ABSTRACT

Title of Thesis: Thermal Decomposition of 1,1,1-trichloroethane-Methane-Oxygen Mixture in Tubular Flow Reactor

Yo-ping Wu, Master of Science in Chemical Engineering, 1989

Thesis Directed by Dr. J. W. Bozzelli

The thermal decomposition of 1,1,1-trichloroethane in methane/oxygen mixtures and argon bath gas was carried out at 1 atmosphere total pressure in a tubular flow reactors. The thermal degradation of 1,1,1-trichloroethane and methane were analyzed systematically over temperature ranges from 500 to 800^{o}C, with average residence times in the range of 0.05 to 2.5 seconds. Five reactants ratio sets in three different size flow reactors were studied.

It was found that the complete decay (99%) of the 1,1,1-trichloroethane at 1 second residence time occurs at about 600^{o}C for all the reactants ratio sets. The major product for 1,1,1-trichloroethane decomposition are 1,1-dichloroethylene and HCl. Oxygen has almost no effect on the decay of 1,1,1-trichloroethane in our study. Formation of CH_2CCl_2 as one of major product from CH_3CCl_3 increases with increasing temperature to a maximum near 600^{o}C at 1.0 sec residence time and is independent of reactant ratio here. It then drops quickly with increasing temperature and increased O_2. Faster decay of compounds, such as C_2H_3Cl, C_2H_2, C_2H_4, C_3H_6+ C_3H_8 formed at lower temperature occurs when the reactor temperature is above 650^{o}C, and higher oxygen levels in the mixture. The higher ratio of O_2 to

CH_4, the lower the temperature needed to observe formation of CO and CO_2. The major products at temperatures above 750°C are HCl and non-chlorinated hydrocarbons: C_2H_2, C_2H_4, C_3H_6, C_3H_8, CO and CO_2.

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

A detailed kinetic reaction mechanism was developed and used to model results obtained from the experimental reaction system. A sensitivity analysis of the model was done to show the most important reactions in the mechanism. The kinetic reaction mechanism was based on thermochemical principles and transition state theory.

Rate constants obtained for initially important decomposition of 1,1,1-trichloroethane over the temperature range 500 - 800°C are:

	$A(sec^{-1})$	Ea(kcal/mol)
$CH_3CCl_3 \dashrightarrow CH_2CCl_2 + HCl$	3.8E+13	47.9
$CH_3CCl_3 \dashrightarrow CH_3CCl_2 + Cl$	2.4E+16	73.2

THERMAL DECOMPOSITION OF 1,1,1-TRICHLOROETHANE-METHANE-OXYGEN MIXTURE IN TUBULAR FLOW REACTOR

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 requirements for the degree of
Master of Science in Chemical Engineering

1989

APPROVAL SHEET

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ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. Joseph W. Bozzelli for his advice and encouragement. I am deeply indebted to him for the opportunities which he made available to me. I acknowledge the helpful corrections and productive comments by Dr. H. Shaw, Dr. E. R. Ritter.

For love and inspiration I shall be eternally grateful to my wife, Sonia and my parents.

It is my pleasure to thank my colleagues at Kinetics Research Laboratory of the New Jersey Institute of Technology: Yangsoo Won for his support and guidance.

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Introduction

The management of chemical hazardous wastes has become a central political issue and environmental concern of the 1980s.<1> High-temperature incineration, which is the most expensive option, is increasingly being used as an effective treatment process for the disposal of hazardous waste, because it is a complete conversion process to safe products.

The incineration process is quite complex involving the interaction of a number of chemical, heat transfer, and fluid dynamic phenomena.<2> Theoretically, incineration could result in the total conversion of hazardous organic compounds to innocuous thermodynamically controlled end products, such as carbon dioxide and water, and other compounds, such as HCl, which maybe easily scrubbed with existing pollution control equipment. In practice, total conversion to innocuous materials cannot be achieved without considerable expense, and for an incinerator of less than optimum design or operating conditions, the most thermally stable components in the waste feed may not be totally decomposed.<3> Louw et al.<4>, have noted the drastic operating conditions of ca 1000 K within a few minutes which are necessary to prevent incinerators from emitting intolerable amounts of polychlorinated dibenzo dioxins (PCDD).

The emission of hazardous organic compounds from poorly designed or inadequately controlled incinerators represents a potentially significant threat to the environment. In addition, since hazardous organic compounds are also subjected to thermal degradation in sources not specifically designed or regulated for their disposal, it is important to obtain the knowledge of the thermal decomposition behavior of hazardous organic materials.

One important family of hazardous wastes is the halogenated hydrocarbons. Such waste include carbon tetrachloride, trichloroethylene, trichloroethane, vinyl chloride, polychlorinated biphenyls (PCB's) and DDT (dichlorodiphenyltrichloroethylene) and others. In order to utilize incineration more effectively, and to better assess the applicability and limitation of the incineration process, the chemical kinetic steps involved in this chlorinated hydrocarbon combustion must be understood in more detail. In addition, the manufacture of useful chemicals by the controlled oxidation and pyrolysis of chlorinated hydrocarbons may be possible through the detailed knowledge of their combustion mechanisms.

Chlorinated compounds are well recognized to inhibit hydrocarbon combustion processes and promote the formation of carbon monoxide, high molecular weight compounds and soot in flames.<5,6> This study on the other hand clearly shows that chlorocarbons facilitate or accelerate the rate of hydrocarbon breakdown. Thus two stages of combustion definitely exist. The presence of chlorocarbons accelerates the first, hydrocarbons degradation to carbon monoxide stage. While the chlorine reactants or product clearly inhibit oxidation of CO to CO_2 in the second stage.

Graham, Hall, and Dellinger[3] have studied the oxidation of a mixture of five priority organic hazardous constituents or POHC's in a 1 mm ID flow reactor at temperatures from $600^{o}C$ - $900^{o}C$. These POHC's consisted of chlorobenzene, carbon tetrachloride, trichloroethylene, freon 113, and toluene. They compiled a list of well over fifty stable products from their partial oxidation study. Twenty seven of these products remained halogenated. These compounds included chlorinated furans, phenols, and polycyclic aromatic hydrocarbons (PAH). All of these are believed to be significantly more toxic than the starting materials.[7]

Chang et al[8] studied the high temperature oxidation of C_2HCl_3. Their study revealed the formation of substantial levels of chlorinated hydrocarbon intermediates, including C_2Cl_2, C_2Cl_4, CCl_4, $CHCl_3$ and $COCl_2$ even under oxygen-rich conditions. Karra et al.[9] investigated the CH3Cl/CH4/O2/Ar flame, they proposed that chlorine has a considerable effect on flame chemistry, as evidenced by the enhanced formation of C_2 hydrocarbons, in particular C_2H_2 and C_2H_4, and inhibited CO conversion to CO_2. The increased levels of CO, C_2H_2 and C_2H_4 in flames containing CH_3Cl is consistent with the flame inhibiting and soot promoting character of chlorinated hydrocarbons.

The current study in this thesis was performed in tubular flow reactors of varied diameter to examine the high temperature dechlorination and thermal reaction of a 1,1,1-Trichloroethane/Methane/Oxygen/Argon mixtures and formulate a detailed reaction mechanism based on fundamental thermochemical and kinetic principles for this system. We characterize reactant loss and product formation as function of both time and temperatures and we developed a detailed kinetic model to accurately describe the reaction process.

Previous Studies

1,1,1 - trichloroethane, also referred to as methyl chloroform and alpha-trichlorothane, is a colorless, nonflammable liquid with an odor similar to that of chloroform. It has a vapor pressure at 127 torr at 25°C and a boiling point of 74.1°C at 760 torr.<45>

Barton and Onyon<11> (1950) studied the thermal decomposition of 1,1,1 - trichloroethane in a batch reactor throughout the temperature range 635.7 to 707.0°K and pressure range 10 to 120 mm Hg. The reaction yielded 1,1 - dichloroethylene and HCl products almost exclusively. They found that the decomposition rate in packed reactor was slower than in empty one indicating that surfaces inhibited the reaction. They proposed the packed reactor has a large surface to volume ratio so the recombination of some radicals to terminate the chain reactions occurred at a faster rate and slowed the overall process. The initiation steps suggested by Barton and Onyon are as follows:

$$CH_3CCl_3 \;\text{--->}\; CH_2CCl_2 + HCl$$

$$CH_3CCl_3 \;\text{--->}\; CH_3CCl_2 + Cl$$

Their results showed that the wall inhibited the decomposition reaction because the proposed " key " free radical CH_3CCl_2 was consumed faster at the wall. They reported that the global first order rate constant for homogeneous unimolecular decomposition can be represented by $10^{14} \times e^{(54,000/RT)}$ sec.

Benson and Spokes<10>(1967), using the very low pressure technique, covered a high temperature range 890 to $1265^{o}K$ (so that the reactor was operated at gas flow rates from 10^{15} to 10^{16} molecules/sec. and most of the collisions made by reactant molecules were with wall rather than with other gas molecule). They calculated the homogeneous rate constant of the thermal decomposition of 1,1,1-trichloroethane at the high pressure limit. Their corresponding high pressure rate equation is $10^{13.8}x$ $e^{(-51700/RT)}$ sec.

Chang<12> investigated reactor modeling and used his model in the calculation of homogeneous bulk and wall rate constants from laminar flow reactor analysis on the reaction of 1,1,1-trichloroethane diluted in hydrogen in the temperature range 828 to 954 K. The activation energies of bulk and wall reaction were determined to be 25.3 Kcal/mol and 37.9 Kcal/mol, respectively. The major products from the reaction were observed to be 1,1-dichloroethylene, chloroform, 1,1-dichloroethane, trichloroethylene, dichloromethane, 1,1,1,2 - tetrachloroethane and HCl.

Won<13> studied the thermal decomposition of a dichloromethane/1,1,1 - trichloroethane mixture diluted in hydrogen at 1 atmosphere total pressure in a tubular flow reactor. The thermal degradation was analyzed systematically over temperature range from 748 to 1083 K and three different surface to volume ratio flow reactor. He found that complete decay occurs at around 843 K for 1,1,1 -

trichloroethane and about 1083 K for dichloromethane at 1 second residence time. An increase in surface to volume ratio of the reactor tube was observed to accelerate the species decomposition in hydrogen, but it had no effect on the distribution of major products. His study demonstrated that selectivity to HCl formation can result from thermal reaction of dichloroethane/1,1,1-trichloroethane mixture and showed that synergistic effects of 1,1,1-trichloroethane decomposition parent (small amount of reaction to CH_3CCl_2. + Cl) relative to molecular elimination (CH_2CCl_2 + HCl) accelerated the rate of dichloromethane decomposition.

Theory

A. Transition-State Theory

This theory was first proposed by Pelzer and Wigner<14> in 1932 and was developed by Eyring, Polanyi, and their coworkers<15> during the 1930's - 1940's. In this theory reaction is presumed to occur as a result of collisions between reacting molecules, but what happens after collision is examined in more detail. This examination is based on the concept that molecules possess vibrational and rotational, as well as translational, energy levels.

Consider the general reaction

$$aA + bB + \ldots \quad <===> M^* \quad ---> \text{Products} \qquad (1)$$

We shall assume that M^*, the activated complex located at the potential-energy maximum, is in virtual equilibrium with A and B and that the order and molecularity of the reaction are equal, namely, a+b+.... The rate of the reaction is given by the equilibrium concentration of transition-state complexes at the top of the barrier M_e^* multiplied by the frequency with which the complex crosses the barrier. The transition state is associated with a distance d along the reaction coordinate, although this quantity cancels out when the final expression for the rate constant is obtained. Half of the transition complex will be moving to the right for the forward reaction and half to the left for the reverse reaction. Therefore, the frequency with which the activated complex crosses the barrier is v/2d, where v is the average speed of the molecule along the reaction coordinate. Thus, for a reaction in any phase

$$\text{rate of reaction} = k\ (A_e)^a(B_e)^b\ldots = n(M_e)^*v/2d \qquad (2)$$

where (A_e) and (B_e) have been written instead of (A) and (B) to emphasize that $(M_e)^*$ is taken to be an equilibrium concentration with respect to the reactants. The constant n, called the transmission coefficient, represents the fraction of transition-state complexes which cross the top of barrier to form products. The transmission coefficient will be assumed to have a value of 1, although there a number of reactions for which this assumption is not valid. The average speed v is

$$v = (2\mathbf{k}T/\ m^*)^{1/2} \qquad (3)$$

where the particles of mass $m^* = am_A + bm_B + \ldots$

In addition,

$$\frac{(M_e)^*}{(A_e)^a(B_e)^b\ldots} = K^*\ \frac{d(2\pi m^*\mathbf{k}T)^{1/2}}{h} = K \qquad (4)$$

where K^* is the equilibrium constant involving the reactants and a transition-state complex which is missing one vibrational degree of freedom.

By combining Eq. (2) to (4) with n=1, we have

$$k = (\mathbf{k}T/h)\ K^* \qquad (5)$$

for the rate constant of a reaction of any order.

Equation (5) may be modified to take account of nonideality in the following simple manner. For the generalized reaction of any order in any phase represented by Eq. (1),

$$\text{rate of reaction} = k\,(A_e)^a(B_e)^b\ldots = n(M_e{}^*)v/2d \qquad (6)$$

where (A_e), (B_e) and $(M_e{}^*)$ represent concentrations. However, since we are treating the reactants and activated complex as the components of a nonideal system in equilibrium, we have

$$K = \frac{(M_e)^*}{(A_e)^a(B_e)^b\ldots}\,\frac{\gamma_M{}^*}{\gamma_A{}^a\gamma_B{}^b\ldots} = \frac{[M_*]}{[A_e]^a[B_e]^b\ldots} \qquad (7)$$

where the bracketed symbols are activities and the γ_i the corresponding coefficients. Substitution of $(M_e{}^*)$ from (7) to (6) leads to the fundamental relation for the rate constant for a nonideal system:

$$k = \frac{kT}{h}\,K^*\,\frac{\gamma_A{}^a\gamma_B{}^b\ldots}{M^*} \qquad (8)$$

The equilibrium constant between the transition-state complex and the reactants is related to thermodynamic state function by

$$\triangle\, G_0{}^* = -\,RT\ \ln K^* = \triangle\, H_0{}^* - T\,\triangle S_0{}^* \qquad (9)$$

where $\triangle\, G_0{}^*$: the standard free energy of activation,
$\triangle\, H_0{}^*$: the standard enthalpy of activation,
$\triangle\, S_0{}^*$: the standard entropy of activation.

However, the standard state normally employed for gases is 1 atm. The relationship between the equilibrium constant expressed in terms of concentration, K_c^*, and the equilibrium constant expressed in terms of pressures, K_p^*, for ideal gases is

$$K_c^* = K_p^* \ (RT)^{-\triangle n*} \qquad (10)$$

where $\triangle n^* = 1 - (a + b + \ldots)$. Combining

$$\frac{d \ln k}{d T} = \frac{\triangle E_0^*}{R T^2} \qquad (11)$$

with Eq. (5) gives

$$\frac{d \ln k}{d T} = \frac{\triangle E_0^* + RT}{R T^2} \qquad (12)$$

Here $\triangle E_0^*$ is the standard internal energy of activation. The Arrhenius activation energy Ea is by definition given by

$$\frac{d \ln k}{d T} = \frac{E_a}{R T^2} \qquad (13)$$

Comparison of Eq. (12) and (13) gives

$$E_a = \triangle E_0^* + RT \qquad (14)$$

The relationship between $\triangle H_0^*$ and $\triangle E_0^*$ is

$$\triangle H_0^* = \triangle E_0^* + \triangle (PV)^* \qquad (15)$$

For ideal gases, $\triangle (PV)^* = \triangle n^* RT$; therefore,

$$E_a = \triangle H_0^* - (\triangle n^* - 1) RT \qquad (16)$$

B. Tubular Flow Reactor

1. Tubular Flow Reactor Theory

The tubular flow reactor is characterized by the fact that there is no mixing in the direction of flow and completing mixing perpendicular to the direction of flow.<16,17> In other words, all elements of fluid must have the same residence time in the reactor and there is no radial concentration gradient.

Generally in tubular flow reactors radial mixing is due to molecular diffusion and axial mixing is due to fluid velocity gradients. To estimate the deviation of a tubular flow reactor with axial diffusion from the plug flow assumption, Reman<18> has used Danckwerts solution of a differential equation which describes a plug flow reactor following first-order kinetics. Using dispersion model<16,19>, we can neglect axial dispersion if D/vl-->0. Here D is diffusion coefficient, v is mean velocity, and l is reactor length. In addition, the ratio of actual reactor to plug flow reactor,

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

should approach 1.<16,19> For our reactor, D/vl is always below 0.05 ($3*10^{-4}-1.5*10^{-2}$) and the highest value of the ratio V_{act}/V_{PF} was 1.08. Hence the axial dispersion can be neglect.

A more rigorous analysis that is applicable to our system is the research by Poirier and Carr<21>. They employed a finite-difference to solve the continuity equation for first-order chemical reactions. They propose that if $D/kR^2 \geq 0.5$ (where R is the radius of reactor, k is homogeneous rate constant), the plug flow approximation is satisfied. Our system has a D/kR^2 values from 10 to 170, so the plug flow model is a good approximation for our present reactor. Chang and Bozzelli<12> solved analytically a laminar flow model for first order reactions in a tubular reactor with simultaneous wall and bulk reactions. They compared the kinetic values found by plug flow analysis with values obtained by applying both numerical and analytical solution of continuity equation for first order kinetics with laminar flow. The comparison turns out to be favourable to the plug flow assumption for our work.

The results obtained by Chuang<22> show that the decomposition of chlorinated hydrocarbons is not only the function of temperature and residence time but also of the radius of reactor. This means, the reaction at wall in addition to the bulk reaction needs to be evaluated to properly characterize the reaction.

If bulk and wall reactions are parallel and indepedent, then observed rate constants can be written as the sum of wall and bulk effects using an equation based on the work of Kaufman<23>. For the first-order reaction of species A we can write:

$$A \xrightarrow{k_{exp}} \text{Products} \qquad -\frac{d[A]}{dt} = k_{exp}\,[A]$$

actually,

$$A \xrightarrow{k_b} \text{Products}$$

$$A + A_w \xrightarrow{k_w'} \text{Products} + A_w$$

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

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

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

assuming rapid radical diffusion, A_w can be written as showed in Kaufman<23>:

$$A_w = (S/V)$$

where A_w : wall concentration,

S/V : surface to volume ratio,

for a cylindrical reactor, $S/V = 2/R$.

From eq.(2) and (3) we obtain:

$$k_{exp} = k_b + k_w * (2/R)$$

In this equation k_b is the first order reaction rate constant for the bulk (homogeneous) reaction and k_w is the rate constant for the wall (heterogeneous) reaction. By running reactions with reactors of different diameters, and keeping all other conditions constant the differences in the reactions parameter value can be evaluated. The overall Arrhenius behavior of wall and bulk rate constants can then be decoupled.

2. Laboratory Scale High Temperature Tubular Flow Reactor

As mentioned in B.1 the ideal tubular-flow reactor is one in which there is no mixing in the direction of flow and complete mixing in the radial direction. When the mixing criteria of ideal forms are not satisfied, mathematical expressions for the conservation equations become more complex. The deviations from ideal tubular flow behavior are : (1) some mixing in the longitudinal direction, that is longitudinal mixing due to vortices and turbulence, and (2) incomplete mixing in the radial direction, for a laminar flow, since the molecular-diffusion process is relatively slow, the annular elements of fluid flowing through the reactor are only slightly mixed in the radial direction. Also, the fluid near the wall will have a longer residence time in the reactor than for ideal tubular-flow performance, while the fluid near the center will have a shorter residence time.

A laboratory scale high temperature tubular flow reactor typically operates isobarically (1 atmosphere pressure in our study)<27> and consists of a flow tube within a furnace. This simple design, however, has several characteristics which complicate its detailed analysis. One of these complication concerns the flow pattern. Typically Reynolds number (N_{Re}) are consistently below 10000 and the length/diameter ratio is rarely over 100.<28> As a result of the flow is laminar, i.e. the parabolic velocity profile is formed across the tube. This results in a residence time distribution in addition to a radial concentration gradient<29,30>. Another complication concerns the expansion of the gas as its temperature increases to that of the reactor. A certain entrance length<31> is required in order for the gas to expand and achieve its finial radial velocity distribution within the reactor tube.

As a result of these complications, several simplifying assumptions are useful to facilitate the analysis of a laboratory scale tubular flow reactor.<28> Generally, assume the reactants and bath gas to be heated instantaneously from a temperature where no reaction occurs to the temperature of the reactor wall. The reactants are then assumed to remain isothermal at this temperature until they exit the heated zone where they are assumed to be quenched instantaneously. In addition. the entrance length is assumed to be zero. This assumption is not bad due to the low Reynold's number typically encountered.<31>

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

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 described below is very important to our model development research. A brief description of this theory from the article by Westmoreland and Dean<32> is therefore, para-phrased below and treated as a quote.

Bimolecular QRRK (Quantum Rice-Ramsperger-Kassel) analysis is a simple method for calculating rate constants of energized complexes which result from addition and recombination reactions. It is based on unimolecular quantum-RRK theory<32>. The decomposition of a radical or molecule has a unimolecular, pressure-independent rate constant in the limit of high pressure, but as pressure is reduced the rate constants fall off or decrease with pressure. In the low-pressure limit, unimolecular rate constants become directly proportional to pressure.

Radical combination or radical addition to on unsaturated molecule produce an energized complex which also exhibits has a fall off behavior or pressure behavior to it's stabilization versus decomposition channels. The adduct species has an energy distribution in thermal equilibrium with surrounding gas molecules, plus an energy equal to newly formed bond.

Additional products can be formed from combination and addition reactions by chemically activated pathways. "The initially formed adduct has a chemical activation energy distribution, different from a thermal energy distribution because the thermal energies of the reactants are augmented by the chemical energy released by making the new bond. The chemical energy is the same as the energy barrier for redissociation of the collisionally stabilized adduct to the original reactants. If the energy in the chemical activation energy distribution extends above the barrier for a new dissociation (or isomerization) of the adduct, then that reaction pathway can also occur."

"Calculations of the bimolecular rate constant involve the concept that the fate of the chemically activated adduct is determined by competition among the possible pathways: stabilization by collisions, redissociation to reactants, or formation of new products by dissociation or isomerization<33>."

1. Unimolecular QRRK Equation

"Dean<33> (1985) has presented equations for bimolecular rate constants based on the QRRK unimolecular reaction theory of Kassel (1928)<24>, which treats the storage of excess energy (relative to the ground state) as quantized vibrational energy."

The general scheme for unimolecular reaction is as follows:

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

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

where M stands for the third body and only serves to raise the reacting molecule to its energized state A^* by collisional activation. For the unimolecular rate constant k_{uni}:

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

then assuming pseudo-steady state for each energy level of A^* as shown in Figure 1-a and evaluated by a sum over all energies with collisional excitation (k_{exc}) or deexcitation (k_{deexc}) rate constant :

$$k_{uni} = \frac{1}{[A]} \sum_{E=E_0}^{\infty} k_{rxn}(E) \cdot [A^*(E)]$$

$$= \sum_{E=E_0}^{\infty} k_{rxn}(E) \quad \frac{k_{deexc}[M]K(E,T)}{k_{deexc}[M] + k_{rxn}(E)} \qquad (2)$$

where K(E,T) is the thermal-energy distribution function (k_{exc}/k_{deexc}). For the high pressure limit, the Arrhenius preexponential factor A_{inf} for dissociation of A to that channel, so the energy-dependent rate constant is:

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

the symbol n is for the variable E and m is the quantized energy for the energy barrier to reaction Eo, s is the vibration of decomposing molecule; quantum levels and the rate processes are illustrated in Figure 1-a.

> "Likewise, Dean<33> derived the quantized thermal energy distribution K(E,T) for the molecule with the geometric mean virbration frequency to be:
>
> $$K(E,T) = a^n\ (1- a)^s \frac{(n+s-1)!}{n!\ (s-1)!} \qquad (4)$$
>
> where $a = e^{(-h<v>/KT)}$."
>
> "In the present developement, a collisional efficiency ß has been applied to modify the strong-

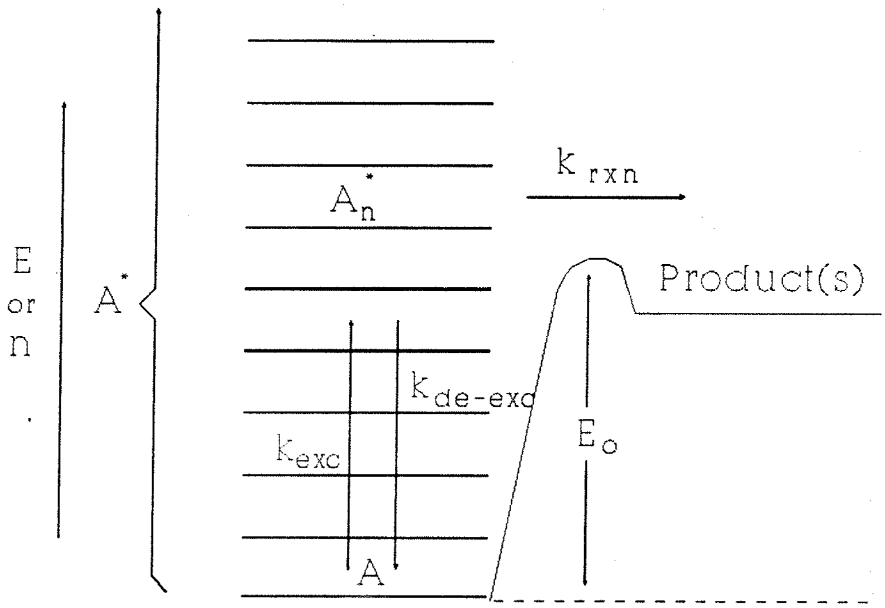

Figure 1-a. Unimolecular Reaction

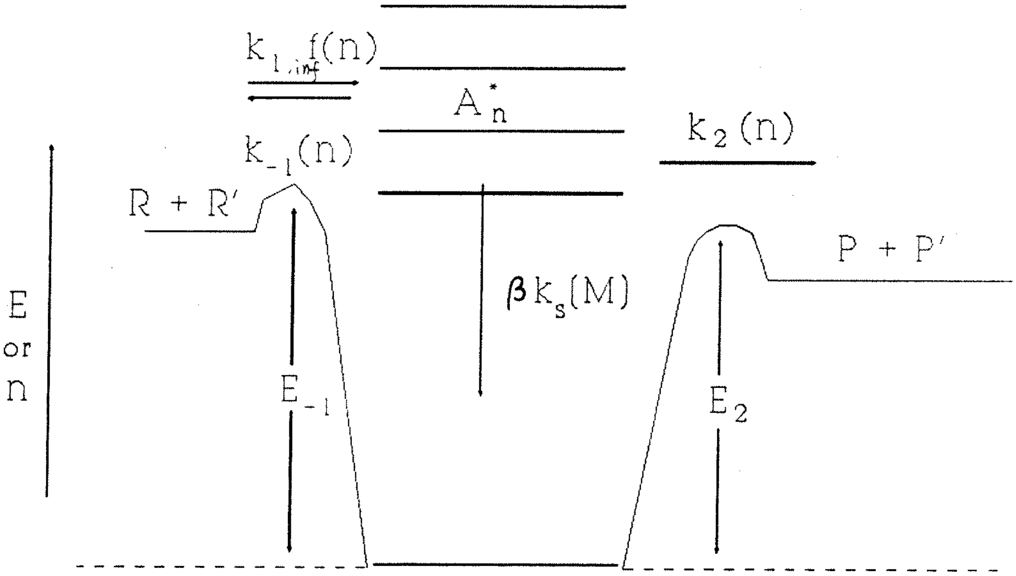

Figure 1-b. Bimolecular Reaction with Chemically Activated pathway

Figure 1. Energy Diagrams for Pressure-dependent Reactions

collision assumption that $k_{deexc} = k_s$ [M], where k_s is the collision frequency rate constant. The strong-collision assumption implies that all collisions between A^* and M would 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." With equation :

$$\frac{\beta}{1-(\beta)^{\frac{1}{2}}} = \frac{-\langle\triangle E_{coll}\rangle}{F_E \cdot kT} \qquad (5)$$

where $\langle\triangle E_{coll}\rangle$ is the average amount of energy transferred per collision and F_E is a factor, Troe<34> (1977) fit most of the temperature dependence of ß over the temperature range of 300 - 2500 K for a series of reactions, $F_E = 1.15$ was a median value. The value of ß depends on the specific third-body M through the value of $\langle\triangle E_{coll}\rangle$.

2. Bimolecular QRRK Equations

"The bimolecular QRRK equations follow (Dean<33>, 1985) from unimolecular QRRK and the definition of the chemical activation distribution function." Consider addition or recombination to occur via the sequence:

$$\begin{tikzcd}
R + R' \arrow[r, leftrightarrow, "k_{1,inf} \cdot f(E,T)"] & {[RR']^*} \arrow[r, "k_2(E)"] \arrow[d, "\beta k_s[M]"] & P + P' \\
& A &
\end{tikzcd}$$

Here, R is a radical, R' is a radical or unsaturated molecule, $[RR']^*$ is the energized complex which can either dissociate or be collisionally stabilized, $k_{1,inf}$ is the high-pressure-limit rate constant for forming adduct, k_s is the collisional rate constant for stabilization, and f(E,T) is the energy distribution for chemical activation:

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

where K(E,T) is the QRRK thermal distribution from Eq.(4). A typical energy diagram for these reaction is shown in Figure 1-b.

> "To obtain the bimolecular rate constant for a particular product channel, a pseudosteady-state analysis is made as before. The rate constant for forming the addition/stabilization product A from R + R′ is:
>
> $$k_{stab} = \frac{d[RR']/dt}{[R][R']} = \sum_{E=E_{-1}}^{\infty} \beta k_s[M] \frac{k_{1,inf}\ f(E,T)}{\beta k_s[M]+k_{-1}(E)+k_2(E)} \qquad (7)$$
>
> and, for forming the addition/decomposition products P + P′:
>
> $$k_{dec} = \sum_{E=E_{-1}}^{\infty} k_2(E) \frac{k_{1,inf} \cdot f(E,T)}{\beta k_s[M]+k_{-1}(E)+k_2(E)} \qquad (8)$$
>
> If more decomposition channels are available, the $k_{rxn}(E)$ for each channel is added in the denominator of Eqs.(7) and (8), and an equation in the form of Eq.(8) is written for each additional channel, the respective $k_{rxn}(E)$ instead of $k_2(E)$ as the multiplier term."

3. Low and High-Pressure Limits

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

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

$$\lim_{[M]\to 0} k_{stab} = [M] \sum_{E=E_{-1}}^{\infty} \beta k_s \frac{k_{1,inf} \cdot f(E,T)}{k_{-1}(E) + k_2(E)} \qquad (9)$$

sometimes written as $[M] \cdot k_0$ (as a termolecular reaction), and the high-pressure limit reduces properly to $k_{1,inf}$. At a given temperature, the fall off curve for stabilization can be plotted as $\log(k_{stab})$ vs $\log(p)$ or $\log([M])$."

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

"Equation (8) implies that chemically activated decomposition has a fall off curve that is the opposite of addition/stabilization, with a rate constant that is pressure-independent at low pressure and inversely proportional to pressure at high pressure. From Eq.(8), low-pressure limit for the chemically activated pathway to P and P′ will be

$$\lim_{[M]\to 0} k_{dec} = k_{1,inf} \sum_{E=E_{-1}}^{\infty} \frac{k_2(E)\ f(E,T)}{k_{-1}(E) + k_2(E)} \qquad (10)$$

and the high-pressure limit will be

$$\lim_{[M]\to 0} k_{dec} = \frac{1}{[M]} \frac{k_{1,inf}}{\beta k_s} \sum_{E=E_{-1}}^{\infty} k_2(E)\ f(E,T) \qquad (11)$$

with an inverse pressure dependence. While this result goes against past intuition about low-and high-pressure limits, it is natural consequence of physics when chemically activated reactions 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 activated complex formation with subsequent rapid decomposition of the complex to products (C + D) before stabilization occurs."

Experimental Method

A schematic diagram of the reactor system is shown in Figure 2. The high temperature tubular flow reactor was operated isothermally and isobarically in the range 773 K-1073 K, and at 1 atm total pressure.

Argon was used as both a carrier and dilution gas. One part of the argon flow was passed through a two stage saturation bubbler to pick up 1,1,1-trichloroethane, which kept at 0°C using an ice bath. The other part of argon flow was used to achieve the desired molar ration between argon, methane, oxygen and 1,1,1-trichloroethane. Before entering the reactor, the methane gas and oxygen were added into the flow, and were preheated to 180 °C to limit cooling at the reactor entrance. Three quartz reactor tubes were utilized in this study of either 4 mm, 10.5 mm, or 16 mm ID. The reactor tube was housed in a three zone Lindberg electric tube furnace. The reactor effluent was monitored using two on line gas chromatographs (GC's), one with Flame Ionization Detector and one with Thermal Conductivity Detector. The outlet lines between reactor and GC analysis were heated to 110°C to limit condensation.

When the inlet switching valves were properly selected the mixture (CH_3CCl_3, CH_4 and O_2) would be transferred directly from the bubbler to the GC samplers via a reactor bypass line. This was necessary to determine the GC peak area which corresponded to the input (initial) concentration of mixture.

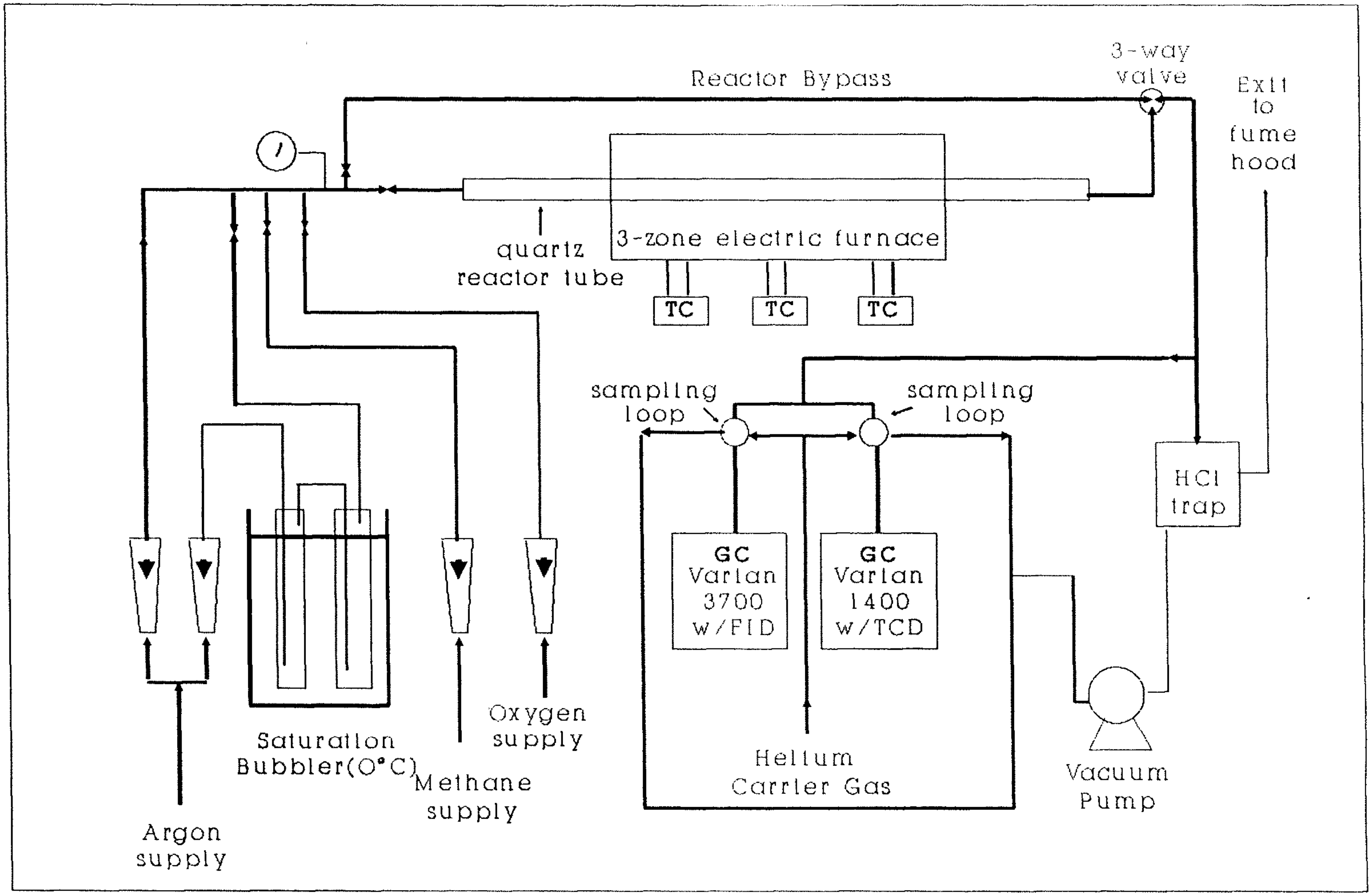

Figure 2. Experimental system

The reactor outlet gases were passed through heated transfer lines, with a loosely packed plug of glass wool to trap any solid like carbon, then to the GC samplers and the exhaust. The bulk of the outlet gases, however, was passed through a sodium-bicarbonate flask to neutralize the HCl, and then released to the atmosphere via a fume hood.

A. Temperature Measurement and Control

The three zone furnace equipped with three independent temperature controllers (NANMAC CORP., Framincham Centre, Mass).

The actual temperature profile of the tubular reactor was obtained using type K thermocouple which could be moved coaxially within reactor from one end to the other. The temperature measurements were performed with steady flow rate of argon gas through reactor. As shown in Figure 3, temperature profiles which were isothermal to within $\pm$ $3^{o}C$ for 80% of the total furnace length were obtained.

An energy balance calculation was done by Won<36> for the reaction system based upon the experimental observed conversion and product and exothermicity. It was determined that the heat, can change the temperature,by $1.5^{o}C$ at most. This is less than 50% of our temperature control error bands and is therefore insignificant. The reaction conditions determined by the temperature profile with no reaction, are therefore considered accurate. The actual temperature

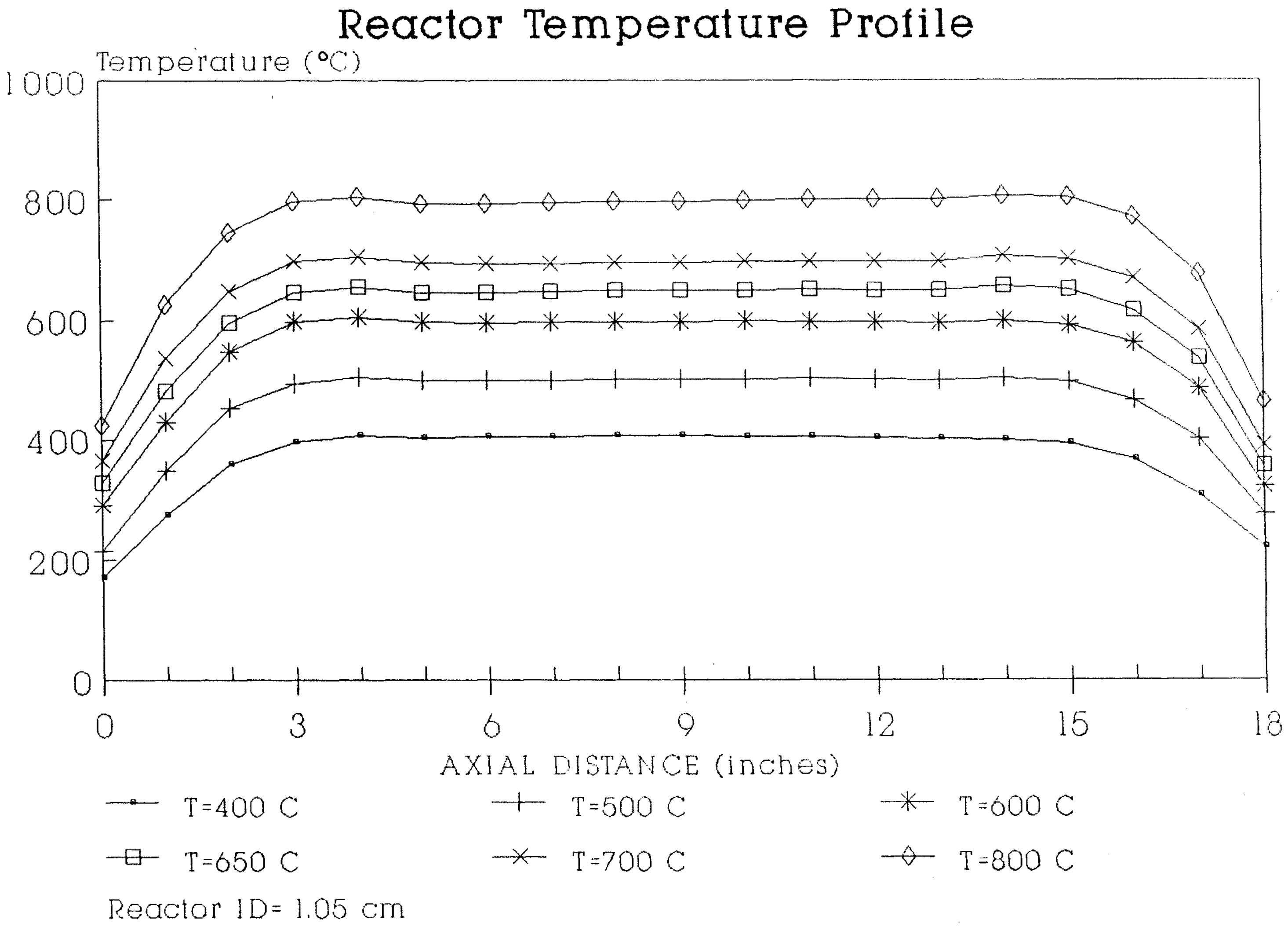

Figure 3. Reactor temperature profile

profile of the tubular reactor with reaction occurring is therefore, that of Figure 3.

B. Quantitative Analysis of Reaction Products

Quantative analysis of the reaction products was performed using a Varian 3700 gas chromatograph with flame ionization detector (FID) and a Varian 1400 gas chromatograph with thermal conductivity detector (TCD). The flame ionization detector was operated as follow:

Column : 5 ft. x 1/8 in. OD stainless steel packed with 1% Alltech At -1000 on graphpac GB.
Temperature : 45°C (5 min.), 15°C/min., 200°C (Final).
Carrier Gas : Helium , 12 ml/min.
Detector : 270°C.
Injector : 170°C, 1 atm pressure.

And the conditions of thermal conductivity detector are:

Column : 6 ft. x 1/8 in. OD stainless steel packed with Carbosphere 80/100.
Temperature : 28°C (2 min.), 20°C/min., 80°C (finial).
Carrier Gas : Helium, 30ml/min..
Detector : 165°C, Sensitivity I = 150 mA.
Injector : 100°C, 1 atm pressure.

Both GC's have a six port gas sample valve (Valco Instrument Co.) with 1.5 ml volume loop. The integration of these two chromatograms were performed with a Varian 4270 integrator using an attenuation of 2 and chart speed of 0.25

cm/min. for channel A (FID) and channel B the TCD. Representative chromatograms are shown in Figure 4, 5 and listed in Table 1 with retention times and peak identification.

Calibration of the flame ionization detector to obtain appropriate molar response factors was done by injecting a known quantity of the relevant compound such as CH_4, C_2H_4, C_2H_6 (flowed through loop at known pressure from SCOTTY^R IV analyzed gases cylinder), CH_2CCl_2, CH_3CCl_3(flowed through loop from bypass line), etc., through the sampling loop, then measuring the corresponding response area. Calibration of the thermal conductivity detector was also done by injecting a known quantity of the relevant compound such as CH_4, CO, CO_2, etc., and then, measuring the corresponding response area. The relative response factors for both detectors, FID and TCD, determined for our compounds are shown in Table 2. The response factors for C_1 compounds are close to each other and the response factor for C_2 compounds are near twice the response of C_1 compounds on the FID. These results agree with the general principle of flame ionization detector which is well known as a carbon counter<35>. Thus, the effect of chlorine in the relative response factor can be neglected for our FID operation and relative response factors of other compounds corresponding to the number of carbon in the molecule were considered accurate. Based on the experimentally verified response factors, the specific component peak area from each set of

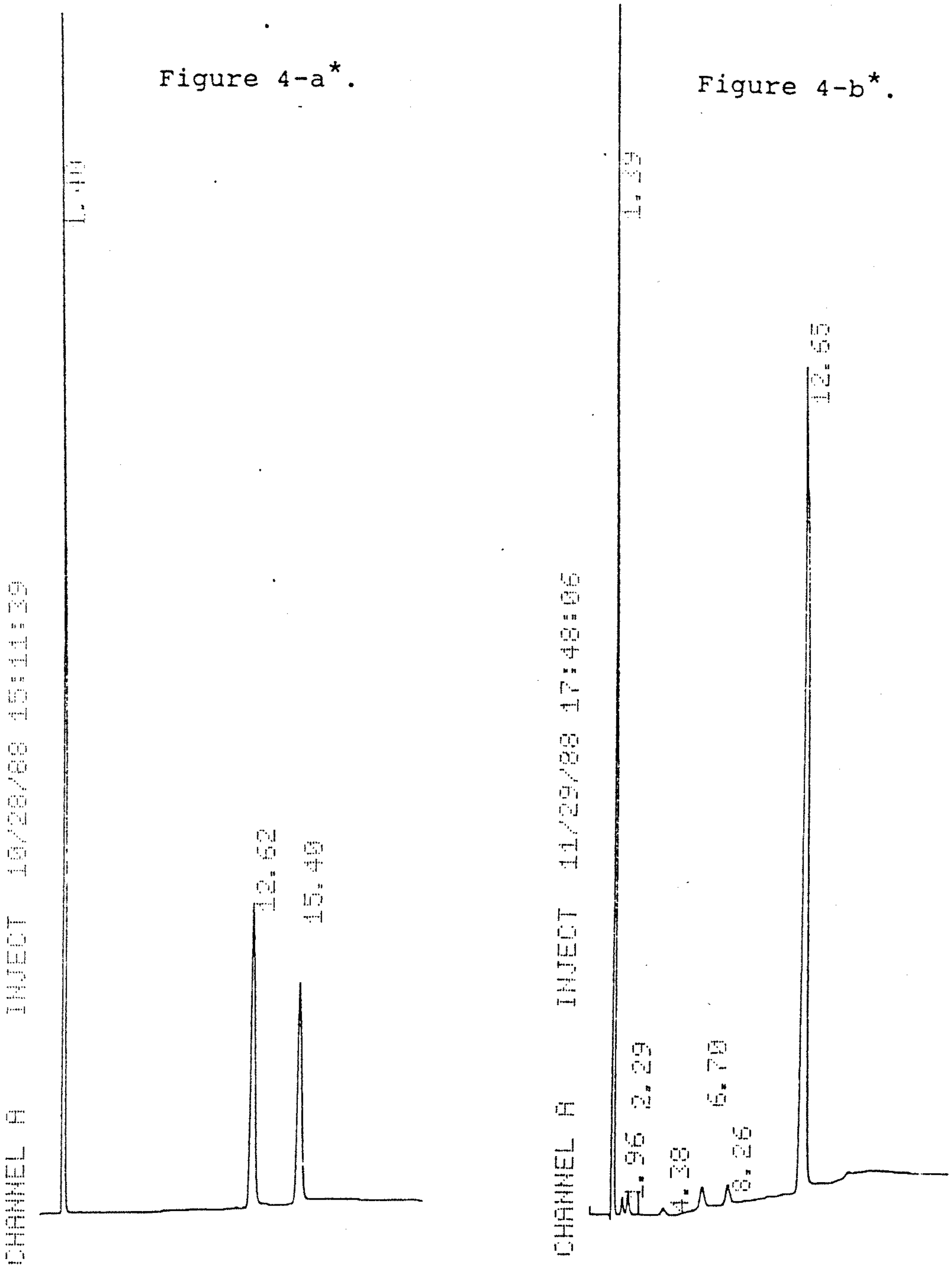
Figure 4-a*.

Figure 4-b*.

Figure 4. Sample Chromatogram

Column: 5 ft x 1/8" OD stainless steel, 1%-AT 1000 on Graphpac GB.
Detector: 270 °C (FID)
Temperature: 45°C(5 min), 15°C/min to 200 °C.
Carrier Gas: Helium supplied at 100 psig.

*Reaction conditions a: $Ar:O_2:CH_4:CH_3CCl_3=95:3:1.5:0.5$
1 sec. under 550°C.
b: $Ar:O_2:CH_4:CH_3CCl_3=95:3.75:0.75:0.5$
1 sec. under 700°C.

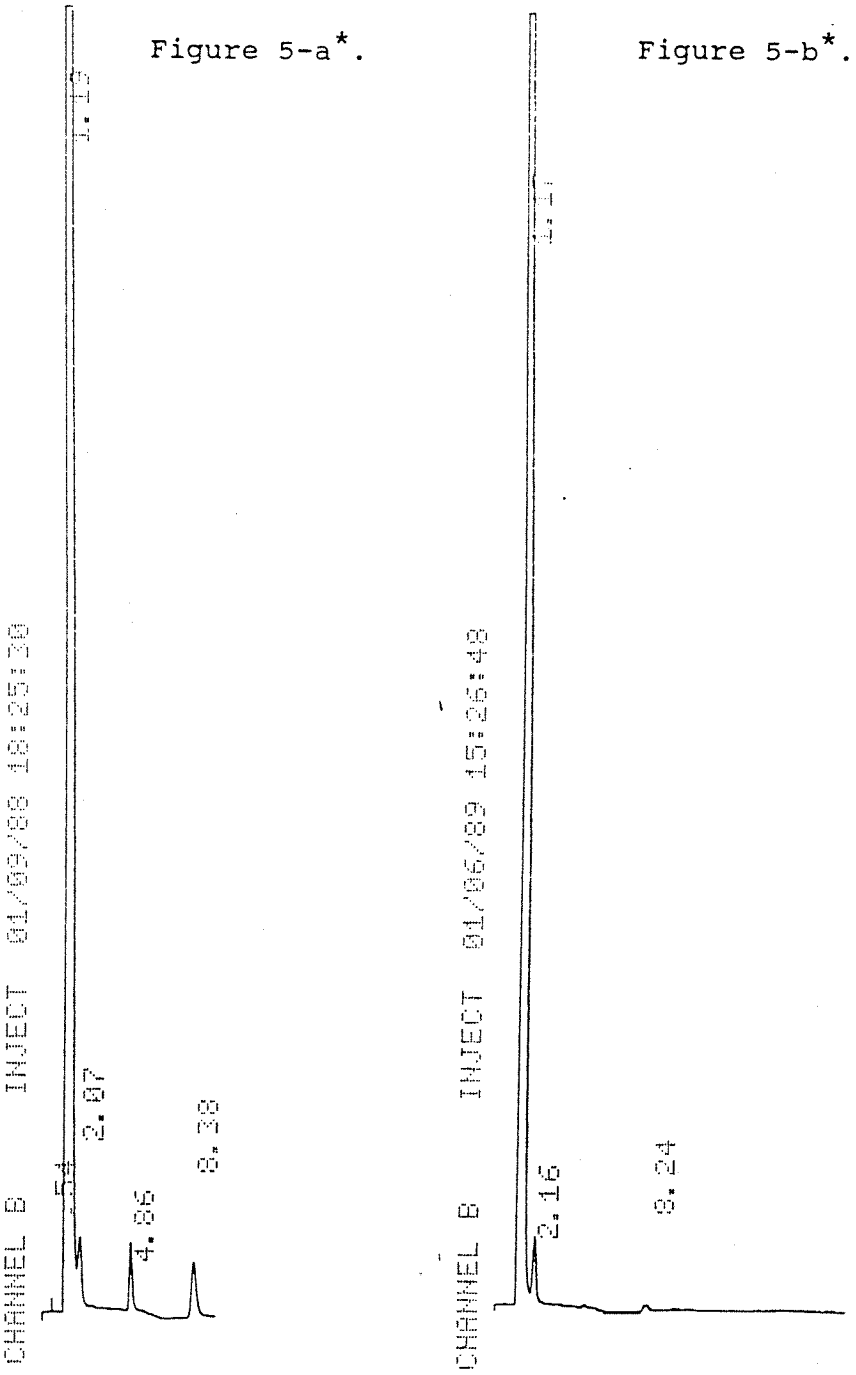

Figure 5-a*.

Figure 5-b*.

Figure 5. Sample Chromatogram

Column: 6 ft x 1/8" OD stainless steel, Carbosphere 80/100.
Detector: 165 °C (TCD), Sensitivity I= 150 mamp.
Temperature: 28°C(2 min), 20°C/min to 80 °C (final).
Carrier Gas: Helium,30 ml/min.
*a: Standard gas $CO:CH_4:CO_2$= 1.0002:0.998:1.0004.
b: Reaction conditions: $Ar:O_2:CH_4:CH_3CCl_3$=95:3.75:0.75:0.5
1 sec. under 800°C.

Table 1

Average Retention Time of Products

Table 1-a Flame Ionization Detector

Compound	Average Retention Time (min.)
CH_4	1.40
CHCH	1.96
CH_2CH_2	2.28
CH_3CH_3	2.60
CHCCl	3.19
CH_3Cl	4.30
C_3H_6 & C_3H_8	6.70
CH_2CHCl	8.24
CH_2Cl_2	10.72
CH_2CCl_2	12.60
CH_3CHCl_2	13.66
CHClCHCl	14.17
CH_3CCl_3	15.40
$CHClCCl_2$	16.70
C_6H_6	17.90
$CH_2ClCHCl_2$	20.95

Table 1-b Thermal Conductivity Detector

Compound	Average Retention Time (min.)
Air	1.20
CO	2.10
CH_4	4.83
CO_2	8.20

Table 2

Relative Response Factor of Several Compounds

Table 2-a Flame Ionization Detector

Compound	Relative Response Factor (RRF)
Methane	1.00
Acethylene	2.13
Ethylene	1.87
Ethane	1.83
Propyne	3.16
Propene	3.24
Propane	3.20
Butane	4.03
Dichloromethane	0.93
1,1,1-Trichloroethane	1.73
1,1-Dichloroethylene	1.96
Chloroform	0.92
Tetrachloromethane	1.10
1,1,2-Trichloroethane	1.96

Table 2-b Thermal Conductivity Detector

Compound	Relative Response Factor (RRF)
Methane	1.00
Carbon monoxide	1.56
Carbon dioxide	1.32

Corrected area = measured area x RRF

samples was converted to the equivalent number of moles of each component.

