing temperature to a maximum near 620 ^oC with 1.0 sec. residence time and then drops quickly with increasing temperature; strongly indicating that CH_2CCl_2 is the initial stable product in unimolecular reaction of this mixture diluted in hydrogen. Figure 16 also specifically illustrates CH_2CCl_2 normalized concentration versus residence time for seven different temperature, and demonstrates that CH_2CCl_2 concentration increases with increasing residence time under 572 ^oC while it increases and then decreasing with residence time over 620 ^oC. The increase in CH_2CCl_2 with residence time suggests that its rate of formation is faster than its destruction of this 572 ^oC temperature and is another indication that the CH_2CCl_2 is a stable intermediate product in overall reaction. Formation of CH_3CHCl_2, CH_2CHCl (vinyl chloride) and CH_3Cl also show a similar trend; These trends may be due to a high formation rate of precursor products (CH_2CCl_2, CH_3CHCl_2 and CH_3Cl) from the chlorinated parent compounds. These products are also dechlorinated to CH_2CHCl, CH_2CH_2, CH_3CH_3 and CH_4 in further reaction steps with increasing temperature.

Formation of CH_2CHCl and CH_2CH_2 increases from 620 to 720 ^oC as the temperature increases. This indicates that the more stable compound, CH_2CHCl is apparently formed from overall reaction of CH_2CCl_2 and CH_3CHCl_2 with hydrogen, and

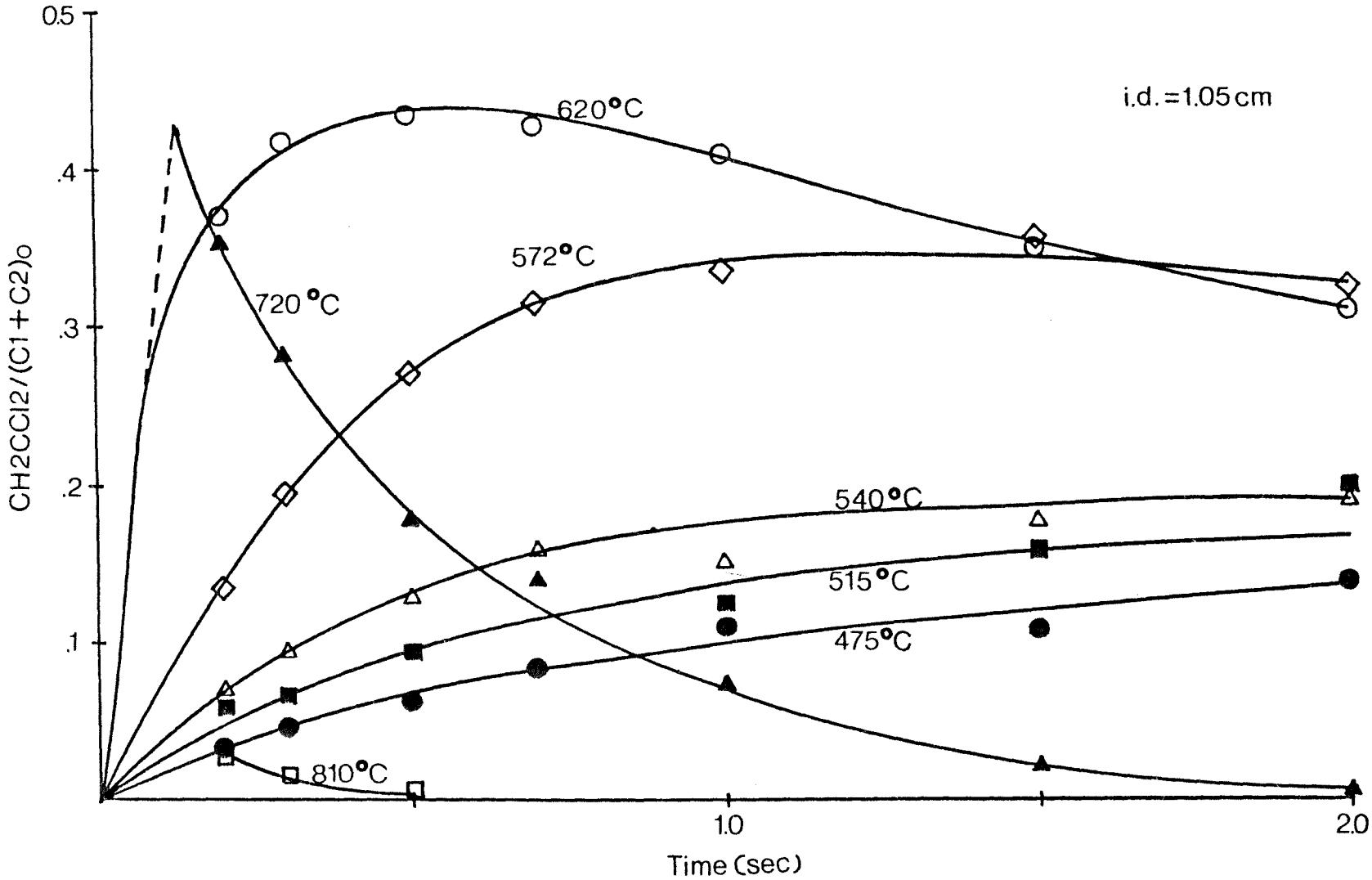


Figure 16. CH2CCl2 Formed per mole of feed

then CH_2CH_2 or CH_3CH_3 is produced from further reaction of CH_2CHCl with hydrogen in this temperature reaction region. The 720 - 810 ^oC temperature range reaction of CH_2CHCl appeares very similar to 620 - 720 ^oC that of CH_2CCl_2.

Formation of CH_4, CH_2CH_2 and CH_3CH_3 increases with increasing temperature to 810 ^oC. This indicates the less chlorinated hydrocarbon is more stable in the reacting system. As shown in Table 5, the greater the bond energy between carbon and chloride, the higher temperature required to observe reaction of the chlorocarbon.

TABLE. 5

Product Maxima Formation Temperatures and Bond Eneregies between Carbon and Chlorine in This Reaction System

Species	Max. Form. Temp. (^oC)	Bond Energy (Kcal/mol)
CH_3CHCl_2	540	78.15
CH_2CCl_2	620	88.59
CH_2CHCl	720	90.90
CH_3CCl_3	< 570	73.20

* Reaction residence time 0.5 sec. with 1.05 cm id tube

The C_2 trace products from pure CH_2Cl_2 reaction could be observed by Tsao<15>, but those quantities cannot be

Table 6

Thermal Reaction Products Distribution with Temperature

CH_2Cl_2 : CH_3CCl_3 : H_2 = 1 : 1 : 24.6
Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

Species	Temperature (^oC)				
	515	572	620	720	810
CH_4	x	x	xx	xxx	****
CHCH		x	x	x	
CH_2CH_2	x	x	x	*	**
CH_3CH_3		x	x	xxx	**
CHCCl	x	x	x	x	xx
CH_3Cl	x	xx	xx	*	xxx
$CHCCH_3$	x	x	x	x	
C_3H_6 & C_3H_8	x	x	x	xx	x
CH_2CHCl	x	xx	xx	*	
CH_3CH_2Cl	x	x	x	xx	
CH_2CCl_2	*	***	****	xxx	
CH_3CHCl_2	xx	xx	xx	x	
CHClCHCl	x	x	x		
$CHClCCl_2$		x	x		
C_6H_6			x	x	xx
$CHCl_2CH_2Cl$	x	x	x	x	

0.1 % < x < 1.0 % < xx < 5.0 % < xxx < 10 %

10 % < * < 20 % < ** < 30 % < *** < 40 % < ****

Percent = (Product Mol Conc.) / (C_1 + C_2)o

Table 7

Thermal Reaction Products Distribution
with Residence Time

CH_2Cl_2 : CH_3CCl_3 : H_2 = 1 : 1 : 24.6
Reactor Diameter : 1.05 cm
Reaction Temperature : 720 ^oC

Species	Residence Time (sec.)				
	0.2	0.5	1.0	1.5	2.0
CH_4	xx	xx	xxx	*	*
CHCH	x	x	x	x	x
CH_2CH_2	xx	xxx	*	*	**
CH_3CH_3	x	xx	xxx	*	**
CHCCl	x	x	x	xx	xx
CH_3Cl	xx	xxx	*	**	**
$CHCCH_3$			x		
C_3H_6 & C_3H_8	x	x	x	x	x
CH_2CHCl	*	*	*	xxx	xx
CH_3CH_2Cl	x	x	xx	xx	x
CH_2CCl_2	***	*	xxx	xx	x
CH_3CHCl_2	x	x	x	x	x
CHClCHCl	x	x			
$CHClCCl_2$		x		x	
C_6H_6	x	x	x	x	xx
$CHCl_2CH_2Cl$	x	x	x		

0.1 % < x < 1.0 % < xx < 5.0 % < xxx < 10 %

10 % < * < 20 % < ** < 30 % < *** < 40 % < ****

Percent = (Product Mol Conc.) / (C_1 + C_2)o

separated from CH_3CCl_3 by product. And these results will be discussed futher detail in the reaction mechanism. No observation of C_1 products from pyrolysis of CH_3CCl_3 in hydrogen occured in this study even though it overlapped the compounds whose bonds are relatively stable. Chuang's study<10> show that very tiny amount of C_1 products from 1,1,2-trichloroethane reaction was seen at above 850 ^oC.

The overall reaction scheme based on analysis of major concentration products and thermochemical kinetics estimation will be discussed in the detailed mechanism section.

Asshown in the semi-quantitative productdistribution Table 6, benzene formation is observed above 620 ^oC and the non-chlorinated C_3 products are also seen above 515 ^oC and over a wide temperature range. C_2H_2 concentration increases slightly and then decreases as more benzene is formed. The formations of benzene and non-chlorinated C_3 hydrocarbon may be due to pyrolysis of methane and C_2 hydrocarbons, followed by ring closure mechanism with olefinic and acetylenic species as intermediates. A general commercial pathway to synthesis of benzene is pyrolysis and hydrogasfication of paraffinic hydrocarbons<32>.

C. Comparison of Dichloromethane/1,1,1-Trichloroethane mixture Reaction with Each Pure Compound Reactions of Previous Studies

It worth comparing the two reagents in the mixturewith

each pure reagent reaction in hydrogen to find effects of mixed system. Tsao[15] (1987) studied thermal decomposition of pure dichloromethane in hydrogen under similar experimental conditions within the temperature range of 700 to 950 ^{o}C and residence time of 0.3 to 3.1 sec.. Dichloromethane feed concentration was 20 %. While, as shown in Figure 17, conversion trends are similar in both cases; here are, however, conversion differences present between the two results. Figure illustrates that conversion difference decreases with temperature rise. For both cases, however, the complete decay (99%) temperature for dichloromethane is the same, about 810 ^{o}C. The conversion of pure dichloromethane reaction increases slowly between 515 and 620 ^{o}C and it appears to reach an apparent steady state value of 13 % in the above temperature range as illustrated in Figure 17. This occurs because dichloromthane by itself does not react to significant degree below 620 ^{o}C but the radicals which are produced from 1,1,1-trichloroethane reaction on subsequent reaction with hydrogen can attack dichloromethane. The pure dichloromethane reaction, however does not follow this kind of behavior (pure CH_2Cl_2 conversion is near 0 % for temperature (515 - 620 ^{o}C) range). As the temperature increases above 700 ^{o}C, the conversion difference decreases. This indicates that unimolecular decomposition reaction of dichloromethane starts and becomes dominant, eventually to

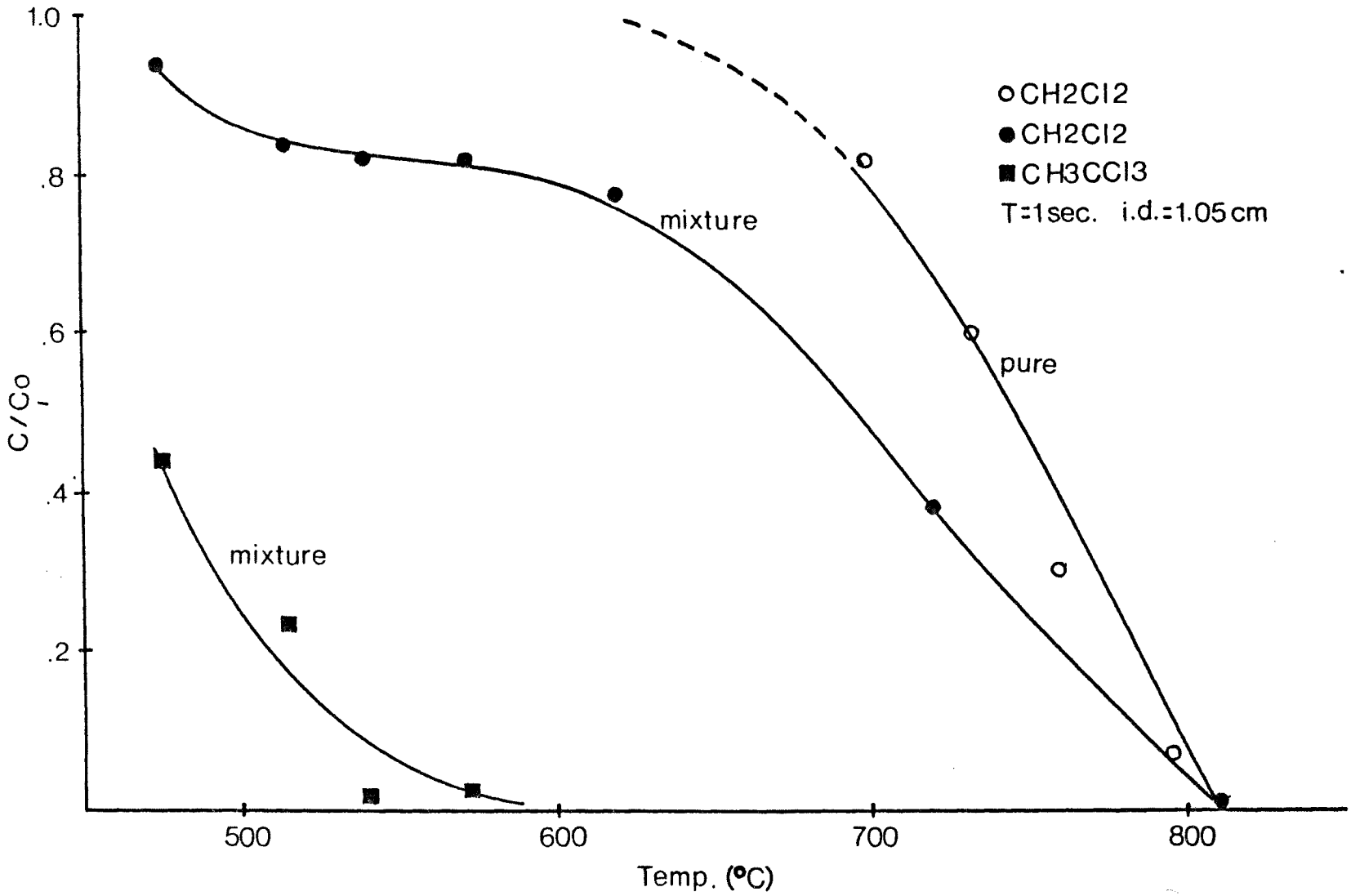


Figure 17. Comparison of Pure and Mixed System of CH2Cl2

overcome the earlier radical initiated reaction.

