ABSTRACT

Title of Thesis: Thermal Decomposition of 1,1,2-Trichloroethane in Hydrogen in Tubular Flow Reactors at Atmospheric Pressure

Chen-Chung Yeh, Master of Science in Chemical Engineering, in 1989

Thesis Directed by Dr. Joseph W. Bozzelli

The decomposition of 1,1,2-trichloroethane in a hydrogen gas bath was carried out at 1 atmosphere total pressure in three different surface to volume ratio flow reactors. Temperature ranged from 440 to 850 ^{o}C and the residence times studied were in the range 0.2 - 2.3 seconds. Application of the first order rate expression to this data yields a linear relationship for each temperature studied and thus global rate constants for loss of reactant were determined.

It was found that conversion of the reagent was a function of both temperature and residence time. The major products observed are 1,2-dichloroethylene (CHClCHCl), 1,1-dichloroethylene (CH_2CCl_2), vinyl chloride (CH_2CHCl), chloroethane (CH_3CH_2Cl), ethylene, and HCl, with methyl chloride (CH_3Cl), dichloromethane (CH_2Cl_2), and benzene as minor products. Complete decay (96 %) of the reagent occurs at 850 ^{o}C and 1.1 sec residence time, where the principal products are ethylene and HCl. Most of the chlorinated by-products have been destroyed at this reaction time at 850 ^{o}C except vinyl chloride (1.0 %) and traces of chloroethane.

A detailed kinetic scheme was formulated considering all reaction products detected by GC. A kinetic reaction mechanism, composed of 73 elementary reactions and 37 species, was developed and used to model results obtained from the experimental reaction system. The detailed kinetic reaction mechanism was based on thermochemical principles and transition state theory. This mechanism is shown to fit the experimental results quite well.

Rate constants for the following reactions were determined by optimization of the reaction mechanism to the experimental data.

	A (1/s)	E (Kcal/mol)
$CH_2ClCHCl_2$ ---> CHClCHCl + HCl	9.5E12	55.3 (△Hr+41)
$CH_2ClCHCl_2$ ---> CH_2CCl_2 + HCl	4.7E12	55.3 (△Hr+41)
$CH_2ClCHCl_2$ ---> $CH_2ClCHCl$ + Cl	2.6E15	77.7 (△Hr)
$CH_2ClCHCl_2$ ---> CH_2CHCl_2 + Cl	1.6E15	81.4 (△Hr)
$CH_2ClCHCl_2$ ---> CH_2Cl + $CHCl_2$	4.2E17	89.1 (△Hr)

For the reaction of 1,1,2-trichloroethane to $CH_2ClCHCl$ + Cl, the energy of activation determined in this study provides a bond energy for the CH_2CHCl--Cl bond of 77.7 kcal/mole.

THERMAL DECOMPOSITION
OF 1,1,2- TRICHLOROETHANE IN HYDROGEN IN TUBULAR FLOW REACTORS AT ATMOSPHERIC PRESSURE

BY

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

1989

APPROVAL SHEET

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Acknowledgement

I appreciate to Dr. Joseph W. Bozzelli for his advice and patience. I am deeply indebted to him for the opportunities which he made available to me. I acknowledge the helpful corrections and productive comments by Dr. R. Parker and Dr. P. Armenante.

I am eternally grateful to my parents for their endless love and inspiration. I am glad to thank all of my colleagues at Kinetics Research Laboratory of the New Jersey Institute of Technology, especially, Dr. Javad Tavakoli and YangSoo Won for their support and guidance.

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I. INTRODUCTION

The disposal of chlorinated hydrocarbons has become an issue of significant environmental concern, with special focus on species such as chlorinated plastics, PCB's, chlorinated dry cleaning solvents, flame inhibitors, and other chlorinated chemicals. Many chlorocarbons are thought to be toxic and in some cases carcinogenic. This includes 1,1,2-trichloroethane<1>. Long term exposure to even low level of these compounds may have significant health effects<2>.

A number of different technologies have been developed or are under development for effective and safe destruction of chlorocarbons. Incineration has been demonstrated in both field testing of operating incinerators<3> and bench scale testing of turbulent diffusion spray flames<4> as an effective technique for eliminating organic hazardous waste<1>. For chlorinated hydrocarbons, this technique may destroy all the initial parent species. However, the reaction products are not all converted to carbon dioxide, as these combustion facilities are often run in an oxygen-rich environment where there is no stable and desirable end adduct for chlorine. If an incinerator with excess oxygen operates under less than optimum conditions, some chlorine-containing carbon products can usually be found in the effluent. This includes partially decomposed and oxidized fragments of the initial chlorocarbon. For example, mixtures of chlorinated and nonchlorinated principal organic hazardous constituents (POHCs) in the waste can lead to the formation of more diverse chlorinated compounds than are formed from a single chlorinated POHC such as carbon tetrachloride alone<5>.

It is important to note that, the HO--H' bond in water is stronger than the H-Cl bond, therefore the O_2-rich conditions can limit hydrogen availability to Cl. Another way of looking at the problem is that oxygen and Cl are both competing for the available fuel, i.e. hydrogen, and by limiting the H available to oxygen, chlorocarbons serve as flame inhibitors. The C-Cl bond is the next strongest when compared with other possible chlorinated products in an combustion environment such as Cl-Cl, N-Cl, or O-Cl bonds. Consequently, C-Cl may persist in an oxygen rich or hydrogen limited atmosphere<6>. 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.

It might also be advantageous to utilize a reducing atmosphere containing excess hydrogen to destroy and detoxify chlorocarbons instead of an oxidizing atmosphere.

This would:

1. allow thermodynamically favorable paths to formation of HCl.
2. possibly reduce fuel requirements, because hydrocarbons (fuels) are product in this reaction system (HCl lost

HC's produced). In addition, the reactions may be made to run in an exothermic regime, and this scheme may also effectively recycle the carbon species for use as a fuel. This could act as an energy resource and eliminate the unnecessary dumping of additional' CO_2 into the atmosphere.

3. provide much-needed kinetic parameters and reaction-product information important to understanding the chemistry of the hitherto largely unexplored carbon/hydrogen/chlorine chemical systems.

The possible drawback to this process is the cost and availability of hydrogen. While acknowledging this, a study of these reactions could demonstrate what reaction products are formed and the feasibility of the chemical mechanism as a means of converting (detoxifing) chlorocarbons. This might also lead to use of less-expensive hydrogen sources such as water vapor<6> or methane<7>.

More importantly, this study provides experimental and theoretical insights into the reactions mechanisms for this elementary carbon, chlorine, and hydrogen chemical system. The mechanisms and kinetic parameters determined are useful to flame, incinerator, and thermal reaction modeling studies as part of larger more complex systems. The current study also develops a detailed reaction model which includes Activated Complex Quantum Rice Ramsberger Kassel<33> analysis on several important addition, beta scission, and recombination reactions of hydrogen atom with radicals or olefins. QRRK theory calculates probability of reaction vs. stabilization as a function of pressure and temperature. Thus activated complex QRRK analysis permits evaluation of reacting system over a wide range of temperatures and pressures.

The use of QRRK allows us to accurately treat combination reactions of atoms and radicals. Plus addition reaction of atoms or molecules or radicals to unsaturates with a theory based upon fundamentals of thermodynamics, statistical mechanics and transition state kinetics. The fundamental bases allow use of the model well beyond the experimental calibration boundary conditions. In this study, three different reactor diameters 0.4, 1.05, and 1.6 cm were studied to vary reactor surface to volume ratio (S/V). This varied ratio allows one to decouple apparent wall and bulk phase decomposition rates using a plug flow assumption based upon the work of Kaufman<8> for a pseudo-first order reaction system. We have performed detailed experimental studies on the 1,1,2-trichloroethane/hydrogen system (1:138 mole ratio, respectively). A detailed kinetic reaction mechanism was developed and used to model results obtained from the experimental reaction system.

II. Previous Studies

Thermal treatment has received a significant amount of attention for conversion of unwanted chlorinated hydrocarbons (ClHC) in the last decade. Several reports are found on gas phase reaction of chlorohydrocarbons in a reducing atmosphere of methane. Murgulescu and Weissman <9-10> studied the effect of methane on pyrolysis of chloroform and reported that production of vinyl chloride is increased by addition of CH_4 to the system. Benson and Weissman <11> investigated high temperature (1200-1300 ^{O}K) reaction of methyl chloride and methane. They reported C_2 hydrocarbons as the major products of their experiment. An overall review of the related and important investigations is presented in the following paragraphs.

Benson and Weissman <12> studied the pyrolysis of pentachloroethane to determine the kinetic parameters and elucidate elementary reactions. They reported different mechanisms for the inhibited (presence of excess toluene) and uninhibited reaction systems. Chain initiation for uninhibited pyrolysis of C_2HCl_5 was reported to be heterogeneous (wall) C-Cl bond breaking:

$$C_2HCl_5 \text{ -----> } Cl + C_2HCl_4$$

While for inhibited reaction homogeneous C-Cl bond cleavage is dominant and accounts for 50% of the reaction. The C-C bond breaking and the molecular HCl elimination pathways were reported to have comparable rates to homogeneous C-Cl bond cleavage and contribute to C_2HCl_5 consumption.

Barton and Onyon[13] (1950) studied 1,1,1-trichloroethane thermal decomposition in batch reactors in temperature range 635.7 to 707.0 °K and pressure range 10 to 120 mm Hg to give primary products 1,1-dichloroethylene and HCl. They found that the decomposition rate in a packed reactor was slower than in an empty reactor. They proposed that 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 follows:

CH_3CCl_3 --------> CH_2CCl_2 + HCl

CH_3CCl_3 --------> 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^{-1}.

Benson and Spokes[14] (1967), using the very low pressure technique, covered a high temperature range 890 to 1265 °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 the wall rather than with other gas molecules) 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 $10^{13.8}\ e^{(-51,700/RT)}\ sec^{-1}$.

Lee et.al.<15> studied thermal (800-1500 ^{o}F) destruction rates of four organic compounds (vinyl chloride, ethyl acrylate, acrolein, and benzene) in air employing a 0.9 mm ID, 135 cm long quartz tube flow reactor. Compounds were run at 1000 ppm in air under uniform temperatures and reaction times of 0.1-1.8 seconds. They <15> reported that, at temperatures above 1450 ^{o}F, 99.8% of C_2H_3Cl was destroyed and no benzene was detected (i.e. more than 2 ppm). Higher temperature (1700-1800 ^{o}F) was required for complete destruction of ethyl acrylate and acrolein.

Louw et.al. <16> investigated thermal dechlorination of (poly) chlorinated organic compounds (C_6H_5Cl, p- and o-$C_6H_4Cl_2$, E-CHCl=CHCl, C_2Cl_4, and 1,2-$C_2H_4Cl_2$) in hydrogen atmosphere. Experiments were performed at 1 atm pressure, using a quartz flow reactor and a temperature range of 500-1000 ^{o}C. They suggested the possibility of more than 99.9% conversion in an atmosphere of excess hydrogen within a few minutes (A long time relative to incineration residence times) in a plug flow reactor at 1000 ^{o}K. Major products, for residence times of 5.9 to 10.6 seconds and various hydrogen/chlorocarbon ratios) were found to be chlorine free hydrocarbons (CH_4, C_2H_4, C_2H_6, C_6H_6) or parent compounds with a smaller number of chlorine atoms. They have also postulated mechanisms for methane formation by pyrolysis of benzene and chlorobenzene in an atmosphere of hydrogen with relative concentration ratios for $C_6H_6:H_2$ and $C_6H_5Cl:H_2$ of about 1:6 <17>.

Chuang and Bozzelli<19-20> studied reactions of chloroform and 1,1,2-trichloroethane with hydrogen or water vapor in a tubular reactor, at atmospheric pressure, and a temperature range of 550 to 1100 ^oC. Reagent loss and product formation were monitored by using an on-line gas chromatograph, where batch samples were analyzed by GC/mass spectrometry. The major products of reactions of 1,1,2-trichloroethane with chloroform and hydrogen above 850 ^oC were observed as the thermodynamically stable species HCl, CH_4, and carbon (solid). The more stable chlorinated byproducts (chloromethane and vinyl chloride) were also observed at low concentrations, and higher temperatures were required for the subsequent decomposition of CH_3Cl and C_2H_3Cl. Complete destruction of the parent reagent (chloroform and 1,1,2-trichloroethane) was observed at temperatures near 700 ^oC with residence times slightly over 1 second. The global activation energies were determined to be 48.6 kcal/mol for reaction of chloroform with hydrogen and 48.8 kcal/mol for reaction of 1,1,2-trichloroethane with hydrogen.

Chang<21-22> investigated the reactor modeling, calculation of homogeneous bulk, and wall rate constants from a laminar flow reactor analysis on his experimental results for hydrogen with 1,1,1-trichloroethane in the temperature range 555 to 681 ^{o}C. The activation energies of bulk and wall reaction were determined to be 50.6 Kcal/mole and 76.0 Kcal/mole. A factors of $1.23 * 10^{13}$ s^{-1} and $5.01 * 10^{17}$ s^{-1} respectively were reported. 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.

The thermal reaction of chloroform and trichloroethylene in a hydrogen atmosphere utilizing tubular flow reactor , ambient pressure, and a temperature range of 550-1000 ^{o}C was investigated by Mahmood<23>in 1985. He reported C_2H_2, C_2H_4, CH_4, HCl, and benzene as major products of the chloroform/trichloroethylene/hydrogen reaction system. No chlorinated hydrocarbons were observed in the effluent of the reactor above 850 ^{o}C for reaction time of less than one second.

Ritter<24> performed studies on the thermal decomposition of chlorobenzene in an atmosphere of hydrogen which report that complete destruction of chlorobenzene in a hydrogen environment can be achieved at a temperature of 1273 ^{o}K and residence time of one second. The major products were identified as HCl, benzene, and C(s).

Tsao<25> studied the thermal decomposition of dichloromethane with hydrogen over the temperature range of 700 to 950 ^{o}C, using almost the same apparatus system we did. 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 the CCl_4/H_2 reaction were $CHCl_3$, HCl, and C_2Cl_6. Chlorine free hydrocarbons were not detected, except at temperatures over 800 °C and one second residence time. Major products reported for the CH_2Cl_2/H_2 reaction system above 950 °C and one second residence time were CH_4, HCl, C_2H_2, C_2H_4, C_2H_6, and benzene.

The decomposition of dichloromethane/1,1,1-trichloroethane mixture in a hydrogen bath gas carried out at 1 atmosphere total pressure in a tubular flow reactor was examined by Won<26> (1988). This study demonstrated that selective formation of HCl can result from thermal reaction of chlorocarbon mixtures 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. Results also suggest 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 the role of a catalyst. A detailed kinetic reaction mechanism was developed and used to model the result obtained from the experimental reaction system.

Reactions of methylene chloride diluted in methane and argon and a mixture of methylene chloride +

trichloroethylene diluted in methane and argon were studied by Tavakoli<7> (1988). First order plug flow model was utilized to analyze the experimental data. In addition the homogeneous and wall rate constants were decoupled and separately evaluated. The following overall rate equations were found to fit the reaction systems studied:

Methylene Chloride in $CH_2Cl_2/C_{H4}/Ar$:

$$k = 1.166E09 * Exp(-44.85/RT) \qquad (1/sec)$$

Methylene Chloride in $C_2HCl_3/CH_2Cl_2/C_{H4}/Ar$:

$$k = 8.11E08 * Exp(-43.2/RT) \qquad (1/sec)$$

Trichloroethylene in $C_2HCl_3/CH_2Cl_2/C_{H4}/Ar$:

$$k = 1.13E05 * Exp(-30.67/RT) \qquad (1/sec)$$

A detailed kinetic reaction mechanism was developed and used to model the reaction systems and fit the experimentally determined product distribution.

III. THEORY

A. Tubular Flow Reactor Theory

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 studied by Chang and Bozzelli[22]. This study showed that the plug flow assumption for our experimental system is accurate to with in 5% to 7% for all temperatures where kinetic information was obtained.

The idealized model of the plug flow reactor assumes that an entering fluid element moves as a plug of material that completely fills the cross section. However, we will limit our discussion to the simplest possible model: the plug flow model. Nontheless, when we attempt to compare the results predicted by the model with what we observe in the real world, we should discuss the deviations from ideal behavior in three categories[27]:

1. There will be velocity gradients in the radial direction so all fluid elements will not have the same residence time in the reactor.

2. There will be an interchange of material between fluid elements at different axial positions by virtue of ordinary molecular diffusion and eddy diffusion processes arising from turbulence and/or the influence of any packing in the bed.

3. There may be radial temperature gradients in the reactor that arise from the interaction between the energy released by reaction and convective transport of energy.

To estimate the deviation of a tubular flow reactor with axial diffusion from the plug flow assumption, Reman<28> has used Danckwerts solution of a differential equation which describes a plug flow reactor following first-order kinetics. He found that for $D/vl < 0.1$ the reactor follows the plug flow assumption, and for $D/vl > 2.0$ the reactor behaves like a well-mixed one<29>. Here D is diffusion coefficient, v is mean velocity, l is reactor length. In addition, the ratio of actual reactor to plug flow reactor should approach 1.

$$\frac{V_{act}}{V_{pf}} = 1 + kt \frac{D}{vl}$$

For our reactor, D/vl is always below 0.05 (3.4E-3 - 6.5E-3) and the highest value of the ratio V_{act}/V_{pf} was 1.04. This would be sufficient for the 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<30>. This is, however, not true for our experiments (We are in the lower laminar flow range).

A more rigorous analysis that is applicable to our system is given in the paper by Poirier and Carr<31>. 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 the homogeneous rate constant) is equal to or greater than 0.5, the plug flow approximation is satisfied.

B. 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 the reactor. This means that, the reaction at the wall in addition to the bulk reaction needs to be evaluated if one is occurring.

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<32>. Hence, for the first order reaction of species A one can write:

$$A \text{ ------> Products}$$

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

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

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

Asuming a rapid radical diffusion, Aw can be written as<36>:

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

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 we 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.

C. Rate of Reaction Predicted by the Theories

Experimental values for rates of reaction are generally either in the order of magnitude of, or are below, those predicted by collision theory. Thus collision theory may be used to estimate the upper bound to the expected rate of reaction. Once in a while a reaction is encountered with much higher rates than predicted. This suggests a complex reaction, frequently catalytic. Occasionally, for the elementary reaction between simpler molecules, enough information is available to allow prediction of the rates from transition-state theory. When available, these predictions usually agree more closely with the experiment than do the predictions of collision theory where references to this are presented by Levenspiel <32>.

1. Transiton-State Theory

For many reactions, particularly elementary, 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 transition-state theory. The reactants combine to form unstable intermediates called activated complexes which then decompose spontaneously into products or back to reactants. It assumes that an equilibrium exists between the concentration of reactants and activated complex at all times. Further, it assumes 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. For the forward elementary reaction of a reversible reaction.

$$A + B \underset{k_r}{\overset{k_f}{\Longleftrightarrow}} AB \qquad (5)$$

we have the following conceptual elementary scheme:

$$A + B \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} AB^* \xrightarrow{k_2} AB \qquad (6)$$

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

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

The observed rate of the forward reaction is then

$$r_{AB,\text{forward}} = \left(\begin{array}{c}\text{conc. of}\\ \text{activated complex}\end{array}\right) \times \left(\begin{array}{c}\text{rate of decomposition}\\ \text{activated complex}\end{array}\right)$$

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

$$= \frac{kT}{h} K^* C_A C_B \qquad (7)$$

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

$$\Delta G^* = \Delta H^* - T\Delta S^* = -RT \ln K^* \qquad (8)$$

$$K^* = \mathrm{EXP}(-\Delta G^*/RT) = \mathrm{EXP}(-\Delta H^*/RT + \Delta S^*/R)$$

the rate becomes

$$r_{AB,\text{foward}} = \frac{kT}{h} \mathrm{EXP}(\Delta S^*/R)\ \mathrm{EXP}(-\Delta H^*/RT)\ C_A\ C_B \qquad (9)$$

Theoretically both ΔS^* and ΔH^* vary slowly with temperature. Hence, of the three terms that make up the rate constant in Eq. 9, the middle one, $\mathrm{EXP}(\Delta S^*/R)$, is much less temperature-senstive than the other two. We may take it to be constant. For the forward reaction, and the reverse reaction of Eq. 5, we have approximately

$$k_f = T\ \mathrm{EXP}(-\Delta H_f{}^*/RT) \qquad (10)$$

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

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

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

$$Z_{AA} = d_A{}^2\, n_A{}^2 \left[\frac{4\ kT}{M_A}\right]^{1/2} = d_A{}^2\, \frac{N^2}{10^6} \left[\frac{4\ kT}{M_A}\right]^{1/2} C_A{}^2$$

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 a mixture of A and B, the kinetic theory gives

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

If every collision 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. Suggesting that only more energetic and violent collisions, those involving energies in excess of a given minimum energy E, lead to a reaction. From the Maxwell Boltzman distribution law of molecular energies the fraction of all bimolecular collisions that involve energies in excess of this minimum energy is given approximately by $e^{(-E/RT)}$, where E is usually much greater than RT. Since we are only considering energetic collisions, this assumption is reasonable. Thus the rate of reaction is given by

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

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

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

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

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

3. Comparison of Two Theories

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

$$A + B \longrightarrow AB^* \longrightarrow AB$$

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 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.It is dependent 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.

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

The significant aspects of this thesis are the experimental results and the detailed chemical kinetic model, both of which are presented later on. The QRRK theory decribed below is very important to our model development research. A brief description of this theory from the article by Westmoreland and Dean<35> is therefore, paraphrased below and treated as a quote.

Bimolecular QRRK (Quantum Rice Ramsperger Kassel)<35> analysis is a simple method for calculating rate constants of addition and recombination reactions, based on unimolecular quantum RRK theory. Input parameters are readily derived, and rate constants and reaction branching can be predicted with remarkable accuracy. Such predictive power makes the method especially useful in developing mechanisms of elementary reactions<33>.

"Predictions by this method can be made quickly, in part because the input data are few and frequently are easy to obtain:

1. Preexponential factors and activation energies in the high pressure limit, A_i and E_{act}.

2. The number of vibrational degrees of freedom for the adduct, s.

3. The geometric mean of the adduct's vibrational frequencies, <v>.

4. Lennard Jones transport properties, sigma and e/k, for the adduct and for the third body gas.

5. The average energy transferred per collision with the third body gas, $\langle E_{coll} \rangle$, which has been experimentally evaluated for a variety of gases.

Obtaining A_i and E_{act} may be the most difficult task. These parameters can come from literature data, from estimates by the methods of Benson (1976,1983), from the generic rate constants of Dean <33> (1985), or from the equilibrium constant and the reverse rate constant (high pressure limit). References are in the Dean's paper<33>."

1. Unimolecular QRRK Equation

"Dean<33> (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. Using a single geometric mean <v> to present all the v's in a molecule is one approximation, and use of the arithmetic mean has been suggested by Thiele et.al.,1980. For the total energy variable E, the symbol n is used. For the number of quanta to the energy barrier to reaction Eo, the quantized energy is m quanta. The quantum level and the rate processes are illustrated in Figure 1a.

The apparent k_{uni}:

$$k_{uni} = \frac{1}{[\ A\ ]} \frac{d\ [\text{Products}]}{dt} \tag{11}$$

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}:

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

$$= \ k_{rxn}(E) \ \frac{k_{deexc}[M]\ K(E,T)}{k_{deexc}[M] + k_{rxn}(E)} \tag{12}$$

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

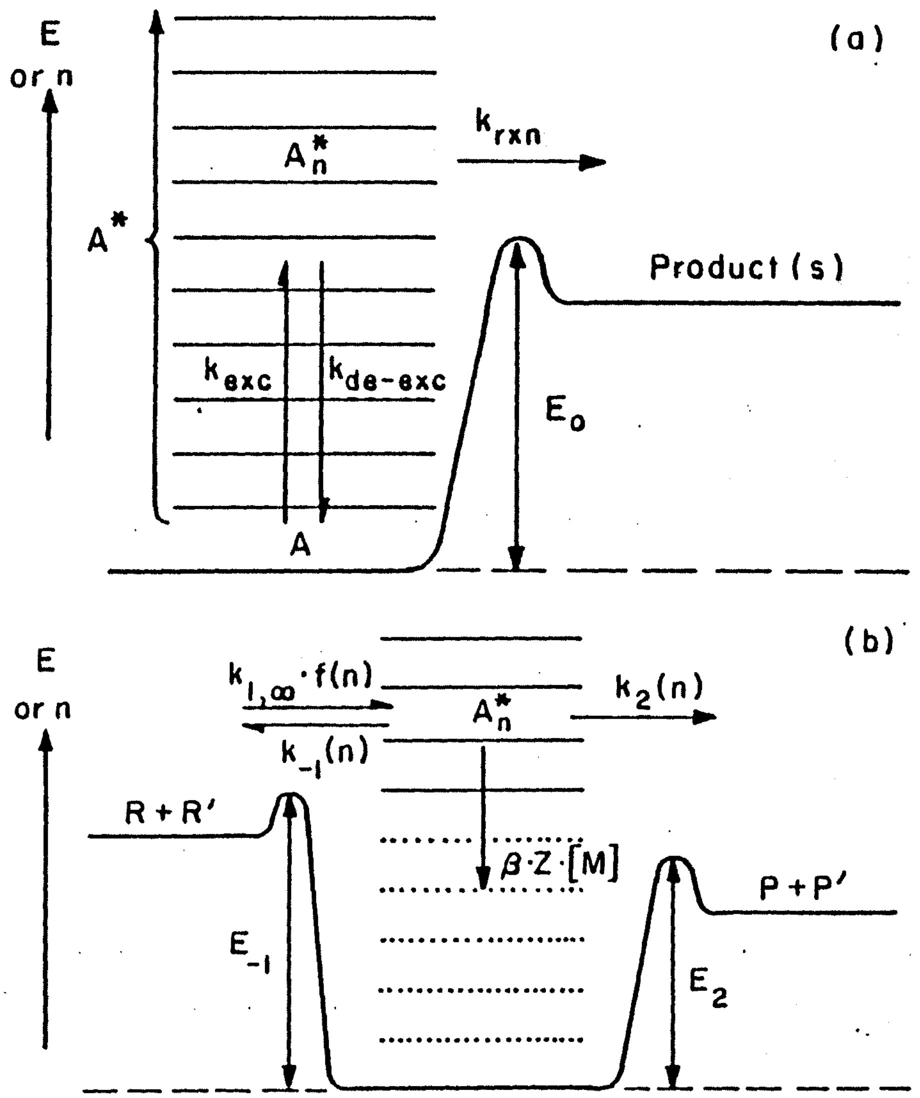


Figure 1. Energy diagrams for pressure-dependent reactions.

a. Unimolecular reaction

b. Bimolecular reaction with chemically activated pathway

reprinted from reference<35>

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 energy-dependent rate constant can be written as:

$$k_{rxn}(E) = A_i \frac{n!\ (n-m_i+s-1)!}{(n-m_i)!\ (n+s-1)!} \tag{13}$$

where A_i is the high pressure Arrhenius preexponential factor for reaction i, and m_i is the number of quanta (E_i/hv) corresponding to the energy threshold for the reaction i. Likewise, he derived the quantized thermal energy distribution K(E,T) to be:

$$K(E,T) = a^n\ (1-a)^s \frac{(n+s-1)!}{n!\ (s-1)!} \tag{14}$$

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

In the present development, we have modified the theory to utilize the Gamma function in place of factorials. 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 energy from A^*. Note that any species included as M would have to accommodate this energy content, regardless of its capacity for accepting the energy. Analyzing collisional energy transfer for master-equation methods, Troe (1977) fit most of the temperature dependence of Beta with the equation:

$$\frac{\text{Beta}}{1-(\text{Beta})^{1/2}} = \frac{-\langle \triangle\ E_{coll} \rangle}{F(E)\ k\ T} \qquad (15)$$

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

2. Bimolecular QRRK Equations

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

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

Here, k_1 is the high-pressure-limit rate constant for forming adduct and f(E,T) is the energy distribution for chemical activation:

$$f(E,T) = \frac{k_{-1}(E)\ K(E,T)}{\sum_{E=E_{-1}}^{\infty} k_{-1}(E)\ K(E,T)} \qquad (16)$$

where K(E,T) is the QRRK thermal distribution from Eq. 14. Rate constants $k_{-1}(E)$ and $k_2(E)$ are calculated from the QRRK equation for $k_{rxn}(E)$ (Eq. 13) using $m_{-1}(E_{-1}/h<v>)$ and $m_2(E_2/h<v>)$, respectively. A typical energy diagram for these reactions is shown in Figure 1-b.

To obtain the bimolecular rate constant for a particular product channel, a pseudo steady-state analysis is made as before. The rate constant for forming the addition/stabilization product $A^*(E)$ from R + R' is:

$$k_{a/s} = \sum_{\substack{E=E_{-1}\\(n=m_{-1})}}^{\infty} \text{Beta } Z[M] \frac{k_{1,\infty} \quad f(E,T)}{\text{Beta } Z[M] + k_{-1}(E) + k_2(E)} \qquad (17)$$

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

$$k_{a/d} = \sum_{\substack{E=E_{-1}\\(n=m_{-1})}}^{\infty} k_2(E) \frac{k_{1,\infty} \quad f(E,T)}{\text{Beta } Z[M] + k_{-1}(E) + k_2(E)} \qquad (18)$$

If more decomposition channels are available, the $k_{rxn}(E)$ for each channel is added in the denominator of Eqs. 17 and 18, and an equation in the form of Eq.18 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. 17 and 18. As pressure changes, the rate constants change because of the relative magnitutes of terms in the denominator, Beta*Z[M] vs. $k_{-1}(E)$ and $k_2(E)$.

The low-pressure limit for addition/stabilization (or recombination) is derived from Eq. 17 to be

$$\lim_{[M]\to 0} k_{a/s} = [M] \sum_{\substack{E=E_{-1} \\ (n=m_{-1})}}^{\infty} \text{Beta } Z \frac{k_{1,\infty} \quad f(E,T)}{k_{-1}(E) + k_2(E)} \qquad (19)$$

sometimes written as $[M]*k_o$ (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 $\log(k_{a/s})$ vs. log(P) or log(M).

Note the presence of $k_2(E)$ in Eq. 19. If chemically activated conversion of $A^*(E)$ is more rapid than decomposition to reactants [$k_2(E) >> k_{-1}(E)$], then Eq. 19 shows that $ko_{a/s}$ 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. 18 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. 18, the low-pressure limit for the chemically activated pathway to P and P' will be

$$\lim_{[M]\to 0} k_{a/d} = k_{1,\infty} \sum_{\substack{E=E_{-1} \\ (n=m_{-1})}}^{\infty} \frac{k_2(E) \; f(E,T)}{k_{-1}(E) + k_2(E)} \qquad (20)$$

and the high-pressure limit will be

$$\lim_{[M] \to oo} k_{a/d} = \frac{1}{[M]} \frac{k_{1,oo}}{\mathrm{Beta}\ Z} \sum_{\substack{E=E-1 \\ (n=m-1)}}^{oo} k_2(E)\ f(E,T) \qquad (21)$$

with an inverse pressure dependence. While this result goes against past intuition 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."

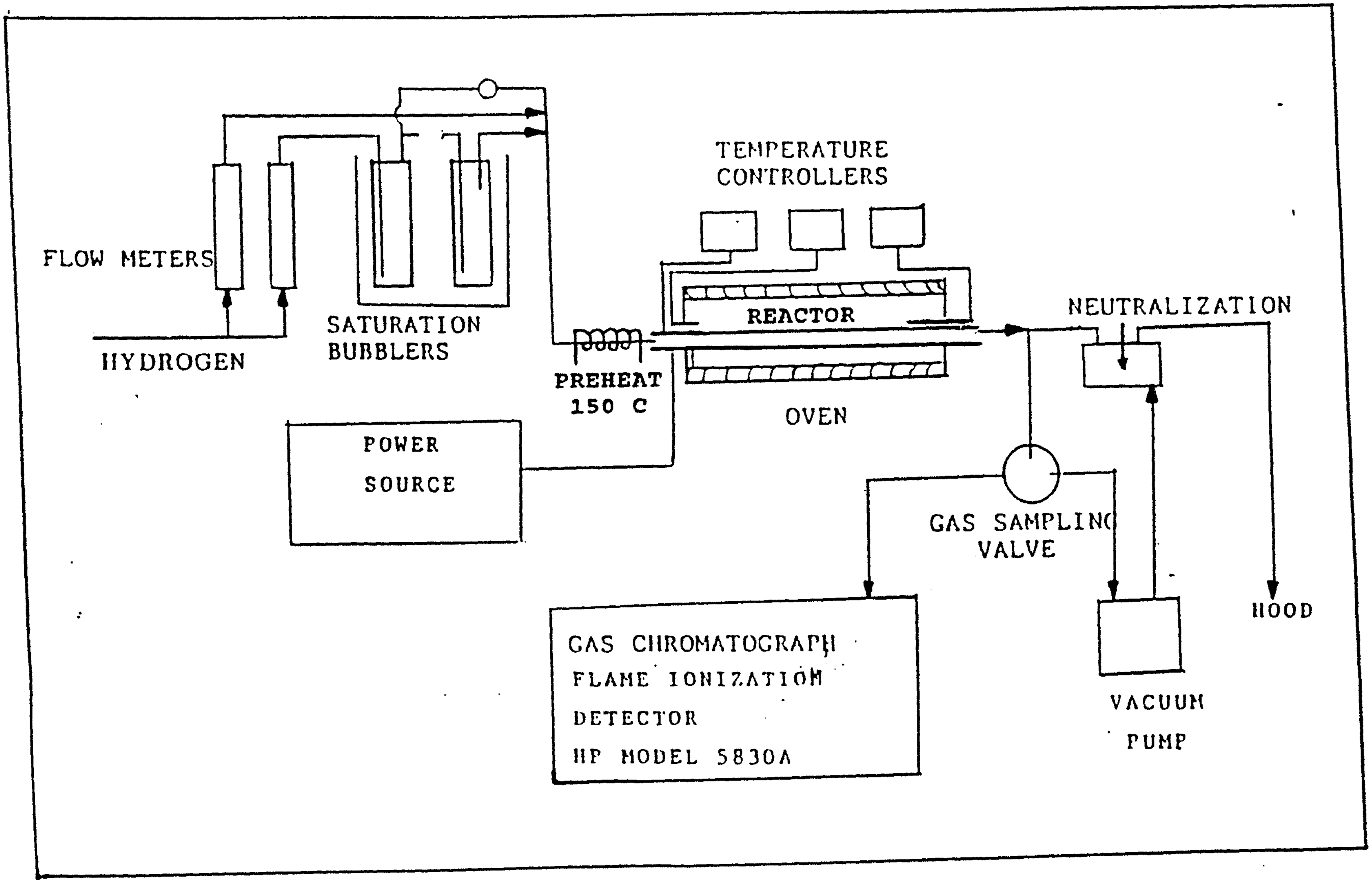
IV. EXPERIMENTAL METHOD

A high temperature tubular flow reactor system, operated isothermally and at atmospheric pressure was used for this study. A block diagram of the entire system is shown in Figure 2.

Hydrogen gas, which acted both as reagent and carrier, was passed through a saturation bubbler filled with the reagent (1,1,2-trichloroethane), and was kept at zero ^{o}C using an ice-water bath. Before the hydrogen/1,1,2-trichloroethane entered the reactor, the mixture was preheated to 150 ^{o}C by use of heating tape to help the reactor achieve uniform temperature profiles. Quartz reactor tubes of 4 mm, 10.5 mm and 16 mm were housed within a three zone Mellen clamshell type furnace, 2.25 inches I.D., and 18 inches long which was used for the reactor oven. Every zone was equipped with an independent Omega CN 300 PI digital temperature controller-indicator with a chromel-alumel TC.

When the inlet switching valves were properly selected, the 1,1,2-trichloroethane vapor would be transferrd directly from the bubbler to the GC sample inlet via a reactor by-pass line. This was necessary to determine the GC peak area which corresponded to the initial input concentration (Co). Effluent from the reactor was filtered to remove solid carbon, by passing all gases through a pyrex wool plug. This limited contamination of the GC sampling loop. The loop was mounted on a six port stainless steel Valco high temperature gas sampling valve.

FIGURE-2 EXPERIMENTAL SET-UP



The reactor effluent was monitored using an on-line gas chromatograph equipped with a Flame Ionization Detector (FID). The lines between reactor exit and GC analysis were heated to 150 °C to prevent product (vapors) condensation or loss. The bulk of the effluent, however, was passed through a sodium - bicarbonate flask before being released into the fume hood.

A. Quantitative Analysis by Gas Chromatography

The Hewlett Packard Gas Chromatograph was equipped with a flame ionization detector (FID) and controlled by a HP 18850C programmable terminal. The terminal also functioned as plotter and integrator. The GC used a 6 ft long by 1/8 inch o.d. stainless steel column packed with 15 % (wt) ov-101 as a stationary phase on Chrompak-R.

The experimental conditions of the reaction of 1,1,2-trichloroethane with hydrogen are listed below:

- Reactants ratio $CH_2ClCHCl_2$: H_2 = 1 : 138
- Reactor temperature (°C) : 440, 470, 500, 530, 570, 600, 630, 660
- Effective reactor length : 40.7 cm
- Reactor Diameter (cm) : 0.40, 1.05, 1.60
- Residence time range (sec.) : 0.44 - 2.55 (i.d. = 1.60)
  0.20 - 2.31 (i.d. = 1.05)
  0.20 - 2.11 (i.d. = 0.40)
- Operating pressure : 1 atm.

1. Regulation and Control

Carrier gases are obtained in a cylinder with 99.9%

purity at 2200 psi. A two-stage regulator is used for constant pressure at the cylinder. Gases were commercial grade from Liquid Carbon Company. The second stage of the regulator is usually set at 40-100 psi.

2. Flow Measurement

A soap-bubble flowmeter was used as a method for measuring gas flowrates in the GC primarily because of its simplicity and independence to the type of gas used. The high flow rates were measured by using a wet test meter (American meter Co. 1 liter per revolation). The FID operated at 30 cc/min hydrogen and 300 cc/min air. Nitrogen at a flowrate of 30 cc/min was used as carrier gas.