C. Hydrochloric Acid Analysis

Quantitative analysis of HCl product was performed for reactions in each diameter reactor and each residence time. The samples for HCl analysis were collected independent from GC sampling as illustrated as Figure 2. In this analysis, the effluent was bubbled through a two stage bubbler before being exhausted to hood. Each stage contained 15 ml of standardized 0.01 M NaOH. The gas was passed through the two stage bubbler until the first stage solution reached its phenolphthalein end point (typically 0.5 to 2 minutes). The time required for this to occur was recorded. At this point the bubbling was stopped, the aliquots were combined, and titrated to their end point with standardized 0.01 M HCl.

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

D. Kinetic Model Computer Integration

The CHEMKIN computer program package is used in interpreting and integrating the detailed reaction mechanism (model) of the reaction system. The CHEMKIN program[38], Chart 1, reads the user's symbolic description of the reaction mechanism. The thermodynamic data base, which has the appropriate thermodynamic information and mass for all species present in mechanism. The information on the elements, species, and reactions in the mechanism; and finally the CHEMKIN gas phase subroutines, which can be called to return information on the elements, species, reactions, equations of state, thermodynamic properties, chemical production rates, and derivatives of thermodynamic properties relative to any time in the integration. The input to these subroutines are usually the state variables of gas pressure or density, temperature and species composition at initial time of reaction. The routines can be called with the species composition defined in terms of either mass fraction or molar concentration. Numerical calculations were carried out using the CHEMKIN computer code coupled to LSODE a linear solver of ordinary differential calculations.

The input data requirement to run CHEMKIN program include:

- Detailed reaction mechanism
- Mole fraction of all gases present in the reaction system

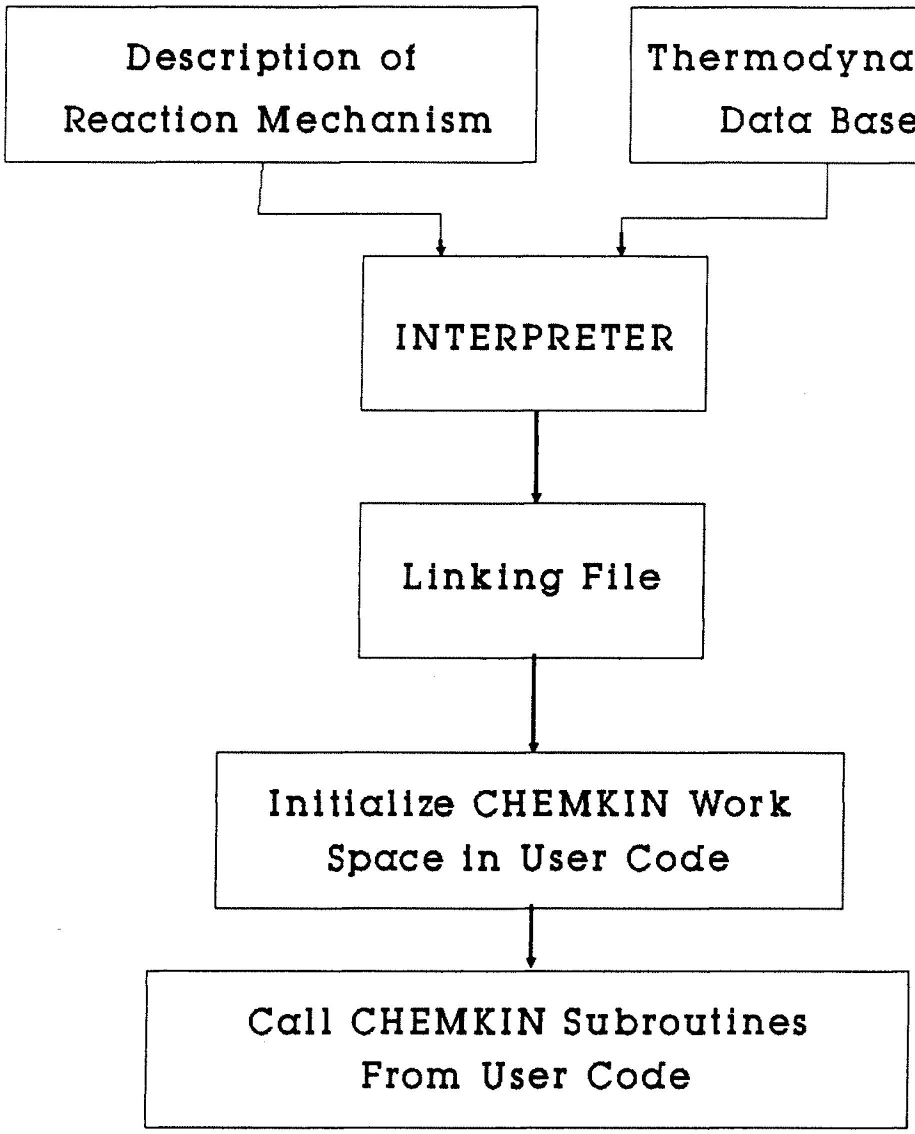

Chart 1. Structure of the CHEMKIN Package

- Pressure and temperature at which the reaction system being studied
- Time increment at which the concentration of species present in the system be reported

A thermodynamic data base for species with C/H/Cl elements is developed at NJIT and used for modeling the kinetic scheme of elementary reactions input to the program. For those species where thermodynamic information was not available in the data base, thermo data was generated utilizing DBGEN program. This program requires heat of formations and entropies, as well as heat capacities, from 298 to 1000 K as input. These were calculated by group additivity method of Benson<41> when not available in literature and computer code THERM<44>.

Results and Discussion

The experimental conditions of the reaction of 1,1,1-trichloroethane/oxygen/methane mixture with argon are listed below:

Reactants Ratio (O_2 : CH_4 : CH_3CCl_3)(Molar Ratios):

1. $O_2 : CH_4 : CH_3CCl_3 = 4.5 : 0 : 0.5$
2. $O_2 : CH_4 : CH_3CCl_3 = 4 : 0.5 : 0.5$
3. $O_2 : CH_4 : CH_3CCl_3 = 3.75 : 0.75 : 0.5$
4. $O_2 : CH_4 : CH_3CCl_3 = 3 : 1.5 : 0.5$
5. $O_2 : CH_4 : CH_3CCl_3 = 0 : 1.5 : 0.5$

Reactor Temperature (^oC) : 500, 525, 550, 575, 600, 650, 700, 750, 800.

Effective Reactor length : 30.5 cm.

Reactor Diameter (cm) : 0.4, 1.05, 1.60.

Residence Time Range (sec.) : 0.05 - 1.0 (I.D. = 0.40)
0.3 - 2.0 (I.D. = 1.05)
0.7 - 2.5 (I.D. = 1.60)

Operating Pressure : 1 atm.

Nine temperatures ranging from 500 to 800 ^oC were studied in the 1.05 cm I.D. reactor, and each temperature study had 6 residence time points from 0.3 to 2.0 sec. For the 0.4 cm and 1.6 cm I.D. reactors, experiments at five temperatures ranging from 500 to 700 ^oC were studied with average residence times in the 0.4 cm I.D. reactor ranging from 0.05 sec. to 1.0 sec. and for the 1.6 cm I.D. reactor ranged from 0.7 sec. to 2.5 sec.

Constant molar ratio of CH_3CCl_3 was maintained at 0.5% through the experiments. The molar ratio of argon was maintained at 95.0% for case 1, 2, 3, 4 and 98.0% for case 5. Oxygen, molar ratios were from 4.5% to 0% and methane ratios were from 0% to 1.5%.

A. Reaction of 1,1,1-Trichloroethane/Oxygen/Methane/Argon mixture.

Experimental results on decomposition of 1,1,1 trichloroethane are in Figure 6a through 6f, which shows normalized concentration (C/C_0) as a function of the average residence time for several temperatures studied and each different i.d. reactor.

The 1,1,1-trichloroethane concentration consistently decreased with increasing reaction time for all temperatures. As shown in Figure 7, we found that oxygen had almost no effect on the 1,1,1-trichloroethane decomposition.

The conditions of excess argon allowed simplification to pseudo-first order kinetics for all experiments. Integrated rate equation plots on the conversion of CH_3CCl_3 over a range of concentration ratios to fit a first order rate equation are shown in Figure 8a through 8f. Here it is seen that for different values of temperature and diameter, as well as chemical ratios the data fit the integrated first order rate equation well. Decomposition was most rapid in the 4 mm id and slowest with the 16 mm id reactors as show in Figure 9a through 9c. This trend is expected since observed reagent loss may be the result of two reaction paths, both contributing under our conditions. One, a

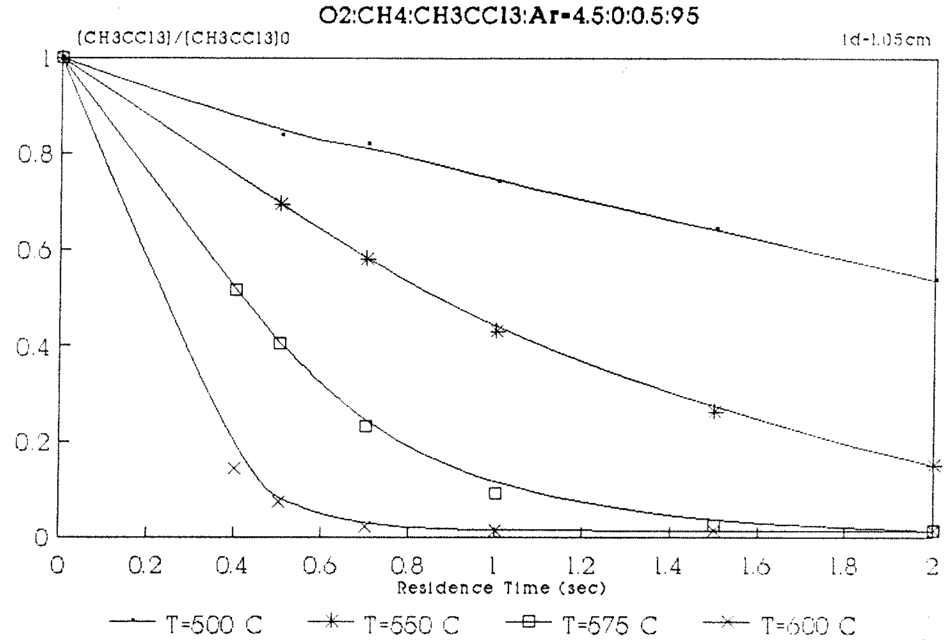

Figure 6-a. 1,1,1 Trichloroethane Decay Curve

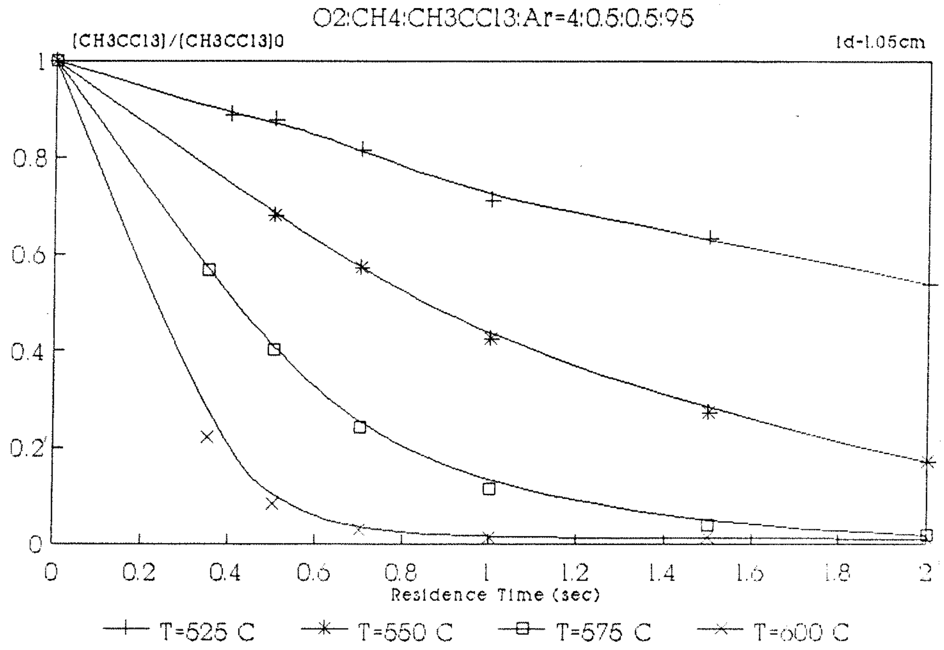

Figure 6-b. 1,1,1 Trichloroethane Decay Curve

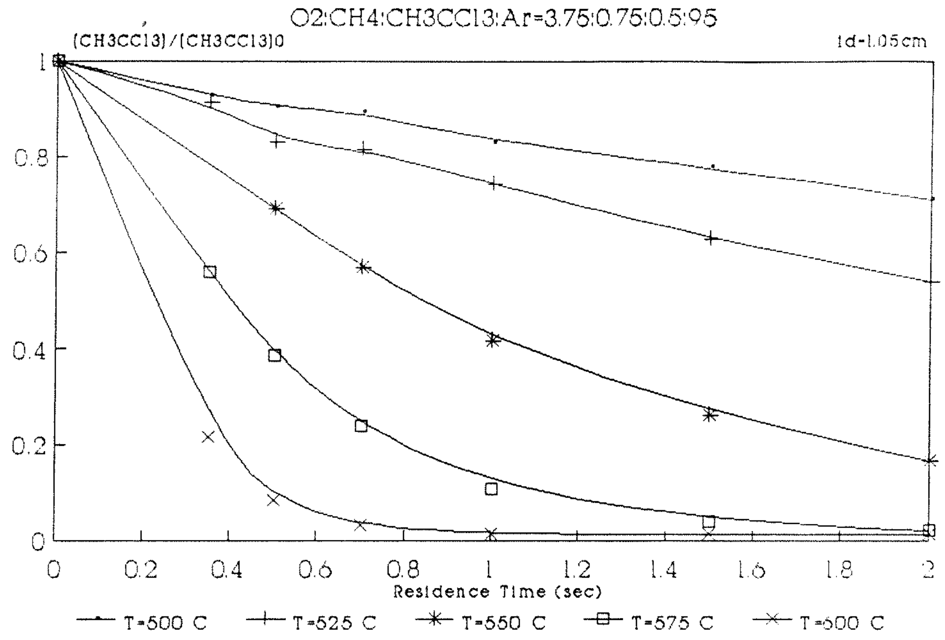

Figure 6-c. 1,1,1 Trichloroethane Decay Curve

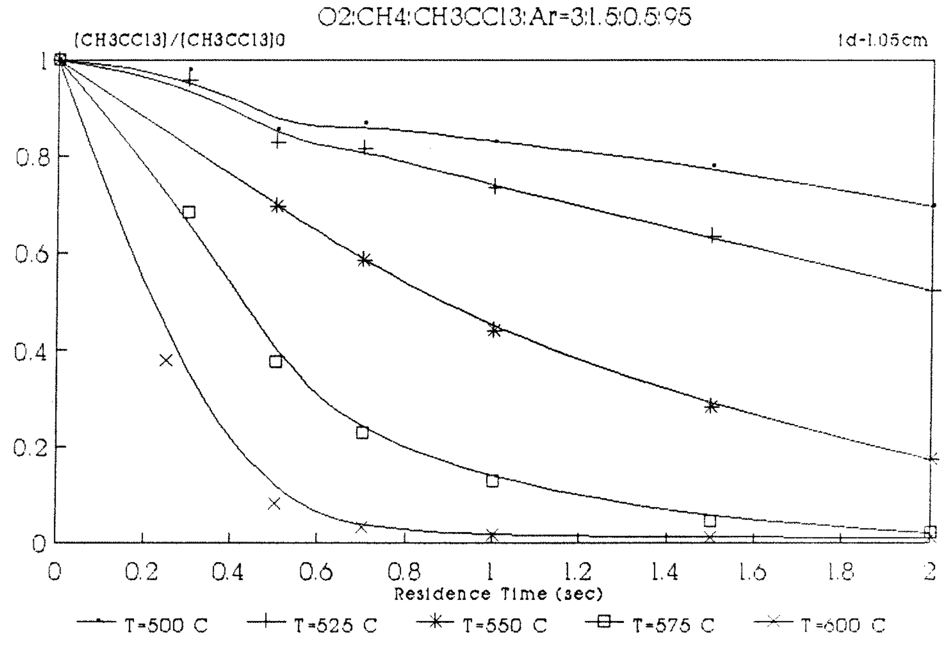

Figure 6-d. 1,1,1 Trichloroethane Decay Curve

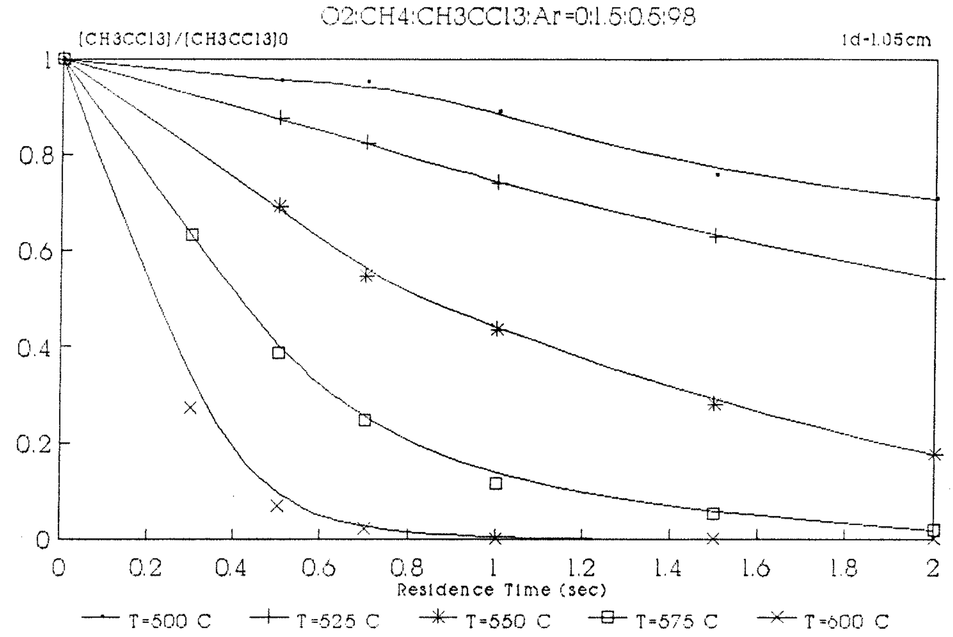

Figure 6–e. 1,1,1–Trichloroethane Decay vs Time

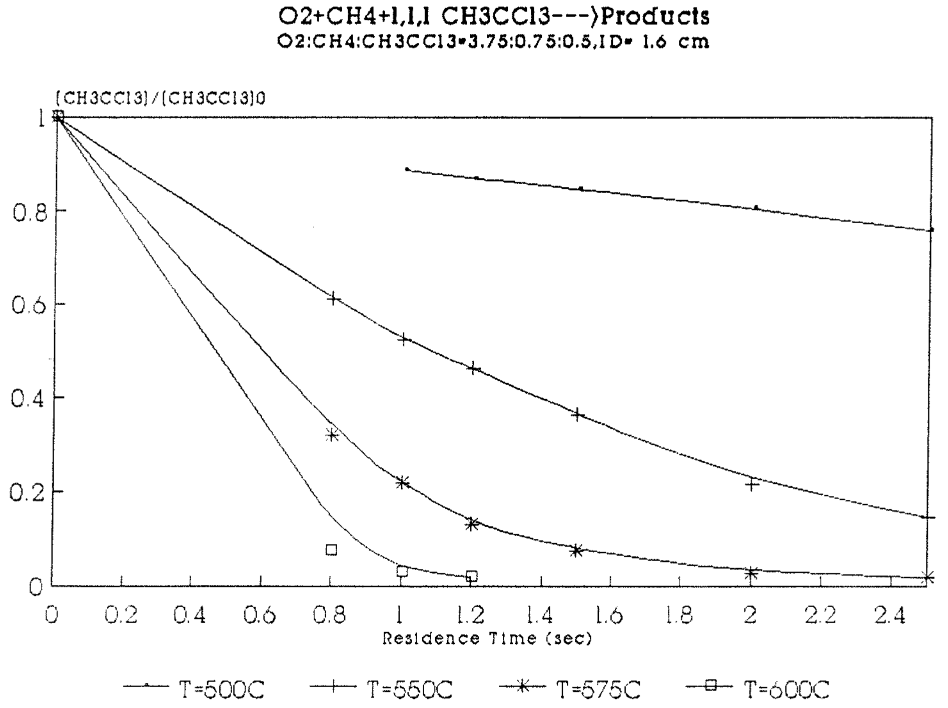

Figure 6–f. 1,1,1–Trichloroethane Decay vs Time

1,1,1-CH_3CCl_3 Decay in All Reactants Ratio Sets vs Time

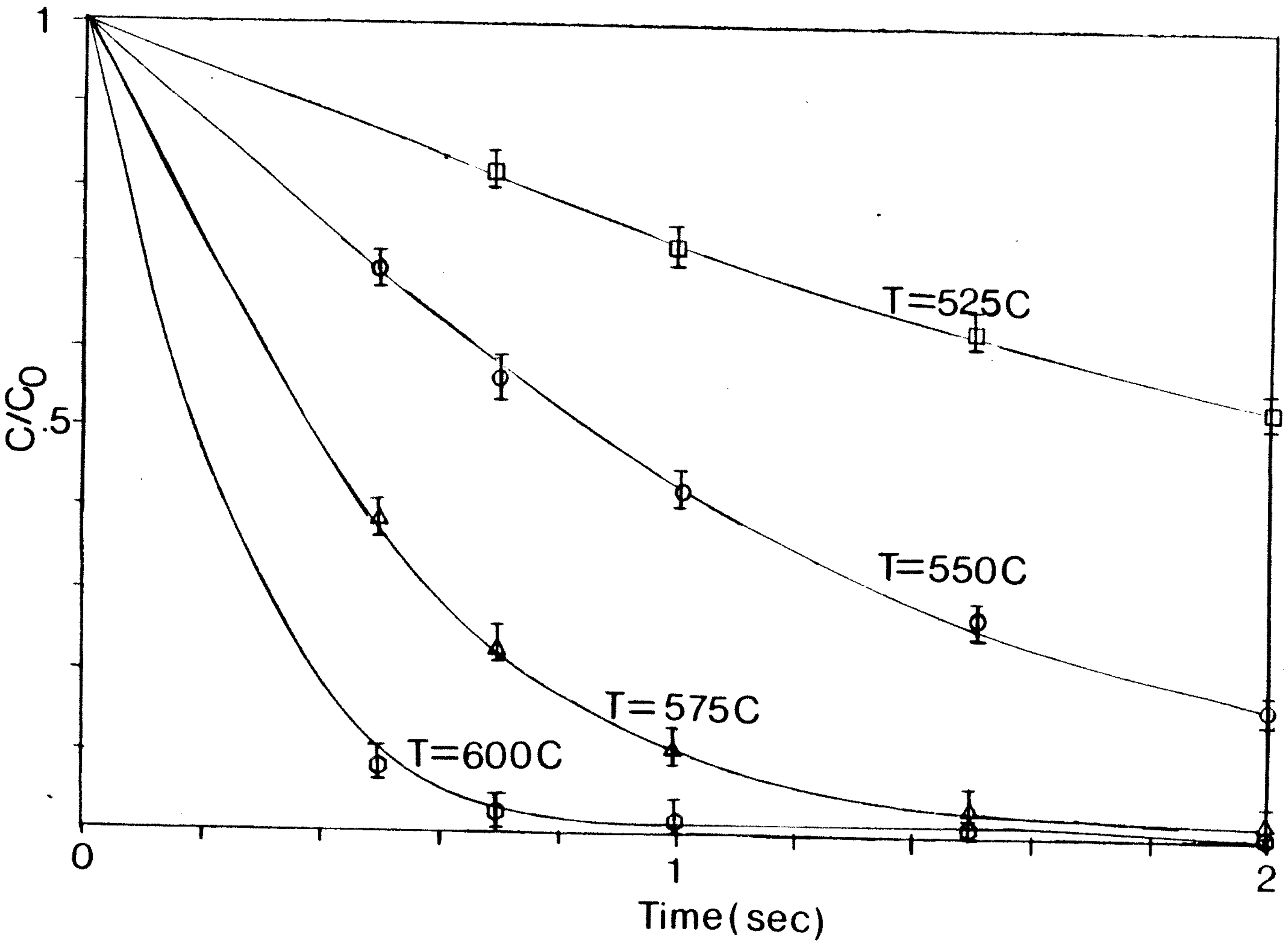

Figure 7. 1,1,1-CH_3CCl_3 Deacy for all Reactants Ratio Sets (Distribute at the same range) vs. Time

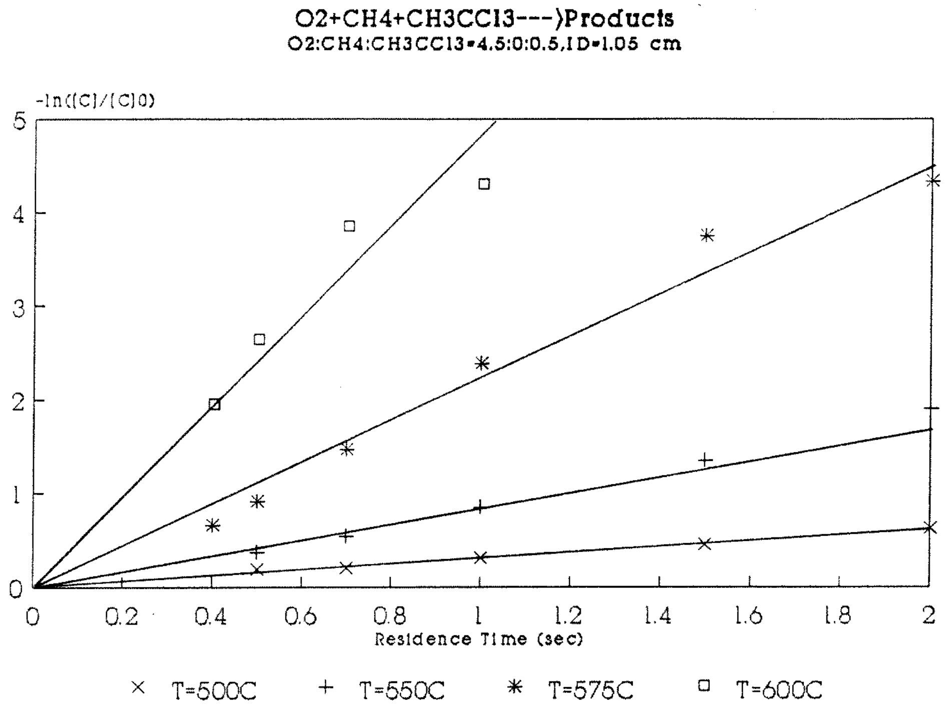

Figure 8-a. 1st-Order Kinetics Fit of CH3CCl3 Decomposition

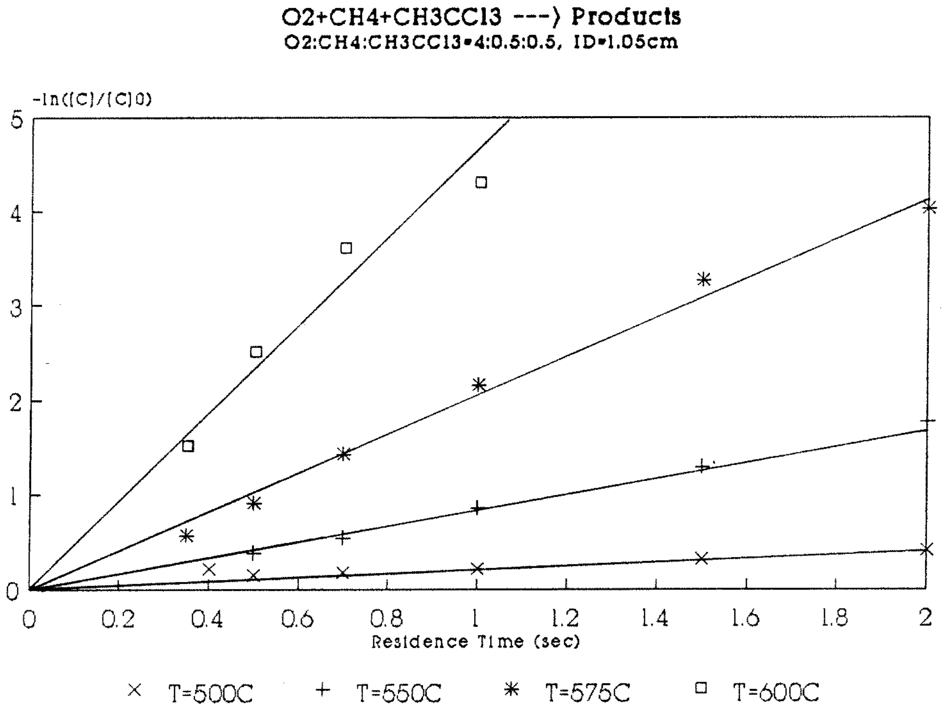

Figure 8-b. 1st-Order Kinetics Fit of CH3CCl3 Decomposition

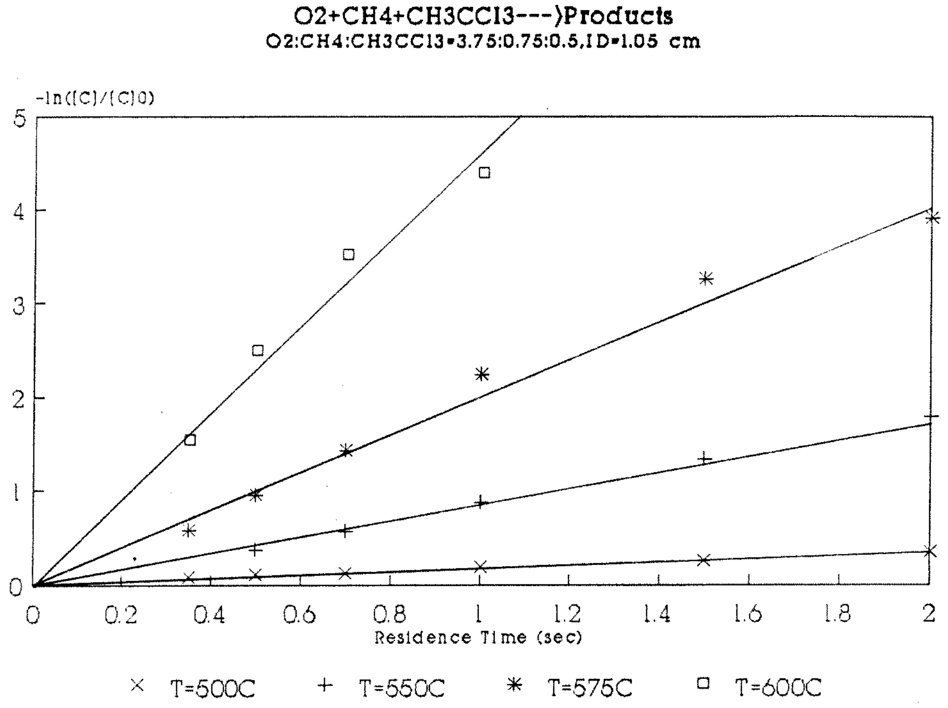

Figure 8-c. 1st-Order Kinetics Fit of Ch3CCl3 Decomposition

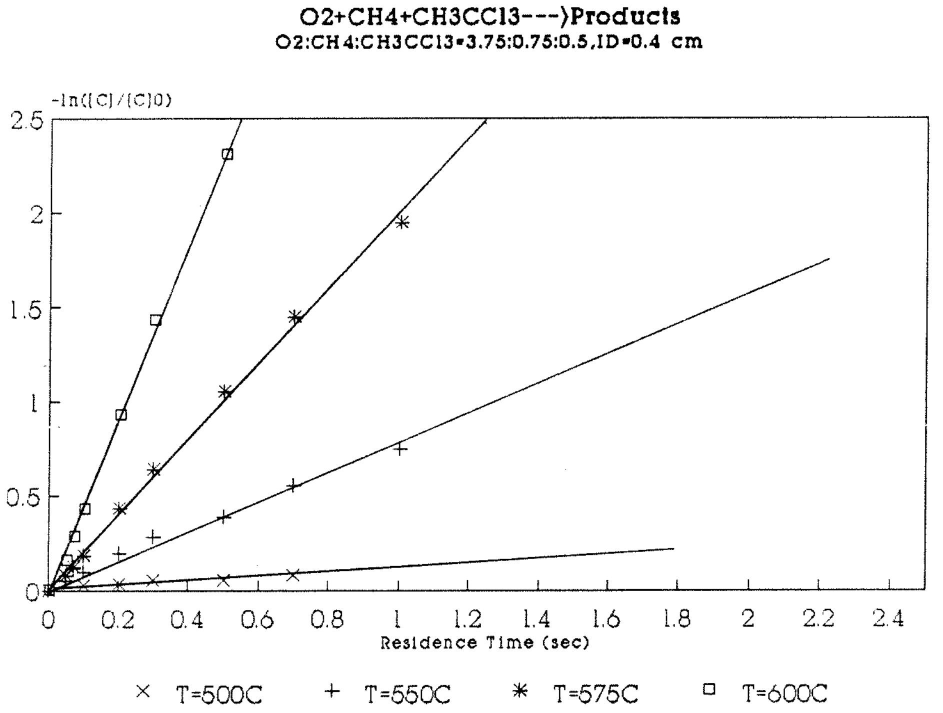

Figure 8-d. 1st-Order Kinetics Fit of Ch3CCl3 Decomposition

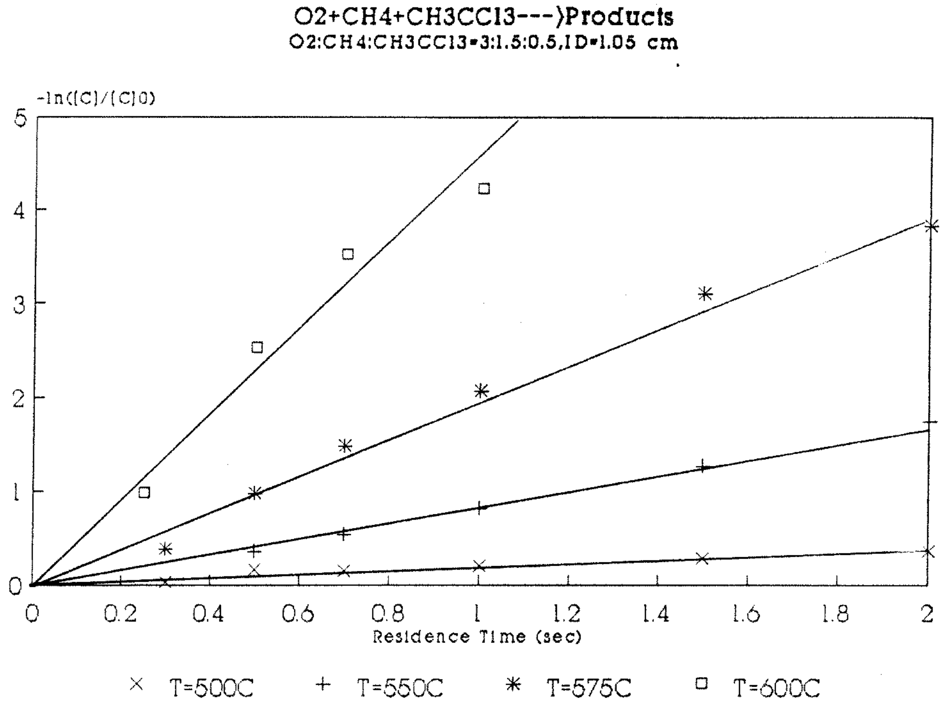
O2+CH4+CH3CCl3---)Products
O2:CH4:CH3CCl3=3:1.5:0.5,ID=1.05 cm

Figure 8-e. 1st-Order Kinetics Fit of CH3CCl3 Decomposition

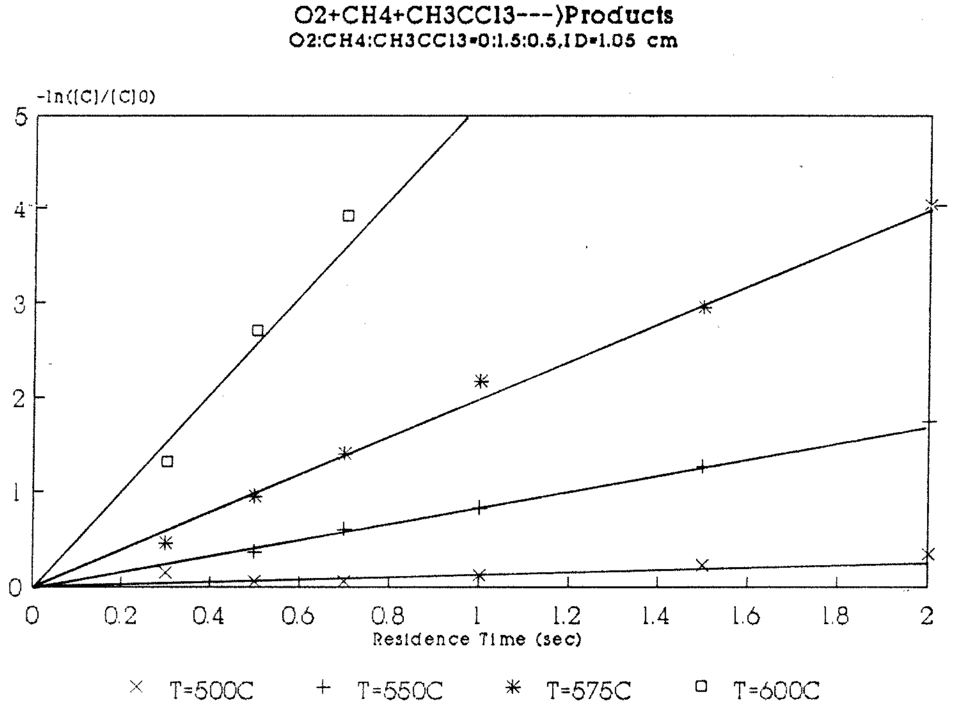
O2+CH4+CH3CCl3---)Products
O2:CH4:CH3CCl3=0:1.5:0.5,ID=1.05 cm

Figure 8-f. 1st-Order Kinetics Fit of CH3CCl3 Decomposition

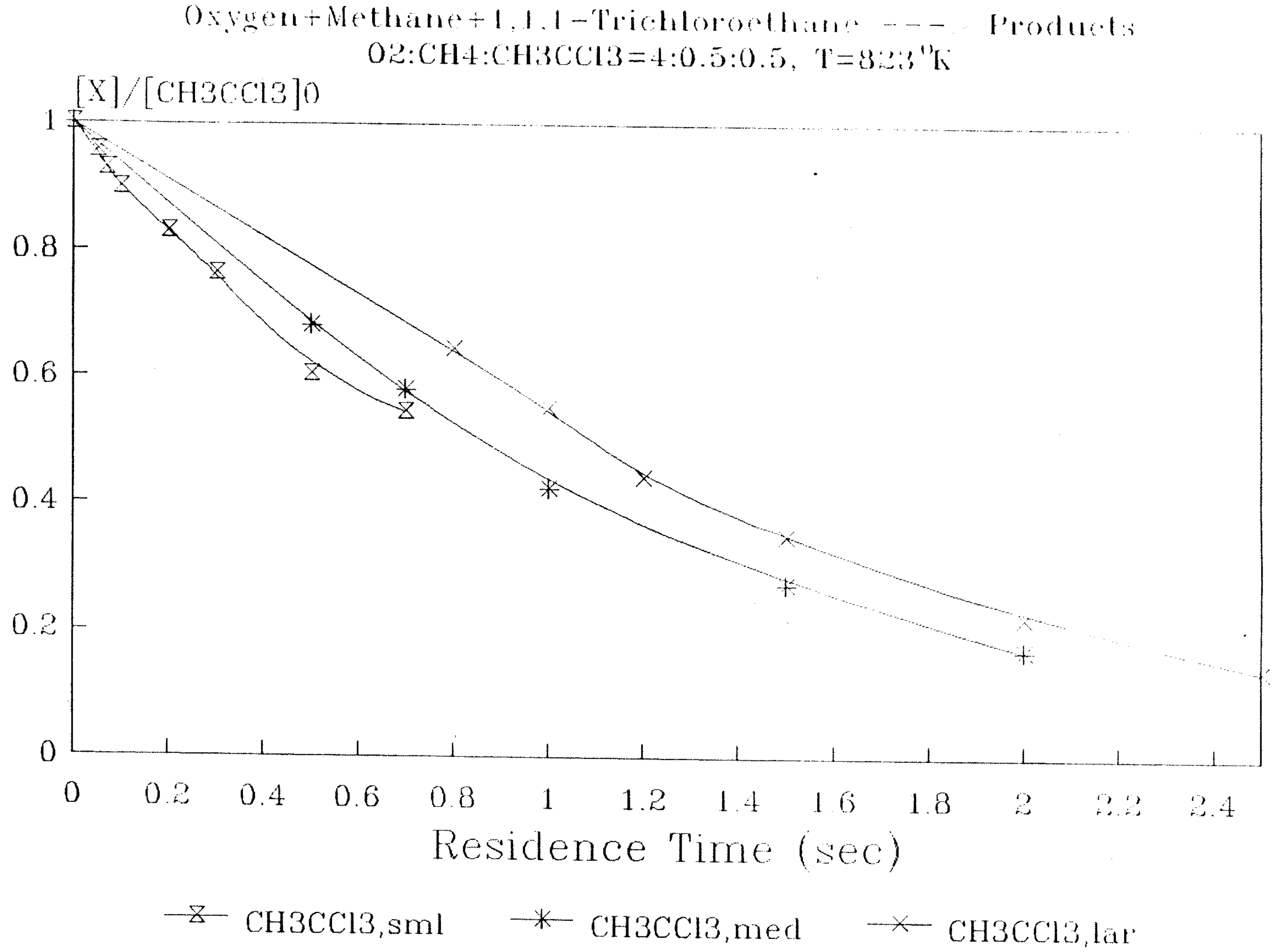

Figure 9-a. 1,1,1-Trichloroethane Decay in varied Reactors
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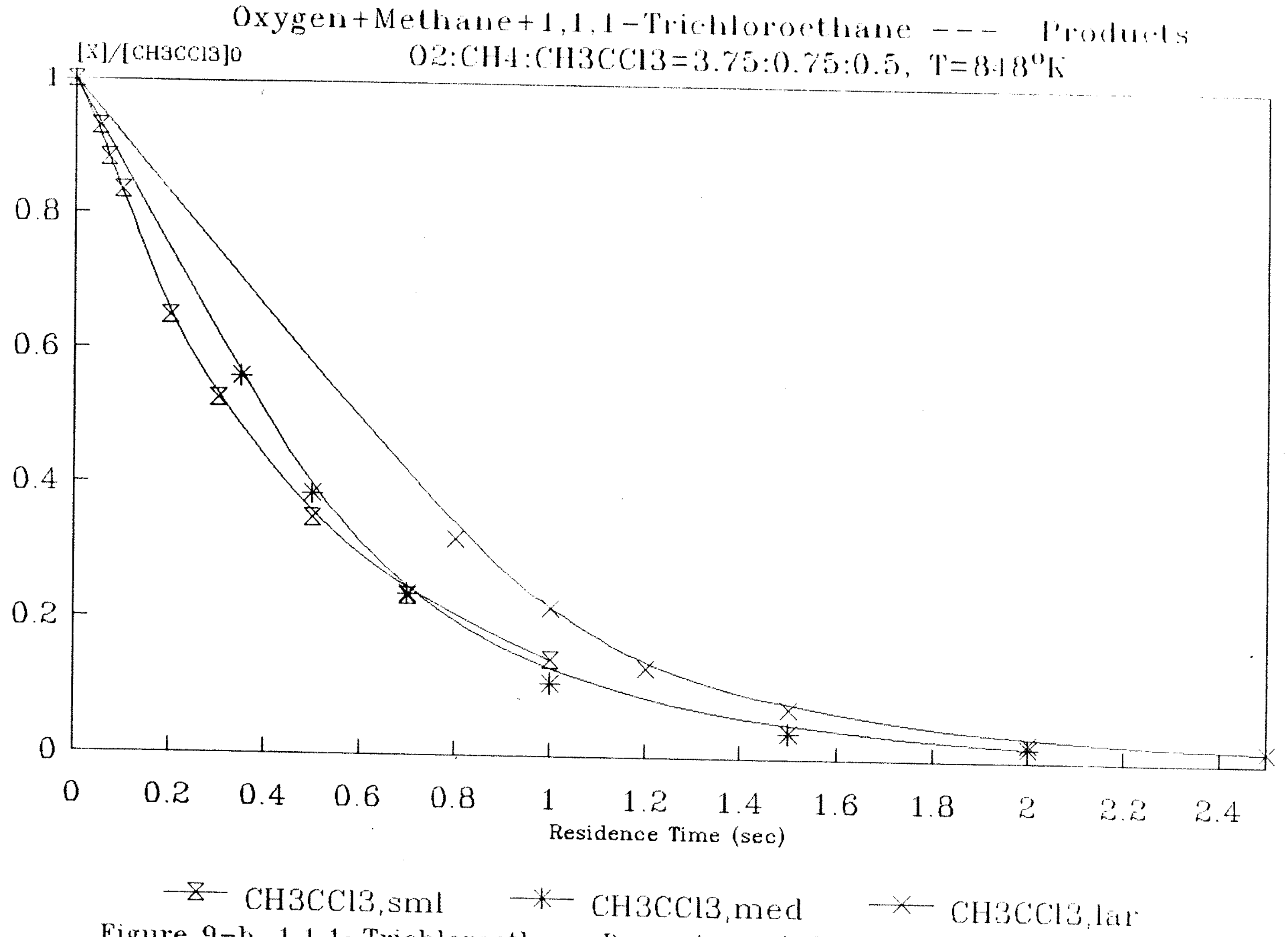

Figure 9-b. 1,1,1-Trichloroethane Decay in varied Reactors

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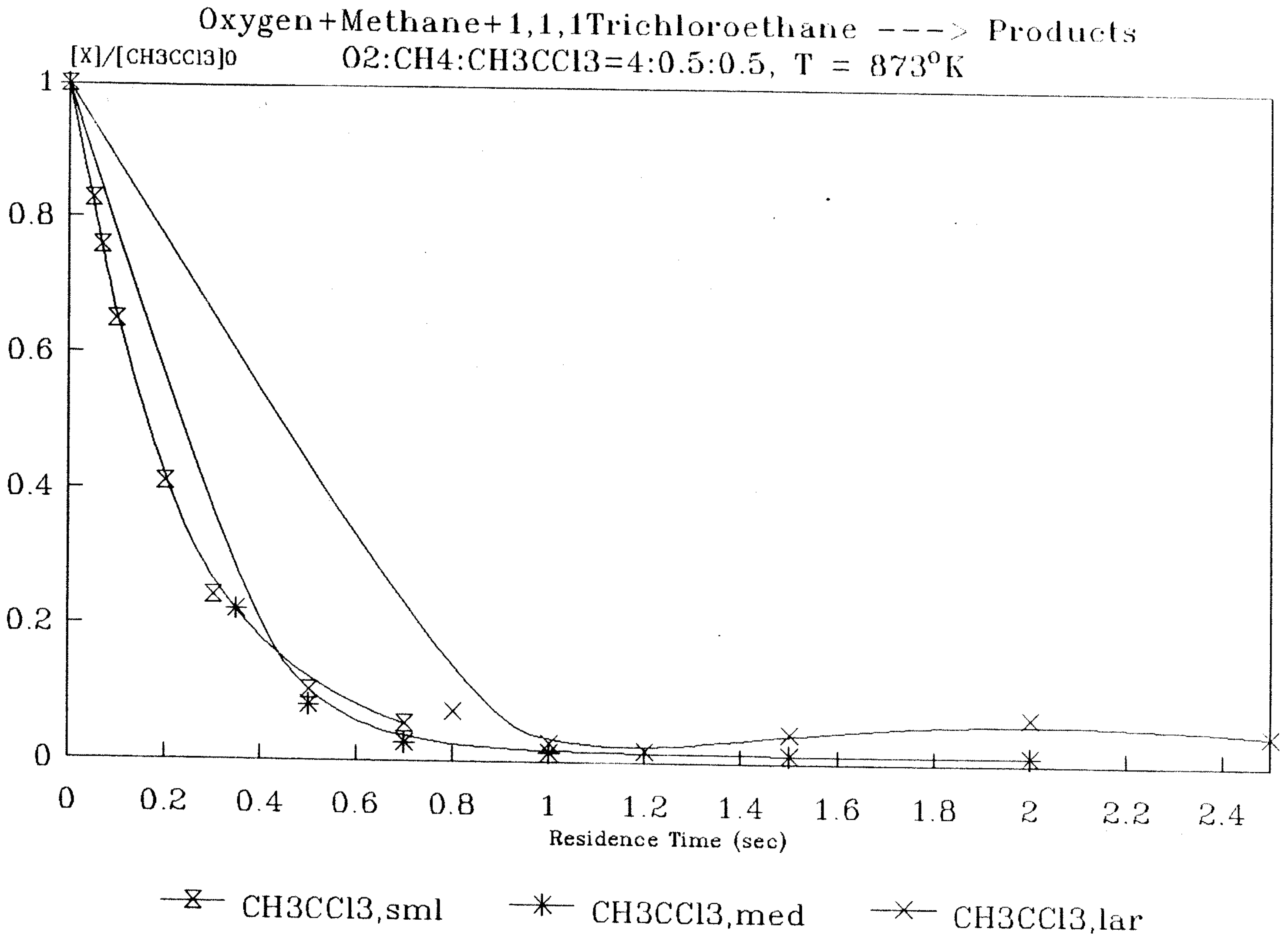


Figure 9-c. 1,1,1-Trichloroethane Decay of varied Reactors

sml:ID=4mm;med:ID=10.5mm;lar:ID=16mm

homogeneous reaction which occurs in the bulk or homogeneous phase of the gas mixture and two, a heterogeneous reaction which occurs on the surface of the flow tube wall. Clearly the relative importance of the wall reaction is greater when the surface to volume ratio (S/V) or relative concentration of the wall surface is greater. The activation energies and Arrhenius frequency factor for the global reaction (loss) of CH_3CCl_3 in the different reactant set ratios are found from Arrhenius plots such as in Figure 10a-e. These global Arrhenius equations for each diameter and reactant set ratio are listed in Table 3.

Wall and bulk rate constants are obtained by plotting k_{exp} versus 2/R, where R is the reactor radius in centimeters. As shown in Figure 11a through 11d, the linear relations described earlier for determining bulk and wall reaction rate constant does not hold. This is probably due to a combination of different effects, these include:

- Synergistic effects of chlorocarbon unimolecular decay to radical and chlorine atoms reaction on oxidation processes.
- Atom and radical loss on the wall (this is probably a manifest of very high wall efficiency at high temperatures.

We note that for all but the highest temperature data, the slope of a best fit straight is almost zero and the observed rate constant is assumed to be the bulk rate constant.