It is valuable to analyze excess hydrogen concentration difference effect on rate constant for each two experimental sets. The difference in the concentration of excess hydrogen may explain the change the rate constant. The reactant to hydrogen ratios are 1:12.3 and 1:4 respectively for mixture and neat studies of dichloromethane. The reactant concentration of two studies change by a factor of three; but the hydrogen concentration does not change significantly. Attempts to explain the effect of change in hydrogen concentration fail to provide reliable results due to the close proximity of the two hydrogen concentration and complicated mixture reaction effects.

Major products from the pure CH_2Cl_2 by Tsao' study<15> reaction are CH_4, CH_3Cl and traces of CHCH, CH_2CH_2, CH_3CH_3 and CH_2CHCl. Methane and methyl chloride normalized concentration the mixture, on the other hand, are slightly higher than that of pure dichloromethane/hydrogen reaction. This occurs because the conversion of mixture reaction is higher than that of pure CH_2Cl_2 reaction. Above 800 ^oC, the methane normalized concentration difference is indicates CH_3CCl_3 dissociates to CH_3 and CCl_3, and then converts to CH_4.

Chang<11>(1985) had studied the thermal decomposition of pure 1,1,1-trichloroethane in hydrogen using similar experimental system at the temperature range of 555 to 681

^{o}C and short residence times between 0.04 to 1.0 sec. for 5.89 % of 1,1,1-trichloroethane present in feed concentration.

Figure 18 shows that both conversion trends are similar with small difference present. The major products from 1,1,1-trichloroethane reaction were observed to be 1,1-dichloroethylene, chloroform, 1,1-dichloroethane, trichloroethylene, methylene chloride and HCl. Propane, proylene and propyne as minor products were seen at all reaction temperature ranges, when a mixture of chlorocarbons were used. These products however, were not identified in each pure compound reaction systems.

In order to simplify the kinetic analysis and obtain global rate parameters, pseudo-first order reaction conditions were utilized by having a large excess of H_2. Decoupling of the wall and bulk reaction constant was achieved by the assuming plug flow reactor conditions (Kaufman<26>) and pseudo first order reaction condition prevail. Apparent bulk activation energies were estimated to be 32 Kcal/mol for CH_3CCl_3 and 36 Kcal/mol for CH_2Cl_2 with H_2 in the mixture reaction system. CH_3CCl_3 apparent bulk activation energy is close to that of pure compound reaction of CH_3CCl_3 (26 Kcal/mol) reported in the literature<18>. But CH_2Cl_2 apparent bulk activation energy is 39 % smaller than that of pure CH_2Cl_2 (50 Kcal/mol) reported in the literature<15>. This is because radicals which are more

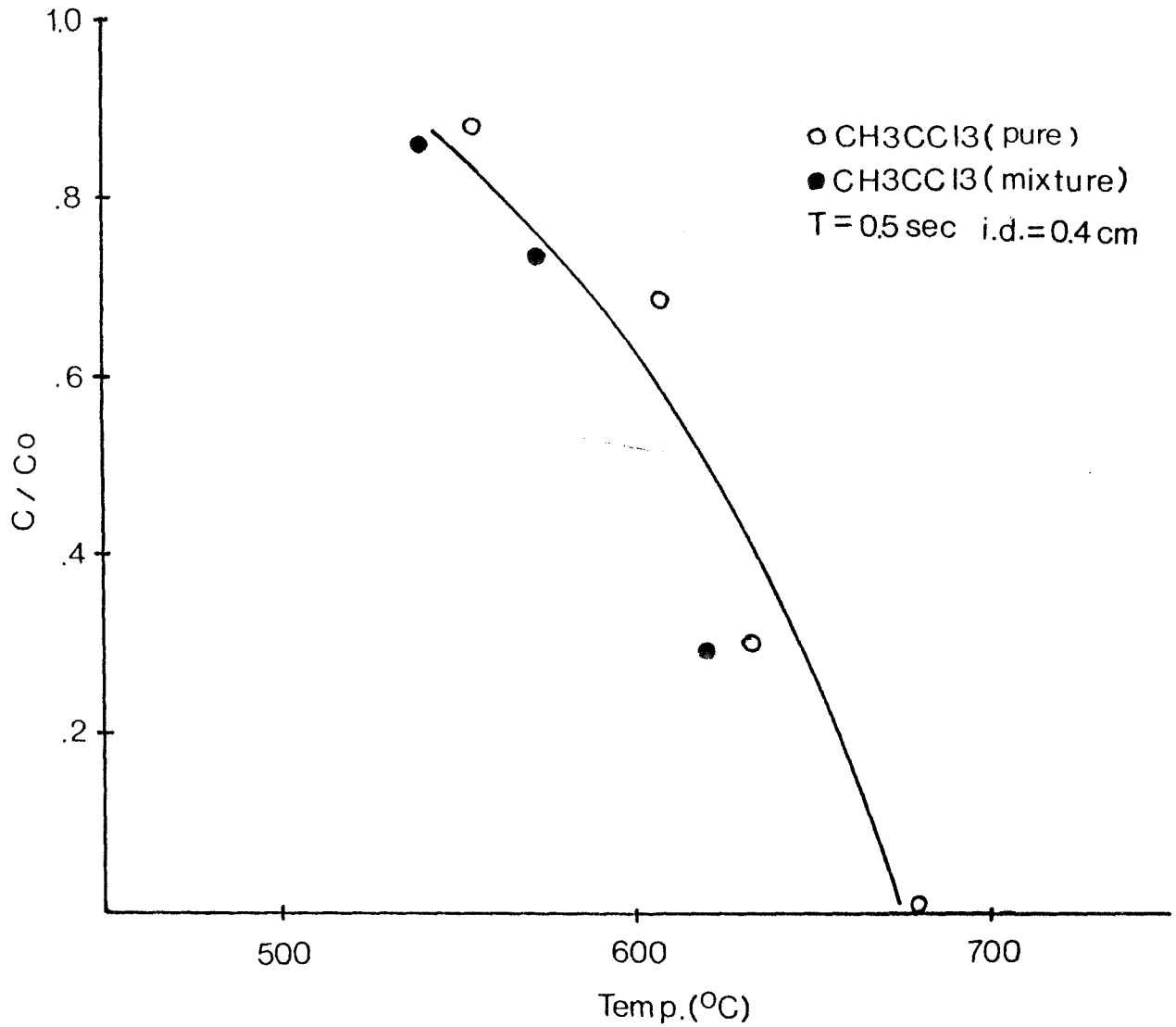


Figure 18. Comparison of Pure and Mixed System for CH_3CCl_3

easily produced from CH_3CCl_3 decomposition initiate CH_2Cl_2 decomposition. These radical reactions decrease the CH_2Cl_2 activation energy similar to the role of a catalyst.

D. Quantum RRK

The decomposition/stabilization of the energized radical and molecule complexes was modeled using the QRRK calculation. The details of the bimolecular QRRK method in theory section and its application to a number of chemically activated reaction systems have been discussed<27,33>.

Energized Complex/QRRK theory as presented by Westmoreland and Dean<33> is used for modelling of radical addition and combination reactions. This has been modified by Ritter and Bozzelli<34> to use gamma function. The QRRK computer code was used to determine the energy dependent rate constants for all channels. The program incorporates QRRK theory to calculate rate constants as function of temperature and pressure. It is important in determination of the mechanism and choice of the paths (accurate product prediction from the activated complex).

A QRRK analysis of the chemically activated system, using generic estimates or literature values for high pressure rate constants and species thermodynamic properties for the enthalpies of reaction, yields apparent rate constantsas will be shown in Figure 20 & 22 and APPENDIX 1. And the results from the calculations input rate parameters

used in these calculations are summarized in APPENDIX Table 1 - 12. The calculations were performed for each of six pressures between 0.76 torr and 7600 torr.

The combination reaction of primary radicals, CH_3CCl_2 (another source : Cl transfer metathetical reaction of H with CH_3CCl_3) and H, is similar but will produce different end-products as shown in all possible reactions which will explain formation procedure of other products

```
CH3CCl2 + H <====> [CH3CHCl2]# -----> CH3CHCl + CL     (1)
 (65.5)                 :                 (45.7)
                        :      -----> CH2CHCl + HCl    (2)
                        :                 (24.8)
                        :      -----> CH2CHCl2 + H     (3)
            STABILIZED  :                 (70.8)
                        :      -----> CH3 + CHCl2      (4)
                        v                 (60.8)
                   CH3CHCl2                            (5)
                    (-31.1)
```

where the energized complex (# denotes energized) further decomposes as shown in reaction (1) to (4). The energy diagram for the above reaction channels(1) to (5) is illustrated in Figure 19. Reactions (3) and (4) do not occur due to thermo limitation (high energy barrier). They are endothermic, while reactions (1), (2) and (5) are thermodynamically favorable channels (low energy barrier) relative to initial energy of the reactants. It must be noted that reaction (2) corresponds to the composite behavior of four-center 1,2 and three-center 1,1 HCl elimination processes, because the CH_3CCl: formed in the latter case rapidly isomerized to CH_2CHCl. Both 1,2 and 1,1

HCl elimination processes are expected to have similar A factors[35] and slightly higher activated energies for 1,1 HCl elimination processes[36].

The calculation results, pressure dependent rate constants and an energy diagram for H atom addition to CH_3CCl_2 are shown in Figure 19 and 20. The QRRK calculations for temperature 773 to 1273 ^oK and pressure range of 0.001 - 10 atm. show that the rate constant for the CH_2CHCl+HCl channel and CH_3CHCl + Cl channel are dominant below 0.1 atm. whereas at pressures above 1 atm. stabilization of activated complex is dominant. The CH_3CHCl radical, from reaction (1) can undergo beta scission to CH_2CHCl+ H or CH_3CH +Cl and stablized CH_3CH_2Cl can also react spliting out HCl forming C_2H_4.

The QRRK calculation results show for this reaction system that the rate constant for CH_2CHCl+HCl channel is close to CH_3CHCl+Cl and three times greater than CH_3CHCl_2 (stabilization) at temperature range 773 -873 ^oK and 1 atm..

For the CH_2CCl_2 + H system, the energy diagram is shown in Figure 21, where the following major reactions are expected to be important:

```
CH2CCl2 + H <======> [C2H3Cl2]# --------> CH2CHCl + Cl   (6)
  (52.8)                 :                    (37.3)
                         :
            STABILIZED   :
                         :
                         v
                      C2H3Cl2                             (7)
                       (15.9)
```

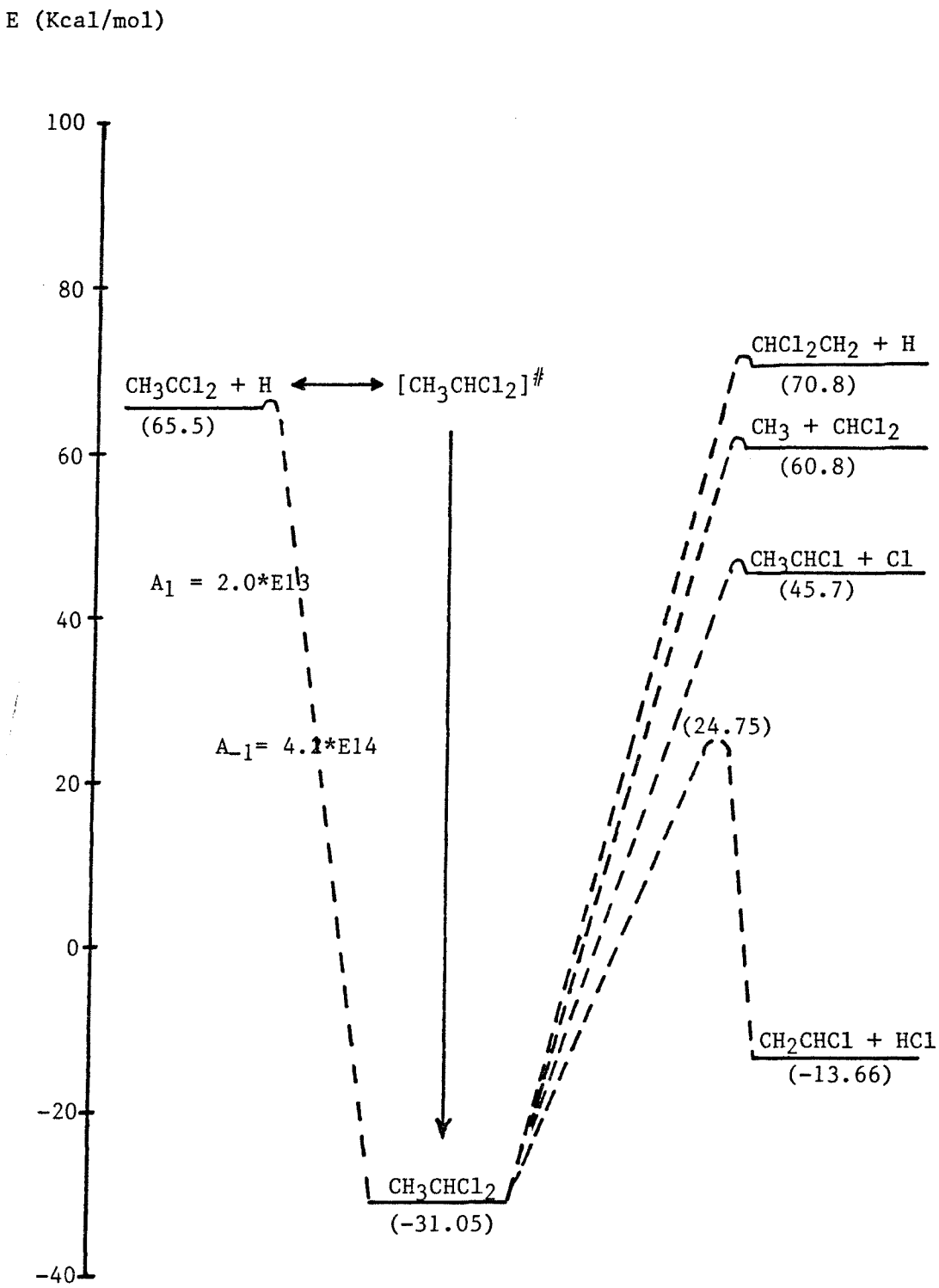


Figure 19. Energies of Activation Complex Theory Calculation for Reaction CH_3CCl_2 + H