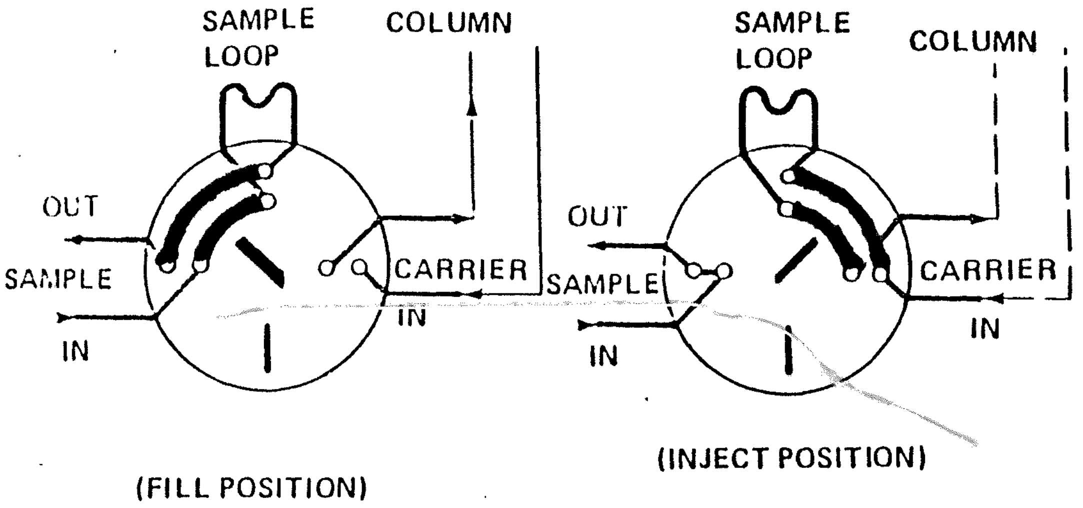


Figure-3 Injection of gas samples by means of a gas sampling valve

3. Gas Sampling

Gas samples are best injected by means of a six port stainless steel Valco high temperature gas sampling valve, model 6UMT, as shown in Figure 3. Steady state conditions were achieved before each sample was injected into the on-line GC. Each sample analysis using the chromatograph took about 20 minutes.

4. Column Temperature

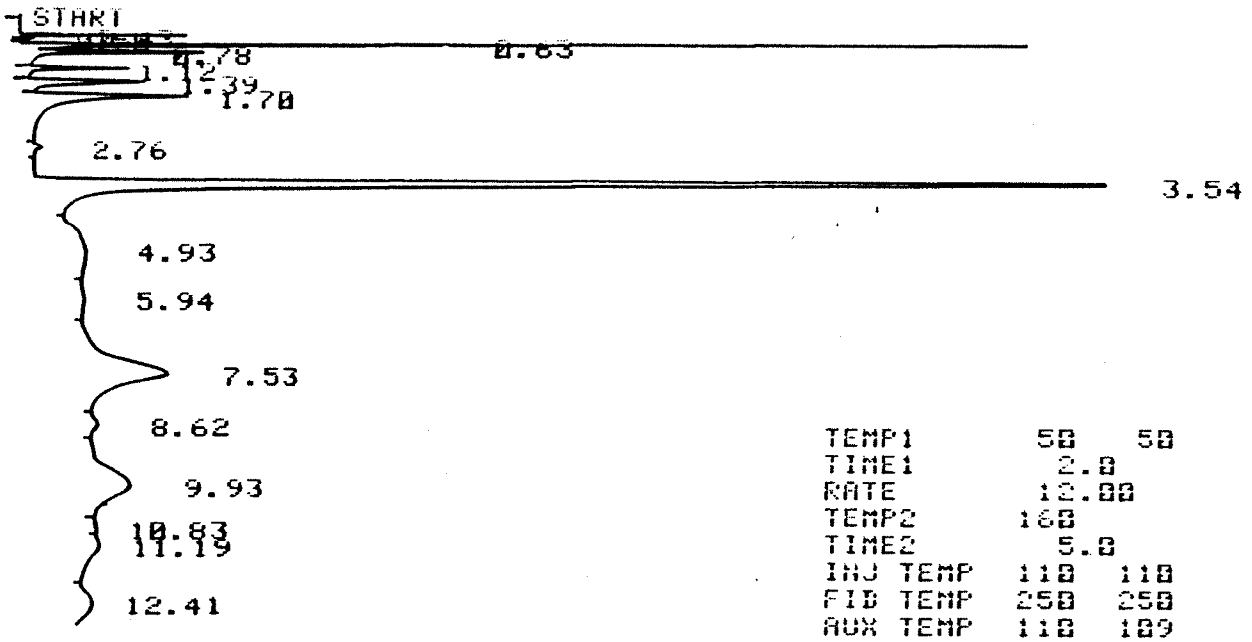
The column oven was programmed to hold at 50 ^{o}C for 2 minutes, then rise to 160 ^{o}C at rate of 12 ^{o}C/min. The initial 2 minutes period allowed enough time for distinct separation of light hydrocarbons.

5. Qualitative Analysis

Qualitative analysis of reactor products was further performed by use of a Kratos MS-25 magnetic sector GC/Mass spectrometer using 25 cc batch samples collected at the reactor exit. A representative chromatogram is shown Figure 4 given in Table 1. with retention times and peak identification.

6. FID Calibration

Calibration of the flame ionization detector to obtain the appropriate molar response factor was done by injecting a known quantity of the relevant compound such as CH_2Cl_2, $CHCl_3$, C_2HCl_3, and $C_2H_4Cl_2$ etc., then measuring the corresponding response area. The relative response factor has been determined in this work for such compounds as shown



```
hp 5830A
AREA %

  RT            AREA        AREA %

 0.43          76700        0.492
 0.50           7366        0.047
 0.63         541200        3.467
 0.78         201700        1.292
 1.12         126700        0.812
 1.39         222000        1.422
 1.70         581600        3.726
 2.76          91080        0.584
 3.54        2968000       19.015
 4.93        1299000        8.322
 5.94         893400        5.724
 7.53        2864000       18.349
 8.62         689600        4.418
 9.93        2421000       15.511
10.83         434400        2.783
11.19        1201000        7.694
12.41         990000        6.343

            XF:    1.0000 E+ 0
```

```
TEMP1          50    50
TIME1           2.0
RATE           12.00
TEMP2         160
TIME2           5.0
INJ TEMP      110   110
FID TEMP      250   250
AUX TEMP      110   109
OVEN MAX      190

CHT SPD         0.10
ATTN 2↑        11
FID SGNL       A
SLP SENS        0.10
AREA REJ     5000
FLOW  A        30
FLOW  B        29
```

---

* Reaction Conditions: 0.86 sec under 600 °C

Figure-4 Sample Chromatogram $CH_2ClCHCl_2/H_2$ Decomposition

Table 1

Average Retention Time of Products

Compound	Average Retention Time (min.)
CH_4	0.39
CH_2CH_2	0.43
CH_3CH_3	0.50
CH_3Cl	0.56
CH_2CHCl	0.63
CH_3CH_2Cl	0.77
CH_2Cl_2	1.12
CH_2CCl_2	1.39
$CHClCHCl$	1.70
CH_3CHCl_2	2.35
CH_2ClCH_2Cl	2.77
C_6H_6	3.20
$CH_2ClCHCl_2$	3.63

in Table 2. The respose factor for C_1 compounds are close to each other, and the response factor of C_2 compounds are nearly twice the response of C_1 compounds. These results agree with the general principle of the flame ionization detector which is well known as a carbon counter<34>. 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 carbons 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.

B. 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 Omega CN 300 PI digital temperature controller-indicators.

The actual temperature inside the tubular reactor was measured with a moveable thermocouple chromel-alumel K, which traversed the length of the reactor. Argon flowed through the reactor at rates of approximately 10 cc/sec. during temperature measurement to minimize radiation effects and to obtain a temperature profile similar to experimental conditions. An Omega type K Thermocouple Thermometer Model

Table 2

Relative Response Factor of Several Compounds

date: 7/21/87
quantity:o.2 ul
TEMP1:70
RATE:15.00
TEMP2:220
AUX TEMP:100
INJ TEMP:120
FID TEMP:250
COLUMN 1:PORAPAK-Q ;50/80 mesh ; 8 ft ; 1/8 IN; S.S.
COLUMN 2:CHROMPAK-R ;40/50 mesh; 6 ft ; 1/8 IN; S.S.

Compound	Relative Response Factor (RRF)				
	1st area	2nd area	3rd area	average	RRF
CH_2CL_2 (COL 1)	4328K	4412K	4637K	4459K**	1.00
$CHCL_3$ (COL 1)	4926K	4994K	4113K	4678K**	1.05
CH_2CLCH_2CL (COL 1)	10060K	10280K	10615K	10318K**	2.31
CCL_2CHCL (COL 2)	7247K	9282K	13890K	10140K	2.27
CCL_2CCL_2 (COL 2)	9026K	8398K (TEMP1 50)	11310K (TEMP1 50)	9578K	2.15
CCL_4 (COL 2)	4174K	4986K (50;RATE 25)	5582K (50;RATE 25)	4914K**	1.10
CH_2CCL_2 (COL 2)	7315K (RATE 20)	8974K (RATE 20)	9769K (RATE 20)	8695K	1.95

** Sampling system was not fully pressure stable.

650, was used for temperature readings inside the reactor, taken at one inch intervals. Temperature profiles obtained as shown in Figure 5 for six different temperatures (500, 550, 600, 650, 700, and 750) were isothermal to within ± 5 ^{O}C for 80 % of reactor length.

C. Hydrochloric Acid Analysis

Quantitative analysis of HCl product was performed for reactions in each diameter reactor for each residence time. The samples for HCl analysis were collected independent H from GC sampling as illustrated as Figure 2.

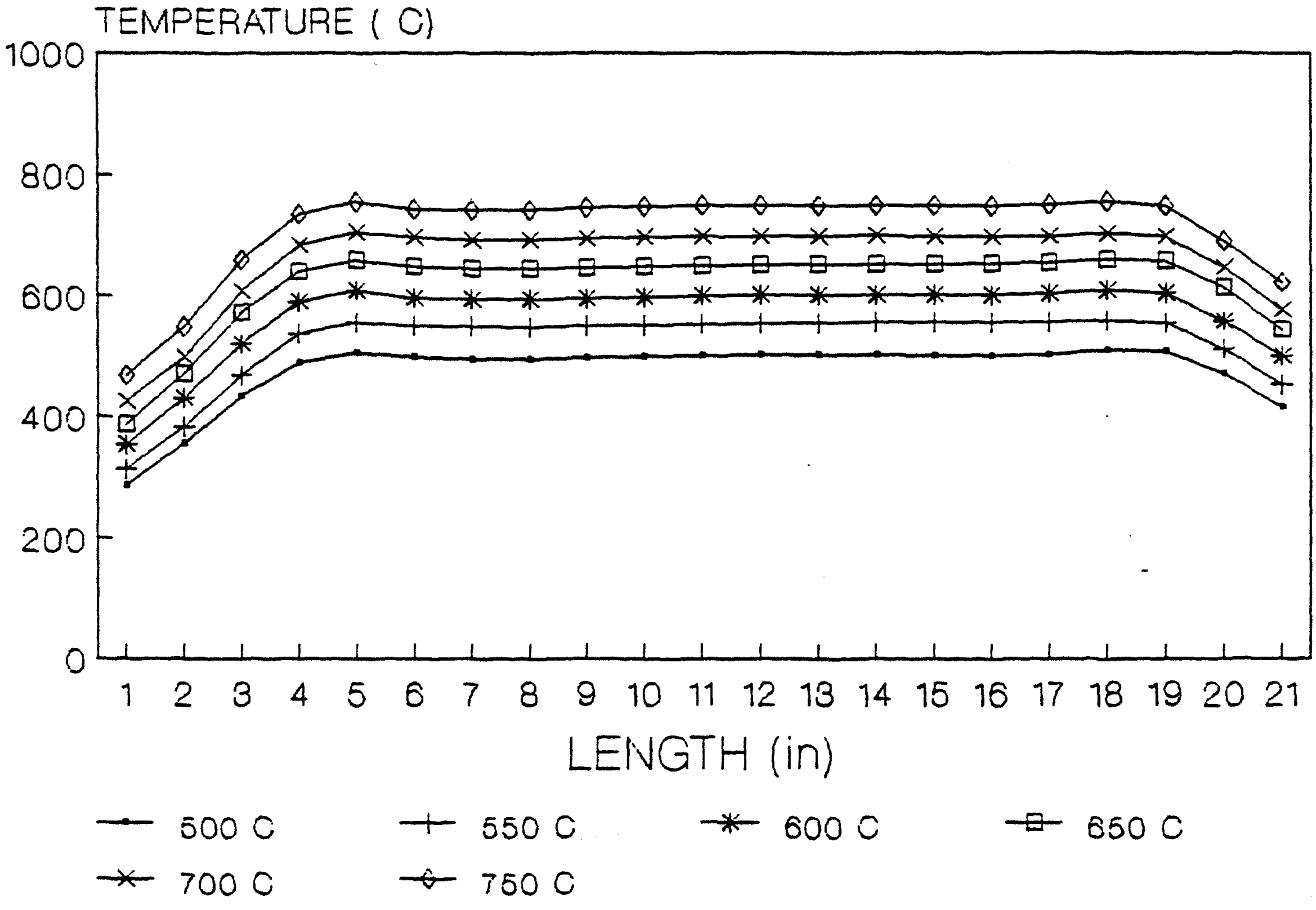
In this analysis, the effluent was bubbled through a two stage bubbler before being exhausted to the hood. Each stage contained 25 ml of standardized 0.01 M NaOH. The gas was passed through the two stage bubbler until the first stage solution reached its phenolphthalein end point. The time required for 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. Since the concentration and molar flow rate of chlorine as 1,1,2-trichloroethane mixture was known, Cl mass balance could be determined from the total HCl produced by reaction. The HCl produced was calculated by:

No. of mol of NaOH =(0.01 M) * (0.05 l) = 5.0E-4 (mole)

No. of mol of HCl gas from reactor = 5.0E-4 - X*1.0E-5 (mol)
(X : Consumed titrated solution (ml))

$$\text{Conc. of gas from reactor} = \frac{5.0E-4 - X*1.0E-5 \text{ (mol)}}{\text{Total flow (liter)}} \qquad (22)$$

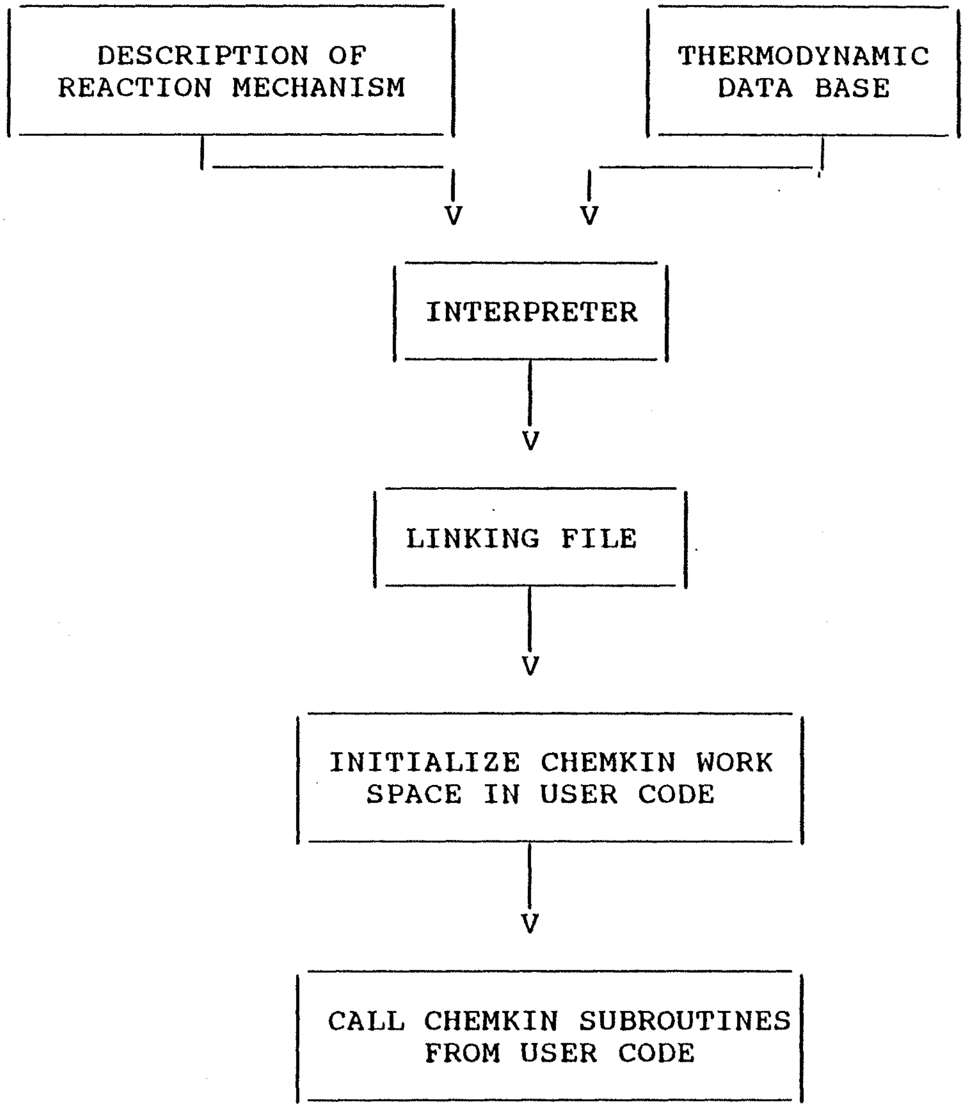
FIGURE-5 TEMPERATURE PROFILE VS REACTOR LENGTH



D. 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<41>, Flow diagram below, reads the user's description of the reaction mechanism, which in this case consists of 73 elementary reactions and 37 species. The thermodynamic data base, THERM has the appropriate thermodynamic information and mass for all species present in the mechanism in 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, can be called to return information on the reactions, equation of state, thermodynamic properties, chemical production rates, and derivatives of thermodynamic properties at 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 Lsode Integrator<41>.

The input data requirement to run the CHEMKIN program Include:



Flow Diagram of the CHEMKIN operation reprinted from reference<41>

- Detailed reaction mechanism of 73 elementary reactions.
- Mole fraction of all gases initially present in the reaction system.
- Pressure and temperature at which the reaction system is being studied.
- Time increment at which the concentration of species present in the system is to be reported.

A thermodynamic data base for species with C/H/Cl elements was developed at NJIT and used for modeling (input to CHEMKIN) the kinetics of the 1,1,2-trichloroethane/H_2 reaction system investigated. For those species that thermodynamic information were not available in the data base, thermo data was generated utilizing the DBGEN 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 the group additivity method of Benson<42> when not available in literature, using "THERM".

This computer work was executed using a Digital equipment corporation (DEC) VAX/VMS 11/785 computer at NJIT.

V. RESULTS and DISCUSSION

The experimental conditions of the reaction of 1,1,2-trichloroethane with hydrogen are listed below. Constant molar ratio $CH_2ClCHCl_2$: H_2 of 1 : 138 was maintained through out the experiment.

. Reactor temperatures (°C) : 440, 470, 500, 530, 570, 600, 630, 660

. Effective reactor length : 40.7 cm

. Reactor Diameter (cm) : 0.40, 1.05, 1.60

. Residence time range (sec.) : 0.44 - 2.55 (i.d. = 1.60)
0.20 - 2.31 (i.d. = 1.05)
0.20 - 2.11 (i.d. = 0.40)

. Operating pressure : 1 atm.

A. Reaction of 1,1,2-trichloroethane with Hydrogen

Figure 6 and Figure 7 show the decrease in the normalized 1,1,2-trichloroethane ($CH_2ClCHCl_2$) concentration (C/Co) as a function of the average residence time for several temperatures studied using the 1.05 cm i.d. and 0.40 cm i.d. reactors. Figure 6 shows decay plots of 1,1,2-trichloroethane vs time for temperatures 570, 600, 630, and 660 °C in the 1.05 cm i.d. reactor. It is apparent from this figure that a conversion of 22%, 41%, 70%, and 80% at 1.1 sec. residence time is obtained at the respective temperatures above. The 1,1,2-trichloroethane concentration consistently decreases with increasing reaction time for all temperatures shown in the each different i.d. reactor and

Figure-6 DECAY OF CHCl2CH2Cl VS TIME FOR 1.05 cm ID REACTOR

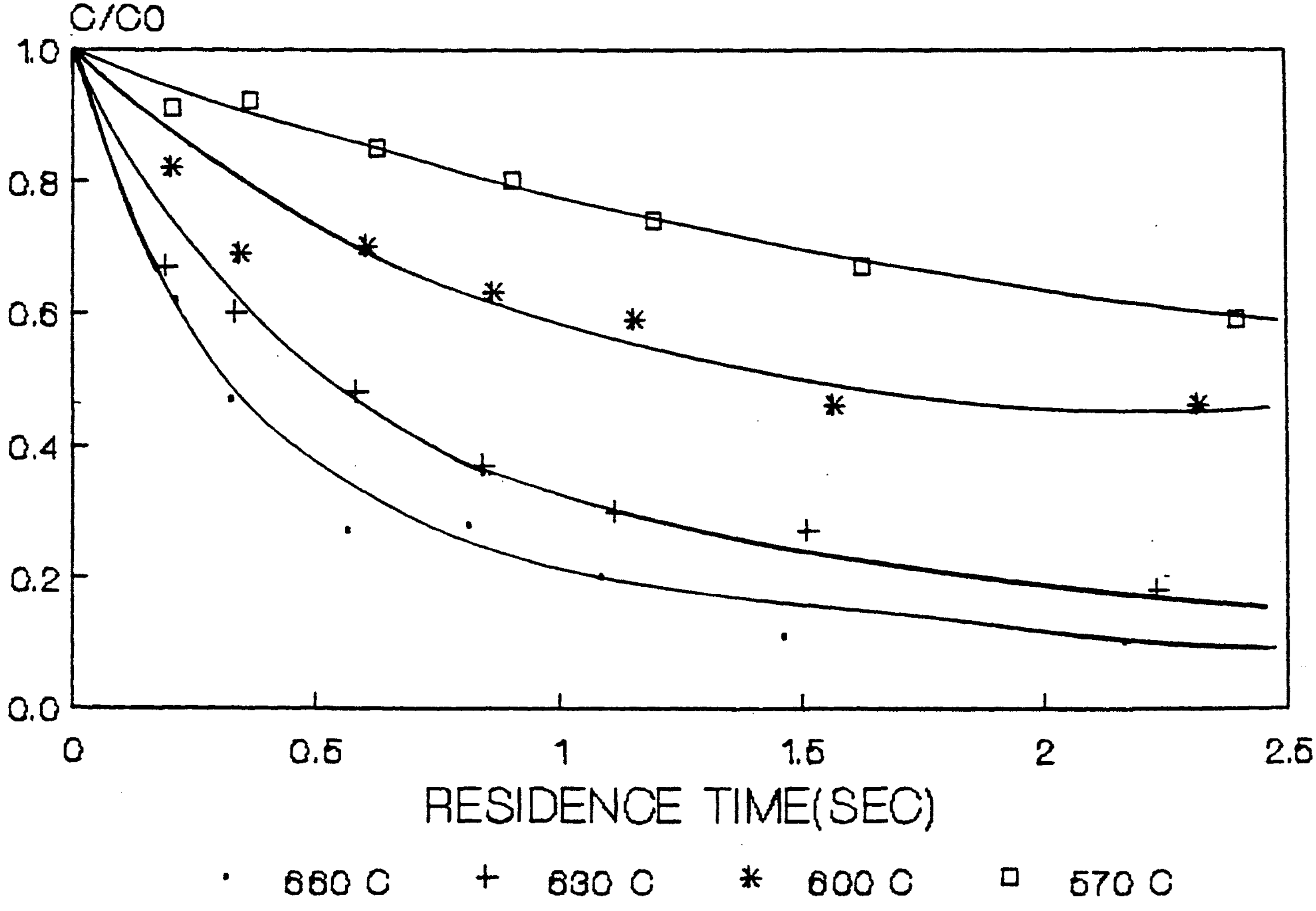
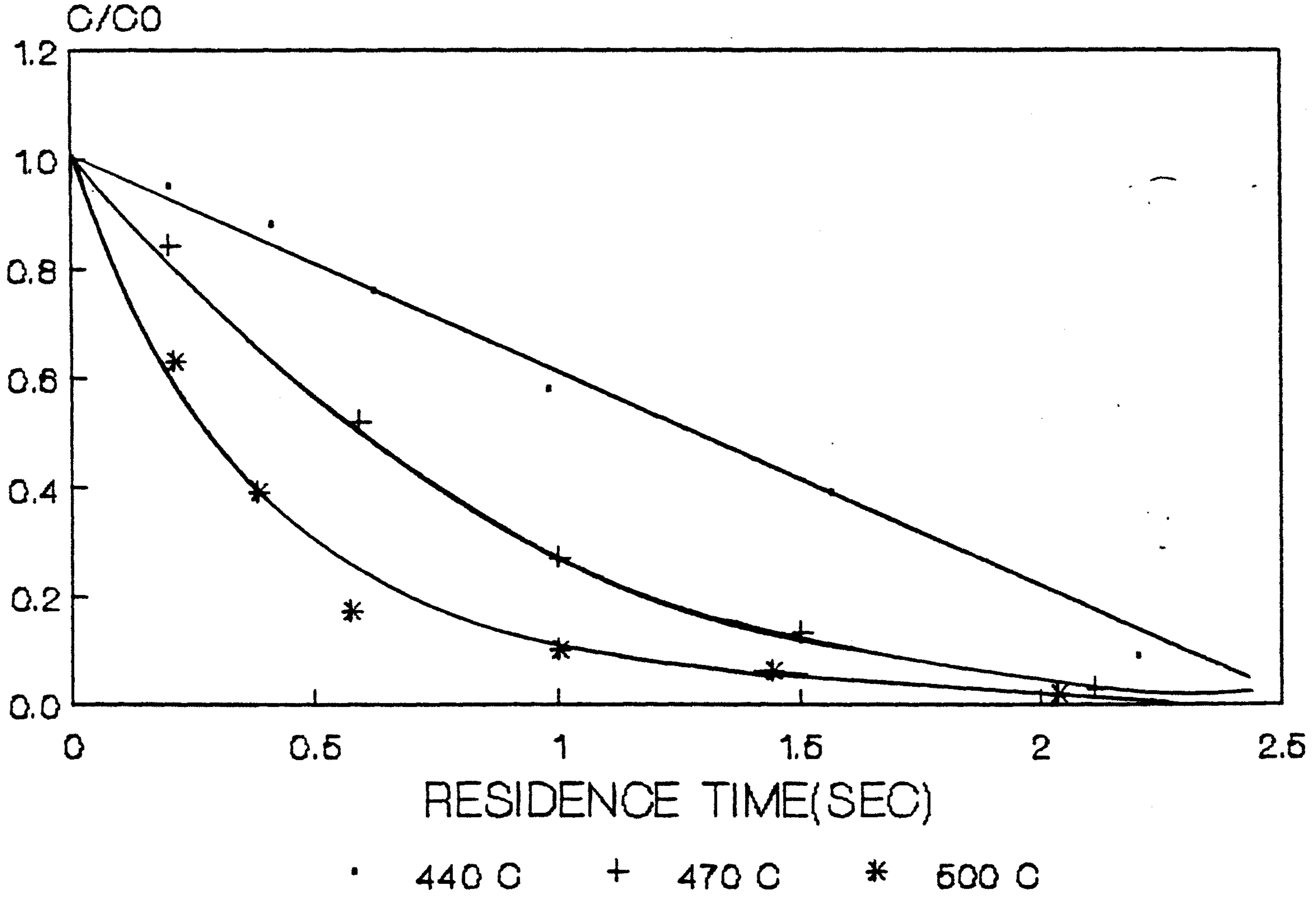


FIGURE-7 DECAY OF CH2ClCHCl2 VS TIME
FOR 0.40 cm ID REACTOR



for constant residence times 1,1,2-trichloroethane conversion consistently increases with temperature.

Application of the first order rate expression to this data yields a linear relationship for each temperature studied. This demonstrates that the overall reaction obeys pseudo-first order kinetics (global reaction). Figure 8 illustrates the first order behavior obtained for several temperatures which were studied in the 1.05 cm i.d. reactor. Here a first order rate plot for decay of $CH_2ClCHCl_2$ shows excellent linearity for all temperatures. Similar results were obtained for the 0.4 cm i.d. reactor as shown in Figure 9.

It is seen that for different values of temperature and reactor diameter, that the data fit the integrated first order rate equation well for reagent loss. Decomposition was most rapid with the 0.40 cm i.d. and slower with the 1.05 cm i.d. reactor as shown in Figure 6 and Figure 7. 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.

Activation energies and Arrhenius frequency factors for the reagent loss are found from Arrhenius plots such as shown in Figure 10. Global rate constants in Arrhenius form for different diameter reactors are listed below:

FIGURE-8 FIRST ORDER DECAY PLOT FOR CH2ClCHCl2/H2 1.05 cm ID REACTOR

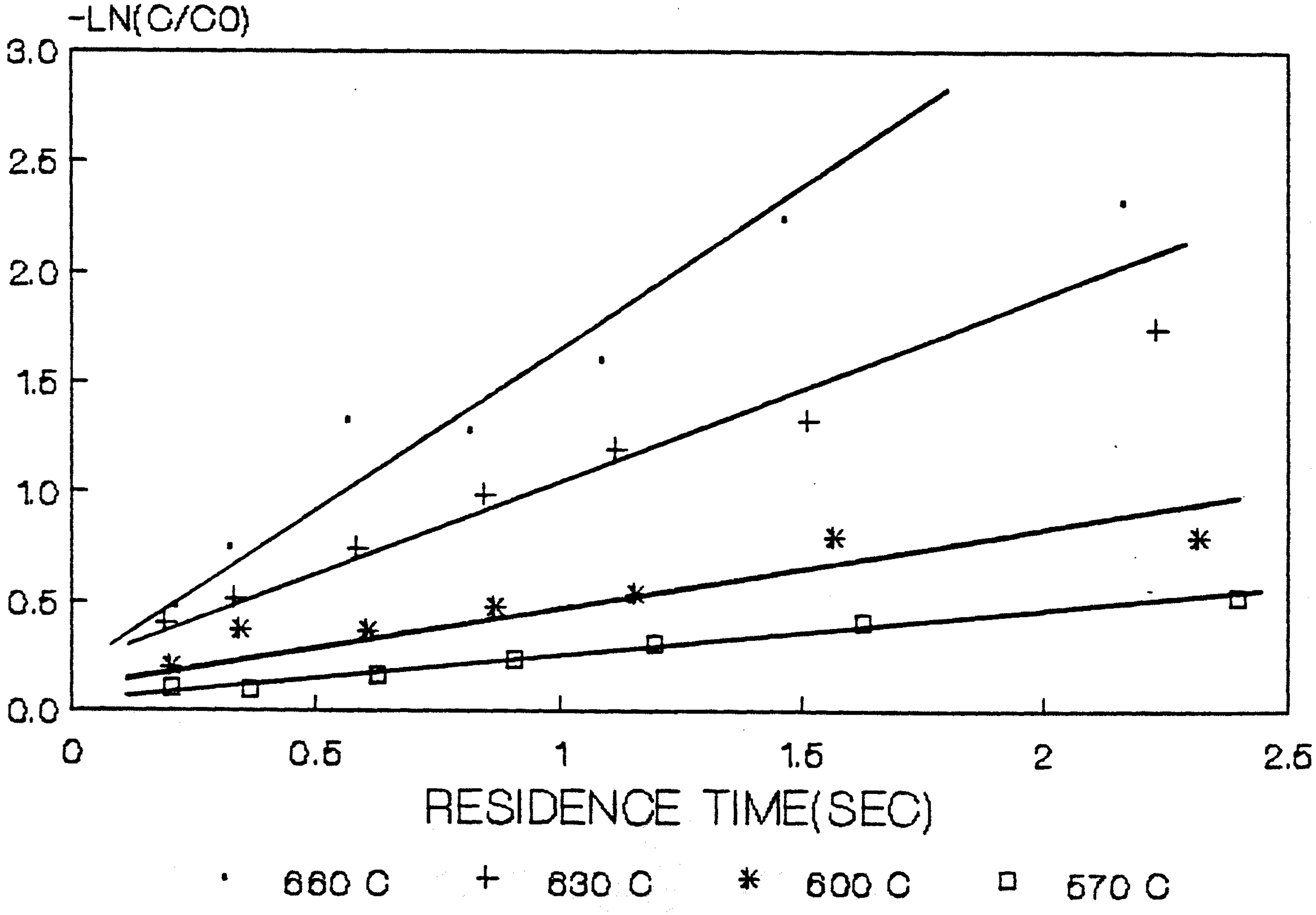


FIGURE-9 FIRST ORDER DECAY PLOT FOR CH2ClCHCl2/H2 0.40 cm ID REACTOR

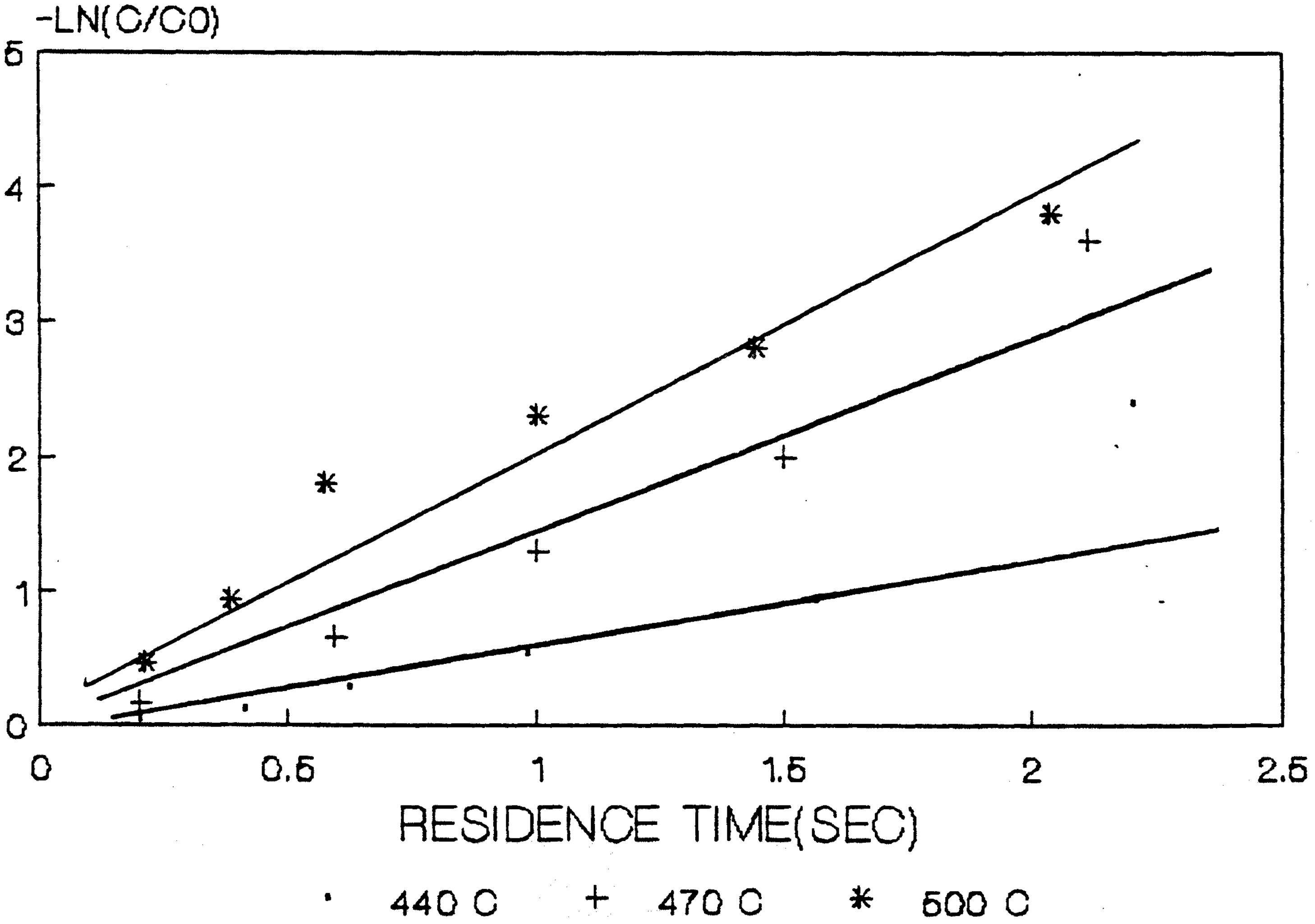
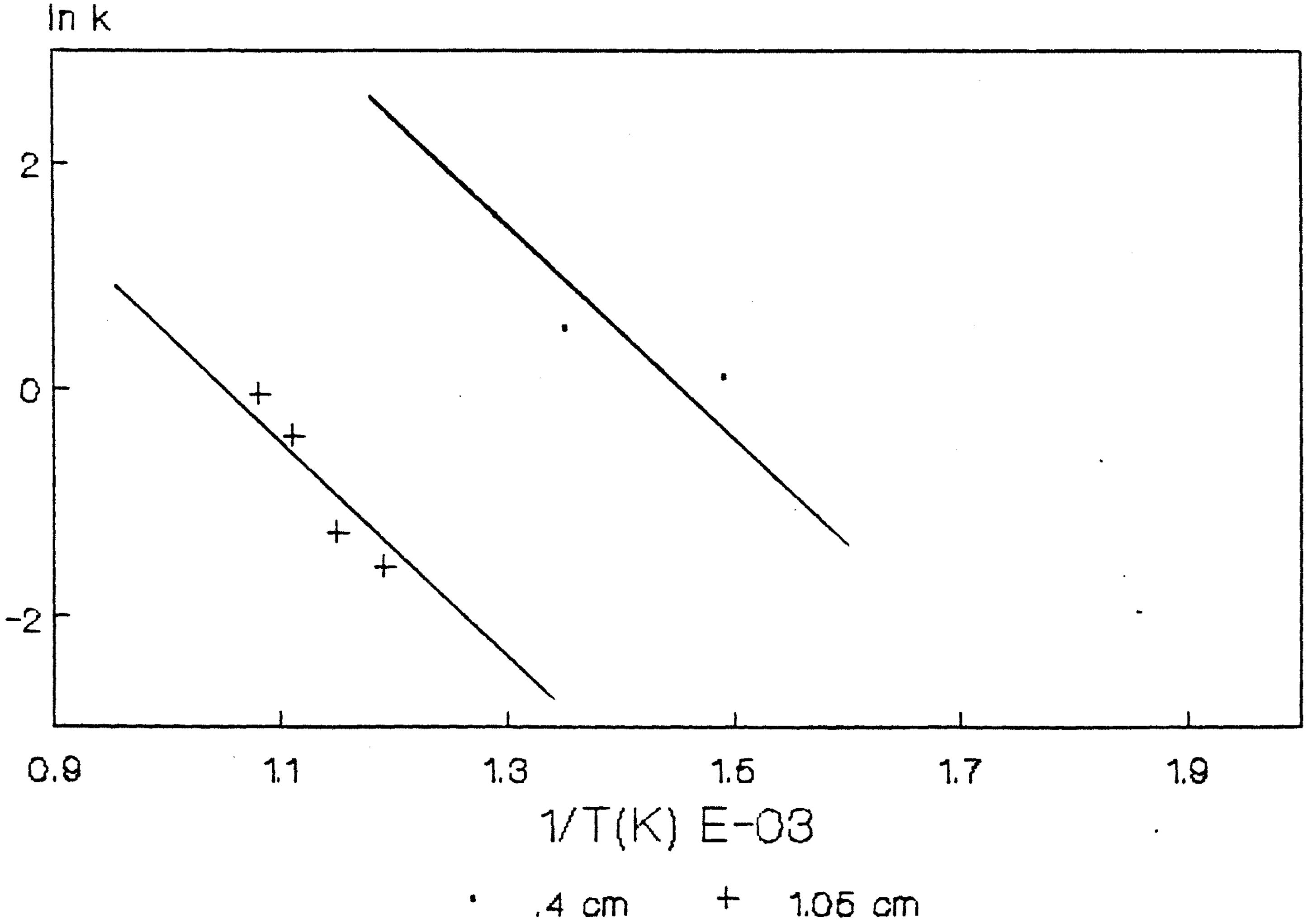


FIGURE-10 ARRHENIUS BEHAVIOR OF Kexp FOR CH2ClCHCl2

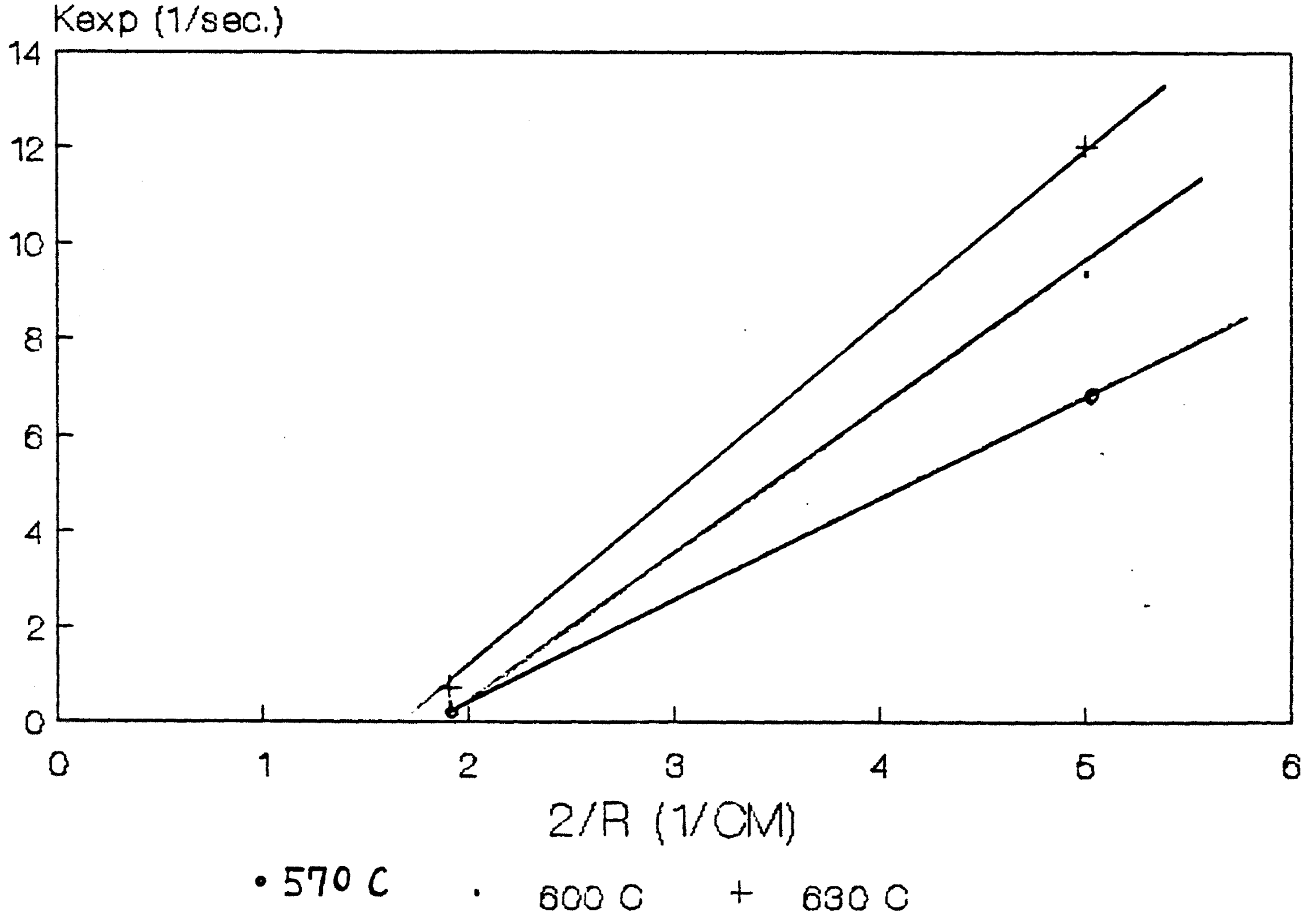


$k_{0.40\ cm}$ = 1.60E+4 * EXP(-13,000/RT) (1/sec.)