Table 3.
Rate Constants For $CH_3CCl_3 + CH_4 + O_2$ in excess Ar

* $O_2 : CH_4 : CH_3CCl_3 : Ar = 4.5 : 0 : 0.5 : 95$

Reactor I.D. (cm)	kexp
0.4	$1.24 * 10^{12}\ e^{(-45588/RT)}$
1.05	$9.29 * 10^{12}\ e^{(-49009/RT)}$
1.6	$2.36 * 10^{12}\ e^{(-47102/RT)}$

* $O_2 : CH_4 : CH_3CCl_3 : Ar = 4 : 0.5 : 0.5 : 95$

Reactor I.D. (cm)	kexp
0.4	$5.71 * 10^{11}\ e^{(-44404/RT)}$
1.05	$5.98 * 10^{12}\ e^{(-48349/RT)}$
1.6	$3.06 * 10^{12}\ e^{(-47627/RT)}$

* $O_2 : CH_4 : CH_3CCl_3 : Ar = 3.75 : 0.75 : 0.5 : 95$

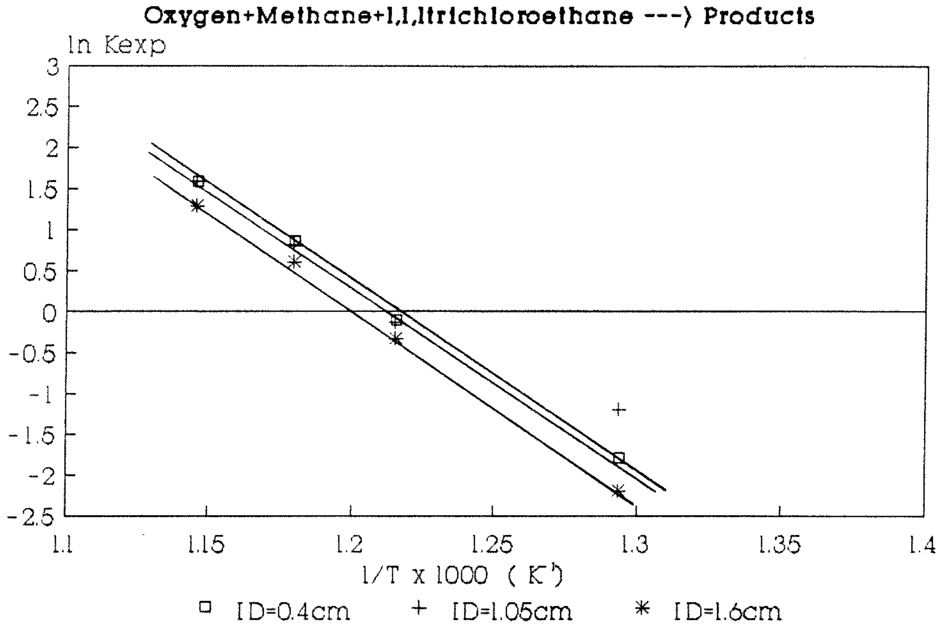
Reactor I.D. (cm)	kexp
0.4	$6.17 * 10^{12}\ e^{(-48429/RT)}$
1.05	$4.44 * 10^{12}\ e^{(-47851/RT)}$
1.6	$1.47 * 10^{12}\ e^{(-46420/RT)}$

* $O_2 : CH_4 : CH_3CCl_3 : Ar = 3 : 1.5 : 0.5 : 95$

Reactor I.D. (cm)	kexp
0.4	$3.98 * 10^{11}\ e^{(-43875/RT)}$
1.05	$1.24 * 10^{11}\ e^{(-41868/RT)}$
1.6	$1.28 * 10^{12}\ e^{(-46267/RT)}$

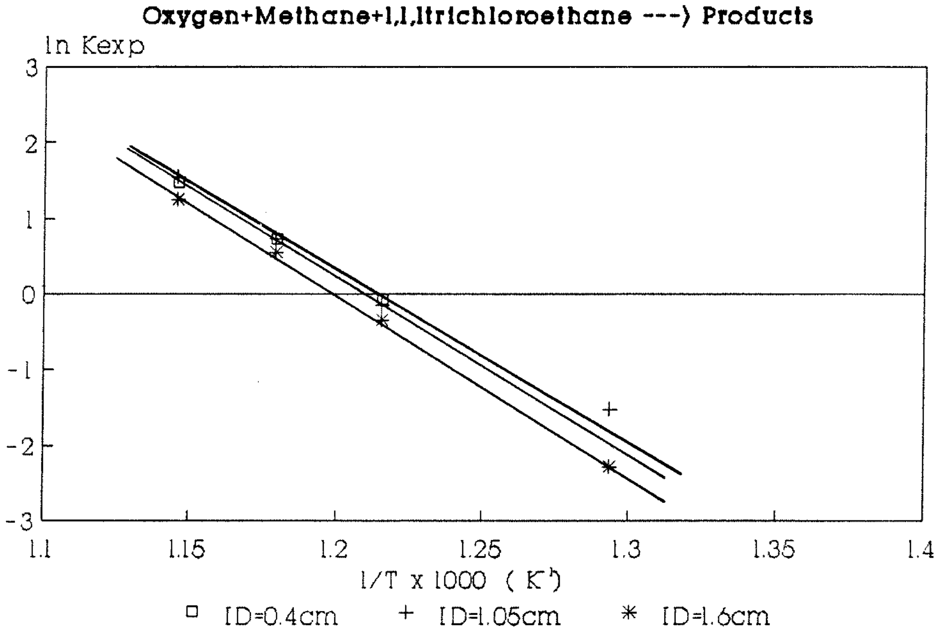
* $O_2 : CH_4 : CH_3CCl_3 : Ar = 0 : 1.5 : 0.5 : 98$

Reactor I.D. (cm)	kexp
0.4	$1.78 * 10^{12}\ e^{(-46378/RT)}$
1.05	$3.56 * 10^{12}\ e^{(-47407/RT)}$
1.6	$7.11 * 10^{11}\ e^{(-45388/RT)}$



O2:CH4:CH3CCl3=4.5:0:0.5

Figure 10-a. Arrhenius Behavior of Kexp for CH3CCl3



O2:CH4:CH3CCl3=4:0.5:0.5

Figure 10-b. Arrhenius Behavior of Kexp for CH3CCl3

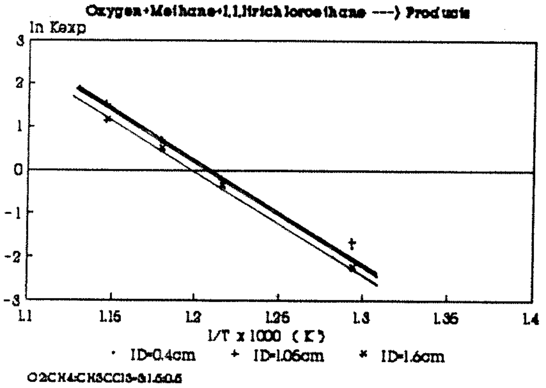


Figure 10-d. Arrhenius Behavior of Kexp for CH3CCl3

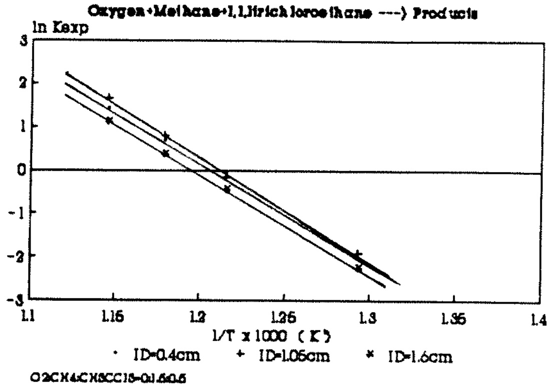
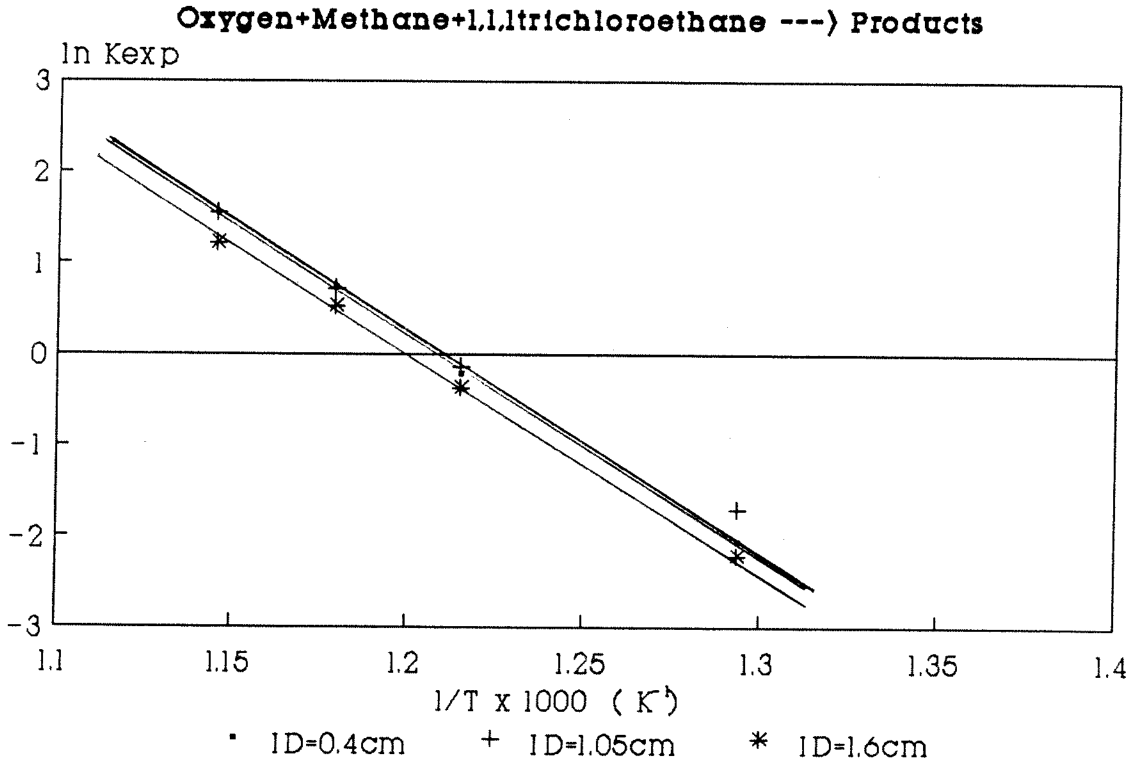


Figure 10-e. Arrhenius Behavior of Kexp for CH3CCl3



O2:CH4:CH3CCl3=3.75:0.75:0.5

Figure 10-c. Arrhenius Behavior of Kexp for CH3CCl3

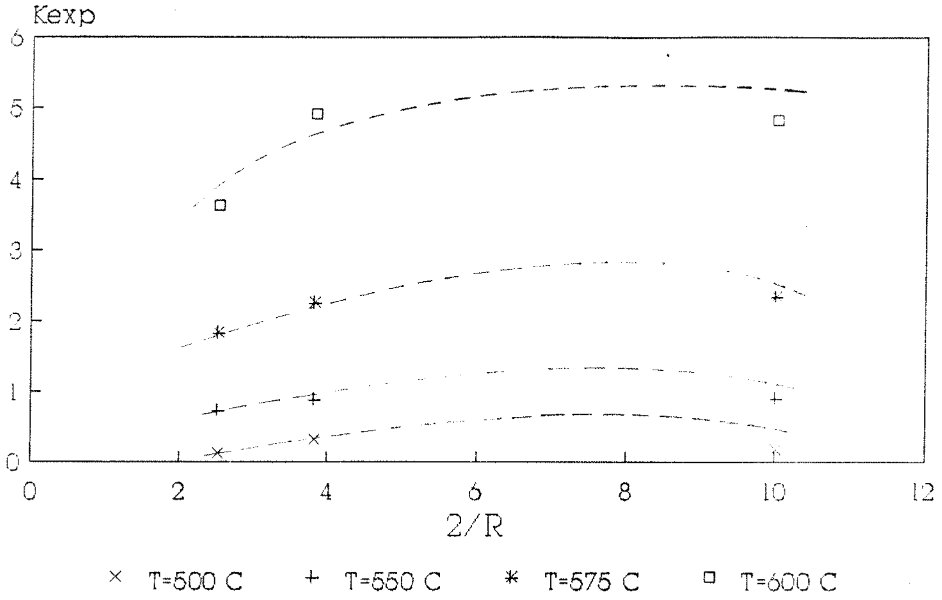


Figure 11-a. Kexp vs S/V of O2:CH4:CH3CCl3=4.5:0:0.5

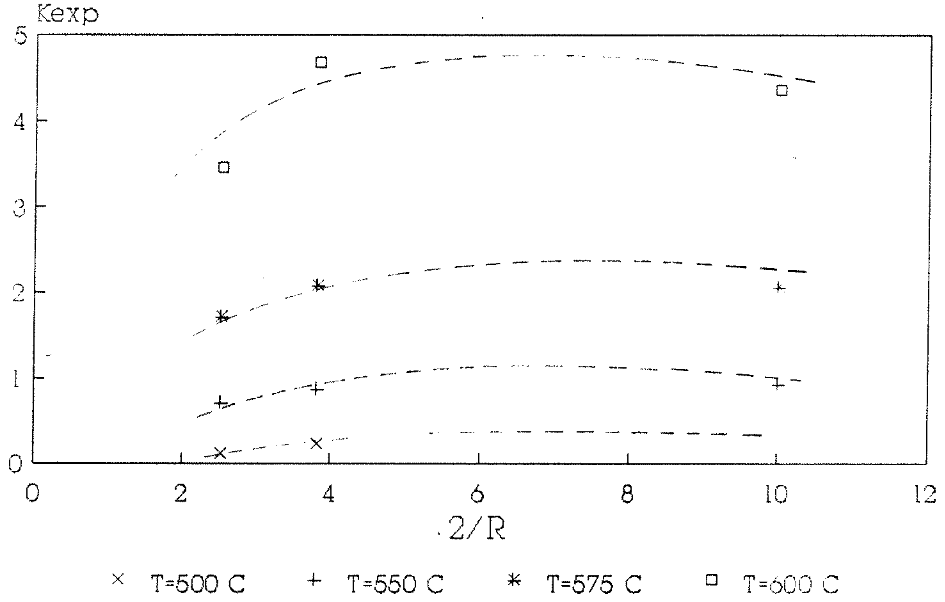
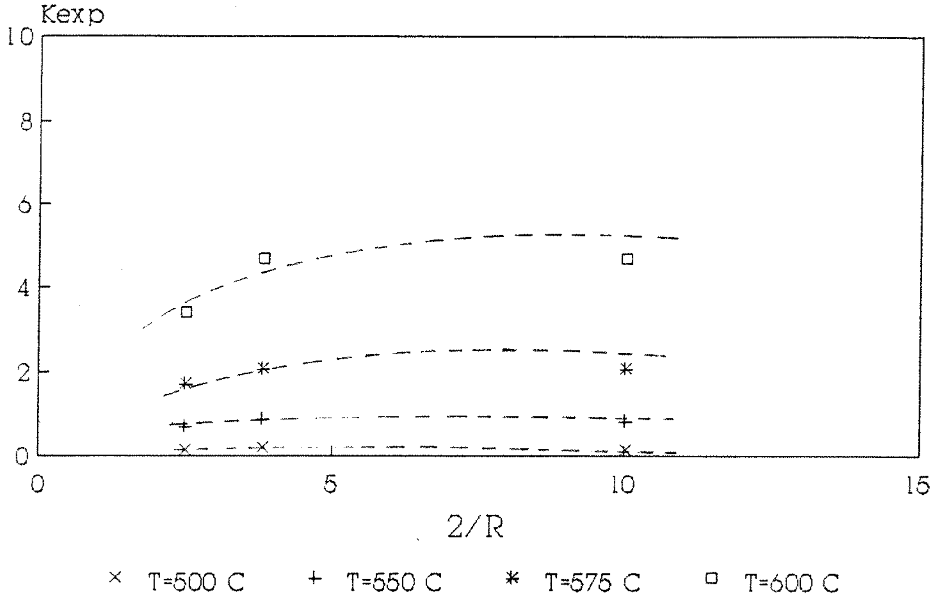
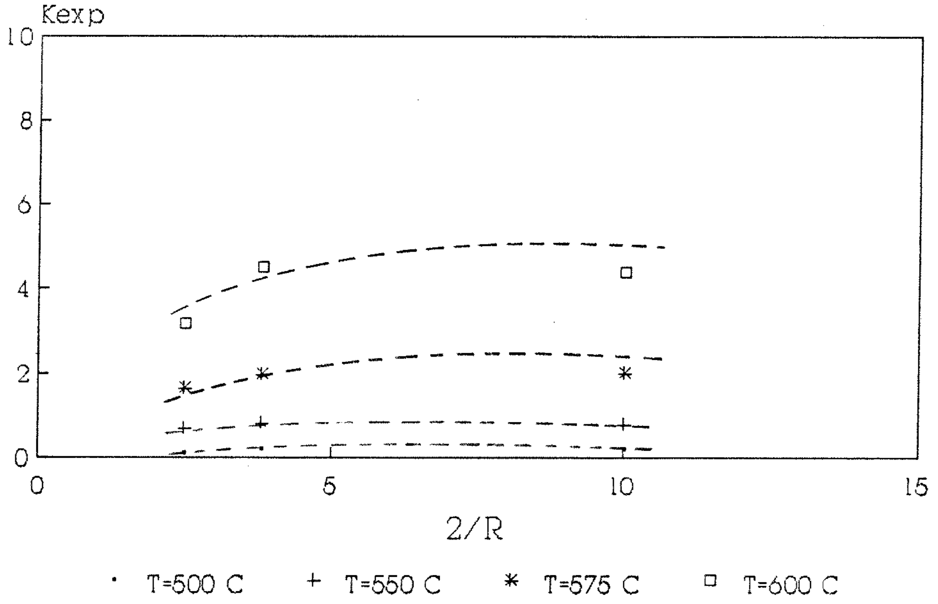


Figure 11-b. Kexp vs S/V of O2:CH4:CH3CCl3=4:0.5:0.5



Figue 11-c. Kexp vs S/V of O2:CH4:CH3CCl3=3.75:0.75:0.5



Figue 11-d. Kexp vs S/V of O2:CH4:CH3CCl3=3:1.5:0.5

B. Reagent Conversion and Product Distribution

Appreciable conversion (50%) of 1,1,1 - trichloroethane is observed at reaction temperature above 550 °C at 1.0 sec residence time even at different reactor set ratios as shown in Figure 6. The distributions for major products CH_2CCl_2, C_2H_2, C_2H_4, CO, CO_2 and C_3H_6 + C_3H_8 (C_3H_n as indicated on figures) are shown in Figure 12 at 1 second residence time for varying temperature and reaction conditions. 1,1-dichloroethylene (CH_2CCl_2) and HCl were the major products over the temperature range from 500 °C to 600 °C, where conversion of CH_3CCl_3 ranged from 5 % to 100 % as shown in both Figure sets 6 and 12. Only a small amount of ethylene, vinyl chloride, propane and propylene were observed at temperatures below or equal to 600°C.

In Figures set 12, clearly one may see that the major product at 1 sec residence time and below 650°C is 1,1-dichloroethylene which results through loss of HCl (molecular elimination) reaction from 1,1,1-trichloroethane. Above 600°C the carbon monoxide concentration rises exponentially and levels off to about 93% at 740°C and above. Figure 12b and 12c show that the presence of 0.5% or 0.75% methane has little effect on 1,1,1-trichloroethane conversion and stabilizes 1,1-dichloroethylene product to a level where it is not significantly destroyed until temperatures above 750°C at 1 sec residence time in this system. Methane shows small amount reaction at 560°C then

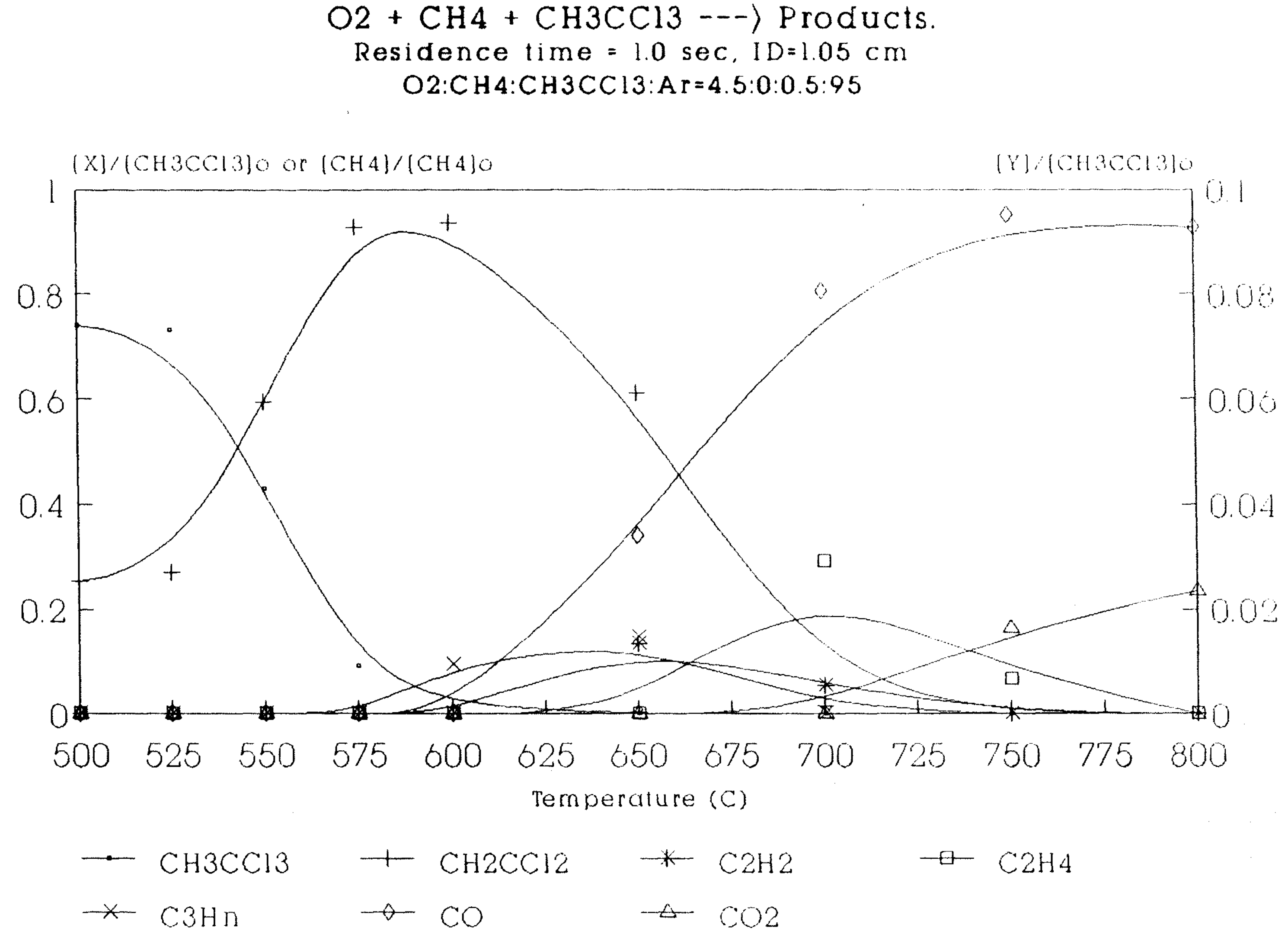


Figure 12-a. Product Distribution

X: CH_3CCl_3, CH_2CCl_2, CO, CO_2
Y: C_2H_2, C_2H_4, C_3H_n(C_3H_6+C_3H_8)

O2 + CH4 + CH3CCl3 ---> Products.

Residence time = 1.0 sec, ID=1.05 cm

O2:CH4:CH3CCl3:Ar=4:0.5:0.5:95

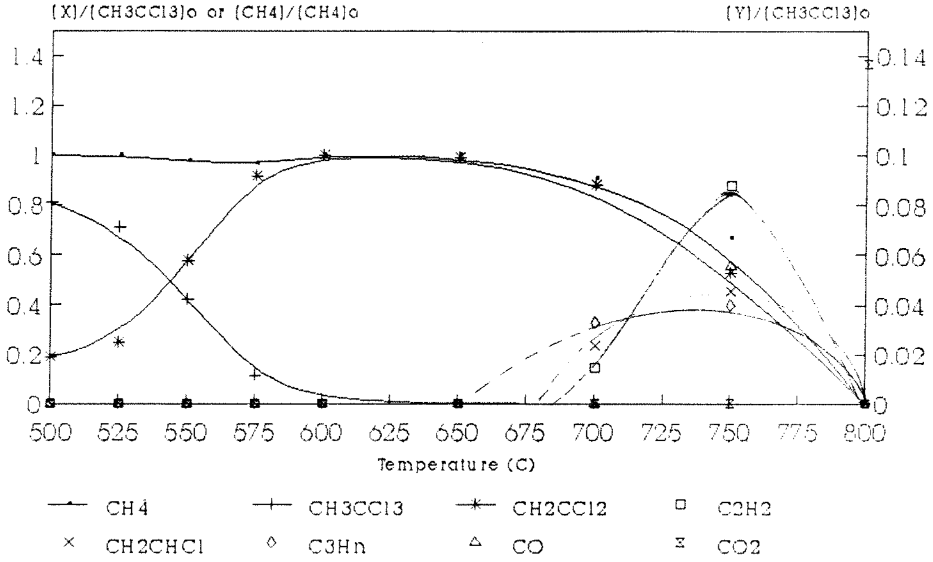


Figure 12-b. Product Distribution.

X: CH3CCl3, CH2CCl2, CO, CO2
Y: C2H2, C2H3Cl, C3Hn(C3H6+C3H8)

O2 + CH4 + CH3CCl3 ---> Products.

Residence time = 1.0 sec, ID=1.05 cm

O2:CH4:CH3CCl3:Ar=3.75:0.75:0.5:95

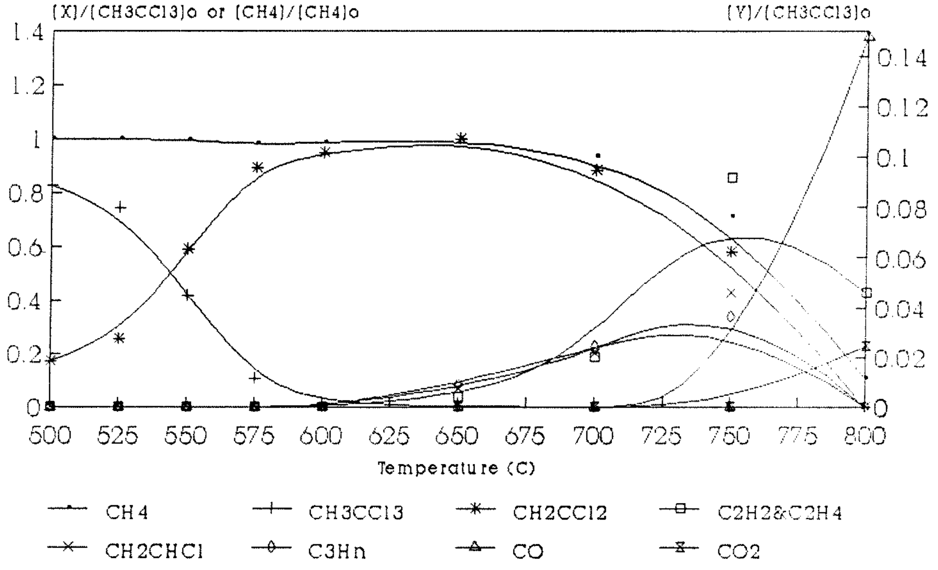


Figure 12-c. Product Distribution.

X: CH3CCl3, CH2CCl2, CO, CO2
Y: C2H2, C2H4, C2H3Cl, C3Hn(C3H6+C3H8)

O2 + CH4 + CH3CCl3 ---⟩ Products.
Residence time = 1.0 sec, ID=1.05 cm
O2:CH4:CH3CCl3:Ar=3:1.5:0.5:95

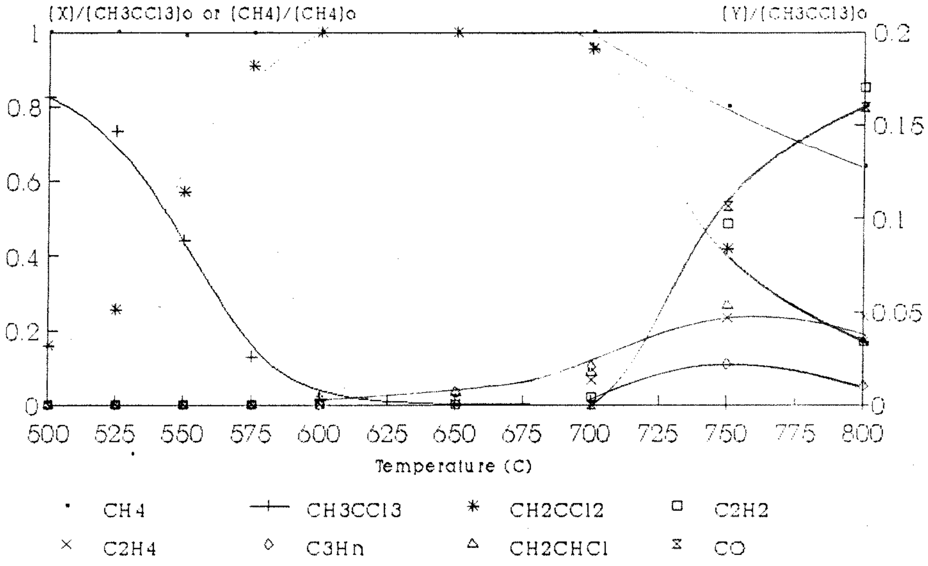


Figure 12-d. Product Distribution

X: CH3CCl3, CH2CCl2, CO
Y: C2H2, C2H4, C2H3Cl, C3Hn(C3H6+C3H8)

O2 + CH4 + CH3CCl3 ---⟩ Products.
Residence time = 1.0 sec, ID=1.05 cm
O2:CH4:CH3CCl3:Ar=0:1.5:0.5:98

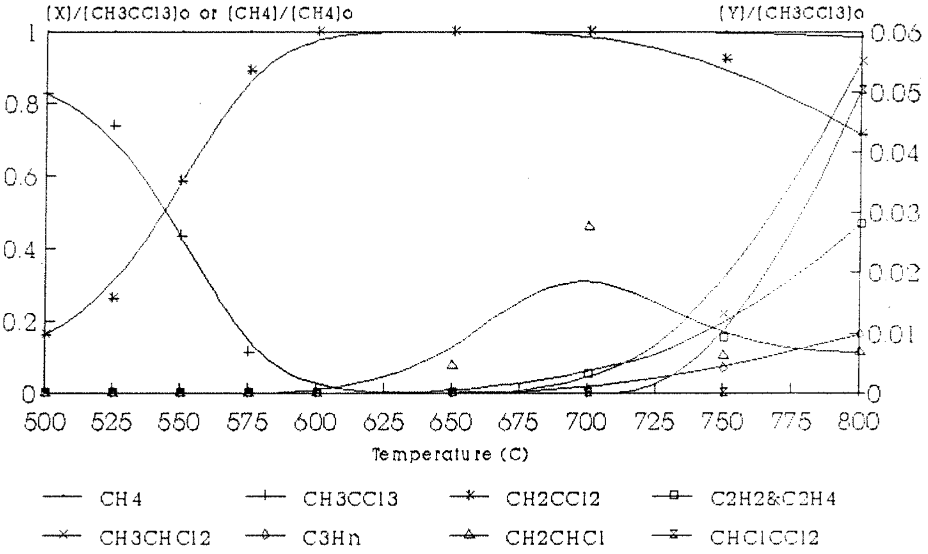


Figure 12-e. Product Distribution.

X: CH3CCl3, CH2CCl2,C3Hn(C3H6+C3H8)
Y: C2H2, C2H4, CH3CHCl2, CH2CHCl,
CHClCCl2

significant decomposition above 700^{o}C. At temperature between 600 to 680^{o}C, 1,1-dichloroethylene represents almost 100% of the parent 1,1,1-trichloroethane concentration. Figure 12d and 12e, which has low or no O_2 concentration and holding methane concentration constant (1.5%), presence 1,1,1-trichloroethane decomposition and 1,1-dichloroethylene production and loss, both similar to conditions for Figure 12 a-c with 1,1-dichloroethylene loss slower at lower [O_2]. CH_4 shows less decomposition and there is more acetylene production higher at high temperature. There was no carbon monoxide measured below 750^{o}C for experiments illustrated in Figures 12 b, c, d and e, and there was no CO observed before 1 sec residence time. Figure 13-a shows product distributions of 1,1-dichloroethylene and CO as a function of time above 700^{o}C. Figure 13-b shows that no CO was observed at the lower O_2 concentration at 700^{o}C. Figure 13c presents product distribution of CH_2CCl_2, CO, CO_2 as a function of time at 800^{o}C. Additional data is also shown in Figure 15a through 15e which is discussed later in this chapter.

As shown in Figure 14, there was an oxygen effect on the major product distribution when the temperature were higher than 600^{o}C. The levels of non-chlorinated hydrocarbons are shown to increase with increasing temperature for all reactant ratio sets. The concentration of chlorine containing hydrocarbon products decrease with increasing temperature, residence time and ratio of O_2/CH_4,

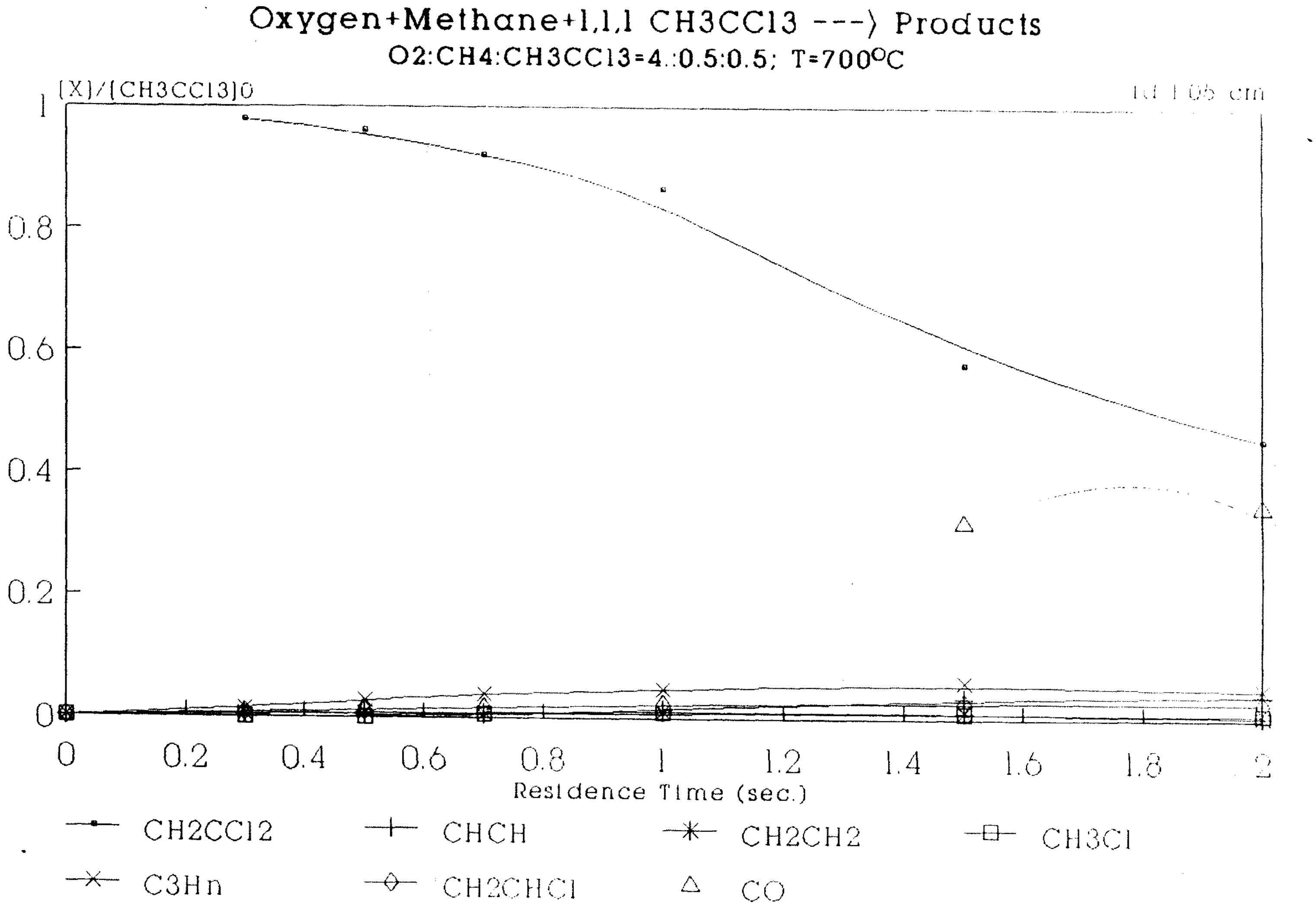


Figure 13-a. Product Distribution at Temp. = 700°C

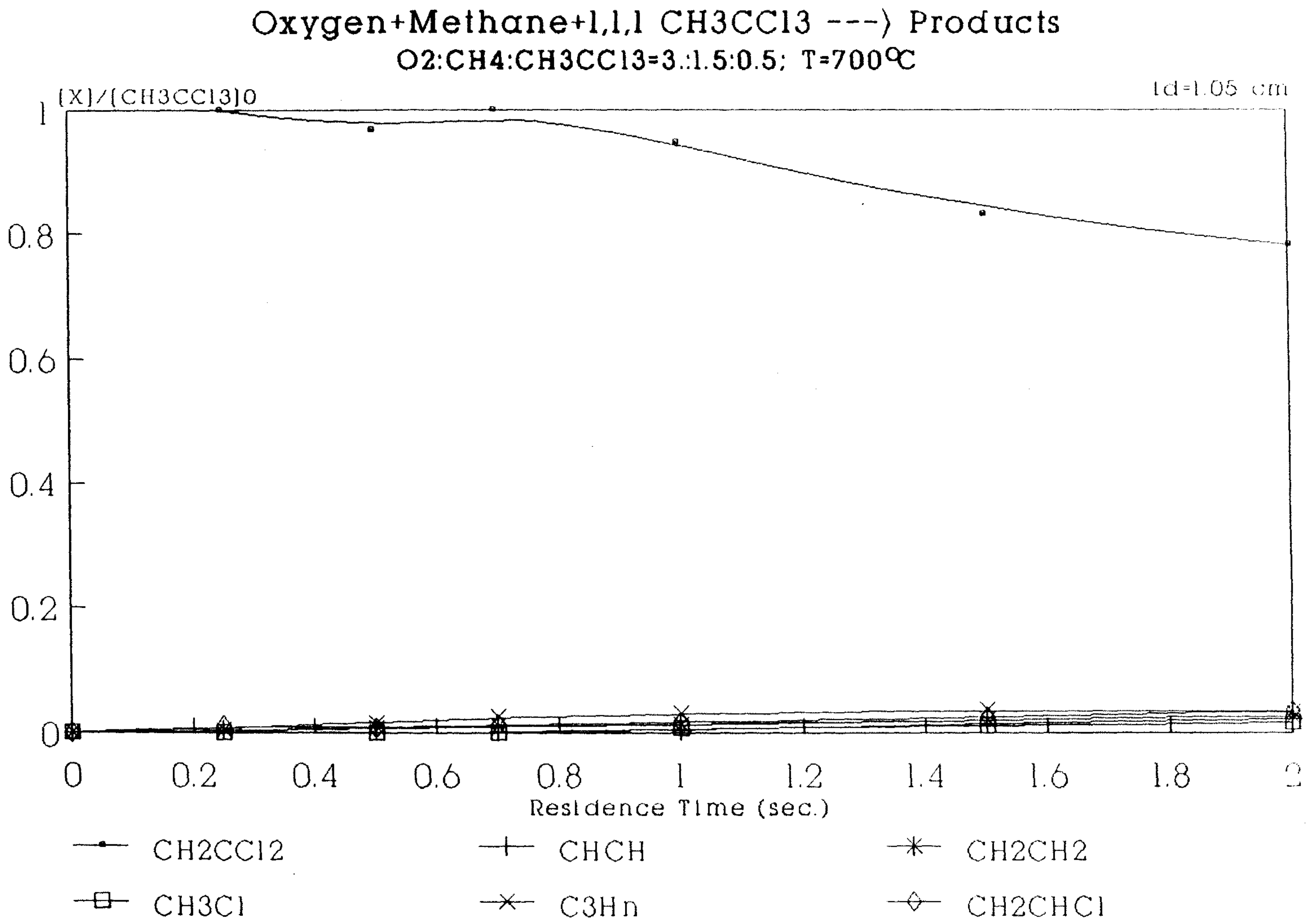


Figure 13-b. Product Distribution at Temp. = 700°C

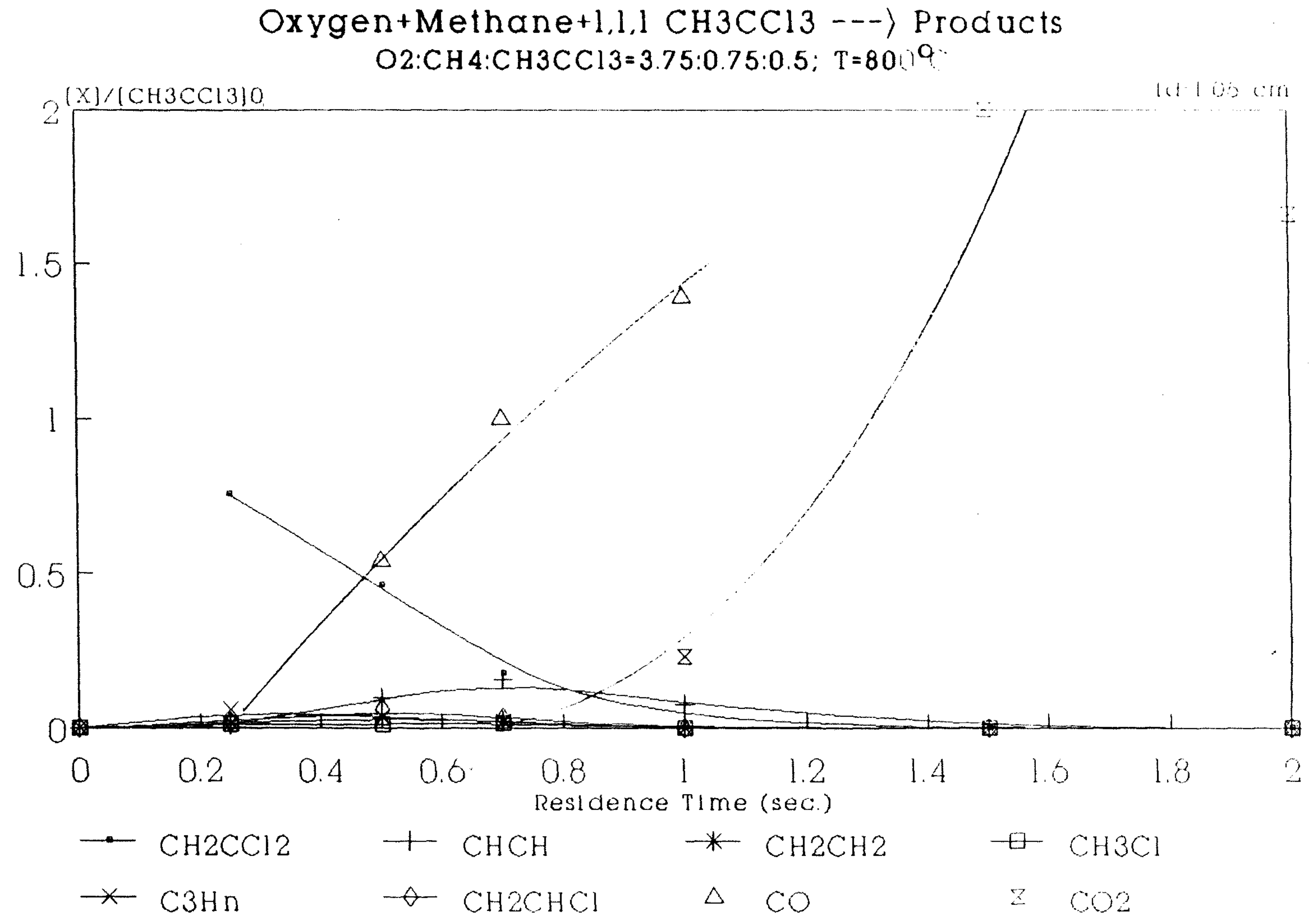


Figure 13-c. Product Distribution at Temp. = 800°C

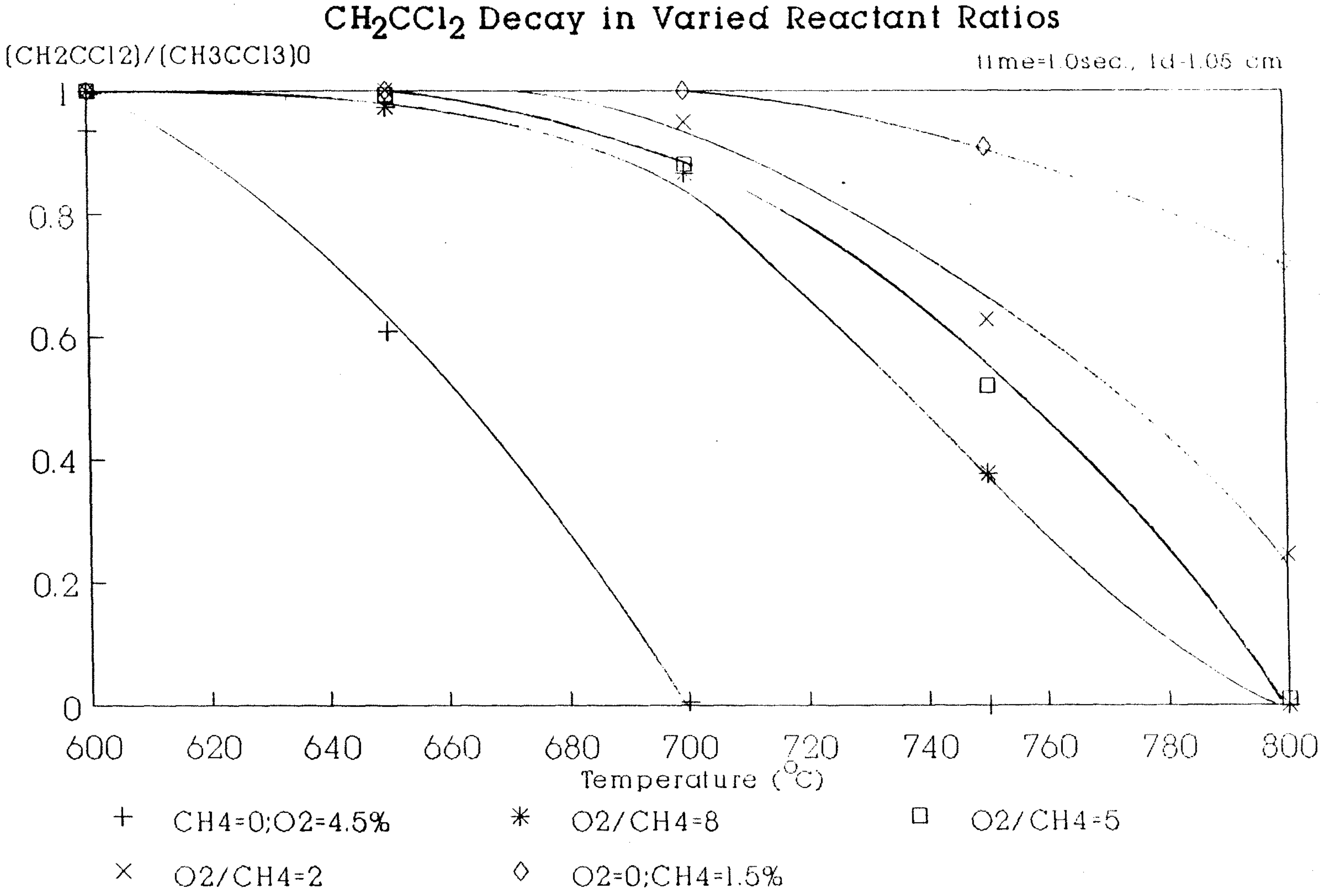


Figure 14. 1,1-Dichloroethylene Distribution versus Temp.

CH3CCl3=0.5%

while HCl formation increased as shown in the chlorine material balance of Table 4.

Formation of CH_2CCl_2 as one of major product from CH_3CCl_3 increases with increasing temperature to a maximum near 600^oC at 1.0 sec residence time and is independent of reactant ratio. It then drops quickly with increasing temperature and/or increased levels of O_2. CH_2CCl_2 is the initial stable product in unimolecular reaction of this mixture. Figures 15a through 15e also specifically illustrate CH_2CCl_2 normalized concentration versus residence time for different temperatures. They demonstrate that the CH_2CCl_2 concentration increase with increasing residence time under 600 ^oC while its survival temperature window which we shall identify as a "stability window" increases with decreasing ratio of O_2 to CH_4. This is further illustrated in Figures 12b through 12e, and particularly in 12d and 12e which show that decreases in $[O_2]$ with CH_4 held constant increases the "stability window" of CH_2CCl_2. Further work needs to be performed here to clearly separate the effects of CH_4 and O_2 on the reaction system. Data shown in Figures 12b through 12e indicates that CH_4 may have a significant stabilizing effect on 1,1 CH_2CCl_2 in this system.

The increase in CH_2CCl_2 with residence time suggests that its rate of formation is faster than its destruction at this 600^oC temperature and is another indication that the CH_2CCl_2 is stable intermediate product in overall reaction.