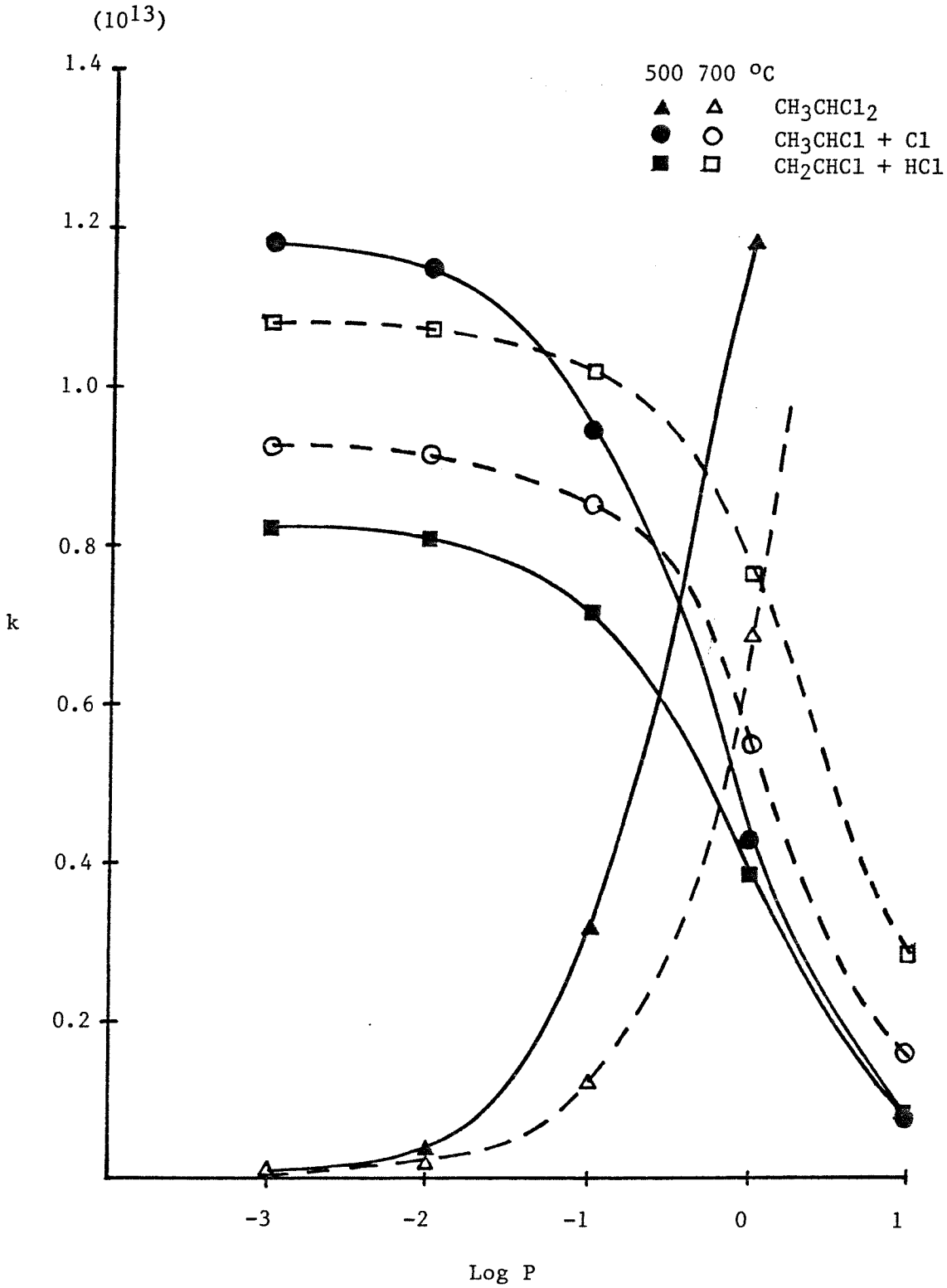


Figure 20. Results of Activated Complex Theory Calculation for Reaction $CH_3CCl_2 + H$

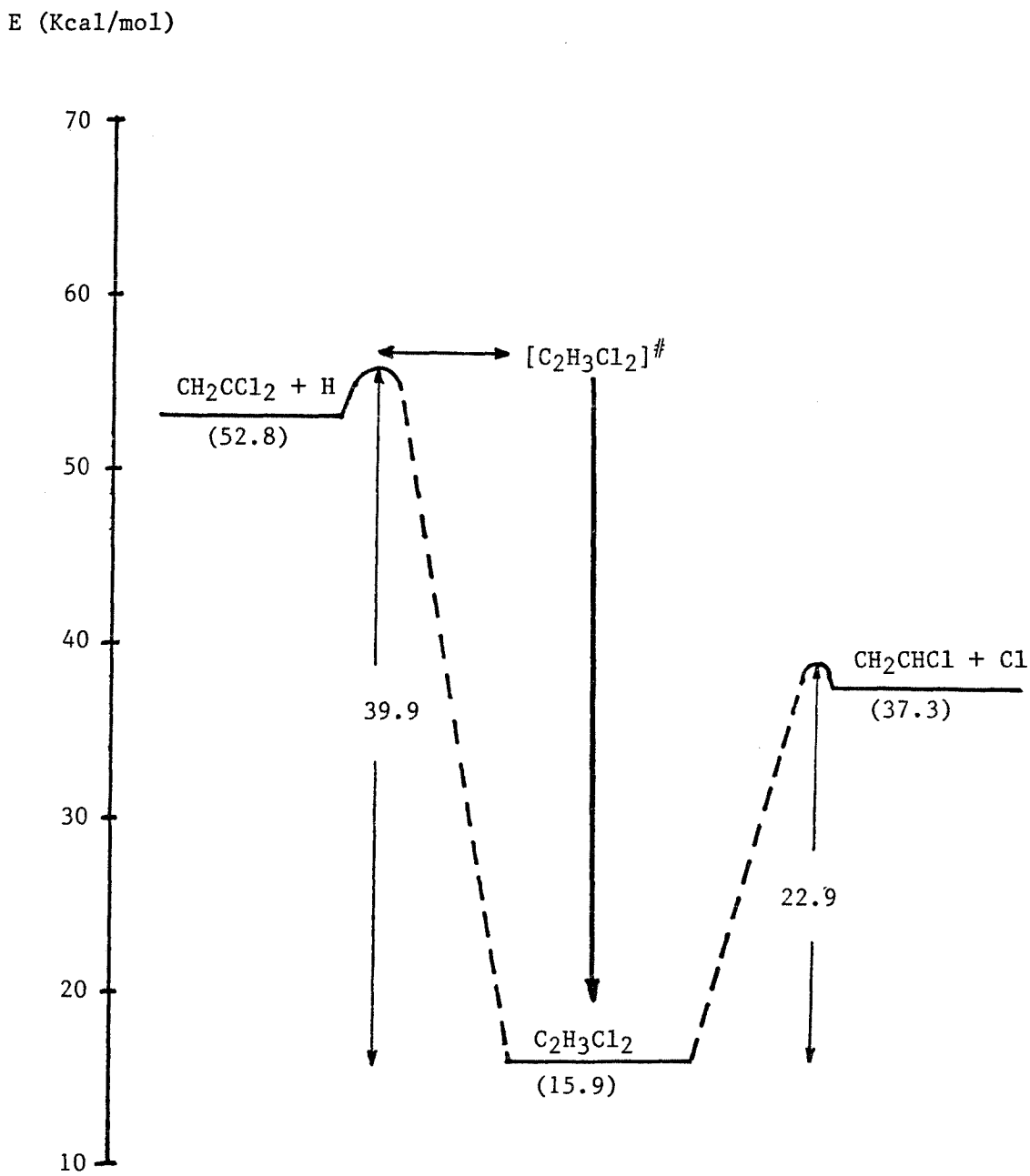


Figure 21. Energy Diagram for CH_2CCl_2 + H

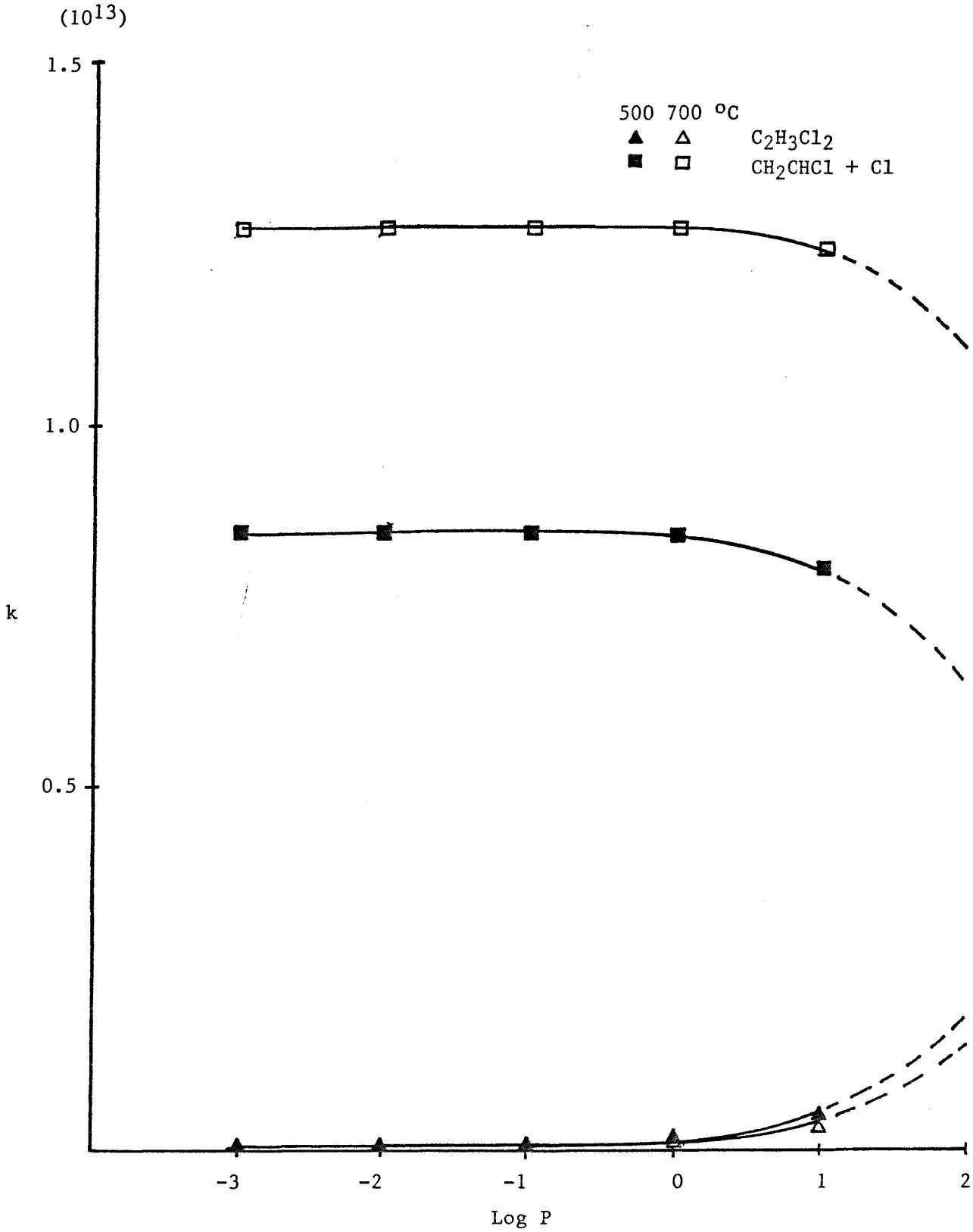


Figure 22. Results of Activated Complex Theory Calculation for Reaction CH_2CCl_2 + H

Atomic H produced from $Cl + H_2 = HCl + H$ will add to CH_2CCl_2 to form $CHCl_2CH_2$ radicals as shown above reactions. The energy diagram of the reaction (6) and (7) is illustrated in Figure 21 and the calculation results are shown in Figure 22.