$k_{1.05\ cm}$ = 6.58E+6 * EXP(-29,200/RT) (1/sec.)

where T is temperature in ^oK and R is gas constant in cal/mol-^oK. Previous studies have demonstrated that a change in the S/V ratio often directly affects the overall rate constants for these reactions<20-26>, because of wall reactions. Clearly the relative importance of the wall reaction in this system is greater when the surface to volume (S/V) ratio or relative extent of the wall surface is greater. This wall reaction is analyzed by plotting k against 2/R and using $R_{exp} = R_b + (2/R) * R_w$, where R is the radius of the reactor in centimeters. The slope is k_w and the intercept k_b, as shown in Figure 11.

FIGURE-11 ARRHENIUS BEHAVIOR OF Kb & Kw FOR CH2ClCHCl2



B. Reagent Conversion and Product Distribution

Appreciable conversion (9.4%) of 1,1,2-trichloroethane could be readily observed at reaction temperatures above 570 ^{o}C at times of 0.2 sec or longer. The destruction of 1,1,2-trichloroethane is shown in Figure 6 with increasing temperature and mean residence time, where 90 % destruction of the reagent was observed at 2.2 sec and 660 ^{o}C. Product distributions as a function of temperature at 1.1 sec residence time are shown in Figure 12, in addition to 1,1,2-trichloroethane loss. The major product distribution curves are shown in Figures 12 and 15 with temperature from 570 ^{o}C to 660 ^{o}C and with varied residence times, Figure 13 and Figure 14, 0.2 sec to 2.2 sec at 600 ^{o}C and 630 ^{o}C respectively. 1,2-dichloroethylene (CHClCHCl), 1,1-dichloroethylene (CH_2CCl_2), vinyl chloride (CH_2CHCl), chloroethane (CH_3CH_2Cl), and HCl are the main observed chlorinated species, with methyl chloride (CH_3Cl) and dichloromethane (CH_2Cl_2) as minor products. The observation of considerable amounts of dichloroethylene (both isomers) strongly indicates that the first step in the reaction series at 570-660 ^{o}C is unimolecular decomposition of 1,1,2-trichloroethane to a corresponding dichloroethylene and hydrogen chloride. The same observation has been reported by Chuang<20> in his study on gas-phase reactions of chloroform and 1,1,2-trichloroethane with hydrogen in a tubular flow reactor in 1986.

As illustrated in Figures 14-15, formation of non-

Figure-12 Product Distribution vs Temp
CH2CLCHCL2/H2 at Time=1.1 sec.

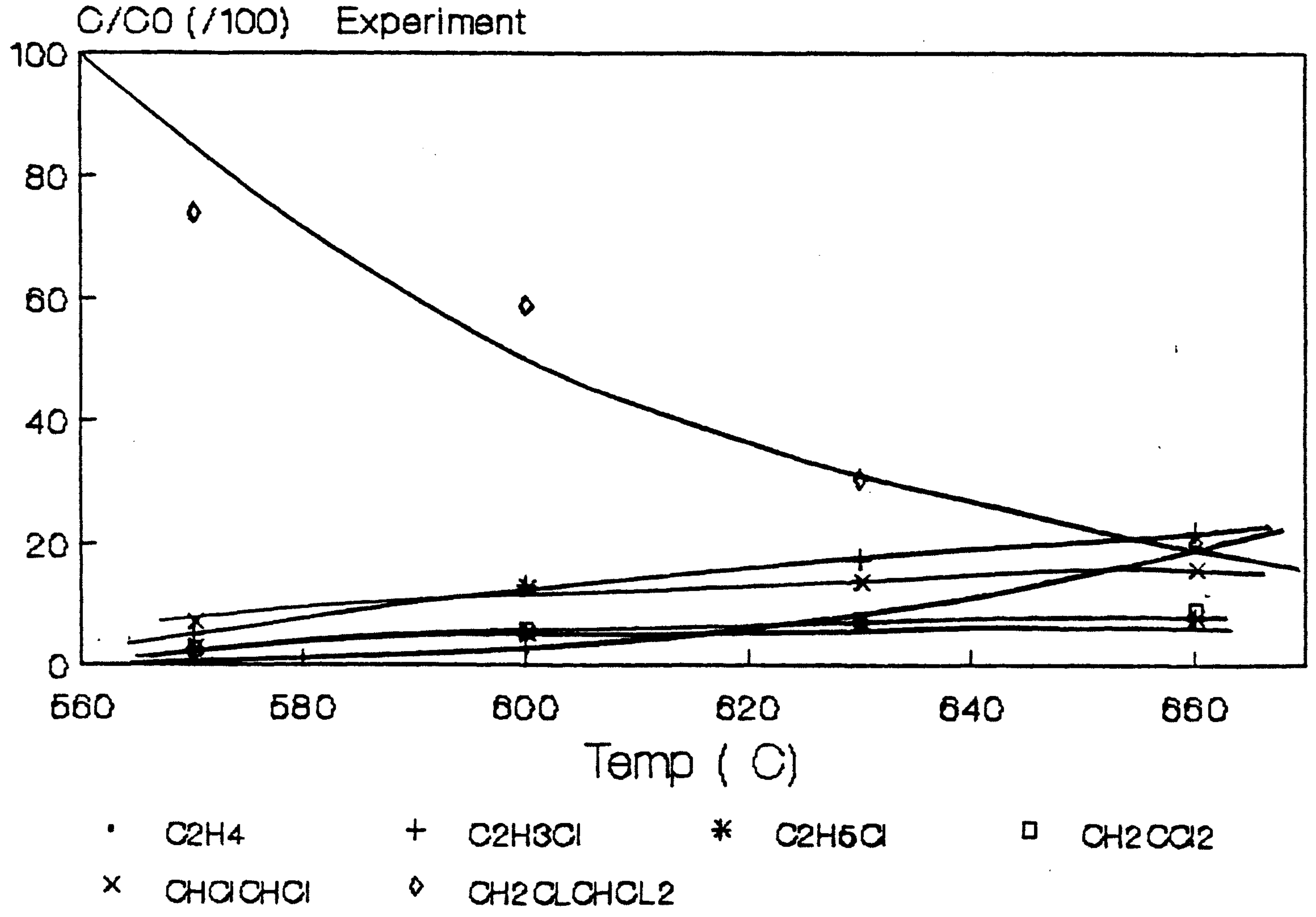


Figure-13 Product Distribution vs Time
CH2ClCHCl2/H2 at Time=600 C

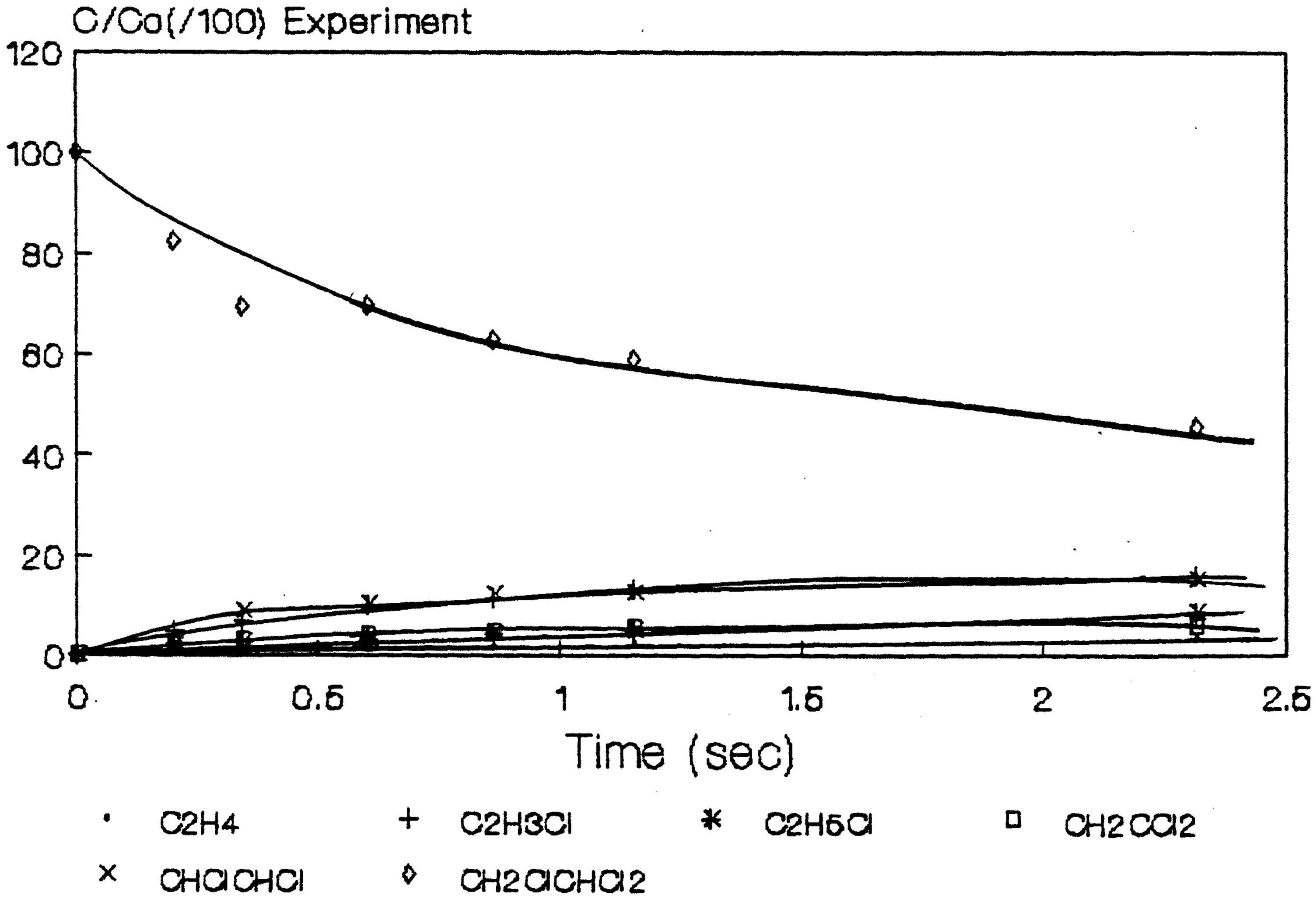


Figure-14 Product Distribution vs Time
CH2ClCHCl2/H2 at Temp=630 C

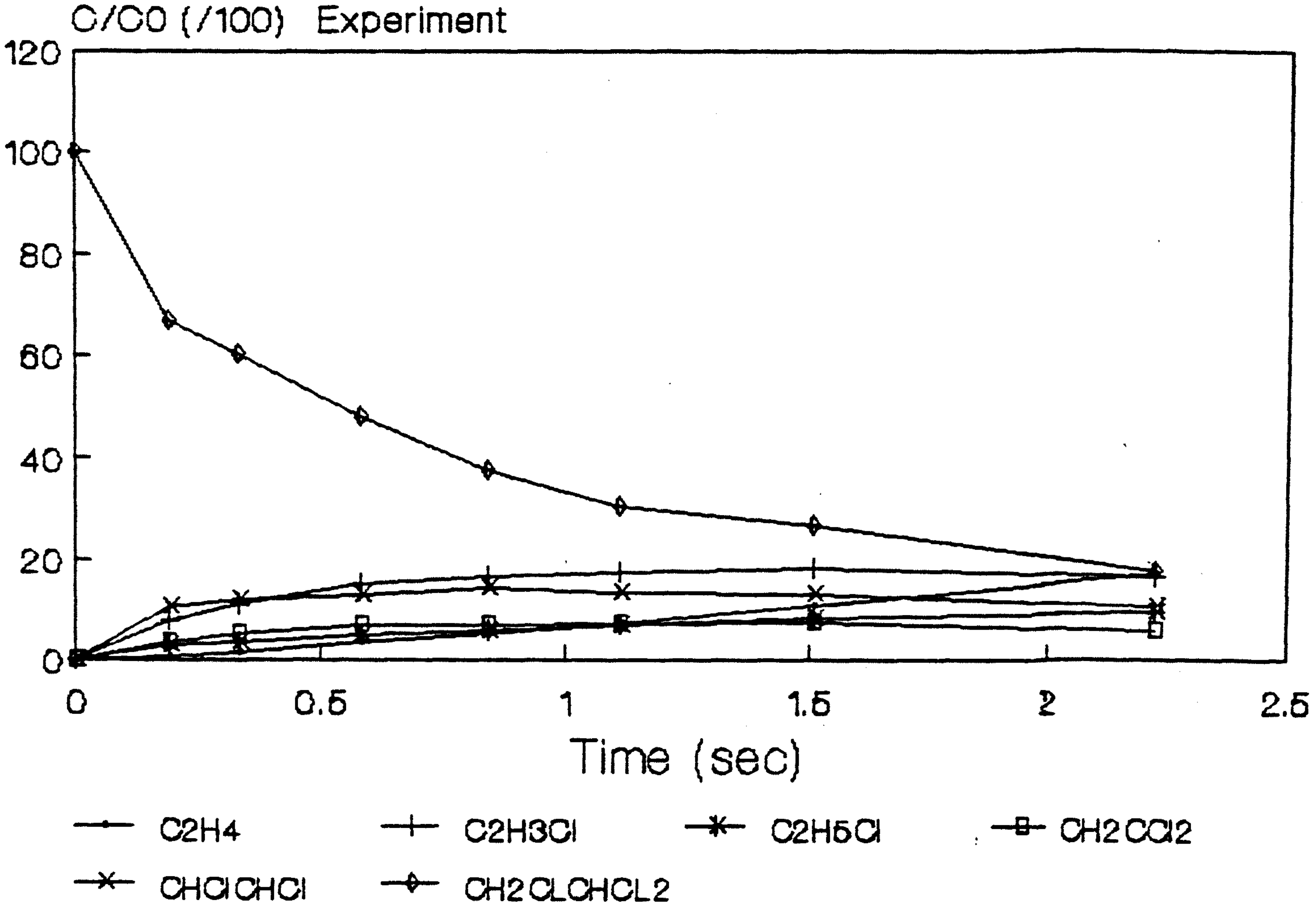
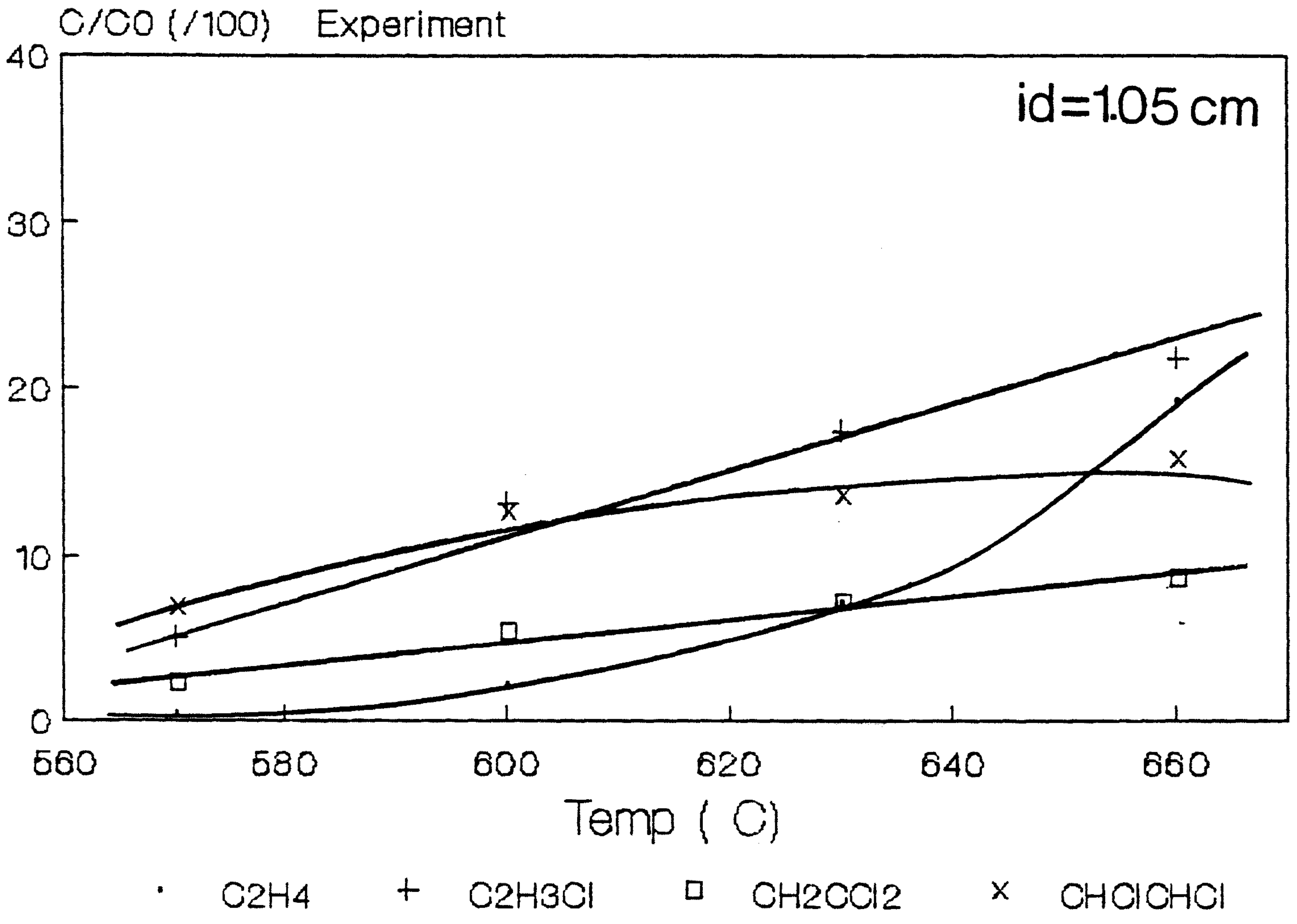


Figure-15 Product Distribution vs Temp
CHClCHCl,CH2CCl2,CH2CHCl,and CH2CH2



chlorinated hydrocarbons are 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 given in Table 3. Table 3 also indicates that excellent Cl material balance is achieved and thus no chlorine is lost into the soot (solid carbon) in this reaction system. Formation of ethylene is observed to increase with increasing temperature as well as formation of benzene (not shown in figures). At 850 ^{o}C and 1.1 sec residence time, the principal products are ethylene and HCl, most chlorinated by-products have been destroyed except vinyl chloride (1.0 %) and traces of chloroethane. The vinyl chloride appears from these studies to be relatively more stable than any other C_2 chlorocarbon and this is consistent with the bond strengths of C-Cl bonds on chlorocarbons which increases with decreasing chlorination. It is interesting to note that very little C_1 chlorocarbons are seen at the high temperature, above 850 ^{o}C. This nonobservation of C_1 chlorocarbons indicates that the carbon-olefinic bonds are relatively stable and persist longer in this reaction zone. Chuang's study<20> also shows that very small amounts of C_1 products are produced from 1,1,2-trichloroethane pyrolysis reaction in H_2 above 850 ^{o}C.

Formation of CHClCHCl and CH_2CCl_2 as two of the major products from CH_2ClCH_2Cl increases with increasing temperature between 570 ^{o}C to 660 ^{o}C at 1.1 sec residence

Table 3

Material Balance for 100 Moles Chlorine

Reactor Diameter : 1.05 cm
Residence Time : 1.1 seo.

Species (%)	Temperature (^{o}C)				
	570	600	630	660	850
CH_3Cl	ND	ND	0.085	0.110	ND
CH_2CHCl	1.696	4.354	5.801	7.247	3.30
CH_3CH_2Cl	0.899	1.642	2.261	2.529	0.71
CH_2Cl_2	2.369	3.631	3.422	2.877	ND
CH_2CCl_2	1.505	3.638	4.754	5.780	0.17
CHClCHCl	4.583	8.391	8.998	10.480	0.42
CH_3CHCl_2	ND	ND	0.809	0.885	ND
CH_2ClCH_2Cl	0.925	1.935	1.627	0.885	ND
$CHCl_2CH_2Cl$	73.872	58.666	30.381	20.169	4.75
HCl	16.723	30.509	47.152	63.277	88.5
Total	102.571	112.765	105.290	114.240	97.85

Fig.-16 CHClCHCl Product Distribution
vs Time at Temp=600,630,and 660 C

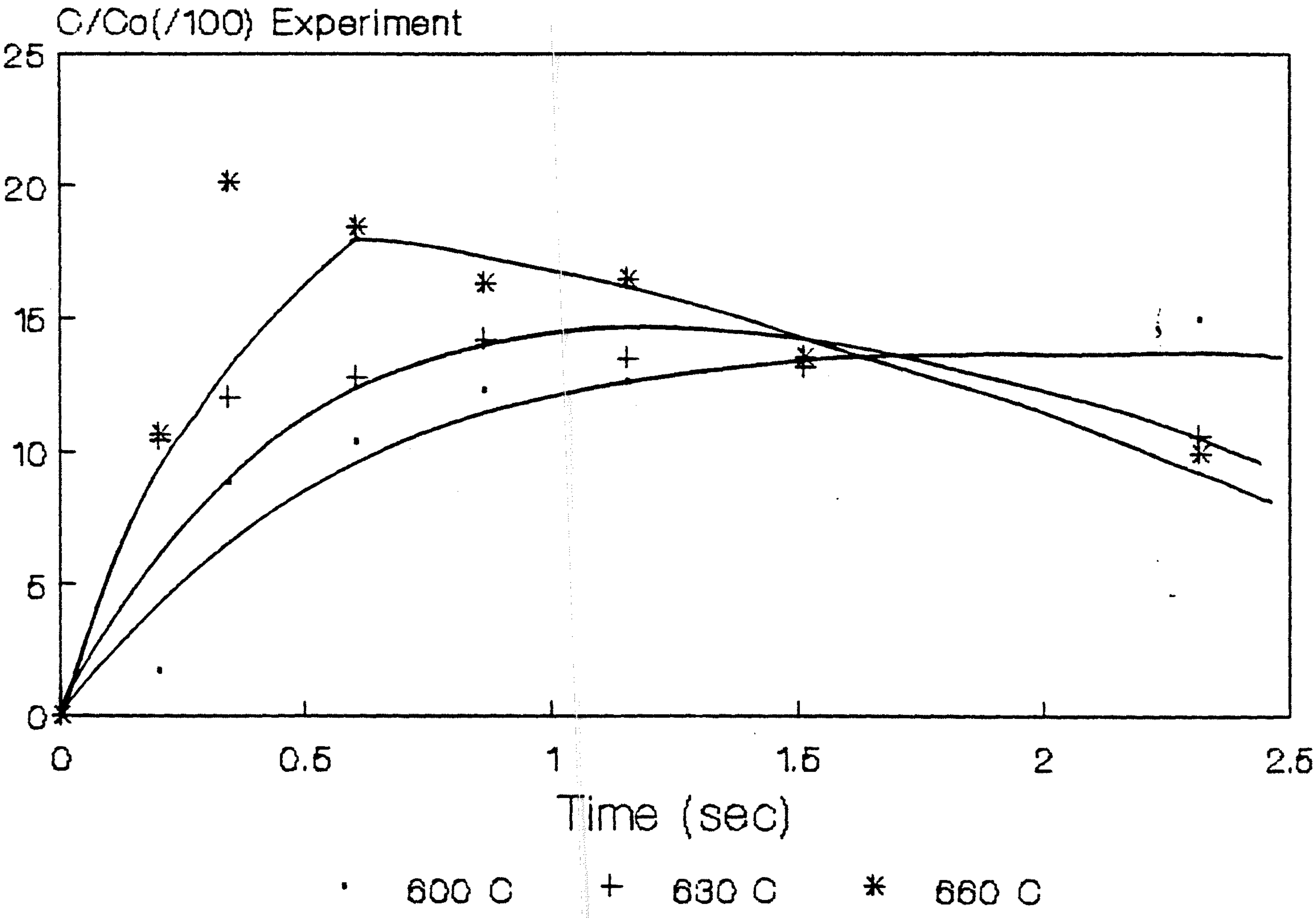
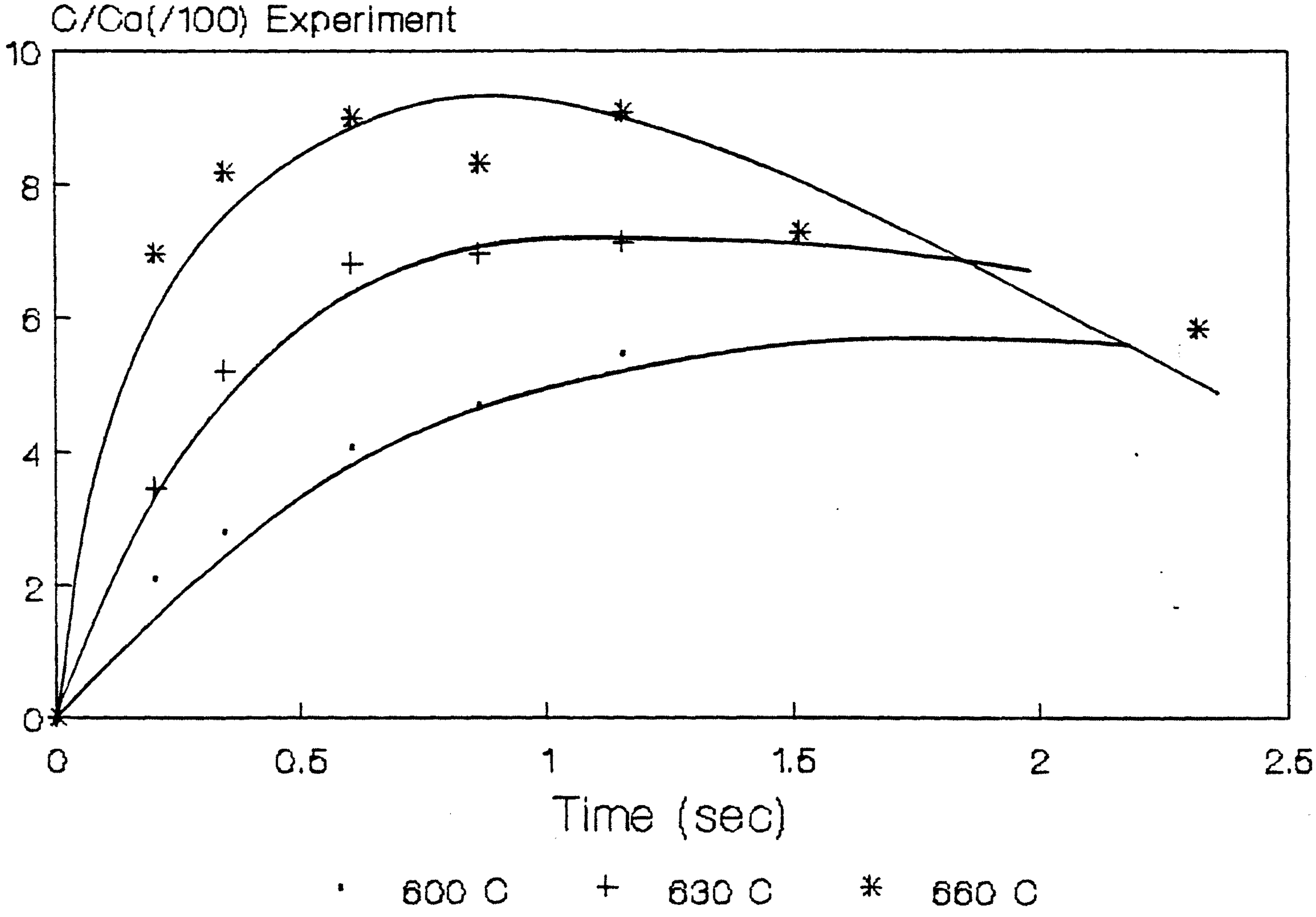


Figure-17 CH2CCl2 Product Distribution vs Time at Temp=600,630,and 660 C



time, 1.05 cm i.d. cm reactor, as shown in Figure 15. Concentration of these species then decreases with further increase in temperature; strongly indicating that CHClCHCl and CH_2CCl_2 are the initial stable product in unimolecular reaction of this mixture diluted in hydrogen. Figure 16 and Figure 17 specifically illustrate CHClCHCl and CH_2CCl_2 normalized concentration data versus residence time for three different temperatures, and demonstrate that CHClCHCl (1,2 DCE) and CH_2CCl_2 (1,1 DCE) concentration increases with increasing residence time under 600 ^{o}C. It is valuable to note that CHClCHCl reaches a maxima of 20% initial 1,1,2-trichloroethane while CH_2CCl_2 only reaches a maxima of 10%. This suggests that 1,1,2-trichloroethane reacts to CHClCHCl about 2 times faster than to CH_2CCl_2 throughout our temperature range - assuming that both have similar (relatively high) stabilities. Formation of CH_3CH_2Cl and CH_2CHCl (vinyl chloride) also increase at temperatures under 600 ^{o}C then decrease similar to the 1,1 and 1,2 DCE. These trends may be due to a high formation rate of precursor products such as CHClCHCl, CH_2CCl_2, CH_2ClCH_2Cl, and CH_3CHCl_2, which are further dechlorinated to CH_2CHCl, CH_2CH_2, and CH_3CH_3 in subsequent reaction steps with increasing temperature.

The increase in formation of CH_2CHCl and CH_2CH_2 with increasing temperature from 570 ^{o}C to 660 ^{o}C as shown in Figure 15. This indicates that the more stable compound, CH_2CHCl is apparently formed from overall reactions of CHClCHCl, CH_2CCl_2, CH_2ClCH_2Cl and CH_3CHCl_2 with hydrogen, and that CH_2CH_2 and/or CH_3CH_3 is produced from further reactions of the CH_2CHCl. Formation of CH_2CH_2 is observed to increase with increasing temperature to 850 ^oC. The less chlorinated hydrocarbons are clearly more stable in this reacting system. Won<26,37> in 1988, showed the greater the carbon chloride bond energy, the higher the temperature required to observe reaction of the chlorocarbon, which we illustrate in Table 4. The maximum concentration (55%) of CH_2CCl_2 was abserved at 620 ^oC and the maximum concentration (16%) of CH_2CHCl was observed at 720 ^oC.

TABLE. 4

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

Table 5 illustrates that a semi-quantitative product distribution of benzene is observed above 630 ^oC. The

Table 5

Material Balance for 100 Moles Carbon

Reactor Diameter : 1.05 cm
Residence Time : 1.1 sec.

Species (%)	Temperature (^{o}C)				
	570	600	630	660	850
CH_2CH_2	0.425	2.219	7.163	19.246	85.24
CH_3CH_3	ND	0.190	0.317	0.832	ND
CH_3Cl	ND	ND	0.127	0.166	ND
CH_2CHCl	5.087	13.063	17.404	21.743	1.1
CH_3CH_2Cl	2.697	4.925	6.782	7.594	0.27
CH_2Cl_2	1.777	2.723	2.567	2.158	ND
CH_2CCl_2	2.257	5.457	7.131	8.669	0.11
CHClCHCl	6.874	12.586	13.497	15.720	0.26
CH_3CHCl_2	ND	ND	1.214	1.327	ND
CH_2ClCH_2Cl	1.387	2.903	2.439	1.327	ND
C_6H_6	ND	ND	4.704	7.900	ND
$CHCl_2CH_2Cl$	73.872	58.666	30.381	20.169	4.75
Total	94.376	102.731	93.726	106.851	90.74

formation of benzene may be due to pyrolysis of C_2 hydrocarbons, followed by a ring closure mechanism with olefinic and acetylenic species as intermediates. A general commercial pathway to synthesis of benzene is pyrolysis and hydrogasification of paraffinic hydrocarbons<38>.

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

C. Detailed Kinetic Mechanism and Modeling

Kinetic Mechanism

A reaction mechanism for decomposition kinetics of $CH_2ClCHCl_2$ in H_2 has been developed.

The first step of this reaction system involves unimolecular decomposition of 1,1,2-trichloroethane. The possible reactions include:

	A (1/s)	E (Kcal/mol)
1. $CH_2ClCHCl_2$ ---> CHClCHCl + HCl	9.5E12	55.3 (ΔHr+41)
2. $CH_2ClCHCl_2$ ---> CH_2CCl_2 + HCl	4.7E12	55.3 (ΔHr+41)
3. $CH_2ClCHCl_2$ ---> $CH_2ClCHCl$ + Cl	2.6E15	77.7 (ΔHr)
4. $CH_2ClCHCl_2$ ---> CH_2CHCl_2 + Cl	1.6E15	81.4 (ΔHr)
5. $CH_2ClCHCl_2$ ---> CH_2Cl + $CHCl_2$	4.2E17	89.1 (ΔHr)

It is observed using the above listing (also see dissociation reactions of parent $CH_2ClCHCl_2$ in APPENDIX Table 1) that reactions (1) and (2) above dominate the other 112 TCE dissociation steps by more than on order of magnitude because of the low Ea's. This is fully consistent with our experimental results. CHClCHCl, CH_2CCl_2 and HCl are the major products detected below 660 ^oC and result from the first reaction step. Although reactions (3) and (4) are about fifty times slower than reactions (1) and (2), the intermediates $CH_2ClC.HCl$ and $C.H_2CHCl_2$ rapidly undergo beta scission reactions (6) and (7) because of the low E_a to Cl loss and one of the major products, CH_2CHCl,. is produced.

A(1/s) E(Kcal/mol)

6. $CH_2ClCHCl$ ----> $CH_2CHCl + Cl$	1.35E14	27.4
7. CH_2CHCl_2 ----> $CH_2CHCl + Cl$	1.35E14	22.9

The C-C bond is weaker than the C-H bond and stronger than the C-Cl bond, thus in considing reactions (1) to (5) breaking the C-C bond requires more energy than needed to break the C-Cl bonds. In the temperature range of 570 °C - 660 °C CH_3Cl and CH_2Cl_2, and C_1 compound are observed only as very minor products which are formed from C-C bond cleavage of parent $CH_2ClCHCl_2$ and further reaction with hydrogen as in (8) and (9) below.