Table 4-a. Material Balance for 100 Moles Chlorine

$O_2 : CH_4 : CH_3CCl_3 = 4.5 : 0 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)					
Species (%)	550	575	600	650	750	800
CH_3CCl_3	32.43	9.28	1.39	-	-	-
CH_2CCl_2	40.17	62.50	63.73	40.98	-	-
CH_3Cl	-	-	-	0.36	-	-
CH_2CHCl	-	-	-	0.23	-	-
HCl	18.60	30.59	35.83	49.18	95.08	104.92
Total	91.20	102.37	100.95	90.75	95.08	104.92

Table 4-b. Material Balance for 100 Moles Chlorine

$O_2 : CH_4 : CH_3CCl_3 = 4 : 0.5 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_3CCl_3	81.40	68.13	42.79	11.42	1.38	-	-	-	-
CH_2CCl_2	12.60	15.71	38.72	61.93	67.98	66.10	58.33	26.23	0.00
CH_3Cl	-	-	-	-	-	0.00	0.62	0.85	-
CH_2CHCl	-	-	-	-	-	0.00	0.77	0.90	-
HCl	6.44	8.28	18.22	28.58	30.37	35.59	41.67	67.21	109.68
Total	100.44	92.12	99.73	101.93	99.73	101.69	101.39	95.19	109.68

Table 4-c. Material Balance for 100 Moles Chlorine

$O_2 : CH_4 : CH_3CCl_3 = 3.75 : 0.75 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_3CCl_3	83.58	73.01	42.27	10.84	1.24	-	-	-	-
CH_2CCL_2	11.51	16.59	39.85	60.35	63.43	67.74	60.00	35.59	0.58
CH_3Cl	-	-	-	-	-	0.00	0.58	1.29	0.00
CH_2CHCl	-	-	-	-	-	0.26	0.72	1.58	0.00
HCl	6.59	7.77	18.39	27.16	30.52	33.87	38.33	59.32	95.16
Total	101.68	97.37	100.51	98.35	95.19	101.87	99.63	97.78	95.74

Table 4-d. Material Balance for 100 Moles Chlorine

$O_2 : CH_4 : CH_3CCl_3 = 3 : 1.5 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_3CCl_3	83.08	67.80	44.33	12.91	1.50	-	-	-	-
CH_2CCl_2	10.52	15.59	38.48	61.54	68.31	68.33	63.93	42.62	16.67
CH_2CHCl	-	-	-	-	0.12	0.22	0.56	1.41	1.82
CH_3Cl	-	-	-	-	-	-	0.48	1.26	1.82
HCl	6.44	8.08	19.07	27.51	30.66	35.00	36.07	52.46	71.21
Total	100.04	91.47	101.88	101.96	100.59	103.55	101.04	97.75	91.52

Table 4-e. Material Balance for 100 Moles Chlorine

$O_2 : CH_4 : CH_3CCl_3 = 0 : 1.5 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_3CCl_3	67.07	38.54	44.03	11.62	-	-	-	-	-
CH_2CCl_2	10.93	9.12	39.47	60.51	69.51	67.24	69.49	61.02	48.39
CH_2CHCl	-	-	-	-	-	0.16	0.92	0.20	0.23
CH_3CHCl_2	-	-	-	-	-	-	-	1.14	3.71
CH_2Cl_2	-	-	-	-	-	-	-	-	3.55
$CHClCCl_2$	-	-	-	-	-	-	-	-	5.00
HCl	5.95	9.09	19.06	27.29	30.45	34.48	33.90	40.68	48.39
Total	83.95	56.75	102.56	99.42	99.96	101.88	104.31	103.04	109.27

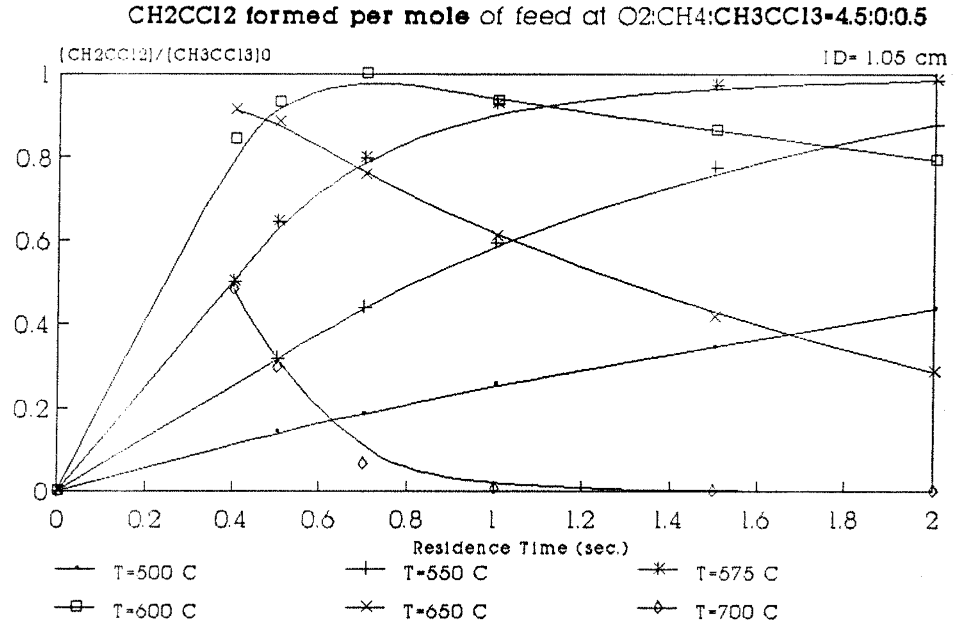


Figure 15-a. CH2CCl2 Distribution

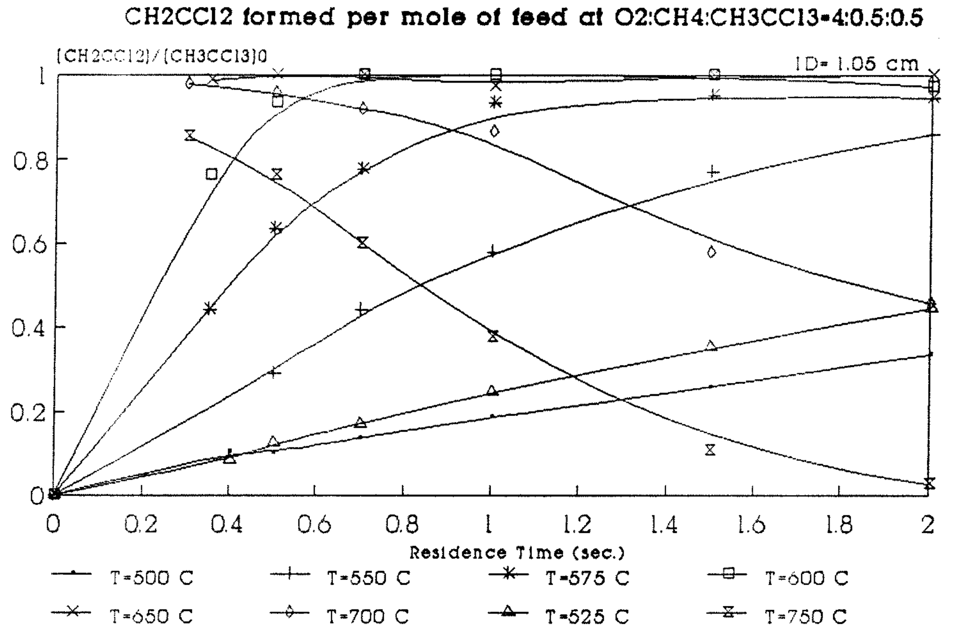
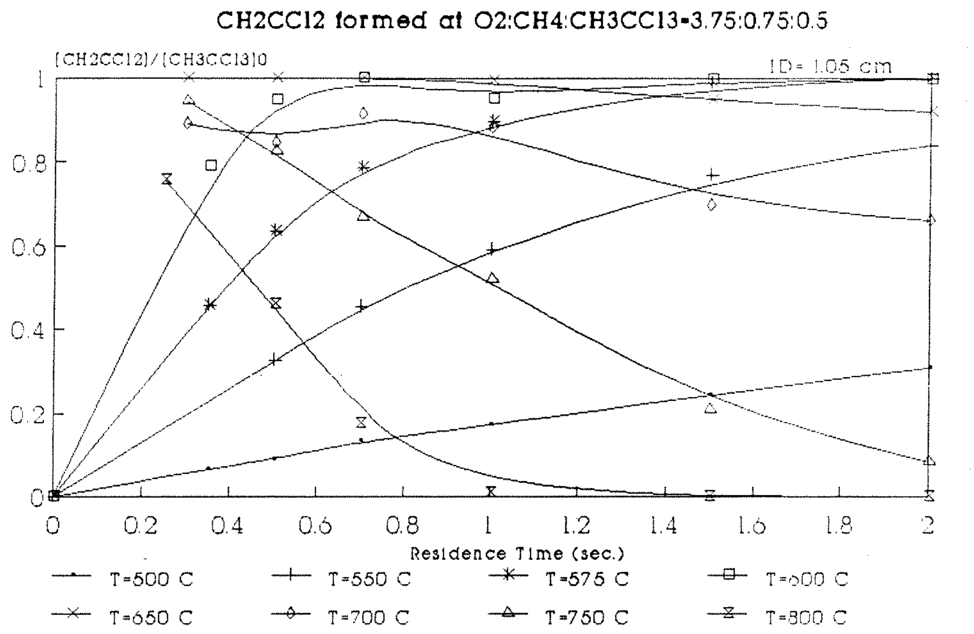
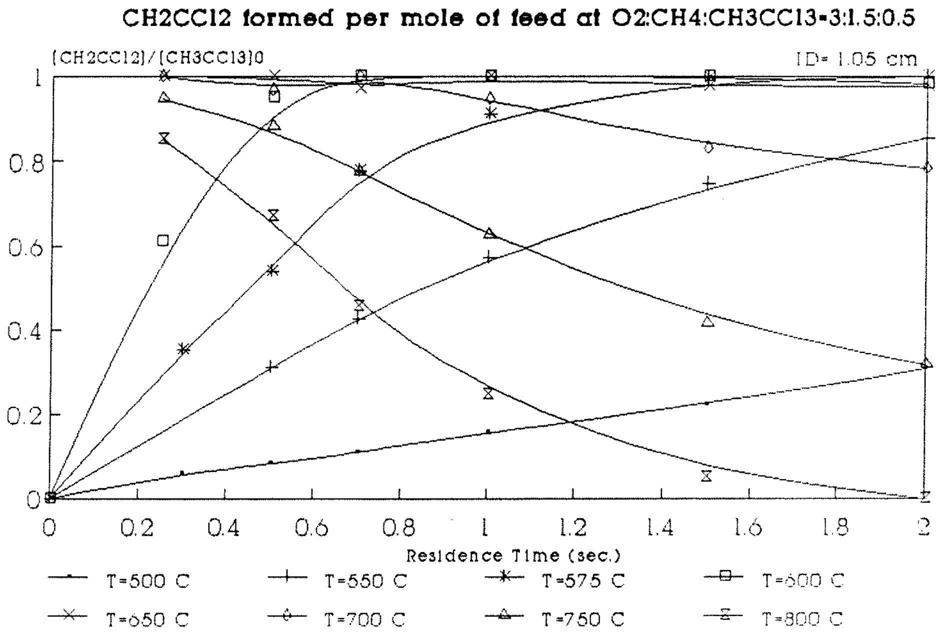


Figure 15-b. CH2CCl2 Distribution



CH2CCl2 formed at O2:CH4:CH3CCl3=3.75:0.75:0.5

Figure 15-c. CH2CCl2 Distribution



CH2CCl2 formed per mole of feed at O2:CH4:CH3CCl3=3:1.5:0.5

Figure 15-d. CH2CCl2 Distribution

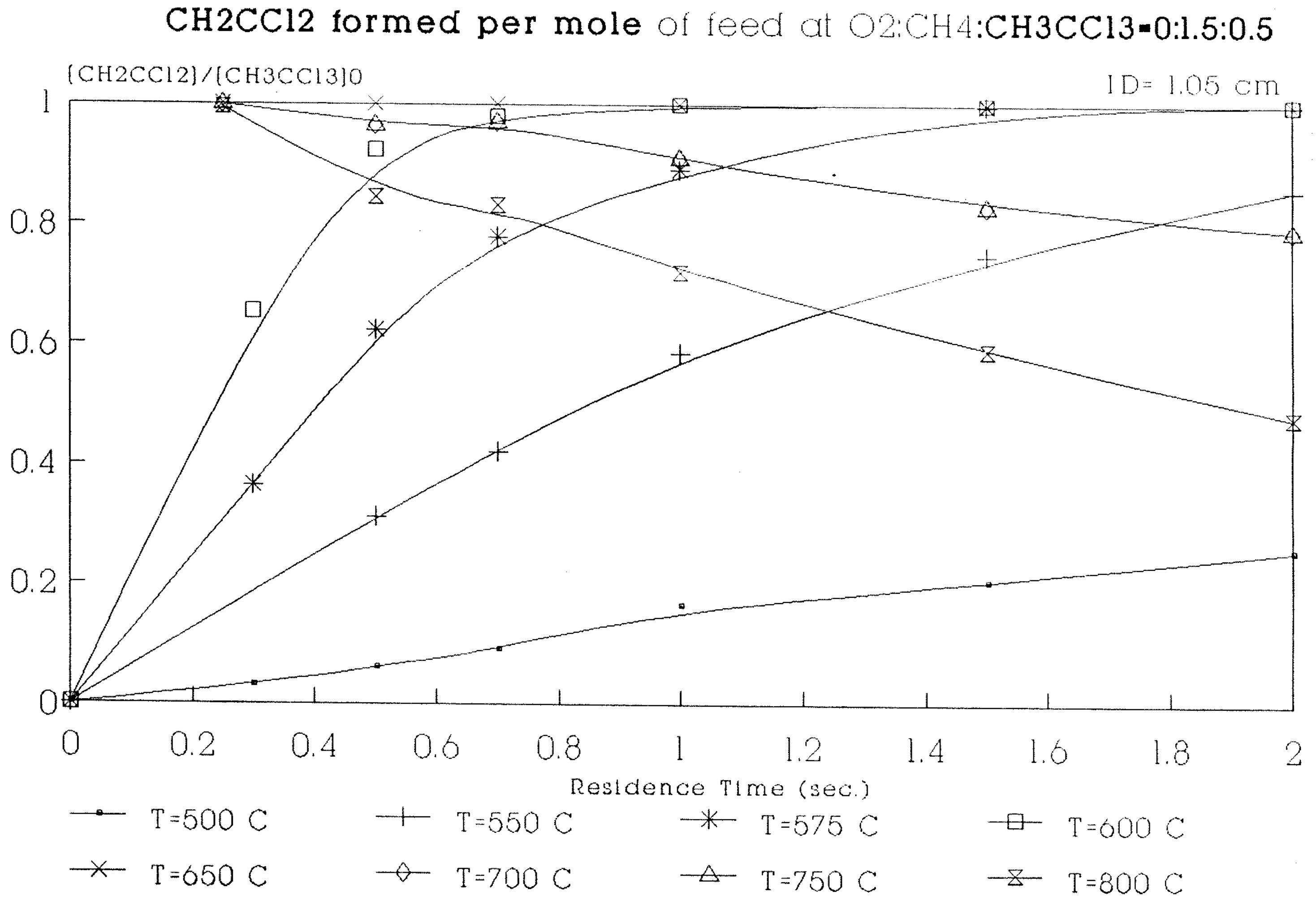


Figure 15-e. CH2CCl2 Distribution vs Time

Figure 12, Table 4 and Table 5, show that concentration of CH_2CHCl, CH_2CH_2, CH_3Cl, C_3H_6 and C_3H_8, increase from 650 to 750^oC as the temperature increases. These same products (except C_2H_2) increase in concentration as residence time increases until a mean residence time longer than 0.7 sec occurs. These products then decrease as residence time increases. C_2H_2 increases with increasing residence time for all cases.

C. Effect of Oxygen

As shown in Figure 6, there is almost no effect by presence of oxygen on the decomposition of parent CH_3CCl_3 in our experiments. Oxygen is in addition, not a significant factor on the formation of CH_2CCl_2 before 600^oC. When the temperature is over 600^oC, CH_2CCl_2 drops quickly in case 1 (O_2 = 4.5%, Ar = 95%, CH_3CCl_3 = 0.5%), high [O_2], where the CH_2CCl_2 decrease is more rapid than for any other case shown in Figure set 15. The lower the amount of oxygen, the slower the observed decay of CH_2CCl_2. This also applies to the other products (such as C_2H_2, C_2H_4, etc.) which are formed and then decrease more quickly in reactants ratio set 1 than in other sets. Generally, a faster decay of compounds which are formed at lower temperature occurs when the reactor temperature is above 650^oC, and when more oxygen is in the mixture. The higher ratio of O_2 to CH_4, the lower the required temperature needed to observed formation of CO and CO_2.

Table 5-a. Material Balance for 100 Moles Carbon

$O_2 : CH_4 : CH_3CCl_3 = 4.5 : 0 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)							
Species (%)	525	550	575	600	650	700	750	800
CH_3CCl_3	73.17	32.00	9.17	1.36	-	-	-	-
CH_2CCl_2	27.12	59.60	92.68	94.22	60.98	1.56	-	-
CHCH	-	-	-	-	1.34	0.54	-	-
C_3H_n	-	-	-	0.31	1.46	-	-	-
CH_2CHCl	-	-	-	-	0.66	-	-	-
$CHClCCl_2$	-	-	-	-	0.68	-	-	-
CO	-	-	-	-	34.15	80.49	95.12	92.68
CH_2CH_2	-	-	-	-	-	2.93	0.66	-
Total	100.29	91.60	101.85	95.89	99.27	85.52	95.78	92.68

Table 5-b. Material Balance for 100 Moles Carbon

$O_2 : CH_4 : CH_3CCl_3 = 4 : 0.5 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_4	32.90	29.80	32.41	32.25	32.25	33.22	30.94	22.80	-
CH_3CCl_3	54.56	45.44	28.50	7.54	0.95	-	-	-	-
CH_2CCl_2	12.65	15.73	38.76	61.40	70.36	63.52	57.00	34.20	-
CHCH	-	-	-	-	-	-	0.91	5.70	-
CH_2CH_2	-	-	-	-	-	0.26	0.77	1.27	-
CH_3Cl	-	-	-	-	-	-	0.60	0.91	-
C_3H_n	-	-	-	-	-	-	2.12	2.61	-
CH_2CHCl	-	-	-	-	-	-	1.51	2.93	-
CO	-	-	-	-	-	-	-	35.83	-
CO_2	-	-	-	-	-	-	-	-	89.58
Total	100.11	90.97	99.67	101.19	103.56	97.00	93.85	106.25	89.58

Table 5-c. Material Balance for 100 Moles Carbon

O_2 : CH_4 : CH_3CCl_3 = 3.75 : 0.75 : 0.5

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_4	43.44	41.20	42.04	40.08	41.48	41.90	40.50	30.73	4.33
CH_3CCl_3	48.32	41.76	24.44	6.54	0.73	-	-	-	-
CH_2CCl_2	10.00	14.25	34.50	54.61	55.73	58.66	50.28	33.52	-
CHCH	-	-	-	-	-	-	0.52	3.91	2.65
CH_2CH_2	-	-	-	-	-	0.24	0.63	1.40	-
CH_3Cl	-	-	-	-	-	-	0.49	0.88	-
C_3H^n	-	-	-	-	-	0.52	1.40	2.09	-
CH_2CHCl	-	-	-	-	-	0.43	1.20	2.65	-
CO	-	-	-	-	-	-	-	25.14	79.61
CO_2	-	-	-	-	-	-	-	-	13.13
Total	101.76	97.21	100.98	101.23	97.94	101.75	95.02	100.32	99.72

Table 5-d. Material Balance for 100 Moles Carbon

$O_2 : CH_4 : CH_3CCl_3 = 3 : 1.5 : 0.5$

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species (%)	500	525	550	575	600	650	700	750	800
CH_4	60.25	65.63	59.77	58.50	61.62	61.52	59.57	46.88	36.13
CH_3CCl_3	34.77	27.15	17.24	5.41	0.59	-	-	-	-
CH_2CCl_2	6.60	9.37	22.46	38.67	40.04	40.04	38.09	17.58	8.11
CH_2CH_2	-	-	-	-	0.11	0.20	0.52	1.95	2.25
CH_2CHCl	-	-	-	-	0.14	0.26	0.67	2.25	1.56
CHCH	-	-	-	-	-	-	0.16	4.10	8.11
CH_3Cl	-	-	-	-	-	-	0.28	1.07	0.83
C_3H_n	-	-	-	-	-	0.25	0.81	0.92	0.48
CO	-	-	-	-	-	-	-	22.46	38.09
Total	101.62	102.15	99.47	102.58	102.50	102.27	100.10	97.21	95.56

Table 5-e. Material Balance for 100 Moles Carbon

O_2 : CH_4 : CH_3CCl_3 = 0 : 1.5 : 0.5

Reactor Diameter : 1.05 cm
Residence Time : 1.0 sec.

	Temperature (°C)								
Species	500	525	550	575	600	650	700	750	800
CH_4	60.84	74.24	61.05	57.90	61.86	62.51	62.51	61.54	58.61
CH_3CCl_3	27.06	19.29	17.08	4.08	-	-	-	-	-
CH_2CCl_2	6.60	6.85	22.97	37.44	41.05	38.10	40.05	35.17	29.30
CH_2CHCl	-	-	-	-	-	0.18	1.07	0.23	0.28
CHCH	-	-	-	-	-	-	-	0.18	0.85
CH_2CH_2	-	-	-	-	-	-	0.12	0.18	0.30
C_3H_n	-	-	-	-	-	-	0.18	2.64	6.64
CH_3CHCl_2	-	-	-	-	-	-	-	0.50	2.25
CH_2Cl_2	-	-	-	-	-	-	-	-	1.07
$CHClCCl_2$	-	-	-	-	-	-	-	-	2.05
C_6H_6	-	-	-	-	-	-	-	-	0.62
Total	94.50	100.38	101.10	99.42	102.91	100.79	103.93	100.44	101.97

Several studies are available on the oxidation of methane in different types of reactors,<25,26> but they have investigated temperature regions which are all above 827°C(1100 K). In our study, methane start to react at about 650°C (923 K) where oxygen is present and at about 750°C for the case without oxygen, this is illustrated in Figure 16a-b for varied residence times. The increased methane conversion with respectively higher [O_2] is shown in Figure 17 a and b at 750 and 800°C. Figures 15a-d along with Tables 4 and 5, show that CH_2CCl_2 decay is more rapid and occurs at lower temperatures e.g. highest conversion for conditions of case 1 with 4.5% O_2.

We found that CO is formed and increases with increasing time in case 1 only for the 650°C reactor temperature. As temperature and O_2 concentration increase CO increases. At 800°C, almost no other products were found except CO, HCl and trace amounts of CO_2 for the case of 4.5% O_2. For the cases with less O_2, the hydrocarbon or halocarbon products were eventually totally converted to HCl and CO or CO_2 at 800°C, and the time needed for this conversion increased with decreasing concentration of oxygen.

D. Comparison of 1,1,1-Trichloroethane/mixture React with Reactions of Previous studies.

It is valuable to compare the reaction of 1,1,1-trichloroethane in these mixture CH_4/O_2 condition with other

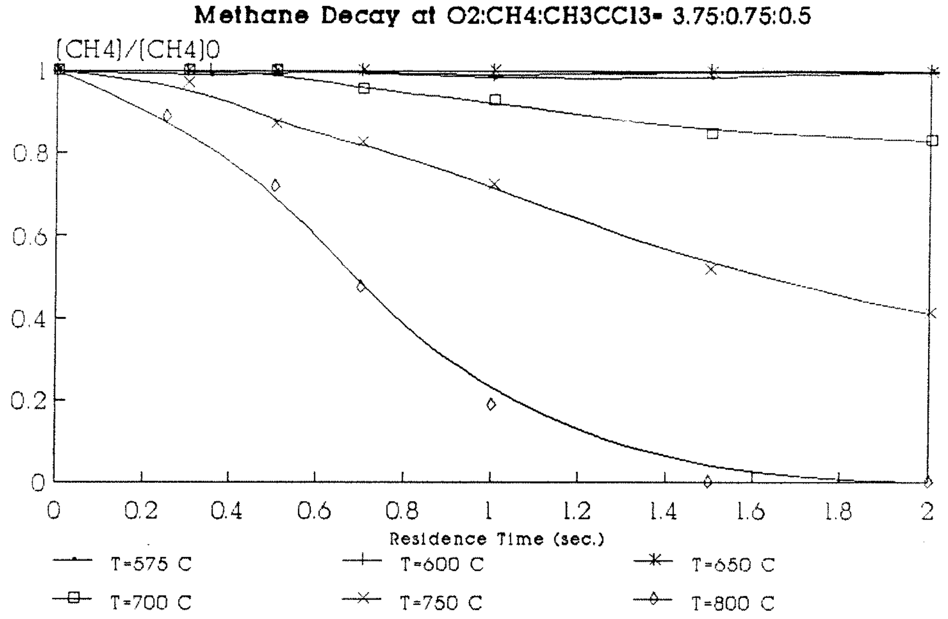


Figure 16-a. Methane Deacy Distribution ,Id=1.05cm

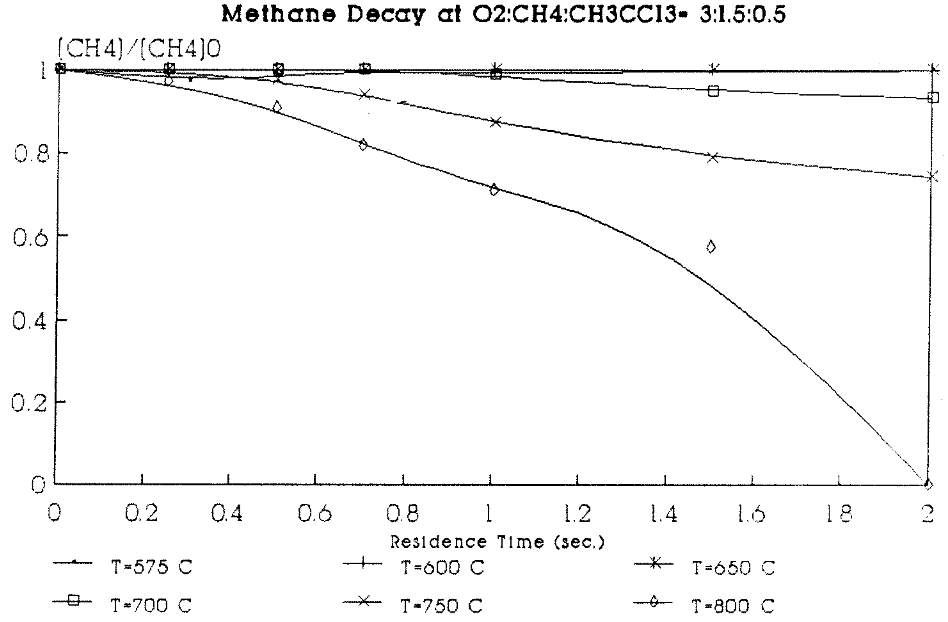


Figure 16-b. Methane Deacy Distribution ,Id=1.05cm

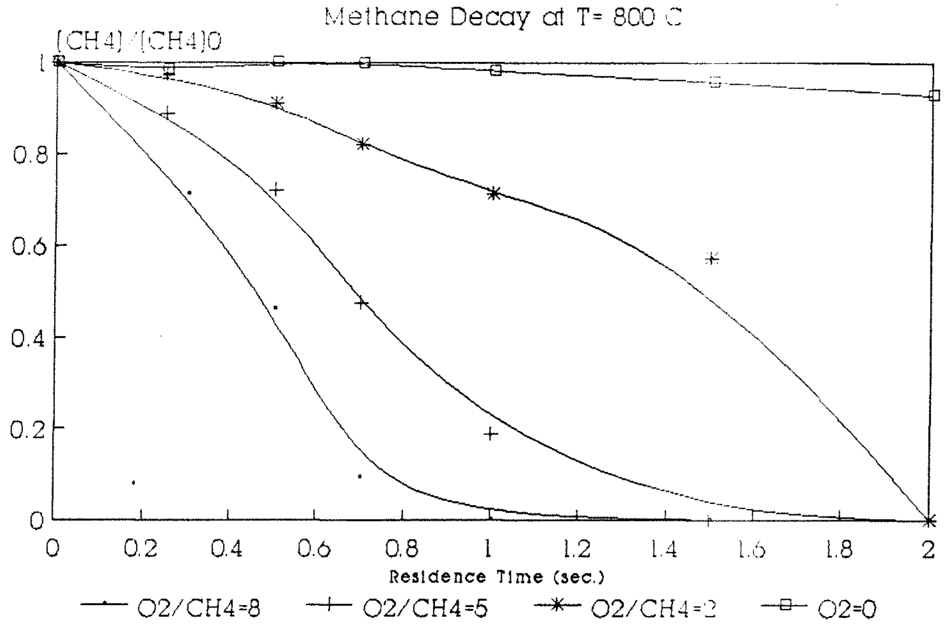


Figure 17–a. Methane Decay vs Time at 800 C

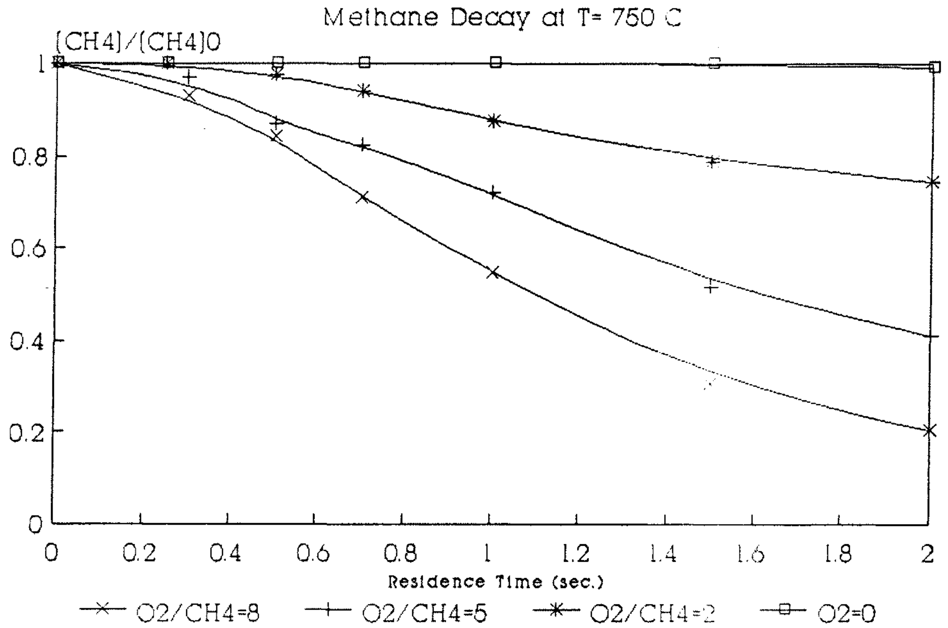


Figure 17–b. Methane Decay vs Time at 750 C

published studies on reactions of 1,1,1-trichloroethane to further evaluate effects of mixture. Chang[30] (1985) studied the thermal decomposition of 1,1,1-trichloroethane diluted in hydrogen using a similar experimental system over the temperature range of 555 to 681°C and residence times between 0.04 to 1.0 sec where initial 1,1,1-trichloroethane was present at the 5.89% concentration. Figure 18-a shows that conversion trend are very similar for both experimental studies.

Won[36,37] (1988) studied the thermal decomposition of 4% dichloromethane and 4% 1,1,1-trichloroethane mixture diluted in hydrogen using a similar experimental system over the temperature range 475 to 810°C, residence time between 0.05 to 2.0 sec and three different diameter reactors. Figure 18-b shows that the decay of CH_3CCl_3 in Won's study (a equal fraction CH_2Cl_2 added) is faster than the present study due to synergistic effects at temperatures below 575°C. The reason for the higher CH_3CCl_3 conversion between these two studies where CH_2Cl_2 was present is the activity of atomic hydrogen relative to CH_3 or HO_2 here. Won's system has excess hydrogen in the mixture which provided a rich hydrogen environment for initial radicals to react with.

CH_2Cl_2 ---> CH_2Cl + Cl

Cl + H_2 ---> HCl + H

H + CH_2Cl_2 ---> HCl + CH_2Cl

---> H_2 + $CHCl_2$

Figure 18-a.

Comparison of Pure and Mixed Systems for CH3CCl3

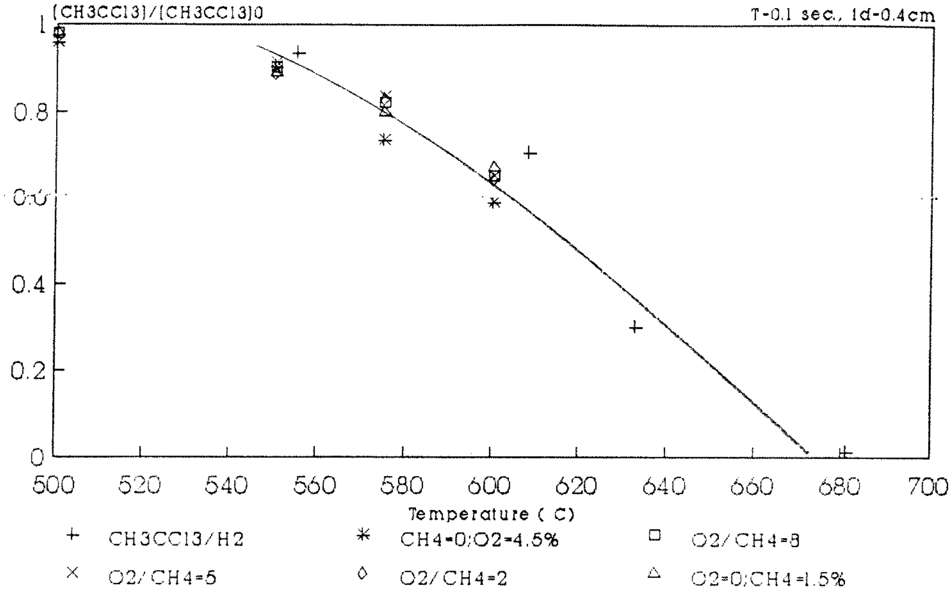
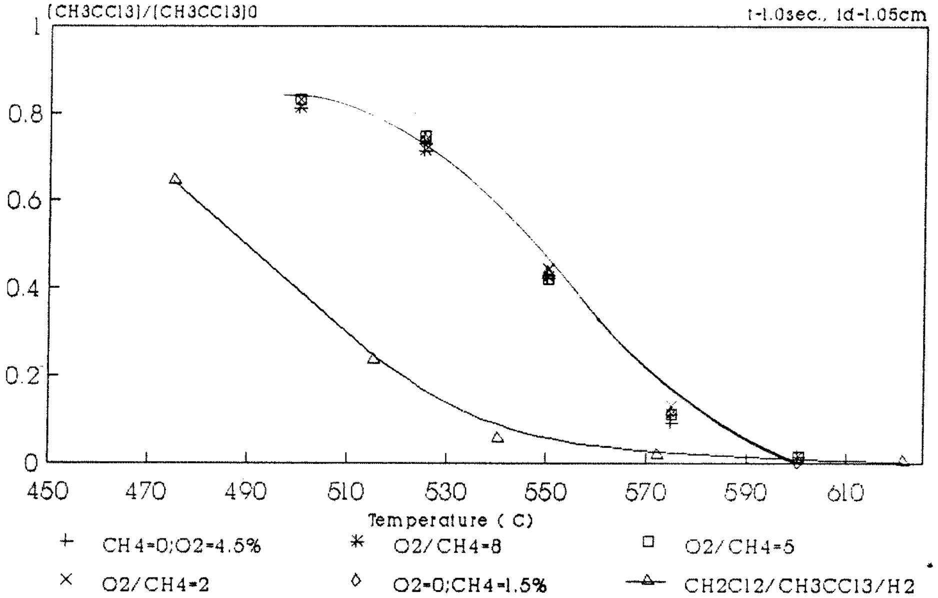


Figure 18-b.

Comparison of Varied Mixed Systems for CH3CCl3



* equal fraction CH2Cl2 added difference from present study due to synergistic effects.

Where in the present study , small amount of HO_2 and CH_3 radicals lead to less reaction with CH_3CCl_3 due to lower reactivity of HO_2 and CH_3 relative to H. In this study, CH_3CCl_3 is just in addition present in a smaller amount, ($CH_4 + O_2 + CH_3CCl_3 = 5\%$).

E. Quantum (Q)RRK

The decomposition/stabilization of the energized radical and molecular complexes was modeled using the QRRK calculations. The details of the bimolecular QRRK method are presented in the theory section and its application to a number of chemically activated reaction systems have been previously discussed<33,39>.

Energized Complex/QRRK theory as presented by Westmoreland and Dean<39> is used for modeling of radical addition reactions to unsaturated bonds and for radical or atom combination reactions. This computer code has been modified by Ritter and Bozzelli<40> to use gamma function instead of factorials. The QRRK computer code was used to determine the energy dependent rate constants for all reaction channels of the energized complexes and calculates rate constants as function of both temperature and pressure. The use of this formalism is important in determination of accurate rate constants needed for input to the mechanism, specifically in choice of the important reaction paths. This also applied to accurate product distribution prediction from the activated complex.

QRRK analysis of the chemically activated system, using generic estimates or literature values for high pressure rate constants and species thermodynamic properties for the enthalpies of reaction, yields thermodynamically and kinetically plausible apparent rate constants. Figure 20, 22 & 24 illustrate the energy level diagrams and apparent rate constants versus temperature and pressure for CH_3CCl_2 + H ---> Products, CH_2CCl_2 + H ---> Products, and CH_3 + O_2 --> Products. The input rate parameters used in these calculations and results from the calculations are summarized in APPENDIX I Table 1 - 9. The calculations were performed for each of six pressures between 0.76 torr and 7600 torr.

CH_3CCl_2 + H Reaction

The reaction of CH_3CCl_2 radical with H atoms will be considered first for these combination reactions. CH_3CCl_2 can arise from unimolecular dissociation of 1,1,1-trichloroethane to Cl atom or from H atom abstracting a Cl from 1,1,1-trichloroethane.

$$\begin{array}{lclr}
\underset{(62.6)}{CH_3CCl_2} + H \Longleftrightarrow [CH_3CHCl_2]^{\#} & \xrightarrow{\quad} & \underset{(45.7)}{CH_3CHCl + CL} & (1) \\
\quad\quad\quad\quad\quad\quad\quad\quad\Big| & \xrightarrow{\quad} & \underset{(24.8)}{CH_2CHCl + HCl} & (2) \\
\quad\quad\quad \text{STABILIZED} \quad \Big| & \xrightarrow{\quad} & \underset{(68.5)}{CH_2CHCl_2 + H} & (3) \\
\quad\quad\quad\quad\quad\quad\quad\quad\Big\downarrow & \xrightarrow{\quad} & \underset{(58.6)}{CH_3 + CHCl_2} & (4) \\
\quad\quad\quad\quad\quad\quad\underset{(-30.6)}{CH_3CHCl_2} & & & (5)
\end{array}$$

The energized complex (# denotes energized) can further decomposes as shown in reaction (1) to (4), be stabilized or return to initial reactants. The energy diagram for the above reaction channels (1) to (5) is illustrated in Figure 19. Reactions (3) and (4) do not occur due to thermo limitations (high energy barrier), they are endothermic. Reactions (1), (2) and (5) are thermodynamically favorable channels (low energy barrier) relative to initial energy of the reactants. It must be noted that reaction (2) corresponds to the composite behavior of four-center 1,2 and three-center 1,1 HCl elimination processes, because the CH_3CCl: formed in the latter case rapidly isomerizes to CH_2CHCl. Both 1,2 and 1,1 HCl elimination processes are expected to have similar A factors<41> with a slightly higher activated energy for the 1,1 HCl elimination processes,<42> then the 1,2 elimination.

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

The QRRK calculation results for this reaction system show that the rate constant for $CH_2CHCl+HCl$ channel is close to $CH_3CHCl+Cl$ and three times greater than

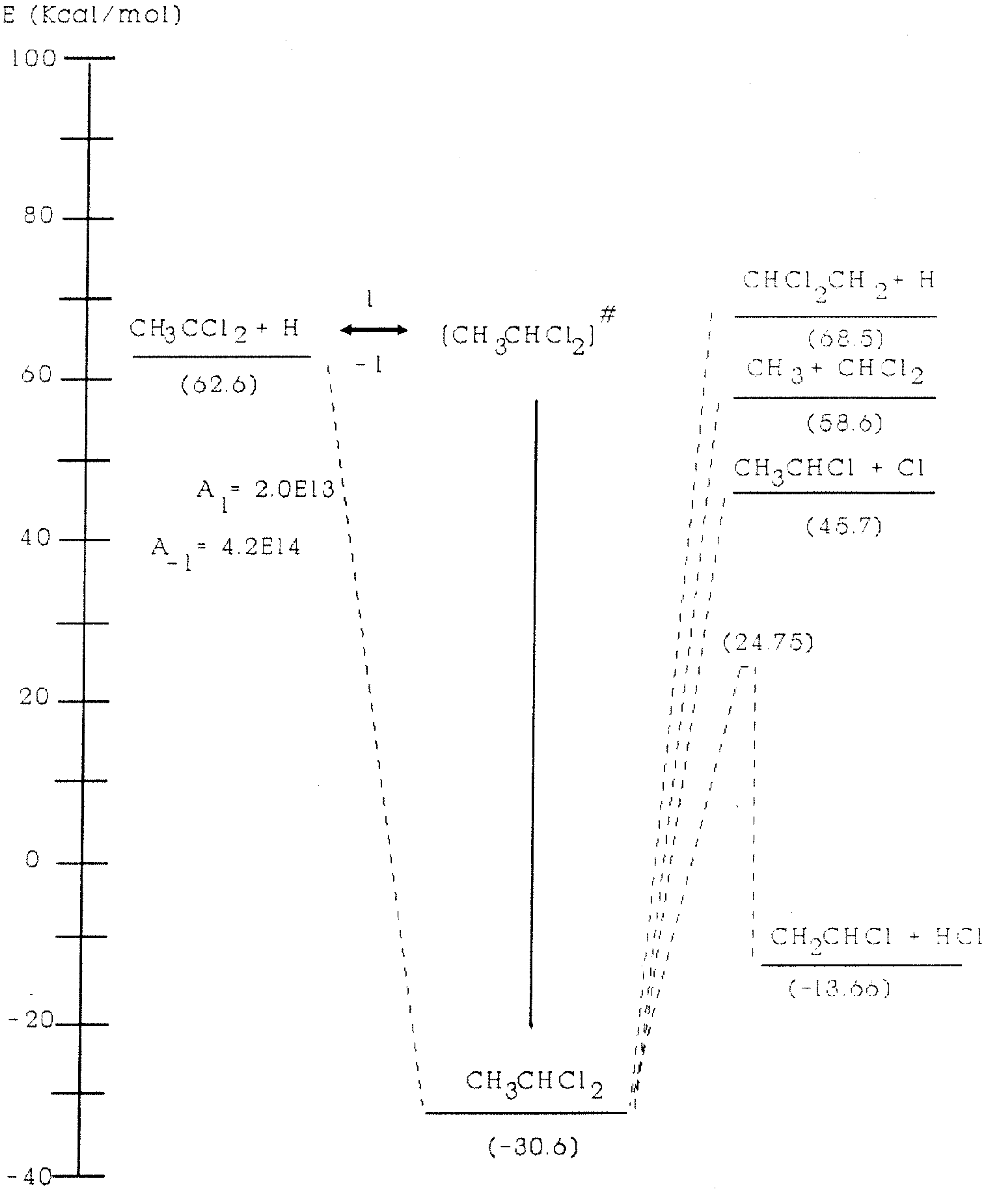


Figure 19. Energies of Activation Complex Theory **Calculation** for Reaction $CH_3CCl_2 + H$

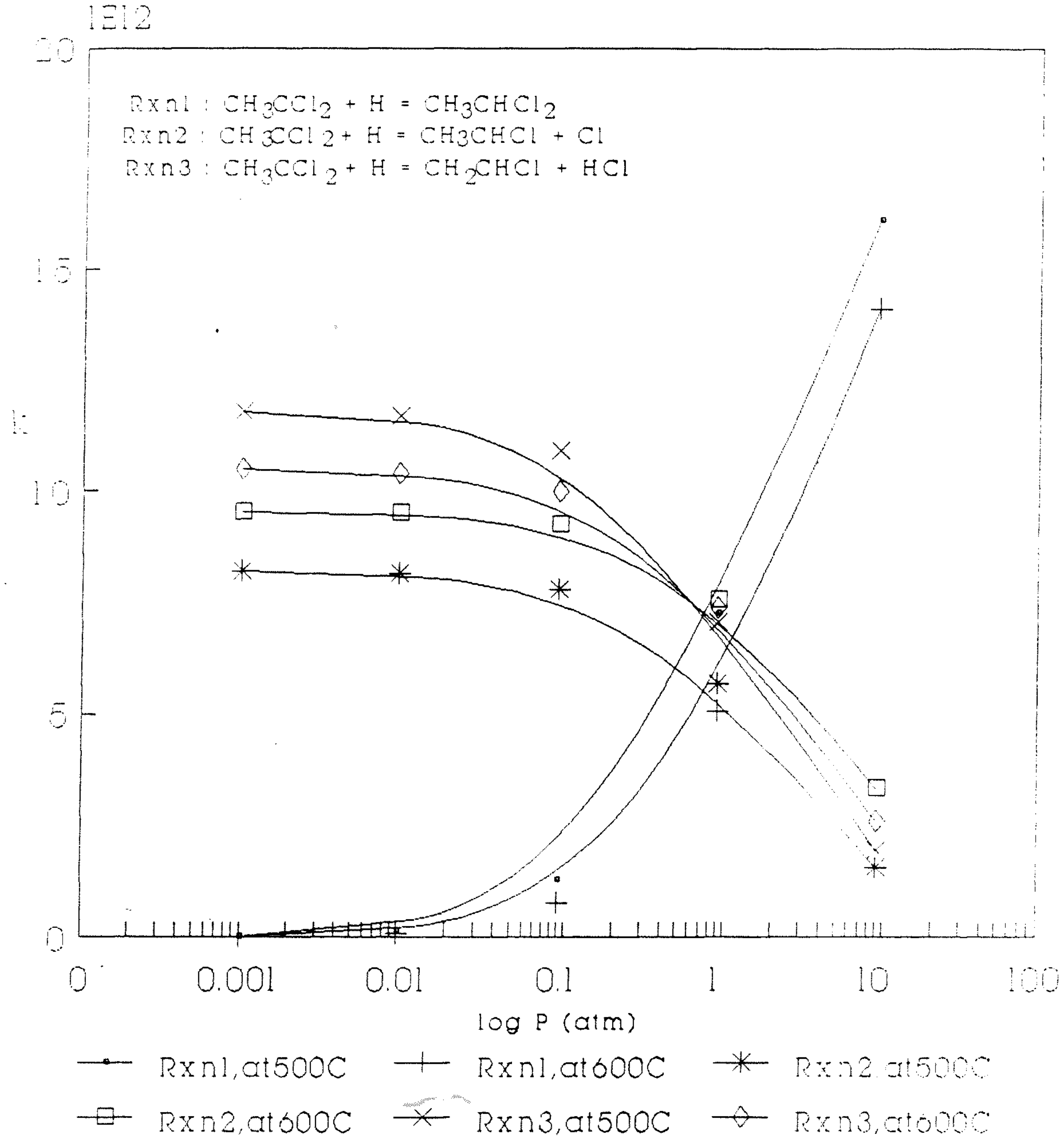
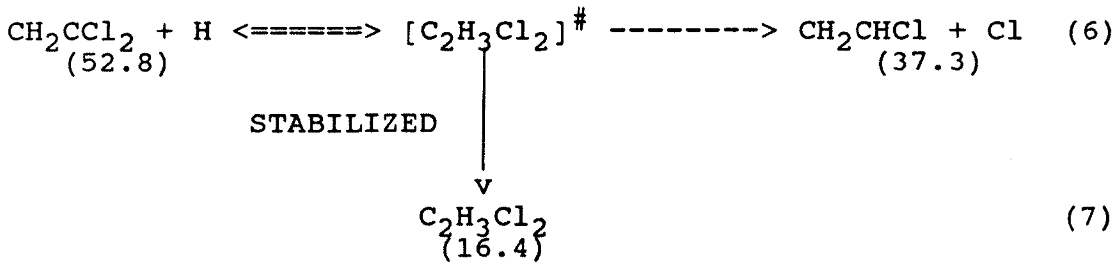


Figure 20. Results of Activated Complex Theory Calculation for Reaction CH_3CCl_2 + H

CH_3CHCl_2 stabilization through the temperature range 773 - 873 K at 1 atm.

CH_2CCl_2 + H Reaction

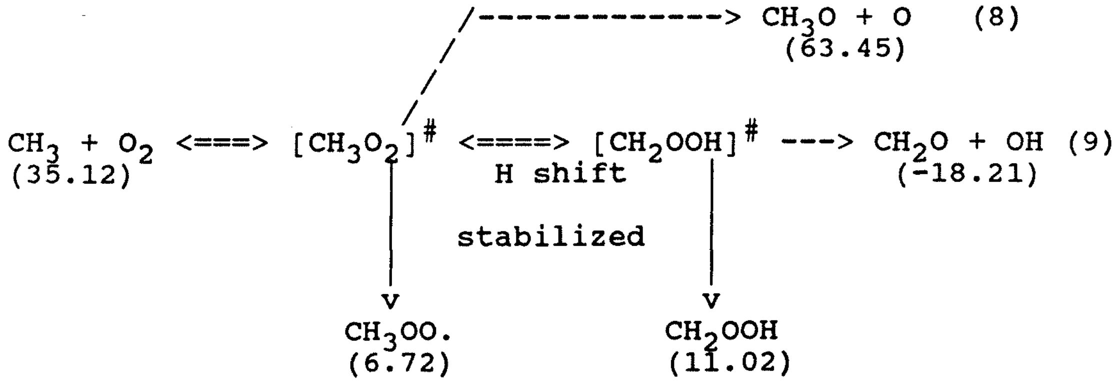
For the CH_2CCl_2 + H system, the energy diagram is shown in Figure 21, with the indicated major reactions are expected to be important:



The energy diagram of the reaction system is illustrated in Figure 21 and the calculation results are shown in Figure 22. Clearly, one may see that all collisions proceed to CH_2CHCl + Cl, the low energy exit channel.

CH_3 + O_2 Reaction

For the CH_3 + O_2 reaction, the energy diagram is shown in Figure 23, where the following reactions are expected to be important:



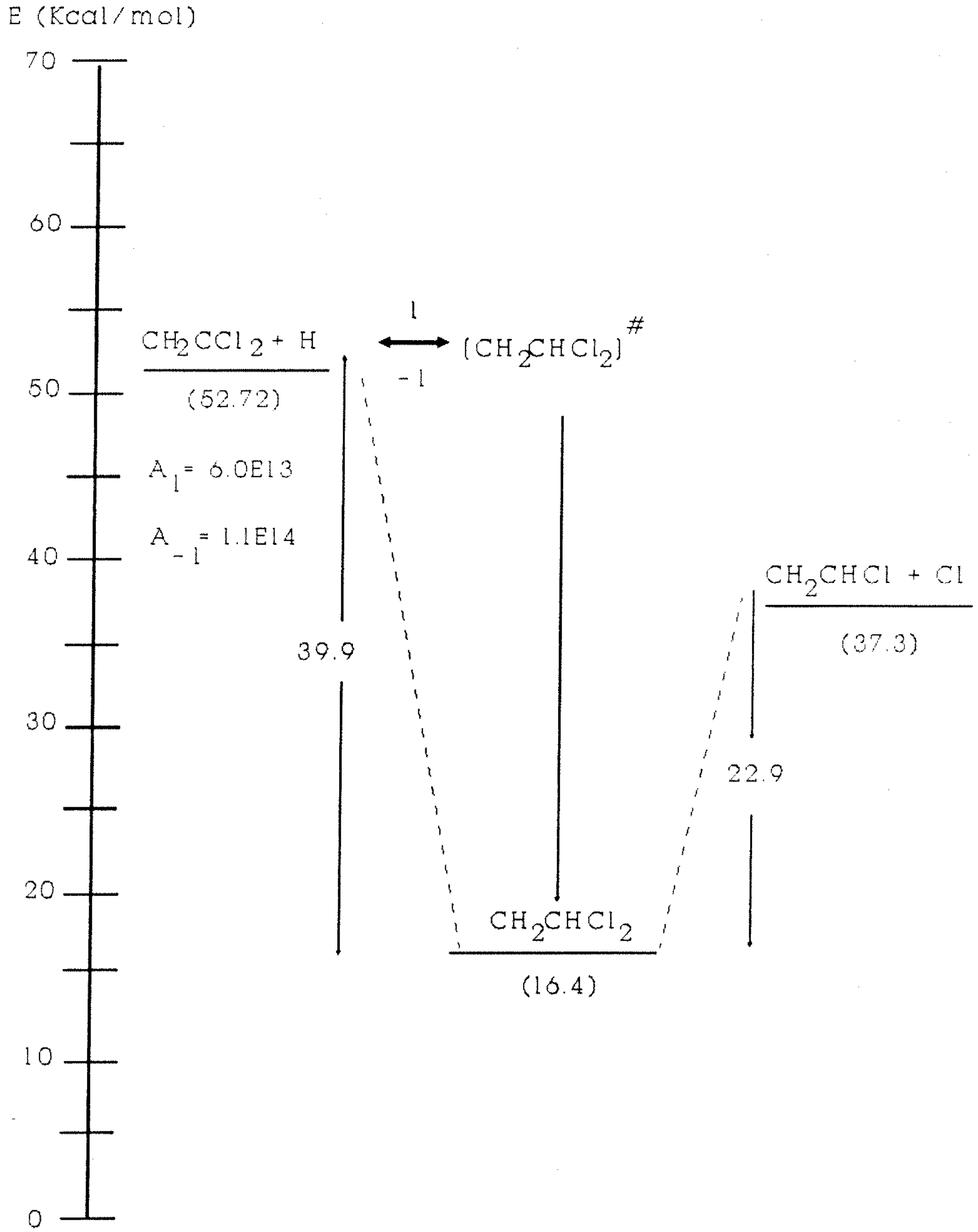


Figure 21. Energy Diagram for CH_2CCl_2 + H

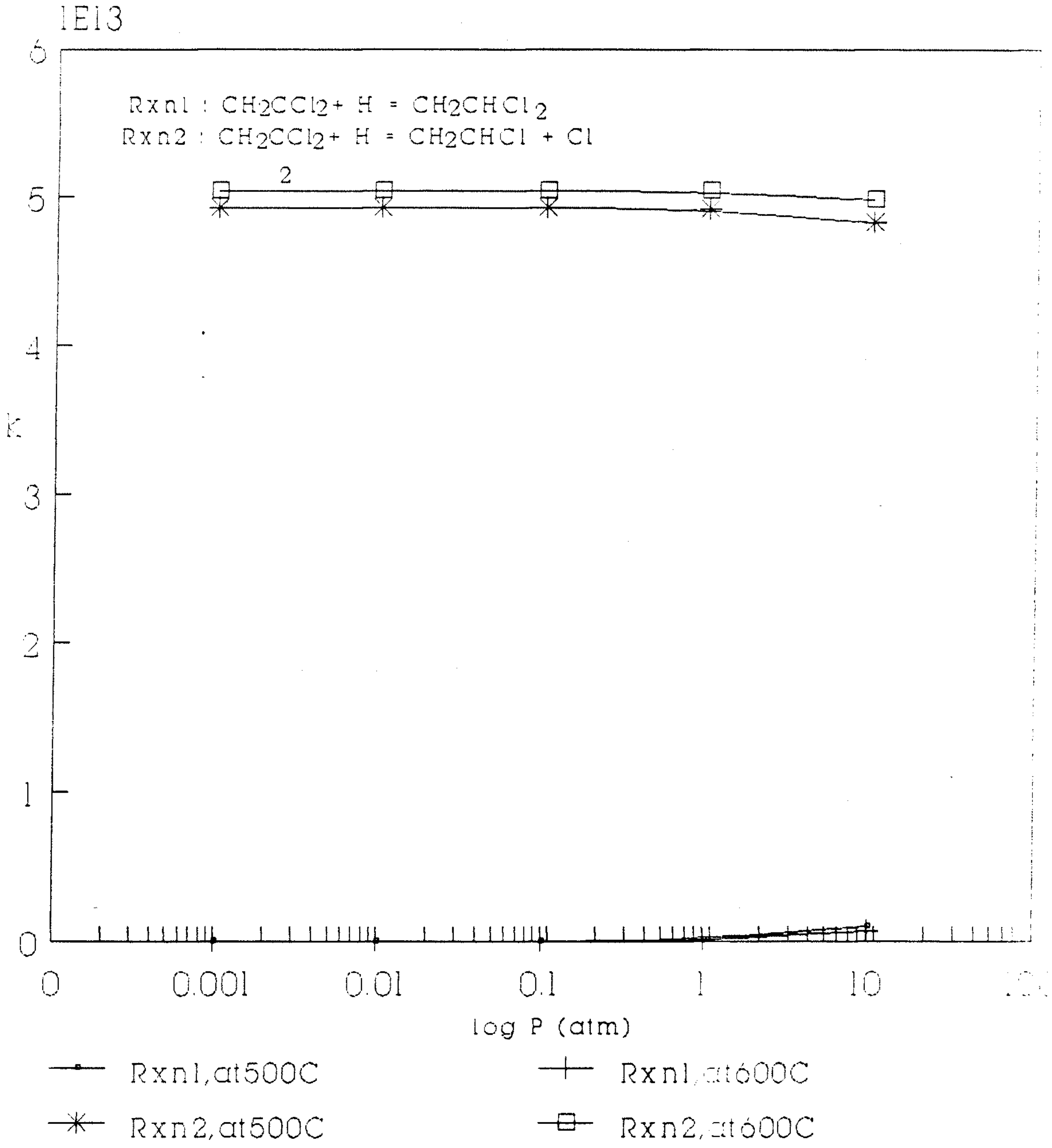


Figure 22. Results of Activated Complex Theory Calculation for Reaction CH_2CCl_2+ H

For the intramolecular transfer:

$$CH_3OO \text{ -----> } CH_2OOH$$

by analogy to other 1,3 hydrogen shifts<41,43>, one can estimate a barrier of approximately 39 kcal/mol (26 kcal for ring strain, 8 kcal for the H-abstraction, and 5 kcal for the reaction endothermicity). The energy diagram for reaction (8) and (9) is illustrated in Figure 23 and the calculation results are shown in Figure 24.