The $CHCl_2CH_2$ complex is initially " hot " since, in addition to the thermal energy, it contains energy resulting from formation of the new chemical bond. Prior to stabilization it may unimolecularly isomerize. It can undergo a hydrogen shift, become a stabilized radical or beta scission to $CH_2CHCl+Cl$.

E. Detailed Kinetic Mechanism and Modeling

The reaction mechanism and decomposition kinetics for CH_2Cl_2/CH_3CCl_3 mixture in H_2 are developed.

The possible initial reactions are unimolecular decomposition of CH_2Cl_2 and CH_3CCl_3 as follows:

		A (1/s)	E (Kcal/mol)		
CH_2Cl_2 ---> CH_2Cl	+ Cl	1.1E16	82.8	(ΔHr)	(1)
CH_2Cl_2 ---> CHCl	+ HCl	1.2E14	105.0	(ΔHr+40)	(2)
CH_3CCl_3 ---> CH_3CCl_2	+ Cl	2.4E16	73.2	(ΔHr)	(3)
CH_3CCl_3 ---> CH_2CCl_2	+ HCl	3.8E13	47.9	(ΔHr+38)	(4)
CH_3CCl_3 ---> CH_3	+ CCl_3	9.1E15	84.7	(ΔHr)	(5)

(kinetic data source refer to source part of Table 8)

It is observed from the above kinetic listing that reaction (4) dominates the other pathways by more than three

orders of magnitude at temperatures below 600 ^{o}C. This is consistentwith our experimental results. CH_2CCl_2 and HCl are the major products detected below 600 ^{o}C. The formation of CH_3CHCl_2 as one of the main products at low temperature results from reaction of CH_3CCl_2 radical with H_2. CH_3CCl_2 results from metathetical reaction (abstraction reaction (7)) of H with CH_3CCl_3 conbined with reaction (3). H is produced from reaction of Cl with H_2 as follows:

				A	E	
Cl	+ H_2	----> H	+ HCl	4.8E13	1.3	(6)
H	+ CH_3CCl_3	----> CH_3CCl_2	+ HCl	3.0E13	3.0	(7)
CH_3CCl_2	+ H_2	----> CH_3CHCl_2	+ H	3.8E13	19.0	(8)
H_2	+ CH_3CCl_3	----> CH_3CHCl_2	+ HCl	overall reaction of (7) and (8)		

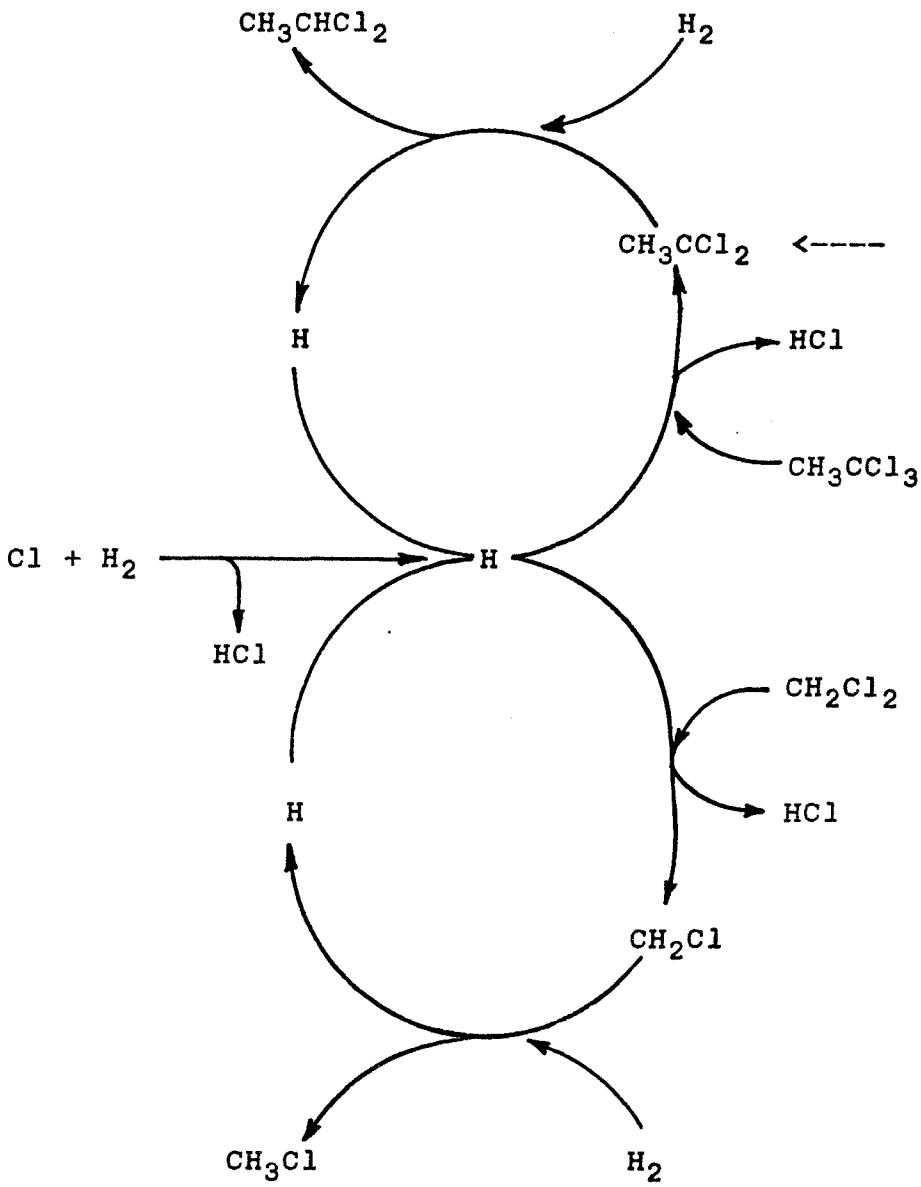
The above three reactions are fast and one sees that H radical plays a catalytic role in formation of CH_3CHCl_2. CH_3CHCl_2 is one of the major products even though reaction (3) only accounts for ca. 0.1 % of the total CH_3CCl_3 decomposition in our low temperature range. In addition, CH_2Cl_2 decay below 620 ^{o}C is explained by a mechanism similar to formation of CH_3CHCl_2.

				A	E	
H	+ CH_2Cl_2	----> CH_2Cl	+ HCl	1.1E13	6.0	(9)
CH_2Cl	+ H_2	----> CH_3Cl	+ H	1.0E13	7.4	(10)
CH_2Cl_2	+ H_2	----> CH_3Cl	+ HCl	overall reaction of (9) and (10)		

The reactions (7 to 10) can be represented in a sort of

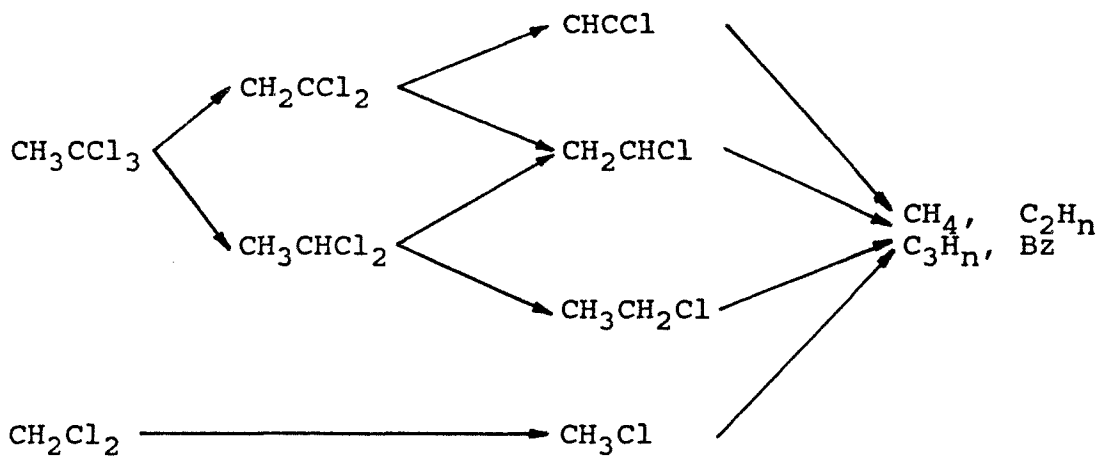
cyclic pathway, Figure 23, driven by unimolecular decomposition reaction (3). Figure 23 illustrated thatH atoms react with both reagents CH_3CCl_3 and CH_2Cl_2 and rapidly form HCl and chlorocarbon radicals. The chlorocarbon radicals then react, rapidly at our temperature with H_2 bath gas to regenerate H atoms and to produce a chlorocarbon molecule with one less Cl than the parent. This process will continue on both the parent and product chlorocarbons until organic hydrocarbons (and HCl) remain.

Distributions of major products vs temperature are shown in Figure 13. Formation of CH_2CCl_2 increases with increasing temperature to a maximum near 620 ^oC and then drops quickly. Formations of CH_2CHCl and CH_3Cl also shows the same trend, but with maximum around 720 ^0C and 810 ^oC respectively. This is consistent with the bond strengths of C-Cl bonds on chlorocarbons which increases with decreasing chlorination<7,37>. The formation of CH_2CCl_2 increases proportionally to decrease in CH_3CCl_3 in temperature range 475 - 620 ^oC, strongly demonstrating that CH_2CCl_2 is the initial stable product in the thermal unimolecular decomposition of CH_3CCl_3 in H_2. CH_2CHCl is then produced from further reaction of primary products CH_2CCl_2 and CH_3CHCl_2 with hydrogen. The overall reaction scheme based on analysis of the major concentration products and thermochemical kinetic estimation can be illustrated as follow:



<---- : addition of CH_3CCl_2 from CH_3CCl_3 unimoleclar reaction

Figure 23. CH_3CHCl_2 and CH_3Cl Formation cycle with H Radical



(plus one HCl from each step). It should be pointed out that this reaction scheme is not a complete detailed mechanism, with the actual mechanism obviously including a significant number of free radical reactions.

Mechanism Modeling by CHEMKIN Program

The CHEMKIN computer program package is used in interpreting and integrating the detailed reaction mechanisms (models) of the systems studied. The CHEMKIN program[38], Figure 24, is reads the user's symbolic description of the reaction mechanism. The thermodynamic data base, which has the appropriate thermodynamic information and mass for all species present in mechanism with a format similar to the one used by the NASA complex chemical equilibrium code. The information on the elements, species , and reactions in the mechanism; and finally the CHEMKIN gas phase subroutines, which can be called to return

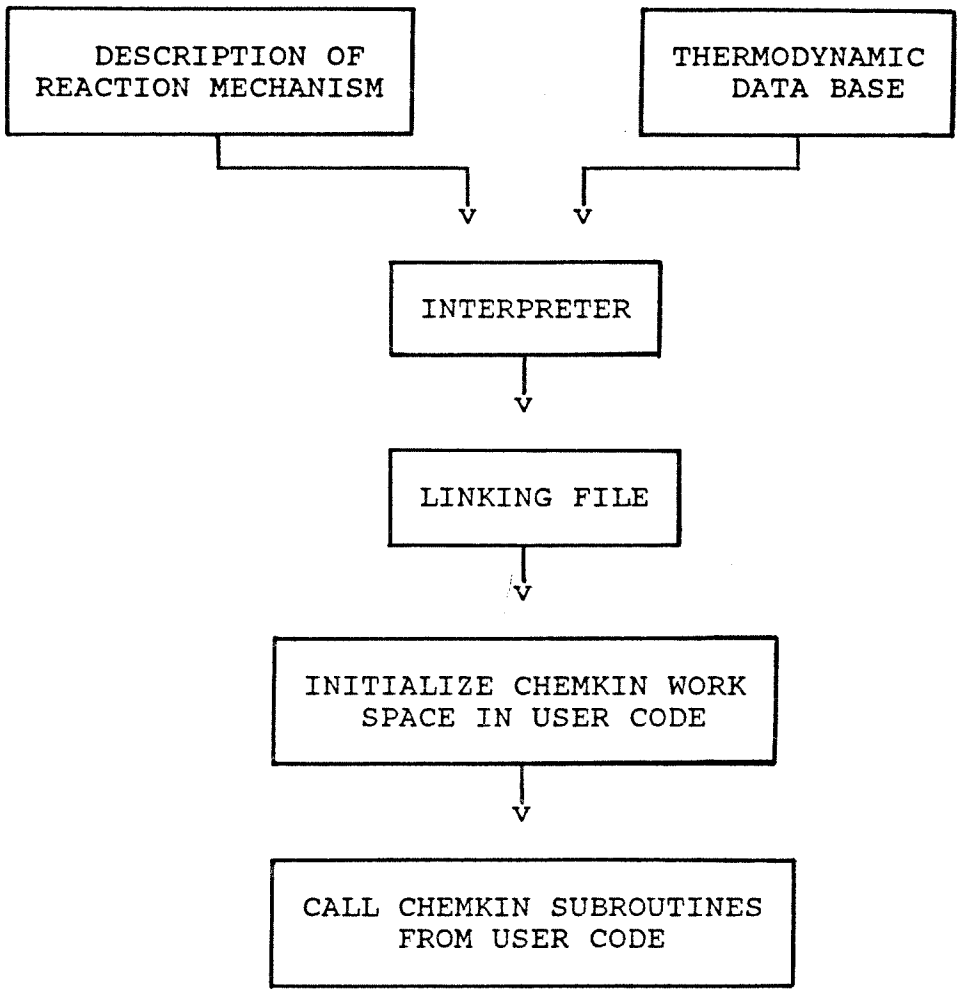


Figure 24. Structure of the CHEMKIN package

information on the elements, species, reactions, equation of state, thermodynamic properties, chemical production rates, and derivatives of thermodynamic properties relative to any time in the integration. Generally the input to these subroutines are the state variables of gas pressure or density, temperature and species composition. All routines can be called with the species composition defined in terms of mass fractions or molar concentrations. Numerical calculations were carried out using the CHEMKIN computer code.