	A(1/s)	E(Kcal/mol)
8. $CH_2Cl + H_2$ ----> $CH_3Cl + H$	2.86E12	14.0
9. $CHCl_2 + H_2$ ----> $CH_2Cl_2 + H$	4.12E12	3.5

The formation of CH_2ClCH_2Cl as one of the minor products at low temperature results from reaction of $CH_2ClCHCl$ radical with H_2. $CH_2ClCHCl$ results from two reactions one the metathetical reaction (abstraction reaction (11)) by H atoms with $CH_2ClCHCl_2$ and two a small but finite and very important amount of reaction (3). CH_3CHCl_2 is not produced at the low temperatures of 570 °C and 600 °C because reaction (4) is much slower than reaction (3)-stronger C--Cl bond required to break.

H is produced from reaction of Cl with H_2 as follows:

	A(1/s)	E(Kcal/mol)
10. $Cl + H_2$ ----> $H + HCl$	4.8E13	5.3

11. $H + CH_2ClCHCl_2 \text{ ----> } CH_2ClCHCl + HCl$ 2.0E13 4.8

12. $CH_2ClCHCl + H_2 \text{ ----> } CH_2ClCH_2Cl + H$ 5.0E12 18.0

$H_2 + CH_2ClCHCl_2 \text{ ----> } CH_2ClCH_2Cl + HCl$
(overall reaction of (11) and (12))

The above three reactions are relatively fast and one sees that H radical plays a catalytic role in formation of CH_2ClCH_2Cl which is a minor product in our experiments. CH_2ClCH_2Cl reacts; it unimolecularly dissociates (APPENDIX Table 2) as follows:

	A(1/s)	E(Kcal/mol)	
13. $CH_2ClCH_2Cl \text{ ---> } CH_2CHCl + HCl$	1.95E13	55.4	$(\Delta Hr+38)$
14. $CH_2ClCH_2Cl \text{ ---> } CH_2ClCH_2 + Cl$	6.17E15	79.7	(ΔHr)
15. $CH_2ClCH_2Cl \text{ ---> } CH_2Cl + CH_2Cl$	3.13E17	88.7	(ΔHr)

H radical plays a very important role in the loss of the major products CHClCHCl and CH_2CCl_2 as follows:

A(1/s) E(Kcal/mol)

$CHClCHCl + H \text{ <---> } [CH_2CLCHCl]^{\#}$

where the activated complex can react to:

16. $\text{---> } CH_2CHCl + Cl$ 2.05E13 5.1

17. $\text{---> } CH_2ClCHCl$ 4.18E09 -2.57

or back to reactants.

$CH_2CCl_2 + H \text{ <---> } [CH_2CHCl_2]^{\#}$

18. $\text{---> } CH_2CHCl + Cl$ 3.01E13 6.0

19. $\text{---> } CH_2CHCl_2$ 6.50E08 -0.97

$CH_2CHCl + H$ <---> $[CH_2ClCH_2]^\#$

20.	---> CH_2ClCH_2	1.39E10	-2.4
21.	---> CH_2CH_2 +Cl	8.51E12	3.5

Quantum RRK

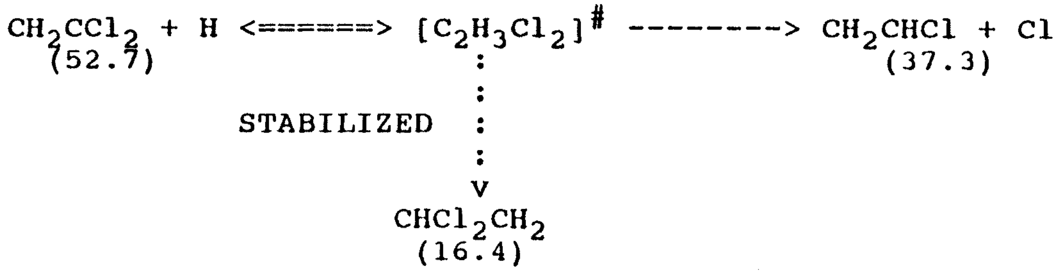
The reactions of atomic hydrogen with CHClCHCl, CH_2CCl_2, and CH_2CHCl were all modeled by using the CHEMACT QRRK calculation. The details of the bimolecular QRRK method are summarized in the theory section.<33,39>

Energized Complex/QRRK theory as described by Westmoreland and Dean<39> is used for the modeling of radical addition to unsaturates and combination reactions. This computer code has been modified by Ritter and Bozzelli<40> to use gamma function in place of factorials. The computer code (CHEMACT) was used to calculate the energy dependent rate constants for all dissociation and stabilzation channels of the activated complexes formed by the above reactions. The code is important in accurate determination rate constants for the correct selection of the important reaction path from the activated complex as a function of temperature and pressure.

This QRRK analysis of the chemically activated system uses generic estimates or literature values for high pressure rate constants and species thermodynamic properties for the enthalpies of reaction. The results from the calculations are apparent rate parameters for our modeling calculations and are summarized in the APPENDIX B Table 6 to

Table 8. The calculations were performed for each of the above listed from reactions (16) to (21).

For the CH_2CCl_2 + H system, the energy diagram is shown in Figure 19, where the following major reactions are important:



22. $$\underset{(52.7)}{CH_2CCl_2} + H \Longleftrightarrow [C_2H_3Cl_2]^{\#} \longrightarrow \underset{(37.3)}{CH_2CHCl + Cl}$$

STABILIZED

23. $$\underset{(16.4)}{CHCl_2CH_2}$$

Atomic H adds to CH_2CCl_2 to form energized $CHCl_2CH_2$ radicals as shown above. The energy diagram of the reaction (22) and (23) is illustrated in Figure 19 and the calculation results are shown in Figure 21.

Atomic H is formed by

$Cl + H_2 \longrightarrow HCl + H$

$CH_2ClCHCl + H_2 \longrightarrow CH_2ClCH_2Cl + H$

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 and prior to stabilization it may unimolecularly isomerize, undergo a hydrogen shift, become a stabilized radical or undergo beta scission to CH_2CHCl+Cl. The CHEMACT calculation results for temperatures of 773 to 933 ^{o}K and the pressure range of 0.001 - 10 atm are shown in Figure 21, and indicate that the rate constant for the CH_2CHCl + Cl channel dominates. The $CHCl_2CH_2$ stabilized channel becomes more important at the higher pressure 100 atm.

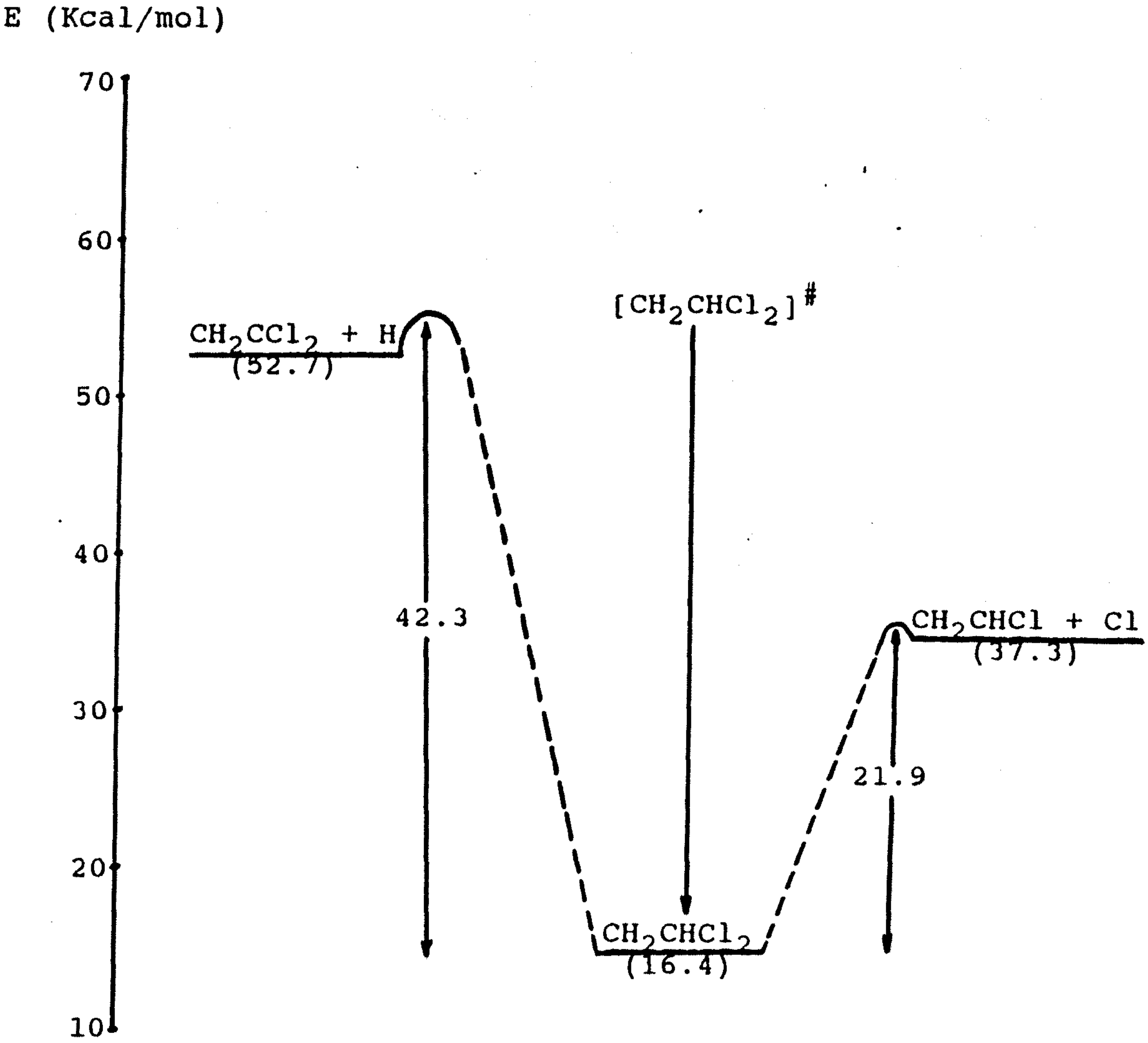


Figure-18 Energy Diagram for CH_2CCl_2 + H

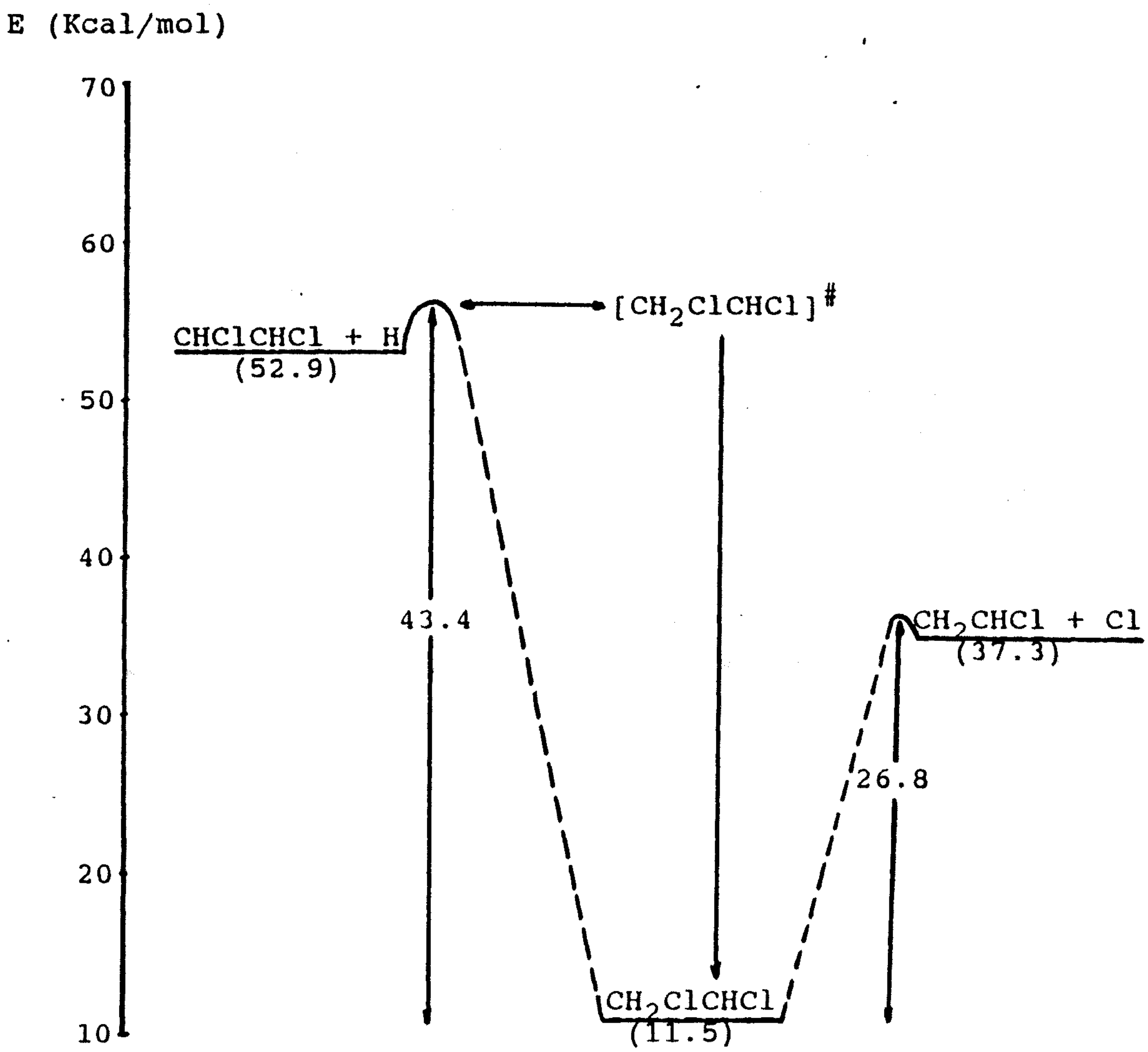


Figure-19 Energy Diagram for CHClCHCl + H

Figure-20 Results of Activated Complex Theory Calc. for Reaction CHClCHCl + H

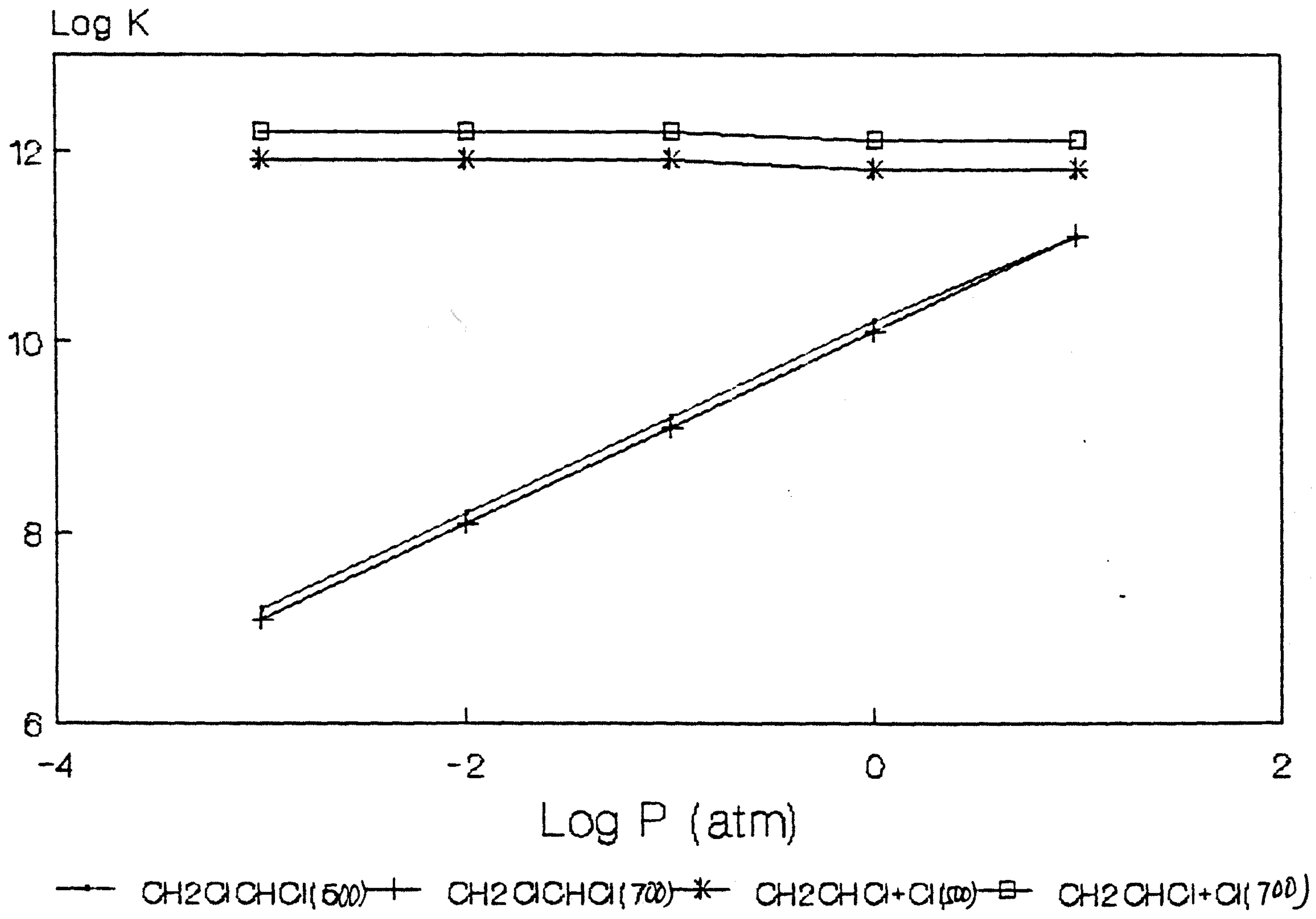
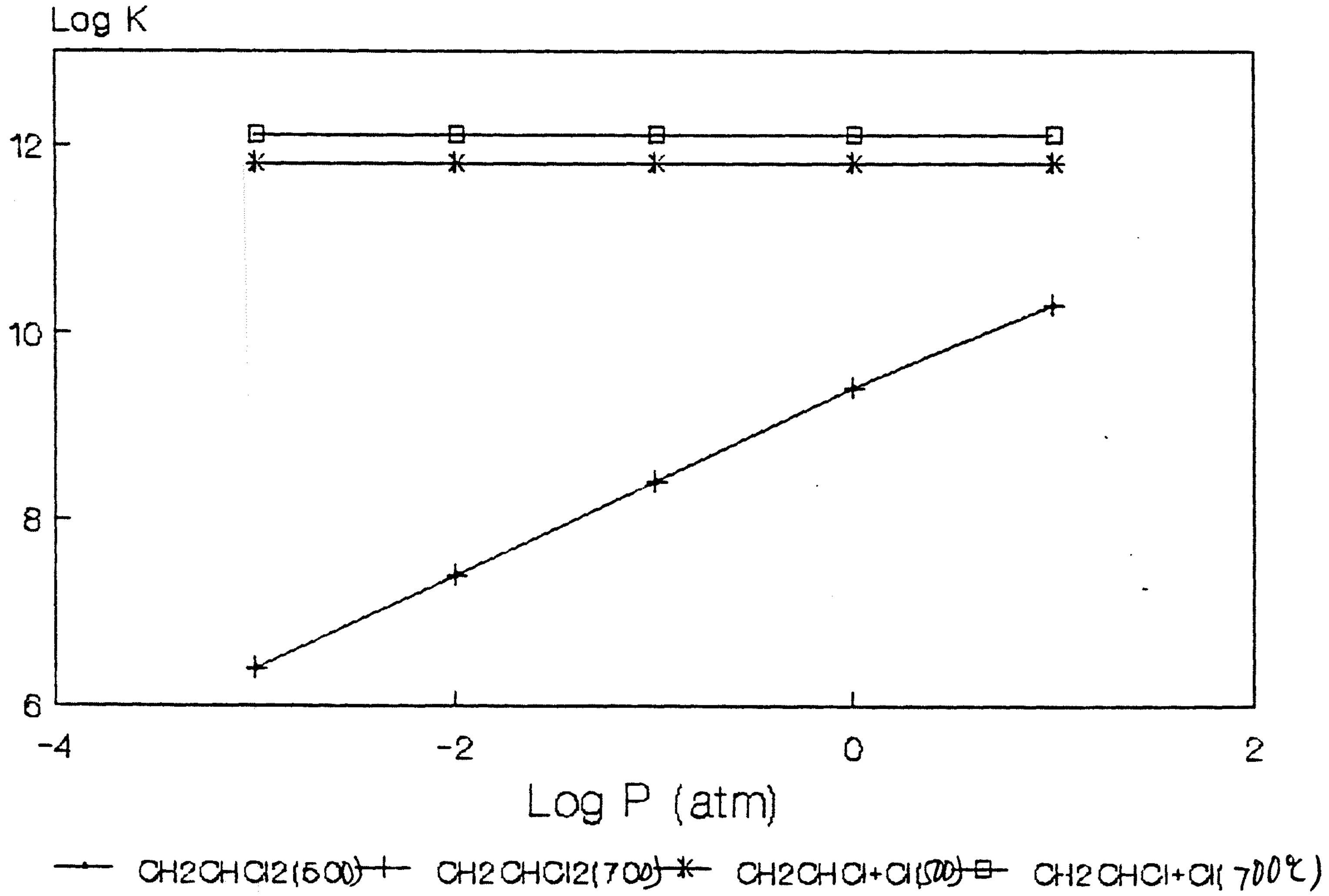


Figure-21 Results of Activated Complex Theory Calc. for Reaction CH2CCl2 + H



CH_2CHCl is therefore produced from further reaction of primary products CHClCHCl, CH_2CCl_2 with H radical. CH_2CH_2 and CH_3CH_3 are then produced from further reaction of CH_2CHCl with hydrogen atoms in this reaction system.

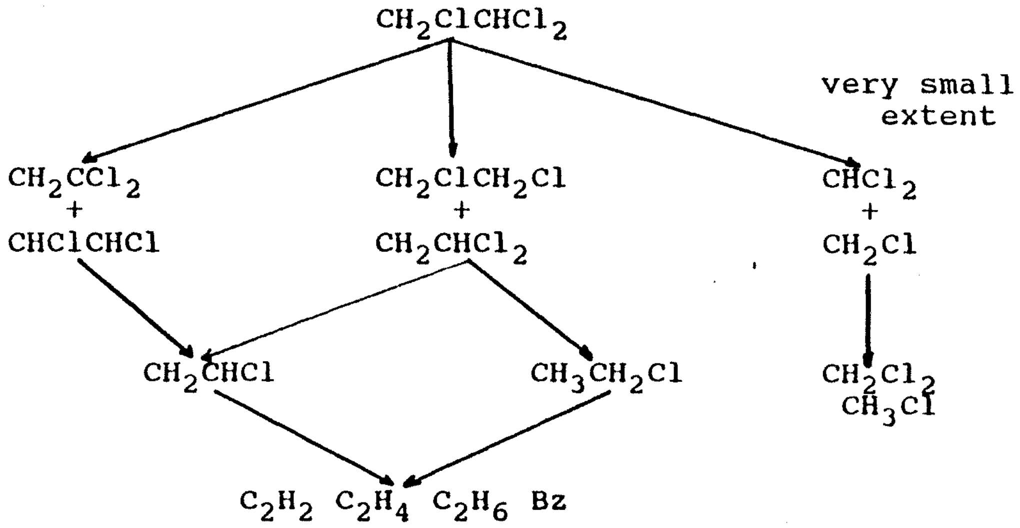
CH_2CCl_2 + H --> [C.H_2CHCl_2] --> CH_2CHCl + Cl (ΔHr = -15.5)

CH_2CHCl + H --> [C.H_2CH_2Cl] --> CH_2CH_2 + Cl (ΔHr = -19.1)

The formation of CH_3CH_2Cl as one of the major products in the temperature range 570 °C - 660 °C results from reaction of $CH_2ClC.H_2$ radical with H_2. $CH_2ClC.H_2$ results from abstraction reaction (24) below in addition to reaction (14). Reactions (24) and (25) show that H atom plays a catalytic role in the formation of CH_3CH_2Cl which is one of the major products in our experiment. CH_3CH_2Cl undergoes dissociation reactions as shown below and in APPENDIX A Table 4.

		A(1/s)	E(Kcal/mol)	
24.	CH_2ClCH_2Cl + H ----> CH_2ClCH_2 + HCl	3.00E13	6.5	
25.	CH_2ClCH_2 + H_2 ----> CH_3CH_2Cl + H	4.00E12	15.7	
	CH_2ClCH_2Cl + H_2 ----> CH_3CH_2Cl + HCl (Overall reaction of (24) and (25))			
26.	CH_3CH_2Cl ----> CH_2CH_2 + HCl	3.03E13	57.4	(ΔHr+39)
27.	CH_3CH_2Cl ----> CH_3CH_2 + Cl	9.26E14	83.2	(ΔHr)
28.	CH_3CH_2Cl ----> CH_3 + CH_2Cl	1.08E17	90.3	(ΔHr)

An overall reaction scheme based on analysis of the major concentration products and thermochemical kinetic estimations can be illustrated as follows:



Plus HCl or H atom is also produced in 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.

A detailed reaction model comprised of 73 elementary reactions is developed to describe the system of reactions studied. This mechanism appears in Table 6 and fits the experimental results well.

The kinetic schemes in Table 6 were formulated considering all reaction products detected by GC. Elementary reaction rate parameters for abstraction reactions are based upon literature values, comparison with similar reactions (generic), thermodynamic estimations, along with Transition State Theory and estimation methods of Benson<42>. QRRK calculations<39,40>, as described in the previous section, were used to estimate apparent rate parameters for addition, combination, and dissociation reactions at the (1 atm) experimental pressure, with H_2 as diluent.

Experimental pyrolysis data are compared with model predictions in Figure 24 and Figure 27 for reagent decomposition and product distribution between 570 and 660 ^{o}C. Predictions for decay of parent 1,1,2-trichloroethane and product distributions for CHClCHCl, CH_2CCl_2, CH_3CH_2Cl, CH_2CHCl, and CH_2CH_2 match experiment well. Figure 25 and Figure 26 shows the calculated concentration of the parent reactant and above listed products versus reaction time at temperatures of 600 ^{o}C and 630 ^{o}C and show quite good agreement with the experimentally observed data in Figure 13 and Figure 14 for decay of reactants and formation of products.

Figures 23 and 12 show the small difference seen between calculated and experimental values for $CH_2ClCHCl_2$, CH_2CHCl, CH_2CH_2, and CH_3CH_2Cl (reagent and products). At 1.1 sec residence time the model over predicts vinyl chloride between 580 and 660 ^{o}C by as much as 30 % at 630 ^{o}C. It also over predicts ethylene at the higher temperatures 600 and 630 ^{o}C. The model over predicts 1,1,2-trichloroethane loss at long reaction times. The possible reasons for this difference can be explained as follows; First, the kinetic scheme does not include all possible products, specifically polyaromatic hydrocarbons and carbon (solid), which are observed in small amounts. Second, the detailed mechanism only considers gaseous phase reactions; heterogeneous reaction effects are not included. Third, the

Figure-23 Product Distribution vs Temp
CH2ClCHCl2/H2 at Time=1.1 sec.

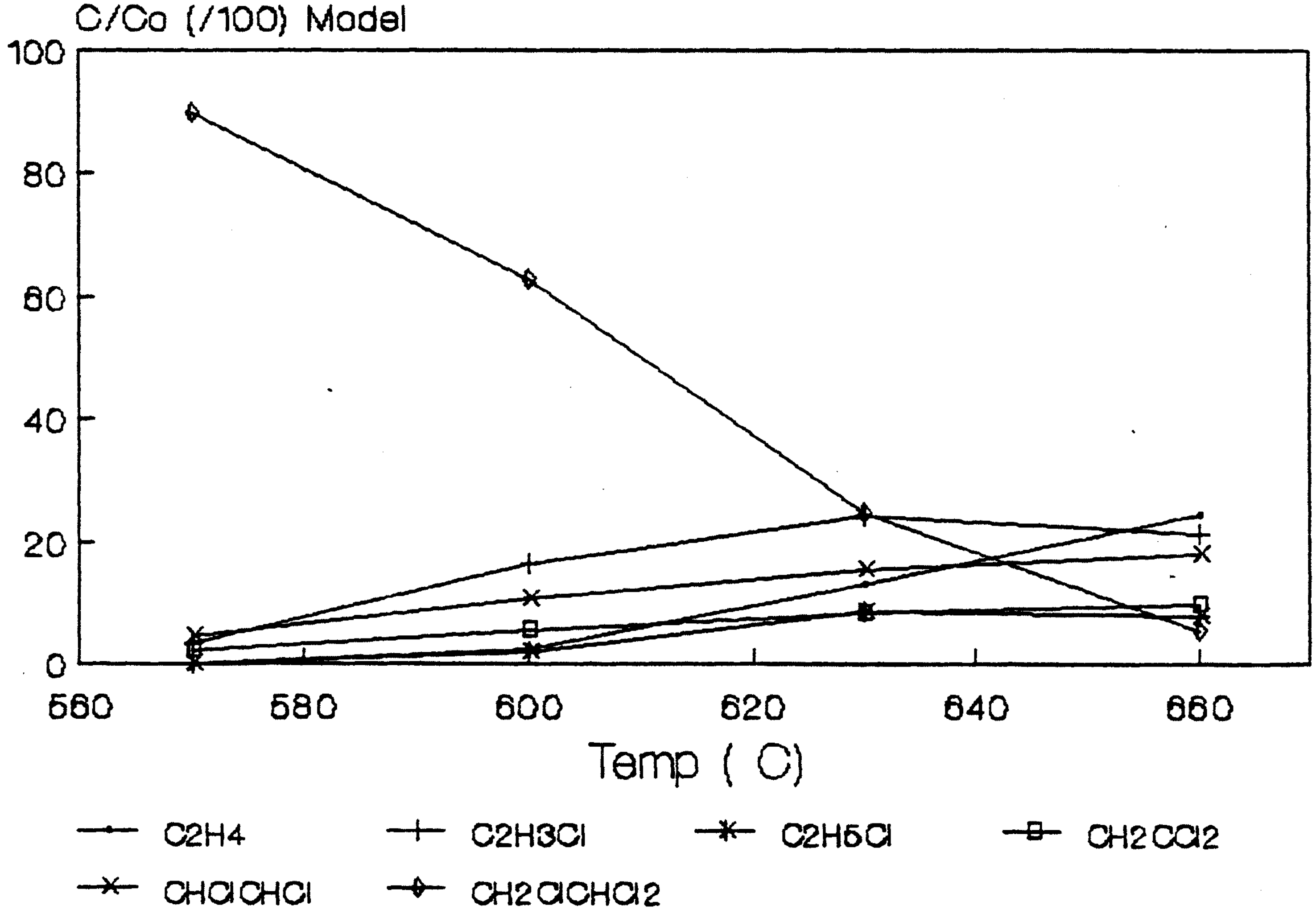


Figure-24 Product Distribution vs Temp
CH2ClCHCl2/H2 at Time=1.1 sec.