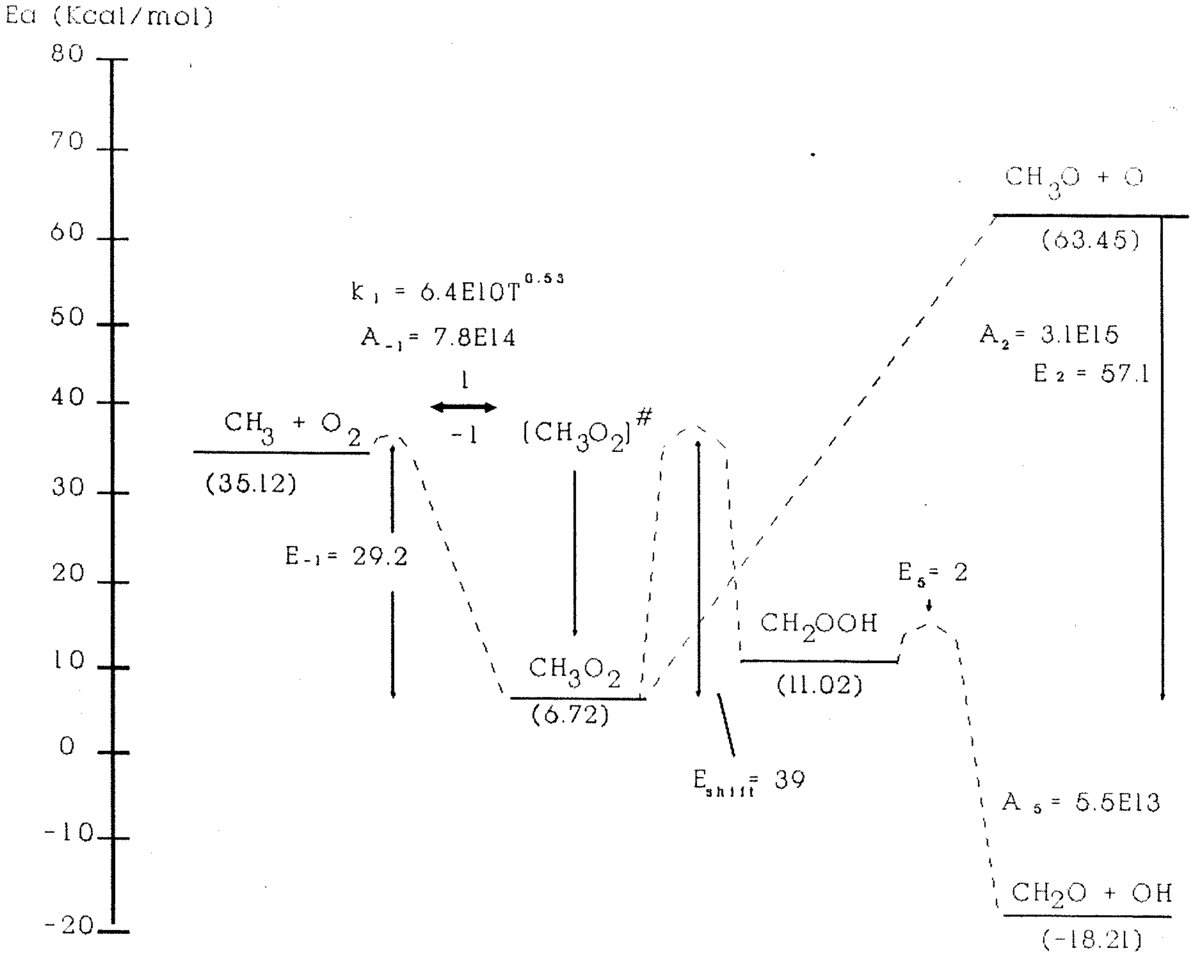


Figure 23. Energy Diagram for the $CH_3 + O_2$ Reaction

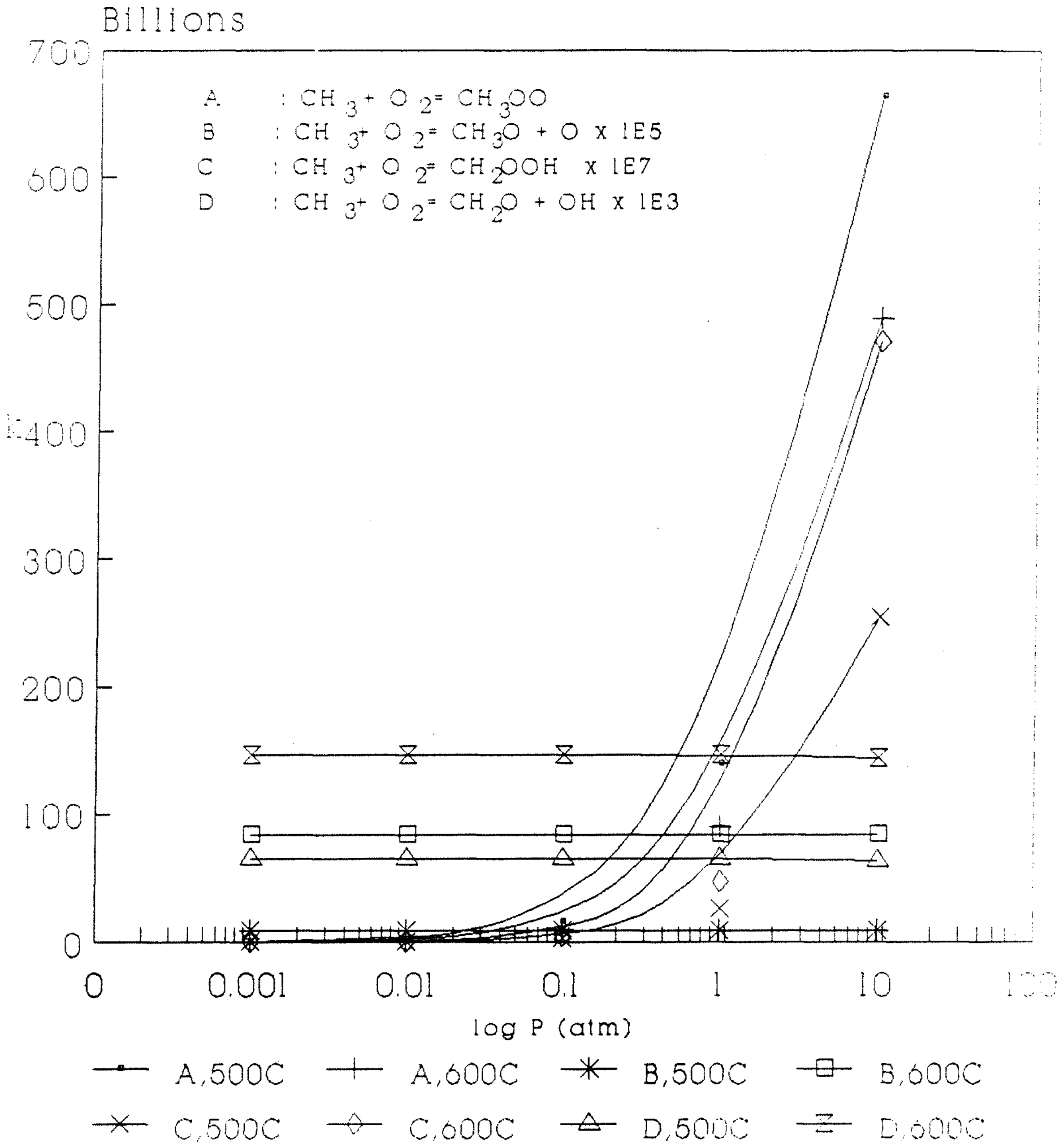


Figure 24. Results of Activated Complex Theory Calculation for Reaction $CH_3 + O_2$

F. Kinetic Mechanism and Modeling

The reaction mechanism and decomposition kinetics for 1,1,1-$CH_3CCl_3/O_2/CH_4$ mixture in Ar are developed.

The probable initial reactions are unimolecular decomposition of CH_3CCl_3 are include:

	A (1/s)	E (Kcal/mol)	
$CH_3CCl_3 \longrightarrow CH_3CCl_2 + Cl$	2.4E16	73.2 (ΔHr)	(1)
$CH_3CCl_3 \longrightarrow CH_2CCl_2 + HCl$	3.8E13	47.9 (ΔHr+38)	(2)
$CH_3CCl_3 \longrightarrow CH_3 + CCl_3$	9.1E15	84.7 (ΔHr)	(3)

(kinetic data sources are referenced in the source part of Table 6)

It is observed from the above kinetic listing that reaction (2) dominates the other pathways by more than three orders of magnitude at temperatures below 600 ^{o}C. This is consistent with our experimental results. CH_2CCl_2 and HCl are the major products detected below 600 ^{o}C.

For the destruction of methane, there has several important metathesis or abstractions reactions as follow:

$$CH_4 + Cl \longrightarrow CH_3 + HCl \qquad (4)$$

$$CH_4 + O_2 \longrightarrow CH_3 + HO_2 \qquad (5)$$

$$CH_4 + O \longrightarrow CH_3 + OH \qquad (6)$$

$$CH_4 + H \longrightarrow CH_3 + H_2 \qquad (7)$$

$$CH_4 + OH \longrightarrow CH_3 + H_2O \qquad (8)$$

$$CH_4 + HO_2 \longrightarrow CH_3 + H_2O_2 \qquad (9)$$

As the methyl radical was formed, it can react with oxygen or other radical as follow:

$$CH_3 + O_2 \longrightarrow CH_3OO \qquad (10)$$

$$CH_3 + O_2 \longrightarrow CH_3O + O \qquad (11)$$

$$CH_3 + O_2 \longrightarrow CH_2O + OH \qquad (12)$$

$$CH_3 + O \longrightarrow CH_3O \qquad (13)$$

$$CH_3 + O \longrightarrow CH_2O + H \qquad (14)$$

$$CH_3 + OH \longrightarrow CH_2O + H + H \text{ (two steps)} \qquad (15)$$

$$\vdots$$

A detailed reaction kinetic mechanism was developed and listed in Table 6 together with the rate parameters and corresponding sources.

This kinetic mechanism consists of 84 elementary reactions reduced from an initial mechanism of 122 elementary reactions (based on the sensitivity analysis which will be discussed later in this chapter). Elementary reaction rate parameters for abstraction reactions are based upon literature comparison, thermodynamic estimations and Transition State Theory methods of Benson<41>. QRRK calculations<39,40>, as described in previous section, were used to estimate apparent rate parameters for addition, combination and dissociation reactions (1 atm).

Experimental pyrolysis data are compared with model predictions in Figure 25a-b and 26a-b for reagent decomposition and product distribution between 500 and 800°C. Predictions for loss of the two reagents and

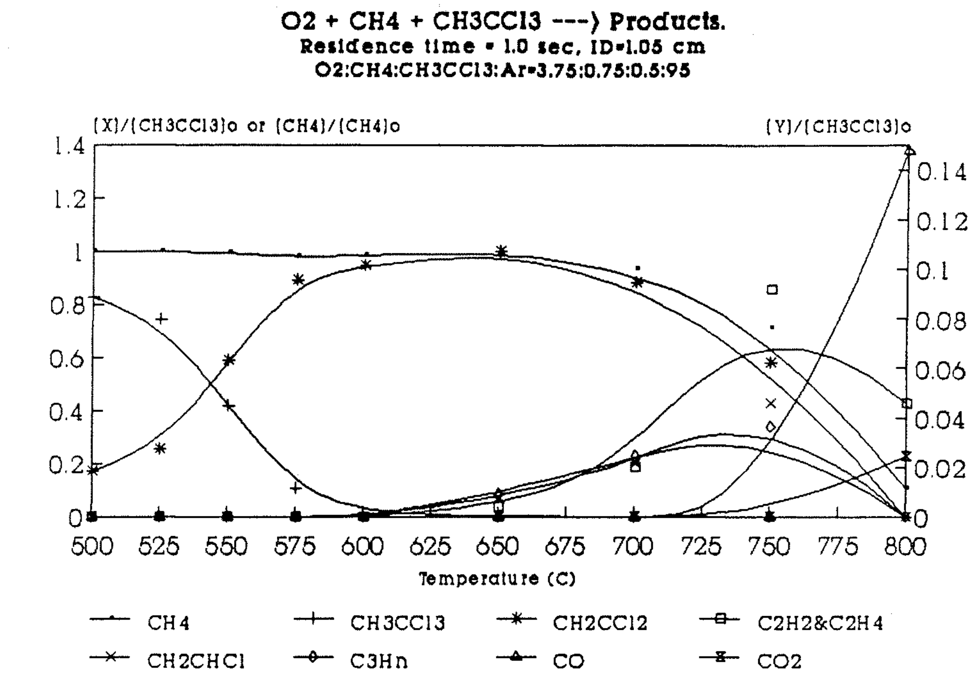


Figure 25-a. Experiment Product Distribution vs Temperature

X: CH3CCl3, CH2CCl2, CO, CO2
Y: C2H2, C2H4, C2H3Cl, C3Hn(C3H6+C3H8)

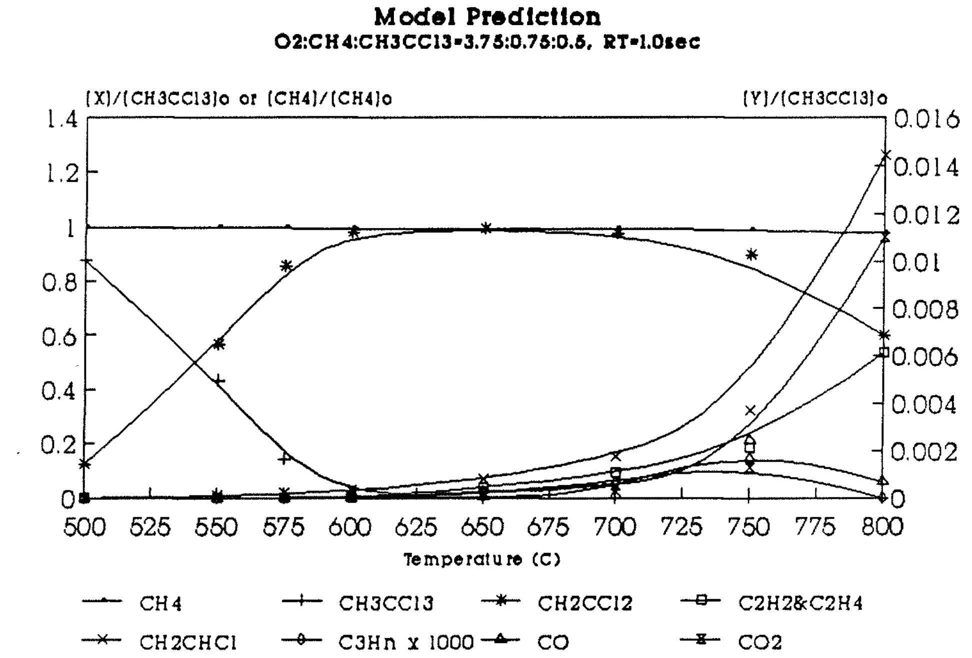
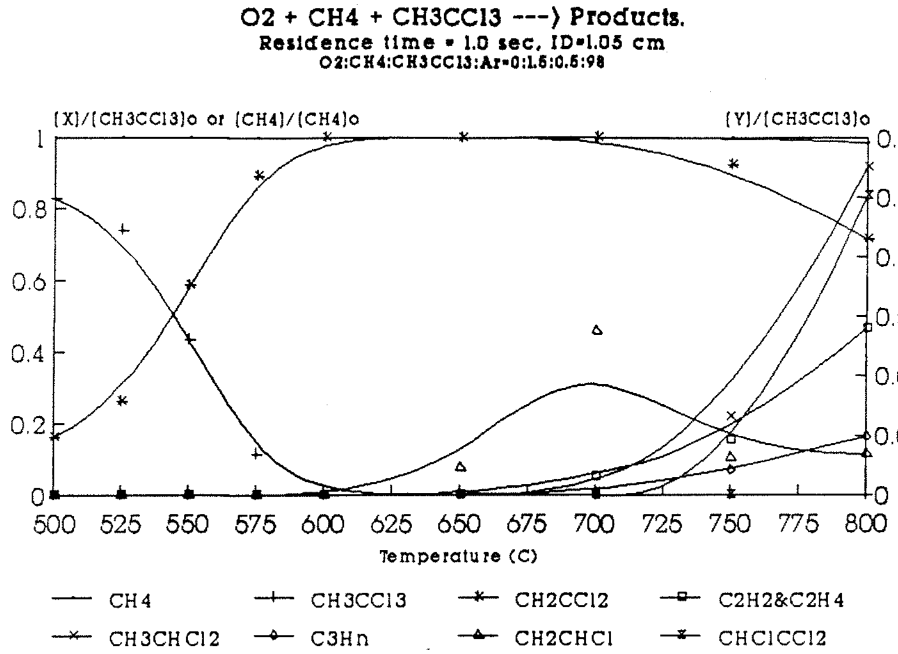


Figure 25-b. Model Product Distribution vs Temperature

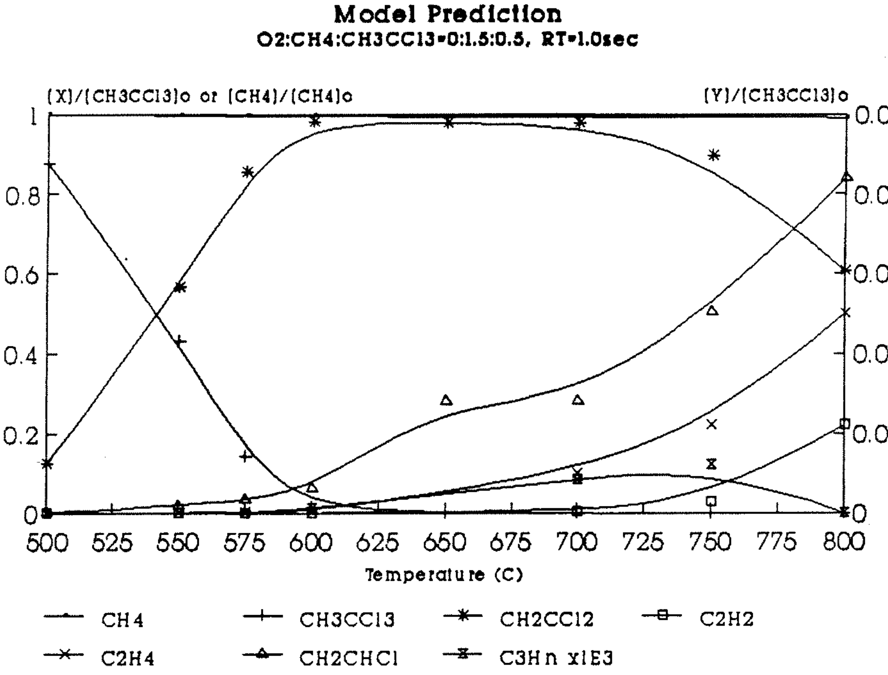
X: CH3CCl3, CH2CCl2
Y: C2H2, C2H4, CH2CHCl, C3Hn(C3H6+C3H8),
CO,CO2



O2 + CH4 + CH3CCl3 ---> Products.
Residence time = 1.0 sec, ID=1.05 cm
O2:CH4:CH3CCl3:Ar=0:1.5:0.5:98

Figure 26-a. Experiment Product Distribution vs Temperature

X: CH3CCl3, CH2CCl2,C3Hn(C3H6+C3H8)
Y: C2H2, C2H4, CH3CHCl2, CH2CHCl,
CHClCCl2



Model Prediction
O2:CH4:CH3CCl3=0:1.5:0.5, RT=1.0sec

Figure 26-b. Model Product Distribution vs Temperature

X: CH3CCl3, CH2CCl2
Y: C2H2, C2H4, CH2CHCl, C3Hn(C3H6+C3H8)

product distribution match experiment well. Figure 27 demonstrates calculated concentration of reactants and products versus reaction time at temperature of 650 ^{o}C and shows good agreement with the experimentally observed data for decay of reactants and formation of products.

Figure 25, 26 and 27 show the small difference seen between calculated and experimental values for reagents and products at 1 sec residence time (Figures 25 and 26) and 650^{o}C (Figure 27) for varied times. The possible reasons for this difference can be explained as following; First, the kinetic scheme does not include all possible products, specifically polyaromatic compound and carbon (solid) production. Second, the detailed mechanism only considers gaseous phase reaction; heterogeneous reaction effects are not included. Finally, the kinetic parameters estimated for several of the elementary reactions in detailed mechanism, are estimated based on best available thermodynamic and kinetic data in literature or for similar reactions. This may produce error when used for our actual reaction conditions. As shown in Figure 26 and 27, the reagent (CH_3CCl_3, CH_4) and major products (CH_2CCl_2), model prediction match the experiment data at lower temperature range (500 - 650^{o}C). As temperature higher than 650^{o}C, the model calculated result still need further work. Improvement of the model is ongoing.

In order to find out the most influential reactions in the large scheme of Table 6, a sensitivity analysis computer

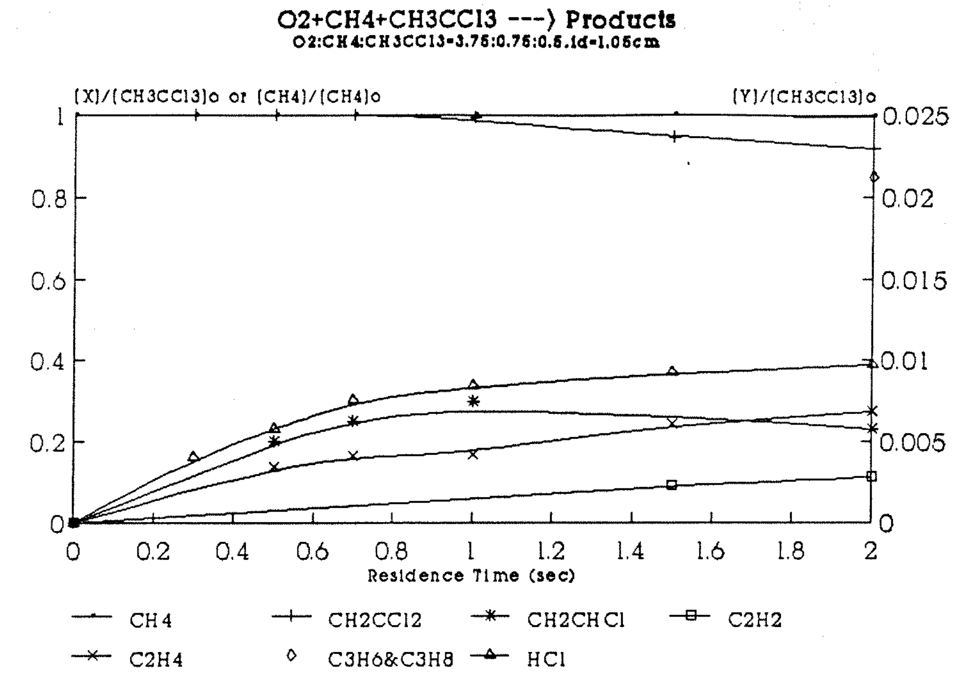


Figure 27-a. Experiment Product Distribution vs Time at 650C

X: CH2CCl2, HCl
Y: CH2CHCl, C2H2, C2H4, C3H6, C3H8

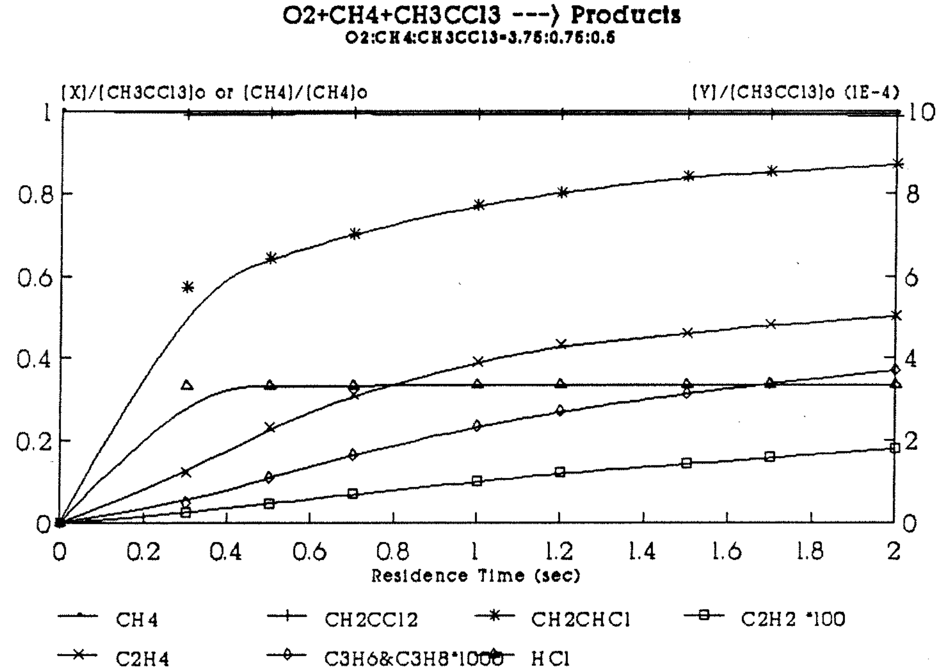


Figure 27-b. Model Product Distribution vs Time at 650C

X: CH2CCl2, HCl
Y: CH2CHCl, C2H2, C2H4, C3H6, C3H8

code SENS and mechanism analysis computer code MECHINFO were applied. As a representative example, the most influential reactions for the reaction products are given in Table 7 at two temperatures. For a more detailed presentation of the sensitivity analysis and mechanism analysis please see APPENDIX II.

Table 6.

	Reaction	A	n	Ea	Source
1.	$CH_3CCl_3 = CH_2CCl_2 + HCl$	3.80E+13$^{\#}$ 2.25E+12*		47.9 46.8	[1] Dissoc
2.	$CH_3CCl_3 = CH_3CCl_2 + Cl$	1.57E+16$^{\#}$ 2.58E+14*		73.2 67.4	[2] Dissoc
3.	$CH_3CCl_3 = CH_3 + CCl_3$	9.10E+16$^{\#}$ 2.06E+14*		84.7 77.1	[3] Dissoc
4.	$CH_2CCl_2 = C_2HCl + HCl$	7.10E+13$^{\#}$ 3.63E+13*		69.1 68.1	[4] Dissoc
5.	$CH_2CCl_2 = CH_2CCl + Cl$	9.34E+15$^{\#}$ 6.69E+13*		88.6 83.5	[5,13] Dissoc
6.	$CH_3CCl_2 = CH_2CCl_2 + H$	2.60E+13		41.4	[6]
7.	$CH_3CCl_2 + H = CH_3CHCl_2$	6.35E+10		-7.49	QRRK7
8.	$CH_3CCl2 + H = C_2H_3Cl + HCl$	4.81E+12		-0.65	QRRK7
9.	$CH_2CCl_2 + H = CH_2CCl + HCl$	1.20E+13		5.5	[8]
10.	$CH_2CCl_2 + H = CHCl_2CH_2$	9.72E+8		-7.32	QRRK1
11.	$CH_2CCl_2 + H = C_2H_3Cl + Cl$	5.99E+13		0.30	QRRK1
12.	$CH_2CCL + H = C_2H_3 + Cl$	1.01E+14		0.76	QRRK2
13.	$CH_2CCL + H = C_2H_2 + HCl$	8.34E+11		-2.12	QRRK2
14.	$CH_3CHCl_2 = C_2H_3Cl + HCl$	2.60E+13$^{\#}$ 1.98E+13*	0	55.8 55.4	[11] Dissoc
15.	$C_2H_3Cl = C_2H_2 + HCl$	3.55E+13$^{\#}$ 1.99E+13*		68.73 67.9	[14] Dissoc
16.	$C_2H_3Cl = C_2H_3 + Cl$	4.08E+15$^{\#}$ 1.16E+14*		87.6 83.1	[15,13] Dissoc
17.	$CH_3Cl = CH_3 + Cl$	2.63E+15$^{\#}$ 1.27E+14*		83.3 79.7	[22,23] Dissoc
18.	$CH_3Cl + H = CH_3+HCl$	7.00E+13		5.0	[20]
19.	$C_2H_6 = CH_3 + CH_3$	7.94E+16$^{\#}$ 3.64E+16*		89.4 89.5	[16] Dissoc
20.	$C_2H_6 + H = C_2H_5 + H_2$	6.61E+13		3.6	[20]

21. $C_2H_6 + CH_3 = C_2H_5 + CH_4$	3.16E+11		10.8	[36]
22. $C_2H_6 + Cl = C_2H_5 + HCl$	4.64E+13		0.179	[37]
23. $C_2H_6 + O = C_2H_5 + OH$	2.51E+13		6.4	[36]
24. $C_2H_6 + OH = C_2H_5 + H_2O$	6.76E+13		3.6	[20]
25. $C_2H_5 = C_2H_4 + H$	5.01E+13		40.9	[16]
26. $C_2H_5 + H = CH_3 + CH_3$	5.10E+14*		2.85	QRRK9
27. $C_2H_5 + O_2 = C_2H_4 + HO_2$	2.00E+12		4.992	[35]
28. $C_2H_5 + CH_3 = C_3H_8$	5.30E+12*		-1.03	QRRK4
29. $C_2H_5 + CH_3 = C_3H_7 + H$	7.37E+13*		23.4	QRRK4
30. $C_2H_4 + O = CH_3 + CHO$	2.24E+13	0	2.7	[28]
31. $C_2H_4 + OH = CH_3 + CH_2O$	1.0E+13	0	0	[28]
32. $C_2H_4 + OH = C_2H_3 + H_2O$	7.08E+13		3.01	[23]
33. $C_2H_4 + H = C_2H_3 + H_2$	6.92E+14	0	14.5	[28]
34. $C_2H_3 + CH_3 = C_3H_6$	9.16E+12	0	-1.08	QRRK5
35. $C_2H_3 + O_2 = C_2H_2 + HO_2$	1E+12	0	0	[23,35]
36. $C_2H_2 + O = CH_2 + CO$	5.25E+13	0	3.7	[28]
37. $C_2H_2 + O_2 = CHO + CHO$	3.98E+12	0	28.0	[26]
38. $C_3H_8 + CH_3 = C_3H_7 + CH_4$	2.00E+12	0	11.3	[35]
39. $C_3H_8 + HO_2 = C_3H_7 + H_2O_2$	6.20E+12	0	17.7	[35]
40. $C_3H_7 = C_3H_6 + H$	1.26E+13		38.5	[16]
41. $C_3H_7 = CH_3 + C_2H_4$	1.00E+13		32.9	[16]
42. $C_3H_7 + O_2 = C_3H_6 + HO_2$	1.00E+12		2.985	[35]
43. $CH_3CCl_3 + Cl = CCl_3CH_2 + HCl$	2.51E+12		3.60	[20]
44. $CH_3CCl_2 + CH_4 = CH_3CHCl_2 + CH_3$	1.58E+12		22.63	[32]
45. $CH_2CCl + CH_4 = C_2H_3Cl + CH_3$	2.90E+11		7.2	[33]
46. $CH_4 + M = CH_3 + H + M$	1.0E+17	0	92.39	[20]
47. $CH_4 + O_2 = CH_3 + HO_2$	7.94E+13		55.887	[39]

48. $CH_4 + O = CH_3 + OH$	1.20E+7	2.1	7.62	[23,30,35]
49. $CH_4 + H = CH_3 + H_2$	2.2E+4	3.0	8.74	[35]
50. $CH_4 + OH = CH_3 + H_2O$	1.60E+6	2.1	2.46	[23,30,35]
51. $CH_4 + Cl = CH_3 + HCl$	2.57E+13	0	3.85	[20,27]
52. $CH_4 + HO_2 = CH_3 + H_2O_2$	2.00E+13	0	18.0	[31]
53. $CH_3 + O_2 = CH_3O + O$	7.00E+12	0	25.65	[26,30]
54. $CH_3 + O = CH_2O + H$	7.00E+13	0	0.	[23,30,35]
55. $CH_3 + OH = CH_2O + H + H$	5.3E+12	0	0	[28]
56. $CH_3 + HO_2 = CH_3O + OH$	2.00E+13	0	0	[30]
57. $CH_3O + O_2 = CH_2O + HO_2$	1.00E+13	0	7.165	[35]
58. $CH_2O + CH_3 = CH_4 + CHO$	1.00E+10	0.5	6.0	[7]
59. $CH_2O + H = CHO + H_2$	2.5E+13	0	3.99	[23,35]
60. $CH_2O + O = CHO + OH$	3.5E+13	0	3.51	[23,30,35]
61. $CH_2O + OH = CHO + H_2O$	3.0E+13	0	1.19	[23]
62. $CH_2O + HO_2 = CHO + H_2O_2$	1E+12	0	8.0	[24,31]
63. $CH_2O + Cl = CHO + HCl$	5.00E+13	0	0.5	[42]
64. $CHO + O_2 = CO + HO_2$	3.0E+12	0	0	[30,35]
65. $CHO + HO_2 = CH_2O + O_2$	5.0E+13	0	3.0	[31]
66. $CO + OH = CO_2 + H$	1.51E+13	1.3	-0.76	[26]
67. $CO + HO_2 = CO_2 + OH$	1.51E+14	0	23.6	[31]
68. $CO + O_2 = CO_2 + O$	1.6E+13	0	41.0	[26]
69. $H + O_2 = O + OH$	2.2E+14	0	16.79	[23]
70. $H + H_2O = H_2 + OH$	4.6E+8	1.6	18.56	[23]
71. $O_2 + M = O + O + M$	1.85E+11	0.5	95.56	[26]
72. $H + HO_2 = OH + OH$	1.5E+14	0	1	[23,30]
73. $H + HO_2 = H_2 + O_2$	2.5E+13		0.69	[23,30,31]
74. $O + HO_2 = OH + O_2$	2.00E+13	0	0.	[23,30]

75.	$OH + HO_2 = H_2O + O_2$	2.0E+13	0	0.	[23]
76.	$O + HCl = OH + Cl$	5.24E+12	0	6.4	[20]
77.	$OH + HCl = Cl + H_2O$	2.45E+12	0	1.1	[20]
78.	$Cl + Cl + M = Cl_2 + M$	2.34E+14	0	-1.8	[20]
79.	$Cl + H_2 = HCl + H$	4.8E+13	0	5.0	[29]
80.	$Cl + HO_2 = HCl + O_2$	1.3E+13	0	0.2	[40]
81.	$Cl + HO_2 = ClO + OH$	7.00E+12	0	2.3	[40]
82.	$ClO + CO = CO_2 + Cl$	2.70E+11	0	4.5	[40]
83.	$CH_3 + ClO = CH_3Cl + O$	6.00E+12	0	4.0	[40]
84.	$CH_3 + ClO = CH_3O + Cl$	9.00E+12	0.	1.0	[40]

High pressure limit value

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

DISSOC : apparent rate constant by DISSOCIATION computer code analysis

QRRK : apparent rate constant by QRRK computer code analysis

$ value selected

SOURCES

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

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

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

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

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

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

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11. A = $10^{13.55} * 10^{(-4/4.6)} * 6$
Ea = ΔHr + 38.5

12. 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 = ΔHr

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

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

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21. 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

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

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32. A factor based upon entropy change for reverse.
A_{-1} taken as that for $n\text{-}C_4H_{10} + CH_3 = 2\text{-}C_4H_9 + CH_4$
(A = 3.98E+11), Ea from Evans-Polanyi Plot.

33. A factor based upon entropy change for reverse.
A_{-1} taken as that for $C_2H_4 + CH_3 = C_2H_3 + CH_4$
(A = 1.58E+11), Ea taken as $C_2H_3 + H_2$,Ea=7.4.

34. A factor based upon entropy change for reverse. A_{-1} taken as that for 2-C_3H_8 + CH_3= 2-C_3H_7 + CH_4 (A = 6.31E+11), Ea from Evans-Polanyi Plot.

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Table 7. Sensitivity Analysis Summary

at 823K , Time = 1.0 sec

Species		Reaction No.	
		Most Important	Important
CH_4	'+'		1^*, 43^*
	'-'		2^*, 19^*
CH_3CCl_3	'+'		19^*
	'-'	1	$2^{\#}$, 11^*, 43^*, 53^*, 69^*
CH_2CCl_2	'+'	1	19^*, 49^*, 79^*
	'-'		$2^{\#}$, $4^{\$}$, 11^*, 43^*
C_2H_3Cl	'+'	2, 11	6, 9, 18
	'-'	1, 49, 79	43, 44, 69
C_2H_2	'+'	2, 11, 15,	6, 9, 12
	'-'	1, 37, 49, 69, 79	43, 45
C_2H_4	'+'	2, 6, 19, 22, 27, 51, 53, 69	3, 26, 47, 52
	'-'	1, 11, 43	49, 79
C_3H_6	'+'	2, 6, 19, 22,26,27, 41, 42, 51, 53,69	3, 47, 52,
	'-'	1, 11, 43	49, 79
C_3H_8	'+'	2, 6, 19, 22, 26, 28, 51, 53, 69	3, 47, 52,
	'-'	1, 11, 27, 43	25, 49, 79
CO	'+'	2, 6, 47, 50,53,56, 58,63,65,69,77	3, 15, 22, 37, 51, 54
	'-'	1, 19, 43, 52, 66	11, 48, 49
CO_2	'+'	2, 6,22,47,51,53,56, 58,63,65,66,69	3,15, 37, 54, 68, 80
	'-'	1, 11, 19, 43, 50, 52, 77, 79	9, 48, 49
HCl	'+'	1	$2^{\#}$,$4^{\$}$,$19^*$
	'-'		43^*, 49^*, 69^*, 79^*

S: Sensitivity Coefficient
'+': $S \geq 0$; '-': $S < 0$
Most Important: $10^{-3} < |S| < 1$; Important: $10^{-4} < |S| < 10^{-2}$
#: $10^{-5} < |S| < 10^{-3}$; $\$$: $10^{-6} < |S| < 10^{-4}$
*: $10^{-7} < |S| < 10^{-5}$

Table 7. (cont'd)

at 923K , Time = 1.0 sec

Species		Reaction No.	
		Most Important	Important
CH_4	'+'	-	1, $19^{\#}$, $52^{\#}$
	'-'		2, 43, 53, 56
CH_3CCl_3	'+'	2, 53	52, 69
	'-'	1, 19, 43	3, 11,17,22,27,47, 51, 54, 63,
CH_2CCl_2	'+'	-	$1^{\#}$, $19^{\#}$
	'-'		2, 4, $56^{\#}$
C_2H_3Cl	'+'	2, 11, 22, 25, 43,53, 56, 63, 66	5, 18, 65
	'-'	1, 17, 19, 27, 47, 49, 50, 52, 77, 79	69, 80
C_2H_2	'+'	2, 11,15,22,25,32, 43, 53, 56, 63	5, 16, 18, 27, 66, 69, 81
	'-'	1, 17,19, 37,47,49,50, 52, 77, 79, 80	65
C_2H_4	'+'	2, 22,25,27,43,52, 53,69	5, 6, 26, 51, 65
	'-'	1,11,17,19,47,56,63,80	49
C_3H_6	'+'	2,22,25,27,40,41,42, 43, 52, 53, 69	5, 6, 26, 51, 65
	'-'	1,11,17,19,47,56,63,80	49, 79
C_3H_8	'+'	2,22,28,43,52,53,69	5, 6, 26, 65
	'-'	1, 11, 17, 19, 25, 27, 47, 56, 63, 80	38, 49
CO	'+'	2, 22, 27, 43,50,53, 56, 63, 65, 77	4, 15, 30, 32, 37, 58, 62, 69, 84
	'-'	1, 17, 19, 25,47,52,66	11,48,49,80,81,83
CO_2	'+'	2, 22, 27,43,53,56, 63,65,66,69	4, 5,6,15,26, 37, 58, 62, 81, 84
	'-'	1, 11,17,19,25,47,50, 52,77,80	49, 51, 79
HCl	'+'	-	$2^{\#}$, 4, $43^{\#}$, $56^{\#}$
	'-'		$1^{\#}$, $19^{\#}$

S: Sensitivity Coefficient

'+': $S \geq 0$; '-': $S < 0$; #: $10^{-5} < |S| < 10^{-3}$

Most Important: $10^{-3} < |S| < 1$; Important: $10^{-4} < |S| < 10^{-2}$

Conclusion

The thermal decomposition of 1,1,1-trichloroethane in methane/oxygen mixtures and argon bath gas was carried out at 1 atmosphere total pressure in tubular flow reactors. Temperature ranged from 500 to 800^{o}C, with the average residence times in the range from 0.05 to 2.5 seconds. Five reactants ratio sets in three size flow reactors were studied.

Complete decay (99%) for the 1,1,1-trichloroethane at 1 second residence time occurs at about 600^{o}C for all the reactants ratio sets. The major products for 1,1,1-trichloroethane decomposition are 1,1-dichloroethylene and HCl. The number and quantity of chlorinated products decrease with increasing temperature and residence time. Oxygen has almost no effect on the decay of 1,1,1-trichloroethane in our study. Formation of CH_2CCl_2 as one of the major products from CH_3CCl_3 increases with increasing temperature to a maximum near 600^{o}C at 1.0 sec residence time and is independent of reactant ratio here. It then drops quickly with increasing temperature and increased O_2. Faster decay of compounds, such as C_2H_3Cl, C_2H_2, C_2H_4, C_3H_6+C_3H_8, formed at lower temperature occurs when the reactor temperature is above 650^{o}C, and higher oxygen levels in the mixture. The higher ratio of O_2 to CH_4, the lower the temperature needed to observe the formation of CO and CO_2. The major products at temperatures above 750^{o}C are HCl and non-chlorinated hydrocarbons: C_2H_2, C_2H_4, C_3H_6, C_3H_8, CO and CO_2.

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

This study demonstrated that the selective ratio of oxygen/methane can optimized the operate conditions to get the non-chlorinated hydrocarbon and HCl from thermal reaction of chlorocarbon mixture.

A detailed kinetic reaction mechanism was developed and used to model results obtained from the experimental reaction system. A sensitivity analysis of the model was done to show the most important reactions in the mechanism. The kinetic reaction mechanism includes 84 elementary reaction steps involving stable compounds and free radical species with the addition, beta scission and recombination type reactions all analyzed by QRRK theory.

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APPENDIX

I. GISOQRRK INPUT DATA and CALCULATION RESULTS

II. SENSITIVITY ANALYSIS & MECHINFO ANALYSIS

APPENDIX. GISOQRRK INPUT DATA and CACULATION RESULTS

Table A-1-a

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

k	A	Ea	source
1	6.0 E+13	3.0	a
-1	1.1 E+14	39.9	a
2	4.0 E+14	22.9	b

<v> = 736/cm c

Lennard-Jones Parameters : d

sigma = 5.103 °A e/k = 435.91 cal

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

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

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

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

Table A-1-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr) (Kcal/mol)	Reaction	A (cc/mol s)	Ea
7.6	$CH_2CCl_2 + H = CH_2CHCl_2$	9.69 E+06	-7.33
76.0		9.67 E+07	-7.33
760.0		9.31 E+08	-7.32
7.6	$CH_2CCl_2 + H = CH_2CHCl + Cl$	5.97 E+13	0.3
76.0		5.97 E+13	0.3
760.0		5.99 E+13	0.3

Table A-2-a

CH_2CCl + H <====> $[CH_2CHCl]^{\#}$ ----> CH_2CH + Cl
----> CHCH + HCl
----> CH_2CHCl (Stab.)

k	A	Ea	source
1	1.0 E+14	0.0	a
-1	3.0 E+15	104.1	a
2	7.9 E+16	87.6	b
3	3.6 E+13	68.7	c

<v> = 1344.3/cm d

LJ Parameters : e

sigma = 4.644 A^{o} e/k = 349 cal

---

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

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

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

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

e
see note (d) Table 1-a

Table A-2-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECUAR QRRK ANALYSIS

P (torr) (Kcal/mol)	Reaction	A (cc/mol s)	Ea
7.6	$CH_2CCl + H = CH_2CHCl$	7.84 E+07	-6.99
76.0		7.84 E+08	-6.98
760.0		7.90 E+09	-6.96
7.6	$CH_2CCl + = CH_2CH + Cl$	1.00 E+14	0.05
76.0		1.00 E+14	0.06
760.0		1.01 E+14	0.08
7.6	$CH_2CCl + H = CHCH + HCl$	8.27 E+11	-2.13
76.0		8.28 E+11	-2.13
760.0		8.34 E+11	-2.10

Table A-3-a

$CH_3 + O_2 \Longleftrightarrow [CH_3OO]^{\#} \Longleftrightarrow [CH_2OOH]^{\#} \longrightarrow CH_2O + OH$
$\quad | \longrightarrow CH_3O + O \qquad\qquad \longrightarrow CH_2OOH(Stab.)$
$\quad | \longrightarrow CH_3O_2(Stab.)$

k	A	Ea	source
1	6.4 E+10	0.0	a
-1	7.8 E+14	29.2	a
2	3.1 E+15	57.1	b
4	1.44E+13	39.0	a
-4	6.39E+11	0.0	a
5	5.5 E+13	2.0	a

<v> = 1190./cm c

LJ Parameters : d

sigma = 5.3 Å e/k = 388.53cal

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[a] Dean, A.M. and Westmoreland, P.R. **Int. J. of Chem. Kinetics**, Vol 19, 207-228, 1987.

[b] estimate a barrier of approximately 39 kcal/mol (26 kcal for ring strain, 8 kcal for the H-abstraction, and 5 kcal for the reaction endothermicity).

[c] see note (c) Table 1-a.
(refer to C_2H_4O)

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

Table A-3-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr) (Kcal/mol)	Reaction	A (cc/mol s)	Ea
7.6	$CH_3 + O_2 = CH_3OO$	6.45 E+06	-8.65
76.0		6.54 E+07	-8.61
760.0		7.32 E+08	-8.21
7.6	$CH_3 + O_2 = CH_3O + O$	2.19 E+13	2.96
76.0		2.19 E+13	2.96
760.0		2.19 E+13	2.96
7.6	$CH_3 + O_2 = CH_2OOH$	3.88 E+03	7.65
76.0		3.88 E+04	7.65
760.0		3.89 E+05	7.66
7.6	$CH_3 + O_2 = CH_2O + OH$	7.83 E+10	10.9
76.0		7.83 E+10	10.9
760.0		7.83 E+10	10.9

Table A-4-a

$$\begin{array}{l} CH_3 + CH_2CH_3 \Longleftrightarrow [CH_3CH_2CH_3]^{\#} \longrightarrow CH_3CH_2CH_2 + H \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \longrightarrow C_3H_8 \text{ (Stab.)} \end{array}$$

k	A	Ea	source
1	1.0 E+13	0.0	a
-1	8.0 E+16	84.4	a
2	1.6 E+16	97.6	a

<v> = 1330/cm b

LJ Parameters : c

sigma = 4.84 A^o e/k = 302 cal

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

b
see note (c) Table 1-a

c
see note (d) Table 1-a

Table A-4-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3 + C_2H_5 = CH_3CH_2CH_3$	2.76 E+11	-5.56
76.0		1.72 E+12	-2.80
760.0		5.30 E+12	-1.03
7.6	$CH_3 + C_2H_5 = CH_3CH_2CH_2 + H$	4.41 E+12	15.2
76.0		1.56 E+13	18.5
760.0		7.37 E+13	23.4

Table A-5-a

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

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

<v> = 1289.5/cm

LJ Parameters :

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

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

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

[c] see note (c) Table 1-a
Geometric mean frequency estimated as follows ;
$<v>_{CH3CHCH2} = (<v>_{CH3CH2CH3} + <v>_{CH2CCH2})/2$

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

Table A-5-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3 + CHCH_2 = CH_3CHCH_2$	4.0 E+11	-5.73
76.0		2.78 E+12	-2.92
760.0		9.12 E+12	-1.09
7.6	$CH_3 + CHCH_2 = CH_2CHCH_2 + H$	1.46 E+13	3.6
76.0		4.73 E+13	7.99
760.0		9.67 E+13	12.3

Table A-6-a

$$\begin{aligned} CH_3 + CH_2CCl <\!\!====\!\!> [CH_2CClCH_3]^{\#} &\ ----> CH_2CCH_2 + HCl \\ &\ ----> CHCCH_3 + HCl \\ &\ ----> CH_2CClCH_3 \text{ (Stab.)} \end{aligned}$$

k	A	Ea	source
1	1.58E+12	0.0	a
-1	1.32E+17	99.92	a
2	1.44E+13	61.86	b
3	3.55E+15	72.28	c

<v> = 1181/cm   d

LJ Parameters :   e

sigma = 5.2 Å   e/k = 418.4 cal

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[a] from Allara, D.L. and Shaw, R., J. Phys. Chem. Ref. Data, 9, 523, 1980, for CC.C + CH_3, log A = 13.2.

[b] $A= 10^{13.55} * 10^{(-4/4.6)} *3$, $E_a = \triangle H + 38.$

[c] $A= 10^{13.55}$, $E_a = \triangle H + 45.$

[d] used the CPfit Program.applied thesee note (c) Table 1-a

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

Table A-6-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr)	Reaction	A (cc/mol s)	Ea (Kcal/mol)
7.6	$CH_3 + CH_2CCl = CH_2CClCH_3$	8.77 E+09	-8.31
76.0		1.72 E+11	-6.08
760.0		2.79 E+12	-2.60
7.6	$CH_3+CH_2CCl= CH_2CCH_2 +HCl$	8.05 E+12	-0.68
76.0		1.60 E+13	1.31
760.0		4.24 E+13	5.26
7.6	$CH_3+CH_2CCl= CHCCH_3 +HCl$	3.59 E+12	1.16
76.0		6.93 E+12	3.00
760.0		2.03 E+13	6.98

Table A-7-a

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

k	A	Ea	source
1	2.0 E+13	0.0	a
-1	4.2 E+14	96.6	a
2	2.9 E+13	55.8	b
3	7.9 E+15	76.8	c

<v> = 797.2/cm d

LJ Parameters : e

sigma = 5.103 A° e/k = 435.9 cal

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

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

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

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

e
see note (d) Table

Table A-7-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P (torr) (Kcal/mol)	Reaction	A (cc/mol s)	Ea
7.6	$CH_3CCl_2 + H = CH_3CHCl_2$	3.13 E+08	-9.6
76.0		3.53 E+09	-9.27
760.0		5.98 E+11	-7.54
7.6	$CH3CCl_2 + H = CH_2CHCl + HCl$	2.54 E+12	-2.40
76.0		2.79 E+12	-2.15
760.0		4.73 E+12	-0.70
7.6	$CH_3CCl_2 + H = CH_3CHCl + Cl$	3.11 E+13	2.06
76.0		3.33 E+13	2.23
760.0		5.06 E+13	3.33

Table A-8-a

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

k	A	Ea	source
1	2.7 E+13	0.0	a
-1	7.6 E+14	94.0	a
2	3.24E+13	56.6	b
3	1.8 E+15	81.5	c

<v> = 1265.3/cm d

LJ Parameters : e
sigma = 4.898 Ao e/k = 300 cal

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

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

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

d
see note (c) Table 1-a

e
see note (d) Table 1-a

Table A-8-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMOLECULAR QRRK ANALYSIS

P Ea (torr) (Kcal/mol)	Reaction	A (cc/mol s)	
7.6	$CH_3CHCl + H = CH_3CH_2Cl$	2.09 E+09	-7.24
76.0		2.28 E+10	-6.99
760.0		3.63 E+11	-5.41
7.6	$CH_3CHCl + H = CH_2CH_2 + HCl$	1.95 E+13	-0.44
76.0		2.11 E+13	-0.22
760.0		3.47 E+13	1.27
7.6	$CH_3CHCl + H = CH_3CH_2 + Cl$	3.05 E+13	5.13
76.0		3.25 E+13	5.30
760.0		4.95 E+13	6.46

Table A-9-a

$$\begin{array}{l} CH_3CH_2 + H \Longleftrightarrow [CH_3CH_3]^{\#} \longrightarrow CH_3 + CH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\;\; \longrightarrow CH_3CH_3 \text{ (Stab.)} \end{array}$$

k source	A	Ea	
1	1.8 E+14	0.0	a
-1	1.3 E+16	100.7	a
2	8.0 E+16	90.4	a

<v> = 1509/cm b

LJ Parameters : c

sigma = 4.342 A^o e/k = 246.8 cal

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

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

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

Table A-9-b

APPARENT REACTION RATE CONSTANTS PREDICTED USING BIMMOLECULAR QRRK ANALYSIS

P (torr) (Kcal/mol)	Reaction	A (cc/mol s)	Ea
7.6	$CH_3CH_2 + H = CH_3CH_3$	8.94 E+09	-9.55
76.0		1.13 E+11	-8.76
760.0		1.98 E+12	-6.22
7.6	$CH_3CH_2 + H = CH_3 + CH_3$	1.84 E+14	0.06
76.0		2.29 E+14	0.64
760.0		5.11 E+14	2.84