The input data requirement to run CHEMKIN program Include:

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

A thermodynamic data base for species with C/H/Cl elements is developed at NJIT and used for modeling of the kinetic scheme of reaction system investigated. For those species that thermodynamic information were not available in the data base, a thermo data was generated utilizing JANAFIT program. This program requires heat capacities in the temperature range of interest, as input. Heat of formations and entropies, as well as heat capacities, were

calculated by group additivity method of Benson[35] when not available in literature.

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

Detailed reaction kinetic mechanism were developed to describe the systems of reactions studied. A mechanism composed of 94 elementary reactions, which appears in Table 8, were found to fit experimental results.

These kinetic schemes were formulated considering all reaction products detected by GC. Elementary reaction rate parameters for abstraction reactions are based upon literature comparison, thermodynamic estimations and Transition State Theory methods of Benson[35]. QRRK calculations[33,34], as described in previous section, were used to estimate apparent rate parameters for addition and dissociation reactions (1 atm).

Experimental pyrolysis data are compared with model predictions in Figure 25 for reagent decomposition and product distribution between 475 and 810 ^{o}C. Predictions for loss of the two reagents and product distribution match experiment well. Figure 27 demonstrates calculated concentration of parent reactants and products versus reaction time at temperature of 720 ^{o}C and shows quite good agreement with the experimentally observed data for decay of reactants and formation of products.

Figure 25 and 27 show the small difference seen between

calculated and experimental values for various species (reagents and products). The important reasons for this difference can be explained as following; First, the kinetic scheme does not include all possible products, specifically polyaromatic compound and carbon (solid) production. Second, the detailed mechanism only considers gaseous phase reaction; heterogeneous reaction effects are not included. Finally, the kinetic parameters estimated for several number of elementary reactions incorporated in detailed mechanism, are estimated based on best available thermodynamic and kinetic collision frequency data in literature or for similar reactions. This may produce error when used for our actual reaction conditions.

Table 8

Detailed Mechanism for $CH_2Cl_2/CH_3CCl_3/H_2$ Reaction System

	REACTION	A	Ea(Kcal/mol)	source
1.	$CH_3CCl_3 = CH_2CCl_2 + HCl$	3.80E+13#	47.9	a
		3.23E+13*	47.8	DISSOC
2.	$CH_3CCl_3 = CH_3CCl_2 + Cl$	2.40E+16#	73.2	b
		2.80E+15*	71.0	DISSOC
3.	$CH_3CCl_3 = CH_3 + CCl_3$	9.10E+16#	84.7	c,k
		4.23E+16*	82.9	DISSOC
4.	$CH_3CHCl_2 = CH_2CHCl + HCl$	2.60E+13#	55.8	d
		2.45E+13*	54.6	DISSOC
5.	$CH_3CHCl_2 = CH_3CHCl + Cl$	7.85E+15#	76.8	e,k
		3.09E+15*	76.1	DISSOC
6.	$CH_3CHCl_2 = CH_3 + CHCl_2$	1.31E+17#	91.6	c
		6.77E+16*	90.1	DISSOC
7.	$CH_3CH_2Cl = CH_2CH_2 + HCl$	3.24E+13#	56.6	f
		3.03E+13*	57.4	DISSOC
8.	$CH_3CH_2Cl = CH_3CH_2 + Cl$	2.18E+15#	81.5	g,k
		7.11E+14*	81.0	DISSOC
9.	$CH_3CH_2Cl = CH_3 + CH_2Cl$	6.84E+15#	89.0	h
		5.81E+15*	89.5	DISSOC
10.	$CH_3CH_3 = CH_3CH_2 + H$	1.26E+16#	98.0	i
		1.15E+15*	95.9	DISSOC
11.	$CH_3CH_3 = CH_3 + CH_3$	7.94E+16#	89.4	i
		1.59E+17*	93.5	DISSOC
12.	$CH_3CCl_2 = CH_2CCl_2 + H$	2.60E+13	41.4	j
13.	$CH_3CHCl = CH_2CHCl + H$	2.76E+13	47.3	j
14.	$CH_3CH_2 = CH_2CH_2 + H$	5.01E+13	40.9	i
15.	$CH_2CH_2 = CH_2CH + H$	2.00E+16	110.0	i
16.	$CH_2CH = CHCH + H$	3.16E+12	38.3	i

17.	$CH_3CHCl + H_2 = CH_3CH_2Cl + H$	5.00E+12	17.2	l,k
18.	$CH_3CCl_2 + H_2 = CH_3CHCl_2 + H$	6.26E+12	16.5	m,w
19.	$CH_3CCl_3 + H = CH_3CCl_2 + HCl$	3.00E+13	1.5	n,w
20.	$CH_3CHCl_2 + H = CH_3CHCl + HCl$	2.00E+13	4.0	o,w
21.	$CH_3CH_2Cl + H = CH_3CH_2 + HCl$	1.50E+13	8.0	p,w
22.	$CH_2CCl_2 = CHCCl + HCl$	7.10E+13#	69.1	q
		2.90E+15*	80.3	DISSOC
23.	$CH_2CCl_2 = CH_2CCl + Cl$	9.34E+15#	88.6	r,k
		7.85E+14*	85.9	DISSOC
24	$CH_2CHCl = CHCH + HCl$	3.55E+13#	68.73	s
		1.76E+15*	82.9	DISSOC
25.	$CH_2CHCl = CH_2CH + Cl$	4.08E+15#	87.6	t,k
		5.34E+14*	85.7	DISSOC
26.	$CH_2CHCl + H = CH_2CH + HCl$	1.00E+13	6.5	l
27.	$CH_2CCl_2 + H = CH_2CCl + HCl$	1.20E+13	5.5	u
28.	$CH_2CCl + H_2 = CH_2CHCl + H$	6.16E+11	6.0	v
29.	$CH_3CH_3 + H = CH_3CH_2 + H_2$	6.61E+13	9.7	w
30.	$CH_2CH_2 + H = CH_2CH + H_2$	1.91E+13	10.3	w
31.	$CHCH + H = CHC + H_2$	2.00E+14	19.0	w
32.	$CH_2Cl_2 = CHCl + HCl$	1.20E+14	105.0	x
33.	$CH_2Cl_2 = CH_2Cl + Cl$	1.06E+16#	82.8	y,k
		2.39E+14*	78.2	DISSOC
34.	$CH_3Cl = CH_2 + HCl$	9.30E+13	130.9	z
35.	$CH_3Cl = CH_3 + Cl$	2.63E+15#	83.3	1,k
		1.27E+14*	79.7	DISSOC
36.	$CH_4 = CH_3 + H$	1.00E+16#	105.0	i
		2.48E+14*	102.0	DISSOC
37.	$CH_2Cl_2 + H = CH_2Cl + HCl$	1.10E+13	6.1	w
38.	$CH_3Cl + H = CH_3 + HCl$	3.72E+13	9.3	w
39.	$CH_4 + H = CH_3 + H_2$	5.00E+12	11.0	w

40.	$CH_2Cl + H_2 = CH_3Cl + H$	2.86E+12	14.0	2,w
41.	$CHCH + H = CHC + H_2$	3.10E+13	3.7	w
42.	$CH_3CCl_3 + Cl = CH_2CCl_3 + HCl$	2.51E+12	3.6	w
43.	$CH_2CCl_3 = CH_2CCl_2 + Cl$	1.35E+14	19.0	3,w
44.	$CH_2Cl_2 + Cl = CHCl_2 + HCl$	5.03E+13	2.9	w
45.	$CH_3Cl + Cl = CH_2Cl + HCl$	1.29E+14	3.6	w
46.	$CH_3 + CH_2Cl_2 = CH_4 + CHCl_2$	6.76E+10	7.2	w
47.	$CH_3 + CH_2Cl_2 = CH_3Cl + CH_2Cl$	1.40E+11	4.9	w
48.	$CH_3 + CH_3Cl = CH_4 + CH_2Cl$	3.30E+11	9.4	w
49.	$CCl_3 + H_2 = CHCl_3 + H$	5.37E+12	14.3	w
50.	$CHCl_3 = CHCl_2 + Cl$	2.52E+16#	78.8	4,k
		2.21E+14*	72.2	DISSOC
51.	$CHCl_2 + H_2 = CH_2Cl_2 + H$	4.12E+12	3.5	2,w
52.	$C_2H_5 + CH_2Cl_2 = C_2H_5Cl + CH_2Cl$	2.80E+11	7.0	5
53.	$CH_3CH_2CH_2 = CH_3 + CH_2CH_2$	1.00E+13	32.9	i
54.	$CH_3CH_2CH_2 = CH_3CHCH_2 + H$	1.26E+13	38.5	i
55.	$CH_2CHCH_2 = CH_2CCH_2 + H$	1.26E+13	61.3	i
56.	$CH_3CH_2CH_2CH_3 = 2CH_3CH_2$	8.00E+16	81.9	i
57.	$CH_2CCl_2 + H = CH_2CHCl_2$	2.67E+09*	-4.7	QRRK 1
58.	$CH_2CCl_2 + H = CH_2CHCl + Cl$	6.02E+13*	3.0	QRRK 1
59.	$CH_2CCl + H = CH_2CHCl$	1.80E+10*	-7.0	QRRK 2
60.	$CH_2CCl + H = CH_2CH + Cl$	1.02E+14*	0.1	QRRK 2
61.	$CH_2CCl + H = CHCH + HCl$	8.31E+11*	-2.1	QRRK 2
62.	$CH_2CHCl + H = CH_2CH_2Cl$	1.39E+10*	-2.4	QRRK 3
63.	$CH_2CHCl + H = CH_2CH_2 + Cl$	8.51E+12*	3.5	QRRK 3
64.	$CH_3 + CH_3CH_2 = C_3H_8$	6.52E+12*	-0.7	QRRK 4

65.	$CH_3 + CH_3CH_2 = CH_3CH_2CH_2 + H$	1.16E+14*	25.2	QRRK 4
66.	$CH_3 + CHCH_2 = C_3H_6$	1.15E+13*	-0.7	QRRK 5
67.	$CH_3 + CHCH_2 = CH_2CHCH_2 + H$	9.80E+13*	13.7	QRRK 5
68.	$CH_3 + CCH = CH_3CCH$	2.11E+11*	-3.9	QRRK 6
69.	$CH_3 + CCH = CH_2CCH + H$	1.24E+13*	4.2	QRRK 6
70.	$CH_3CCl_2 + H = CH_3CHCl_2$	2.54E+11*	-6.1	QRRK 7
71.	$CH_3CCl_2 + H = CH_2CHCl + HCl$	7.50E+12*	0.7	QRRK 7
72.	$CH_3CCl_2 + H = CH_3CHCl + Cl$	7.92E+13*	4.6	QRRK 7
73.	$CH_3CHCl + H = CH_3CH_2Cl$	1.30E+12*	-4.2	QRRK 8
74.	$CH_3CHCl + H = CH_2CH_2 + HCl$	5.12E+13*	2.7	QRRK 8
75.	$CH_3CHCl + H = CH_3CH_2 + Cl$	7.64E+14*	7.8	QRRK 8
76.	$CH_3CH_2 + H = CH_3 + CH_3$	7.65E+14*	4.1	QRRK 9
77.	$CH_2Cl + CH_2Cl = CH_2ClCH_2Cl$	1.34E+11*	-5.0	QRRK 10
78.	$CH_2Cl + CH_2Cl = CH_2CHCl + HCl$	2.51E+12*	1.6	QRRK 10
79.	$CH_2Cl + CH_2Cl = CH_2ClCH_2 + Cl$	7.37E+12*	6.5	QRRK 10
80.	$CH_2Cl + CH_3 = CH_2CH_2 + HCl$	1.67E+13*	2.5	QRRK 11
81.	$CH_2Cl + CH_3 = CH_3CH_2 + Cl$	1.76E+12*	7.9	QRRK 11
82.	$CH_2Cl + CHCl_2 = CH_2ClCHCl_2$	4.88E+11*	-4.4	QRRK 12
83.	$CH_2Cl + CHCl_2 = CH_2CCl_2 + HCl$	4.81E+10*	4.1	QRRK 12
84.	$CH_2Cl + CHCl_2 = CHClCHCl + HCl$	1.84E+11*	4.1	QRRK 12
85.	$CH_2ClCH_2 + H_2 = CH_3CH_2Cl + H$	4.00E+12	15.7	6,l
86.	$CHCl_2CH_2 + H_2 = CH_3CHCl_2 + H$	5.26E+12	15.0	7
87.	$CH_3CH_2CH_2 + H_2 = C_3H_8 + H$	2.63E+12	14.8	w
88.	$C_3H_6 + H = CH_2CHCH_2 + H_2$	2.80E+12	1.1	w
89.	$C_4H_{10} = C_3H_7 + CH_3$	1.00E+17	84.7	i
90.	$H_2 = H + H$	5.26E+08	105.0	8

91.	$Cl_2 = Cl + Cl$	7.69E+08	55.6	8
92.	$HCl = H + Cl$	6.09E+08	97.3	8
93.	$Cl + H_2 = HCl + H$	4.80E+13	1.3	w,8
94.	$H + Cl_2 = HCl + Cl$	4.57E+12	1.4	w,8

High pressure limit value

* Pressure dependent : rate expression given for 760 torr
Temperature range : 773 - 1273 ^{o} K