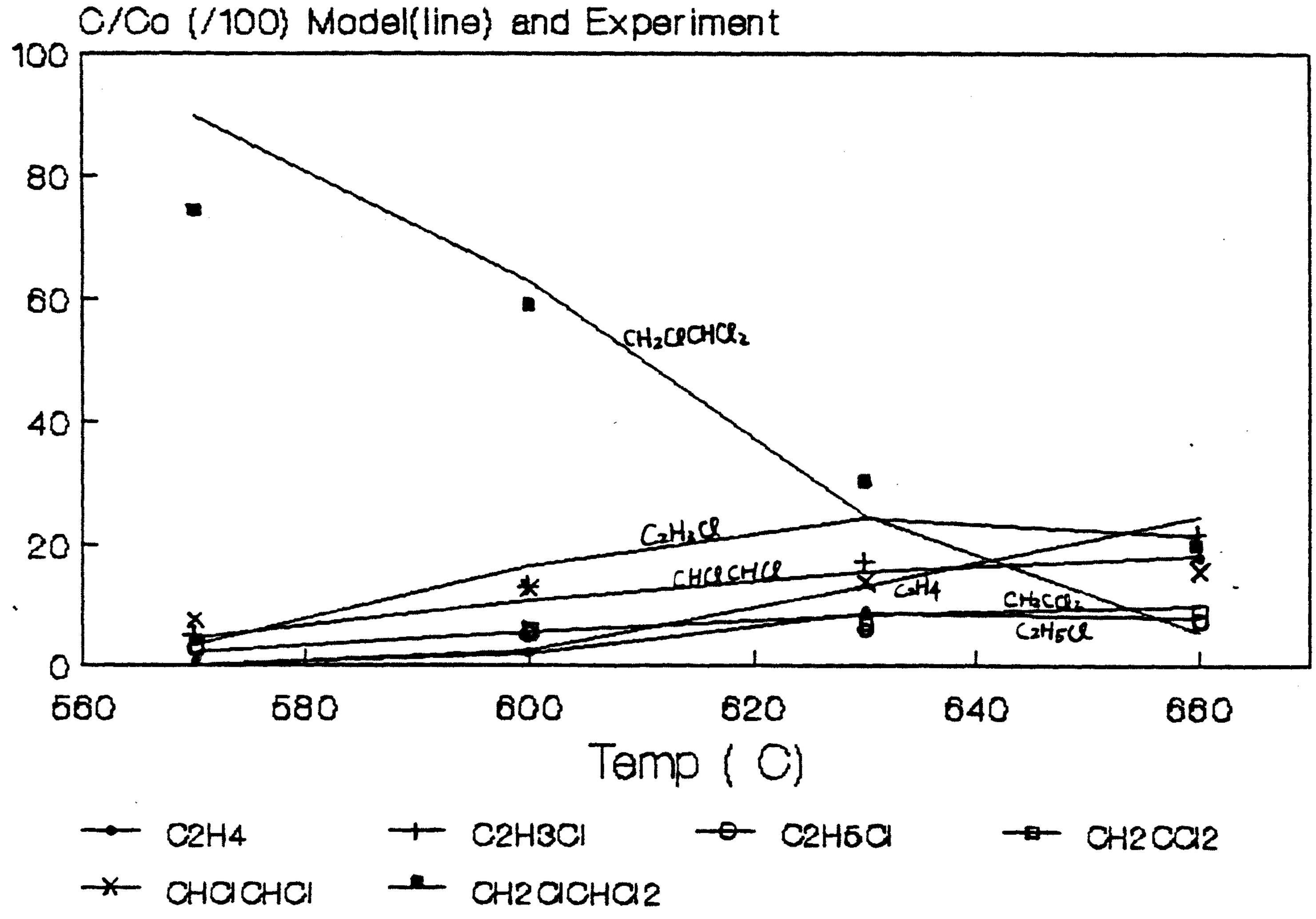


Figure-13 Product Distribution vs Time
$CH_2ClCHCl_2/H_2$ at Time=600 C

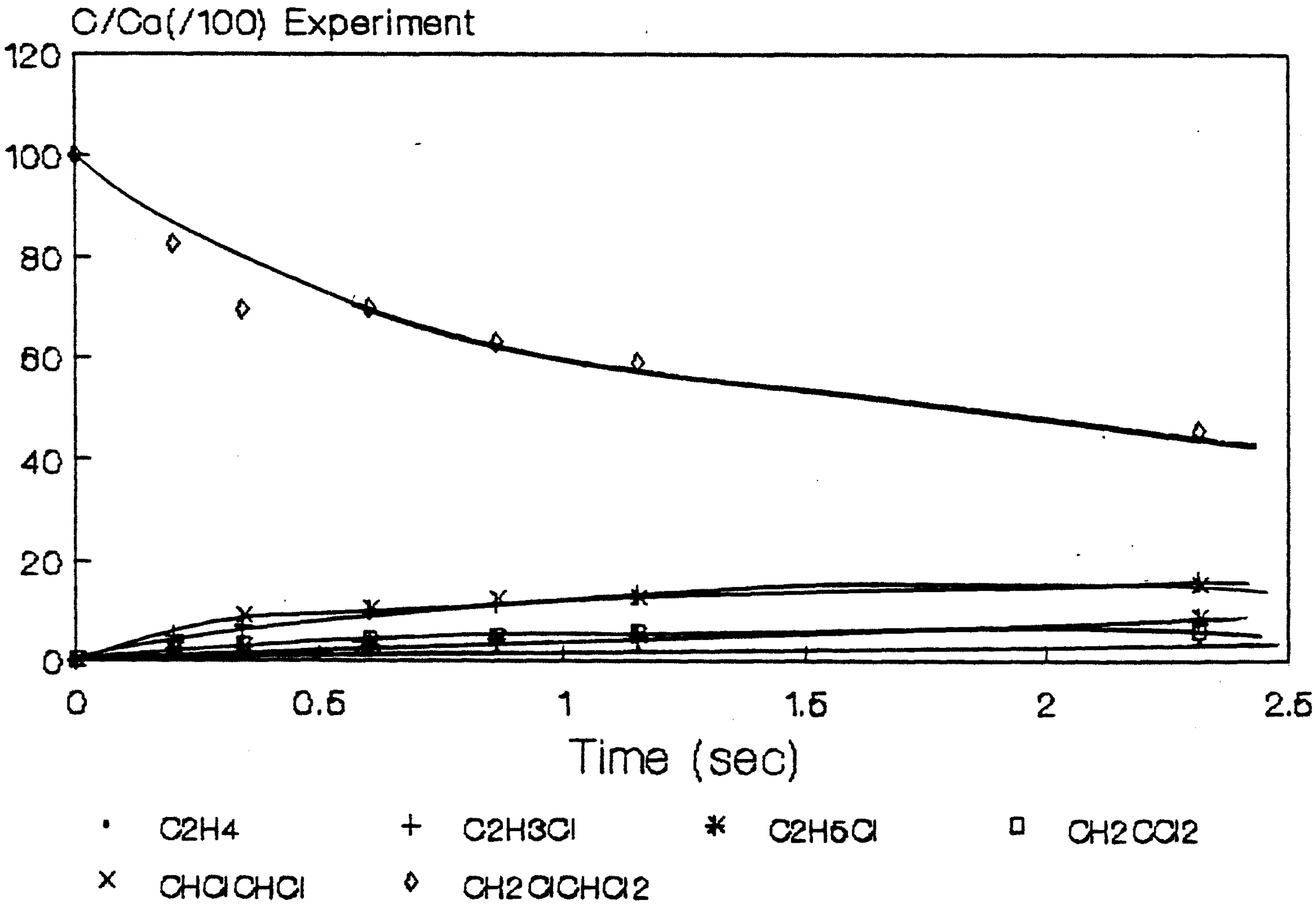


Figure-25 Product Distribution vs Time
CH2ClCHCl2/H2 at Temp=600 C

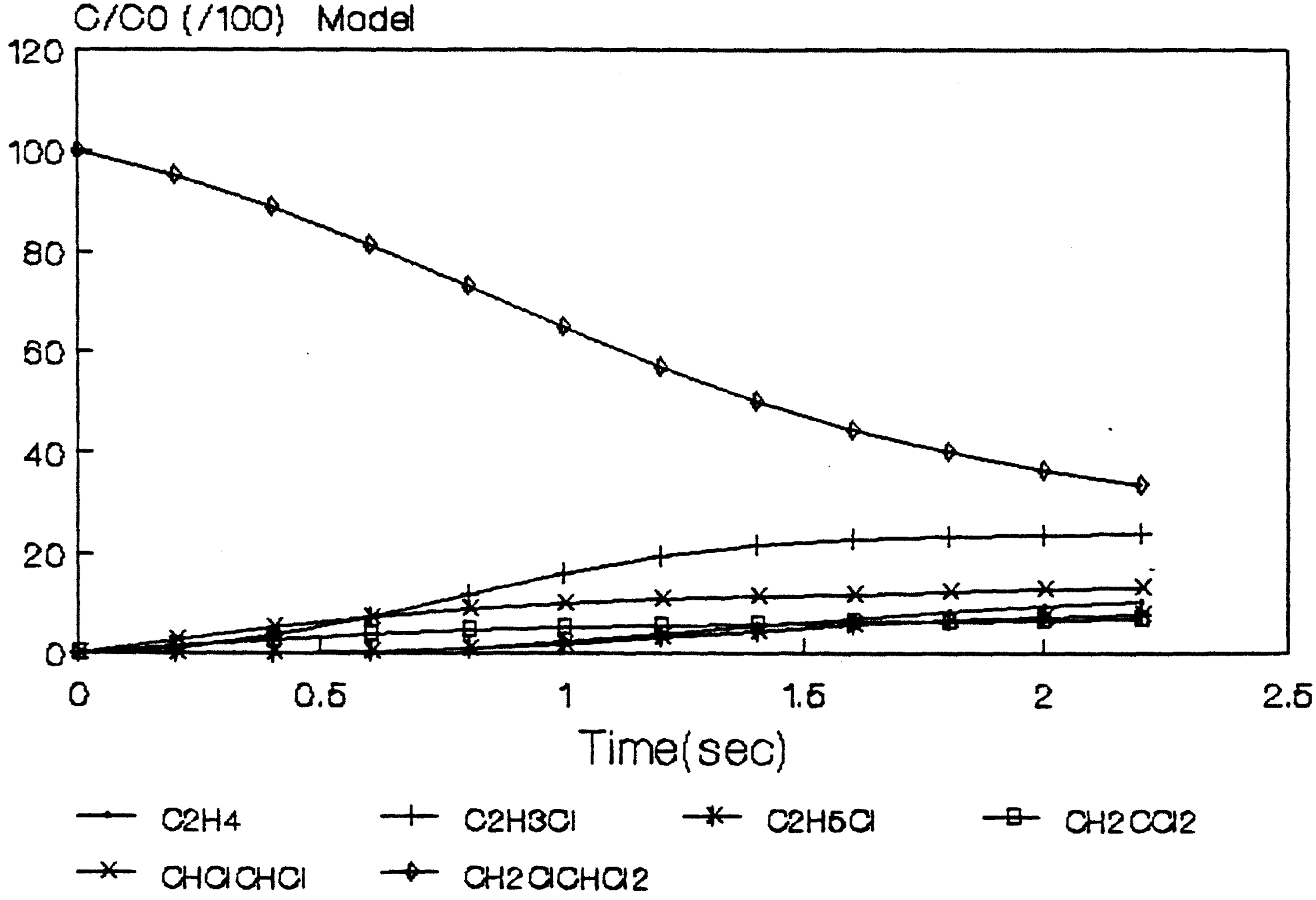


Figure-14 Product Distribution vs Time
CH2ClCHCl2/H2 at Temp=630 C

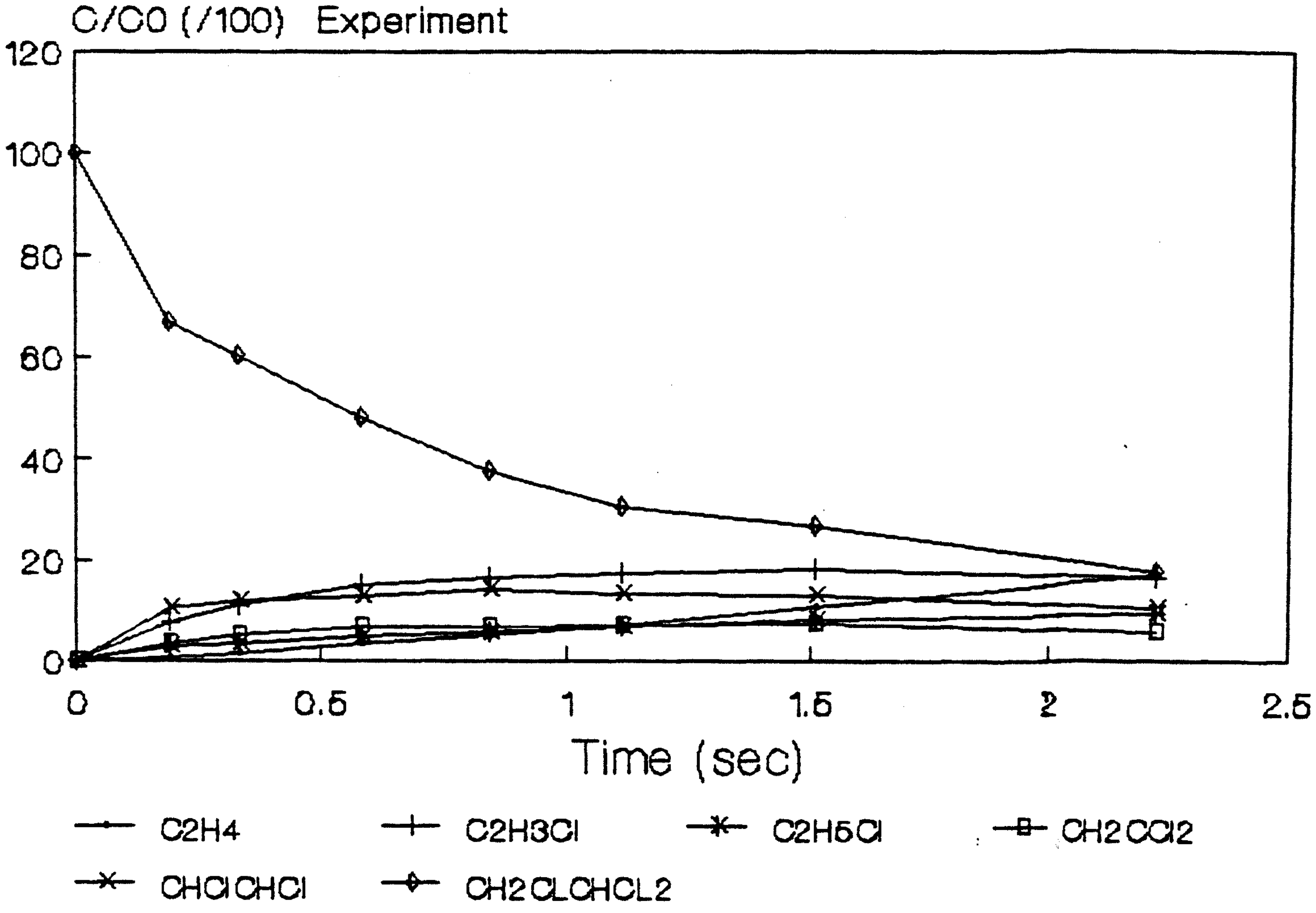


Figure-26 Product Distribution vs Time CH2ClCHCl2/H2 at Temp=630 C

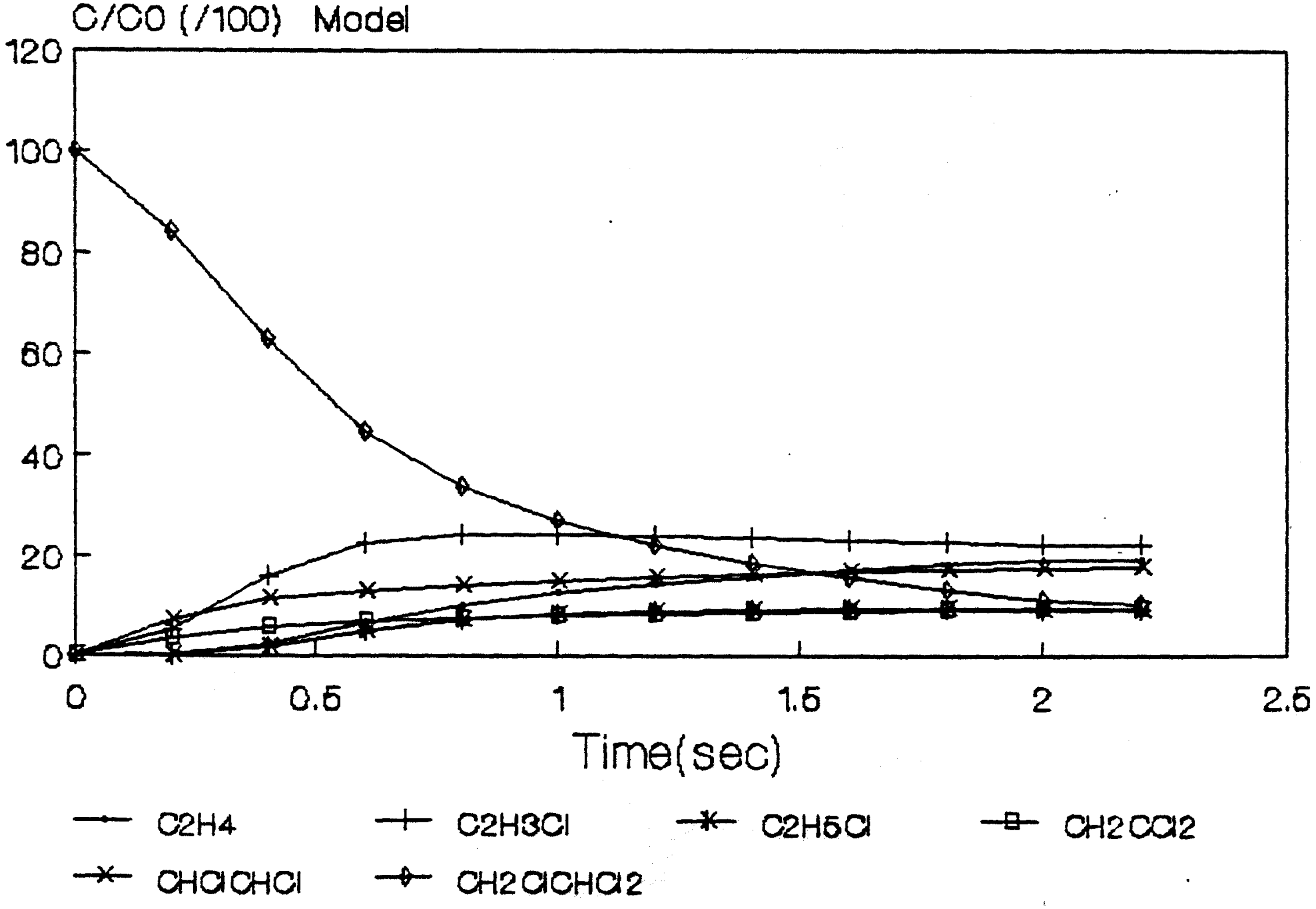
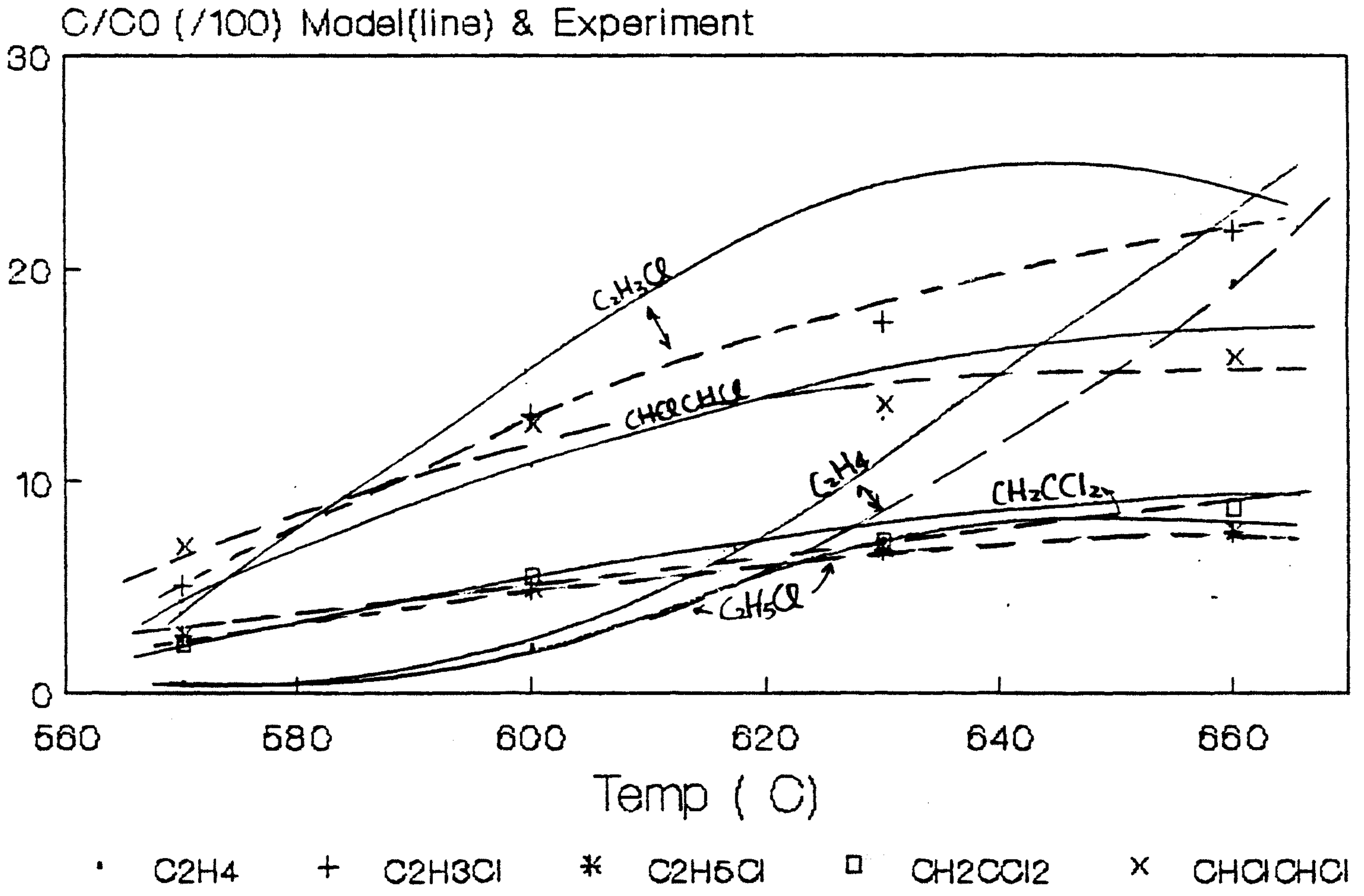


Figure-27 Product Distribution vs Temp
CH2CLCHCL2/H2 at Time=1.1 sec.



kinetic parameters estimated for several elementary reactions are estimated based on best available thermodynamic and kinetic collision frequency data in the literature or for similar reactions.

A computer code "SENS" was utilized to determine the reactions important to the mechanism in this work and they are shown in Table 7 (Reactions important to nine principal species are listed for 600 ^{o}C and 1.0 sec residence time). Complete results from the sensitivity analysis on the 73 elementary reactions relative to the nine major species (0 to 2.0 sec residence time) with temperatures 600 ^{o}C and 660 ^{o}C are shown in APPENDIX D. These sensitivity results are very helpful for selecting the important reactions to optimize for better fits of experimental results to mathematical models.

Table 7 shows that reactions (1), (3), and (28) are very important and (2), (4), (5), (19), and (24) are important for $CH_2ClCHCl_2$. We find that Ea = $\triangle$Hr + 40.8 for reactions (1) and (2). Reactions (17) and (18), the succeeding steps from reactions (3) and (4), are not important reactions for $CH_2ClCHCl_2$. The lack of sensitivity to Reactions (17) and (18) is because they are very fast in this study. They go immediately, via beta scission, because they are unimolecular and have low Ea's.

		A(1/s)	E(kcal/mol)
17.	$CH_2ClCHCl = CH_2CHCl + Cl$	1.35E+14	27.4
18.	$CH_2CHCl_2 = CH_2CHCl + Cl$	1.35E+14	22.9

Table 7

Sensitivity Analysis of Mechanism Reactions*

Temperature : 600 ^{o}C
Residence Time : 1.0 sec.

Species	Most Important Reactions by Number (see Table 6)									
CH_2CH_2	3 +	28 +	64 +	5 +	2 -	62 +	21 -	4 +	20 -	24 +
CH_3CH_3	3 +	28 +	64 +	21 +	5 +	2 -	32 +	4 +	24 +	62 +
CH_2CHCl	28 +	3 +	20 -	5 +	64 -	2 -	56 +	4 +	49 +	1 +
CH_3CH_2Cl	3 +	20 +	28 +	5 +	2 -	4 +	24 +	64 -	1 +	56 +
CH_2CCl_2	2 +	3 -	49 -	1 -	28 -	5 -				
CHClCHCl	1 +	3 -	56 -	5 -	2 -	4 -				
CH_2ClCH_2Cl	17 -	23 +	28 +	3 +	5 +	6 -	1 -	30 -	4 +	20 -
$CHCl_2CH_2Cl$	28 -	3 -	1 -	2 -	5 -	4 -				
HCl	28 +	3 +	1 +	5 +	4 +	20 -	24 +	56 +	64 +	2 +

* Detailed results of sensitivity analysis are shown in APPENDIX D. Reaction numbers are identical to those in Table 6. Decreasing order of importance sensitivity value cut off 0.01. (+) = increase, (-) = decrease species concentration.

Reactions (1), (3), and (56) are important reactions for the major product CHClCHCl and reactions (2), (3), and (49) are important for CH_2CCl_2. Reactions (49) and (56) were both modeled by using the CHEMACT QRRK calculations. The high sensitivity to these reactions combined with the good model fit to the experimental data indicate the theory provides a reasonable method to determine these rate constants.

		A(1/s)	E(kcal/mol)
49.	CH_2CCl_2 + H = CH_2CHCl + Cl	3.00E+13	6.0 (this work)
56.	CHClCHCl + H = CH_2CHCl + Cl	2.00E+13	5.0 (this work)

Optimization of the mechanism to fit the experimental data has allowed determination of several elementary reaction rate constants. These include:

		A(1/s)	E(kcal/mol)
1.	$CH_2ClCHCl_2$ = CHClCHCl + HCl	9.56E+12	54.9 (this work)
2.	$CH_2ClCHCl_2$ = CH_2CCl_2 + HCl	4.79E+12	54.9 (this work)
3.	$CH_2ClCHCl_2$ = $CH_2ClCHCl$ + Cl	2.60E+15	77.8 (this work)
4.	$CH_2ClCHCl_2$ = CH_2CHCl_2 + Cl	1.73E+15	81.7 (this work)

where the Arrhenius parameters given are the high pressure limits used as input to the DISSOC program. The rate constants were determined by DISSOC for our temperatures and pressure regime. k/k_{oo} for our T & P ranges are 0.93 for reactions (3) and (4) and 0.80 for reactions (1) and (2).

Table 6

Detailed Mechanism for $CH_2ClCHCl_2/H_2$ Reaction System

	REACTION	A	Ea(Kcal/mol)	source
(dissociation)				
1.	$CH_2ClCHCl_2 = CHClCHCl + HCl$	9.56E+12$^{\#}$ 9.50E+12*	54.9 55.3	a,** DISSOC
2.	$CH_2ClCHCl_2 = CH_2CCl_2 + HCl$	4.79E+12$^{\#}$ 4.72E+12*	54.9 55.3	b,** DISSOC
3.	$CH_2ClCHCl_2 = CH_2ClCHCl + Cl$	2.60E+15$^{\#}$ 2.57E+15*	77.8 77.7	c,** DISSOC
4.	$CH_2ClCHCl_2 = CH_2CHCl_2 + Cl$	1.73E+15$^{\#}$ 1.58E+15*	81.7 81.4	c,** DISSOC
5.	$CH_2ClCHCl_2 = CH_2Cl + CHCl_2$	5.28E+17$^{\#}$ 4.15E+17*	89.6 89.1	d,k,** DISSOC
6.	$CH_2ClCH_2Cl = CH_2CHCl + HCl$	1.99E+13$^{\#}$ 1.97E+13*	55.3 54.7	e,** DISSOC
7.	$CH_2ClCH_2Cl = CH_2ClCH_2 + Cl$	6.65E+15$^{\#}$ 6.17E+15*	80.7 79.7	c DISSOC
8.	$CH_2ClCH_2Cl = CH_2Cl + CH_2Cl$	4.26E+17$^{\#}$ 3.13E+17*	88.6 88.7	f,k DISSOC
9.	$CH_3CHCl_2 = CH_2CHCl + HCl$	1.96E+13$^{\#}$ 1.94E+13*	55.4 54.7	e,** DISSOC
10.	$CH_3CHCl_2 = CH_3CHCl + Cl$	3.92E+15$^{\#}$ 3.75E+15*	76.2 75.2	c DISSOC
11.	$CH_3CHCl_2 = CH_3 + CHCl_2$	2.07E+17$^{\#}$ 1.32E+17*	91.3 90.9	g,k DISSOC
12.	$CH_3CH_2Cl = CH_2CH_2 + HCl$	3.24E+13$^{\#}$ 3.03E+13*	56.6 57.4	h DISSOC
13.	$CH_3CH_2Cl = CH_3CH_2 + Cl$	9.80E+14$^{\#}$ 9.26E+14*	84.1 83.2	i,k DISSOC
14.	$CH_3CH_2Cl = CH_3 + CH_2Cl$	1.34E+17$^{\#}$ 1.08E+17*	90.3 90.3	j,k DISSOC

15.	$CH_3CH_3 = CH_3CH_2 + H$	1.25E+16$^{\#}$ 6.18E+15*	100.1 98.8	1 DISSOC
16.	$CH_3CH_3 = CH_3 + CH_3$	7.94E+16$^{\#}$ 2.35E+18*	90.3 98.1	1 DISSOC
(Beta Scission)				
17.	$CH_2ClCHCl = CH_2CHCl + Cl$	1.35E+14	27.4	3,o
18.	$CH_2CHCl_2 = CH_2CHCl + Cl$	1.35E+14	22.9	3,o
19.	$CH_2ClCH_2 = CH_2CH_2 + Cl$	1.69E+14	23.9	1
20.	$CH_3CHCl = CH_2CHCl + H$	2.76E+13	47.3	m
21.	$CH_3CH_2 = CH_2CH_2 + H$	5.01E+13	40.9	1
22.	$CH_2CH = CHCH + H$	3.16E+12	38.3	1
(Abstraction)				
23.	$CH_2ClCHCl + H_2 = CH_2ClCH_2Cl+H$	5.00E+12	18.0	n,p
24.	$CH_3CHCl + H_2 = CH_3CH_2Cl + H$	5.00E+12	17.2	n,p
25.	$CH_2ClCH_2 + H_2 = CH_3CH_2Cl + H$	4.00E+12	15.7	5,p
26.	$CHCl_2CH_2 + H_2 = CH_3CHCl_2 + H$	5.26E+12	15.0	6
27.	$C_2H_2Cl_3 + H_2 = CH_2ClCHCl_2 + H$	5.00E+12	18.0	n,p
(Abstraction)				
28.	$CH_2ClCHCl_2 +H =CH_2ClCHCl +HCl$	2.00E+13	4.8	q,o
29.	$CH_3CHCl_2 + H = CH_3CHCl + HCl$	2.00E+13	6.2	q,o
30.	$CH_2ClCH_2Cl +H =CH_2ClCH_2 +HCl$	3.00E+13	6.5	r,o
31.	$CH_3CH_2Cl + H = CH_3CH_2 + HCl$	1.50E+13	8.0	s,o
32.	$CH_3CH_3 + H = CH_3CH_2 + H_2$	6.61E+13	9.7	o
33.	$CH_2CH_2 + H = CH_2CH + H_2$	1.91E+13	10.3	o
34.	$CHCH + H = CHC + H_2$	2.00E+14	19.0	o
35.	$CH_2ClCHCl_2+Cl=C_2H_2Cl_3 + HCl$	1.00E+13	0.5	4
(1 carbon reactions)				
36.	$CHCl_2 + H_2 = CH_2Cl_2 + H$	4.12E+12	3.5	1,o

37.	$CH_2Cl_2 = CH_2Cl + Cl$	1.05E+16# 1.66E+14*	80.2 74.6	y,k DISSOC
38.	$CH_2Cl_2 = CHCl + HCl$	1.20E+14	105.0	x
39.	$CH_2Cl_2 + H = CH_2Cl + HCl$	1.10E+13	6.1	o
40.	$CH_2Cl + H_2 = CH_3Cl + H$	2.86E+12	14.0	1,o
41.	$CH_3Cl = CH_3 + Cl$	1.28E+15# 1.27E+14*	83.0 79.7	2,k DISSOC
42.	$CH_3Cl = CH_2 + HCl$	4.75E+13	124.9	z
43.	$CH_3Cl + H = CH_3 + HCl$	3.72E+13	9.3	o
44.	$CH_4 + H = CH_3 + H_2$	5.00E+12	11.0	o
(CH_2CCl_2 reactions)				
45.	$CH_2CCl_2 = CH_2CCl + Cl$	9.34E+15	88.6	10,k
46.	$CH_2CCl_2 = CHCCl + HCl$	3.55E+13	69.1	11
47.	$CH_2CCl_2 + H = CH_2CHCl_2$	6.50E+08*	-0.97	QRRK1,**
48.	CH2CCl2 + H = CH3CCl2	4.30E+09*	-5.03	QRRK1,**
49.	$CH_2CCl_2 + H = CH_2CHCl + Cl$	3.01E+13*	6.0	QRRK1,**
50.	$CH_2CCl_2 + H = CH_2CCl + HCl$	6.00E+12	9.5	u,p
51.	$CH_2CCl_2 + Cl = CCl_2CH + HCl$	1.00E+13	7.1	4
52.	$CCl_2CH + H_2 = CH_2CCl_2 + H$	4.11E+11	4.7	w
(CHClCHCl reactions)				
53.	CHClCHCl = CHClCH + Cl	9.34E+15	90.0	8,k
54.	CHClCHCl = CHCCl + HCl	3.50E+13	69.1	9
55.	$CHClCHCl + H = CH_2ClCHCl$	4.18E+09*	-2.57	QRRK2,**
56.	$CHClCHCl + H = CH_2CHCl + Cl$	2.05E+13*	5.06	QRRK2,**
57.	CHClCHCl + H = CHClCH + HCl	1.00E+13	9.5	t,p
58.	CHClCHCl + Cl = CHClCCl + HCl	1.00E+13	7.5	4
59.	$CHClCCl + H_2 = CHClCHCl + H$	6.16E+11	6.0	v
(CH_2CHCl reactions)				

60.	$CH_2CHCl = CH_2CH + Cl$	4.08E+15	87.6	12,k
61.	$CH_2CHCl = CHCH + HCl$	3.55E+13	68.7	13
62.	$CH_2CHCl + H = CH_2CH + HCl$	1.00E+13	6.5	p
63.	$CH_2CHCl + H = CH_2CH_2Cl$	1.39E+10*	-2.4	QRRK 3
64.	$CH_2CHCl + H = CH_2CH_2 + Cl$	8.51E+12*	3.5	QRRK 3
65.	$CH_2CHCl + Cl = CHClCH + HCl$	1.00E+13	3.0	4
66.	$CH_2CHCl + Cl = CH_2CCl + HCl$	1.00E+13	1.6	4
67.	$CH_2CCl + H_2 = CH_2CHCl + H$	6.16E+11	6.0	v
68.	$CHClCH + H_2 = CHClCH_2 + H$	4.10E+11	4.7	w
69.	$H + H + M = H_2 + M$	1.00E+17	0.0	7
70.	$Cl_2 = Cl + Cl$	7.69E+08	55.6	7
71.	$HCl = H + Cl$	6.09E+08	97.3	7
72.	$Cl + H_2 = HCl + H$	4.80E+13	5.3	o,7
73.	$H + Cl_2 = HCl + Cl$	4.57E+12	1.4	o,7

High pressure limit value

* Pressure dependent : rate expression given for 760 torr

Temperature range : 773 - 933 °K

** Reactions determined in this work by optimization.

DISSOC : apparent rate constant by DISSOCIATION computer code analysis (APPENDIX).

QRRK : apparent rate constant by QRRK computer code analysis (APPENDIX).

SOURCES

a. $A = 10^{13.55} * 10^{(-4/4.6)} * 4 = 1.92E+13$
Ea = 55.9 ($\triangle$Hr + 40.8), This study A= 1/2 A

b. $A = 10^{13.55} * 10^{(-4/4.6)} * 1 = 4.79E+12$
Ea = 55.9 ($\triangle$Hr + 40.8)

c. A factor based upon entropy change for reverse.
A_{-1} taken as that for CH_3CCl_2 + Cl = CH_3CCl_3 (A = 1.0 E+13)
Ea = $\triangle$Hr

d. A factor based upon entropy change for reverse.
A_{-1} taken as that for CCC. + C_2H_5 log A = 12.9
CC.C + C_2H_5 log A = 12.9
This study $A_r = 1/2 * 10^{12.9}$.
Ea = $\triangle$Hr

e. Weissman and Benson, I. J. of Chem. Kinetics, vol. 16, 1984,
for CH_2CLCH_2Cl = C_2H_3Cl + HCl log A = 13.6. This study 1/2 A
Ea = $\triangle$Hr + 38

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

g. A factor based upon $\triangle$S for reverse
A_{-1} taken as that for CH_3 + CH_3 log A = 13.4,
CH_3 + C_2H_5 log A = 13.3,
C_2H_5 + C_2H_5 log A = 12.6,
This study $A_r = 2 * 10^{13}$.
Ea = $\triangle$Hr

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

i. A factor based upon $\triangle$S for reverse
A_{-1} taken as that for C_2H_5 + CH_3 log A = 13.4
Ea = $\triangle$Hr

j. A factor based upon entropy change for reverse.
A_{-1} taken as that for CH_2 + CH_3 log A = 13.4
estimat $A_r = 2/3 * 10^{13.4}$.
Ea = $\triangle$Hr

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

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

m. 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 = $\triangle$Hr + 2.0

n. (A factor taken that for 2-C_4H_9 + H_2)

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

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

q. A factor taken as 2/3 that for $CH_3Cl + H = CH_3 + HCl$
Ea from "Evans-Polanyi" plot as shown in APPENDIX C.
("Evans-Polanyi" plot for a set of abstraction reactions: This is a plot of Ea versus $\triangle$Hr from similar reactions using data of w. After completing the plot obtain the best slope and put into the form of the general equation for determination of Ea knowing only $\triangle$Hr.)

r. A factor taken as that for $CH_3Cl + H = CH_3 + HCl$
Ea from "Evans-Polanyi" plot as shown in APPENDIX C.

s. A factor taken as 1/2 that for $CH_3Cl + H = CH_3 + Cl$
Ea from "Evans-Polanyi" plot as shown in APPENDIX C.

t. A factor taken as 2.4 that for reaction (62)

u. A factor taken as 1.2 that for reaction (62)

v. A factor taken as 1.5 that for reverse reaction (33) with
A = 4.1 E+11 Ea from "Evans-Polanyi" plot

w. A factor taken as 1.5 that for reverse reaction (33) with
A = 4.1 E+11 Ea from "Evans-Polanyi" plot

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

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

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

1. 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 the "Evans-Polanyi" plot

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

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 = $\triangle$Hr + 1.5

4. $A = 1.0\ E{+}13$
   $E = \triangle Hr + 0.5$

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

6. $A = A_{85} + \triangle A \quad \triangle A = A_{CHCl2+H2} - A_{CH2Cl+H2}$

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

8. A based upon $\triangle S$ for reverse.
   A_{-1} taken as that for $2\text{-}C_4H_9 + CH_3$ ($A = 1.6\ E{+}13$)
   $Ea = \triangle Hr$

9. $A = 10^{13.55} * 2$
   $Ea = \triangle Hr + 45$ (ref: Skinner)

10. A based upon $\triangle S$ for reverse.
    A_{-1} taken as that for $2\text{-}C_4H_9 + CH_3$ ($A = 1.6\ E{+}13$)
    $Ea = \triangle Hr$

11. $A = 10^{13.55} * 2$
    $Ea = \triangle Hr + 45$ (ref: Skinner)

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

13. $A = 10^{13.55} * 1$, $Ea = \triangle Hr + 45$ (ref: Zabel, F. Int'l J. Chem Kin., 9, 651, 1977)

References of Thermochemical Properties

<1> JANAF Thermochemical Tables issued as supplement No.1, Vol. 14, (1985) J. Phys. Chem. Ref. Data

<2> Wagman, D.D. and Evans, W.H., The NBS Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data, Vol.11 (1982)

<3> Pedley, J.B., Naylor, R.D. and Kirby, S.P., "Thermochemical Data of Organic Compounds", 2nd ed., Chapman and Hall, NY (1986)

<4> Stull, D.R., Westrum, E.F. and Sinke, G.C., "The Chemical Thermodynamic of Organic Compounds", Robert Krieger Publishing Co. FL (1987)

<5> Benson, S.W., "Thermochemical Kinetics", 2nd ed. John Wiley & Son, NY (1976)

<6> Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, Vol.9, 523 (1980)

<7> Ritter, E. and Bozzelli, J.W., "Thermochemical Estimation of Molecule and Radical", computer code submitted to J. Phys. Chem. Ref. Data for publication.

VI. CONCLUSION

The decomposition of 1,1,2-trichloroethane in a hydrogen gas bath was carried out at 1 atmosphere total pressure in a tubular flow reactor. Temperature ranged from 440 - 850 ^{o}C; and residence times studied were in the range from 0.2 - 2.3 seconds.

Decoupling of the wall and bulk reaction constant was achieved with the plug flow model, which was found to be valid under the conditions studied. Application of the first order rate expression to this data yields a linear relationship for each temperature studied. This demonstrates that the overall global reaction obeys a pseudo-first order kinetics. A first-order rate plot for the decay of $CH_2ClCHCl_2$ shows excellent linearity for all temperatures. The global activation energies were determined to be 29.2 Kcal/mol for the reactions of 1,1,2-trichloroethane with hydrogen in the 1.05 cm i.d. reactor.

The major reaction products include 1,2-dichloroethylene (CHClCHCl), 1,1-dichloroethylene (CH_2CCl_2), vinyl chloride (CH_2CHCl), chloroethane (CH_3CH_2Cl), ethylene, and HCl, with methyl chloride (CH_3Cl), dichloromethane (CH_2Cl_2), and benzene observed as minor products. The observation of considerable amounts of dichloroethylene, both isomers, strongly indicates that the first step in the reaction series at 570-660 ^{o}C is the primarily unimolecular decomposition of 1,1,2-trichloroethane to a corresponding dichloroethylene and hydrogen chloride. Complete decay (96

%) of the reagent occurs at 850 °C and 1.1 sec residence time, the principal products are ethylene and HCl; most chlorinated by-products have been destroyed except vinyl chloride (1.0 %) and traces of chloroethane. The vinyl chloride appears from these studies to be relatively more stable than any other C_2 chlorocarbon.

The method of CHEMACT QRRK calculations is shown to provide useful preditions for effects of pressure and temperature on the rate constant. A detailed kinetic reaction mechanism, composed of 73 elementary reactions and 37 species, was developed and used to model the experimental results obtained from the reaction system. This mechanism appears in Table 6 and fits experimental results quite well as shown in Figures 23 - 27.

Reaction rate constants determined in this research are:

	A (1/s)	E (Kcal/mol)
$CH_2ClCHCl_2$ ---> CHClCHCl + HCl	9.5E12	55.3 (ΔHr+41)
$CH_2ClCHCl_2$ ---> CH_2CCl_2 + HCl	4.7E12	55.3 (ΔHr+41)
$CH_2ClCHCl_2$ ---> $CH_2ClCHCl$ + Cl	2.6E15	77.7 (ΔHr)
$CH_2ClCHCl_2$ ---> CH_2CHCl_2 + Cl	1.6E15	81.4 (ΔHr)
$CH_2ClCHCl_2$ ---> CH_2Cl + $CHCl_2$	4.2E17	89.1 (ΔHr)

For the reaction of 1,1,2-trichloroethane to $CH_2ClCHCl$ + Cl, the energy of activation determined in this study provides a bond energy for the CH_2CHCl--Cl bond of 77.7 kcal/mole.

VII. REFERENCES

<1> Sittig, M., Handbook of Toxic and Hazardous Chemicals and Carcinogens, Noyes Data Corporation (1985).

<2> Kebbekus, B.B., and Bozzelli, J.W., "Determination of Selected Toxic Organic Vapors in Air by Adsorbent Trapping and Capillary Gas Chromatography", J. Environ. Sci. Health, A17(5), 713, (1982).

<3> A. Trenholm, P. Gorman, B. Smith, D. Oberacker, "Emissions Test Results for a Hazardous Waste Incineration RIA," in Ninth Annual Research Symposium on Hazardous Waste, EPA 600/9-84-015, U.S. EPA, July 1984, P.160.

<4> J.C. Kramlich, M.P. Heap, W.R. Seelcer, G.S. Samuelsen, "Flame-Mode Destruction of Hazardous Waste Compounds," in 20th Symposium on Combustion, The Combustion Institute, pittsburgh, PA, 1985.

<5> W.P. Linak, J.A. McSorley, J.O.L. Wendt, J.E. Dunn, J. Air Pollut. Cont. Assoc. 37, 934 (1987).

<6> Chuang, S.C. and Bozzelli, J.W., Environ. Sci. Tech., 20, 568 (1986)

<7> Tavakoli, J. and Bozzelli J.W., Paper presented at the Central States Technolgy Meeting, The combustion Institute, Argonne, IL, May 11 - 12 (1987)

<8> Kaufman, F., Progress in Reaction Kinetics, Vol. VI, Pergamon Press, NY (1961)

<9> Karra, S.B., Senkan, S.M. "Chemical Structure of Sooting CH3Cl/CH4/O2/Ar and CH4/O2/Ar Flame", Central States

Technical Meeting of The Combustion Institute, 1987.