APPENDIX II

A. SENSITIVITY ANALYSIS

```
     PROGRAM SID       Version 1.4
      Double PreCision


    Sensitivity analysis will be performed.
                WORKING SPACE REQUIREMENTS
                 PROVIDED        REQUIRED
Integer            40000            7500
Real              400000           60494


    Temperature is held Constant.


 Initial Conditions:

 PRESSURE (ATM)  =  1.0000E+00      TIM =   0.0000E+00
 Temperature (K) =  8.2300E+02
 Density (gm/CC) =  5.9141E-04

 Mole FraCtions:


 Time Integration:



T(SEC)= 0.0000E+00   P(ATM)= 1.0000E+00   T(K)= 8.2300E+02
 CH3CCL3     5.00E-03  CH3CL       0.00E+00  CH2CCL2     0.00E+00  CH2O        0.00E+00
 H2O         0.00E+00  H2O2        0.00E+00  C3H8        0.00E+00  O2          3.75E-02
 CO2         0.00E+00  CH4         7.50E-03  CH3         0.00E+00  H           0.00E+00
 C2H6        0.00E+00  CH3CCL2     0.00E+00  C2H5        0.00E+00  CCL3CH2     0.00E+00
 CH3CHCL2    0.00E+00  C3H7        0.00E+00  CH3CHCL     0.00E+00  CHCL2       0.00E+00
 CH2CL       0.00E+00  C2H5CL      0.00E+00  CL          0.00E+00  CL2         0.00E+00
 CCL3        0.00E+00  CH2CCL      0.00E+00  CHCL2CH2    0.00E+00  C2H3        0.00E+00
 C2H         0.00E+00  CH2CL2      0.00E+00  C2H2        0.00E+00  C*C*C       0.00E+00
 C3H5        0.00E+00  C2HCL       0.00E+00  CH          0.00E+00  CH2         0.00E+00
 O           0.00E+00  H2          0.00E+00  HCL         0.00E+00  C3H6        0.00E+00
 C2H4        0.00E+00  OH          0.00E+00  HO2         0.00E+00  CHO         0.00E+00
 CH2CO       0.00E+00  CH3O        0.00E+00  CO          0.00E+00  C2H3CL      0.00E+00
 AR          9.50E-01  CLO         0.00E+00
```

```
T(SEC)= 1.0168E+00   P(ATM)= 1.0000E+00   T(K)= 8.2300E+02
 CH3CCL3      2.13E-03  CH3CL        1.78E-10  CH2CCL2      2.86E-03  CH2O         2.39E-09
 H2O          1.00E-08  H2O2         3.31E-09  C3H8         9.77E-15  O2           3.74E-02
 CO2          2.50E-12  CH4          7.48E-03  CH3          4.96E-09  H            1.21E-13
 C2H6         1.35E-08  CH3CCL2      1.33E-09  C2H5         1.98E-14  CCL3CH2      8.38E-07
 CH3CHCL2     3.52E-10  C3H7         2.56E-19  CH3CHCL      0.00E+00  CHCL2        0.00E+00
 CH2CL        0.00E+00  C2H5CL       0.00E+00  CL           1.40E-10  CL2          1.20E-15
 CCL3         1.86E-09  CH2CCL       5.75E-12  CHCL2CH2     1.21E-11  C2H3         1.38E-20
 C2H          0.00E+00  CH2CL2       0.00E+00  C2H2         4.12E-12  C*C*C        0.00E+00
 C3H5         0.00E+00  C2HCL        4.93E-08  CH           0.00E+00  CH2          1.42E-17
 O            9.43E-14  H2           2.24E-08  HCL          2.86E-03  C3H6         9.05E-15
 C2H4         5.99E-10  OH           2.51E-14  HO2          9.67E-11  CHO          1.14E-16
 CH2CO        0.00E+00  CH3O         2.34E-14  CO           8.49E-11  C2H3CL       4.01E-07
 AR           9.47E-01  CLO          1.72E-13
                    SENSITIVITY (KSPEC,IIRXN) KSPEC = 1, KK
RXN     A FACTOR         CH3CCL3     CH3CL       CH2CCL2     CH2O        H2O         H2O2        C3H8        O2          CO2

  1 CH3CCL3=CH2CCL2+HCL
             2.250E+12  -8.497E-01  -2.618E-02   6.335E-01  -6.305E-01  -8.782E-01  -5.242E-01  -7.423E-01   1.854E-07  -1.643E+00
  2 CH3CCL3=CH3CCL2+CL
             1.000E+14  -3.726E-04   1.589E+00  -1.473E-04   1.017E+00   1.011E+00   1.119E+00   1.912E+00  -2.734E-07   2.931E+00
  3 CH3CCL3=CH3+CCL3
             2.060E+14  -7.824E-07   2.820E-03  -3.984E-07   2.075E-03   5.239E-04   2.294E-03   3.911E-03  -3.504E-10   4.755E-03
  4 CH2CCL2=C2HCL+HCL
             3.630E+13   1.862E-08   3.067E-07  -1.726E-05  -3.998E-06   9.419E-07  -2.123E-06  -2.460E-06   1.933E-13  -2.602E-06
  5 CH2CCL2=CH2CCL+CL
             6.690E+13  -5.062E-09   2.442E-05  -2.443E-09   1.079E-05   2.797E-06   1.152E-05   1.918E-05  -1.848E-12   2.613E-05
  6 CH3CCL2=CH2CCL2+H
             2.600E+13  -4.637E-09   4.633E-03   6.595E-08   1.241E-02   6.550E-02   1.457E-02   2.624E-02  -1.052E-08   2.343E-02
  7 CH3CCL2+H=CH3CHCL2
             5.930E+10   7.919E-11  -9.732E-07   1.103E-10  -1.068E-06  -2.963E-06  -1.250E-06  -2.343E-06   5.473E-13  -2.462E-06
  8 CH3CCL2+H=C2H3CL+HCL
             4.690E+12   9.517E-11  -1.165E-06   1.318E-10  -1.279E-06  -3.547E-06  -1.497E-06  -2.805E-06   6.552E-13  -2.945E-06
  9 CH2CCL2+H=CH2CCL+HCL
             1.200E+13   1.257E-08  -8.823E-07  -5.990E-08   1.855E-05  -5.196E-03  -2.940E-06  -6.793E-05   6.964E-10  -4.296E-03
 10 CH2CCL2+H=CHCL2CH2
             9.720E+08  -3.419E-10  -1.358E-06  -1.199E-10  -2.238E-05  -1.293E-04  -2.876E-05  -5.446E-05   2.070E-11  -3.967E-05
 11 CH2CCL2+H=C2H3CL+CL
             5.990E+13   1.287E-06  -1.363E-02  -7.445E-06  -1.505E-02  -6.274E-01  -1.611E-02  -2.953E-02   8.611E-08  -5.401E-01
 12 CH2CCL+H=C2H3+CL
             1.020E+14  -5.989E-13   1.294E-09   3.423E-12   6.218E-07   8.387E-08   3.894E-06  -1.291E-08  -4.013E-13   2.667E-05
 13 CH2CCL+H=C2H2+HCL
             8.340E+11   1.310E-13  -1.645E-09   2.115E-13  -7.795E-10  -2.440E-09   1.190E-08  -3.786E-09  -1.402E-15   8.001E-07
 14 CH3CHCL2=C2H3CL+HCL
             1.980E+13   4.633E-12   5.308E-11  -3.497E-12  -5.064E-10  -2.260E-10   3.311E-10  -2.885E-10  -1.719E-17   1.033E-08
 15 C2H3CL=C2H2+HCL
             1.990E+13  -8.200E-11   3.609E-07  -1.443E-11   3.701E-06   4.699E-07   6.634E-05   2.602E-07  -9.772E-12   1.738E-03
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16 C2H3CL=C2H3+CL
         1.160E+14  -1.612E-12   7.572E-09  -3.520E-13   4.277E-08   1.027E-08   6.858E-07   5.769E-09  -6.866E-14   9.850E-07
17 CH3CL=CH3+CL
         1.270E+14   6.847E-08   6.638E-01   2.610E-08  -2.884E-04  -7.321E-05  -3.168E-04  -5.628E-04   4.907E-11  -6.588E-04
18 CH3CL+H=CH3+HCL
         7.000E+13  -1.550E-10   3.357E-01  -1.997E-08  -1.590E-06   5.262E-05  -1.256E-06  -1.600E-06  -6.890E-12   9.548E-05
19 C2H6=2CH3
         3.640E+16   5.846E-06  -6.814E-02   3.902E-06  -5.129E-02  -1.289E-02   9.609E-02   3.707E-01  -5.604E-09  -1.188E-01
20 C2H6+H=C2H5+H2
         6.610E+13   3.060E-14  -1.519E-09   4.513E-12   3.984E-07   7.543E-08   3.683E-06   2.027E-05  -3.527E-13   5.647E-07
21 C2H6+CH3=C2H5+CH4
         3.160E+11   1.738E-12  -4.647E-08   2.682E-13   1.005E-05   2.496E-06   1.121E-04   5.080E-04  -1.085E-11   1.398E-05
22 C2H6+CL=C2H5+HCL
         4.640E+13   8.490E-09  -3.808E-05   1.124E-09   9.673E-03   2.378E-03   1.522E-01   4.653E-01  -1.478E-08   1.226E-02
23 C2H6+O=C2H5+OH
         2.510E+13  -4.478E-15  -1.813E-09   7.632E-16   4.679E-07   1.190E-07   4.631E-06   2.402E-05  -4.481E-13   6.698E-07
24 C2H6+OH=C2H5+H2O
         6.760E+13  -2.435E-13  -1.156E-08  -2.077E-14   3.156E-06   7.902E-07   2.805E-05   1.621E-04  -2.722E-12  -1.022E-05
25 C2H5=C2H4+H
         5.010E+13  -1.255E-10   6.076E-07  -2.609E-09  -1.313E-04  -2.644E-05  -2.042E-03  -6.332E-03   1.977E-10  -1.543E-04
26 C2H5+H=2CH3
         5.100E+14  -7.704E-11  -5.467E-07  -1.651E-09   2.463E-04   8.035E-05   1.421E-03   1.263E-02  -1.462E-10   4.147E-04
27 C2H5+O2=C2H4+HO2
         2.000E+12   1.176E-09  -4.391E-06   2.700E-09   7.881E-04   1.867E-04   1.380E-02  -4.819E-01  -1.356E-09   9.805E-04
28 C2H5+CH3=C3H8
         5.200E+12   5.875E-12  -3.499E-08   1.997E-12  -2.394E-07  -5.947E-08  -2.640E-06   5.196E-01   2.594E-13  -3.518E-07
29 C2H5+CH3=C3H7+H
         7.170E+13   1.116E-19  -3.457E-16   1.602E-19  -1.308E-13  -3.260E-14  -1.388E-12   7.811E-11   1.370E-19  -1.893E-13
30 C2H4+O=CH3+CHO
         2.240E+13   3.133E-14  -1.326E-10  -1.177E-14   3.300E-08  -1.880E-07   5.441E-07  -3.159E-10  -5.301E-14   2.396E-05
31 C2H4+OH=CH3+CH2O
         1.000E+13  -4.010E-14  -8.528E-10   1.400E-14  -2.327E-05   5.699E-06  -4.529E-07   3.501E-09   4.497E-14   2.191E-06
32 C2H4+OH=C2H3+H2O
         7.080E+13  -1.517E-14   3.219E-11   2.465E-15   3.257E-08   7.120E-09   5.105E-07  -1.874E-10  -5.100E-14   5.008E-07
33 C2H4+H=C2H3+H2
         6.920E+14  -1.396E-15   9.943E-12   2.677E-14   1.627E-09   3.330E-10   2.573E-08   5.218E-12  -2.549E-15   5.139E-08
34 C2H3+CH3=C3H6
         9.160E+12   2.261E-17  -2.433E-13   1.451E-17  -5.987E-12  -1.440E-12  -3.218E-11  -4.396E-13   3.457E-18  -2.362E-10
35 C2H3+O2=C2H2+HO2
         1.000E+12   1.477E-15  -5.084E-12   2.709E-16   1.801E-12   7.618E-13  -1.130E-09   7.589E-13   4.601E-16   4.838E-10
36 C2H2+O=CH2+CO
         5.250E+13   1.246E-14  -5.779E-11   2.606E-15  -3.692E-11  -1.760E-09  -2.306E-10  -4.289E-11   3.437E-17   1.357E-07
37 C2H2+O2=2CHO
         3.980E+12  -8.034E-11   3.566E-07  -1.477E-11   3.663E-06   4.623E-07   6.551E-05   2.577E-07  -9.642E-12   1.739E-03
38 C3H8+CH3=C3H7+CH4
         2.000E+12  -4.553E-17   3.127E-13  -2.346E-17   3.960E-12   9.867E-13   4.379E-11  -9.336E-06  -4.139E-18   5.396E-12
39 C3H8+HO2=C3H7+H2O2
         6.200E+12  -2.376E-19   1.162E-15  -5.605E-20   1.102E-14   2.707E-15   1.715E-13  -3.962E-08  -1.682E-20   1.461E-14
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40 C3H7=C3H6+H
               1.260E+13   1.113E-14  -4.620E-11  -1.093E-14  -1.027E-09  -2.177E-10  -1.748E-08  -2.136E-07   1.724E-15  -1.249E-09
41 C3H7=CH3+C2H4
               1.000E+13   2.029E-13  -1.126E-09   4.826E-14   1.206E-07   2.946E-08   2.093E-06   2.560E-05  -2.068E-13   1.524E-07
42 C3H7+O2=C3H6+HO2
               1.000E+12   2.387E-14  -1.044E-10   1.422E-14   2.559E-08   6.220E-09   4.430E-07  -2.539E-05  -4.377E-14   3.234E-08
43 CH3CCL3+CL=CCL3CH2+HCL
               2.510E+12  -8.006E-06  -1.139E+00  -6.704E-06  -7.394E-01  -1.875E-01  -8.036E-01  -1.341E+00   1.238E-07  -1.772E+00
44 CH3CCL2+CH4=CH3CHCL2+CH3
               1.580E+12   1.108E-09   4.540E-06  -6.305E-09   1.559E-05  -5.553E-04   1.547E-05   2.234E-05   7.255E-11  -4.385E-04
45 CH2CCL+CH4=C2H3CL+CH3
               2.900E+11   3.339E-10   1.790E-05  -7.438E-10   4.431E-05   1.097E-05   5.090E-05   1.032E-04  -7.567E-12   6.357E-05
46 CH4+AR=CH3+H+AR
               1.000E+17   2.260E-09  -3.282E-05   3.771E-09  -3.668E-05  -5.285E-05  -4.356E-05  -8.377E-05   1.229E-11  -7.881E-05
47 CH4+O2=CH3+HO2
               7.940E+13  -2.749E-07   1.589E-03  -9.210E-08   1.113E-02   2.757E-03   1.336E-01   1.620E-03  -1.294E-08   1.603E-02
48 CH4+O=CH3+OH
               1.200E+07  -1.103E-09   3.403E-05   4.657E-10  -1.691E-03   4.333E-04  -2.592E-06   7.835E-05   2.740E-13  -3.142E-03
49 CH4+H=CH3+H2
               2.200E+04   8.281E-08  -9.899E-04   1.802E-06  -1.361E-03  -5.087E-02  -1.547E-03  -2.866E-03   7.006E-09  -6.067E-03
50 CH4+OH=CH3+H2O
               1.600E+06   1.107E-09   4.876E-05   1.628E-09   2.925E-05   1.787E-04   6.156E-05   4.329E-06  -1.085E-11  -5.751E-01
51 CH4+CL=CH3+HCL
               2.570E+13   1.098E-07   8.971E-04   1.174E-07   5.600E-03   1.382E-03   7.237E-03   1.454E-02  -1.032E-09   1.187E-02
52 CH4+HO2=CH3+H2O2
               2.000E+13  -1.879E-08   3.726E-04  -1.367E-08  -8.404E-02  -2.083E-02   2.967E-02   1.157E-03   5.217E-09  -1.195E-01
53 CH3+O2=CH3O+O
               7.260E+11  -1.152E-06   8.853E-03  -5.355E-07   9.822E-01   2.425E-01   6.841E-01   1.250E-02  -1.271E-07   1.402E+00
54 CH3+O=CH2O+H
               7.000E+13   1.597E-09  -2.227E-05  -2.018E-10   1.799E-03  -4.330E-04   3.231E-05  -5.472E-05  -5.359E-12   2.752E-03
55 CH3+OH=CH2O+2H
               5.300E+12  -4.367E-12   4.616E-08  -1.117E-10   6.970E-05  -1.506E-05   2.410E-06   5.681E-08  -5.469E-13   1.147E-04
56 CH3+HO2=CH3O+OH
               2.000E+13  -3.522E-10  -2.005E-06   7.110E-11   1.016E-01   2.517E-02   2.805E-03   1.004E-06  -7.022E-09   1.508E-01
57 CH3O+O2=CH2O+HO2
               1.000E+13   3.541E-12   1.102E-07   1.976E-13   1.487E-05   1.431E-06   7.578E-06   7.085E-07  -1.073E-12   5.816E-05
58 CH2O+CH3=CH4+CHO
               1.000E+10   1.028E-11  -1.137E-07  -1.107E-11  -3.848E-04   4.485E-07   2.820E-04  -2.381E-07  -2.735E-11   1.995E-02
59 CH2O+H=CHO+H2
               2.500E+13   8.589E-14  -2.023E-09   6.284E-12  -7.551E-06  -3.789E-08   5.739E-06  -6.787E-09  -5.483E-13   5.799E-04
60 CH2O+O=CHO+OH
               3.500E+13   6.929E-14  -1.794E-09  -2.827E-13  -6.555E-06   2.327E-10   4.910E-06  -5.534E-09  -4.744E-13   4.434E-04
61 CH2O+OH=CHO+H2O
               3.000E+13   2.538E-14  -2.472E-09  -4.757E-13  -8.845E-06  -8.251E-09   6.724E-06  -9.670E-09  -6.503E-13   7.011E-04
62 CH2O+HO2=CHO+H2O2
               1.000E+12   5.684E-15  -9.477E-11  -2.065E-13  -6.500E-06  -6.187E-08   4.694E-06  -1.091E-10  -4.165E-13   2.565E-04
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 63 CH2O+CL=CHO+HCL
           5.000E+13   1.789E-09  -7.037E-06  -2.297E-10  -3.275E-02   1.056E-04   2.311E-02  -7.682E-06  -2.265E-09   9.245E-01
 64 CHO+O2=CO+HO2
           3.000E+12  -9.899E-15   1.075E-10  -1.136E-14  -2.895E-07   1.427E-09   2.356E-07   1.313E-10  -2.371E-14   8.121E-06
 65 CHO+HO2=CH2O+O2
           5.000E+13  -1.752E-09   8.830E-06  -4.945E-10  -1.018E-03   1.559E-05   1.568E-03   7.038E-06  -1.516E-10   3.786E-02
 66 CO+OH=CO2+H
           1.510E+13  -2.965E-12  -3.165E-08  -8.069E-10  -3.903E-08  -2.392E-04  -4.032E-08  -6.115E-08  -2.114E-13   9.624E-01
 67 CO+HO2=CO2+OH
           1.510E+14   2.615E-16  -1.159E-12   9.044E-17  -4.434E-11   1.862E-10  -8.170E-10  -6.999E-13   2.692E-18   1.179E-06
 68 CO+O2=CO2+O
           1.600E+13  -2.490E-12   1.108E-08  -4.088E-13   4.697E-09   3.426E-07   4.625E-09   8.139E-09  -9.100E-14   1.317E-03
 69 H+O2=O+OH
           2.200E+14  -1.434E-06   1.660E-02   1.772E-07   2.031E-02   7.250E-01   2.227E-02   4.093E-02  -9.993E-08   5.787E-01
 70 H+H2O=H2+OH
           4.600E+08  -4.291E-14   2.075E-10  -2.966E-12  -2.757E-11   2.013E-08  -1.696E-11   1.296E-11  -2.746E-15  -1.621E-06
 71 O2+AR=2O+AR
           1.850E+11   1.429E-14  -2.377E-10   1.247E-14  -3.725E-10  -4.840E-09  -4.213E-10  -7.839E-10   8.457E-16  -1.363E-09
 72 H+HO2=2OH
           1.500E+14   1.472E-12   9.166E-09   3.397E-11  -5.114E-06   1.901E-05  -3.087E-05   1.130E-07   3.758E-13   5.145E-06
 73 H+HO2=H2+O2
           2.500E+13   8.472E-12  -9.534E-08   1.249E-11  -1.110E-06  -3.570E-07  -6.162E-06  -1.708E-07   6.342E-13  -1.885E-06
 74 O+HO2=OH+O2
           2.000E+13   4.455E-12  -4.627E-08   2.861E-12  -5.246E-07  -1.292E-07  -3.102E-06  -7.862E-08   3.127E-13  -8.750E-07
 75 OH+HO2=H2O+O2
           2.000E+13   1.953E-12  -2.206E-08   1.360E-12  -2.599E-07  -6.608E-08  -1.439E-06  -3.981E-08   1.456E-13  -7.323E-07
 76 O+HCL=OH+CL
           5.240E+12  -3.022E-10  -1.252E-05  -1.768E-10  -8.489E-05   1.412E-05  -1.903E-05  -2.608E-05   2.963E-12  -1.005E-04
 77 OH+HCL=CL+H2O
           2.450E+12  -1.043E-09  -4.911E-05  -6.799E-10  -8.839E-05   7.874E-05  -9.276E-05  -1.607E-04   1.409E-11  -3.881E-01
 78 2CL+AR=CL2+AR
           2.340E+14   8.291E-13  -4.027E-09   1.888E-13  -1.810E-09  -4.687E-10  -1.932E-09  -3.358E-09   3.117E-16  -4.316E-09
 79 CL+H2=HCL+H
           4.800E+13   4.900E-08  -5.707E-04   5.516E-06  -6.271E-04  -2.628E-02  -6.752E-04  -1.234E-03   3.606E-09  -2.260E-02
 80 CL+HO2=HCL+O2
           1.300E+13  -3.285E-08   1.568E-04  -7.700E-09   8.795E-04   2.161E-04   1.402E-02   1.211E-04  -1.363E-09   1.170E-03
 81 CL+HO2=CLO+OH
           7.000E+12   5.079E-11   1.856E-05   1.634E-11   8.623E-06   1.989E-05  -5.033E-05  -2.709E-07  -5.836E-13   6.215E-05
 82 CLO+CO=CL+CO2
           2.700E+11  -4.226E-16  -3.356E-11  -5.540E-17  -2.464E-11   6.469E-13  -1.515E-11   1.279E-12   1.538E-18   3.518E-07
 83 CH3+CLO=CH3CL+O
           6.000E+12  -9.644E-13   1.861E-05  -2.635E-13  -1.799E-07   3.295E-07  -1.206E-07   4.390E-09   1.172E-14   1.063E-06
 84 CH3+CLO=CH3O+CL
           9.000E+12  -8.498E-12  -2.361E-06  -2.304E-12   1.180E-05   9.174E-08   8.082E-06   3.534E-08  -7.914E-13   5.413E-06
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T(SEC)= 1.0168E+00   P(ATM)= 1.0000E+00   T(K)= 8.2300E+02
 CH4          7.48E-03  CH3CCL3     2.13E-03  CH2CCL2     2.86E-03  C2H3CL      4.01E-07
 HCL          2.86E-03  C2H2        4.12E-12  C2H4        5.99E-10  C3H6        9.05E-15
 CO           8.49E-11  CH3         4.96E-09  H           1.21E-13  C2H6        1.35E-08
 CH3CCL2      1.33E-09  C2H5        1.98E-14  CCL3CH2     8.38E-07  CH3CHCL2    3.52E-10
 C3H7         2.56E-19  CH3CHCL     0.00E+00  CHCL2       0.00E+00  CH2CL       0.00E+00
 C2H5CL       0.00E+00  CL          1.40E-10  CL2         1.20E-15  CCL3        1.86E-09
 CH2CCL       5.75E-12  CHCL2CH2    1.21E-11  C2H3        1.38E-20  C2H         0.00E+00
 CH2CL2       0.00E+00  C*C*C       0.00E+00  C3H5        0.00E+00  C2HCL       4.93E-08
 CH           0.00E+00  CH2         1.42E-17  O           9.43E-14  H2          2.24E-08
 CH3CL        1.78E-10  H2O         1.00E-08  H2O2        3.31E-09  O2          3.74E-02
 OH           2.51E-14  HO2         9.67E-11  CHO         1.14E-16  CH2CO       0.00E+00
 CH3O         2.34E-14  C3H8        9.77E-15  CO2         2.50E-12  CH2O        2.39E-09
 AR           9.47E-01  CLO         1.72E-13


                      SENSITIVITY (KSPEC,IIRXN) KSPEC = 1, KK
RXN      A FACTOR          CH4          CH3CCL3       CH2CCL2       C2H3CL        HCL           C2H2          C2H4          C3H6          CO

  1 CH3CCL3=CH2CCL2+HCL
              2.250E+12   4.559E-06   -8.497E-01    6.335E-01   -3.512E-01    6.332E-01   -2.283E-01   -9.300E-01   -6.716E-01   -3.101E-01
  2 CH3CCL3=CH3CCL2+CL
              1.000E+14  -7.981E-06   -3.725E-04   -1.474E-04    9.999E-01    1.342E-04    1.000E+00    2.749E+00    1.809E+00    1.932E+00
  3 CH3CCL3=CH3+CCL3
              2.060E+14   1.770E-07   -7.768E-07   -3.978E-07    1.442E-07   -3.977E-07    2.969E-06    5.738E-03    3.670E-03    3.657E-03
  4 CH2CCL2=C2HCL+HCL
              3.630E+13   2.129E-11    2.600E-09   -1.725E-05   -6.336E-07    1.724E-05   -4.340E-07    4.607E-07   -3.456E-06    1.663E-06
  5 CH2CCL2=CH2CCL+CL
              6.690E+13  -6.647E-11   -5.061E-09   -2.873E-09    1.825E-05    1.359E-09    1.360E-05    2.522E-05    1.892E-05    2.651E-05
  6 CH3CCL2=CH2CCL2+H
              2.600E+13  -1.474E-07   -4.740E-09    6.629E-08    1.217E-03   -4.543E-08    4.205E-03    4.351E-02    2.407E-02    1.663E-02
  7 CH3CCL2+H=CH3CHCL2
              5.930E+10   1.198E-11    7.912E-11    1.102E-10   -8.397E-07   -5.945E-11   -1.268E-06   -3.671E-06   -2.128E-06   -1.604E-06
  8 CH3CCL2+H=C2H3CL+HCL
              4.690E+12   1.435E-11    9.497E-11    1.319E-10   -4.401E-07   -7.403E-11   -6.579E-07   -4.396E-06   -2.548E-06   -1.918E-06
  9 CH2CCL2+H=CH2CCL+HCL
              1.200E+13   2.460E-10    1.254E-08   -5.998E-08    4.814E-04    7.934E-08    3.160E-03   -1.514E-04   -6.386E-05    9.661E-05
 10 CH2CCL2+H=CHCL2CH2
              9.720E+08   3.204E-10   -3.427E-10   -5.320E-10    4.417E-06    4.191E-10    4.736E-06   -9.466E-05   -5.176E-05   -2.939E-05
 11 CH2CCL2+H=C2H3CL+CL
              5.990E+13   1.476E-07    1.282E-06   -7.446E-06    5.937E-02    9.107E-06    6.333E-02   -4.557E-02   -2.689E-02   -8.203E-03
 12 CH2CCL+H=C2H3+CL
              1.020E+14  -1.298E-13   -5.829E-13    3.423E-12   -5.436E-08    5.324E-13    2.616E-03   -2.376E-08    4.535E-06    1.801E-05
 13 CH2CCL+H=C2H2+HCL
              8.340E+11   1.913E-14    1.318E-13    2.137E-13   -1.711E-09   -1.203E-14    8.195E-05   -5.955E-09   -3.462E-09    5.377E-07
 14 CH3CHCL2=C2H3CL+HCL
              1.980E+13   2.759E-15    4.725E-12   -3.506E-12    1.917E-05    2.672E-09    1.217E-05    1.900E-10   -1.973E-10    2.530E-08
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15 C2H3CL=C2H2+HCL
            1.990E+13  -2.119E-12  -8.202E-11  -1.445E-11  -1.050E-05   9.308E-10   9.927E-01   3.311E-07   2.559E-07   2.749E-03
16 C2H3CL=C2H3+CL
            1.160E+14  -3.135E-14  -1.612E-12  -3.520E-13  -5.011E-09   4.571E-13   5.317E-04   7.453E-09   3.109E-07   1.504E-06
17 CH3CL=CH3+CL
            1.270E+14  -1.339E-08   6.846E-08   2.611E-08  -6.323E-08  -1.537E-08  -4.210E-07  -8.058E-04  -5.192E-04  -5.449E-04
18 CH3CL+H=CH3+HCL
            7.000E+13  -8.000E-09  -1.510E-10  -1.997E-08   1.414E-04   1.239E-09   1.046E-04  -1.493E-06  -1.574E-06  -3.441E-06
19 C2H6=2CH3
            3.640E+16  -3.107E-06   5.852E-06   3.897E-06   9.768E-06   3.907E-06   2.989E-04   7.832E-01   3.566E-01  -8.784E-02
20 C2H6+H=C2H5+H2
            6.610E+13  -1.046E-13   1.665E-14   4.513E-12  -3.134E-08  -4.250E-12  -1.577E-08   2.092E-05   2.022E-05   4.595E-07
21 C2H6+CH3=C2H5+CH4
            3.160E+11  -2.673E-12   1.573E-12   3.832E-13   1.184E-08   5.118E-12   5.126E-07   6.464E-04   5.000E-04   1.036E-05
22 C2H6+CL=C2H5+HCL
            4.640E+13  -2.967E-09   8.229E-09   1.315E-09   1.654E-05   8.619E-09   3.852E-04   8.975E-01   4.455E-01   7.041E-03
23 C2H6+O=C2H5+OH
            2.510E+13  -1.206E-13  -1.390E-14   3.995E-15   4.604E-10   1.944E-13   2.542E-08   2.647E-05   2.375E-05   5.206E-07
24 C2H6+OH=C2H5+H2O
            6.760E+13  -7.912E-13  -2.790E-13   3.329E-15   2.812E-09   1.159E-12   1.684E-07   1.596E-04   1.580E-04   4.112E-06
25 C2H5=C2H4+H
            5.010E+13   3.968E-11  -1.263E-10  -2.608E-09   1.814E-05   2.474E-09   1.278E-05   9.204E-04   3.314E-04  -9.655E-05
26 C2H5+H=2CH3
            5.100E+14  -1.381E-09  -7.480E-11  -1.652E-09   1.148E-05   1.589E-09   2.949E-05   8.096E-03   1.041E-02   3.137E-04
27 C2H5+O2=C2H4+HO2
            2.000E+12  -2.426E-10   1.154E-09   2.716E-09  -1.684E-05  -3.545E-09   6.809E-06   6.989E-02   2.515E-02   4.389E-04
28 C2H5+CH3=C3H8
            5.200E+12  -1.093E-12   5.881E-12   2.007E-12  -2.863E-10   1.900E-12  -1.034E-08  -1.538E-05   2.361E-05  -2.499E-07
29 C2H5+CH3=C3H7+H
            7.170E+13   1.095E-18  -5.631E-20   7.044E-20  -8.965E-16  -3.076E-19  -3.967E-14  -5.909E-11   2.065E-06  -1.327E-13
30 C2H4+O=CH3+CHO
            2.240E+13   2.455E-13   2.982E-14  -9.620E-15   1.405E-10   3.154E-14  -1.333E-09  -3.185E-06  -1.478E-06   2.176E-05
31 C2H4+OH=CH3+CH2O
            1.000E+13  -7.634E-12  -5.088E-15  -2.949E-14   1.550E-11  -6.635E-14   6.263E-08   9.553E-05   6.057E-05  -1.862E-05
32 C2H4+OH=C2H3+H2O
            7.080E+13  -1.024E-14  -1.474E-14   2.704E-15   2.883E-12   4.414E-15   3.886E-04  -2.772E-06  -1.202E-06   1.326E-06
33 C2H4+H=C2H3+H2
            6.920E+14  -6.207E-16  -3.938E-16   2.745E-14  -1.953E-10  -2.748E-14   1.944E-05  -1.375E-07  -6.137E-08   6.679E-08
34 C2H3+CH3=C3H6
            9.160E+12   4.079E-18   2.255E-17   1.455E-17  -1.405E-15   1.414E-17  -2.139E-08  -6.648E-13   5.120E-06  -1.523E-10
35 C2H3+O2=C2H2+HO2
            1.000E+12   2.243E-17   1.308E-15   2.650E-16   1.212E-15   2.658E-16   2.467E-08  -3.405E-12  -5.120E-06   1.624E-10
36 C2H2+O=CH2+CO
            5.250E+13   1.157E-16   1.054E-14   2.148E-15   7.958E-13   2.411E-15  -3.340E-06  -4.778E-11  -3.638E-11   1.556E-07
37 C2H2+O2=2CHO
            3.980E+12  -2.096E-12  -8.033E-11  -1.478E-11   1.037E-08  -1.186E-11  -2.838E-02   3.280E-07   2.516E-07   2.712E-03
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38 C3H8+CH3=C3H7+CH4
          2.000E+12   1.396E-18  -4.592E-17  -2.362E-17   1.270E-15  -2.320E-17   4.463E-14   4.987E-11   7.881E-06   4.458E-12
39 C3H8+HO2=C3H7+H2O2
          6.200E+12   9.507E-21  -2.365E-19  -5.731E-20   5.939E-18  -5.556E-20   8.206E-17   2.072E-13   3.278E-08   8.304E-15
40 C3H7=C3H6+H
          1.260E+13  -1.337E-15   1.030E-14  -9.916E-15   9.229E-11   1.613E-14   3.035E-11  -2.135E-08   6.892E-04  -6.338E-10
41 C3H7=CH3+C2H4
          1.000E+13  -1.048E-12   2.084E-13   5.092E-14   7.349E-11   7.104E-14  -3.620E-09  -1.257E-05   4.063E-01   6.772E-08
42 C3H7+O2=C3H6+HO2
          1.000E+12  -2.104E-13   2.952E-14   1.689E-14  -7.215E-11  -3.604E-15  -7.577E-10  -2.533E-06   8.194E-02   1.438E-08
43 CH3CCL3+CL=CCL3CH2+HCL
          2.510E+12   5.431E-06  -8.022E-06  -6.692E-06  -2.196E-04  -6.670E-06  -1.118E-03  -1.908E+00  -1.267E+00  -1.363E+00
44 CH3CCL2+CH4=CH3CHCL2+CH3
          1.580E+12  -1.412E-10   1.102E-09  -6.308E-09  -8.193E-04  -1.138E-07  -8.207E-04   3.302E-05   1.976E-05   2.387E-05
45 CH2CCL+CH4=C2H3CL+CH3
          2.900E+11  -5.799E-10   3.337E-10  -7.441E-10   1.373E-05  -7.528E-10  -2.526E-03   1.711E-04   8.973E-05   4.166E-05
46 CH4+AR=CH3+H+AR
          1.000E+17   4.345E-10   2.259E-09   3.772E-09  -1.380E-05  -1.053E-10  -2.203E-05  -1.318E-04  -7.540E-05  -5.385E-05
47 CH4+O2=CH3+HO2
          7.940E+13  -9.747E-09  -2.748E-07  -9.219E-08   2.903E-07  -9.208E-08   3.164E-06   2.255E-03   1.559E-03   1.124E-02
48 CH4+O=CH3+OH
          1.200E+07   3.685E-11  -1.096E-09   4.608E-10  -9.699E-06  -1.785E-09  -1.229E-05   1.357E-04   7.099E-05  -2.368E-03
49 CH4+H=CH3+H2
          2.200E+04   1.508E-08   8.089E-08   1.803E-06  -1.226E-02  -1.643E-06  -1.773E-02  -4.620E-03  -2.648E-03  -2.007E-03
50 CH4+OH=CH3+H2O
          1.600E+06  -7.645E-10   1.112E-09   1.625E-09  -4.098E-06   1.480E-09  -2.431E-04   9.320E-05  -4.131E-06   1.681E-02
51 CH4+CL=CH3+HCL
          2.570E+13  -8.047E-08   1.099E-07   1.173E-07   7.265E-07   1.179E-07   1.329E-05   2.420E-02   1.343E-02   7.604E-03
52 CH4+HO2=CH3+H2O2
          2.000E+13   2.181E-08  -1.902E-08  -1.350E-08  -4.486E-07  -1.437E-08  -1.139E-05   1.839E-03   1.013E-03  -8.697E-02
53 CH3+O2=CH3O+O
          7.260E+11  -3.799E-07  -1.149E-06  -5.383E-07   1.267E-05  -5.341E-07   1.767E-04   1.835E-02   1.152E-02   9.754E-01
54 CH3+O=CH2O+H
          7.000E+13  -3.292E-10   1.593E-09  -1.985E-10   1.008E-05   2.642E-09   1.550E-05  -8.529E-05  -4.890E-05   2.299E-03
55 CH3+OH=CH2O+2H
          5.300E+12  -2.366E-11  -4.483E-12  -1.115E-10   7.643E-07   1.035E-10   1.217E-06   9.658E-08   6.088E-08   9.123E-05
56 CH3+HO2=CH3O+OH
          2.000E+13  -3.377E-08  -2.796E-11  -1.765E-10   9.092E-07   2.031E-10   1.392E-05   9.249E-06   8.344E-06   1.082E-01
57 CH3O+H=CH2O+H2
          2.000E+13   1.369E-15   6.440E-15   1.168E-14  -4.420E-11  -7.463E-16  -7.181E-11  -3.079E-10  -1.779E-10  -1.274E-09
58 CH3O+O2=CH2O+HO2
          1.000E+13  -5.901E-12   3.575E-12   1.551E-13   3.581E-10   3.048E-13   8.034E-10   1.191E-06   6.444E-07   2.489E-05
59 CH2O+CH3=CH4+CHO
          1.000E+10  -6.024E-12   1.027E-11  -1.107E-11   1.179E-07   2.181E-11   1.044E-07  -3.887E-07  -2.214E-07   1.089E-02
60 CH2O+H=CHO+H2
          2.500E+13  -1.481E-13   7.198E-14   6.265E-12  -4.346E-08  -5.961E-12  -4.806E-08  -1.155E-08  -6.281E-09   2.117E-04
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61 CH2O+O=CHO+OH
          3.500E+13  -1.161E-13   6.931E-14  -2.827E-13   2.595E-09   4.441E-13   2.485E-09  -9.247E-09  -5.094E-09   1.843E-04
62 CH2O+OH=CHO+H2O
          3.000E+13  -1.733E-13   2.488E-14  -4.761E-13   4.130E-09   6.847E-13   2.445E-09  -1.617E-08  -8.905E-09   2.481E-04
63 CH2O+HO2=CHO+H2O2
          1.000E+12  -1.763E-15   4.968E-15  -2.062E-13   1.519E-09   2.136E-13   1.161E-09  -4.978E-10  -2.525E-10   1.757E-04
64 CH2O+CL=CHO+HCL
          5.000E+13  -4.211E-10   1.789E-09  -2.301E-10   5.476E-06   1.517E-09   3.736E-06  -1.331E-05  -7.401E-06   9.349E-01
65 CHO+O2=CO+HO2
          3.000E+12  -4.424E-15  -7.777E-15  -8.938E-15   4.803E-11  -2.610E-13   3.342E-11   1.510E-10   1.068E-10   9.704E-06
66 CHO+HO2=CH2O+O2
          5.000E+13  -5.636E-11  -1.751E-09  -4.949E-10   2.255E-07  -4.321E-10   1.803E-07   9.190E-06   6.935E-06   3.051E-02
67 CO+OH=CO2+H
          1.510E+13   2.237E-13  -4.863E-12  -8.055E-10   5.711E-06   8.035E-10   3.483E-06  -7.791E-08  -5.856E-08  -2.842E-02
68 CO+HO2=CO2+OH
          1.510E+14   8.821E-18   1.537E-16   4.640E-17  -1.169E-13   1.261E-17   3.034E-13  -6.810E-13  -5.589E-13  -3.497E-08
69 CO+O2=CO2+O
          1.600E+13  -3.022E-14  -2.487E-12  -4.104E-13  -1.377E-10  -4.547E-13   4.571E-10   1.043E-08   7.911E-09  -3.888E-05
70 H+O2=O+OH
          2.200E+14  -2.096E-07  -1.425E-06   1.708E-07  -8.020E-03  -2.086E-06  -1.132E-02   6.420E-02   3.732E-02   1.473E-02
71 H+H2O=H2+OH
          4.600E+08  -2.120E-16  -4.109E-14  -2.967E-12   2.082E-08   2.892E-12   2.246E-08   4.901E-11   3.974E-12   4.774E-08
72 H+HO2=2OH
          1.500E+14   1.091E-12   1.653E-12   3.383E-11  -2.358E-07  -3.252E-11  -3.376E-07   1.870E-07   1.011E-07  -6.891E-06
73 H+HO2=H2+O2
          2.500E+13   1.170E-12   8.448E-12   1.249E-11  -4.608E-08  -4.615E-13  -6.837E-08  -2.571E-07  -1.529E-07  -1.439E-06
74 O+HO2=OH+O2
          2.000E+13   5.385E-13   4.449E-12   2.866E-12  -3.079E-11   2.858E-12  -1.221E-10  -1.175E-07  -7.048E-08  -6.706E-07
75 OH+HO2=H2O+O2
          2.000E+13   2.732E-13   1.949E-12   1.362E-12  -6.347E-12   1.361E-12  -1.734E-10  -5.984E-08  -3.557E-08  -3.278E-07
76 O+HCL=OH+CL
          5.240E+12   1.612E-10  -2.990E-10  -1.791E-10  -3.954E-07  -5.225E-10   7.009E-08  -3.576E-05  -2.347E-05  -1.137E-04
77 OH+HCL=CL+H2O
          2.450E+12   7.534E-10  -1.043E-09  -6.799E-10  -2.405E-06   1.001E-09  -1.504E-04  -2.374E-04  -1.458E-04   1.128E-02
78 2CL+AR=CL2+AR
          2.340E+14   1.285E-14   8.290E-13   1.893E-13  -6.506E-13  -6.476E-13  -2.046E-12  -4.446E-09  -3.212E-09  -4.391E-09
79 CL+H2=HCL+H
          4.800E+13   6.163E-09   4.676E-08   5.517E-06  -3.895E-02  -5.434E-06  -3.857E-02  -1.906E-03  -1.123E-03  -4.595E-04
80 CL+HO2=HCL+O2
          1.300E+13  -6.806E-10  -3.284E-08  -7.706E-09   3.091E-08  -7.169E-09   3.263E-07   1.587E-04   1.198E-04   6.773E-04
81 CL+HO2=CLO+OH
          7.000E+12  -2.240E-12   5.095E-11   1.624E-11   3.496E-10  -4.512E-11   2.213E-08  -3.660E-07  -2.563E-07   2.515E-06
82 CLO+CO=CL+CO2
          2.700E+11   5.823E-18  -2.679E-16  -2.509E-17  -2.767E-14   2.027E-16  -1.150E-14   9.926E-13   7.340E-13  -7.631E-09
83 CH3+CLO=CH3CL+O
          6.000E+12  -4.083E-13  -9.500E-13  -2.567E-13   9.735E-12  -4.078E-13   4.092E-10   5.586E-09   4.047E-09  -1.311E-07
84 CH3+CLO=CH3O+CL
          9.000E+12  -3.934E-12  -8.479E-12  -2.299E-12   3.707E-11   7.382E-12   1.143E-10   4.734E-08   3.455E-08   8.009E-06
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     PROGRAM SID       Version 1.4
      Double PreCision


    Sensitivity analysis will be performed.
                WORKING SPACE REQUIREMENTS
                 PROVIDED        REQUIRED
Integer            40000           7500
Real              400000          60494


    Temperature is held Constant.


 Initial Conditions:

 PRESSURE (ATM)   =  1.0000E+00      TIM =   0.0000E+00
 Temperature (K) =  9.2300E+02
 Density (gm/CC) =  5.2734E-04

 Mole FraCtions:


 Time Integration:



T(SEC)= 0.0000E+00   P(ATM)= 1.0000E+00   T(K)= 9.2300E+02
 CH4         7.50E-03  CH3CCL3     5.00E-03  CH2CCL2     0.00E+00  C2H3CL      0.00E+00
 HCL         0.00E+00  C2H2        0.00E+00  C2H4        0.00E+00  C3H6        0.00E+00
 CO          0.00E+00  CH3         0.00E+00  H           0.00E+00  C2H6        0.00E+00
 CH3CCL2     0.00E+00  C2H5        0.00E+00  CCL3CH2     0.00E+00  CH3CHCL2    0.00E+00
 C3H7        0.00E+00  CH3CHCL     0.00E+00  CHCL2       0.00E+00  CH2CL       0.00E+00
 C2H5CL      0.00E+00  CL          0.00E+00  CL2         0.00E+00  CCL3        0.00E+00
 CH2CCL      0.00E+00  CHCL2CH2    0.00E+00  C2H3        0.00E+00  C2H         0.00E+00
 CH2CL2      0.00E+00  C*C*C       0.00E+00  C3H5        0.00E+00  C2HCL       0.00E+00
 CH          0.00E+00  CH2         0.00E+00  O           0.00E+00  H2          0.00E+00
 CH3CL       0.00E+00  H2O         0.00E+00  H2O2        0.00E+00  O2          3.75E-02
 OH          0.00E+00  HO2         0.00E+00  CHO         0.00E+00  CH2CO       0.00E+00
 CH3O        0.00E+00  C3H8        0.00E+00  CO2         0.00E+00  CH2O        0.00E+00
 AR          9.50E-01  CLO         0.00E+00
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T(SEC)= 1.0091E+00   P(ATM)= 1.0000E+00   T(K)= 9.2300E+02
 CH4         7.46E-03  CH3CCL3     6.56E-08  CH2CCL2     4.96E-03  CH2HCL      3.86E-06
 HCL         4.99E-03  C2H2        4.99E-09  C2H4        1.97E-06  C3H6        7.49E-10
 CO          2.19E-07  CH3         6.58E-08  H           2.74E-13  C2H6        7.60E-07
 CH3CCL2     6.67E-11  C2H5        1.35E-11  CCL3CH2     3.47E-07  CH3CHCL2    1.83E-10
 C3H7        8.28E-15  CH3CHCL     0.00E+00  CHCL2       0.00E+00  CH2CL       0.00E+00
 C2H5CL      0.00E+00  CL          2.75E-09  CL2         2.66E-12  CCL3        1.40E-10
 CH2CCL      6.45E-11  CHCL2CH2    3.86E-12  C2H3        1.37E-15  C2H         0.00E+00
 CH2CL2      0.00E+00  C*C*C       0.00E+00  C3H5        0.00E+00  C2HCL       1.28E-05
 CH          0.00E+00  CH2         9.26E-13  O           2.75E-12  H2          2.30E-07
 CH3CL       1.17E-07  H2O         1.06E-06  H2O2        2.86E-06  O2          3.73E-02
 OH          1.71E-12  HO2         5.49E-08  CHO         7.35E-13  CH2CO       0.00E+00
 CH3O        1.08E-11  C3H8        4.21E-10  CO2         9.17E-07  CH2O        7.55E-07
 AR          9.45E-01  CLO         8.52E-10
                    SENSITIVITY (KSPEC,IIRXN) KSPEC = 1, KK
RXN     A FACTOR         CH4          CH3CCL3      CH2CCL2      C2H3CL       HCL          C2H2         C2H4         C3H6         CO

  1 CH3CCL3=CH2CCL2+HCL
          2.250E+12   1.084E-03  -2.607E+00   9.457E-04  -1.232E+00  -6.572E-04  -1.302E+00  -1.028E+00  -1.496E+00  -8.335E-01
  2 CH3CCL3=CH3CCL2+CL
          1.000E+14  -1.119E-03   7.099E-01  -1.030E-03   1.249E+00   8.888E-04   1.375E+00   1.124E+00   1.651E+00   1.065E+00
  3 CH3CCL3=CH3+CCL3
          2.060E+14   8.433E-08  -1.449E-03   2.501E-07  -1.396E-04   5.067E-08  -8.635E-05  -1.168E-04  -4.495E-05  -9.577E-04
  4 CH2CCL2=C2HCL+HCL
          3.630E+13  -2.798E-07  -5.936E-04  -2.580E-03   2.638E-04   2.564E-03   1.267E-04   6.531E-04   5.412E-04   2.960E-03
  5 CH2CCL2=CH2CCL+CL
          6.690E+13  -2.111E-06   2.041E-04  -1.944E-06   2.474E-03   1.853E-06   1.945E-03   1.860E-03   2.986E-03   3.816E-04
  6 CH3CCL2=CH2CCL2+H
          2.600E+13  -9.492E-07  -4.855E-04   7.685E-07  -9.105E-04  -6.449E-07  -5.752E-04   1.231E-03   1.769E-03   8.547E-04
  7 CH3CCL2+H=CH3CHCL2
          5.930E+10   8.966E-10  -4.099E-07   6.550E-10  -9.234E-07  -6.709E-10  -1.216E-06  -9.507E-07  -1.390E-06  -8.310E-07
  8 CH3CCL2+H=C2H3CL+HCL
          4.690E+12   1.688E-09  -7.716E-07   1.233E-09  -1.504E-06  -1.323E-09  -1.762E-06  -1.791E-06  -2.618E-06  -1.562E-06
  9 CH2CCL2+H=CH2CCL+HCL
          1.200E+13   1.651E-07  -1.283E-04  -5.016E-07   6.519E-04   5.233E-07   8.493E-04  -1.695E-04  -2.521E-04  -4.081E-05
 10 CH2CCL2+H=CHCL2CH2
          9.720E+08   2.071E-09   1.753E-06   2.582E-10   1.927E-06   1.309E-09   1.586E-06  -2.653E-06  -3.852E-06  -2.249E-06
 11 CH2CCL2+H=C2H3CL+CL
          5.990E+13   1.382E-05  -5.790E-03  -4.329E-05   5.633E-02   4.422E-05   4.712E-02  -1.419E-02  -2.095E-02  -3.310E-03
 12 CH2CCL+H=C2H3+CL
          1.020E+14  -1.076E-09   3.082E-09  -7.309E-10   2.788E-07   1.233E-09   3.258E-04   7.032E-09   4.853E-07   5.149E-06
 13 CH2CCL+H=C2H2+HCL
          8.340E+11   1.293E-11  -1.257E-08   9.009E-12  -2.814E-08  -6.400E-12   8.794E-06  -2.033E-08  -2.887E-08   5.577E-08
 14 CH3CHCL2=C2H3CL+HCL
          1.980E+13  -2.866E-11  -4.112E-08  -1.810E-11   5.900E-05   4.631E-08   4.971E-05   3.054E-08   4.028E-08   3.046E-07
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15 C2H3CL=C2H2+HCL
         1.990E+13  -4.218E-07   5.131E-06  -3.655E-07  -8.533E-04   1.378E-06   8.411E-01   2.652E-04   4.683E-04   4.156E-03
16 C2H3CL=C2H3+CL
         1.160E+14  -4.012E-09   2.271E-07  -2.181E-09   8.393E-07   3.557E-09   1.235E-03   2.780E-06   5.137E-06   6.285E-06
17 CH3CL=CH3+CL
         1.270E+14   2.585E-05  -6.737E-03   1.591E-05  -1.974E-02  -3.354E-05  -2.329E-02  -3.602E-02  -5.337E-02  -3.058E-02
18 CH3CL+H=CH3+HCL
         7.000E+13  -2.489E-06   1.052E-05  -3.512E-06   4.514E-03  -1.869E-07   2.809E-03   2.662E-05   3.999E-05  -5.479E-05
19 C2H6=2CH3
         3.640E+16   2.223E-04  -2.603E-01   2.742E-04  -3.248E-01  -2.076E-04  -2.987E-01  -6.531E-02  -5.754E-01  -6.133E-01
20 C2H6+H=C2H5+H2
         6.610E+13  -2.448E-10  -3.357E-08   3.635E-10  -4.640E-07  -3.550E-10  -3.172E-07   2.997E-07   1.272E-06   9.546E-07
21 C2H6+CH3=C2H5+CH4
         3.160E+11  -3.242E-08  -2.581E-06  -4.110E-08   5.311E-05   4.151E-08   8.307E-05   1.596E-04   2.330E-04   1.223E-04
22 C2H6+CL=C2H5+HCL
         4.640E+13  -5.831E-05  -4.926E-03  -7.407E-05   9.575E-02   7.491E-05   1.554E-01   3.181E-01   4.340E-01   2.172E-01
23 C2H6+O=C2H5+OH
         2.510E+13  -1.573E-09  -1.102E-07  -1.904E-09   2.460E-06   1.920E-09   3.826E-06   6.841E-06   1.065E-05   5.370E-06
24 C2H6+OH=C2H5+H2O
         6.760E+13  -2.264E-08  -1.736E-06  -1.083E-08   1.411E-05   1.121E-08  -4.677E-05   9.333E-05   1.634E-04   4.993E-04
25 C2H5=C2H4+H
         5.010E+13   1.494E-05   9.407E-04  -3.055E-05   3.918E-02   3.009E-05   1.751E-02   1.446E-02   2.026E-02  -3.083E-02
26 C2H5+H=2CH3
         5.100E+14  -8.841E-07  -8.319E-06  -7.563E-07   9.733E-04   7.547E-07   9.940E-04   1.105E-03   1.501E-03   7.322E-04
27 C2H5+O2=C2H4+HO2
         2.000E+12  -2.343E-05  -1.570E-03   1.981E-05  -2.530E-02  -1.924E-05   5.340E-03   3.389E-02   4.232E-02   6.186E-02
28 C2H5+CH3=C3H8
         5.200E+12   1.403E-07  -2.024E-05   1.055E-07  -1.334E-04  -9.818E-08  -1.791E-04  -3.473E-04   4.013E-04  -2.133E-04
29 C2H5+CH3=C3H7+H
         7.170E+13  -3.573E-13  -4.252E-11  -1.571E-12   2.024E-09   1.553E-12   9.926E-10  -1.186E-09   5.283E-06  -7.864E-10
30 C2H4+O=CH3+CHO
         2.240E+13   2.752E-08  -3.765E-07  -2.820E-08   3.630E-05   2.823E-08  -7.576E-05  -1.649E-04  -1.163E-04   1.037E-03
31 C2H4+OH=CH3+CH2O
         1.000E+13  -1.352E-08   1.199E-07  -4.810E-09   6.163E-06   4.737E-09   2.220E-05   5.945E-05   3.092E-05  -3.364E-04
32 C2H4+OH=C2H3+H2O
         7.080E+13  -1.284E-07  -1.005E-06  -6.794E-08   8.740E-05   6.669E-08   1.565E-01  -4.579E-04  -2.524E-04   1.868E-03
33 C2H4+H=C2H3+H2
         6.920E+14  -1.978E-10  -3.019E-09   1.053E-10  -1.351E-07  -1.056E-10   2.647E-04  -7.705E-07  -4.016E-07   1.187E-06
34 C2H3+CH3=C3H6
         9.160E+12   2.276E-11  -9.490E-10   1.609E-11  -2.058E-08  -1.531E-11  -8.439E-06  -2.144E-08   7.037E-05  -6.795E-08
35 C2H3+O2=C2H2+HO2
         1.000E+12  -2.337E-11   1.038E-09  -1.651E-11   2.101E-08   1.580E-11   8.484E-06   2.110E-08  -6.899E-05   7.268E-08
36 C2H2+O=CH2+CO
         5.250E+13   4.329E-10  -1.087E-08   1.685E-10  -2.153E-07  -1.562E-10  -1.573E-04  -3.543E-07  -6.020E-07   2.654E-06
37 C2H2+O2=2CHO
         3.980E+12  -4.415E-07   5.472E-06  -3.850E-07   4.941E-04   3.739E-07  -1.892E-01   2.776E-04   4.860E-04   4.262E-03
38 C3H8+CH3=C3H7+CH4
         2.000E+12   8.766E-11  -7.420E-10  -3.173E-11   4.087E-08   3.191E-11   8.701E-08   4.156E-07   7.399E-04  -1.650E-08
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39 C3H8+HO2=C3H7+H2O2
        6.200E+12   6.290E-12   4.231E-11  -2.963E-13   3.758E-10   2.585E-13   1.682E-09   2.573E-08   4.263E-05  -1.392E-10
40 C3H7=C3H6+H
        1.260E+13  -4.486E-09   3.336E-08  -1.148E-08   1.475E-05   1.139E-08   3.584E-06  -2.012E-05   5.459E-02   1.037E-06
41 C3H7=CH3+C2H4
        1.000E+13  -5.176E-08  -3.109E-07  -1.641E-08   2.112E-05   1.648E-08   6.452E-06  -1.568E-04   3.956E-01  -1.781E-05
42 C3H7+O2=C3H6+HO2
        1.000E+12  -7.443E-08  -5.070E-07  -1.355E-08   1.746E-05   1.374E-08   6.262E-06  -2.190E-04   5.487E-01  -2.819E-05
43 CH3CCL3+CL=CCL3CH2+HCL
        2.510E+12  -1.551E-04  -8.004E-01   8.691E-05   8.076E-02   2.056E-04   9.329E-02   1.170E-01   1.030E-01   4.267E-01
44 CH3CCL2+CH4=CH3CHCL2+CH3
        1.580E+12   3.130E-09  -3.799E-06  -7.608E-09  -3.613E-05  -2.744E-08  -7.508E-05  -2.806E-06  -4.275E-06  -2.775E-06
45 CH2CCL+CH4=C2H3CL+CH3
        2.900E+11  -4.472E-09  -5.037E-05   6.939E-09   5.463E-06   3.249E-09  -2.347E-04   2.111E-05   2.726E-05   1.898E-06
46 CH4+AR=CH3+H+AR
        1.000E+17   5.851E-08  -2.795E-05   5.094E-08  -6.254E-05  -4.537E-08  -7.078E-05  -6.112E-05  -8.950E-05  -5.349E-05
47 CH4+O2=CH3+HO2
        7.940E+13   5.419E-05  -2.655E-03   2.576E-05  -3.283E-02  -2.423E-05  -3.739E-02  -3.835E-02  -5.931E-02  -3.334E-02
48 CH4+O=CH3+OH
        1.200E+07  -1.889E-07   7.710E-05   2.081E-07  -2.758E-04  -2.255E-07   1.926E-04   4.761E-04   6.086E-04  -1.626E-03
49 CH4+H=CH3+H2
        2.200E+04   1.194E-06  -7.257E-04   8.152E-06  -1.041E-02  -7.978E-06  -1.118E-02  -1.228E-03  -1.802E-03  -1.174E-03
50 CH4+OH=CH3+H2O
        1.600E+06   9.691E-08  -1.408E-04   1.070E-05  -1.374E-02  -1.061E-05  -6.461E-02   2.059E-04   3.940E-05   2.513E-01
51 CH4+CL=CH3+HCL
        2.570E+13   8.656E-08  -8.850E-03   1.426E-06  -8.950E-04   2.346E-07  -2.414E-04   1.258E-03   1.154E-03   3.104E-04
52 CH4+HO2=CH3+H2O2
        2.000E+13   1.000E-04   6.557E-03   9.564E-05  -1.236E-01  -9.695E-05  -1.181E-01   4.402E-02   6.504E-02  -2.745E-01
53 CH3+O2=CH3O+O
        7.260E+11  -1.461E-04   1.354E-02  -8.983E-05   1.140E-01   8.547E-05   1.106E-01   6.737E-02   1.035E-01   1.731E-01
54 CH3+O=CH2O+H
        7.000E+13   1.824E-07  -1.214E-04  -2.076E-07   2.798E-04   2.338E-07  -3.238E-05  -4.058E-04  -5.994E-04   9.700E-04
55 CH3+OH=CH2O+2H
        5.300E+12  -1.711E-08   2.527E-07  -4.454E-08   5.724E-05   4.427E-08   2.925E-05  -1.079E-06  -1.661E-06   1.082E-04
56 CH3+HO2=CH3O+OH
        2.000E+13  -2.757E-04  -9.923E-04  -2.182E-04   2.806E-01   2.174E-04   3.010E-01  -1.836E-02  -2.738E-02   3.187E-01
57 CH3O+O2=CH2O+HO2
        1.000E+13  -8.598E-09   1.219E-06  -1.110E-08   1.414E-05   1.086E-08   7.793E-06   2.245E-07  -5.918E-07   3.568E-05
58 CH2O+CH3=CH4+CHO
        1.000E+10  -2.184E-07  -9.945E-06  -7.257E-07   9.340E-04   7.255E-07   1.282E-04  -1.232E-04  -1.917E-04   5.889E-03
59 CH2O+H=CHO+H2
        2.500E+13  -3.322E-10  -3.548E-08   7.627E-10  -9.766E-07  -7.490E-10  -7.894E-07  -1.898E-07  -2.903E-07   6.431E-06
60 CH2O+O=CHO+OH
        3.500E+13  -4.330E-09  -1.893E-07  -1.367E-08   1.760E-05   1.367E-08   3.002E-06  -2.032E-06  -3.305E-06   1.084E-04
61 CH2O+OH=CHO+H2O
        3.000E+13  -1.635E-08  -7.677E-07  -3.150E-08   4.058E-05   3.163E-08  -8.917E-05  -8.436E-06  -1.302E-05   7.254E-04
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62 CH2O+HO2=CHO+H2O2
           1.000E+12   1.354E-08   3.448E-08  -2.941E-07   3.780E-04   2.925E-07  -2.300E-04  -4.688E-06  -1.218E-05   5.899E-03
63 CH2O+CL=CHO+HCL
           5.000E+13  -2.942E-05  -1.337E-03  -9.873E-05   1.271E-01   9.872E-05   1.572E-02  -1.700E-02  -2.624E-02   8.136E-01
64 CHO+O2=CO+HO2
           3.000E+12  -4.590E-09   1.845E-08  -7.098E-09   9.122E-06   6.914E-09   2.901E-06   1.129E-06   1.866E-06   4.643E-05
65 CHO+HO2=CH2O+O2
           5.000E+13  -6.756E-06   1.212E-04  -4.166E-06   5.341E-03   4.000E-06   4.216E-03   4.432E-03   7.571E-03   1.346E-02
66 CO+OH=CO2+H
           1.510E+13  -1.324E-07   1.198E-05  -2.407E-05   3.094E-02   2.392E-05  -9.754E-03   2.576E-04   2.503E-04  -5.765E-01
67 CO+HO2=CO2+OH
           1.510E+14   8.935E-10   1.089E-08   9.585E-10  -1.234E-06  -9.666E-10   6.650E-06   5.273E-07   9.240E-07  -1.271E-04
68 CO+O2=CO2+O
           1.600E+13  -5.630E-08   7.647E-07  -2.365E-08   3.028E-05   2.206E-08   6.828E-05   4.647E-05   8.311E-05  -6.808E-04
69 H+O2=O+OH
           2.200E+14  -1.627E-05   6.825E-03   8.080E-07  -1.767E-03  -2.129E-06   2.077E-03   1.677E-02   2.473E-02   5.327E-03
70 H+H2O=H2+OH
           4.600E+08  -2.170E-11   8.223E-09  -2.295E-09   2.951E-06   2.281E-09   2.496E-08   3.169E-08   3.789E-08   9.562E-06
71 O2+AR=AR+2O
           1.850E+11   1.378E-12  -4.731E-10   5.504E-13  -6.575E-10  -4.559E-13  -9.103E-10  -1.452E-09  -2.118E-09  -1.139E-09
72 H+HO2=2OH
           1.500E+14   5.179E-09   3.100E-07   1.160E-08  -1.495E-05  -1.162E-08  -2.893E-06   1.981E-06   2.981E-06  -7.053E-05
73 H+HO2=H2+O2
           2.500E+13   4.399E-09  -9.578E-07   3.922E-09  -4.941E-06  -3.682E-09  -4.431E-06  -2.768E-06  -4.258E-06  -4.773E-06
74 O+HO2=OH+O2
           2.000E+13   3.309E-08  -2.137E-06   1.607E-08  -2.042E-05  -1.505E-08  -2.265E-05  -2.308E-05  -3.590E-05  -2.121E-05
75 OH+HO2=H2O+O2
           2.000E+13   4.114E-08  -2.307E-06   2.223E-08  -2.833E-05  -2.103E-08  -4.391E-05  -2.884E-05  -4.328E-05   2.231E-05
76 O+HCL=OH+CL
           5.240E+12  -5.053E-08   4.133E-05   2.760E-08  -3.988E-05  -3.569E-08   8.884E-05   1.169E-04   1.412E-04  -4.676E-04
77 OH+HCL=CL+H2O
           2.450E+12   1.019E-07   1.327E-04   1.352E-05  -1.740E-02  -1.347E-05  -8.174E-02   2.997E-04   1.415E-04   3.205E-01
78 2CL+AR=CL2+AR
           2.340E+14   1.062E-09  -1.494E-07   4.316E-10  -5.390E-07  -1.447E-09  -6.334E-07  -9.752E-07  -1.446E-06  -8.232E-07
79 CL+H2=HCL+H
           4.800E+13   7.056E-07  -2.848E-04   2.840E-05  -3.650E-02  -2.820E-05  -3.436E-02  -7.316E-04  -1.075E-03  -7.004E-04
80 CL+HO2=HCL+O2
           1.300E+13   1.614E-05  -6.958E-04   7.634E-06  -9.738E-03  -7.190E-06  -1.114E-02  -1.147E-02  -1.775E-02  -9.590E-03
81 CL+HO2=CLO+OH
           7.000E+12  -6.225E-07  -3.102E-05  -5.017E-07   6.481E-04   1.998E-07   1.070E-03  -1.556E-04  -2.069E-04  -2.028E-03
82 CLO+CO=CL+CO2
           2.700E+11   1.193E-09   1.585E-08   2.157E-09  -2.774E-06  -2.194E-10   1.819E-06   1.614E-06   2.842E-06  -7.591E-05
83 CH3+CLO=CH3CL+O
           6.000E+12   1.924E-10   3.070E-06   1.847E-08  -2.407E-05  -1.221E-07   9.611E-05   3.331E-05   4.967E-05  -1.166E-03
84 CH3+CLO=CH3O+CL
           9.000E+12  -4.124E-07   1.367E-05  -2.714E-07   3.474E-04   5.251E-07   1.250E-04   9.085E-05   1.193E-04   2.646E-03
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T(SEC)= 1.0091E+00   P(ATM)= 1.0000E+00   T(K)= 9.2300E+02
 CH3CCL3     6.56E-08  CH3CL       1.17E-07  CH2CCL2     4.96E-03  CH2O        7.55E-07
 H2O         1.06E-06  H2O2        2.86E-06  C3H8        4.21E-10  O2          3.73E-02
 CO2         9.17E-07  CH4         7.46E-03  CH3         6.58E-08  H           2.74E-13
 C2H6        7.60E-07  CH3CCL2     6.67E-11  C2H5        1.35E-11  CCL3CH2     3.47E-07
 CH3CHCL2    1.83E-10  C3H7        8.28E-15  CH3CHCL     0.00E+00  CHCL2       0.00E+00
 CH2CL       0.00E+00  C2H5CL      0.00E+00  CL          2.75E-09  CL2         2.66E-12
 CCL3        1.40E-10  CH2CCL      6.45E-11  CHCL2CH2    3.86E-12  C2H3        1.37E-15
 C2H         0.00E+00  CH2CL2      0.00E+00  C2H2        4.99E-09  C*C*C       0.00E+00