DISSOC : apparent rate constant by DISSOCIATION computer code analysis

QRRK : apparent rate constant by QRRK computer code analysis

SOURCES

a. $A = 10^{13.55} * 10^{(-4/4.6)} * 9$
$Ea = 47.9\ (\Delta Hr + 38)$ (ref: Bamford,D.H. and Tipper,C.F., Comprehensive Chemical Kinetics, Vol.5 1972)

b. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CH_3CCl_2 + Cl = CH_3CCl_3$ (A = 3.0 E+13)
$Ea = \Delta Hr$

c. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CH_3 + 1\text{-}C_4H_9$ (A = 2.0 E+13)
$Ea = \Delta Hr$

d. $A = 10^{13.55} * 10^{(-4/4.6)} * 6$
$Ea = \Delta Hr + 38.5$

e. A factor based upon entropy change for reverse.
A_{-1} taken as that for $1\text{-}C_3H_7 + CH_3$ (A = 2.0E+13)
$Ea = \Delta Hr$

f. $Ea = \Delta Hr + 39.4$
Benson, S.W., "Thermochemical Kinetics", 2nd ed., John Wiley & Son, (1976)

g. A factor based upon ΔS for reverse
A_{-1} taken as that for $C_2H_5 + CH_3$ (A= 2.0 E+13)
$Ea = \Delta Hr$

h. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CH_3 + CH_3CH_2$ (A = 2.0E+13 and Ea = 0)
Ea = ΔHr

i. Dean, A.M., J. Phys. Chem., 89, 4600, 1985

j. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CH_3CCl_2 = CH_2CCl_2 + H$ (A = 1.6E+13)
Ea = ΔHr + 2.0

k. Allara,D.L. and Shaw,R., J. Phys. Chem. Ref. Data, 9,523,1980

l. Barat, R.B. and Bozzelli, J.W., "Reaction of Atomic Hydrogen with Vinyl Chloride", submitted to J. Phys. Chem. (1988)
(A factor taken that for $2\text{-}C_4H_9 + H_2$)

m. $A = A_{17} + \Delta A$ $\Delta A = A_{CHCl2+H2} - A_{CH2Cl+H2}$
($A_{CHCl2+H2}$ and $A_{CH2Cl+H2}$ from source No.2)
Ea from "Evans-Polanyi" plot
("Evans-Polanyi" plot for a set of abstraction reaction. This is a plot of Ea versus ΔHr from similar reactions using data of w. After completing the plot obtain the best slop and put into form of general equation for determination of Ea knowing only ΔHr.)

n. A factor taken as that for $CH_3Cl + H = CH_3 + HCl$
Ea from "Evans-Polanyi" plot

o. A factor taken as 2/3 that for $CH_3Cl + H = CH_3 + HCl$
Ea from "Evans-Polanyi" plot

p. A factor taken as 1/2 that for $CH_3Cl + H = CH_3 + HCl$
Ea from "Evans-Polanyi" plot

q. $A = 10^{13.55} * 2$
Ea = ΔHr + 45 (ref: Skinner)

r. A factor based upon entropy change for reverse.
A_{-1} taken as that for $2\text{-}C_4H_9 + CH_3$ (A = 1.6 E+13)
Ea = ΔHr

s. $A = 10^{13.55} * 1$
Ea = ΔHr + 45 (ref: Zabel, F., Int. J. Chem. Kinetics, 9,651, 1977)

t. A factor based upon ΔS for reverse.
A_{-1} taken as that for $C_2H_5 + CH_3$ (A = 2.0 E+13)
Ea = ΔHr

u. A factor taken as 1.2 that for raction (26)

v. A factor taken as 1.5 that for reverse reaction (30) with A = 4.1 E+11

w. Kerr, J.A. and Moss, S.J.," Handbook of Bimolecular and Termolecular Gas Reaction, Vol.I & II", CRC Press Inc., 1981

x. $A = 10^{13.55} * 4$, $Ea = \Delta Hr + 40$ (ref: Setser, D.W. and Lee, T., Am. Chem. Soc., 89, 5799, 1985)

y. A based upon ΔS for reverse.
A_{-1} taken as that for $C_2H_5 + CH_3$ (A = 2.0 E+13)
$Ea = \Delta Hr$

z. $A = 10^{13.55} * 3$
$Ea = \Delta Hr + 40$ (ref: same with x)

1. A based upon ΔS for reverse.
A_{-1} taken as that for $CH_3 + CH_3$ (A = 2.5 E+13)
$Ea = \Delta Hr$

2. A factor taken as that for interpolation between CH_3+H_2 (1.6 E+12) and $CCl_3 + H_2$ (5.37 E+12) with chlorine number Ea from "Evans-Polanyi" plot

3. A factor based upon entropy change for reverse.
A_{-1} taken as that for $C_2H_3Cl + Cl$ (A = 2.0 E+13)
$Ea = \Delta Hr + 1.5$

4. A factor based upon entropy change for reverse.
A_{-1} taken as that for $2\text{-}C_3H_7 + CH_3$ (A = 1.6 E+13)

5. A factor taken as 2 that for reaction (47)

6. A factor taken as that for reaction $1\text{-}C_4H_9 + H_2$

7. $A = A_{85} + \Delta A$ $\Delta A = A_{CHCl2+H2} - A_{CH2Cl+H2}$

8. Ritter, E. ,Bozzelli, J.W. and Dean, A.M.'s paper accepted in J. Phys. Chem. (1988)

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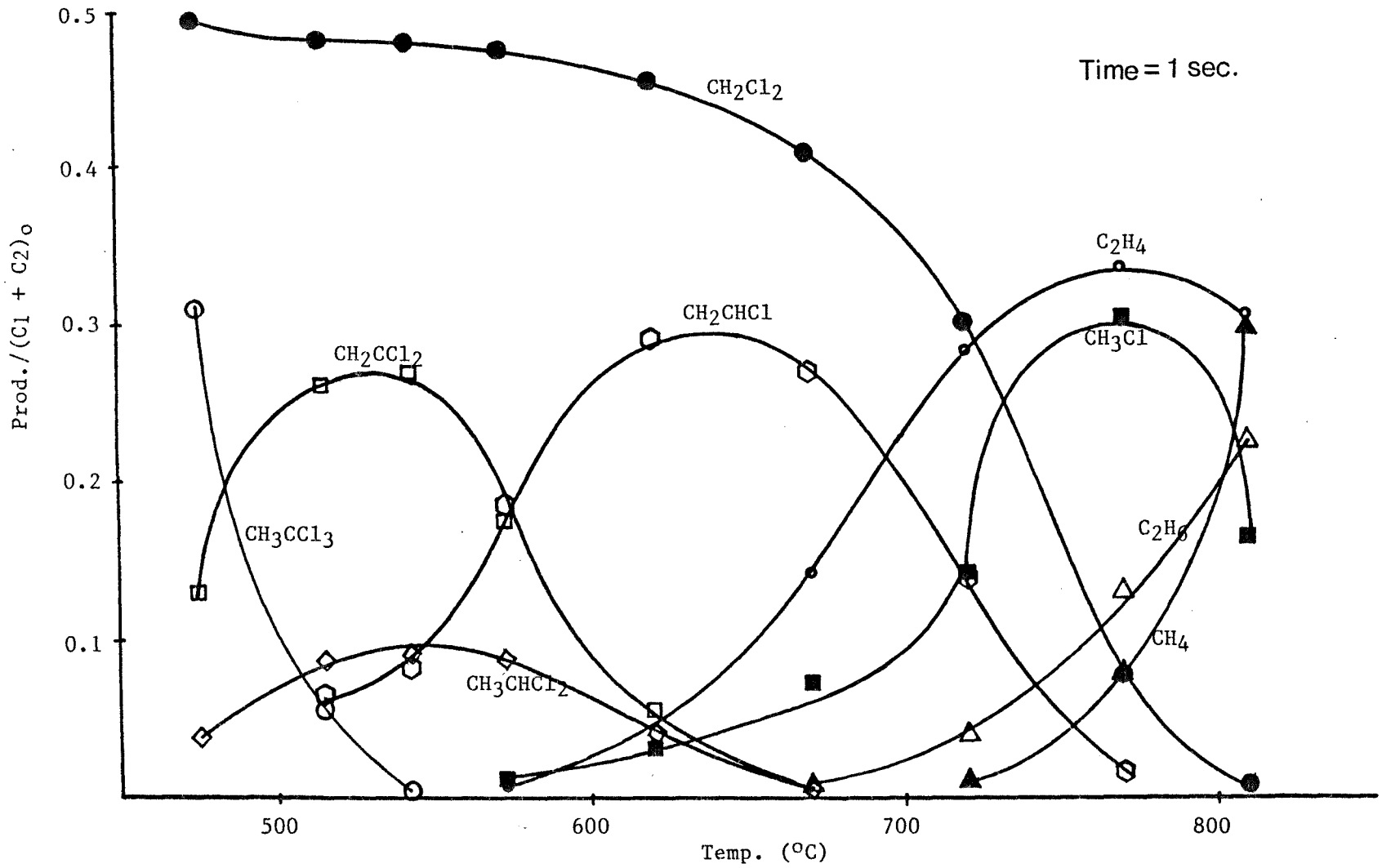

Figure 25. Model Prediction: Product Distribution vs Temperature

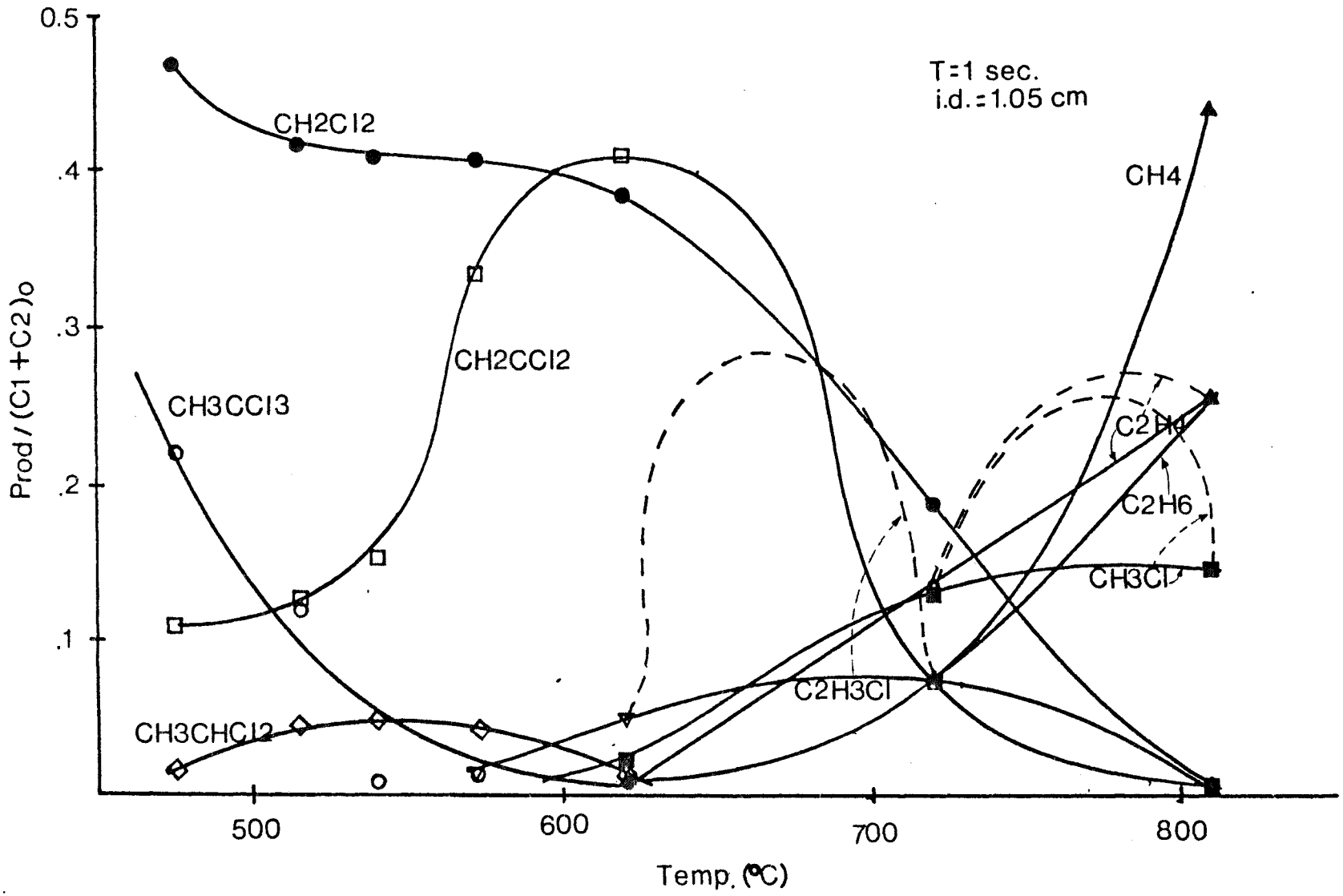

Figure 26. Modified Experimental Product Distribution vs. Temp.
(dash lines based on the model prediction results)