<10> Supelco Chromatography Supplies, Catalog 21, 1983, State college, Penn.

<11> Benson S.W., Weissman, M., "Pyrolysis of Catalyzed polymerization of Methane," Int'l J. Chem. Kin., Vol. 16, 307 (1984).

<12> Benson, S.W., Weissman, M., "Mechanism of the Pyrolysis of C2HCl5, Molecular and Radical Steps," Int'l J. Chem. Kin., Vol. 14, 1287 (1982).

<13> Barton, D.H.R. and Onyon, P.F., J. Am. Chem. Soc. 72, 988 (1950)

<14> Benson, S.W. and Spokes, G.N., Symp. Comb., 11, 95 (1966)

<15> Lee, K.C., Jahnes, H.J., MaCauley, D.C., "Thermal Oxidation Kinetics of Selected Organic Compounds," J. Air Pollution Control Ass., Vol. 29, 7, 749 (1979).

<16> Louw, R.,Dijks, H., and Mulder, P., "Thermal Hydro-Dechlorination of (Poly) Chlorinated Organic Compounds" Chemistry and Industry, 19, 759 (1983).

<17> Louw, R., Dijks, H. M., and Mulder, P., "Pyrolysis of Benzene and Chlorobenzene in an Atmosphere of Hydrogen; Formation of Methane", J. of the Royal Netherland Chemical Soc., 103/10, 271 (1984).

<18> Huang, S.H., M. Sc. Thesis, NJIT (1987).

<19> Chuang, S.C., M.Sc. Thesis, New Jersey Institute of Technology (1982).

<20> Chuang, S.C. and Bozzelli, J.W., Ind. Eng. Chem. Process Design and Development, 25, 317 (1986)

<21> Chang, S.H. and Bozzelli, J.W., AIChE J., 33, 1207 (1987)

<22> Chang, S.H., Doctoral Dissertation, New Jersey Institute of Technology (1985)

<23> Mahmood, M., M.Sc. Thesis, NJIT (1985)

<24> Ritter, E.R., M.Sc. Thesis, NJIT (1986)

<25> Tsao, H., M.Sc. Thesis, NJIT (1987)

<26> Won, Y.S. M.Sc. Thesis, NJIT (1988)

<27> Hill, C.G., Chemical Engineering Kinetics & Reactor Design, John Wiley & Son Inc., (1977).

<28> Reman, G.H., Chem. & Ind., 46 (1955)

<29> Cremer, H.W. and Watkins, S.B., Chemical Enginering Practice, Vol. 8, Butterworth, London (1965)

<30> Butt, J.B., Reaction kinetics and Reactor Design, Prentice Hall (1980)

<31> Poirier, R.V. and Carr, R.W., J. Phys. Chem., 74, 1593, (1971)

<32> Levenspiel, O., Chemical Reaction Engineering, 2nd ed., John Wiley & Son Inc., NY (1962)

<33> Dean, A.M., J. Phys. Chem., 89, 4600 (1985)

<34> Leathard, D.A. and Shwrlock, Indentification Techniques in Gas Chromatography, Wiley, NY (1970)

<35> Kassel, L.S., "Studies in Homogeneous Gas Reactions II. Introduction of Quantum Theory," J. Phys. Chem., 32, 1065 (1928).

<36> Kaufman, F., Progress in Reaction Kinetics, Vol. VI, Pergamon Press, NY (1961)

<37> Won, Y.S. and Bozzelli, J.W., The American Society of Mechanical Engineers Annual Meeting, HTD-Volume 104, 131-135 Nov., 1988, Chicago, Ill.

<38> Viek, P.S., Chember, L.E. and Wosbcke, H.N., Advances in Chemical Series 131

<39> Westmoreland, P.R. and Dean, A.M., AIChE J., 32, 171 (1986)

<40> Ritter, E., and Bozzelli, J. W., and Dean, A.M., paper Accepted in J. Phys. Chem. (1988)

<41> Kee, R.J., Miller, T.H. and Jefferson, T.H., CHEMKIN: A Gereral-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package, SANDIA (1980)

<42> Benson, S.W., Themochemical Kinetics, 2nd ed. Wiley, NY (1976)

APPENDIX A.

INPUT DATA

and

RESULTS

DISSOC CALCULATION

Table 1-a

$$
\begin{aligned}
CH_2ClCHCl_2 &\text{ ----> } CHClCHCl + HCl \\
&\text{ ----> } CH_2CCl_2 + HCl \\
&\text{ ----> } CH_2ClCHCl + Cl \\
&\text{ ----> } CH_2CHCl_2 + Cl \\
&\text{ ----> } CH_2Cl + CHCl_2
\end{aligned}
$$

k	A	Ea	source
1	9.56E+12	54.9	a
2	4.79E+12	54.9	b
3	3.69E+15	77.8	c
4	1.73E+15	81.7	c
5	5.28E+17	89.6	d

<v> = 678.7/cm e

Lennard-Jones Parameters : f

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

a. $A = 10^{13.55} * 10^{(-4/4.6)} * 4 = 1.92E+13$
Ea = 55.9 ($\triangle$Hr + 40.8), this study A = 1/2 A above

b. $A = 10^{13.55} * 10^{(-4/4.6)} * 1 = 4.79E+12$
Ea = 55.9 ($\triangle$Hr + 40.8)

c. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CH_3CCl_2 + Cl = CH_3CCl_3$ (A = 1.0E+13)
Ea = $\triangle$Hr

d. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CCl_3 + C_2H_5$ log A = 12.9
This study $A_r = 1/2 * 10^{12.9}$, Ea = $\triangle$Hr
Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980

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

f. 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 CALCULATED USING DISSOC

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2ClCHCl_2$ = CHClCHCl + HCl	8.11 E+12	55.2
76.0		9.22 E+12	55.3
760.0		9.50 E+12	55.3
7.6	$CH_2ClCHCl_2$ = CH_2CCl_2	4.38 E+12	55.2
76.0		4.56 E+12	55.3
760.0		4.72 E+12	55.3
7.6	$CH_2ClCHCl_2$ = $CH_2ClCHCl$ + Cl	2.25 E+15	77.3
76.0		3.16 E+15	77.7
760.0		3.57 E+15	77.7
7.6	$CH_2ClCHCl_2$ = $CH_2ClCHCl$ + Cl	6.07 E+14	80.8
76.0		1.20 E+15	81.3
760.0		1.58 E+15	81.4
7.6	$CH_2ClCHCl_2$ = CH_2Cl + $CHCl_2$	1.27 E+17	88.3
76.0		2.72 E+17	88.8
760.0		4.15 E+17	89.1

Table 2-a

$$
\begin{aligned}
CH_2ClCH_2Cl &\longrightarrow CH_2CHCl + HCl \\
&\longrightarrow CH_2ClCH_2 + Cl \\
&\longrightarrow CH_2Cl + CH_2Cl
\end{aligned}
$$

k	A	Ea	source
1	1.99E+13	55.3	a
2	6.65E+15	80.7	b
3	4.26E+17	88.6	c

<v> = 797. /cm d

Lennard-Jones Parameters : e

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

a. Weissman and Benson, I. J. of Chem. Kinetics, vol. 16, 1984, for $CH_2CLCH_2Cl = C_2H_3Cl + HCl$ log A = 13.6, this study 1/2 A. Ea = $\triangle$Hr + 38

b. A factor based upon entropy change for reverse.
A_{-1} taken as that for $CH_3CCl_2 + Cl = CH_3CCl_3$ (A = 1.0E+13)
Ea = $\triangle$Hr

c. 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 = $\triangle$Hr
Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980

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

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

Table 2-b

APPARENT REACTION RATE CONSTANTS CALCULATED USING DISSOC

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2ClCH_2Cl = CH_2CHCl + HCl$	1.59 E+13	54.6
76.0		1.90 E+13	54.7
760.0		1.97 E+13	54.7
7.6	$CH_2ClCH_2Cl = CH_2ClCH_2 + Cl$	3.52 E+15	79.3
76.0		5.18 E+15	79.6
760.0		6.17 E+15	79.7
7.6	$CH_2ClCH_2Cl = CH_2Cl + CH_2Cl$	5.66 E+16	87.5
76.0		1.73 E+17	88.3
760.0		3.10 E+17	88.7

Table 3-a

CH_3CHCl_2 ----> CH_2CHCl + HCl
----> CH_3CHCl + Cl
----> CH_3 + $CHCl_2$

k	A	Ea	source
1	1.96E+13	55.4	a
2	3.51E+15	76.1	b
3	2.07E+17	91.3	c

<v> = 797. /cm d

Lennard-Jones Parameters : e

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

a. Weissman and Benson, I. J. of Chem. Kinetics, vol. 16, 1984, for CH_2ClCH_2Cl = C_2H_3Cl + HCl log A = 13.6, this study 1/2 A
Ea = ΔHr + 38

b. A factor based upon entropy change for reverse.
A_{-1} taken as that for CH_3CCl_2 + Cl = CH_3CCl_3 (A = 1.0E+13)
Ea = ΔHr

c. A factor based upon ΔS for reverse
A_{-1} taken as that for CH_3 + CH_3 log A = 13.4,
CH_3 + C_2H_5 log A = 13.3,
This study A_r = 2.0E13
Ea = ΔHr
Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980

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

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

Table 3-b

APPARENT REACTION RATE CONSTANTS CALCULATED USING DISSOC

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	CH_3CHCl_2 = CH_2CHCl + HCl	1.57 E+13	54.6
76.0		1.87 E+13	54.7
760.0		1.94 E+14	54.7
7.6	CH_3CHCl_2 = CH_3CHCl + Cl	2.00 E+15	74.8
76.0		2.93 E+15	75.1
760.0		3.37 E+15	75.2
7.6	CH_3CHCl_2 = CH_3 + $CHCl_2$	7.90 E+15	89.1
76.0		5.18 E+16	90.2
760.0		1.32 E+17	90.9

Table 4-a

CH_3CH_2Cl ----> CH_2CH_2 + HCl
----> CH_3CH_2 + Cl
----> CH_3 + CH_2Cl

k	A	Ea	source
1	3.24E+13	56.6	a
2	9.80E+14	84.1	b
3	1.34E+17	90.3	c

<v> = 1265.3 /cm d

Lennard-Jones Parameters : e

sigma = 2.83 ^{o}A e/k = 621.1 ^{o}K

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

b. A factor based upon $\triangle$S for reverse
A_{-1} taken as that for C_2H_5 + CH_3 log A = 13.4
Ea = $\triangle$Hr
Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980

c. A factor based upon entropy change for reverse.
A_{-1} taken as that for CH_2 + CH_3 log A = 13.4
estimat $A_r = 2/3 * 10^{13.4}$.
Ea = $\triangle$Hr
Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980

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

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

Table 4-b

APPARENT REACTION RATE CONSTANTS CALCULATED USING DISSOC

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3CH_2Cl = CH_2CH_2 + HCl$	9.82 E+13	56.1
76.0		1.06 E+14	57.2
760.0		3.03 E+14	57.4
7.6	$CH_3CH_2Cl = CH_3CH_2 + Cl$	5.81 E+14	82.9
76.0		8.02 E+14	83.1
760.0		9.26 E+14	83.2
7.6	$CH_3CH_2Cl = CH_3 + CH_2Cl$	2.93 E+16	89.4
76.0		7.11 E+16	90.0
760.0		1.10 E+17	90.3

Table 5-a

CH_3CH_3 ----> CH_3CH_2 + H
----> CH_3 + CH_3

k	A	Ea	source
1	1.25E+16	100.1	a
2	7.94E+16	90.3	a

<v> = 1509 /cm b

Lennard-Jones Parameters : c

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

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

b. 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 $CH_2ClCHCl$)

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

Table 5-b

APPARENT REACTION RATE CONSTANTS CALCULATED
USING DISSOC

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3CH_3 = CH_3CH_2 + H$	1.77 E+14	97.0
76.0		1.65 E+15	98.0
760.0		6.18 E+15	98.8
7.6	$CH_3CH_3 = CH_3 + CH_3$	1.23 E+17	96.7
76.0		9.35 E+17	97.6
760.0		2.35 E+18	98.1

APPENDIX B.

INPUT DATA

and

RESULTS

CHEMACT QRRK CALCULATIONS

Table 6-a

$$\begin{array}{l}CH_2CCl_2 + H \Longleftrightarrow [CH_2CHCl_2]^{\#} \longrightarrow CH_2CHCl + Cl \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \longrightarrow CH_2CHCl_2 \text{ (Stab.)}\end{array}$$

k	A	Ea	source
1	3.0 E+13	6.0	a
-1	5.4 E+13	42.3	a
2	3.3 E+14	21.9	b

<v> = 736/cm   c

Lennard-Jones Parameters :   d

sigma = 5.103 ^{o}A   e/k = 435.91 ^{o}K

---

a

A factor taken as that for C2H4 + H (A=3.0E+13) (ref: Kerr, J.A. and Moss, S.J., "Handbook of Bimolecular and Termolecular Gas Reaction Vol. I & II," CRC Press inc., 1981)
A_{-1} factor based upon $\triangle$ S for reverse.

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)
Ea = $\triangle$Hr + 1

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.

d

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

Table 6-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	6.46 E+06	-0.99
76.0		6.46 E+07	-0.98
760.0		6.50 E+08	-0.97
7.6	CH_2CCl_2 + H = CH_2CHCl + Cl	3.00 E+13	6.00
76.0		3.00 E+13	6.00
760.0		3.01 E+13	6.01

Table 7-a

$CHClCHCl + H \Longleftrightarrow [CH_2ClCHCl]^{\#} \longrightarrow CH_2CHCl + Cl$
$\longrightarrow CH_2ClCHCl$ (Stab.)

k	A	Ea	source
1	2.0 E+13	5.0	a
-1	1.0 E+13	46.84	a
2	1.6 E+14	26.9	b

<v> = 736/cm c

Lennard-Jones Parameters : d

sigma = 5.103 ^{o}A e/k = 435.91 ^{o}K

a
A factor taken as that for C_2H_4 + H (A=2.0E+13) (ref: Kerr, J.A. and Moss, S.J., "Handbook of Bimolecular and Termolecular Gas Reaction Vol.I & II," CRC Press inc., 1981)
A_{-1} factor based upon $\triangle$ S for reverse.

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)
Ea = $\triangle$Hr + 1

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_2CHCl_2)

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

Table 7-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	CHClCHCl + H = $CH_2ClCHCl$	4.05 E+07	-2.65
76.0		4.06 E+08	-2.65
760.0		4.18 E+09	-2.57
7.6	CHClCHCl + H = CH_2CHCl + Cl	2.00 E+13	5.00
76.0		2.00 E+13	5.01
760.0		2.05 E+13	5.06

Table 8-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 ^{o}K		

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

c
see note (c) Table 5-a.
(refer to CH_2CHCl_2)

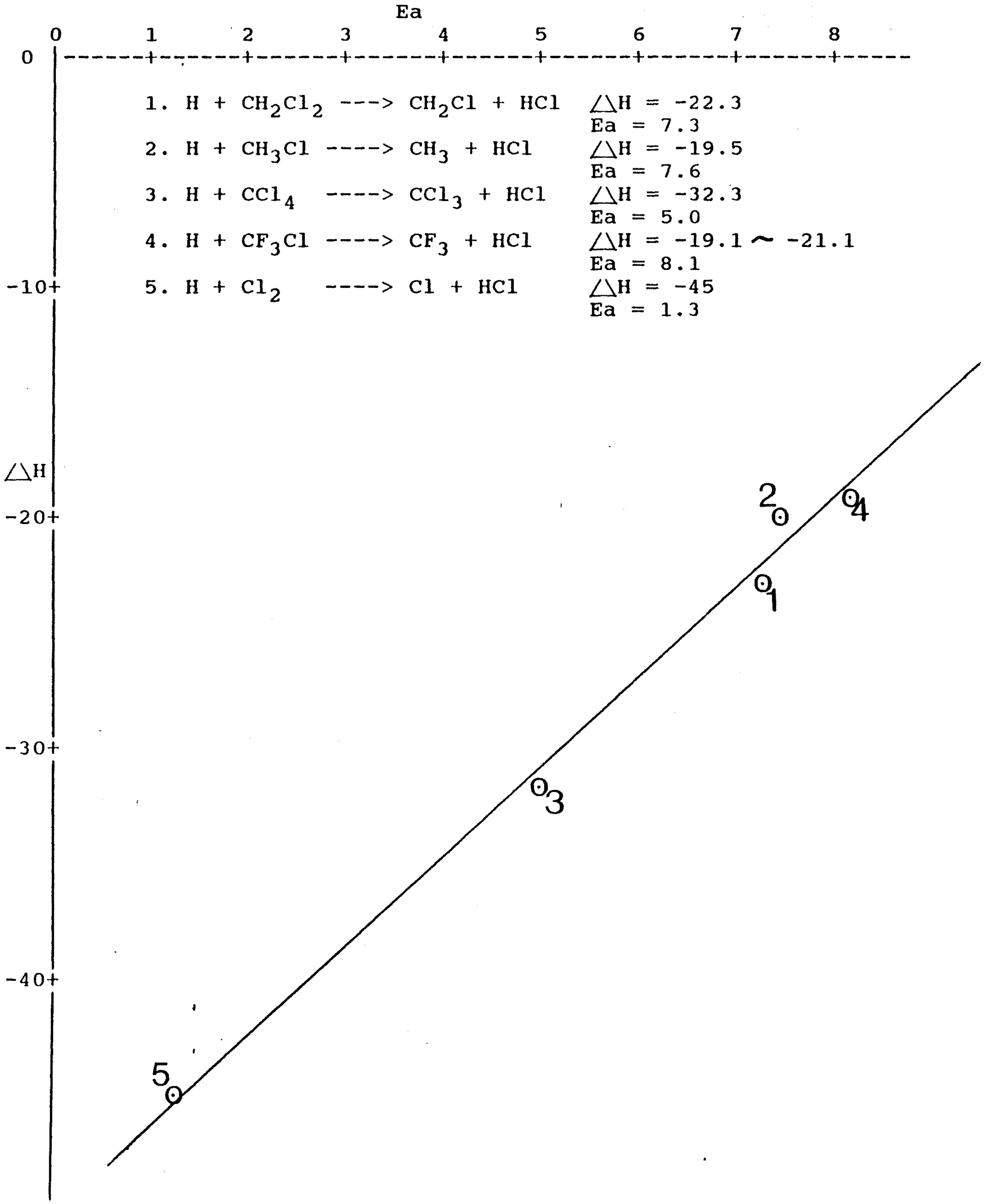
d
see note (d) Table 5-a

Table 8-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_2CHCl + H = CH_2CH_2Cl$	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

APPENDIX C. EVANS-POLANYI PLOT



1\. H + CH_2Cl_2 ---> CH_2Cl + HCl △H = -22.3
Ea = 7.3
2\. H + CH_3Cl ----> CH_3 + HCl △H = -19.5
Ea = 7.6
3\. H + CCl_4 ----> CCl_3 + HCl △H = -32.3
Ea = 5.0
4\. H + CF_3Cl ----> CF_3 + HCl △H = -19.1 ~ -21.1
Ea = 8.1
5\. H + Cl_2 ----> Cl + HCl △H = -45
Ea = 1.3

APPENDIX D.1-D.4

D.1 RESULTS OF SENSITIVITY ANALYSIS CALCULATIONS AT 1 ATM, 600 ^{o}C, 1.0 SEC.

D.2 RESULTS OF SENSITIVITY ANALYSIS CALCULATIONS AT 1 ATM, 660 ^{o}C, 1.0 SEC.

D.3 THERMO DATA IN THIS WORK

D.4 RESULTS OF MECHANINFO CALCULATIONS AT 1 ATM, 800-1000 ^{o}K.