 C3H5        0.00E+00  C2HCL       1.28E-05  CH          0.00E+00  CH2         9.26E-13
 O           2.75E-12  H2          2.30E-07  HCL         4.99E-03  C3H6        7.49E-10
 C2H4        1.97E-06  OH          1.71E-12  HO2         5.49E-08  CHO         7.35E-13
 CH2CO       0.00E+00  CH3O        1.08E-11  CO          2.19E-07  C2H3CL      3.86E-06
 AR          9.45E-01  CLO         8.52E-10
                   SENSITIVITY (KSPEC,IIRXN) KSPEC = 1, KK
RXN     A FACTOR          CH3CCL3     CH3CL       CH2CCL2     CH2O        H2O         H2O2        C3H8        O2          CO2

  1 CH3CCL3=CH2CCL2+HCL
           2.250E+12  -2.607E+00  -7.365E-01   9.457E-04  -1.492E+00  -1.327E+00  -1.228E+00  -1.471E+00   1.832E-04  -2.040E+00
  2 CH3CCL3=CH3CCL2+CL
           1.000E+14   7.099E-01   7.486E-01  -1.030E-03   1.419E+00   1.317E+00   1.315E+00   1.590E+00  -1.904E-04   2.081E+00
  3 CH3CCL3=CH3+CCL3
           2.060E+14  -1.449E-03  -7.788E-04   2.482E-07  -9.824E-05  -2.732E-04  -3.142E-04  -6.485E-04   4.543E-08  -5.722E-04
  4 CH2CCL2=C2HCL+HCL
           3.630E+13  -5.934E-04   1.041E-03  -2.580E-03  -4.432E-04   3.189E-04   9.050E-04   7.054E-04  -1.074E-07   1.148E-03
  5 CH2CCL2=CH2CCL+CL
           6.690E+13   2.041E-04   1.823E-03  -1.945E-06   3.180E-03   2.364E-03   2.266E-03   2.618E-03  -3.548E-07   4.289E-03
  6 CH3CCL2=CH2CCL2+H
           2.600E+13  -4.855E-04  -7.953E-04   7.720E-07   8.848E-04   5.618E-03   1.121E-03   1.170E-03  -2.089E-07   1.232E-03
  7 CH3CCL2+H=CH3CHCL2
           5.930E+10  -4.094E-07  -3.596E-07   6.539E-10  -1.081E-06  -1.418E-06  -1.048E-06  -1.243E-06   1.539E-10  -1.561E-06
  8 CH3CCL2+H=C2H3CL+HCL
           4.690E+12  -7.723E-07  -6.774E-07   1.234E-09  -2.038E-06  -2.673E-06  -1.976E-06  -2.343E-06   2.901E-10  -2.942E-06
  9 CH2CCL2+H=CH2CCL+HCL
           1.200E+13  -1.283E-04  -9.764E-05  -4.995E-07  -2.083E-04  -9.770E-04  -1.915E-04  -2.256E-04   3.922E-08  -3.269E-04
 10 CH2CCL2+H=CHCL2CH2
           9.720E+08   1.753E-06   1.697E-06  -1.829E-10  -1.910E-06  -1.199E-05  -2.549E-06  -2.660E-06   4.671E-10  -2.958E-06
 11 CH2CCL2+H=C2H3CL+CL
           5.990E+13  -5.789E-03  -6.816E-03  -4.329E-05  -1.729E-02  -8.258E-02  -1.605E-02  -1.902E-02   3.282E-06  -2.693E-02
 12 CH2CCL+H=C2H3+CL
           1.020E+14   2.544E-09   1.360E-07  -7.304E-10   3.130E-06   1.459E-06   3.157E-06   1.913E-08  -4.820E-10   6.813E-06
 13 CH2CCL+H=C2H2+HCL
           8.340E+11  -1.257E-08  -5.689E-09   9.013E-12   9.715E-10  -3.846E-08   1.983E-09  -2.660E-08  -5.780E-13   3.181E-08
 14 CH3CHCL2=C2H3CL+HCL
           1.980E+13  -4.107E-08   4.844E-08  -2.098E-11   4.460E-08   4.119E-09   7.657E-08   3.814E-08  -1.072E-11   1.306E-07
 15 C2H3CL=C2H2+HCL
           1.990E+13   5.121E-06   2.763E-04  -3.655E-07   1.079E-03  -7.195E-05   1.021E-03   3.434E-04  -1.535E-07   2.003E-03
 16 C2H3CL=C2H3+CL
           1.160E+14   2.270E-07   2.795E-06  -2.181E-09   8.628E-06   4.997E-06   7.701E-06   3.811E-06  -1.074E-09   1.145E-05
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17 CH3CL=CH3+CL
          1.270E+14  -6.737E-03   8.042E-01   1.591E-05  -5.461E-02  -4.557E-02  -4.438E-02  -5.372E-02   6.659E-06  -7.614E-02
18 CH3CL+H=CH3+HCL
          7.000E+13   1.054E-05   1.568E-01  -3.512E-06   3.729E-05   1.334E-04   3.657E-05   3.760E-05  -7.223E-09   8.938E-05
19 C2H6=2CH3
          3.640E+16  -2.603E-01  -9.088E-01   2.742E-04  -8.363E-01  -7.289E-01  -4.856E-01  -5.649E-01   9.361E-05  -1.396E+00
20 C2H6+H=C2H5+H2
          6.610E+13  -3.365E-08  -5.764E-08   3.635E-10   7.045E-07   6.622E-07   7.136E-07   1.173E-06  -1.168E-10   1.706E-06
21 C2H6+CH3=C2H5+CH4
          3.160E+11  -2.581E-06  -1.023E-05  -4.110E-08   1.390E-04   1.252E-04   1.521E-04   1.925E-04  -2.006E-08   1.899E-04
22 C2H6+CL=C2H5+HCL
          4.640E+13  -4.926E-03  -2.046E-02  -7.407E-05   2.630E-01   2.336E-01   2.888E-01   3.603E-01  -3.730E-05   3.333E-01
23 C2H6+O=C2H5+OH
          2.510E+13  -1.101E-07  -4.014E-07  -1.904E-09   6.251E-06   6.006E-06   6.790E-06   8.923E-06  -9.174E-10   9.125E-06
24 C2H6+OH=C2H5+H2O
          6.760E+13  -1.736E-06  -7.102E-06  -1.083E-08   9.158E-05   1.693E-04   9.622E-05   1.284E-04  -1.315E-08   3.586E-05
25 C2H5=C2H4+H
          5.010E+13   9.407E-04   6.407E-03  -3.055E-05  -8.204E-02  -6.384E-02  -9.559E-02  -1.187E-01   1.138E-05  -8.482E-02
26 C2H5+H=2CH3
          5.100E+14  -8.320E-06  -5.943E-05  -7.563E-07   9.642E-04   8.724E-04   1.060E-03   1.432E-03  -1.406E-07   1.368E-03
27 C2H5+O2=C2H4+HO2
          2.000E+12  -1.571E-03  -9.261E-03   1.981E-05   1.211E-01   9.823E-02   1.385E-01  -8.273E-01  -1.687E-05   1.325E-01
28 C2H5+CH3=C3H8
          5.200E+12  -2.024E-05  -1.355E-04   1.055E-07  -3.787E-04  -3.160E-04  -3.505E-04   9.992E-01   4.841E-08  -4.870E-04
29 C2H5+CH3=C3H7+H
          7.170E+13  -1.139E-11   6.840E-10  -1.627E-12  -9.519E-10  -7.544E-10  -1.442E-09  -2.789E-09   1.536E-13  -8.369E-10
30 C2H4+O=CH3+CHO
          2.240E+13  -3.769E-07  -6.213E-06  -2.820E-08   9.621E-05  -3.006E-04   1.200E-04  -9.795E-06  -1.321E-08   1.651E-04
31 C2H4+OH=CH3+CH2O
          1.000E+13   1.202E-07   8.147E-07  -4.810E-09  -1.130E-04   6.728E-05  -1.536E-05   1.255E-06   1.720E-09   2.726E-05
32 C2H4+OH=C2H3+H2O
          7.080E+13  -1.008E-06   3.171E-05  -6.794E-08   5.193E-04   4.324E-04   5.713E-04   2.923E-05  -7.137E-08   3.809E-04
33 C2H4+H=C2H3+H2
          6.920E+14  -3.023E-09   4.204E-08   1.054E-10   8.126E-07   3.253E-07   9.172E-07   3.788E-08  -1.138E-10   1.009E-06
34 C2H3+CH3=C3H6
          9.160E+12  -8.712E-10  -2.075E-08   1.579E-11  -6.336E-08  -3.928E-08  -5.787E-08  -2.986E-08   8.008E-12  -8.311E-08
35 C2H3+O2=C2H2+HO2
          1.000E+12   9.849E-10   2.100E-08  -1.647E-11   6.486E-08   3.995E-08   5.933E-08   3.043E-08  -8.696E-12   8.684E-08
36 C2H2+O=CH2+CO
          5.250E+13  -1.089E-08  -3.639E-07   1.687E-10  -7.480E-07  -1.450E-06  -5.403E-07  -4.802E-07   8.491E-11  -8.367E-07
37 C2H2+O2=2CHO
          3.980E+12   5.471E-06   2.888E-04  -3.850E-07   1.129E-03  -8.069E-05   1.069E-03   3.610E-04  -1.604E-07   2.109E-03
38 C3H8+CH3=C3H7+CH4
          2.000E+12  -7.835E-10  -1.120E-08  -3.185E-11   1.597E-07   1.109E-07   1.971E-07  -3.318E-03  -2.186E-11   1.324E-07
39 C3H8+HO2=C3H7+H2O2
          6.200E+12   3.672E-11   3.246E-10   2.700E-13  -6.350E-09  -4.105E-09   7.785E-09  -1.912E-04  -4.786E-13  -4.844E-09
40 C3H7=C3H6+H
          1.260E+13   3.338E-08   6.179E-07  -1.148E-08  -7.444E-06  -4.699E-06  -9.303E-06  -8.329E-06   1.010E-09  -5.716E-06
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41 C3H7=CH3+C2H4
          1.000E+13  -3.108E-07  -5.633E-06  -1.641E-08   8.300E-05   5.613E-05   1.038E-04   9.313E-05  -1.138E-08   6.705E-05
42 C3H7+O2=C3H6+HO2
          1.000E+12  -5.069E-07  -9.206E-06  -1.354E-08   1.340E-04   9.030E-05   1.675E-04  -1.074E-04  -1.837E-08   1.080E-04
43 CH3CCL3+CL=CCL3CH2+HCL
          2.510E+12  -8.004E-01   2.556E-01   8.690E-05   2.249E-01   2.498E-01   1.934E-01   2.911E-01  -2.951E-05   3.174E-01
44 CH3CCL2+CH4=CH3CHCL2+CH3
          1.580E+12  -3.801E-06  -3.459E-06  -7.590E-09  -4.479E-06  -1.905E-05  -3.725E-06  -4.394E-06   7.845E-10  -6.763E-06
45 CH2CCL+CH4=C2H3CL+CH3
          2.900E+11  -5.038E-05  -6.675E-05   5.826E-09  -1.441E-05  -8.985E-06   2.899E-06   1.455E-06   7.974E-10  -2.875E-05
46 CH4+AR=CH3+H+AR
          1.000E+17  -2.795E-05  -2.779E-05   5.094E-08  -7.183E-05  -7.174E-05  -6.830E-05  -8.148E-05   9.793E-09  -1.035E-04
47 CH4+O2=CH3+HO2
          7.940E+13  -2.655E-03  -3.792E-02   2.576E-05  -1.114E-01  -8.687E-02  -1.006E-01  -5.552E-02   1.367E-05  -1.335E-01
48 CH4+O=CH3+OH
          1.200E+07   7.710E-05   2.240E-04   2.081E-07  -5.291E-05   1.640E-03  -3.159E-05   5.061E-04  -5.078E-09  -4.340E-04
49 CH4+H=CH3+H2
          2.200E+04  -7.257E-04  -5.996E-04   8.152E-06  -1.492E-03  -7.275E-03  -1.407E-03  -1.646E-03   2.857E-07  -2.171E-03
50 CH4+OH=CH3+H2O
          1.600E+06  -1.408E-04  -2.464E-04   1.070E-05  -4.231E-04   5.182E-02  -4.751E-04  -1.603E-04   6.568E-08  -6.101E-02
51 CH4+CL=CH3+HCL
          2.570E+13  -8.850E-03  -7.720E-03   1.426E-06  -1.991E-03  -1.400E-03  -3.824E-04  -5.479E-04   1.757E-07  -4.121E-03
52 CH4+HO2=CH3+H2O2
          2.000E+13   6.557E-03   3.699E-02   9.564E-05  -5.014E-01  -4.170E-01  -1.325E-01   6.550E-02   3.663E-05  -5.656E-01
53 CH3+O2=CH3O+O
          7.260E+11   1.354E-02   6.324E-02  -8.982E-05   3.687E-01   2.989E-01   2.646E-01   9.772E-02  -4.121E-05   4.851E-01
54 CH3+O=CH2O+H
          7.000E+13  -1.214E-04  -2.977E-04  -2.075E-07   1.013E-04  -1.627E-03  -6.890E-05  -5.825E-04   1.809E-08   2.785E-04
55 CH3+OH=CH2O+2H
          5.300E+12   2.526E-07  -9.264E-07  -4.454E-08   5.092E-05  -9.304E-05   3.032E-05  -1.793E-06  -3.777E-09   7.745E-05
56 CH3+HO2=CH3O+OH
          2.000E+13  -9.929E-04  -1.554E-02  -2.182E-04   1.221E+00   9.401E-01   3.950E-01  -2.637E-02  -8.858E-05   1.257E+00
57 CH3O+O2=CH2O+HO2
          1.000E+13   1.219E-06  -9.067E-07  -1.110E-08   1.399E-05   7.663E-06   2.457E-05   7.352E-07  -3.657E-09   6.303E-05
58 CH2O+CH3=CH4+CHO
          1.000E+10  -9.951E-06  -1.101E-04  -7.257E-07  -3.832E-03  -1.481E-03   1.593E-03  -1.811E-04  -1.851E-07   4.205E-03
59 CH2O+H=CHO+H2
          2.500E+13  -3.553E-08  -1.512E-07   7.629E-10  -3.809E-06  -1.408E-06   1.902E-06  -2.689E-07  -2.389E-10   5.305E-06
60 CH2O+O=CHO+OH
          3.500E+13  -1.894E-07  -1.924E-06  -1.367E-08  -7.164E-05  -2.672E-05   3.002E-05  -3.203E-06  -3.512E-09   7.961E-05
61 CH2O+OH=CHO+H2O
          3.000E+13  -7.681E-07  -7.810E-06  -3.150E-08  -2.157E-04  -1.499E-06   1.002E-04  -1.335E-05  -1.222E-08   1.840E-04
62 CH2O+HO2=CHO+H2O2
          1.000E+12   3.078E-08  -6.292E-06  -2.941E-07  -3.844E-03  -1.504E-03   9.804E-04  -7.458E-06  -7.348E-08   1.689E-03
63 CH2O+CL=CHO+HCL
          5.000E+13  -1.337E-03  -1.549E-02  -9.873E-05  -5.287E-01  -2.042E-01   2.177E-01  -2.483E-02  -2.518E-05   5.723E-01
64 CHO+O2=CO+HO2
          3.000E+12   1.846E-08   1.231E-06  -7.097E-09  -2.373E-05  -7.713E-06   1.778E-05   1.530E-06  -2.160E-09   4.028E-05
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65 CHO+HO2=CH2O+O2
              5.000E+13   1.212E-04   4.580E-03  -4.166E-06   5.228E-03   6.635E-03   1.459E-02   5.915E-03  -1.901E-06   2.230E-02
66 CO+OH=CO2+H
              1.510E+13   1.208E-05   1.585E-04  -2.407E-05   6.087E-05  -1.177E-01   6.450E-05   1.746E-04  -2.088E-08   1.377E-01
67 CO+HO2=CO2+OH
              1.510E+14   1.095E-08   5.383E-07   9.585E-10  -7.840E-06   2.364E-05  -1.051E-05   7.586E-07   2.954E-10   2.648E-05
68 CO+O2=CO2+O
              1.600E+13   7.648E-07   4.858E-05  -2.365E-08   9.144E-05   1.933E-04   5.569E-05   6.041E-05  -1.310E-08   2.748E-04
69 H+O2=O+OH
              2.200E+14   6.825E-03   7.742E-03   8.084E-07   2.029E-02   9.668E-02   1.897E-02   2.234E-02  -3.858E-06   3.143E-02
70 H+H2O=H2+OH
              4.600E+08   8.207E-09   2.306E-08  -2.295E-09   1.887E-08   2.105E-06   1.709E-08   3.061E-08  -4.315E-12  -2.248E-06
71 O2+AR=2O+AR
              1.850E+11  -4.730E-10  -5.392E-10   5.515E-13  -1.672E-09  -4.855E-09  -1.616E-09  -1.906E-09   2.682E-13  -2.469E-09
72 H+HO2=2OH
              1.500E+14   3.101E-07   1.415E-06   1.160E-08  -2.134E-05   5.475E-05  -2.375E-05   2.912E-06   1.939E-09  -1.809E-05
73 H+HO2=H2+O2
              2.500E+13  -9.578E-07  -2.403E-06   3.922E-09  -8.924E-06  -7.508E-06  -8.388E-06  -3.916E-06   1.183E-09  -1.275E-05
74 O+HO2=OH+O2
              2.000E+13  -2.137E-06  -2.269E-05   1.607E-08  -6.812E-05  -5.269E-05  -6.166E-05  -3.334E-05   8.405E-09  -8.309E-05
75 OH+HO2=H2O+O2
              2.000E+13  -2.307E-06  -2.821E-05   2.223E-08  -8.386E-05  -5.558E-05  -7.721E-05  -4.279E-05   1.050E-08  -1.167E-04
76 O+HCL=OH+CL
              5.240E+12   4.133E-05   9.742E-05   2.760E-08  -9.980E-06   3.697E-04   8.945E-06   1.162E-04  -4.191E-09  -1.445E-05
77 OH+HCL=CL+H2O
              2.450E+12   1.326E-04   1.028E-04   1.352E-05  -5.336E-04   6.607E-02  -4.535E-04  -1.043E-04   6.065E-08  -7.735E-02
78 2CL+AR=CL2+AR
              2.340E+14  -1.494E-07  -9.189E-07   4.316E-10  -1.496E-06  -1.245E-06  -1.206E-06  -1.460E-06   1.815E-10  -2.081E-06
79 CL+H2=HCL+H
              4.800E+13  -2.850E-04  -3.524E-04   2.840E-05  -8.811E-04  -4.136E-03  -8.598E-04  -9.730E-04   1.709E-07  -1.369E-03
80 CL+HO2=HCL+O2
              1.300E+13  -6.958E-04  -1.138E-02   7.634E-06  -3.319E-02  -2.581E-02  -2.995E-02  -1.659E-02   4.064E-06  -3.957E-02
81 CL+HO2=CLO+OH
              7.000E+12  -3.102E-05   5.674E-03  -5.017E-07   3.177E-03   3.968E-03   1.743E-04  -2.421E-04  -1.816E-07   2.964E-03
82 CLO+CO=CL+CO2
              2.700E+11   1.587E-08  -1.465E-05   2.157E-09  -1.530E-05   8.514E-06  -5.338E-06   2.116E-06   4.412E-10   1.381E-05
83 CH3+CLO=CH3CL+O
              6.000E+12   3.071E-06   5.277E-03   1.847E-08  -5.417E-04   4.207E-04  -2.701E-04   5.217E-05   2.853E-08  -1.239E-04
84 CH3+CLO=CH3O+CL
              9.000E+12   1.367E-05  -4.263E-03  -2.714E-07   1.605E-03  -3.344E-05   1.120E-03   1.440E-04  -1.372E-07   1.499E-03
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APPENDIX II

B. MECHINFO ANALYSIS

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RXN1

P= 1.00ATM     KEQ IN MOLE CC UNITS

REACTION # 1     CH3CCL3=CH2CCL2+HCL
DELTA N =   1   DELTA H(T =   300. K)=  9.446E+03 CAL/MOLE     DELTA S (T =   300. K) =  3.527E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.694E+02     DELTA H= 0.123E+06
        T          EF-EREV         LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        0.773E+04        0.550E+01      0.782010E-02     0.74E-08          0.55E-02       0.58E-02
      800.        0.737E+04        0.526E+01      0.630443E-20     0.45E-03          0.37E+00       0.20E+00
      900.        0.699E+04        0.503E+01      0.737422E+08     0.24E+01          0.97E+01       0.31E+01
     1000.        0.660E+04        0.483E+01      0.518625E+10     0.22E+04          0.13E+03       0.29E+02
     1100.        0.619E+04        0.463E+01      0.479864E+10     0.61E+06          0.11E+04       0.19E+03
     1200.        0.578E+04        0.445E+01      0.763138E+01     0.65E+08          0.67E+04       0.88E+03

REACTION # 2     CH3CCL3=CH3CCL2+CL
DELTA N =   1   DELTA H(T =   300. K)=  7.027E+04 CAL/MOLE     DELTA S (T =   300. K) =  3.448E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.503E+01     DELTA H= 0.684E+05
        T          EF-EREV         LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        0.688E+05        0.533E+01      0.667521E-19     0.68E-19          0.90E-07       0.14E+13
      800.        0.686E+05        0.518E+01      0.321238E-16     0.32E-16          0.39E-04       0.12E+13
      900.        0.684E+05        0.504E+01      0.385717E-14     0.38E-14          0.43E-02       0.11E+13
     1000.        0.681E+05        0.492E+01      0.175535E-12     0.17E-12          0.19E+00       0.11E+13
     1100.        0.679E+05        0.482E+01      0.394942E-11     0.40E-11          0.41E+01       0.10E+13
     1200.        0.677E+05        0.472E+01      0.524365E-10     0.54E-10          0.53E+02       0.10E+13

REACTION # 3     CH3CCL3=CH3+CCL3
DELTA N =   1   DELTA H(T =   300. K)=  8.498E+04 CAL/MOLE     DELTA S (T =   300. K) =  3.878E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.714E+01     DELTA H= 0.828E+05
        T          EF-EREV         LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        0.836E+05        0.767E+01      0.166632E-22     0.17E-22          0.17E-09       0.10E+14
      800.        0.832E+05        0.742E+01      0.301435E-19     0.30E-19          0.18E-06       0.59E+13
      900.        0.828E+05        0.718E+01      0.100217E-16     0.97E-17          0.39E-04       0.39E+13
     1000.        0.824E+05        0.695E+01      0.101873E-14     0.99E-15          0.29E-02       0.28E+13
     1100.        0.819E+05        0.673E+01      0.437861E-13     0.44E-13          0.99E-01       0.23E+13
     1200.        0.815E+05        0.652E+01      0.987827E-12     0.10E-11          0.19E+01       0.19E+13

REACTION # 4     CH2CCL2=C2HCL+HCL
DELTA N =   1   DELTA H(T =   300. K)=  2.421E+04 CAL/MOLE     DELTA S (T =   300. K) =  3.350E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.545E+01     DELTA H= 0.230E+05
        T          EF-EREV         LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        0.235E+05        0.580E+01      0.147774E-04     0.15E-04          0.20E-07       0.13E-02
      800.        0.233E+05        0.564E+01      0.121443E-03     0.12E-03          0.90E-05       0.74E-01
      900.        0.230E+05        0.549E+01      0.614237E-03     0.60E-03          0.11E-02       0.17E+01
     1000.        0.227E+05        0.533E+01      0.221118E-02     0.22E-02          0.47E-01       0.21E+02
     1100.        0.224E+05        0.518E+01      0.621851E-02     0.62E-02          0.11E+01       0.17E+03
     1200.        0.221E+05        0.504E+01      0.145415E-01     0.15E-01          0.14E+02       0.99E+03
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REACTION #  5     CH2CCL2=CH2CCL+CL
DELTA N =   1   DELTA H(T =  300. K)=  8.864E+04 CAL/MOLE     DELTA S (T =  300. K) =  3.470E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.600E+01     DELTA H= 0.878E+05
         T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.877E+05        0.599E+01      0.159039E-24     0.16E-24          0.57E-12       0.36E+13
      800.        0.877E+05        0.597E+01      0.423012E-21     0.42E-21          0.10E-08       0.24E+13
      900.        0.877E+05        0.598E+01      0.194914E-18     0.20E-18          0.35E-06       0.18E+13
     1000.        0.877E+05        0.600E+01      0.263697E-16     0.26E-16          0.38E-04       0.14E+13
     1100.        0.878E+05        0.603E+01      0.146507E-14     0.15E-14          0.17E-02       0.12E+13
     1200.        0.879E+05        0.607E+01      0.418006E-13     0.42E-13          0.41E-01       0.99E+12

REACTION #  6     CH3CCL2=CH2CCL2+H
DELTA N =   1   DELTA H(T =  300. K)=  4.221E+04 CAL/MOLE     DELTA S (T =  300. K) =  2.302E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.750E+00     DELTA H= 0.418E+05
         T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.419E+05        0.817E+00      0.187532E-12     0.19E-12          0.31E+01       0.16E+14
      800.        0.419E+05        0.800E+00      0.809495E-11     0.81E-11          0.13E+03       0.16E+14
      900.        0.418E+05        0.766E+00      0.150913E-09     0.15E-09          0.23E+04       0.15E+14
     1000.        0.417E+05        0.720E+00      0.156088E-08     0.16E-08          0.23E+05       0.15E+14
     1100.        0.416E+05        0.665E+00      0.105084E-07     0.11E-07          0.15E+06       0.15E+14
     1200.        0.415E+05        0.606E+00      0.512410E-07     0.52E-07          0.75E+06       0.15E+14

REACTION #  7     CH3CCL2+H=CH3CHCL2
DELTA N =  -1   DELTA H(T =  300. K)= -9.316E+04 CAL/MOLE     DELTA S (T =  300. K) = -2.808E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.355E+01     DELTA H=-0.931E+05
         T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.930E+05       -0.353E+01      0.326864E+28     0.33E+28          0.14E+14       0.41E-14
      800.       -0.930E+05       -0.355E+01      0.762706E+24     0.76E+24          0.69E+13       0.90E-11
      900.       -0.930E+05       -0.356E+01      0.113980E+22     0.11E+22          0.40E+13       0.35E-08
     1000.       -0.930E+05       -0.355E+01      0.625855E+19     0.63E+19          0.26E+13       0.42E-06
     1100.       -0.930E+05       -0.353E+01      0.886421E+17     0.89E+17          0.19E+13       0.21E-04
     1200.       -0.929E+05       -0.350E+01      0.255761E+16     0.26E+16          0.14E+13       0.55E-03

REACTION #  8     CH3CCL2+H=C2H3CL+HCL
DELTA N =   0   DELTA H(T =  300. K)= -7.624E+04 CAL/MOLE     DELTA S (T =  300. K) =  6.749E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.163E+01     DELTA H=-0.782E+05
         T          EF-EREV         LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.775E+05        0.208E+01      0.127701E+26     0.13E+26          0.77E+13       0.61E-12
      800.       -0.778E+05        0.186E+01      0.118793E+23     0.12E+23          0.73E+13       0.61E-09
      900.       -0.781E+05        0.166E+01      0.509343E+20     0.49E+20          0.69E+13       0.14E-06
     1000.       -0.785E+05        0.149E+01      0.637822E+18     0.63E+18          0.67E+13       0.10E-04
     1100.       -0.788E+05        0.133E+01      0.174435E+17     0.17E+17          0.65E+13       0.37E-03
     1200.       -0.791E+05        0.118E+01      0.858184E+15     0.89E+15          0.63E+13       0.73E-02
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REACTION #  9     CH2CCL2+H=CH2CCL+HCL
DELTA N =   0   DELTA H(T =   300. K)= -1.439E+04 CAL/MOLE     DELTA S (T =  300. K) =  1.247E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  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
      700.      -0.152E+05      0.534E+01      0.120600E+08      0.12E+08          0.23E+12       0.19E+05
      800.      -0.154E+05      0.525E+01      0.304653E+07      0.30E+07          0.38E+12       0.12E+06
      900.      -0.155E+05      0.520E+01      0.103657E+07      0.10E+07          0.55E+12       0.53E+06
     1000.      -0.155E+05      0.518E+01      0.435868E+06      0.44E+06          0.75E+12       0.17E+07
     1100.      -0.155E+05      0.518E+01      0.214321E+06      0.21E+06          0.97E+12       0.45E+07
     1200.      -0.155E+05      0.520E+01      0.118723E+06      0.12E+06          0.12E+13       0.10E+08

REACTION # 10     CH2CCL2+H=CHCL2CH2
DELTA N =  -1   DELTA H(T =   300. K)= -3.631E+04 CAL/MOLE     DELTA S (T =  300. K) = -2.232E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.372E+00     DELTA H=-0.359E+05
        T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.      -0.360E+05     -0.444E+00      0.110001E+12      0.11E+12          0.19E+12       0.17E+01
      800.      -0.359E+05     -0.425E+00      0.433787E+10      0.43E+10          0.97E+11       0.22E+02
      900.      -0.359E+05     -0.388E+00      0.352000E+09      0.35E+09          0.58E+11       0.17E+03
     1000.      -0.358E+05     -0.340E+00      0.474037E+08      0.48E+08          0.39E+11       0.82E+03
     1100.      -0.357E+05     -0.284E+00      0.923586E+07      0.92E+07          0.28E+11       0.30E+04
     1200.      -0.355E+05     -0.222E+00      0.237505E+07      0.24E+07          0.21E+11       0.88E+04

REACTION # 11     CH2CCL2+H=C2H3CL+CL
DELTA N =   0   DELTA H(T =   300. K)= -1.542E+04 CAL/MOLE     DELTA S (T =  300. K) =  5.957E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.166E+01     DELTA H=-0.168E+05
        T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.      -0.164E+05      0.191E+01      0.897996E+06      0.91E+06          0.48E+14       0.54E+08
      800.      -0.166E+05      0.178E+01      0.203763E+06      0.20E+06          0.50E+14       0.24E+09
      900.      -0.168E+05      0.167E+01      0.634644E+05      0.63E+05          0.51E+14       0.80E+09
     1000.      -0.169E+05      0.159E+01      0.247218E+05      0.24E+05          0.51E+14       0.21E+10
     1100.      -0.171E+05      0.151E+01      0.113473E+05      0.11E+05          0.52E+14       0.46E+10
     1200.      -0.172E+05      0.145E+01      0.589672E+04      0.60E+04          0.53E+14       0.90E+10

REACTION # 12     CH2CCL+H=C2H3+CL
DELTA N =   0   DELTA H(T =   300. K)= -1.649E+04 CAL/MOLE     DELTA S (T =  300. K) =  3.877E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.691E+00     DELTA H=-0.181E+05
        T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.      -0.173E+05      0.121E+01      0.833119E+06      0.86E+06          0.97E+14       0.12E+09
      800.      -0.176E+05      0.975E+00      0.173741E+06      0.17E+06          0.97E+14       0.56E+09
      900.      -0.180E+05      0.746E+00      0.500257E+05      0.48E+05          0.98E+14       0.20E+10
     1000.      -0.184E+05      0.524E+00      0.180643E+05      0.18E+05          0.98E+14       0.54E+10
     1100.      -0.189E+05      0.312E+00      0.769670E+04      0.77E+04          0.99E+14       0.13E+11
     1200.      -0.193E+05      0.109E+00      0.371557E+04      0.39E+04          0.99E+14       0.27E+11
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REACTION # 13     CH2CCL+H=C2H2+HCL
DELTA N =   0   DELTA H(T =   300. K)= -8.034E+04 CAL/MOLE     DELTA S (T =   300. K) =  8.371E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.444E+00     DELTA H=-0.816E+05
       T         EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.      -0.808E+05        0.660E-01     0.183910E+26     0.19E+26         0.38E+13       0.21E-12
      800.      -0.811E+05       -0.155E+00     0.127109E+23     0.12E+23         0.32E+13       0.25E-09
      900.      -0.815E+05       -0.383E+00     0.431703E+20     0.42E+20         0.27E+13       0.63E-07
     1000.      -0.819E+05       -0.611E+00     0.446734E+18     0.43E+18         0.24E+13       0.54E-05
     1100.      -0.824E+05       -0.835E+00     0.103971E+17     0.10E+17         0.22E+13       0.21E-03
     1200.      -0.829E+05       -0.105E+01     0.444645E+15     0.46E+15         0.20E+13       0.46E-02

REACTION # 14     CH3CHCL2=C2H3CL+HCL
DELTA N =   1   DELTA H(T =   300. K)=  1.692E+04 CAL/MOLE     DELTA S (T =   300. K) =  3.483E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.518E+01     DELTA H= 0.149E+05
       T         EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       0.155E+05        0.561E+01     0.390684E-02     0.40E-02         0.10E-03       0.26E-01
      800.       0.152E+05        0.541E+01     0.155752E-01     0.15E-01         0.14E-01       0.93E+00
      900.       0.149E+05        0.522E+01     0.446872E-01     0.43E-01         0.70E+00       0.16E+02
     1000.       0.146E+05        0.504E+01     0.101912E+00     0.10E+00         0.15E+02       0.15E+03
     1100.       0.142E+05        0.486E+01     0.196786E+00     0.20E+00         0.19E+03       0.99E+03
     1200.       0.138E+05        0.468E+01     0.335542E+00     0.35E+00         0.16E+04       0.48E+04

REACTION # 15     C2H3CL=C2H2+HCL
DELTA N =   1   DELTA H(T =   300. K)=  2.372E+04 CAL/MOLE     DELTA S (T =   300. K) =  2.958E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.389E+01     DELTA H= 0.230E+05
       T         EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       0.233E+05        0.415E+01     0.325711E-05     0.33E-05         0.13E-07       0.38E-02
      800.       0.232E+05        0.404E+01     0.263879E-04     0.26E-04         0.56E-05       0.21E+00
      900.       0.230E+05        0.392E+01     0.132586E-03     0.13E-03         0.64E-03       0.49E+01
     1000.       0.227E+05        0.380E+01     0.476512E-03     0.47E-03         0.29E-01       0.60E+02
     1100.       0.225E+05        0.368E+01     0.134240E-02     0.13E-02         0.64E+00       0.48E+03
     1200.       0.222E+05        0.357E+01     0.315199E-02     0.32E-02         0.85E+01       0.27E+04

REACTION # 16     C2H3CL=C2H3+CL
DELTA N =   1   DELTA H(T =   300. K)=  8.756E+04 CAL/MOLE     DELTA S (T =   300. K) =  3.262E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.503E+01     DELTA H= 0.865E+05
       T         EF-EREV         LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       0.869E+05        0.529E+01     0.147549E-24     0.15E-24         0.13E-11       0.89E+13
      800.       0.867E+05        0.517E+01     0.360687E-21     0.36E-21         0.23E-08       0.64E+13
      900.       0.865E+05        0.505E+01     0.153641E-18     0.15E-18         0.76E-06       0.50E+13
     1000.       0.863E+05        0.493E+01     0.192684E-16     0.19E-16         0.80E-04       0.41E+13
     1100.       0.860E+05        0.483E+01     0.993740E-15     0.99E-15         0.36E-02       0.36E+13
     1200.       0.858E+05        0.473E+01     0.263389E-13     0.27E-13         0.85E-01       0.32E+13
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REACTION # 17     CH3CL=CH3+CL
DELTA N =   1   DELTA H(T =   300. K)=  8.358E+04 CAL/MOLE     DELTA S (T =   300. K) =  2.988E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.437E+01     DELTA H= 0.833E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.        0.834E+05      0.448E+01      0.781225E-24     0.79E-24        0.17E-10      0.21E+14
      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     0.47E-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
     1100.        0.830E+05      0.424E+01      0.224959E-14     0.22E-14        0.19E-01      0.82E+13
     1200.        0.828E+05      0.417E+01      0.531137E-13     0.54E-13        0.39E+00      0.73E+13

REACTION # 18     CH3CL+H=CH3+HCL
DELTA N =   0   DELTA H(T =   300. K)= -1.945E+04 CAL/MOLE     DELTA S (T =   300. K) =  7.655E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.359E+01     DELTA H=-0.199E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.       -0.195E+05      0.384E+01      0.592406E+08     0.60E+08        0.19E+13      0.32E+05
      800.       -0.197E+05      0.373E+01      0.101510E+08     0.10E+08        0.30E+13      0.30E+06
      900.       -0.199E+05      0.361E+01      0.254223E+07     0.25E+07        0.43E+13      0.17E+07
     1000.       -0.201E+05      0.350E+01      0.830343E+06     0.82E+06        0.57E+13      0.68E+07
     1100.       -0.203E+05      0.339E+01      0.329085E+06     0.33E+06        0.71E+13      0.22E+08
     1200.       -0.206E+05      0.329E+01      0.150854E+06     0.15E+06        0.86E+13      0.57E+08

REACTION # 19     C2H6=2CH3
DELTA N =   1   DELTA H(T =   300. K)=  9.045E+04 CAL/MOLE     DELTA S (T =   300. K) =  3.793E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.831E+01     DELTA H= 0.899E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.        0.903E+05      0.860E+01      0.342604E-24     0.35E-24        0.41E-11      0.12E+14
      800.        0.901E+05      0.849E+01      0.114146E-20     0.11E-20        0.13E-07      0.11E+14
      900.        0.899E+05      0.835E+01      0.618528E-18     0.60E-18        0.67E-05      0.11E+14
     1000.        0.896E+05      0.820E+01      0.937849E-16     0.92E-16        0.10E-02      0.11E+14
     1100.        0.893E+05      0.804E+01      0.562587E-14     0.56E-14        0.60E-01      0.11E+14
     1200.        0.889E+05      0.788E+01      0.168293E-12     0.17E-12        0.18E+01      0.11E+14

REACTION # 20     C2H6+H=C2H5+H2
DELTA N =   0   DELTA H(T =   300. K)= -3.495E+03 CAL/MOLE     DELTA S (T =   300. K) =  6.907E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.363E+01     DELTA H=-0.348E+04
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.       -0.329E+04      0.375E+01      0.456787E+03     0.46E+03        0.62E+11      0.14E+09
      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     0.26E+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
     1100.       -0.372E+04      0.352E+01      0.185748E+03     0.19E+03        0.78E+12      0.42E+10
     1200.       -0.388E+04      0.345E+01      0.160706E+03     0.16E+03        0.11E+13      0.70E+10
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REACTION # 21     C2H6+CH3=C2H5+CH4
DELTA N =   0   DELTA H(T =  300. K)= -4.420E+03 CAL/MOLE     DELTA S (T =  300. K) =  1.143E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.396E-01     DELTA H=-0.505E+04
        T         EF-EREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.      -0.490E+04         0.673E-01      0.361758E+02      0.36E+02          0.13E+09       0.37E+07
      800.      -0.499E+04         0.355E-02      0.231978E+02      0.23E+02          0.35E+09       0.15E+08
      900.      -0.507E+04        -0.415E-01      0.163210E+02      0.16E+02          0.75E+09       0.46E+08
     1000.      -0.512E+04        -0.717E-01      0.122734E+02      0.12E+02          0.14E+10       0.11E+09
     1100.      -0.516E+04        -0.906E-01      0.969910E+01      0.97E+01          0.23E+10       0.23E+09
     1200.      -0.519E+04        -0.101E+00      0.796178E+01      0.80E+01          0.34E+10       0.43E+09

REACTION # 22     C2H6+CL=C2H5+HCL
DELTA N =   0   DELTA H(T =  300. K)= -2.366E+03 CAL/MOLE     DELTA S (T =  300. K) =  8.195E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.411E+01     DELTA H=-0.253E+04
        T         EF-EREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.      -0.231E+04         0.425E+01      0.369996E+03      0.37E+03          0.41E+14       0.11E+12
      800.      -0.240E+04         0.419E+01      0.299510E+03      0.30E+03          0.41E+14       0.14E+12
      900.      -0.251E+04         0.413E+01      0.252337E+03      0.25E+03          0.42E+14       0.17E+12
     1000.      -0.264E+04         0.406E+01      0.218548E+03      0.22E+03          0.42E+14       0.19E+12
     1100.      -0.277E+04         0.399E+01      0.193119E+03      0.19E+03          0.43E+14       0.22E+12
     1200.      -0.292E+04         0.393E+01      0.173259E+03      0.18E+03          0.43E+14       0.25E+12

REACTION # 23     C2H6+O=C2H5+OH
DELTA N =   0   DELTA H(T =  300. K)= -1.456E+03 CAL/MOLE     DELTA S (T =  300. K) =  8.466E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.441E+01     DELTA H=-0.145E+04
        T         EF-EREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.      -0.127E+04         0.452E+01      0.230014E+03      0.23E+03          0.25E+12       0.11E+10
      800.      -0.133E+04         0.448E+01      0.204703E+03      0.20E+03          0.45E+12       0.22E+10
      900.      -0.143E+04         0.442E+01      0.185913E+03      0.18E+03          0.70E+12       0.38E+10
     1000.      -0.155E+04         0.436E+01      0.171107E+03      0.17E+03          0.10E+13       0.59E+10
     1100.      -0.168E+04         0.430E+01      0.158953E+03      0.16E+03          0.13E+13       0.84E+10
     1200.      -0.182E+04         0.424E+01      0.148695E+03      0.15E+03          0.17E+13       0.12E+11

REACTION # 24     C2H6+OH=C2H5+H2O
DELTA N =   0   DELTA H(T =  300. K)= -1.868E+04 CAL/MOLE     DELTA S (T =  300. K) =  4.271E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.200E+01     DELTA H=-0.189E+05
        T         EF-EREV          LN AF/AREV         KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.      -0.187E+05         0.212E+01      0.597115E+07      0.60E+07          0.51E+13       0.85E+06
      800.      -0.188E+05         0.207E+01      0.110393E+07      0.11E+07          0.70E+13       0.64E+07
      900.      -0.189E+05         0.202E+01      0.295207E+06      0.29E+06          0.90E+13       0.31E+08
     1000.      -0.190E+05         0.196E+01      0.102208E+06      0.10E+06          0.11E+14       0.11E+09
     1100.      -0.191E+05         0.191E+01      0.427053E+05      0.43E+05          0.13E+14       0.30E+09
     1200.      -0.192E+05         0.186E+01      0.205504E+05      0.21E+05          0.15E+14       0.73E+09
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REACTION # 25     C2H5=C2H4+H
DELTA N =   1   DELTA H(T =   300. K)=  3.627E+04 CAL/MOLE     DELTA S (T =   300. K) =  2.186E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.237E+00     DELTA H= 0.360E+05
        T          EF-EREV        LN AF/AREV       KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.        0.360E+05       0.223E+00     0.730639E-11    0.73E-11        0.85E+01      0.12E+13
      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
     1100.        0.359E+05       0.214E+00     0.893770E-07    0.89E-07        0.37E+06      0.42E+13
     1200.        0.359E+05       0.185E+00     0.351604E-06    0.35E-06        0.18E+07      0.51E+13

REACTION # 26     C2H5+H=2CH3
DELTA N =   0   DELTA H(T =   300. K)= -1.021E+04 CAL/MOLE     DELTA S (T =   300. K) =  7.504E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.342E+01     DELTA H=-0.108E+05
        T          EF-EREV        LN AF/AREV       KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.       -0.104E+05       0.370E+01     0.702164E+05    0.72E+05        0.66E+14      0.94E+09
      800.       -0.105E+05       0.358E+01     0.274475E+05    0.27E+05        0.85E+14      0.31E+10
      900.       -0.108E+05       0.345E+01     0.130357E+05    0.13E+05        0.10E+15      0.79E+10
     1000.       -0.110E+05       0.332E+01     0.709311E+04    0.70E+04        0.12E+15      0.17E+11
     1100.       -0.113E+05       0.320E+01     0.426156E+04    0.43E+04        0.14E+15      0.32E+11
     1200.       -0.115E+05       0.308E+01     0.275881E+04    0.28E+04        0.15E+15      0.56E+11

REACTION # 27     C2H5+O2=C2H4+HO2
DELTA N =   0   DELTA H(T =   300. K)= -1.232E+04 CAL/MOLE     DELTA S (T =   300. K) =  2.060E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.290E-01     DELTA H=-0.124E+05
        T          EF-EREV        LN AF/AREV       KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.       -0.124E+05      -0.137E-01     0.741590E+04    0.74E+04        0.55E+11      0.75E+07
      800.       -0.124E+05      -0.182E-01     0.242957E+04    0.24E+04        0.87E+11      0.36E+08
      900.       -0.124E+05      -0.245E-01     0.101938E+04    0.10E+04        0.12E+12      0.12E+09
     1000.       -0.124E+05      -0.335E-01     0.508458E+03    0.51E+03        0.16E+12      0.32E+09
     1100.       -0.125E+05      -0.455E-01     0.287529E+03    0.29E+03        0.20E+12      0.71E+09
     1200.       -0.125E+05      -0.602E-01     0.178602E+03    0.18E+03        0.25E+12      0.14E+10

REACTION # 28     C2H5+CH3=C3H8
DELTA N =  -1   DELTA H(T =   300. K)= -8.826E+04 CAL/MOLE     DELTA S (T =   300. K) = -3.977E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.822E+01     DELTA H=-0.867E+05
        T          EF-EREV        LN AF/AREV       KEQ          KEQ FIT        K FORWARD     K REVERSE
      700.       -0.873E+05      -0.868E+01     0.318380E+24    0.31E+24        0.11E+14      0.35E-10
      800.       -0.870E+05      -0.848E+01     0.125552E+21    0.13E+21        0.10E+14      0.80E-07
      900.       -0.867E+05      -0.827E+01     0.289251E+18    0.30E+18        0.94E+13      0.32E-04
     1000.       -0.863E+05      -0.806E+01     0.229228E+16    0.23E+16        0.88E+13      0.38E-02
     1100.       -0.859E+05      -0.787E+01     0.445841E+14    0.45E+14        0.84E+13      0.19E+00
     1200.       -0.854E+05      -0.768E+01     0.169891E+13    0.16E+13        0.81E+13      0.48E+01
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REACTION # 29      C2H5+CH3=C3H7+H
DELTA N =   0   DELTA H(T =  300. K)=  1.260E+04 CAL/MOLE     DELTA S (T =  300. K) = -7.844E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.265E+01     DELTA H= 0.142E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT         K FORWARD      K REVERSE
      700.        0.135E+05       -0.310E+01     0.276530E-05     0.27E-05         0.38E+07       0.14E+13
      800.        0.138E+05       -0.288E+01     0.942559E-05     0.96E-05         0.31E+08       0.33E+13
      900.        0.141E+05       -0.268E+01     0.250365E-04     0.26E-04         0.16E+09       0.63E+13
     1000.        0.145E+05       -0.251E+01     0.557147E-04     0.57E-04         0.58E+09       0.10E+14
     1100.        0.148E+05       -0.236E+01     0.108780E-03     0.11E-03         0.17E+10       0.15E+14
     1200.        0.151E+05       -0.223E+01     0.192210E-03     0.19E-03         0.41E+10       0.21E+14

REACTION # 30      C2H4+O=CH3+CHO
DELTA N =   0   DELTA H(T =  300. K)= -2.655E+04 CAL/MOLE     DELTA S (T =  300. K) =  9.188E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.461E+01     DELTA H=-0.268E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT         K FORWARD      K REVERSE
      700.       -0.265E+05        0.481E+01     0.227453E+11     0.23E+11         0.32E+13       0.14E+03
      800.       -0.266E+05        0.473E+01     0.209584E+10     0.21E+10         0.41E+13       0.20E+04
      900.       -0.267E+05        0.464E+01     0.324868E+09     0.32E+09         0.49E+13       0.15E+05
     1000.       -0.269E+05        0.454E+01     0.724348E+08     0.72E+08         0.58E+13       0.79E+05
     1100.       -0.271E+05        0.445E+01     0.210376E+08     0.21E+08         0.65E+13       0.31E+06
     1200.       -0.273E+05        0.436E+01     0.745106E+07     0.76E+07         0.72E+13       0.97E+06

REACTION # 31      C2H4+OH=CH3+CH2O
DELTA N =   0   DELTA H(T =  300. K)= -1.460E+04 CAL/MOLE     DELTA S (T =  300. K) =  2.371E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.870E+00     DELTA H=-0.150E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT         K FORWARD      K REVERSE
      700.       -0.148E+05        0.993E+00     0.115361E+06     0.12E+06         0.10E+14       0.87E+08
      800.       -0.149E+05        0.931E+00     0.303047E+05     0.30E+05         0.10E+14       0.33E+09
      900.       -0.150E+05        0.876E+00     0.106449E+05     0.11E+05         0.10E+14       0.94E+09
     1000.       -0.151E+05        0.831E+00     0.458649E+04     0.46E+04         0.10E+14       0.22E+10
     1100.       -0.152E+05        0.792E+00     0.229423E+04     0.23E+04         0.10E+14       0.44E+10
     1200.       -0.153E+05        0.758E+00     0.128417E+04     0.13E+04         0.10E+14       0.78E+10

REACTION # 32      C2H4+OH=C2H3+H2O
DELTA N =   0   DELTA H(T =  300. K)= -1.272E+04 CAL/MOLE     DELTA S (T =  300. K) =  5.037E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.264E+01     DELTA H=-0.127E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT         K FORWARD      K REVERSE
      700.       -0.126E+05        0.275E+01     0.132842E+06     0.13E+06         0.81E+13       0.61E+08
      800.       -0.126E+05        0.271E+01     0.427993E+05     0.43E+05         0.11E+14       0.25E+09
      900.       -0.127E+05        0.266E+01     0.176402E+05     0.17E+05         0.13E+14       0.75E+09
     1000.       -0.128E+05        0.260E+01     0.863179E+04     0.86E+04         0.16E+14       0.18E+10
     1100.       -0.130E+05        0.254E+01     0.478369E+04     0.48E+04         0.18E+14       0.37E+10
     1200.       -0.131E+05        0.248E+01     0.291036E+04     0.29E+04         0.20E+14       0.69E+10
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REACTION # 33     C2H4+H=C2H3+H2
DELTA N =   0   DELTA H(T =   300. K)=  2.464E+03 CAL/MOLE     DELTA S (T =   300. K) =  7.672E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.427E+01     DELTA H= 0.270E+04
        T          EF-EREV        LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        0.288E+04       0.439E+01      0.101623E+02      0.10E+02          0.21E+11       0.20E+10
      800.        0.283E+04       0.435E+01      0.131391E+02      0.13E+02          0.76E+11       0.58E+10
      900.        0.273E+04       0.430E+01      0.159639E+02      0.16E+02          0.21E+12       0.13E+11
     1000.        0.260E+04       0.423E+01      0.185367E+02      0.18E+02          0.47E+12       0.25E+11
     1100.        0.244E+04       0.415E+01      0.208068E+02      0.21E+02          0.91E+12       0.44E+11
     1200.        0.226E+04       0.407E+01      0.227593E+02      0.23E+02          0.16E+13       0.69E+11

REACTION # 34     C2H3+CH3=C3H6
DELTA N =  -1   DELTA H(T =   300. K)= -9.730E+04 CAL/MOLE     DELTA S (T =   300. K) = -3.879E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.827E+01     DELTA H=-0.963E+05
        T          EF-EREV        LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.       -0.968E+05      -0.863E+01      0.300070E+27      0.29E+27          0.20E+14       0.66E-13
      800.       -0.966E+05      -0.848E+01      0.503963E+23      0.51E+23          0.18E+14       0.36E-09
      900.       -0.963E+05      -0.831E+01      0.594605E+20      0.61E+20          0.17E+14       0.28E-06
     1000.       -0.959E+05      -0.813E+01      0.274982E+18      0.28E+18          0.16E+14       0.57E-04
     1100.       -0.955E+05      -0.795E+01      0.343591E+16      0.34E+16          0.15E+14       0.44E-02
     1200.       -0.951E+05      -0.777E+01      0.904768E+14      0.88E+14          0.14E+14       0.16E+00

REACTION # 35     C2H3+O2=C2H2+HO2
DELTA N =   0   DELTA H(T =   300. K)= -9.404E+03 CAL/MOLE     DELTA S (T =   300. K) = -2.462E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.619E+00     DELTA H=-0.876E+04
        T          EF-EREV        LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.       -0.893E+04      -0.734E+00      0.295471E+03      0.29E+03          0.10E+13       0.34E+10
      800.       -0.883E+04      -0.669E+00      0.132946E+03      0.13E+03          0.10E+13       0.75E+10
      900.       -0.875E+04      -0.620E+00      0.718862E+02      0.72E+02          0.10E+13       0.14E+11
     1000.       -0.868E+04      -0.584E+00      0.441430E+02      0.44E+02          0.10E+13       0.23E+11
     1100.       -0.862E+04      -0.555E+00      0.297072E+02      0.30E+02          0.10E+13       0.34E+11
     1200.       -0.857E+04      -0.531E+00      0.214028E+02      0.21E+02          0.10E+13       0.47E+11

REACTION # 36     C2H2+O=CH2+CO
DELTA N =   0   DELTA H(T =   300. K)= -4.779E+04 CAL/MOLE     DELTA S (T =   300. K) =  7.043E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.246E+01     DELTA H=-0.491E+05
        T          EF-EREV        LN AF/AREV        KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.       -0.485E+05       0.280E+01      0.239448E+17      0.24E+17          0.37E+13       0.15E-03
      800.       -0.488E+05       0.263E+01      0.301455E+15      0.30E+15          0.51E+13       0.17E-01
      900.       -0.490E+05       0.248E+01      0.985579E+13      0.96E+13          0.66E+13       0.67E+00