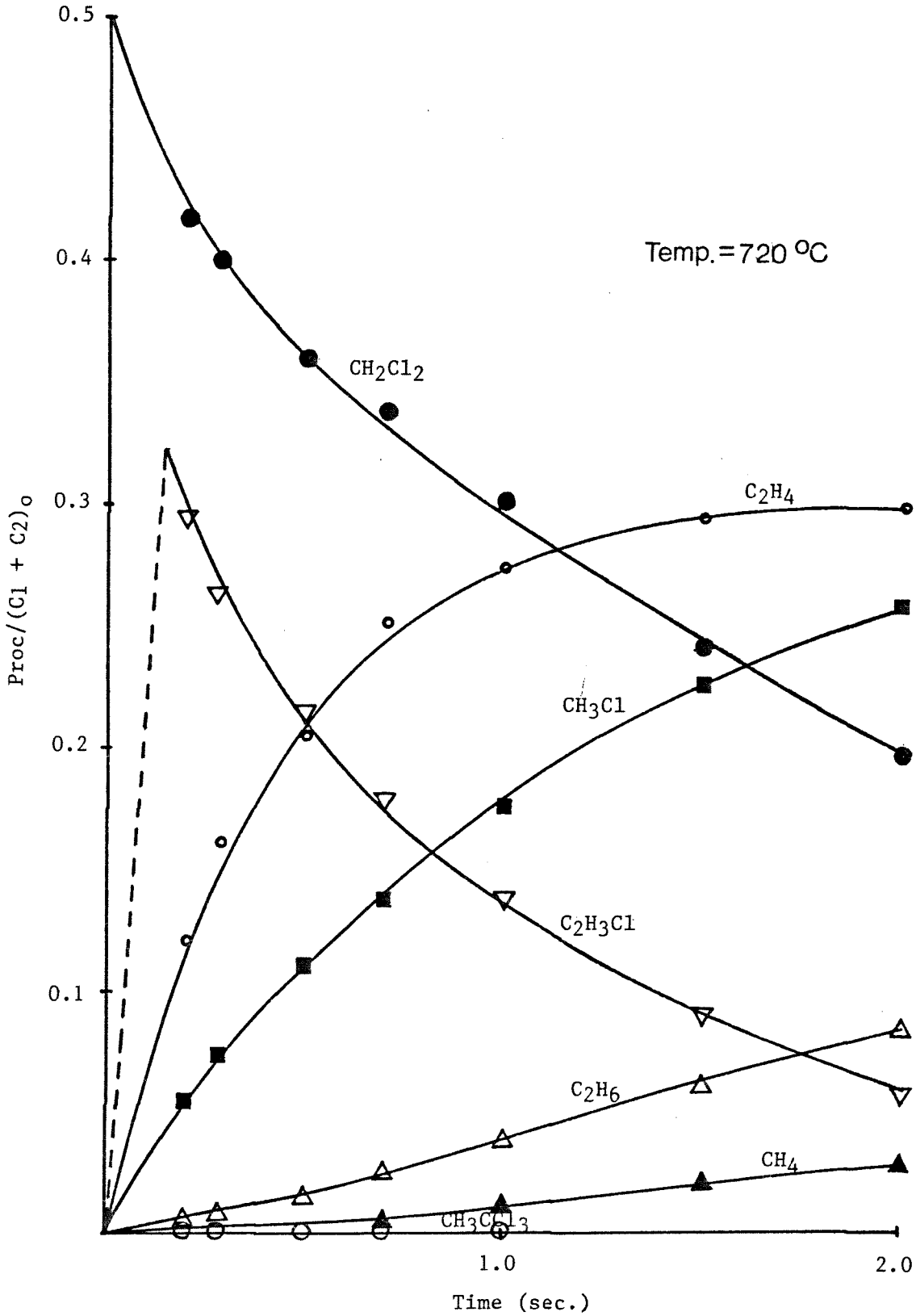

Figure 27. Model Prediction: Product Distribution vs Time

VI. CONCLUSION

The decomposition of dichloromethane/1,1,1-trichloroethane mixture in a hydrogen bath gas was carried out at 1 atmosphere total pressure in a tubular flow reactor. Temperature ranged from 475 - 810 ^{o}C; and residence times studied were in the range from 0.02 - 2.0 seconds.

Complete decay (99 %) occurs at about 810 oC for dichloromethane and around 572 ^{o}C for 1,1,1-trichloroethane at 1 second residence time. The number and quantity of chlorinated products decrease with increasing temperature and residence time, with HCl formation decreasing. The major products at our high temperature ranges (above 720 ^{o}C) were HCl and non-chlorinated hydrocarbons: methane, ethylene and ethane. The most thermodynamically stable (resistant to reaction) chlorocarbon product observed in this system was methyl chloride with excess hydrocarbon.

An increase in surface to volume ratio of reactor tube was observed to accelerate the decomposition process in hydrogen bath, but it had no effect on distribution of principal products.

This study demonstrated that selective formation of HCl can result from thermal reaction of chlorocarbon mixture and showed that synergistic effects of 1,1,1-trichloroethane decomposition accelerate the rate of dichloromethane

decomposition. There is strong interaction of decay products from 1,1,1-trichloroethane with parent dichloromethane.

Decoupling of the wall and bulk reaction constant was achieved by the assuming plug flow reactor condition (Kaufman) and pseudo 1st order reactions prevail. Apparent bulk activation energies were estimated to be 32 Kcal/mol for 1,1,1-trichloroethane and 36 Kcal/mol for dichloromethane with hydrogen in the mixture reaction system. 1,1,1-trichloroethane apparent bulk activation energy is close to that of pure compound reaction. But dichloromethane apparent bulk activation energy is 39 % smaller than that of pure dichloromethane. This suggests that radicals which are more easily produced from 1,1,1-trichloroethane decomposition initiate dichloromethane decomposition. These radical reactions decrease the dichloromethane activation energy similar to thr role of a catalyst.

A detailed kinetic reaction mechanism was developed and used to model result obtained from the experimental reaction system. The kinetic reaction mechanism includes 94 elementary reaction steps involving stable compounds and free radical species with the addition, beta scission and recombination type reactions all analyzed by Quantum RRK theory.

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APPENDIX

1. GISOQRRK INPUT DATA and CALCULATION RESULTS

2. ENERGY BALANCE CALCULATION

APPENDIX 1. GISOQRRK INPUT DATA and CACULATION RESULTS

Table 1-a

$$CH_2CCl_2 + H \Longleftrightarrow [CH_2CHCl_2]^{\#} \longrightarrow CH_2CHCl + Cl$$
$$\longrightarrow CH_2CHCl_2 \text{ (Stab.)}$$

k	A	Ea	source
1	6.0 E+13	3.0	a
-1	1.1 E+14	39.9	a
2	4.0 E+14	22.9	b
<v> = 736/cm			c
Lennard-Jones Parameters :			d
sigma = 5.103 ^{o}A		e/k = 435.91 cal	

a
A factor taken as that for C2H4 + H (A=6.0 E+13) (ref: Kerr, J.A. and Moss, S.J., "Handbook of Bimolecular and Termolecular Gas Reaction Vol.I & II", CRC Press inc., 1981)

b
based upon (del S) for $CH_2CH_2 + Cl = CH_2CH_2Cl$ with A_{-2} = 1.8 E+13 cc/mol sec (Ref: Kerr)

c
Shimanouchi,T., Tables of Molecular Vibration Frequencies Consolidated Vol.I, Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) 1972, NSRDS-NBS 39. (refer to $CH_2ClCHCl$)

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

Table 1-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2CCl_2 + H = CH_2CHCl_2$	2.64 E+07	-4.71
76.0		2.64 E+08	-4.70
760.0		2.67 E+09	-4.68
7.6	$CH_2CCl_2 + H = CH_2CHCl + Cl$	5.97 E+13	2.99
76.0		5.98 E+13	2.99
760.0		6.02 E+13	3.01

Table 2-a

$$CH_2CCl + H \Longleftrightarrow [CH_2CHCl]^{\#} \begin{array}{l} \longrightarrow CH_2CH + Cl \\ \longrightarrow CHCH + HCl \\ \longrightarrow CH_2CHCl \text{ (Stab.)} \end{array}$$

k	A	Ea	source
1	1.0 E+14	0.0	a
-1	3.0 E+15	104.1	a
2	7.9 E+16	87.6	b
3	3.6 E+13	68.7	c
<v> = 1344.3/cm			d
LJ Parameters :			e
sigma = 4.644 A^o	e/k = 349 cal		

a
A factor taken as that for H + 2-C_4H_9
A_{-1} based upon entropy change for reverse.
(ref: Allara, D.L. and Shaw, R.,J. Phys. Chem. Ref. Data, 9, 523, 1980)

b
A factor based upon entropy change for reverse.
$CH_2CH + CH_3 = CH_2CHCH_3$ with A = 1.8 E+13 and Ea = 0.0
(ref: Dean, A.M.,J. Phys. Chem., 89, 4600, 1985)

c
$A = 10^{13.55} * 1$
$Ea = \Delta Hr + 45$ (ref: Zabel, F., Int. Che. Kineticb, 9, 651, 1977)

d
see note (c) Table 1-a.
Geometric mean frequency estimated as follows:
$\langle v \rangle_{CH2CHCl} = \langle v \rangle_{CH2CH2} - \Delta\langle v \rangle$
$\Delta\langle v \rangle = \langle v \rangle_{CH3CH3} - \langle v \rangle_{CH3CH2Cl}$

e
see note (d) Table 1-a

Table 2-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECUAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2CCl + H = CH_2CHCl$	1.78 E+08	-7.09
76.0		1.77 E+09	-7.08
760.0		1.80 E+10	-7.03
7.6	$CH_2CCl + = CH_2CH + Cl$	1.00 E+14	0.05
76.0		1.00 E+14	0.06
760.0		1.02 E+14	0.11
7.6	$CH_2CCl + H = CHCH + HCl$	8.15 E+11	-2.16
76.0		8.16 E+11	-2.16
760.0		8.31 E+11	-2.11

Table 3-a

$$CH_2CHCl + H \Longleftrightarrow [CH_2CH_2Cl]^{\#} \longrightarrow CH_2CH_2 + Cl$$
$$\longrightarrow CH_2CH_2Cl \text{ (Stab.)}$$

k	A	Ea	source
1	8.0 E+12	3.3	a
-1	7.7 E+12	45.1	a
2	1.0 E+13	22.7	b

<v> = 1265.3/cm		c
LJ Parameters :		d
sigma = 4.898 A^o	e/k = 300 cal	

a
A factor taken as that for CH_3CHCH_2 + H
A_{-1} factor based upon entropy change fro reverse.
(ref: Dean)

b
A factor based upon entropy change for reverse.
A_{-1} taken as that for CH_3 + CH_2CH_3 (A = 2.0 E+13, Ea = $\triangle$Hr)
(ref: Dean)

c
see note (c) Table 1-a.
(refer to CH_3CH_2Cl)

d
see note (d) Table 1-a

Table 3-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2CHCl + H = CH_2CH_2Cl$	1.30 E+08	-2.57
76.0		1.30 E+09	-2.55
760.0		1.39 E+10	-2.36
7.6	$CH_2CHCl + H = CH_2CH_2 + Cl$	7.97 E+12	3.29
76.0		8.02 E+12	3.31
760.0		8.51 E+12	3.49

Table 4-a

$$CH_3 + CH_2CH_3 \Longleftrightarrow [CH_3CH_2CH_3]^{\#} \longrightarrow CH_3CH_2CH_2 + H$$
$$\longrightarrow C_3H_8 \text{ (Stab.)}$$

k	A	Ea	source
1	1.0 E+13	0.0	a
-1	8.0 E+16	84.4	a
2	1.6 E+16	97.6	a
<v> = 1330/cm			b
LJ Parameters :			c
sigma = 4.84 A^o		e/k = 302 cal	

a Dean, A.M., J. Phys. Chem., 98, 4600, 1985

b see note (c) Table 1-a

c see note (d) Table 1-a

Table 4-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3 + C_2H_5 = CH_3CH_2CH_3$	5.45 E+11	-4.63
76.0		2.69 E+12	-2.15
760.0		6.52 E+12	-0.72
7.6	$CH_3 + C_2H_5 = CH_3CH_2CH_2 + H$	6.55 E+12	16.2
76.0		2.75 E+13	20.2
760.0		1.16 E+14	25.0

Table 5-a

$$CH_3 + CHCH_2 \Longleftrightarrow [CH_3CHCH_2]^{\#} \longrightarrow CH_2CHCH_2 + H$$
$$\longrightarrow CH_3CHCH_2 \text{ (Stab.)}$$

k	A	Ea	source
1	1.8 E+13	0.0	a
-1	8.0 E+16	99.5	a
2	6.3 E+14	89.2	b

<v> = 1289.5/cm

LJ Parameters :

sigma = 4.685 A^o e/k = 298 cal

a
Dean, A.M. J. Phys. Chem., 89, 4600, 1985

b
Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980

c
see note (c) Table 1-a
Geometric mean frequency estimated as follows ;
$\langle v \rangle_{CH3CHCH2} = (\langle v \rangle_{CH3CH2CH3} + \langle v \rangle_{CH2CCH2})/2$

d
see note (d) Table 1-a

Table 5-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3 + CHCH_2 = CH_3CHCH_2$	8.65 E+11	-4.72
76.0		4.59 E+12	-2.21
760.0		1.15 E+13	-0.74
7.6	$CH_3 + CHCH_2 = CH_2CHCH_2 + H$	2.27 E+13	5.18
76.0		6.51 E+13	9.66
760.0		9.79 E+13	13.70

Table 6-a

$$CH_3 + CCH \Longleftrightarrow [CH_3CCH]^{\#} \longrightarrow CH_2CCH + H$$
$$\longrightarrow CH_3CCH \text{ (Stab.)}$$

k	A	Ea	source
1	3.2 E+12	0.0	a
-1	5.0 E+15	125.5	a
2	3.0 E+15	101.4	a
<v> = 1238/cm			b
LJ Parameters :			c
sigma = 4.522 A^{o}		e/k = 333.4 cal	

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

[b] see note (c) Table 1-a

[c] see note (d) Table 1-a

Table 6-a

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3 + CCH = CH_3CCH$	8.11 E+08	-8.05
76.0		1.16 E+10	-6.88
760.0		2.11 E+11	-3.88
7.6	$CH_3 + CCH = CH_2CCH + H$	3.36 E+12	0.14
76.0		4.77 E+12	1.10
760.0		1.24 E+13	4.17

Table 7-a

$$CH_3CCl_2 + H \Longleftrightarrow [CH_3CHCl_2]^{\#} \begin{array}{l} \longrightarrow CH_2CHCl + HCl \\ \longrightarrow CH_3CHCl + Cl \\ \longrightarrow CH_3CHCl_2 \text{ (Stab.)} \end{array}$$

k	A	Ea	source
1	2.0 E+13	0.0	a
-1	4.2 E+14	96.6	a
2	2.9 E+13	55.8	b
3	7.9 E+15	76.8	c
<v> = 797.2/cm			d
LJ Parameters :			e
sigma = 5.103 A^o	e/k = 435.9 cal		

a
A factor taken as 1/2 that for H + CH_3CH_3 (A= 4.0 E+13)
Reverse reaction (A_{-1}) from thermodynamics
(ref: Allara and Shaw)

b
$A = 10^{13.55} * 10^{(-4/4.6)} * 6$
$Ea = \Delta H + 38.5$

c
A factor based upon entropy change for reverse.
A_{-3} factor taken as that for $C_3H_7 + CH_3$ (A = 4.0E+12)
$Ea = \Delta H$

d
see note (c) Table 1-a.
(refer to CH_2ClCH_2Cl)

e
see note (d) Table

Table 7-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3CCl_2 + H = CH_3CHCl_2$	8.57 E+08	-9.66
76.0		1.12 E+10	-8.89
760.0		2.54 E+11	-6.11
7.6	$CH3CCl_2 + H = CH_2CHCl + HCl$	2.52 E+12	-2.39
76.0		3.19 E+12	-1.79
760.0		7.50 E+12	0.74
7.6	$CH_3CCl_2 + H = CH_3CHCl + Cl$	3.15 E+13	2.09
76.0		3.72 E+13	2.51
760.0		7.92 E+13	4.59