APPENDIX D.1 (1 ATM, 600 C, 1.0 SEC)

```
     PROGRAM SID       Version 1.4
      Double PreCision


    Sensitivity analysis will be performed.
                WORKING SPACE REQUIREMENTS
                 PROVIDED         REQUIRED
Integer            40000            6109
Real              400000           47746


    Temperature is held Constant.


 Initial Conditions:

 PRESSURE (ATM)  =  1.0000E+00      TIM =    0.0000E+00
 Temperature (K) =  8.7300E+02
 Density (gm/CC) =  4.1349E-05

 Mole FraCtions:


 Time Integration:



T(SEC)= 1.0051E+00   P(ATM)= 1.0000E+00   T(K)= 8.7300E+02
 C2H3CLCL2  4.79E-03  CHCLCHCL    7.32E-04  CH2CCL2     3.73E-04  C2H3CL      1.05E-03
 C2H5CL     1.01E-04  C2H4        1.26E-04  HCL         3.83E-03  C2H6        1.43E-05
 C2H4CLCL   1.08E-07  CH4         2.51E-09  C2H2CL3     9.44E-07  CH2CL2      1.21E-07
 C2H4CL2    1.28E-09  CH3CL       1.27E-07  CH3CCL2     2.63E-07  CH3CHCL     1.09E-07
 C2H2       2.94E-07  CCC         0.00E+00  C*CC        0.00E+00  C#CC        0.00E+00
 CCCC       0.00E+00  CHCLCH      2.01E-10  C2HCL       1.11E-07  C2H         3.12E-20
 C2H3       1.63E-09  C2H5        6.19E-09  CH2         1.72E-25  CH3         8.95E-13
 C3H7       0.00E+00  C3H5        0.00E+00  C3H3        0.00E+00  CH2CL       9.78E-12
 CHCLCCL    2.13E-11  CCL2CH      4.19E-12  CHCL2       7.79E-13  CHCL        4.07E-20
 H          2.11E-08  CL          1.68E-10  CH2CCL      4.26E-10  CHCL2CH2    2.60E-14
 CH2CLCH2   2.79E-13  CH2CLCHCL   9.60E-11  CCL3CH2     0.00E+00  H2          9.89E-01
 CL2        3.27E-17
                          SENSITIVITY (KSPEC,IIRXN) KSPEC = 1, KK
RXN      A FACTOR          C2H3CLCL2   CHCLCHCL    CH2CCL2     C2H3CL      C2H5CL      C2H4        HCL         C2H6        C2H4CLCL

  1 C2H3CLCL2=CHCLCHCL+HCL
           9.500E+12  -1.422E-01   9.284E-01  -7.075E-02   1.466E-02   4.784E-02   4.670E-02   1.868E-01   7.955E-02  -6.427E-02
  2 C2H3CLCL2=CH2CCL2+HCL
           4.750E+12  -4.568E-02  -1.207E-02   9.859E-01  -8.587E-02  -2.028E-01  -1.980E-01   1.283E-02
```

```
  3 C2H3CLCL2=CH2CLCHCL+CL
           2.570E+15  -1.502E-01  -1.414E-01  -1.281E-01   5.192E-01   1.308E+00   1.287E+00   4.649E-01   2.083E+00   5.842E-01
  4 C2H3CLCL2=CHCL2CH2+CL
           1.580E+15  -1.094E-02  -1.030E-02  -9.334E-03   3.782E-02   9.525E-02   9.376E-02   3.387E-02   1.517E-01   4.252E-02
  5 C2H3CLCL2=CH2CL+CHCL2
           4.150E+17  -3.393E-02  -3.195E-02  -2.895E-02   1.172E-01   2.953E-01   2.907E-01   1.050E-01   4.705E-01   1.319E-01
  6 C2H4CLCL=C2H3CL+HCL
           1.950E+13   9.079E-08   8.076E-08   7.174E-08   7.619E-06   5.768E-06   2.372E-06   2.296E-06   1.666E-06  -8.714E-02
  7 C2H4CLCL=CH2CLCH2+CL
           6.170E+15  -4.761E-07  -4.419E-07  -3.929E-07   1.636E-06   4.167E-06   4.059E-06   1.470E-06   6.600E-06  -2.134E-05
  8 C2H4CLCL=2CH2CL
           3.130E+17  -1.179E-07  -1.094E-07  -9.716E-08   4.052E-07   1.032E-06   9.998E-07   3.636E-07   1.628E-06  -6.052E-06
  9 C2H4CL2=C2H3CL+HCL
           1.920E+13  -8.720E-09  -7.956E-09  -7.033E-09  -6.021E-08   4.657E-08   1.030E-08  -3.211E-09   7.349E-08   3.395E-08
 10 C2H4CL2=CH3CHCL+CL
           3.370E+15   1.017E-04   9.365E-05   8.258E-05  -3.484E-04  -9.031E-04  -8.575E-04  -3.132E-04  -1.403E-03  -4.003E-04
 11 C2H4CL2=CH3+CHCL2
           1.320E+17  -4.336E-11  -3.989E-11  -3.519E-11   1.484E-10   3.806E-10   3.650E-10   1.333E-10   5.978E-10   1.706E-10
 12 C2H5CL=C2H4+HCL
           3.030E+13   4.473E-05   4.049E-05   3.557E-05  -1.532E-04  -2.790E-02   1.990E-02   5.880E-04   1.460E-02  -1.753E-04
 13 C2H5CL=C2H5+CL
           9.260E+14  -1.265E-06  -1.174E-06  -1.041E-06   4.350E-06   1.102E-05   1.074E-05   3.905E-06   1.784E-05   4.965E-06
 14 C2H5CL=CH3+CH2CL
           1.080E+17  -5.840E-06  -5.382E-06  -4.748E-06   2.001E-05   5.069E-05   4.923E-05   1.797E-05   8.051E-05   2.298E-05
 15 C2H6=C2H5+H
           6.180E+15   3.204E-03   2.941E-03   2.589E-03  -1.096E-02  -2.815E-02  -2.698E-02  -9.845E-03  -4.361E-02  -1.262E-02
 16 C2H6=2CH3
           2.350E+18  -1.056E-07  -9.688E-08  -8.526E-08   3.610E-07   9.279E-07   8.868E-07   3.244E-07   1.353E-06   4.160E-07
 17 CH2CLCHCL=C2H3CL+CL
           1.350E+14  -1.405E-05  -1.339E-05  -1.216E-05   1.361E-04   2.163E-04   1.657E-04   7.336E-05   2.451E-04  -9.950E-01
 18 CHCL2CH2=C2H3CL+CL
           1.350E+14   8.275E-08   7.637E-08   6.759E-08  -2.808E-07  -7.253E-07  -6.960E-07  -2.542E-07  -1.141E-06  -3.253E-07
 19 CH2CLCH2=C2H4+CL
           1.690E+14  -8.107E-08  -7.520E-08  -6.730E-08   2.779E-07  -2.313E-06   2.903E-06   3.298E-07   2.911E-06   3.133E-07
 20 CH3CHCL=C2H3CL+H
           2.760E+13   8.077E-03   7.529E-03   6.699E-03  -1.165E-01   8.584E-01  -7.905E-02  -2.513E-02  -7.153E-02  -3.200E-02
 21 C2H5=C2H4+H
           5.010E+13   2.504E-03   2.302E-03   2.027E-03  -8.568E-03  -2.200E-02  -1.004E-01  -7.697E-03   6.663E-01  -9.864E-03
 22 C2H3=C2H2+H
           3.160E+12  -4.784E-06  -4.465E-06  -3.950E-06   1.643E-05   4.209E-05  -7.338E-04   1.475E-05  -9.977E-04   1.885E-05
 23 CH2CLCHCL+H2=C2H4CLCL+H
           5.000E+12  -1.731E-06  -1.561E-06  -1.394E-06  -7.615E-05  -7.522E-05  -2.833E-05  -2.276E-05  -2.440E-05   9.378E-01
 24 CH3CHCL+H2=C2H5CL+H
           5.000E+12  -8.243E-03  -7.659E-03  -6.811E-03   2.732E-02   8.386E-02   6.995E-02   2.543E-02   1.145E-01   3.231E-02
 25 CH2CLCH2+H2=C2H5CL+H
           4.000E+12   5.295E-05   4.800E-05   4.219E-05  -1.814E-04  -3.426E-02   2.470E-02   7.285E-04   1.595E-02  -2.013E-04
 26 CHCL2CH2+H2=C2H4CL2+H
           5.260E+12   4.912E-08   4.749E-08   4.378E-08  -2.257E-07  -4.398E-07  -4.678E-07  -1.712E-07  -7.110E-07  -1.893E-07
 27 C2H2CL3+H2=C2H3CLCL2+H
           5.000E+12  -2.886E-03  -2.725E-03  -2.477E-03   9.996E-03   2.513E-02   2.481E-02   8.949E-03   4.010E-02   1.122E-02
 28 C2H3CLCL2+H=CH2CLCHCL+HCL
           2.000E+13  -1.976E-01  -6.217E-02  -6.205E-02   7.790E-01   8.138E-01   8.154E-01   5.420E-01   8.239E-01   8.829E-01
 29 C2H4CL2+H=CH3CHCL+HCL
           2.000E+13   8.106E-08   7.477E-08   6.560E-08  -2.794E-07  -4.105E-07  -6.764E-07
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30 C2H4CLCL+H=CH2CLCH2+HCL
         3.000E+13   2.031E-07   1.875E-07   1.677E-07  -1.242E-06  -2.061E-06   4.561E-05   2.684E-06   4.377E-05  -5.587E-02
31 C2H5CL+H=C2H5+HCL
         1.500E+13   1.714E-04   1.574E-04   1.386E-04  -5.865E-04  -9.603E-03  -5.028E-04  -3.133E-04   4.656E-02  -6.750E-04
32 C2H6+H=C2H5+H2
         6.610E+13  -2.854E-03  -2.621E-03  -2.307E-03   9.764E-03   2.508E-02   3.867E-03   8.772E-03   2.176E-01   1.124E-02
33 C2H4+H=C2H3+H2
         1.910E+13  -1.174E-04  -1.090E-04  -9.701E-05   4.037E-04   1.026E-03   2.671E-03   3.621E-04   3.456E-03   4.599E-04
34 C2H2+H=C2H+H2
         2.000E+14  -2.941E-16  -2.930E-16  -2.725E-16   1.055E-15   2.564E-15   2.642E-15   9.385E-16   4.205E-15   1.142E-15
35 C2H3CLCL2+CL=C2H2CL3+HCL
         1.000E+13   2.931E-03   2.771E-03   2.523E-03  -1.016E-02  -2.552E-02  -2.521E-02  -9.092E-03  -4.075E-02  -1.142E-02
36 CHCL2+H2=CH2CL2+H
         1.070E+14   3.927E-11   6.384E-10   1.044E-09  -1.121E-09   3.355E-09  -5.900E-09  -7.647E-10  -1.677E-09   1.077E-09
37 CH2CL2=CH2CL+CL
         1.660E+14  -4.876E-07  -4.551E-07  -4.074E-07   1.680E-06   4.257E-06   4.154E-06   1.507E-06   6.746E-06   1.906E-06
38 CH2CL2=CHCL+HCL
         1.200E+14   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00
39 CH2CL2+H=CH2CL+HCL
         1.100E+13   5.446E-08   5.271E-08   4.921E-08  -1.904E-07  -4.663E-07  -4.774E-07   9.774E-07  -7.587E-07  -2.031E-07
40 CH2CL+H2=CH3CL+H
         2.860E+12  -2.901E-06  -2.775E-06  -2.576E-06   1.008E-05   2.519E-05   2.507E-05   9.008E-06   4.046E-05   1.105E-05
41 CH3CL=CH3+CL
         1.270E+14  -8.120E-09  -7.576E-09  -6.774E-09   2.797E-08   7.094E-08   6.917E-08   2.508E-08   1.123E-07   3.176E-08
42 CH3CL=CH2+HCL
         4.750E+13   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00
43 CH3CL+H=CH3+HCL
         3.720E+13   3.905E-08   4.071E-08   4.041E-08  -1.405E-07  -3.247E-07  -3.604E-07   5.071E-07  -5.527E-07  -1.440E-07
44 CH4+H=CH3+H2
         5.000E+12  -6.648E-08  -6.222E-08  -5.562E-08   2.293E-07   5.796E-07   5.684E-07   2.056E-07   9.200E-07   2.597E-07
45 CH2CCL2=CH2CCL+CL
         9.340E+15  -2.316E-05  -2.161E-05  -1.964E-05   7.987E-05   2.024E-04   1.974E-04   7.156E-05   3.205E-04   9.057E-05
46 CH2CCL2=C2HCL+HCL
         3.550E+13  -1.691E-06  -1.580E-06  -9.437E-05   3.470E-06   1.330E-05   1.284E-05   1.422E-05   2.228E-05   6.654E-06
47 CH2CCL2+H=CHCL2CH2
         6.500E+08  -1.311E-06  -1.207E-06  -1.246E-04   4.158E-05   4.140E-05   4.085E-05   1.715E-05   4.364E-05   5.391E-06
48 CH2CCL2+H=CH3CCL2
         4.300E+09   2.057E-03   1.942E-03   1.736E-03  -7.118E-03  -1.790E-02  -1.767E-02  -6.373E-03  -2.856E-02  -7.993E-03
49 CH2CCL2+H=C2H3CL+CL
         3.010E+13  -1.112E-03  -1.026E-03  -1.038E-01   3.471E-02   3.465E-02   3.421E-02   1.435E-02   3.663E-02   4.564E-03
50 CH2CCL2+H=CH2CCL+HCL
         6.000E+12  -3.077E-05  -2.843E-05  -2.752E-03   9.244E-04   9.298E-04   9.180E-04   3.843E-04   9.891E-04   1.247E-04
51 CH2CCL2+CL=HCL+CCL2CH
         1.000E+13  -6.948E-09  -8.246E-09  -6.881E-09   2.660E-08   5.213E-08   7.170E-08   2.450E-08   1.027E-07  -1.226E-08
52 CCL2CH+H2=CH2CCL2+H
         4.100E+11  -4.308E-08  -4.033E-08  -3.551E-08   1.486E-07   3.763E-07   3.680E-07   1.332E-07   5.972E-07   1.670E-07
53 CHCLCHCL=CHCLCH+CL
         9.340E+15  -2.079E-05  -1.954E-05  -1.735E-05   7.169E-05   1.817E-04   1.772E-04   6.424E-05   2.877E-04   8.130E-05
54 CHCLCHCL=C2HCL+HCL
         3.500E+13  -1.025E-08  -9.132E-05  -3.523E-08  -5.314E-06  -3.353E-06  -3.351E-06   1.738E-05  -2.348E-06  -2.018E-08
55 CHCLCHCL+H=CH2CLCHCL
         4.180E+09   1.443E-05  -1.978E-03   1.189E-05   1.123E-03   8.254E-04   8.265E-04   3.708E-04   6.178E-04   1.376E-03
56 CHCLCHCL+H=C2H3CL+CL
         2.050E+13   8.515E-04  -1.166E-01   7.014E-04   6.619E-02   4.863E-02   4.870E-02   2.185E-02   3.639E-02  -3.012E-02
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57 CHCLCHCL+H=CHCLCH+HCL
          1.000E+13   2.780E-05  -4.505E-03   2.280E-05   2.573E-03   1.922E-03   1.923E-03   8.593E-04   1.475E-03  -1.012E-04
58 CHCLCHCL+CL=HCL+CHCLCCL
          1.000E+13  -8.751E-08  -8.366E-08  -7.230E-08   3.014E-07   7.671E-07   7.446E-07   2.710E-07   1.211E-06   2.869E-07
59 CHCLCCL+H2=CHCLCHCL+H
          6.160E+11  -3.225E-08  -2.935E-08  -2.736E-08   1.113E-07   2.832E-07   2.743E-07   9.970E-08   4.484E-07   1.250E-07
60 C2H3CL=C2H3+CL
          4.080E+15  -2.677E-05  -2.485E-05  -2.208E-05   9.188E-05   2.342E-04   2.283E-04   8.261E-05   3.712E-04   1.050E-04
61 C2H3CL=C2H2+HCL
          3.550E+13   4.538E-07   3.936E-07   3.437E-07  -7.456E-05  -6.164E-05   2.217E-04   2.015E-05   1.910E-04  -2.056E-06
62 C2H3CL+H=C2H3+HCL
          1.000E+13   5.233E-04   4.817E-04   4.249E-04  -2.009E-02  -1.679E-02   1.396E-01   3.727E-03   1.338E-01  -2.120E-03
63 C2H3CL+H=CH2CLCH2
          1.390E+10   1.061E-04   9.757E-05   8.597E-05  -4.665E-03  -3.798E-03   3.337E-02   9.283E-04   3.213E-02  -4.242E-04
64 C2H3CL+H=C2H4+CL
          8.510E+12   2.170E-03   1.995E-03   1.758E-03  -9.521E-02  -7.758E-02   6.810E-01   1.893E-02   6.556E-01  -8.671E-03
65 C2H3CL+CL=HCL+CHCLCH
          2.000E+13  -1.395E-06  -1.304E-06  -1.164E-06   4.816E-06   1.222E-05   1.192E-05   4.322E-06   1.935E-05   3.949E-06
66 C2H3CL+CL=HCL+CH2CCL
          2.000E+13  -2.785E-06  -2.606E-06  -2.330E-06   9.614E-06   2.440E-05   2.381E-05   8.637E-06   3.865E-05   7.208E-06
67 CH2CCL+H2=C2H3CL+H
          6.160E+11  -3.901E-06  -3.630E-06  -3.235E-06   1.346E-05   3.415E-05   3.320E-05   1.205E-05   5.397E-05   1.487E-05
68 CHCLCH+H2=C2H3CL+H
          4.100E+11  -3.404E-06  -3.175E-06  -2.837E-06   1.175E-05   2.978E-05   2.902E-05   1.052E-05   4.713E-05   1.296E-05
69 2H+H2=2H2
          1.000E+17   4.564E-04   4.234E-04   3.760E-04  -1.569E-03  -3.996E-03  -3.871E-03  -1.407E-03  -6.305E-03  -1.790E-03
70 CL2=2CL
          7.690E+08  -1.288E-13  -1.184E-13  -1.042E-13   4.409E-13   1.132E-12   1.084E-12   3.968E-13   1.775E-12   5.074E-13
71 HCL=H+CL
          6.090E+08   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00
72 CL+H2=HCL+H
          4.800E+13  -3.036E-03  -2.868E-03  -2.609E-03   1.052E-02   2.644E-02   2.610E-02   9.414E-03   4.219E-02   1.017E-02
73 H+CL2=HCL+CL
          4.570E+12  -9.484E-16   1.668E-15   4.088E-15  -5.539E-16   2.061E-14  -1.177E-14   2.104E-16   5.320E-15   9.482E-15
END
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PPENDIX D.2 (1 ATM, 660 C, 1.0 SEC)

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     PROGRAM SID       Version 1.4
      Double PreCision



    Sensitivity analysis will be performed.
                WORKING SPACE REQUIREMENTS
                 PROVIDED        REQUIRED
Integer            40000           6109
Real              400000          47746


    Temperature is held Constant.


 Initial Conditions:

 PRESSURE (ATM)  =  1.0000E+00      TIM =    0.0000E+00
 Temperature (K) =  9.3300E+02
 Density (gm/CC) =  3.8690E-05

 Mole FraCtions:


 Time Integration:



T(SEC)= 1.0088E+00   P(ATM)= 1.0000E+00   T(K)= 9.3300E+02
 C2H3CLCL2  4.79E-04  CHCLCHCL    1.30E-03  CH2CCL2     6.94E-04  C2H3CL      1.56E-03
 C2H5CL     5.80E-04  C2H4        1.68E-03  HCL         1.39E-02  C2H6        8.60E-04
 C2H4CLCL   3.41E-08  CH4         2.09E-07  C2H2CL3     6.00E-08  CH2CL2      1.04E-06
 C2H4CL2    1.39E-08  CH3CL       1.35E-06  CH3CCL2     1.10E-07  CH3CHCL     1.07E-07
 C2H2       5.08E-06  CCC         0.00E+00  C*CC        0.00E+00  C#CC        0.00E+00
 CCCC       0.00E+00  CHCLCH      3.08E-10  C2HCL       3.80E-06  C2H         1.33E-18
 C2H3       2.86E-09  C2H5        4.35E-08  CH2         2.51E-22  CH3         1.75E-11
 C3H7       0.00E+00  C3H5        0.00E+00  C3H3        0.00E+00  CH2CL       3.01E-11
 CHCLCCL    4.80E-11  CCL2CH      9.85E-12  CHCL2       5.77E-12  CHCL        2.38E-17
 H          2.03E-08  CL          3.50E-10  CH2CCL      5.99E-10  CHCL2CH2    3.60E-14
 CH2CLCH2   1.20E-12  CH2CLCHCL   4.62E-12  CCL3CH2     0.00E+00  H2          9.79E-01
 CL2        1.69E-15
                           SENSITIVITY (KSPEC,IIRXN) KSPEC = 1, KK
RXN      A FACTOR          C2H3CLCL2   CHCLCHCL     CH2CCL2      C2H3CL       C2H5CL       C2H4         HCL          C2H6         C2H4CLCL

  1 C2H3CLCL2=CHCLCHCL+HCL
           9.500E+12  -9.462E-01   7.174E-01  -2.814E-01   4.944E-02  -1.112E-01  -6.672E-02  -9.253E-03  -2.166E-01  -3.231E-01
  2 C2H3CLCL2=CH2CCL2+HCL
           4.750E+12  -4.786E-01  -1.458E-01   8.564E-01   1.037E-02  -5.308E-02  -4.195E-02
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  3 C2H3CLCL2=CH2CLCHCL+CL
           2.570E+15  -2.012E-01  -1.966E-01  -1.907E-01  -9.392E-02   8.742E-02   1.509E-01   8.350E-02   3.809E-01  -4.088E-02
  4 C2H3CLCL2=CHCL2CH2+CL
           1.580E+15  -1.681E-02  -1.643E-02  -1.594E-02  -7.847E-03   7.304E-03   1.261E-02   6.976E-03   3.182E-02  -3.519E-03
  5 C2H3CLCL2=CH2CL+CHCL2
           4.150E+17  -6.951E-02  -6.791E-02  -6.588E-02  -3.270E-02   2.998E-02   5.183E-02   2.863E-02   1.312E-01  -1.464E-02
  6 C2H4CLCL=C2H3CL+HCL
           1.950E+13   4.536E-06   4.246E-06   3.870E-06   1.063E-05   6.121E-06   1.782E-06   1.122E-06  -4.901E-06  -8.597E-01
  7 C2H4CLCL=CH2CLCH2+CL
           6.170E+15  -5.409E-06  -5.122E-06  -4.700E-06  -2.633E-06   4.361E-06   3.213E-06   2.101E-06   1.015E-05  -6.654E-04
  8 C2H4CLCL=2CH2CL
           3.130E+17  -2.111E-06  -1.997E-06  -1.830E-06  -1.028E-06   1.727E-06   1.230E-06   8.142E-07   3.951E-06  -2.606E-04
  9 C2H4CL2=C2H3CL+HCL
           1.920E+13   5.838E-06   5.433E-06   4.890E-06   6.065E-06  -5.374E-06  -5.173E-07  -1.052E-06  -9.610E-06   1.604E-06
 10 C2H4CL2=CH3CHCL+CL
           3.370E+15   3.376E-03   3.239E-03   3.030E-03   1.611E-03  -1.882E-03  -2.408E-03  -1.360E-03  -6.193E-03   5.643E-04
 11 C2H4CL2=CH3+CHCL2
           1.320E+17  -8.630E-08  -8.107E-08  -7.349E-08  -4.244E-08   7.989E-08   4.607E-08   3.271E-08   1.624E-07  -7.989E-09
 12 C2H5CL=C2H4+HCL
           3.030E+13   2.301E-02   2.150E-02   1.959E-02   1.045E-02  -5.356E-01   1.246E-01   1.282E-02   3.790E-02   5.810E-03
 13 C2H5CL=C2H5+CL
           9.260E+14  -7.660E-04  -7.132E-04  -6.382E-04  -3.804E-04   8.596E-04   3.335E-04   2.827E-04   1.480E-03  -4.116E-05
 14 C2H5CL=CH3+CH2CL
           1.080E+17  -2.885E-03  -2.703E-03  -2.441E-03  -1.417E-03   2.865E-03   1.426E-03   1.083E-03   5.482E-03  -2.255E-04
 15 C2H6=C2H5+H
           6.180E+15   2.986E-01   2.843E-01   2.628E-01   1.426E-01  -2.018E-01  -1.959E-01  -1.178E-01  -5.491E-01   4.204E-02
 16 C2H6=2CH3
           2.350E+18  -8.622E-04  -8.038E-04  -7.209E-04  -4.276E-04   9.718E-04   3.770E-04   3.183E-04   1.651E-03  -4.832E-05
 17 CH2CLCHCL=C2H3CL+CL
           1.350E+14   1.150E-05   1.049E-05   9.254E-06  -2.460E-06   8.216E-06   2.752E-06  -3.237E-07  -5.383E-06  -7.773E-01
 18 CHCL2CH2=C2H3CL+CL
           1.350E+14  -1.520E-07  -1.419E-07  -1.282E-07  -7.407E-08   1.567E-07   7.512E-08   5.778E-08   2.914E-07  -1.041E-08
 19 CH2CLCH2=C2H4+CL
           1.690E+14   4.426E-07   4.134E-07   3.758E-07   1.953E-07  -6.306E-06   9.750E-07   8.099E-08   8.214E-07  -2.329E-07
 20 CH3CHCL=C2H3CL+H
           2.760E+13   1.143E-02   1.220E-02   1.219E-02  -3.757E-01   6.827E-01   7.671E-02   8.907E-03   3.701E-02  -7.068E-02
 21 C2H5=C2H4+H
           5.010E+13   1.172E-01   1.122E-01   1.041E-01   5.585E-02  -7.438E-02  -2.752E-01  -4.662E-02   1.673E-01   1.739E-02
 22 C2H3=C2H2+H
           3.160E+12  -8.028E-05  -8.196E-05  -8.313E-05  -3.509E-05  -2.682E-05   5.831E-04   3.701E-05   3.748E-05  -2.810E-05
 23 CH2CLCHCL+H2=C2H4CLCL+H
           5.000E+12  -9.285E-06  -8.865E-06  -8.304E-06   3.642E-06  -8.206E-06  -8.755E-07   7.408E-07   4.610E-06   5.381E-01
 24 CH3CHCL+H2=C2H5CL+H
           5.000E+12   2.090E-03   1.271E-03   9.759E-05  -1.330E-02   1.656E-02   5.431E-03   3.478E-04  -6.590E-04  -4.470E-03
 25 CH2CLCH2+H2=C2H5CL+H
           4.000E+12   1.605E-02   1.514E-02   1.395E-02   7.254E-03  -2.084E-01   3.233E-02   2.000E-03   2.116E-02   4.380E-03
 26 CHCL2CH2+H2=C2H4CL2+H
           5.260E+12   5.158E-07   4.805E-07   4.340E-07   2.911E-07  -4.406E-07  -5.565E-08  -1.113E-07  -7.668E-07   1.331E-07
 27 C2H2CL3+H2=C2H3CLCL2+H
           5.000E+12   6.550E-05  -1.061E-05  -1.342E-04   4.789E-05  -6.239E-04   1.828E-04   2.985E-05   6.889E-05  -1.686E-04
 28 C2H3CLCL2+H=CH2CLCHCL+HCL
           2.000E+13  -7.849E-01  -2.132E-01  -2.226E-01   2.594E-01   1.238E-01   2.238E-01   1.090E-01  -5.280E-02   4.387E-01
 29 C2H4CL2+H=CH3CHCL+HCL
           2.000E+13   1.425E-06   1.340E-06   1.218E-06  -1.666E-06
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30 C2H4CLCL+H=CH2CLCH2+HCL
          3.000E+13   6.879E-06   6.561E-06   6.097E-06  -8.082E-06  -1.014E-05   4.281E-06   4.313E-09   4.352E-06  -2.492E-01
31 C2H5CL+H=C2H5+HCL
          1.500E+13   1.236E-02   1.182E-02   1.100E-02   5.763E-03  -5.501E-02  -1.155E-02  -2.937E-03   1.556E-02   2.350E-03
32 C2H6+H=C2H5+H2
          6.610E+13  -1.884E-01  -1.791E-01  -1.655E-01  -8.986E-02   1.276E-01  -2.741E-02   7.420E-02   6.404E-01  -2.653E-02
33 C2H4+H=C2H3+H2
          1.910E+13   7.405E-04   7.014E-04   6.335E-04   3.570E-04  -5.676E-04   3.885E-04  -2.871E-04   6.849E-04   8.119E-05
34 C2H2+H=C2H+H2
          2.000E+14  -8.850E-13  -8.350E-13  -7.691E-13  -4.292E-13   8.188E-13   2.473E-13   3.378E-13   1.133E-12  -8.657E-14
35 C2H3CLCL2+CL=C2H2CL3+HCL
          1.000E+13  -3.399E-06   7.786E-05   2.080E-04  -1.531E-05   5.934E-04  -2.311E-04  -5.861E-05  -2.094E-04   1.562E-04
36 CHCL2+H2=CH2CL2+H
          1.070E+14  -2.700E-08  -2.906E-08  -3.134E-08  -1.078E-08  -3.504E-08   4.237E-08   1.404E-08   4.479E-08  -1.478E-08
37 CH2CL2=CH2CL+CL
          1.660E+14  -3.384E-05  -3.180E-05  -2.886E-05  -1.660E-05   3.324E-05   1.712E-05   1.282E-05   6.453E-05  -2.852E-06
38 CH2CL2=CHCL+HCL
          1.200E+14   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00
39 CH2CL2+H=CH2CL+HCL
          1.100E+13   5.004E-06   4.732E-06   4.313E-06   2.474E-06  -5.038E-06  -2.460E-06   1.296E-05  -9.720E-06   4.025E-06
40 CH2CL+H2=CH3CL+H
          2.860E+12  -4.925E-07  -9.861E-07  -1.687E-06  -1.987E-07  -3.092E-06   1.821E-06   5.592E-07   2.038E-06  -5.584E-06
41 CH3CL=CH3+CL
          1.270E+14  -2.044E-06  -1.919E-06  -1.739E-06  -1.005E-06   2.076E-06   1.001E-06   7.708E-07   3.915E-06  -1.606E-07
42 CH3CL=CH2+HCL
          4.750E+13   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00   0.000E+00
43 CH3CL+H=CH3+HCL
          3.720E+13   4.499E-07   5.176E-07   5.370E-07   2.561E-07   7.186E-08  -4.839E-07   1.010E-05  -1.039E-06   2.045E-06
44 CH4+H=CH3+H2
          5.000E+12  -3.385E-07  -3.719E-07  -4.147E-07  -1.435E-07  -3.173E-07   4.576E-07   1.758E-07   6.685E-07  -1.786E-07
45 CH2CCL2=CH2CCL+CL
          9.340E+15  -7.032E-04  -6.618E-04  -6.125E-04  -3.414E-04   6.752E-04   3.644E-04   2.674E-04   1.340E-03  -6.239E-05
46 CH2CCL2=C2HCL+HCL
          3.550E+13  -7.323E-06  -8.237E-06  -1.502E-03  -1.140E-04  -4.301E-05  -3.171E-05   7.196E-05  -6.476E-06  -7.383E-06
47 CH2CCL2+H=CHCL2CH2
          6.500E+08   1.547E-05   1.468E-05  -4.284E-04   8.784E-05   5.130E-05   5.053E-05   2.647E-05   2.264E-05   2.488E-05
48 CH2CCL2+H=CH3CCL2
          4.300E+09   3.964E-04   4.159E-04   4.466E-04   1.952E-04  -1.272E-04  -3.105E-04  -1.799E-04  -8.737E-04   1.233E-04
49 CH2CCL2+H=C2H3CL+CL
          3.010E+13   1.667E-02   1.583E-02  -4.620E-01   9.474E-02   5.538E-02   5.449E-02   2.855E-02   2.445E-02   2.684E-02
50 CH2CCL2+H=CH2CCL+HCL
          6.000E+12   5.014E-04   4.760E-04  -1.394E-02   2.858E-03   1.672E-03   1.645E-03   8.623E-04   7.410E-04   7.892E-04
51 CH2CCL2+CL=HCL+CCL2CH
          1.000E+13  -4.220E-08  -4.010E-08  -3.738E-08  -2.191E-08   5.953E-08   1.162E-08   1.498E-08   9.043E-08  -3.170E-07
52 CCL2CH+H2=CH2CCL2+H
          4.100E+11   1.971E-07   1.842E-07   1.651E-07   9.588E-08  -1.824E-07  -1.058E-07  -7.441E-08  -3.666E-07  -2.017E-08
53 CHCLCHCL=CHCLCH+CL
          9.340E+15  -6.336E-04  -6.015E-04  -5.433E-04  -3.074E-04   6.018E-04   3.314E-04   2.413E-04   1.207E-03  -5.754E-05
54 CHCLCHCL=C2HCL+HCL
          3.500E+13  -1.002E-05  -1.460E-03  -1.070E-05  -2.352E-04  -9.075E-05  -7.269E-05   1.273E-04  -2.509E-05  -2.301E-05
55 CHCLCHCL+H=CH2CLCHCL
          4.180E+09   4.274E-04  -6.155E-03   3.796E-04   2.379E-03   1.495E-03   1.409E-03   7.401E-04   6.884E-04   7.432E-03
56 CHCLCHCL+H=C2H3CL+CL
          2.050E+13   3.347E-02  -4.820E-01   2.973E-02   1.863E-01   1.171E-01   1.104E-01
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57 CHCLCHCL+H=CHCLCH+HCL
          1.000E+13  1.515E-03  -2.191E-02   1.346E-03   8.462E-03   5.325E-03   5.019E-03   2.636E-03   2.461E-03   2.292E-03
58 CHCLCHCL+CL=HCL+CHCLCCL
          1.000E+13 -5.695E-08  -5.429E-08  -4.985E-08  -2.900E-08   6.474E-08   2.375E-08   2.047E-08   1.142E-07  -5.501E-07
59 CHCLCCL+H2=CHCLCHCL+H
          6.160E+11  2.989E-09  -1.578E-09  -5.832E-09   2.832E-09  -4.841E-08   1.944E-08   2.235E-09  -5.502E-09  -3.675E-08
60 C2H3CL=C2H3+CL
          4.080E+15 -1.292E-03  -1.214E-03  -1.103E-03  -6.384E-04   1.228E-03   6.776E-04   4.906E-04   2.455E-03  -1.161E-04
61 C2H3CL=C2H2+HCL
          3.550E+13  1.376E-04   1.293E-04   1.188E-04  -1.501E-03  -8.047E-04   5.912E-04   1.515E-04   2.215E-04  -1.909E-04
62 C2H3CL+H=C2H3+HCL
          1.000E+13  2.917E-02   2.792E-02   2.601E-02  -7.866E-02  -8.304E-02   4.029E-02   1.443E-03   3.704E-02  -1.100E-02
63 C2H3CL+H=CH2CLCH2
          1.390E+10  5.063E-03   4.847E-03   4.511E-03  -1.323E-02  -1.413E-02   6.862E-03   1.917E-04   6.362E-03  -1.750E-03
64 C2H3CL+H=C2H4+CL
          8.510E+12  1.286E-01   1.231E-01   1.146E-01  -3.360E-01  -3.589E-01   1.743E-01   4.870E-03   1.616E-01  -4.443E-02
65 C2H3CL+CL=HCL+CHCLCH
          2.000E+13 -9.372E-07  -9.032E-07  -8.666E-07  -4.297E-07   3.811E-07   7.193E-07   3.836E-07   1.710E-06  -3.167E-06
66 C2H3CL+CL=HCL+CH2CCL
          2.000E+13 -3.068E-06  -2.881E-06  -2.640E-06  -1.439E-06   2.200E-06   1.930E-06   1.188E-06   5.556E-06  -2.304E-05
67 CH2CCL+H2=C2H3CL+H
          6.160E+11  2.993E-07  -1.315E-07  -7.569E-07   2.317E-07  -4.305E-06   1.550E-06   2.278E-07   1.506E-07  -1.154E-05
68 CHCLCH+H2=C2H3CL+H
          4.100E+11 -6.917E-08  -5.373E-07  -1.180E-06   6.500E-08  -4.472E-06   1.976E-06   4.110E-07   9.100E-07  -1.456E-05
69 2H+H2=2H2
          1.000E+17  3.695E-03   3.594E-03   3.432E-03   1.724E-03  -1.462E-03  -2.874E-03  -1.529E-03  -6.802E-03   7.485E-04
70 CL2=2CL
          7.690E+08  1.982E-12   1.858E-12   1.672E-12   9.415E-13  -1.208E-12  -1.402E-12  -6.987E-13  -3.426E-12   2.844E-13
71 HCL=H+CL
          6.090E+08  1.607E-07   1.536E-07   1.424E-07   7.739E-08  -1.180E-07  -9.986E-08  -6.329E-08  -3.030E-07   2.165E-08
72 CL+H2=HCL+H
          4.800E+13 -8.946E-04  -9.486E-04  -1.036E-03  -4.081E-04  -2.217E-04   9.271E-04   4.292E-04   1.858E-03  -8.302E-03
73 H+CL2=HCL+CL
          4.570E+12  7.752E-12   7.354E-12   6.763E-12   3.682E-12  -4.696E-12  -5.378E-12  -3.049E-12  -1.393E-11   1.155E-12
END
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APPENDIX D3-Thermo Data

SPECIES	HF(298)	S (298)	CP300	CP500	CP800	CP1000	CP1500	CP2000	COMMENTS	ELEMENTS								
AR	-0.01	36.95	4.97	4.97	4.97	4.97	4.97	4.97		C	0	H	0	CL	0	AR	1	G
C(S)	0.00	21.83	2.06	3.50	4.74	5.15	5.65	5.89	J 3/61	C	1	0	0	0	0	0	0	S
C	170.88	38.31	4.98	4.97	4.97	4.97	4.97	5.01	J 3/61	C	1	00	0	00	0	00	0	G
CL	28.90	39.50	5.20	5.40	5.35	5.30	5.24	3.40		CL	1	0	0	0	0	0	0	G
H2	0.00	31.21	6.90	6.99	7.10	7.21	7.72	8.17		H	2	0	0	0	0	0	0	G
H	52.10	27.36	4.97	4.97	4.97	4.97	4.97	4.97		C	0	H	1	CL	0	0	0	G
H2O	-57.80	29.78	8.02	8.41	9.25	9.85	11.23	12.20	J 3/61	H	2	O	1	00	0	00	0	G
H2O2	-32.53	69.07	10.42	12.35	14.29	15.21	16.85	17.88	L 2/69	H	2	O	2	0	0	0	0	G
CH	142.00	29.05	6.97	7.03	7.40	7.78	8.74	9.36	J12/67	C	1	H	1	0	0	0	0	G
HCL	-22.07	44.60	6.96	6.99	7.29	7.56	8.10	8.40		C	0	H	1	CL	1	0	0	G
CL2	0.00	53.30	8.10	8.59	8.91	8.99	9.10	9.16		CL	2	0	0	0	0	0	0	G
C3O2	-22.38	116.09	16.07	19.32	22.14	23.34	24.93	25.76	J 6/68	C	3	O	2	0	0	0	0	G
CH2	92.35	46.32	8.28	8.99	10.15	10.88	12.22	13.00	J12/72	C	1	H	2		0		0	G
CH3	35.12	46.38	9.26	10.81	12.90	14.09	16.26	17.56	J 6/69	C	1	H	3	0	0	0	0	G
CH4	-17.90	44.48	8.51	11.10	15.00	17.20	20.61	22.61	J 3/61	C	1	H	4	00	0	00	0	G
C2H	132.00	49.58	8.88	10.22	11.54	12.16	13.32	14.11		C	2	H	1	CL	0	0	0	G
C2H2	54.19	48.01	10.60	13.08	15.31	16.29	18.31	19.57	J 3/61	C	2	H	2	00	0	00	0	G
C2H3	67.10	56.20	10.89	13.87	17.16	18.73	21.34	23.20		C	2	H	3	CL	0	0	0	G
C2H4	12.54	52.39	10.28	14.91	20.03	22.45	26.21	28.35	J 9/65	C	2	H	4	00	0	00	0	G
C2H5	28.36	57.90	12.26	17.13	22.85	25.74	30.54	33.31		C	2	H	5	CL	0	0	0	G
C2H6	-20.24	54.85	12.58	18.68	25.80	29.33	34.91	38.37	L 5/72	C	2	H	6		0		0	G
C3H2	106.65	117.98	12.96	16.94	20.26	21.59	23.85	25.59		C	3	H	2					G
C3H3	77.26	89.99	14.05	18.28	22.39	24.24	27.23	28.88		C	3	H	3					G
C*C*C	45.79	79.49	14.72	19.73	24.96	27.31	31.63	34.12		C	3	H	4					G
C3H5	41.00	62.09	14.75	21.68	28.44	31.53	36.44	39.44	U12/77	C	3	H	5		0		0	G
C*CC	4.91	63.89	15.26	22.67	30.51	34.32	40.48	43.87	T12/81	C	3	H	6		0		0	G
CCC	-24.79	64.62	17.63	27.01	37.11	41.88	49.27	53.43		C	3	H	8		0	0	0	G
CC.C	22.30	69.24	15.73	23.98	32.85	37.31	44.26	48.30		C	3	H	7					G
C3H7	24.02	69.17	16.85	25.39	33.87	37.11	44.58	48.61		C	3	H	7	CL	0	0	0	G
C#CC	44.35	59.39	14.56	19.71	25.06	27.64	31.85	34.00		C	3	H	4	CL	0	0	0	G
C3H3	83.33	56.99	14.06	18.27	22.33	24.19	27.21	28.85		C	3	H	3	CL	0	0	0	G
C4	232.02	54.62	12.05	15.06	17.50	18.39	19.55	20.14		C	4							G
CCCC	-30.11	74.26	23.31	35.36	47.98	54.03	63.68	69.66		C	4	H	10	CL	0	0	0	G
C#CC#C	108.29	126.53	17.12	21.87	25.25	26.47	28.79	30.27		C	4	H	2					G
C#CC*C	62.84	98.86	17.64	24.11	30.44	33.20	37.66	39.90		C	4	H	4					G
C*CC*C	34.97	123.08	18.81	26.39	35.17	39.30	45.45	49.16	T12/82	C	4	H	6		0		0	G
CCC*C	-0.13	83.45	20.51	30.79	41.82	46.85	55.10	58.89	T 6/83	C	4	H	8		0		0	G
C5	234.00	138.26	14.70	18.97	22.23	23.48	25.05	25.85	J12/69	C	5	0	0	0	0	0	0	G
C6H	233.20	167.88	21.67	27.63	31.84	33.20	35.59	37.07		C	6	H	1					G
C6H2	162.61	133.69	21.42	28.87	34.59	36.75	40.66	42.84		C	6	H	2					G
CC6H6	19.82	64.32	19.70	32.80	45.10	50.20	57.30	61.11		C	6	H	6		0		0	G
C*CC*CC*C	37.95	79.13	28.11	36.35	50.44	58.05	66.38	74.10		C	6	H	8	CL	0	0	0	G
C6H9	50.85	87.74	27.73	36.89	52.44	60.88	70.59	79.59		C	6	H	9	CL	0	0	0	G
CC6H7	56.05	44.94	27.42	35.43	49.17	56.53	64.28	71.40		C	6	H	7	CL	0	0	0	G
CC6H8	25.86	46.76	23.26	33.10	50.20	59.16	67.11	74.19		C	6	H	8	CL	0	0	0	G
CC6H9	41.36	76.65	25.45	35.64	53.03	62.41	72.71	82.19		C	6	H	9	CL	0	0	0	G
C8H	287.40	217.28	26.38	35.08	41.21	43.17	46.28	48.30		C	8	H	1	CL	0	0	0	G
C8H2	216.83	209.94	28.65	38.25	44.79	46.89	50.67	52.92		C	8	H	2	CL	0	0	0	G
CC6H5C6H5	37.90	106.45	35.73	59.45	81.17	90.06	96.67	103.62		C	12	H	10	CL	0	0	0	G
CHCL	71.00	56.17	8.80	10.13	12.11	13.22	14.78	14.96		C	1	H	1	CL	1	0	0	G

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CCL          103.29    53.64     7.72     8.28     8.69     8.81     8.98     9.07              C   1 H   0 CL  1 0    0 G
CH2CL         29.10    59.60     9.32    11.14    14.10    15.83    18.31    18.93              C   1 H   2 CL  1 0    0 G
CCL2          38.98    48.94    11.09    12.52    13.61    14.09    15.41    15.84              C   1 H   0 CL  2 0    0 G
CHCL2         25.70    67.40    13.11    14.68    16.83    17.98    19.80    21.20              C   1 H   1 CL  2 0    0 G
CCL3          19.00    71.01    15.25    17.53    18.89    19.14    19.56    19.69              C   1 H   0 CL  3 0    0 G
CH3CL        -19.59    56.01     9.77    13.20    17.02    18.87    21.80    23.40              C   1 H   3 CL  1 0    0 G
CH2CL2       -22.80    64.59    12.26    15.88    19.36    20.81    22.90    24.00              C   1 H   2 CL  2 0    0 G
CHCL3        -24.20    70.66    15.77    19.31    21.96    22.82    24.21    24.60              C   1 H   1 CL  3 0    0 G
CCL4         -22.90    74.22    19.90    23.00    24.60    25.00    25.51    25.80              C   1 H   0 CL  4 0    0 G
C2CL         125.99    59.33    11.51    12.43    13.50    14.04    15.01    15.90              C   2 H   0 CL  1 0    0 G
C2HCL         46.90    58.10    13.17    15.18    16.88    17.55    18.80    19.55              C   2 H   1 CL  1 0    0 G
C2CL2         39.87    63.96    15.79    17.42    18.76    19.23    19.90    20.10              C   2 H   0 CL  2 0    0 G
CHCLCCL       58.63    70.65    17.52    22.16    25.74    26.90    28.60    29.86              C   2 H   1 CL  2 0    0 G
CCL2CH        58.20    68.88    17.52    22.16    25.74    26.90    28.60    29.86              C   2 H   1 CL  2 0    0 G
C2CL3         56.47    78.91    20.90    25.21    28.10    28.80    29.70    30.50              C   2 H   0 CL  3 0    0 G
C2H3CL         8.40    63.09    12.33    17.73    22.47    24.26    26.88    28.80              C   2 H   3 CL  1 0    0 G
CHCLCHCL       1.14    69.25    15.81    20.56    24.68    26.19    28.21    29.60              C   2 H   2 CL  2 0    0 G
CH2CCL2        0.57    69.25    15.81    20.56    24.68    26.19    28.21    29.60              C   2 H   2 CL  2 0    0 G
CHCLCH        61.83    64.46    11.39    16.35    21.23    23.38    26.87    28.80              C   2 H   2 CL  1 0    0 G
CH2CCL        60.40    64.46    11.39    16.35    21.23    23.38    26.87    28.80              C   2 H   2 CL  1 0    0 G
C2HCL3        -1.44    77.52    19.22    23.75    26.80    27.60    28.98    30.10              C   2 H   1 CL  3 0    0 G
C2CL4         -3.40    81.48    22.73    26.72    29.27    30.04    30.52    31.79              C   2 H   0 CL  4 0    0 G
CH2CLCH2      17.51    67.31    14.10    19.79    25.42    27.99    32.50    34.70              C   2 H   4 CL  1 0    0 G
CH3CHCL       16.80    67.31    14.10    19.79    25.42    27.99    32.50    34.70              C   2 H   4 CL  1 0    0 G
CH3CCL2       13.40    73.60    17.28    22.86    28.09    30.18    33.09    35.01              C   2 H   3 CL  2 0    0 G
CH2CLCHCL     11.40    75.80    16.81    22.56    27.67    29.75    33.21    34.50              C   2 H   3 CL  2 0    0 G
CHCL2CH2      15.90    74.30    17.35    22.95    28.03    30.29    33.07    34.55              C   2 H   3 CL  2 0    0 G
C2H2CL3        9.66    82.98    20.21    25.68    30.14    31.77    34.50    36.10              C   2 H   2 CL  3 0    0 G
CCL3CH2       12.10    82.90    20.21    25.68    30.14    31.77    34.50    36.10              C   2 H   2 CL  3 0    0 G
C2HCL4         9.46    89.16    23.89    28.93    32.65    33.84    35.80    36.40              C   2 H   1 CL  4 0    0 G
C2CL5          7.45    92.04    27.59    32.22    35.37    36.12    36.87    37.30              C   2 H   0 CL  5 0    0 G
C2H5CL       -26.72    66.03    15.06    21.67    28.43    31.47    36.27    39.17              C   2 H   5 CL  1 0    0 G
C2H4CL2      -31.05    72.89    18.29    24.81    30.87    33.44    37.80    40.16              C   2 H   4 CL  2 0    0 G
C2H4CLCL     -31.01    73.78    18.99    24.74    30.32    33.06    38.79    40.77              C   2 H   4 CL  2 0    0 G
CH3CCL3      -30.90    78.60    22.52    28.45    33.70    35.73    38.91    41.60              C   2 H   3 CL  3 0    0 G
C2H3CLCL2    -31.40    81.50    21.01    27.67    33.26    35.36    38.91    41.60              C   2 H   3 CL  3 0    0 G
C2H2CL4      -37.25    85.86    25.23    31.32    36.05    37.59    39.82    41.10              C   2 H   2 CL  4 0    0 G
C2HCL5       -34.00    90.97    28.24    34.36    38.55    39.82    40.51    41.10              C   2 H   1 CL  5 0    0 G
C2CL6        -33.86    94.58    32.69    38.24    41.38    42.05    44.17    46.20              C   2 H   0 CL  6 0    0 G
PHCL2          7.11    81.45    27.76    40.24    50.56    54.64    56.08    59.53              C   6 H   4 CL  2 0    0 G
CC6H5CL       12.35    74.78    23.26    36.50    47.90    52.45    82.72   226.25              C   6 H   5 CL  1 0    0 G
PHPHCL        38.39   113.80    39.89    63.19    83.83    92.05   140.20   366.27              C  12 H   9 CL  1 0    0 G
PHCLPHCL      38.88   121.14    44.05    66.98    86.49    94.04   144.90   390.72              C  12 H   8 CL  2 0    0 G
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APPENDIX D4. "MECHANINFO"

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P= 1.00ATM     KEQ IN MOLE CC UNITS

REACTION #  1     C2H3CLCL2=CHCLCHCL+HCL
DELTA N =   1   DELTA H(T =  800. K)=  1.037E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.239E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.153E+02     DELTA H=-0.269E+05
          T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
       800.        0.878E+04        0.421E+01      0.172795E+02     0.53E+01          0.74E-02        0.27E-01
       900.        0.844E+04        0.401E+01      0.564751E-01     0.81E+00          0.35E+00        0.72E+00
      1000.        0.809E+04        0.382E+01      0.783880E+00     0.18E+00          0.78E+01        0.99E+01

REACTION #  2     C2H3CLCL2=CH2CCL2+HCL
DELTA N =   1   DELTA H(T =  800. K)=  9.797E+03 CAL/MOLE     DELTA S (T =  800. K) =  3.239E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.403E+01     DELTA H= 0.790E+04
          T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
       800.        0.821E+04        0.421E+01      0.386618E+00     0.39E+00          0.37E-02        0.96E-02
       900.        0.787E+04        0.401E+01      0.678715E+00     0.67E+00          0.18E+00        0.26E+00
      1000.        0.752E+04        0.382E+01      0.104429E+01     0.10E+01          0.39E+01        0.37E+01

REACTION #  3     C2H3CLCL2=CH2CLCHCL+CL
DELTA N =   1   DELTA H(T =  800. K)=  7.178E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.412E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.496E+01     DELTA H= 0.700E+05
          T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
       800.        0.702E+05        0.508E+01      0.105582E-16     0.11E-16          0.15E-05        0.14E+12
       900.        0.700E+05        0.495E+01      0.141915E-14     0.14E-14          0.35E-03        0.24E+12
      1000.        0.697E+05        0.482E+01      0.706699E-13     0.71E-13          0.27E-01        0.38E+12

REACTION #  4     C2H3CLCL2=CHCL2CH2+CL
DELTA N =   1   DELTA H(T =  800. K)=  7.648E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.302E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.443E+01     DELTA H= 0.748E+05
          T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
       800.        0.749E+05        0.452E+01      0.315342E-18     0.32E-18          0.91E-07        0.29E+12
       900.        0.747E+05        0.442E+01      0.589511E-16     0.59E-16          0.27E-04        0.46E+12
      1000.        0.745E+05        0.432E+01      0.383243E-14     0.38E-14          0.26E-02        0.67E+12

REACTION #  5     C2H3CLCL2=CH2CL+CHCL2
DELTA N =   1   DELTA H(T =  800. K)=  8.535E+04 CAL/MOLE     DELTA S (T =  800. K) =  4.420E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.993E+01     DELTA H= 0.834E+05
          T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
       800.        0.838E+05        0.102E+02      0.330431E-18     0.33E-18          0.19E-06        0.57E+12
       900.        0.833E+05        0.990E+01      0.113927E-15     0.11E-15          0.95E-04        0.84E+12
      1000.        0.830E+05        0.971E+01      0.119408E-13     0.12E-13          0.14E-01        0.12E+13

REACTION #  6     C2H4CLCL=C2H3CL+HCL
DELTA N =   1   DELTA H(T =  800. K)=  1.728E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.386E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.480E+01     DELTA H= 0.154E+05
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      T          EF-EREV         LN AF/AREV          KEQ            KEQ FIT            K FORWARD      K REVERSE
     800.        0.157E+05       0.495E+01       0.728514E-02      0.73E-02            0.14E-01       0.20E+01
     900.        0.154E+05       0.479E+01       0.216333E-01      0.22E-01            0.69E+00       0.32E+02
    1000.        0.151E+05       0.463E+01       0.508558E-01      0.51E-01            0.15E+02       0.30E+03

REACTION #  7      C2H4CLCL=CH2CLCH2+CL
DELTA N =   1   DELTA H(T =  800. K)=  7.760E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.343E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.465E+01     DELTA H= 0.759E+05
      T          EF-EREV         LN AF/AREV          KEQ            KEQ FIT            K FORWARD      K REVERSE
     800.        0.760E+05       0.473E+01       0.191820E-18      0.19E-18            0.10E-05       0.54E+13
     900.        0.759E+05       0.464E+01       0.388223E-16      0.39E-16            0.27E-03       0.70E+13
    1000.        0.757E+05       0.455E+01       0.269200E-14      0.27E-14            0.23E-01       0.87E+13

REACTION #  8      C2H4CLCL=2CH2CL
DELTA N =   1   DELTA H(T =  800. K)=  8.809E+04 CAL/MOLE     DELTA S (T =  800. K) =  4.343E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.956E+01     DELTA H= 0.862E+05
      T          EF-EREV         LN AF/AREV          KEQ            KEQ FIT            K FORWARD      K REVERSE
     800.        0.865E+05       0.976E+01       0.398965E-19      0.40E-19            0.18E-06       0.46E+13
     900.        0.861E+05       0.953E+01       0.166778E-16      0.17E-16            0.90E-04       0.54E+13
    1000.        0.858E+05       0.934E+01       0.204186E-14      0.21E-14            0.13E-01       0.63E+13

REACTION #  9      C2H4CL2=C2H3CL+HCL
DELTA N =   1   DELTA H(T =  800. K)=  1.726E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.474E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.522E+01     DELTA H= 0.154E+05
      T          EF-EREV         LN AF/AREV          KEQ            KEQ FIT            K FORWARD      K REVERSE
     800.        0.157E+05       0.539E+01       0.115016E-01      0.12E-01            0.22E-01       0.19E+01
     900.        0.154E+05       0.520E+01       0.340539E-01      0.34E-01            0.10E+01       0.29E+02
    1000.        0.150E+05       0.502E+01       0.796409E-01      0.80E-01            0.21E+02       0.27E+03

REACTION # 10      C2H4CL2=CH3CHCL+CL
DELTA N =   1   DELTA H(T =  800. K)=  7.688E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.432E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.507E+01     DELTA H= 0.751E+05