     1000.       -0.493E+05       0.235E+01      0.629667E+12      0.62E+12          0.82E+13       0.13E+02
     1100.       -0.495E+05       0.223E+01      0.655817E+11      0.66E+11          0.97E+13       0.15E+03
     1200.       -0.498E+05       0.212E+01      0.986550E+10      0.10E+11          0.11E+14       0.11E+04
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REACTION # 37     C2H2+O2=2CHO
DELTA N =   0   DELTA H(T =   300. K)= -3.338E+04 CAL/MOLE     DELTA S (T =   300. K) =  1.029E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.417E+01     DELTA H=-0.345E+05
        T          EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.       -0.341E+05       0.442E+01      0.377150E+13     0.38E+13         0.72E+04       0.19E-08
      800.       -0.343E+05       0.429E+01      0.174171E+12     0.17E+12         0.89E+05       0.51E-06
      900.       -0.345E+05       0.418E+01      0.157205E+11     0.15E+11         0.63E+06       0.40E-04
     1000.       -0.347E+05       0.409E+01      0.227303E+10     0.23E+10         0.30E+07       0.13E-02
     1100.       -0.348E+05       0.402E+01      0.463669E+09     0.46E+09         0.11E+08       0.23E-01
     1200.       -0.350E+05       0.395E+01      0.122548E+09     0.12E+09         0.32E+08       0.26E+00

REACTION # 38     C3H8+CH3=C3H7+CH4
DELTA N =   0   DELTA H(T =   300. K)= -4.211E+03 CAL/MOLE     DELTA S (T =   300. K) =  2.649E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.638E+00     DELTA H=-0.492E+04
        T          EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.       -0.474E+04       0.757E+00      0.643962E+02     0.65E+02         0.59E+09       0.92E+07
      800.       -0.484E+04       0.691E+00      0.418768E+02     0.42E+02         0.16E+10       0.39E+08
      900.       -0.492E+04       0.640E+00      0.297727E+02     0.30E+02         0.36E+10       0.12E+09
     1000.       -0.499E+04       0.601E+00      0.225616E+02     0.22E+02         0.68E+10       0.30E+09
     1100.       -0.506E+04       0.572E+00      0.179257E+02     0.18E+02         0.11E+11       0.64E+09
     1200.       -0.511E+04       0.548E+00      0.147663E+02     0.15E+02         0.18E+11       0.12E+10

REACTION # 39     C3H8+HO2=C3H7+H2O2
DELTA N =   0   DELTA H(T =   300. K)=  1.278E+04 CAL/MOLE     DELTA S (T =   300. K) =  5.495E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.334E+01     DELTA H= 0.133E+05
        T          EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.        0.132E+05       0.328E+01      0.194025E-02     0.19E-02         0.19E+08       0.97E+10
      800.        0.133E+05       0.332E+01      0.640250E-02     0.64E-02         0.92E+08       0.14E+11
      900.        0.133E+05       0.335E+01      0.162622E-01     0.16E-01         0.32E+09       0.19E+11
     1000.        0.134E+05       0.335E+01      0.343266E-01     0.34E-01         0.85E+09       0.25E+11
     1100.        0.133E+05       0.335E+01      0.632556E-01     0.63E-01         0.19E+10       0.30E+11
     1200.        0.133E+05       0.334E+01      0.105201E+00     0.11E+00         0.37E+10       0.36E+11

REACTION # 40     C3H7=C3H6+H
DELTA N =   1   DELTA H(T =   300. K)=  3.298E+04 CAL/MOLE     DELTA S (T =   300. K) =  2.210E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.155E+00     DELTA H= 0.324E+05
        T          EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.        0.325E+05       0.215E+00      0.860625E-10     0.86E-10         0.12E+02       0.14E+12
      800.        0.325E+05       0.189E+00      0.160037E-08     0.16E-08         0.38E+03       0.24E+12
      900.        0.324E+05       0.159E+00      0.154949E-07     0.15E-07         0.56E+04       0.36E+12
     1000.        0.324E+05       0.128E+00      0.949775E-07     0.95E-07         0.48E+05       0.51E+12
     1100.        0.323E+05       0.955E-01      0.417468E-06     0.42E-06         0.28E+06       0.68E+12
     1200.        0.322E+05       0.628E-01      0.142984E-05     0.14E-05         0.12E+07       0.86E+12
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REACTION # 41     C3H7=CH3+C2H4
DELTA N =   1   DELTA H(T =  300. K)=  2.366E+04 CAL/MOLE     DELTA S (T =  300. K) =  2.970E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.289E+01     DELTA H= 0.218E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.225E+05      0.332E+01     0.264217E-05     0.27E-05          0.53E+03       0.20E+09
      800.        0.222E+05      0.312E+01     0.196955E-04     0.19E-04          0.10E+05       0.52E+09
      900.        0.219E+05      0.293E+01     0.919088E-04     0.89E-04          0.10E+06       0.11E+10
     1000.        0.215E+05      0.275E+01     0.309316E-03     0.30E-03          0.64E+06       0.21E+10
     1100.        0.212E+05      0.257E+01     0.821634E-03     0.82E-03          0.29E+07       0.35E+10
     1200.        0.208E+05      0.242E+01     0.182927E-02     0.19E-02          0.10E+08       0.56E+10

REACTION # 42     C3H7+O2=C3H6+HO2
DELTA N =   0   DELTA H(T =  300. K)= -1.560E+04 CAL/MOLE     DELTA S (T =  300. K) =  4.483E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.112E+00     DELTA H=-0.160E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.158E+05     -0.218E-01     0.873524E+05     0.88E+05          0.12E+12       0.13E+07
      800.       -0.159E+05     -0.701E-01     0.209448E+05     0.21E+05          0.15E+12       0.73E+07
      900.       -0.160E+05     -0.109E+00     0.686430E+04     0.68E+04          0.19E+12       0.27E+08
     1000.       -0.160E+05     -0.140E+00     0.280223E+04     0.28E+04          0.22E+12       0.79E+08
     1100.       -0.161E+05     -0.164E+00     0.134301E+04     0.13E+04          0.26E+12       0.19E+09
     1200.       -0.161E+05     -0.183E+00     0.726307E+03     0.73E+03          0.29E+12       0.39E+09

REACTION # 43     CH3CCL3+CL=CCL3CH2+HCL
DELTA N =   0   DELTA H(T =  300. K)= -8.167E+03 CAL/MOLE     DELTA S (T =  300. K) =  9.432E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.407E+01     DELTA H=-0.895E+04
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.862E+04      0.429E+01     0.361302E+05     0.37E+05          0.19E+12       0.52E+07
      800.       -0.878E+04      0.419E+01     0.165343E+05     0.16E+05          0.26E+12       0.16E+08
      900.       -0.894E+04      0.409E+01     0.890104E+04     0.88E+04          0.34E+12       0.38E+08
     1000.       -0.911E+04      0.400E+01     0.537305E+04     0.53E+04          0.41E+12       0.76E+08
     1100.       -0.928E+04      0.392E+01     0.352755E+04     0.35E+04          0.48E+12       0.14E+09
     1200.       -0.945E+04      0.384E+01     0.246801E+04     0.25E+04          0.55E+12       0.22E+09

REACTION # 44     CH3CCL2+CH4=CH3CHCL2+CH3
DELTA N =   0   DELTA H(T =  300. K)=  1.192E+04 CAL/MOLE     DELTA S (T =  300. K) =  1.200E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.138E+01     DELTA H= 0.127E+05
        T          EF-EREV        LN AF/AREV        KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.125E+05      0.130E+01     0.440864E-03     0.44E-03          0.14E+06       0.31E+09
      800.        0.126E+05      0.135E+01     0.136732E-02     0.14E-02          0.10E+07       0.76E+09
      900.        0.127E+05      0.139E+01     0.331365E-02     0.33E-02          0.50E+07       0.15E+10
     1000.        0.127E+05      0.140E+01     0.674227E-02     0.68E-02          0.18E+08       0.27E+10
     1100.        0.127E+05      0.140E+01     0.120651E-01     0.12E-01          0.50E+08       0.42E+10
     1200.        0.127E+05      0.140E+01     0.195960E-01     0.20E-01          0.12E+09       0.61E+10
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REACTION # 45     CH2CCL+CH4=C2H3CL+CH3
DELTA N =   0   DELTA H(T =  300. K)=  1.023E+03 CAL/MOLE     DELTA S (T =  300. K) =  5.401E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.594E+00     DELTA H= 0.119E+04
        T          EF-EREV         LN AF/AREV         KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.        0.142E+04        0.746E+00      0.761568E+00     0.77E+00         0.16E+10      0.22E+10
      800.        0.137E+04        0.712E+00      0.863543E+00     0.86E+00         0.31E+10      0.36E+10
      900.        0.124E+04        0.641E+00      0.946602E+00     0.93E+00         0.52E+10      0.55E+10
     1000.        0.105E+04        0.541E+00      0.100997E+01     0.10E+01         0.77E+10      0.77E+10
     1100.        0.801E+03        0.419E+00      0.105420E+01     0.11E+01         0.11E+11      0.10E+11
     1200.        0.491E+03        0.283E+00      0.108084E+01     0.11E+01         0.14E+11      0.13E+11

REACTION # 46     CH4+AR=CH3+H+AR
DELTA N =   1   DELTA H(T =  300. K)=  1.051E+05 CAL/MOLE     DELTA S (T =  300. K) =  2.928E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.493E+01     DELTA H= 0.106E+06
        T          EF-EREV         LN AF/AREV         KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.        0.106E+06        0.483E+01      0.134877E-30     0.13E-30         0.14E-11      0.11E+20
      800.        0.106E+06        0.491E+01      0.179272E-26     0.18E-26         0.57E-08      0.32E+19
      900.        0.106E+06        0.494E+01      0.290724E-23     0.29E-23         0.37E-05      0.13E+19
     1000.        0.106E+06        0.495E+01      0.107729E-20     0.11E-20         0.64E-03      0.59E+18
     1100.        0.106E+06        0.493E+01      0.136110E-18     0.14E-18         0.44E-01      0.32E+18
     1200.        0.106E+06        0.490E+01      0.766186E-17     0.77E-17         0.15E+01      0.19E+18

REACTION # 47     CH4+O2=CH3+HO2
DELTA N =   0   DELTA H(T =  300. K)=  5.650E+04 CAL/MOLE     DELTA S (T =  300. K) =  7.629E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.466E+01     DELTA H= 0.573E+05
        T          EF-EREV         LN AF/AREV         KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.        0.572E+05        0.459E+01      0.136898E-15     0.14E-15         0.28E-03      0.20E+13
      800.        0.573E+05        0.465E+01      0.234621E-13     0.24E-13         0.42E-01      0.18E+13
      900.        0.573E+05        0.467E+01      0.128792E-11     0.13E-11         0.21E+01      0.16E+13
     1000.        0.573E+05        0.468E+01      0.317844E-10     0.32E-10         0.48E+02      0.15E+13
     1100.        0.573E+05        0.467E+01      0.437871E-09     0.44E-09         0.62E+03      0.14E+13
     1200.        0.573E+05        0.466E+01      0.389196E-08     0.39E-08         0.52E+04      0.13E+13

REACTION # 48     CH4+O=CH3+OH
DELTA N =   0   DELTA H(T =  300. K)=  2.964E+03 CAL/MOLE     DELTA S (T =  300. K) =  7.323E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.445E+01     DELTA H= 0.361E+04
        T          EF-EREV         LN AF/AREV         KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.        0.363E+04        0.446E+01      0.635825E+01     0.64E+01         0.47E+11      0.74E+10
      800.        0.366E+04        0.448E+01      0.882425E+01     0.88E+01         0.12E+12      0.14E+11
      900.        0.364E+04        0.447E+01      0.113911E+02     0.11E+02         0.27E+12      0.24E+11
     1000.        0.358E+04        0.443E+01      0.139413E+02     0.14E+02         0.52E+12      0.37E+11
     1100.        0.348E+04        0.439E+01      0.163884E+02     0.16E+02         0.90E+12      0.55E+11
     1200.        0.336E+04        0.434E+01      0.186761E+02     0.19E+02         0.14E+13      0.77E+11
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REACTION # 49      CH4+H=CH3+H2
DELTA N =    0    DELTA H(T =   300. K)=  9.245E+02 CAL/MOLE      DELTA S (T =   300. K) =  5.764E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.367E+01      DELTA H= 0.158E+04
        T           EF-EREV         LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.        0.160E+04        0.369E+01      0.126269E+02      0.13E+02          0.14E+11       0.11E+10
      800.        0.163E+04        0.371E+01      0.146090E+02      0.15E+02          0.46E+11       0.32E+10
      900.        0.161E+04        0.370E+01      0.163688E+02      0.16E+02          0.12E+12       0.74E+10
     1000.        0.154E+04        0.366E+01      0.178834E+02      0.18E+02          0.27E+12       0.15E+11
     1100.        0.144E+04        0.361E+01      0.191510E+02      0.19E+02          0.54E+12       0.28E+11
     1200.        0.131E+04        0.355E+01      0.201847E+02      0.20E+02          0.97E+12       0.48E+11

REACTION # 50      CH4+OH=CH3+H2O
DELTA N =    0    DELTA H(T =   300. K)= -1.426E+04 CAL/MOLE      DELTA S (T =   300. K) =  3.128E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.204E+01      DELTA H=-0.139E+05
        T           EF-EREV         LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.       -0.138E+05        0.206E+01      0.165059E+06      0.17E+06          0.26E+12       0.16E+07
      800.       -0.138E+05        0.207E+01      0.475875E+05      0.48E+05          0.43E+12       0.89E+07
      900.       -0.138E+05        0.206E+01      0.180876E+05      0.18E+05          0.65E+12       0.36E+08
     1000.       -0.139E+05        0.203E+01      0.832760E+04      0.83E+04          0.93E+12       0.11E+09
     1100.       -0.140E+05        0.200E+01      0.440302E+04      0.44E+04          0.13E+13       0.29E+09
     1200.       -0.140E+05        0.196E+01      0.258113E+04      0.26E+04          0.17E+13       0.65E+09

REACTION # 51      CH4+CL=CH3+HCL
DELTA N =    0    DELTA H(T =   300. K)=  2.054E+03 CAL/MOLE      DELTA S (T =   300. K) =  7.052E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.415E+01      DELTA H= 0.253E+04
        T           EF-EREV         LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.        0.259E+04        0.418E+01      0.102277E+02      0.10E+02          0.16E+13       0.16E+12
      800.        0.259E+04        0.419E+01      0.129111E+02      0.13E+02          0.23E+13       0.18E+12
      900.        0.256E+04        0.417E+01      0.154609E+02      0.15E+02          0.30E+13       0.19E+12
     1000.        0.249E+04        0.413E+01      0.178066E+02      0.18E+02          0.37E+13       0.21E+12
     1100.        0.239E+04        0.408E+01      0.199111E+02      0.20E+02          0.44E+13       0.22E+12
     1200.        0.227E+04        0.403E+01      0.217614E+02      0.22E+02          0.51E+13       0.23E+12
REACTION # 52      CH4+HO2=CH3+H2O2
DELTA N =    0    DELTA H(T =   300. K)=  1.699E+04 CAL/MOLE      DELTA S (T =   300. K) =  2.846E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.270E+01      DELTA H= 0.182E+05
        T           EF-EREV         LN AF/AREV          KEQ           KEQ FIT          K FORWARD      K REVERSE
      700.        0.180E+05        0.252E+01      0.301299E-04      0.30E-04          0.48E+08       0.16E+13
      800.        0.181E+05        0.263E+01      0.152889E-03      0.15E-03          0.24E+09       0.16E+13
      900.        0.183E+05        0.271E+01      0.546213E-03      0.55E-03          0.85E+09       0.16E+13
     1000.        0.184E+05        0.275E+01      0.152146E-02      0.15E-02          0.23E+10       0.15E+13
     1100.        0.184E+05        0.278E+01      0.352876E-02      0.35E-02          0.53E+10       0.15E+13
     1200.        0.184E+05        0.279E+01      0.712442E-02      0.71E-02          0.11E+11       0.15E+13
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REACTION # 53     CH3+O2=CH3O+O
DELTA N =   0   DELTA H(T =   300. K)=  2.831E+04 CAL/MOLE     DELTA S (T =  300. K) = -3.681E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.227E+01     DELTA H= 0.280E+05
          T         EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.279E+05       -0.233E+01      0.184524E-09     0.18E-09          0.27E+05       0.14E+15
      800.        0.279E+05       -0.232E+01      0.227211E-08     0.23E-08          0.33E+06       0.14E+15
      900.        0.280E+05       -0.229E+01      0.160521E-07     0.16E-07          0.23E+07       0.15E+15
     1000.        0.281E+05       -0.225E+01      0.769904E-07     0.77E-07          0.11E+08       0.15E+15
     1100.        0.282E+05       -0.219E+01      0.278878E-06     0.28E-06          0.41E+08       0.15E+15
     1200.        0.283E+05       -0.214E+01      0.818748E-06     0.81E-06          0.12E+09       0.15E+15

REACTION # 54     CH3+O=CH2O+H
DELTA N =   0   DELTA H(T =   300. K)= -7.024E+04 CAL/MOLE     DELTA S (T =  300. K) = -5.234E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.280E+01     DELTA H=-0.703E+05
          T         EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.704E+05       -0.286E+01      0.565881E+21     0.56E+21          0.70E+14       0.12E-06
      800.       -0.704E+05       -0.284E+01      0.100890E+19     0.10E+19          0.70E+14       0.69E-04
      900.       -0.703E+05       -0.281E+01      0.736247E+16     0.74E+16          0.70E+14       0.95E-02
     1000.       -0.703E+05       -0.277E+01      0.144207E+15     0.14E+15          0.70E+14       0.49E+00
     1100.       -0.702E+05       -0.274E+01      0.579351E+13     0.58E+13          0.70E+14       0.12E+02
     1200.       -0.701E+05       -0.270E+01      0.398940E+12     0.40E+12          0.70E+14       0.18E+03

REACTION # 55     CH3+OH=CH2O+2H
DELTA N =   1   DELTA H(T =   300. K)=  3.188E+04 CAL/MOLE     DELTA S (T =  300. K) =  1.672E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.231E+01     DELTA H= 0.318E+05
          T         EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.315E+05       -0.249E+01      0.120040E-10     0.12E-10          0.53E+13       0.44E+24
      800.        0.316E+05       -0.241E+01      0.204966E-09     0.21E-09          0.53E+13       0.26E+23
      900.        0.318E+05       -0.233E+01      0.187906E-08     0.19E-08          0.53E+13       0.28E+22
     1000.        0.319E+05       -0.226E+01      0.111434E-07     0.11E-07          0.53E+13       0.48E+21
     1100.        0.320E+05       -0.219E+01      0.481166E-07     0.48E-07          0.53E+13       0.11E+21
     1200.        0.322E+05       -0.214E+01      0.163665E-06     0.16E-06          0.53E+13       0.32E+20

REACTION # 56     CH3+HO2=CH3O+OH
DELTA N =   0   DELTA H(T =   300. K)= -2.522E+04 CAL/MOLE     DELTA S (T =  300. K) = -3.987E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.249E+01     DELTA H=-0.257E+05
          T         EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.256E+05       -0.246E+01      0.857023E+07     0.86E+07          0.20E+14       0.23E+07
      800.       -0.257E+05       -0.249E+01      0.854556E+06     0.85E+06          0.20E+14       0.23E+08
      900.       -0.257E+05       -0.250E+01      0.141973E+06     0.14E+06          0.20E+14       0.14E+09
     1000.       -0.257E+05       -0.249E+01      0.337695E+05     0.34E+05          0.20E+14       0.59E+09
     1100.       -0.256E+05       -0.248E+01      0.104377E+05     0.10E+05          0.20E+14       0.19E+10
     1200.       -0.256E+05       -0.246E+01      0.392887E+04     0.39E+04          0.20E+14       0.51E+10
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REACTION # 57      CH3O+O2=CH2O+HO2
DELTA N =   0   DELTA H(T =   300. K)= -2.809E+04 CAL/MOLE     DELTA S (T =   300. K) =  4.733E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.252E+01     DELTA H=-0.280E+05
        T           EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.       -0.280E+05       0.255E+01      0.689108E+10     0.69E+10         0.58E+11      0.84E+01
      800.       -0.280E+05       0.254E+01      0.558006E+09     0.56E+09         0.11E+12      0.20E+03
      900.       -0.280E+05       0.252E+01      0.788854E+08     0.79E+08         0.18E+12      0.23E+04
     1000.       -0.280E+05       0.250E+01      0.164626E+08     0.16E+08         0.27E+12      0.16E+05
     1100.       -0.281E+05       0.248E+01      0.455881E+07     0.46E+07         0.38E+12      0.83E+05
     1200.       -0.281E+05       0.245E+01      0.156040E+07     0.16E+07         0.50E+12      0.32E+06

REACTION # 58      CH2O+CH3=CH4+CHO
DELTA N =   0   DELTA H(T =   300. K)= -1.491E+04 CAL/MOLE     DELTA S (T =   300. K) = -5.055E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.703E+00     DELTA H=-0.154E+05
        T           EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.       -0.153E+05      -0.639E+00      0.310094E+05     0.31E+05         0.35E+10      0.11E+06
      800.       -0.153E+05      -0.680E+00      0.783736E+04     0.78E+04         0.65E+10      0.83E+06
      900.       -0.154E+05      -0.706E+00      0.267917E+04     0.27E+04         0.10E+11      0.39E+07
     1000.       -0.154E+05      -0.722E+00      0.113283E+04     0.11E+04         0.15E+11      0.14E+08
     1100.       -0.154E+05      -0.730E+00      0.559527E+03     0.56E+03         0.21E+11      0.38E+08
     1200.       -0.154E+05      -0.735E+00      0.310676E+03     0.31E+03         0.28E+11      0.90E+08

REACTION # 59      CH2O+H=CHO+H2
DELTA N =   0   DELTA H(T =   300. K)= -1.399E+04 CAL/MOLE     DELTA S (T =   300. K) =  5.258E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.297E+01     DELTA H=-0.138E+05
        T           EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.       -0.137E+05       0.305E+01      0.391552E+06     0.39E+06         0.14E+13      0.36E+07
      800.       -0.137E+05       0.303E+01      0.114496E+06     0.11E+06         0.20E+13      0.18E+08
      900.       -0.138E+05       0.299E+01      0.438547E+05     0.44E+05         0.27E+13      0.61E+08
     1000.       -0.139E+05       0.294E+01      0.202588E+05     0.20E+05         0.34E+13      0.17E+09
     1100.       -0.140E+05       0.288E+01      0.107155E+05     0.11E+05         0.40E+13      0.38E+09
     1200.       -0.141E+05       0.282E+01      0.627089E+04     0.63E+04         0.47E+13      0.75E+09

REACTION # 60      CH2O+O=CHO+OH
DELTA N =   0   DELTA H(T =   300. K)= -1.195E+04 CAL/MOLE     DELTA S (T =   300. K) =  6.818E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.374E+01     DELTA H=-0.118E+05
        T           EF-EREV         LN AF/AREV        KEQ           KEQ FIT          K FORWARD     K REVERSE
      700.       -0.116E+05       0.382E+01      0.197165E+06     0.20E+06         0.28E+13      0.14E+08
      800.       -0.117E+05       0.380E+01      0.691588E+05     0.69E+05         0.38E+13      0.56E+08
      900.       -0.117E+05       0.376E+01      0.305186E+05     0.30E+05         0.49E+13      0.16E+09
     1000.       -0.118E+05       0.371E+01      0.157931E+05     0.16E+05         0.60E+13      0.38E+09
     1100.       -0.119E+05       0.366E+01      0.916978E+04     0.92E+04         0.70E+13      0.77E+09
     1200.       -0.121E+05       0.360E+01      0.580222E+04     0.59E+04         0.80E+13      0.14E+10
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REACTION # 61      CH2O+OH=CHO+H2O
DELTA N =   0    DELTA H(T =   300. K)= -2.917E+04 CAL/MOLE      DELTA S (T =   300. K) =  2.623E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.134E+01      DELTA H=-0.292E+05
        T           EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.291E+05        0.142E+01       0.511839E+10      0.51E+10          0.13E+14       0.25E+04
      800.        -0.292E+05        0.139E+01       0.372960E+09      0.37E+09          0.14E+14       0.38E+05
      900.        -0.292E+05        0.135E+01       0.484597E+08      0.48E+08          0.15E+14       0.32E+06
     1000.        -0.293E+05        0.131E+01       0.943374E+07      0.94E+07          0.16E+14       0.17E+07
     1100.        -0.294E+05        0.127E+01       0.246361E+07      0.25E+07          0.17E+14       0.71E+07
     1200.        -0.295E+05        0.123E+01       0.801894E+06      0.81E+06          0.18E+14       0.23E+08

REACTION # 62      CH2O+HO2=CHO+H2O2
DELTA N =   0    DELTA H(T =   300. K)=  2.072E+03 CAL/MOLE      DELTA S (T =   300. K) =  2.340E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.200E+01      DELTA H= 0.288E+04
        T           EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.         0.272E+04        0.188E+01       0.934309E+00      0.93E+00          0.32E+10       0.34E+10
      800.         0.282E+04        0.195E+01       0.119825E+01      0.12E+01          0.65E+10       0.54E+10
      900.         0.290E+04        0.200E+01       0.146340E+01      0.15E+01          0.11E+11       0.78E+10
     1000.         0.295E+04        0.203E+01       0.172355E+01      0.17E+01          0.18E+11       0.10E+11
     1100.         0.299E+04        0.205E+01       0.197444E+01      0.20E+01          0.26E+11       0.13E+11
     1200.         0.300E+04        0.205E+01       0.221339E+01      0.22E+01          0.35E+11       0.16E+11

REACTION # 63      CH2O+CL=CHO+HCL
DELTA N =   0    DELTA H(T =   300. K)= -1.286E+04 CAL/MOLE      DELTA S (T =   300. K) =  6.547E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.344E+01      DELTA H=-0.128E+05
        T           EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.127E+05        0.354E+01       0.317156E+06      0.32E+06          0.35E+14       0.11E+09
      800.        -0.127E+05        0.351E+01       0.101189E+06      0.10E+06          0.37E+14       0.36E+09
      900.        -0.128E+05        0.346E+01       0.414224E+05      0.41E+05          0.38E+14       0.91E+09
     1000.        -0.129E+05        0.341E+01       0.201719E+05      0.20E+05          0.39E+14       0.19E+10
     1100.        -0.130E+05        0.335E+01       0.111408E+05      0.11E+05          0.40E+14       0.36E+10
     1200.        -0.132E+05        0.329E+01       0.676073E+04      0.68E+04          0.41E+14       0.60E+10

REACTION # 64      CHO+O2=CO+HO2
DELTA N =   0    DELTA H(T =   300. K)= -3.330E+04 CAL/MOLE      DELTA S (T =   300. K) = -7.294E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.458E+00      DELTA H=-0.334E+05
        T           EF-EREV          LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.333E+05       -0.404E+00       0.174264E+11      0.17E+11          0.30E+13       0.17E+03
      800.        -0.334E+05       -0.426E+00       0.868027E+09      0.87E+09          0.30E+13       0.35E+04
      900.        -0.334E+05       -0.451E+00       0.839861E+08      0.84E+08          0.30E+13       0.36E+05
     1000.        -0.335E+05       -0.475E+00       0.129322E+08      0.13E+08          0.30E+13       0.23E+06
     1100.        -0.335E+05       -0.500E+00       0.279186E+07      0.28E+07          0.30E+13       0.11E+07
     1200.        -0.336E+05       -0.522E+00       0.776648E+06      0.78E+06          0.30E+13       0.39E+07
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REACTION # 65     CHO+HO2=CH2O+O2
DELTA N =   0   DELTA H(T =  300. K)= -4.158E+04 CAL/MOLE     DELTA S (T =  300. K) = -7.124E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.396E+01     DELTA H=-0.419E+05
        T            EF-EREV        LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.419E+05      -0.395E+01      0.235564E+12      0.24E+12         0.58E+13       0.25E+02
      800.        -0.419E+05      -0.397E+01      0.543831E+10      0.54E+10         0.76E+13       0.14E+04
      900.        -0.419E+05      -0.397E+01      0.289809E+09      0.29E+09         0.93E+13       0.32E+05
     1000.        -0.419E+05      -0.396E+01      0.277729E+08      0.28E+08         0.11E+14       0.40E+06
     1100.        -0.419E+05      -0.394E+01      0.408162E+07      0.41E+07         0.13E+14       0.31E+07
     1200.        -0.418E+05      -0.392E+01      0.827036E+06      0.83E+06         0.14E+14       0.17E+08

REACTION # 66     CO+OH=CO2+H
DELTA N =   0   DELTA H(T =  300. K)= -2.501E+04 CAL/MOLE     DELTA S (T =  300. K) = -1.266E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.555E+01     DELTA H=-0.240E+05
        T            EF-EREV        LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.245E+05      -0.589E+01      0.122919E+06      0.12E+06         0.13E+18       0.11E+13
      800.        -0.242E+05      -0.573E+01      0.137375E+05      0.14E+05         0.14E+18       0.11E+14
      900.        -0.240E+05      -0.558E+01      0.254259E+04      0.26E+04         0.16E+18       0.63E+14
     1000.        -0.237E+05      -0.544E+01      0.669166E+03      0.68E+03         0.18E+18       0.26E+15
     1100.        -0.235E+05      -0.531E+01      0.227255E+03      0.23E+03         0.19E+18       0.85E+15
     1200.        -0.232E+05      -0.519E+01      0.933492E+02      0.91E+02         0.21E+18       0.22E+16

REACTION # 67     CO+HO2=CO2+OH
DELTA N =   0   DELTA H(T =  300. K)= -6.161E+04 CAL/MOLE     DELTA S (T =  300. K) = -6.982E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.294E+01     DELTA H=-0.610E+05
        T            EF-EREV        LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.612E+05      -0.308E+01      0.595816E+18      0.59E+18         0.65E+07       0.11E-10
      800.        -0.611E+05      -0.301E+01      0.244203E+16      0.25E+16         0.54E+08       0.22E-07
      900.        -0.610E+05      -0.295E+01      0.342084E+14      0.35E+14         0.28E+09       0.82E-05
     1000.        -0.609E+05      -0.290E+01      0.113151E+13      0.11E+13         0.10E+10       0.93E-03
     1100.        -0.608E+05      -0.286E+01      0.698584E+11      0.70E+11         0.31E+10       0.44E-01
     1200.        -0.607E+05      -0.282E+01      0.688377E+10      0.68E+10         0.76E+10       0.11E+01

REACTION # 68     CO+O2=CO2+O
DELTA N =   0   DELTA H(T =  300. K)= -8.076E+03 CAL/MOLE     DELTA S (T =  300. K) = -6.676E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.273E+01     DELTA H=-0.732E+04
        T            EF-EREV        LN AF/AREV          KEQ            KEQ FIT          K FORWARD      K REVERSE
      700.        -0.765E+04      -0.295E+01      0.128284E+02      0.13E+02         0.25E+01       0.20E+00
      800.        -0.749E+04      -0.284E+01      0.649292E+01      0.65E+01         0.10E+03       0.15E+02
      900.        -0.732E+04      -0.274E+01      0.386773E+01      0.39E+01         0.18E+04       0.46E+03
     1000.        -0.715E+04      -0.265E+01      0.257970E+01      0.26E+01         0.17E+05       0.68E+04
     1100.        -0.698E+04      -0.257E+01      0.186650E+01      0.19E+01         0.11E+06       0.61E+05
     1200.        -0.681E+04      -0.250E+01      0.143453E+01      0.14E+01         0.54E+06       0.38E+06
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REACTION # 69     H+O2=O+OH
DELTA N =   0    DELTA H(T =   300. K)=  1.693E+04 CAL/MOLE      DELTA S (T =   300. K) =  5.980E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.282E+01      DELTA H= 0.167E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.        0.168E+05       0.294E+01      0.104365E-03     0.11E-03          0.13E+10       0.12E+14
     800.        0.168E+05       0.289E+01      0.472642E-03     0.47E-03          0.57E+10       0.12E+14
     900.        0.167E+05       0.284E+01      0.152118E-02     0.15E-02          0.18E+11       0.12E+14
    1000.        0.166E+05       0.278E+01      0.385510E-02     0.38E-02          0.47E+11       0.12E+14
    1100.        0.165E+05       0.274E+01      0.821323E-02     0.82E-02          0.10E+12       0.12E+14
    1200.        0.164E+05       0.269E+01      0.153673E-01     0.16E-01          0.19E+12       0.13E+14

REACTION # 70     H+H2O=H2+OH
DELTA N =   0    DELTA H(T =   300. K)=  1.518E+04 CAL/MOLE      DELTA S (T =   300. K) =  2.635E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.109E+02      DELTA H=-0.103E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.        0.154E+05       0.163E+01      0.949257E+00     0.30E-01          0.26E+08       0.28E+08
     800.        0.155E+05       0.164E+01      0.306993E-03     0.12E-01          0.17E+09       0.56E+12
     900.        0.155E+05       0.164E+01      0.904974E-03     0.58E-02          0.76E+09       0.84E+12
    1000.        0.154E+05       0.163E+01      0.214749E-02     0.33E-02          0.25E+10       0.12E+13
    1100.        0.154E+05       0.161E+01      0.434952E-02     0.20E-02          0.69E+10       0.16E+13
    1200.        0.154E+05       0.159E+01      0.782010E-02     0.14E-02          0.16E+11       0.21E+13

REACTION # 71     O2+AR=AR+2O
DELTA N =   1    DELTA H(T =   300. K)=  1.190E+05 CAL/MOLE      DELTA S (T =   300. K) =  2.794E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.358E+02      DELTA H= 0.254E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.        0.119E+06       0.331E+01      0.221388E-35     0.31E-23          0.71E-17       0.32E+19
     800.        0.119E+06       0.332E+01      0.187281E+01     0.31E-22          0.41E-13       0.22E-13
     900.        0.119E+06       0.331E+01      0.388237E-27     0.18E-21          0.34E-10       0.89E+17
    1000.        0.119E+06       0.330E+01      0.297897E-24     0.76E-21          0.76E-08       0.26E+17
    1100.        0.119E+06       0.328E+01      0.682130E-22     0.24E-20          0.63E-06       0.93E+16
    1200.        0.119E+06       0.326E+01      0.630443E-20     0.64E-20          0.25E-04       0.40E+16

REACTION # 72     H+HO2=2OH
DELTA N =   0    DELTA H(T =   300. K)= -3.660E+04 CAL/MOLE      DELTA S (T =   300. K) =  5.673E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.110E+01      DELTA H=-0.330E+05
       T          EF-EREV        LN AF/AREV        KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.       -0.367E+05       0.281E+01      0.484723E+13     0.61E+11          0.73E+14       0.15E+02
     800.       -0.368E+05       0.272E+01      0.177764E+12     0.32E+10          0.80E+14       0.45E+03
     900.       -0.370E+05       0.263E+01      0.309563E+01     0.31E+09          0.86E+14       0.28E+14
    1000.       -0.372E+05       0.254E+01      0.169092E+10     0.50E+08          0.91E+14       0.54E+05
    1100.       -0.373E+05       0.245E+01      0.307401E+09     0.11E+08          0.95E+14       0.31E+06
    1200.       -0.375E+05       0.237E+01      0.737422E+08     0.31E+07          0.99E+14       0.13E+07
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REACTION # 73      H+HO2=H2+O2
DELTA N =    0   DELTA H(T =   300. K)= -5.557E+04 CAL/MOLE     DELTA S (T =   300. K) = -1.866E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.152E+02      DELTA H=-0.739E+05
        T            EF-EREV         LN AF/AREV          KEQ             KEQ FIT            K FORWARD      K REVERSE
      700.        -0.556E+05       -0.904E+00       0.922357E+17       0.30E+17            0.15E+14       0.17E-03
      800.        -0.556E+05       -0.940E+00       0.622666E+15       0.39E+14            0.16E+14       0.26E-01
      900.        -0.557E+05       -0.980E+00       0.127095E+14       0.22E+12            0.17E+14       0.13E+01
     1000.        -0.558E+05       -0.102E+01       0.452879E+01       0.35E+10            0.18E+14       0.39E+13
     1100.        -0.559E+05       -0.106E+01       0.437367E+11       0.12E+09            0.18E+14       0.42E+03
     1200.        -0.559E+05       -0.110E+01       0.518625E+10       0.71E+07            0.19E+14       0.36E+04

REACTION # 74      O+HO2=OH+O2
DELTA N =    0   DELTA H(T =   300. K)= -5.353E+04 CAL/MOLE     DELTA S (T =   300. K) = -3.063E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.218E+02      DELTA H=-0.862E+05
        T            EF-EREV         LN AF/AREV          KEQ             KEQ FIT            K FORWARD      K REVERSE
      700.        -0.535E+05       -0.134E+00       0.464451E+17       0.28E+18            0.20E+14       0.43E-03
      800.        -0.536E+05       -0.171E+00       0.376107E+15       0.12E+15            0.20E+14       0.53E-01
      900.        -0.537E+05       -0.209E+00       0.884456E+13       0.30E+12            0.20E+14       0.23E+01
     1000.        -0.537E+05       -0.248E+00       0.438619E+12       0.24E+10            0.20E+14       0.46E+02
     1100.        -0.538E+05       -0.285E+00       0.607122E+01       0.46E+08            0.20E+14       0.33E+13
     1200.        -0.539E+05       -0.321E+00       0.479864E+10       0.17E+07            0.20E+14       0.42E+04

REACTION # 75      OH+HO2=H2O+O2
DELTA N =    0   DELTA H(T =   300. K)= -7.076E+04 CAL/MOLE     DELTA S (T =   300. K) = -4.501E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.351E+02      DELTA H=-0.123E+06
        T            EF-EREV         LN AF/AREV          KEQ             KEQ FIT            K FORWARD      K REVERSE
      700.        -0.710E+05       -0.254E+01       0.120571E+22       0.13E+24            0.20E+14       0.17E-07
      800.        -0.711E+05       -0.258E+01       0.202827E+19       0.20E+19            0.20E+14       0.99E-05
      900.        -0.711E+05       -0.262E+01       0.140441E+17       0.38E+15            0.20E+14       0.14E-02
     1000.        -0.712E+05       -0.265E+01       0.262002E+15       0.39E+12            0.20E+14       0.76E-01
     1100.        -0.713E+05       -0.267E+01       0.100555E+14       0.14E+10            0.20E+14       0.20E+01
     1200.        -0.713E+05       -0.270E+01       0.763138E+01       0.13E+08            0.20E+14       0.26E+13

REACTION # 76      O+HCL=OH+CL
DELTA N =    0   DELTA H(T =   300. K)=  9.099E+02 CAL/MOLE     DELTA S (T =   300. K) =  2.709E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.298E+00      DELTA H= 0.108E+04
        T            EF-EREV         LN AF/AREV          KEQ             KEQ FIT            K FORWARD      K REVERSE
      700.         0.104E+04        0.274E+00       0.621667E+00       0.62E+00            0.53E+11       0.85E+11
      800.         0.107E+04        0.290E+00       0.683460E+00       0.68E+00            0.93E+11       0.14E+12
      900.         0.108E+04        0.299E+00       0.736766E+00       0.74E+00            0.15E+12       0.20E+12
     1000.         0.109E+04        0.304E+00       0.782926E+00       0.78E+00            0.21E+12       0.27E+12
     1100.         0.109E+04        0.306E+00       0.823082E+00       0.82E+00            0.28E+12       0.34E+12
     1200.         0.110E+04        0.307E+00       0.858223E+00       0.86E+00            0.36E+12       0.42E+12
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REACTION # 77     OH+HCL=CL+H2O
DELTA N =   0   DELTA H(T =  300. K)= -1.631E+04 CAL/MOLE     DELTA S (T =  300. K) = -3.924E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.211E+01     DELTA H=-0.164E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.164E+05      -0.213E+01     0.161384E+05     0.16E+05          0.11E+13       0.69E+08
      800.       -0.164E+05      -0.212E+01     0.368577E+04     0.37E+04          0.12E+13       0.33E+09
      900.       -0.164E+05      -0.211E+01     0.116989E+04     0.12E+04          0.13E+13       0.11E+10
     1000.       -0.164E+05      -0.210E+01     0.467668E+03     0.47E+03          0.14E+13       0.30E+10
     1100.       -0.163E+05      -0.208E+01     0.221134E+03     0.22E+03          0.15E+13       0.67E+10
     1200.       -0.163E+05      -0.207E+01     0.118611E+03     0.12E+03          0.15E+13       0.13E+11

REACTION # 78     2CL+AR=CL2+AR
DELTA N =  -1   DELTA H(T =  300. K)= -5.778E+04 CAL/MOLE     DELTA S (T =  300. K) = -2.570E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.189E+01     DELTA H=-0.572E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.573E+05      -0.192E+01     0.112244E+18     0.11E+18          0.85E+15       0.76E-02
      800.       -0.572E+05      -0.191E+01     0.652733E+15     0.65E+15          0.73E+15       0.11E+01
      900.       -0.572E+05      -0.189E+01     0.119305E+14     0.12E+14          0.64E+15       0.54E+02
     1000.       -0.572E+05      -0.187E+01     0.486329E+12     0.49E+12          0.58E+15       0.12E+04
     1100.       -0.571E+05      -0.186E+01     0.355320E+11     0.36E+11          0.53E+15       0.15E+05
     1200.       -0.571E+05      -0.184E+01     0.402138E+10     0.40E+10          0.50E+15       0.12E+06

REACTION # 79     CL+H2=HCL+H
DELTA N =   0   DELTA H(T =  300. K)=  1.129E+03 CAL/MOLE     DELTA S (T =  300. K) =  1.288E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N = 0.475E+00     DELTA H= 0.953E+03
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.        0.982E+03       0.496E+00     0.809997E+00     0.81E+00          0.11E+13       0.13E+13
      800.        0.958E+03       0.479E+00     0.883777E+00     0.88E+00          0.17E+13       0.19E+13
      900.        0.945E+03       0.471E+00     0.944536E+00     0.94E+00          0.25E+13       0.26E+13
     1000.        0.942E+03       0.470E+00     0.995706E+00     0.10E+01          0.33E+13       0.33E+13
     1100.        0.947E+03       0.472E+00     0.103969E+01     0.10E+01          0.42E+13       0.41E+13
     1200.        0.956E+03       0.476E+00     0.107811E+01     0.11E+01          0.52E+13       0.48E+13

REACTION # 80     CL+HO2=HCL+O2
DELTA N =   0   DELTA H(T =  300. K)= -5.444E+04 CAL/MOLE     DELTA S (T =  300. K) = -5.772E-01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=  700. TO 1200.  DELTA S/R - DELTA N =-0.517E+00     DELTA H=-0.548E+05
        T          EF-EREV        LN AF/AREV         KEQ          KEQ FIT          K FORWARD      K REVERSE
      700.       -0.546E+05      -0.408E+00     0.747106E+17     0.75E+17          0.11E+14       0.15E-03
      800.       -0.547E+05      -0.461E+00     0.550298E+15     0.55E+15          0.11E+14       0.21E-01
      900.       -0.547E+05      -0.508E+00     0.120046E+14     0.12E+14          0.12E+14       0.97E+00
     1000.       -0.548E+05      -0.552E+00     0.560231E+12     0.56E+12          0.12E+14       0.21E+02
     1100.       -0.549E+05      -0.591E+00     0.454724E+11     0.45E+11          0.12E+14       0.26E+03
     1200.       -0.550E+05      -0.628E+00     0.559137E+10     0.56E+10          0.12E+14       0.21E+04
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REACTION # 81     CL+HO2=CLO+OH
DELTA N =   0    DELTA H(T =   300. K)=  1.291E+03 CAL/MOLE     DELTA S (T =   300. K) =  3.755E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N = 0.206E+01     DELTA H= 0.139E+04
       T           EF-EREV        LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.        0.146E+04       0.210E+01      0.287332E+01      0.29E+01          0.13E+13       0.47E+12
     800.        0.144E+04       0.209E+01      0.327353E+01      0.33E+01          0.16E+13       0.50E+12
     900.        0.140E+04       0.207E+01      0.361574E+01      0.36E+01          0.19E+13       0.53E+12
    1000.        0.135E+04       0.204E+01      0.390530E+01      0.39E+01          0.22E+13       0.56E+12
    1100.        0.128E+04       0.201E+01      0.414824E+01      0.41E+01          0.24E+13       0.59E+12
    1200.        0.121E+04       0.198E+01      0.435053E+01      0.44E+01          0.27E+13       0.61E+12

REACTION # 82     CLO+CO=CL+CO2
DELTA N =   0    DELTA H(T =   300. K)= -6.290E+04 CAL/MOLE     DELTA S (T =   300. K) = -1.074E+01 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.500E+01     DELTA H=-0.624E+05
       T           EF-EREV        LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.       -0.627E+05      -0.519E+01      0.207362E+18      0.20E+18          0.11E+11       0.51E-07
     800.       -0.625E+05      -0.510E+01      0.745993E+15      0.75E+15          0.16E+11       0.21E-04
     900.       -0.624E+05      -0.502E+01      0.946096E+13      0.96E+13          0.22E+11       0.23E-02
    1000.       -0.622E+05      -0.494E+01      0.289736E+12      0.29E+12          0.28E+11       0.97E-01
    1100.       -0.621E+05      -0.487E+01      0.168405E+11      0.17E+11          0.34E+11       0.20E+01
    1200.       -0.619E+05      -0.479E+01      0.158228E+10      0.16E+10          0.41E+11       0.26E+02

REACTION # 83     CH3+CLO=CH3CL+O
DELTA N =   0    DELTA H(T =   300. K)= -1.935E+04 CAL/MOLE     DELTA S (T =   300. K) = -6.008E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.334E+01     DELTA H=-0.196E+05
       T           EF-EREV        LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.       -0.197E+05      -0.341E+01      0.458072E+05      0.46E+05          0.34E+12       0.74E+07
     800.       -0.196E+05      -0.339E+01      0.782720E+04      0.78E+04          0.48E+12       0.62E+08
     900.       -0.196E+05      -0.336E+01      0.198662E+04      0.20E+04          0.64E+12       0.32E+09
    1000.       -0.195E+05      -0.331E+01      0.666025E+03      0.67E+03          0.80E+12       0.12E+10
    1100.       -0.194E+05      -0.326E+01      0.273584E+03      0.27E+03          0.96E+12       0.35E+10
    1200.       -0.193E+05      -0.320E+01      0.130923E+03      0.13E+03          0.11E+13       0.86E+10

REACTION # 84     CH3+CLO=CH3O+CL
DELTA N =   0    DELTA H(T =   300. K)= -2.651E+04 CAL/MOLE     DELTA S (T =   300. K) = -7.742E+00 CAL/DEG/MOLE
(THERMO VALUES IN PREVIOUS LINE HAVE 1 ATMSTANDARD STATE)
 T(K)=   700. TO 1200.  DELTA S/R - DELTA N =-0.455E+01     DELTA H=-0.271E+05
       T           EF-EREV        LN AF/AREV         KEQ           KEQ FIT          K FORWARD      K REVERSE
     700.       -0.271E+05      -0.457E+01      0.298269E+07      0.30E+07          0.44E+13       0.15E+07
     800.       -0.271E+05      -0.458E+01      0.261050E+06      0.26E+06          0.48E+13       0.18E+08
     900.       -0.271E+05      -0.457E+01      0.392653E+05      0.39E+05          0.51E+13       0.13E+09
    1000.       -0.270E+05      -0.453E+01      0.864707E+04      0.87E+04          0.54E+13       0.63E+09
    1100.       -0.269E+05      -0.449E+01      0.251618E+04      0.25E+04          0.57E+13       0.23E+10
    1200.       -0.268E+05      -0.444E+01      0.903080E+03      0.90E+03          0.59E+13       0.66E+10
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