Table 8-a

$$CH_3CHCl + H \Longleftrightarrow [CH_3CH_2Cl]^{\#} \begin{array}{l} \longrightarrow CH_2CH_2 + HCl \\ \longrightarrow CH_3CH_2 + Cl \\ \longrightarrow CH_3CH_2Cl \text{ (Stab.)} \end{array}$$

k	A	Ea	source
1	2.7 E+13	0.0	a
-1	7.6 E+14	94.0	a
2	3.24E+13	56.6	b
3	1.8 E+15	81.5	c
<v> = 1265.3/cm			d
LJ Parameters : sigma = 4.898 Ao	e/k = 300 cal		e

a
A factor as 2/3 that for CH_3CH_2 + H with A = 4.0 E13
Reverse reaction (k_{-1}) from thermodynamics
(ref: Allara and Shaw)

b
Benson, S. W., "Thermochemical Kinetics", N.Y. John & Son, 1976 (Ea = ΔH + 39.4)

c
A factor based upon entropy change for reverse.
A_{-3} taken as that for C_2H_5 + CH_3 (A = 2.0 E13)
(ref; Allara & Shaw)

d
see note (c) Table 1-a

e
see note (d) Table 1-a

Table 8-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3CHCl + H = CH_3CH_2Cl$	5.63 E+09	-7.30
76.0		6.89 E+10	-6.67
760.0		1.30 E+12	-4.15
7.6	$CH_3CHCl + H = CH_2CH_2 + HCl$	1.96 E+13	-4.18
76.0		2.38 E+13	0.14
760.0		5.12 E+13	2.65
7.6	$CH_3CHCl + H = CH_3CH_2 + Cl$	3.14 E+13	5.18
76.0		3.67 E+13	5.60
760.0		7.64 E+13	7.75

Table 9-a

$$CH_3CH_2 + H \Longleftrightarrow [CH_3CH_3]^{\#} \longrightarrow CH_3 + CH_3$$
$$\longrightarrow CH_3CH_3 \text{ (Stab.)}$$

k	A	Ea	source
1	1.8 E+14	0.0	a
-1	1.3 E+16	100.7	a
2	8.0 E+16	90.4	a
<v> = 1509/cm			b
LJ Parameters :			c
sigma = 4.342 A^o		e/k = 246.8 cal	

a
Dean, A. M., J. Phys. Chem., 89, 4600, 1985

b
see note (c) Table 1-a

c
see note (d) Table 1-a

Table 9-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3CH_2 + H = CH_3CH_3$	1.99 E+10	-9.57
76.0		2.91 E+11	-8.21
760.0		4.93 E+12	-5.21
7.6	$CH_3CH_2 + H = CH_3 + CH_3$	1.91 E+14	0.16
76.0		2.82 E+14	1.18
760.0		7.65 E+14	4.08

Table 10-a

$$CH_2Cl + CH_2Cl \Longleftrightarrow [CH_2ClCH_2Cl]^{\#} \longrightarrow CH_2CHCl + HCl$$
$$\longrightarrow CH_2ClCH_2 + Cl$$
$$\longrightarrow CH_2ClCH_2Cl \text{ (Stab.)}$$

k	A	Ea	source
1	4.0 E+12	0.0	a
-1	4.8 E+17	89.3	a
2	1.9 E+13	52.4	b
3	6.0 E+15	78.6	c

<v> = 797.2/cm — d

LJ Parameters : — e

sigma = 5.116 A^o e/k = 471.2 cal

a
A factor taken as that for $1\text{-}C_3H_7 + 1\text{-}C_3H_7$
A_{-1} factor based upon entropy change for reverse.
(ref: Allara & Shaw)

b
$A = 10^{13.55} * 10^{(-4/4.6)} * 4$
$Ea = \Delta H + 35$

c
A factor based upon entropy change for reverse.
A_{-3} taken as that for $C_3H_7 + CH_3$ (A = 2.0E+13)
(ref: Allara & Shaw)

d
see note (c) Table 1-a

e
see note (d) Table 1-a

Table 10-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2Cl + CH_2Cl = CH_2Cl + CH_2Cl$	4.19 E+08	-9.42
76.0		6.28 E+09	-8.19
760.0		1.34 E+11	-4.98
7.6	$CH_2Cl + CH_2Cl = CH_2CHCl + HCl$	6.98 E+11	-2.52
76.0		9.96 E+11	-1.53
760.0		2.51 E+12	1.61
7.6	$CH_2Cl + CH_2Cl = CH_2ClCH_2 + Cl$	2.41 E+12	3.26
76.0		3.05 E+12	3.89
760.0		7.37 E+12	6.46

Table 11-a

$$CH_2Cl + CH_3 \Longleftrightarrow [CH_2ClCH_3]^{\#} \begin{array}{l} \longrightarrow CH_2CH_2 + HCl \\ \longrightarrow CH_3CH_2 + H \\ \longrightarrow CH_2ClCH_3 \text{ (Stab.)} \end{array}$$

k	A	Ea	Source
1	1.67 E+13	0.0	a
-1	1.36 E+17	91.0	a
2	1.44 E+13	56.6	b
3	2.17 E+15	84.0	c
<v> = 1265.3/cm			d
LJ Parameters :			e
sigma = 4.898 A^o		e/k = 300 cal	

a
A factor taken as 2/3 that for $CH_3 + CH_3$ (A =2.5 E+13)
A_{-1} based upon entropy change for reverse.

b
$A = 10^{13.55} * 10^{(-4/4.6)} * 3$
$Ea = \triangle H + 39.4$

d
see note (c) Table 1-a

e
see note (d) Table 1-a

Table 11-a

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2Cl + CH_3 = CH_2ClCH_3$	5.19 E+09	-7.84
76.0		7.37 E+10	-6.78
760.0		1.30 E+12	-3.75
7.6	$CH_2Cl + CH_3 = CH_2CH_2 + HCl$	5.11 E+12	-1.73
76.0		7.30 E+12	-0.68
760.0		1.67 E+13	2.51
7.6	$CH_2Cl + CH_3 = CH_3CH_2 + Cl$	5.40 E+12	4.35
76.0		7.05 E+12	5.07
760.0		1.76 E+13	7.86

Table 12-a

$$CH_2Cl + CHCl_2 \Longleftrightarrow [CH_2ClCHCl_2]^{\#} \begin{array}{l} \longrightarrow CH_2CCl_2 + HCl \\ \longrightarrow CHClCHCl + HCl \\ \longrightarrow CH_2ClCHCl_2 \text{ (Stab.)} \end{array}$$

k	A	Ea	source
-1	8.0 E+12	0.0	a
1	1.0 E+18	86.2	a
2	4.8 E+12	68.1	b
3	2.0 E+13	68.5	c

<v> = 678.7/cm		d
LJ Parameters :		e
sigma = 5.72 A^o	e/k = 498.9 cal	

a
A factor as that for $1\text{-}C_3H_7 + 1\text{-}C_4H_9$
A_{-1} based upon entropy change for reverse.

b
$A = 10^{13.55} * 10^{(-4/4.6)} * 1$
$Ea = \Delta H + 36$

c
A = 1013.55 * 10(-4/4.6) * 4
$Ea = \Delta H + 36$

d
see note (c) Table 1-a
Geometric mean frequency estimated as folloes:
$\langle v \rangle_{CH2ClCHCl2} = (\langle v \rangle_{CHCl2CHCl2} + \langle v \rangle_{CH2ClCH2Cl})/2$

e
see note (d) Table 1-a

Table 12-b

APPARENT REACTION RATE CONSTANTS PREDICTED

USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2Cl + CHCl_2 = CH_2ClCHCl_2$	4.84 E+09	-10.60
76.0		5.85 E+10	-7.41
760.0		4.88 E+11	-4.40
7.6	$CH_2Cl + CHCl_2 = CH_2CCl_2 + HCl$	6.54 E+09	-3.65
76.0		1.82 E+10	-0.05
760.0		4.81 E+10	4.05
7.6	$CH_2Cl + CHCl_2 = CHClCHCl + HCl$	2.46 E+10	-3.85
76.0		6.91 E+10	0.01
760.0		1.84 E+11	4.12

APPENDIX 2. ENERGY BALANCE CALCULATION

This calculation is based upon the experimental results and detailed reaction mechanism.

CASE 1.

Reaction conditions

- .Reaction temperature = 572 ^{o}C
- .Residence time = 1.0 second
- .Reactor diameter = 1.05 cm
- .Mole fraction for each reagent = 0.0376
- .Mole flow rate = 0.562 l/min * 1/24.45 * 0.0376

  = 8.55×10^{-4} mol/min for each reagent

Rxn. 1 90 % conversion

CH_3CCl_3 ----> CH_2CCl_2 + HCl ΔH = 9.57 Kcal/mol

Rxn. 2 10 % conversion

CH_3CCl_3 + H ----> CH_3CCl_2 + HCl

CH_3CCl_2 + H_2 ----> CH_3CHCl_2 + H

CH_3CCl_3 + H_2 ----> CH_3CHCl_2 + HCl overall reaction ΔH = -22.21 Kcal/mol

Rxn. 3 17 % conversion

CH_2Cl_2 + H ----> CH_2Cl + HCl

CH_2Cl + H_2 ----> CH_3Cl + H

CH_2Cl_2 + H_2 ----> CH_3Cl + HCl overall reaction ΔH = -18.89 Kcal/mol

Total energy balance

Rxn. 1 $(8.55 \times 10^{-4}) * (9.57) * 0.9 = 7.36 \times 10^{-3}$

Rxn. 2 $(8.55 \times 10^{-4}) * (-22.21) * 0.1 = -1.90 \times 10^{-3}$

Rxn. 3 $(8.55 \times 10^{-4}) * (-18.89) * 0.17 = -2.75 \times 10^{-3}$

2.71×10^{-3}

= (2.71 cal/min) * (1/60) * (4.2 Joule/cal) = 0.19 J/sec.

CASE 2

Reaction conditions

.Reaction temperature = 720 ^{o}C

.Residence time = 1.0 second

.Reactor diameter = 1.05 cm

.Mole fraction for each reagent = 0.0376

.Mole flow rate = 0.479 l/min * 1/24.45 * 0.0376

= 7.37×10^{-4} g mol/min for each reagent

Rxn. 1 90 % conversion

CH_3CCl_3 ----> CH_2CCl_2 + HCl

CH_2CCl_2 + H ----> CH_2CCl + HCl

CH_2CCl + H_2 ----> CH_2CHCl + H

CH_3CCl_3 + H_2 ----> CH_2CHCl + 2HCl overall reaction ΔH =-4.82 Kcal/mol

Rxn. 2 10 % conversion

CH_3CCl_3 + H ----> CH_3CCl_2 + HCl

CH_3CCl_2 + H_2 ----> CH_3CHCl_2 + H

CH_3CHCl_2 ----> CH_2CHCl + HCl

CH_3CCl_3 + H_2 ----> CH_2CHCl + 2HCl overall reaction ΔH = -4.82 Kcal/mol

Rxn. 3 90 % conversion

CH_2Cl_2 ----> CH_2Cl + Cl

Cl + H_2 ----> HCl + H

CH_2Cl + H ----> CH_3Cl

CH_2Cl_2 + H_2 ----> CH_3Cl + HCl

overall reaction
ΔH = -18.9 Kcal/mol

Rxn. 4 10 % conversion

CH_3Cl ----> CH_3 + Cl

Cl + H2 ----> HCl + H

CH_3 + H ----> CH_4

CH_3Cl + H_2 ----> CH_4 + HCl

overall reaction
ΔH = -20.4 Kcal/mol

Total energy balance

Rxn. 1 $(7.37 \times 10^{-4}) * (-4.82) * 0.9 = -3.20 \times 10^{-3}$

Rxn. 2 $(7.37 \times 10^{-4}) * (-4.82) * 0.1 = -3.55 \times 10^{-4}$

Rxn. 3 $(7.37 \times 10^{-4}) * (-18.9) * 0.9 = -1.25 \times 10^{-2}$

Rxn. 4 $(7.37 \times 10^{-4}) * (-20.4) * 0.1 = -1.50 \times 10^{-3}$

-2.08×10^{-2}

= (20.8 cal/min) * (1/60) * (4.2 J/cal) = -1.45 Joule/sec

Heating Element Capacity in Furnace

Position	Length	Watt	Volt	F_{time}	Heating Capacity#
R	3"	500	50	0.5	114 watt
M	12"	1500	100	0.5	682 watt
L	3"	500	50	0.5	144 watt

see sample calculation.
F_{time} = time fraction the furnace element is required to be for designated temperature.

Total heating capacity = 910 watt

Case 1. error in temperature due to endothermic reaction described

$$\text{Error} = \frac{0.19}{910} * (572\ ^{o}C) = 0.12\ ^{o}C$$

Case 2. error due to exothermic reaction described

$$\text{Error} = \frac{-1.45}{910} * (720\ ^{o}C) = -1.14\ ^{o}C$$

NOTE Our temperature is only $\pm$ 3 ^{o}C. These error from reaction exo. or endo. thermicity is less than our temperature uncertainty.

SAMPLE CALCULATION

Heating capacity = (500 watt) * (50/110) * (0.5) = 114 watt