      T          EF-EREV         LN AF/AREV          KEQ            KEQ FIT            K FORWARD      K REVERSE
     800.        0.753E+05       0.518E+01       0.473343E-18      0.47E-18            0.96E-05       0.20E+14
     900.        0.751E+05       0.506E+01       0.908941E-16      0.90E-16            0.18E-02       0.20E+14
    1000.        0.749E+05       0.494E+01       0.602616E-14      0.60E-14            0.12E+00       0.20E+14

REACTION # 11      C2H4CL2=CH3+CHCL2
DELTA N =   1   DELTA H(T =  800. K)=  9.213E+04 CAL/MOLE     DELTA S (T =  800. K) =  4.190E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.882E+01     DELTA H= 0.903E+05
      T          EF-EREV         LN AF/AREV          KEQ            KEQ FIT            K FORWARD      K REVERSE
     800.        0.905E+05       0.900E+01       0.145626E-20      0.15E-20            0.19E-07       0.13E+14
     900.        0.902E+05       0.880E+01       0.809576E-18      0.80E-18            0.11E-04       0.14E+14
    1000.        0.899E+05       0.863E+01       0.124823E-15      0.13E-15            0.18E-02       0.14E+14

REACTION # 12      C2H5CL=C2H4+HCL
DELTA N =   1   DELTA H(T =  800. K)=  1.724E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.133E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.350E+01     DELTA H= 0.154E+05
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       T          EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
     800.        0.157E+05         0.368E+01       0.209581E-02       0.21E-02          0.63E-02       0.30E+01
     900.        0.153E+05         0.349E+01       0.619535E-02       0.62E-02          0.35E+00       0.56E+02
    1000.        0.150E+05         0.331E+01       0.144750E-01       0.15E-01          0.86E+01       0.60E+03

REACTION # 13     C2H5CL=C2H5+CL
DELTA N =   1    DELTA H(T =  800. K)=  8.432E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.232E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.405E+01     DELTA H= 0.826E+05
       T          EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
     800.        0.827E+05         0.418E+01       0.159944E-20       0.16E-20          0.17E-07       0.11E+14
     900.        0.825E+05         0.404E+01       0.516563E-18       0.51E-18          0.58E-05       0.11E+14
    1000.        0.823E+05         0.391E+01       0.518487E-16       0.52E-16          0.61E-03       0.12E+14

REACTION # 14     C2H5CL=CH3+CH2CL
DELTA N =   1    DELTA H(T =  800. K)=  9.100E+04 CAL/MOLE     DELTA S (T =  800. K) =  4.055E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.813E+01     DELTA H= 0.891E+05
       T          EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
     800.        0.894E+05         0.832E+01       0.150080E-20       0.15E-20          0.23E-07       0.15E+14
     900.        0.891E+05         0.811E+01       0.770401E-18       0.76E-18          0.13E-04       0.16E+14
    1000.        0.887E+05         0.792E+01       0.111295E-15       0.11E-15          0.20E-02       0.18E+14

REACTION # 15     C2H6=C2H5+H
DELTA N =   1    DELTA H(T =  800. K)=  1.023E+05 CAL/MOLE     DELTA S (T =  800. K) =  3.378E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.491E+01     DELTA H= 0.101E+06
       T          EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
     800.        0.101E+06         0.491E+01       0.415871E-25       0.42E-25          0.63E-11       0.15E+15
     900.        0.101E+06         0.490E+01       0.474489E-22       0.47E-22          0.63E-08       0.13E+15
    1000.        0.101E+06         0.488E+01       0.132220E-19       0.13E-19          0.16E-05       0.12E+15

REACTION # 16     C2H6=2CH3
DELTA N =   1    DELTA H(T =  800. K)=  9.172E+04 CAL/MOLE     DELTA S (T =  800. K) =  4.090E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.837E+01     DELTA H= 0.899E+05
       T          EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
     800.        0.901E+05         0.849E+01       0.114146E-20       0.11E-20          0.37E-08       0.32E+13
     900.        0.899E+05         0.835E+01       0.618528E-18       0.62E-18          0.35E-05       0.57E+13
    1000.        0.896E+05         0.820E+01       0.937849E-16       0.94E-16          0.85E-03       0.91E+13

REACTION # 17     CH2CLCHCL=C2H3CL+CL
DELTA N =   1    DELTA H(T =  800. K)=  2.613E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.730E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.155E+01     DELTA H= 0.244E+05
       T          EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
     800.        0.245E+05         0.165E+01       0.102435E-05       0.10E-05          0.44E+07       0.43E+13
     900.        0.244E+05         0.154E+01       0.566286E-05       0.56E-05          0.30E+08       0.53E+13
    1000.        0.241E+05         0.142E+01       0.219904E-04       0.22E-04          0.14E+09       0.63E+13

REACTION # 18     CHCL2CH2=C2H3CL+CL
DELTA N =   1    DELTA H(T =  800. K)=  2.144E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.841E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.208E+01     DELTA H= 0.196E+05
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       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT         K FORWARD     K REVERSE
      800.       0.198E+05       0.220E+01      0.342969E-04     0.34E-04         0.75E+08      0.22E+13
      900.       0.196E+05       0.206E+01      0.136324E-03     0.14E-03         0.37E+09      0.27E+13
     1000.       0.194E+05       0.193E+01      0.405503E-03     0.41E-03         0.13E+10      0.33E+13

REACTION # 19      CH2CLCH2=C2H4+CL
DELTA N =   1   DELTA H(T =  800. K)=  2.416E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.516E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.457E+00      DELTA H= 0.224E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT         K FORWARD     K REVERSE
      800.       0.226E+05       0.569E+00      0.120367E-05     0.12E-05         0.50E+08      0.41E+14
      900.       0.224E+05       0.446E+00      0.579339E-05     0.58E-05         0.27E+09      0.46E+14
     1000.       0.221E+05       0.330E+00      0.201228E-04     0.20E-04         0.10E+10      0.50E+14

REACTION # 20      CH3CHCL=C2H3CL+H
DELTA N =   1   DELTA H(T =  800. K)=  4.505E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.592E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.946E+00      DELTA H= 0.435E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT         K FORWARD     K REVERSE
      800.       0.435E+05       0.952E+00      0.344248E-11     0.34E-11         0.33E+01      0.96E+12
      900.       0.434E+05       0.943E+00      0.718817E-10     0.72E-10         0.90E+02      0.13E+13
     1000.       0.434E+05       0.914E+00      0.815807E-09     0.82E-09         0.13E+04      0.16E+13

REACTION # 21      C2H5=C2H4+H
DELTA N =   1   DELTA H(T =  800. K)=  3.758E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.451E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.247E+00      DELTA H= 0.360E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT         K FORWARD     K REVERSE
      800.       0.360E+05       0.241E+00      0.185641E-09     0.19E-09         0.34E+03      0.18E+13
      900.       0.360E+05       0.244E+00      0.230108E-08     0.23E-08         0.58E+04      0.25E+13
     1000.       0.360E+05       0.234E+00      0.172335E-07     0.17E-07         0.58E+05      0.33E+13

REACTION # 22      C2H3=C2H2+H
DELTA N =   1   DELTA H(T =  800. K)=  4.117E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.321E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.353E+00      DELTA H= 0.397E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT         K FORWARD     K REVERSE
      800.       0.396E+05      -0.410E+00      0.101583E-10     0.10E-10         0.11E+03      0.11E+14
      900.       0.397E+05      -0.352E+00      0.162270E-09     0.16E-09         0.16E+04      0.97E+13
     1000.       0.397E+05      -0.316E+00      0.149616E-08     0.15E-08         0.13E+05      0.90E+13

REACTION # 23      CH2CLCHCL+H2=C2H4CLCL+H
DELTA N =   0   DELTA H(T =  800. K)=  9.810E+03 CAL/MOLE     DELTA S (T =  800. K) = -5.640E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.280E+01      DELTA H= 0.988E+04
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT         K FORWARD     K REVERSE
      800.       0.981E+04      -0.284E+01      0.121790E-03     0.12E-03         0.60E+08      0.50E+12
      900.       0.987E+04      -0.280E+01      0.242320E-03     0.24E-03         0.21E+09      0.88E+12
     1000.       0.997E+04      -0.275E+01      0.421971E-03     0.42E-03         0.58E+09      0.14E+13

REACTION # 24      CH3CHCL+H2=C2H5CL+H
DELTA N =   0   DELTA H(T =  800. K)=  8.586E+03 CAL/MOLE     DELTA S (T =  800. K) = -5.262E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.259E+01      DELTA H= 0.868E+04
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        T          EF-EREV        LN AF/AREV         KEQ            KEQ FIT           K FORWARD     K REVERSE
      800.        0.859E+04       -0.265E+01      0.318269E-03      0.32E-03           0.10E+09      0.31E+12
      900.        0.869E+04       -0.259E+01      0.582012E-03      0.58E-03           0.33E+09      0.57E+12
     1000.        0.880E+04       -0.253E+01      0.949052E-03      0.95E-03           0.87E+09      0.92E+12

REACTION # 25     CH2CLCH2+H2=C2H5CL+H
DELTA N =   0   DELTA H(T =  800. K)=  7.876E+03 CAL/MOLE     DELTA S (T =  800. K) = -5.262E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.259E+01     DELTA H= 0.797E+04
        T          EF-EREV        LN AF/AREV         KEQ            KEQ FIT           K FORWARD     K REVERSE
      800.        0.788E+04       -0.265E+01      0.497459E-03      0.50E-03           0.21E+09      0.41E+12
      900.        0.798E+04       -0.259E+01      0.865652E-03      0.87E-03           0.62E+09      0.71E+12
     1000.        0.809E+04       -0.253E+01      0.135663E-02      0.14E-02           0.15E+10      0.11E+13

REACTION # 26     CHCL2CH2+H2=C2H4CL2+H
DELTA N =   0   DELTA H(T =  800. K)=  5.130E+03 CAL/MOLE     DELTA S (T =  800. K) = -5.423E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.269E+01     DELTA H= 0.520E+04
        T          EF-EREV        LN AF/AREV         KEQ            KEQ FIT           K FORWARD     K REVERSE
      800.        0.513E+04       -0.273E+01      0.258284E-02      0.26E-02           0.42E+09      0.16E+12
      900.        0.520E+04       -0.269E+01      0.370580E-02      0.37E-02           0.12E+10      0.32E+12
     1000.        0.529E+04       -0.264E+01      0.496875E-02      0.50E-02           0.28E+10      0.56E+12

REACTION # 27     C2H2CL3+H2=C2H3CLCL2+H
DELTA N =   0   DELTA H(T =  800. K)=  1.108E+04 CAL/MOLE     DELTA S (T =  800. K) = -5.406E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.266E+01     DELTA H= 0.112E+05
        T          EF-EREV        LN AF/AREV         KEQ            KEQ FIT           K FORWARD     K REVERSE
      800.        0.111E+05       -0.272E+01      0.614702E-04      0.61E-04           0.60E+08      0.98E+12
      900.        0.112E+05       -0.266E+01      0.133909E-03      0.13E-03           0.21E+09      0.16E+13
     1000.        0.113E+05       -0.259E+01      0.251316E-03      0.25E-03           0.58E+09      0.23E+13

REACTION # 28     C2H3CLCL2+H=CH2CLCHCL+HCL
DELTA N =   0   DELTA H(T =  800. K)= -3.288E+04 CAL/MOLE     DELTA S (T =  800. K) =  8.623E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.416E+01     DELTA H=-0.332E+05
        T          EF-EREV        LN AF/AREV         KEQ            KEQ FIT           K FORWARD     K REVERSE
      800.       -0.329E+05        0.434E+01      0.745244E+11      0.75E+11           0.98E+12      0.13E+02
      900.       -0.332E+05        0.415E+01      0.739675E+10      0.73E+10           0.14E+13      0.18E+03
     1000.       -0.335E+05        0.398E+01      0.114483E+10      0.11E+10           0.18E+13      0.16E+04

REACTION # 29     C2H4CL2+H=CH3CHCL+HCL
DELTA N =   0   DELTA H(T =  800. K)= -2.779E+04 CAL/MOLE     DELTA S (T =  800. K) =  8.824E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.427E+01     DELTA H=-0.281E+05
        T          EF-EREV        LN AF/AREV         KEQ            KEQ FIT           K FORWARD     K REVERSE
      800.       -0.278E+05        0.444E+01      0.334108E+10      0.34E+10           0.40E+12      0.12E+03
      900.       -0.281E+05        0.426E+01      0.473749E+09      0.47E+09           0.62E+12      0.13E+04
     1000.       -0.284E+05        0.410E+01      0.976222E+08      0.98E+08           0.88E+12      0.90E+04

REACTION # 30     C2H4CLCL+H=CH2CLCH2+HCL
DELTA N =   0   DELTA H(T =  800. K)= -2.706E+04 CAL/MOLE     DELTA S (T =  800. K) =  7.937E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.385E+01     DELTA H
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         T           EF-EREV          LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
       800.       -0.271E+05        0.399E+01       0.135395E+10     0.14E+10          0.50E+12       0.37E+03
       900.       -0.273E+05        0.384E+01       0.202346E+09     0.20E+09          0.79E+12       0.39E+04
      1000.       -0.276E+05        0.371E+01       0.436097E+08     0.44E+08          0.11E+13       0.26E+05

REACTION # 31      C2H5CL+H=C2H5+HCL
DELTA N =    0    DELTA H(T =   800. K)= -2.034E+04 CAL/MOLE      DELTA S (T =  800. K) =  6.826E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.325E+01      DELTA H=-0.206E+05
         T           EF-EREV          LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
       800.       -0.203E+05        0.344E+01       0.112896E+08     0.11E+08          0.98E+11       0.87E+04
       900.       -0.207E+05        0.324E+01       0.269237E+07     0.27E+07          0.17E+12       0.64E+05
      1000.       -0.210E+05        0.307E+01       0.839936E+06     0.84E+06          0.27E+12       0.32E+06

REACTION # 32      C2H6+H=C2H5+H2
DELTA N =    0    DELTA H(T =   800. K)= -3.357E+03 CAL/MOLE      DELTA S (T =  800. K) =  7.375E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.366E+01      DELTA H=-0.345E+04
         T           EF-EREV          LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
       800.       -0.336E+04        0.371E+01       0.338898E+03     0.34E+03          0.15E+12       0.44E+09
       900.       -0.346E+04        0.365E+01       0.267154E+03     0.27E+03          0.29E+12       0.11E+10
      1000.       -0.358E+04        0.359E+01       0.219490E+03     0.22E+03          0.50E+12       0.23E+10

REACTION # 33      C2H4+H=C2H3+H2
DELTA N =    0    DELTA H(T =   800. K)=  2.827E+03 CAL/MOLE      DELTA S (T =  800. K) =  8.650E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.430E+01      DELTA H= 0.274E+04
         T           EF-EREV          LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
       800.        0.283E+04        0.435E+01       0.131391E+02     0.13E+02          0.29E+11       0.22E+10
       900.        0.273E+04        0.430E+01       0.159639E+02     0.16E+02          0.60E+11       0.38E+10
      1000.        0.260E+04        0.423E+01       0.185367E+02     0.19E+02          0.11E+12       0.58E+10

REACTION # 34      C2H2+H=C2H+H2
DELTA N =    0    DELTA H(T =   800. K)=  2.524E+04 CAL/MOLE      DELTA S (T =  800. K) =  4.662E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.225E+01      DELTA H= 0.251E+05
         T           EF-EREV          LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
       800.        0.252E+05        0.235E+01       0.132365E-05     0.13E-05          0.13E+10       0.97E+15
       900.        0.251E+05        0.225E+01       0.768633E-05     0.77E-05          0.49E+10       0.63E+15
      1000.        0.249E+05        0.215E+01       0.310852E-04     0.31E-04          0.14E+11       0.45E+15

REACTION # 35      C2H3CLCL2+CL=C2H2CL3+HCL
DELTA N =    0    DELTA H(T =   800. K)= -1.013E+04 CAL/MOLE      DELTA S (T =  800. K) =  6.318E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.311E+01      DELTA H=-0.102E+05
         T           EF-EREV          LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
       800.       -0.101E+05        0.318E+01       0.140908E+05     0.14E+05          0.73E+13       0.52E+09
       900.       -0.102E+05        0.311E+01       0.691299E+04     0.69E+04          0.76E+13       0.11E+10
      1000.       -0.104E+05        0.304E+01       0.388301E+04     0.39E+04          0.78E+13       0.20E+10

REACTION # 36      CHCL2+H2=CH2CL2+H
DELTA N =    0    DELTA H(T =   800. K)=  3.229E+03 CAL/MOLE      DELTA S (T =  800. K) = -7.646E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.382E+01
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         T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
       800.        0.323E+04      -0.385E+01     0.279071E-02     0.28E-02          0.12E+14      0.42E+16
       900.        0.328E+04      -0.382E+01     0.350296E-02     0.35E-02          0.15E+14      0.43E+16
      1000.        0.333E+04      -0.379E+01     0.421401E-02     0.42E-02          0.18E+14      0.44E+16

REACTION # 37     CH2CL2=CH2CL+CL
DELTA N =   1   DELTA H(T =  800. K)=  8.111E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.536E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.561E+01     DELTA H= 0.794E+05
         T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
       800.        0.795E+05       0.570E+01     0.556338E-19     0.56E-19          0.69E-06      0.12E+14
       900.        0.793E+05       0.559E+01     0.143711E-16     0.14E-16          0.13E-03      0.88E+13
      1000.        0.792E+05       0.550E+01     0.121008E-14     0.12E-14          0.82E-02      0.68E+13

REACTION # 38     CH2CL2=CHCL+HCL
DELTA N =   1   DELTA H(T =  800. K)=  7.229E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.762E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.674E+01     DELTA H= 0.706E+05
         T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
       800.        0.707E+05       0.684E+01     0.447058E-16     0.45E-16          0.25E-14      0.55E+02
       900.        0.705E+05       0.673E+01     0.623306E-14     0.62E-14          0.38E-11      0.61E+03
      1000.        0.703E+05       0.662E+01     0.320092E-12     0.32E-12          0.13E-08      0.42E+04

REACTION # 39     CH2CL2+H=CH2CL+HCL
DELTA N =   0   DELTA H(T =  800. K)= -2.356E+04 CAL/MOLE     DELTA S (T =  800. K) =  9.859E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.481E+01     DELTA H=-0.238E+05
         T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
       800.       -0.236E+05       0.496E+01     0.392689E+09     0.39E+09          0.24E+12      0.60E+03
       900.       -0.238E+05       0.479E+01     0.749037E+08     0.74E+08          0.36E+12      0.48E+04
      1000.       -0.241E+05       0.466E+01     0.196030E+08     0.20E+08          0.51E+12      0.26E+05

REACTION # 40     CH2CL+H2=CH3CL+H
DELTA N =   0   DELTA H(T =  800. K)=  3.437E+03 CAL/MOLE     DELTA S (T =  800. K) = -7.567E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.376E+01     DELTA H= 0.351E+04
         T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
       800.        0.344E+04      -0.381E+01     0.254673E-02     0.25E-02          0.43E+09      0.17E+12
       900.        0.352E+04      -0.376E+01     0.324745E-02     0.33E-02          0.11E+10      0.35E+12
      1000.        0.360E+04      -0.372E+01     0.396255E-02     0.40E-02          0.25E+10      0.63E+12

REACTION # 41     CH3CL=CH3+CL
DELTA N =   1   DELTA H(T =  800. K)=  8.495E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.286E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.440E+01     DELTA H= 0.833E+05
         T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD     K REVERSE
       800.        0.834E+05       0.445E+01     0.140947E-20     0.14E-20          0.21E-07      0.15E+14
       900.        0.833E+05       0.439E+01     0.478037E-18     0.48E-18          0.56E-05      0.12E+14
      1000.        0.831E+05       0.432E+01     0.502352E-16     0.50E-16          0.48E-03      0.96E+13

REACTION # 42     CH3CL=CH2+HCL
DELTA N =   1   DELTA H(T =  800. K)=  9.108E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.778E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.682E+01     DELTA H= 0.894E+05
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         T           EF-EREV         LN AF/AREV         KEQ            KEQ FIT           K FORWARD      K REVERSE
       800.         0.895E+05        0.692E+01      0.353370E-21      0.35E-21           0.36E-20       0.10E+02
       900.         0.893E+05        0.681E+01      0.183442E-18      0.18E-18           0.22E-16       0.12E+03
      1000.         0.891E+05        0.669E+01      0.269639E-16      0.27E-16           0.24E-13       0.88E+03

REACTION # 43     CH3CL+H=CH3+HCL
DELTA N =   0   DELTA H(T =  800. K)= -1.971E+04 CAL/MOLE     DELTA S (T =  800. K) =  7.367E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.360E+01     DELTA H=-0.199E+05
         T           EF-EREV         LN AF/AREV         KEQ            KEQ FIT           K FORWARD      K REVERSE
       800.        -0.197E+05        0.371E+01      0.994868E+07      0.10E+08           0.11E+12       0.11E+05
       900.        -0.199E+05        0.359E+01      0.249157E+07      0.25E+07           0.21E+12       0.82E+05
      1000.        -0.201E+05        0.348E+01      0.813796E+06      0.82E+06           0.35E+12       0.42E+06

REACTION # 44     CH4+H=CH3+H2
DELTA N =   0   DELTA H(T =  800. K)=  1.633E+03 CAL/MOLE     DELTA S (T =  800. K) =  7.368E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.369E+01     DELTA H= 0.161E+04
         T           EF-EREV         LN AF/AREV         KEQ            KEQ FIT           K FORWARD      K REVERSE
       800.         0.163E+04        0.371E+01      0.146090E+02      0.15E+02           0.49E+10       0.34E+09
       900.         0.161E+04        0.370E+01      0.163688E+02      0.16E+02           0.11E+11       0.65E+09
      1000.         0.154E+04        0.366E+01      0.178834E+02      0.18E+02           0.20E+11       0.11E+10

REACTION # 45     CH2CCL2=CH2CCL+CL
DELTA N =   1   DELTA H(T =  800. K)=  8.934E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.590E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.599E+01     DELTA H= 0.878E+05
         T           EF-EREV         LN AF/AREV         KEQ            KEQ FIT           K FORWARD      K REVERSE
       800.         0.878E+05        0.597E+01      0.409915E-21      0.41E-21           0.58E-08       0.14E+14
       900.         0.878E+05        0.598E+01      0.189540E-18      0.19E-18           0.28E-05       0.15E+14
      1000.         0.878E+05        0.600E+01      0.257145E-16      0.26E-16           0.40E-03       0.16E+14

REACTION # 46     CH2CCL2=C2HCL+HCL
DELTA N =   1   DELTA H(T =  800. K)=  2.495E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.520E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.548E+01     DELTA H= 0.231E+05
         T           EF-EREV         LN AF/AREV         KEQ            KEQ FIT           K FORWARD      K REVERSE
       800.         0.234E+05        0.562E+01      0.115338E-03      0.12E-03           0.47E-05       0.41E-01
       900.         0.231E+05        0.547E+01      0.585399E-03      0.58E-03           0.59E-03       0.10E+01
      1000.         0.228E+05        0.531E+01      0.211327E-02      0.21E-02           0.28E-01       0.13E+02

REACTION # 47     CH2CCL2+H=CHCL2CH2
DELTA N =  -1   DELTA H(T =  800. K)= -3.798E+04 CAL/MOLE     DELTA S (T =  800. K) = -2.487E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.393E+00     DELTA H=-0.363E+05
         T           EF-EREV         LN AF/AREV         KEQ            KEQ FIT           K FORWARD      K REVERSE
       800.        -0.364E+05       -0.425E+00      0.575719E+10      0.58E+10           0.12E+10       0.21E+00
       900.        -0.363E+05       -0.388E+00      0.452707E+09      0.45E+09           0.11E+10       0.25E+01
      1000.        -0.362E+05       -0.340E+00      0.594510E+08      0.59E+08           0.11E+10       0.18E+02

REACTION # 48     CH2CCL2+H=CH3CCL2
DELTA N =  -1   DELTA H(T =  800. K)= -4.050E+04 CAL/MOLE     DELTA S (T =  800. K) = -2.562E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.771E+00     DELTA H=-0.388E+05
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      T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD     K REVERSE
    800.       -0.389E+05      -0.800E+00      0.193146E+11     0.19E+11          0.10E+12      0.52E+01
    900.       -0.389E+05      -0.766E+00      0.127326E+10     0.13E+10          0.70E+11      0.55E+02
   1000.       -0.388E+05      -0.720E+00      0.145181E+09     0.15E+09          0.53E+11      0.37E+03

REACTION # 49      CH2CCL2+H=C2H3CL+CL
DELTA N =   0    DELTA H(T =   800. K)= -1.655E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.537E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.168E+01      DELTA H=-0.167E+05
      T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD     K REVERSE
    800.       -0.165E+05       0.178E+01      0.197454E+06     0.20E+06          0.69E+12      0.35E+07
    900.       -0.167E+05       0.167E+01      0.617147E+05     0.61E+05          0.11E+13      0.17E+08
   1000.       -0.169E+05       0.159E+01      0.241076E+05     0.24E+05          0.15E+13      0.61E+08

REACTION # 50      CH2CCL2+H=CH2CCL+HCL
DELTA N =   0    DELTA H(T =   800. K)= -1.532E+04 CAL/MOLE     DELTA S (T =  800. K) =  1.040E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.519E+01      DELTA H=-0.154E+05
      T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD     K REVERSE
    800.       -0.153E+05       0.523E+01      0.289337E+07     0.29E+07          0.15E+11      0.53E+04
    900.       -0.154E+05       0.518E+01      0.987902E+06     0.99E+06          0.30E+11      0.30E+05
   1000.       -0.155E+05       0.516E+01      0.416567E+06     0.42E+06          0.50E+11      0.12E+06

REACTION # 51      CH2CCL2+CL=HCL+CCL2CH
DELTA N =   0    DELTA H(T =   800. K)=  8.249E+03 CAL/MOLE     DELTA S (T =  800. K) =  7.897E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.414E+01      DELTA H= 0.852E+04
      T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD     K REVERSE
    800.        0.825E+04       0.397E+01      0.296578E+00     0.30E+00          0.11E+12      0.38E+12
    900.        0.855E+04       0.415E+01      0.533358E+00     0.54E+00          0.19E+12      0.35E+12
   1000.        0.884E+04       0.431E+01      0.867311E+00     0.86E+00          0.28E+12      0.32E+12

REACTION # 52      CCL2CH+H2=CH2CCL2+H
DELTA N =   0    DELTA H(T =   800. K)= -7.291E+03 CAL/MOLE     DELTA S (T =  800. K) = -6.985E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.369E+01      DELTA H=-0.758E+04
      T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD     K REVERSE
    800.       -0.729E+04      -0.352E+01      0.292053E+01     0.29E+01          0.21E+11      0.73E+10
    900.       -0.760E+04      -0.370E+01      0.173563E+01     0.17E+01          0.30E+11      0.17E+11
   1000.       -0.790E+04      -0.386E+01      0.112516E+01     0.11E+01          0.39E+11      0.34E+11

REACTION # 53      CHCLCHCL=CHCLCH+CL
DELTA N =   1    DELTA H(T =   800. K)=  9.020E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.590E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.599E+01      DELTA H= 0.887E+05
      T          EF-EREV        LN AF/AREV          KEQ           KEQ FIT          K FORWARD     K REVERSE
    800.        0.886E+05       0.597E+01      0.238645E-21     0.24E-21          0.24E-08      0.10E+14
    900.        0.886E+05       0.598E+01      0.117183E-18     0.12E-18          0.13E-05      0.11E+14
   1000.        0.887E+05       0.600E+01      0.166811E-16     0.17E-16          0.20E-03      0.12E+14

REACTION # 54      CHCLCHCL=C2HCL+HCL
DELTA N =   1    DELTA H(T =   800. K)=  2.438E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.520E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.
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        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      800.        0.228E+05      0.562E+01      0.165078E-03     0.17E-03        0.46E-05      0.28E-01
      900.        0.225E+05      0.547E+01      0.805131E-03     0.80E-03        0.58E-03      0.72E+00
     1000.        0.222E+05      0.531E+01      0.281532E-02     0.28E-02        0.28E-01      0.98E+01

REACTION # 55     CHCLCHCL+H=CH2CLCHCL
DELTA N =  -1   DELTA H(T =  800. K)= -4.325E+04 CAL/MOLE     DELTA S (T =  800. K) = -2.377E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.136E+00     DELTA H=-0.417E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      800.       -0.417E+05      0.131E+00      0.275888E+12     0.28E+12        0.21E+11      0.76E-01
      900.       -0.416E+05      0.140E+00      0.149888E+11     0.15E+11        0.18E+11      0.12E+01
     1000.       -0.416E+05      0.163E+00      0.146047E+10     0.15E+10        0.15E+11      0.10E+02

REACTION # 56     CHCLCHCL+H=C2H3CL+CL
DELTA N =   0   DELTA H(T =  800. K)= -1.712E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.537E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.168E+01     DELTA H=-0.173E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      800.       -0.171E+05      0.178E+01      0.282606E+06     0.28E+06        0.83E+12      0.29E+07
      900.       -0.173E+05      0.167E+01      0.848796E+05     0.85E+05        0.12E+13      0.14E+08
     1000.       -0.175E+05      0.159E+01      0.321163E+05     0.32E+05        0.16E+13      0.49E+08

REACTION # 57     CHCLCHCL+H=CHCLCH+HCL
DELTA N =   0   DELTA H(T =  800. K)= -1.446E+04 CAL/MOLE     DELTA S (T =  800. K) =  1.040E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.519E+01     DELTA H=-0.145E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      800.       -0.145E+05      0.523E+01      0.168447E+07     0.17E+07        0.25E+11      0.15E+05
      900.       -0.146E+05      0.518E+01      0.610771E+06     0.61E+06        0.49E+11      0.81E+05
     1000.       -0.146E+05      0.516E+01      0.270230E+06     0.27E+06        0.84E+11      0.31E+06

REACTION # 58     CHCLCHCL+CL=HCL+CHCLCCL
DELTA N =   0   DELTA H(T =  800. K)=  8.109E+03 CAL/MOLE     DELTA S (T =  800. K) =  9.666E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.503E+01     DELTA H= 0.838E+04
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      800.        0.811E+04      0.486E+01      0.789256E+00     0.79E+00        0.87E+11      0.11E+12
      900.        0.841E+04      0.504E+01      0.140555E+01     0.14E+01        0.15E+12      0.10E+12
     1000.        0.871E+04      0.520E+01      0.226780E+01     0.23E+01        0.22E+12      0.99E+11

REACTION # 59     CHCLCCL+H2=CHCLCHCL+H
DELTA N =   0   DELTA H(T =  800. K)= -7.151E+03 CAL/MOLE     DELTA S (T =  800. K) = -8.754E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.458E+01     DELTA H=-0.744E+04
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      800.       -0.715E+04     -0.441E+01      0.109745E+01     0.11E+01        0.14E+11      0.13E+11
      900.       -0.746E+04     -0.459E+01      0.658611E+00     0.65E+00        0.22E+11      0.33E+11
     1000.       -0.776E+04     -0.475E+01      0.430314E+00     0.43E+00        0.30E+11      0.70E+11

REACTION # 60     C2H3CL=C2H3+CL
DELTA N =   1   DELTA H(T =  800. K)=  8.827E+04 CAL/MOLE     DELTA S (T =  800. K) =  3.430E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.506E+01     DELTA H= 0.865E+05
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        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT         K FORWARD      K REVERSE
      800.        0.867E+05       0.517E+01      0.360687E-21     0.36E-21         0.48E-08       0.13E+14
      900.        0.865E+05       0.505E+01      0.153641E-18     0.15E-18         0.22E-05       0.14E+14
     1000.        0.863E+05       0.493E+01      0.192684E-16     0.19E-16         0.29E-03       0.15E+14

REACTION # 61     C2H3CL=C2H2+HCL
DELTA N =   1    DELTA H(T =  800. K)=  2.477E+04 CAL/MOLE      DELTA S (T =  800. K) =  3.201E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.391E+01      DELTA H= 0.230E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT         K FORWARD      K REVERSE
      800.        0.232E+05       0.402E+01      0.258620E-04     0.26E-04         0.59E-05       0.23E+00
      900.        0.230E+05       0.390E+01      0.129944E-03     0.13E-03         0.72E-03       0.56E+01
     1000.        0.227E+05       0.378E+01      0.467016E-03     0.47E-03         0.34E-01       0.72E+02

REACTION # 62     C2H3CL+H=C2H3+HCL
DELTA N =   0    DELTA H(T =  800. K)= -1.640E+04 CAL/MOLE      DELTA S (T =  800. K) =  8.801E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.426E+01      DELTA H=-0.167E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT         K FORWARD      K REVERSE
      800.       -0.164E+05       0.443E+01      0.254590E+07     0.26E+07         0.17E+12       0.66E+05
      900.       -0.167E+05       0.425E+01      0.800789E+06     0.80E+06         0.26E+12       0.33E+06
     1000.       -0.170E+05       0.409E+01      0.312142E+06     0.31E+06         0.38E+12       0.12E+07

REACTION # 63     C2H3CL+H=CH2CLCH2
DELTA N =  -1    DELTA H(T =  800. K)= -4.434E+04 CAL/MOLE      DELTA S (T =  800. K) = -2.592E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.946E+00      DELTA H=-0.428E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT         K FORWARD      K REVERSE
      800.       -0.428E+05      -0.952E+00      0.185851E+12     0.19E+12         0.63E+11       0.34E+00
      900.       -0.427E+05      -0.943E+00      0.935342E+10     0.94E+10         0.53E+11       0.57E+01
     1000.       -0.427E+05      -0.914E+00      0.857516E+09     0.86E+09         0.47E+11       0.54E+02

REACTION # 64     C2H3CL+H=C2H4+CL
DELTA N =   0    DELTA H(T =  800. K)= -2.018E+04 CAL/MOLE      DELTA S (T =  800. K) = -7.607E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.489E+00      DELTA H=-0.204E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT         K FORWARD      K REVERSE
      800.       -0.202E+05      -0.383E+00      0.223704E+06     0.22E+06         0.94E+12       0.42E+07
      900.       -0.204E+05      -0.497E+00      0.541880E+05     0.54E+05         0.12E+13       0.22E+08
     1000.       -0.205E+05      -0.584E+00      0.172557E+05     0.17E+05         0.15E+13       0.85E+08

REACTION # 65     C2H3CL+CL=HCL+CHCLCH
DELTA N =   0    DELTA H(T =  800. K)=  2.655E+03 CAL/MOLE      DELTA S (T =  800. K) =  6.864E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.351E+01      DELTA H= 0.274E+04
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT         K FORWARD      K REVERSE
      800.        0.265E+04       0.345E+01      0.596049E+01     0.60E+01         0.31E+13       0.52E+12
      900.        0.274E+04       0.351E+01      0.719573E+01     0.72E+01         0.38E+13       0.53E+12
     1000.        0.286E+04       0.357E+01      0.841409E+01     0.84E+01         0.45E+13       0.53E+12

REACTION # 66     C2H3CL+CL=HCL+CH2CCL
DELTA N =   0    DELTA H(T =  800. K)=  1.225E+03 CAL/MOLE      DELTA S (T =  800. K) =  6.864E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
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       T           EF-EREV        LN AF/AREV         KEQ            KEQ FIT          K FORWARD     K REVERSE
     800.         0.123E+04       0.345E+01      0.270126E+00      0.46E+00          0.74E+13      0.28E+14
     900.         0.131E+04       0.351E+01      0.160076E+02      0.49E+01          0.83E+13      0.52E+12
    1000.         0.143E+04       0.357E+01      0.172795E+02      0.33E+02          0.91E+13      0.53E+12

REACTION # 67      CH2CCL+H2=C2H3CL+H
DELTA N =   0    DELTA H(T =   800. K)= -2.673E+02 CAL/MOLE     DELTA S (T =   800. K) = -5.952E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.163E+01     DELTA H= 0.897E+03
       T           EF-EREV        LN AF/AREV         KEQ            KEQ FIT          K FORWARD     K REVERSE
     800.        -0.267E+03      -0.300E+01      0.591102E-01      0.11E+00          0.14E+11      0.24E+12
     900.        -0.367E+03      -0.305E+01      0.493484E+00      0.12E+00          0.22E+11      0.44E+11
    1000.        -0.490E+03      -0.312E+01      0.564751E-01      0.12E+00          0.30E+11      0.53E+12

REACTION # 68      CHCLCH+H2=C2H3CL+H
DELTA N =   0    DELTA H(T =   800. K)= -1.697E+03 CAL/MOLE     DELTA S (T =   800. K) = -5.952E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.580E+01     DELTA H= 0.128E+05
       T           EF-EREV        LN AF/AREV         KEQ            KEQ FIT          K FORWARD     K REVERSE
     800.        -0.170E+04      -0.300E+01      0.145318E+00      0.11E+00          0.21E+11      0.15E+12
     900.        -0.180E+04      -0.305E+01      0.128648E+00      0.26E+00          0.30E+11      0.23E+12
    1000.        -0.192E+04      -0.312E+01      0.783880E+00      0.53E+00          0.39E+11      0.49E+11

REACTION # 69      2H+H2=2H2
DELTA N =  -1    DELTA H(T =   800. K)= -1.056E+05 CAL/MOLE     DELTA S (T =   800. K) = -2.641E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N =-0.125E+01     DELTA H=-0.104E+06
       T           EF-EREV        LN AF/AREV         KEQ            KEQ FIT          K FORWARD     K REVERSE
     800.        -0.104E+06      -0.120E+01      0.814910E+28      0.82E+28          0.10E+18      0.12E-10
     900.        -0.104E+06      -0.125E+01      0.563035E+25      0.56E+25          0.10E+18      0.18E-07
    1000.        -0.104E+06      -0.129E+01      0.166004E+23      0.17E+23          0.10E+18      0.60E-05

REACTION # 70      CL2=2CL
DELTA N =   1    DELTA H(T =   800. K)=  5.883E+04 CAL/MOLE     DELTA S (T =   800. K) =  2.782E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.190E+01     DELTA H= 0.572E+05
       T           EF-EREV        LN AF/AREV         KEQ            KEQ FIT          K FORWARD     K REVERSE
     800.         0.572E+05       0.191E+01      0.153202E-14      0.15E-14          0.50E-06      0.32E+09
     900.         0.572E+05       0.189E+01      0.838187E-13      0.84E-13          0.24E-04      0.29E+09
    1000.         0.572E+05       0.187E+01      0.205622E-11      0.21E-11          0.54E-03      0.26E+09

REACTION # 71      HCL=H+CL
DELTA N =   1    DELTA H(T =   800. K)=  1.047E+05 CAL/MOLE     DELTA S (T =   800. K) =  2.550E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.798E+00     DELTA H= 0.103E+06
       T           EF-EREV        LN AF/AREV         KEQ            KEQ FIT          K FORWARD     K REVERSE
     800.         0.103E+06       0.740E+00      0.141674E-27      0.14E-27          0.16E-17      0.11E+11
     900.         0.103E+06       0.797E+00      0.191862E-24      0.19E-24          0.14E-14      0.74E+10
    1000.         0.103E+06       0.839E+00      0.617294E-22      0.62E-22          0.33E-12      0.53E+10

REACTION # 72      CL+H2=HCL+H
DELTA N =   0    DELTA H(T =   800. K)=  9.579E+02 CAL/MOLE     DELTA S (T =   800. K) =  9.120E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.453E+00     DELTA H= 0.948E+03
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          T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT         K FORWARD     K REVERSE
        800.       0.958E+03       0.459E+00     0.866165E+00     0.87E+00         0.17E+13      0.20E+13
        900.       0.945E+03       0.451E+00     0.925714E+00     0.93E+00         0.25E+13      0.27E+13
       1000.       0.942E+03       0.450E+00     0.975864E+00     0.98E+00         0.33E+13      0.34E+13

REACTION # 73     H+CL2=HCL+CL
DELTA N =   0   DELTA H(T =  800. K)= -4.583E+04 CAL/MOLE     DELTA S (T =  800. K) =  2.321E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  800. TO 1000.  DELTA S/R - DELTA N = 0.110E+01     DELTA H=-0.460E+05
          T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT         K FORWARD     K REVERSE
        800.      -0.458E+05       0.117E+01     0.108137E+14     0.11E+14         0.19E+13      0.18E+00
        900.      -0.460E+05       0.110E+01     0.436871E+12     0.44E+12         0.21E+13      0.48E+01
       1000.      -0.461E+05       0.104E+01     0.333102E+11     0.33E+11         0.23E+13      0.68E+02
ND
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