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# High Temperature Combustion of Selected Chlorinated Hydrocarbons.

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HIGH TEMPERATURE COMBUSTION OF SELECTED CHLORINATED HYDROCARBONS

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# HIGH TEMPERATURE COMBUSTION OF SELECTED CHLORINATED HYDROCARBONS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical Engineering

by
David Leslie Miller
B.S.M.E., Louisiana State University, 1976
M.S.M.E., Louisiana State University, 1979
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Most importantly, the author wishes to express his appreciation to his parents for their encouragement and support in this and all other undertakings.

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# ABSTRACT

A study combining ignition delay measurements and quenched product distributions from shock-tube experiments with chlorinated hydrocarbons has been conducted to develop a better understanding of the combustion characteristics of these compounds which are candidates for incineration. The ignition delay times of selected $C_1$, $C_2$ and $C_6$ chlorinated hydrocarbon- stoichiometric oxygen mixtures have been measured behind reflected shock waves at a pressure of 1.8 atm over the temperature range 1200- 1700 K. Studies were also conducted with mixtures of chlorinated and non-chlorinated hydrocarbons to examine the effect of chlorine atom/ hydrogen atom ratio on ignition delay behavior. The results indicate that contrary to conventional wisdom the chlorinated hydrocarbons are not more difficult to ignite than the analogous hydrocarbon. Quenched product distributions in shock- tube studies of the pyrolysis and oxidation of methane, methyl chloride and dichloromethane were determined at a total density of $7.5 \pm 0.5 \times 10^{-7}$ mol/cc over the temperature range 1200- 2700 K. The product distributions indicate that there is a much larger propensity to produce soot and priority organic pollutants as the chlorine atom/ hydrogen atom ratio of the reactants increased. The first chemical kinetic mechanism including detailed chemistry for the $C_1$ and $C_2$ chlorinated hydrocarbons has been developed. The mechanism contains

432 reactions and 59 chemical species. This model was used to identify the importance of $C_2$ chlorinated hydrocarbons during the pre-ignition oxidation of methyl chloride.

# CHAPTER I

# INTRODUCTION

The United States Environmental Protection Agency (USEPA) estimates that between 90 and 110 million metric tons of the chemical by-products generated annually are hazardous(1- 3). The production of hazardous compounds in these magnitudes threatens to pose a significant health problem. Since the hazardous nature of many of these wastes has only recently been identified, economic considerations have been the principal factors controlling the design of chemical processes in which they are generated. With the verification of the hazardous nature (toxic, carcinogenic, mutagenic and tutagenic) of many of these waste products, judicial and/or legislative actions have begun to force industries in the United States to accept responsibility for the environmental fate of the by-products from their processes.

The major legislation controlling the handling of hazardous chemicals is the Resource Conservation and Recovery Act of 1976 (RCRA) (4). This law mandates the USEPA to develop a national plan minimizing the hazards involved in all aspects of hazardous waste management: transportation, disposal, treatment and storage. There are two complementary laws which have as a similar goal the protection of the public:

1. Toxic Substance Control Act, 1976 (5). Under the auspices of this legislation the manufacture, transport and use of toxic substances may be regulated. The first compounds to be controlled were polychlorinated biphenyls (PCB's) for which the manufacture and use was banned and strict requirements were established for proper disposal methods(6).
2. Comprehensive Environmental Response, Compensation and Liability Act, 1980 (CERCLA or Superfund) (7). CERCLA was established to remedy the problems caused by the improper waste disposal practices used in the past.

Historically, industry has disposed of hazardous wastes in various ways. The first is to release the wastes into a flowing waterway, reasoning that dilution and biological action would passify the wastes. This method of "disposal" has been illegal since 1972 with the passage of the Clean Water Act (8). The major techniques which are still used include: storage in secure landfills, deep well injection into a stable geological structure and incineration. Several new technologies appear promising - destruction by genetically engineered microbes, wet-oxidation, and supercritical extraction - but require further development for practical use. With the nationwide publicity of Love Canal, New York and similar situations (9), the technical community has begun to realize that landfills and deep-well injection are not permanent solutions to the disposal of hazardous wastes. Since the environmental lifetime of many hazardous wastes is measured in hundreds of years, landfills and injection wells are nothing more than methods of storing the waste for future generations. Additionally, the understanding of these processes is not developed to a stage where their safety can be guaranteed for long periods of time; earthquakes, floods, tornadoes, hurricanes, et cetera can affect their integrity. Therefore, incineration has become the preferred hazardous waste control technology for combustible organic compounds (1, 10).

In principle, a properly designed and operated incinerator reduces a hazardous waste into water, carbon dioxide, low-volume ash, a hydrogen-X atom (HXn) chemical species - such as a hydrogen halide acid for halogenated hazardous wastes and metal salts if the waste stream contains dissolved metals. Unfortunately, the present understanding of the incineration process is incomplete and cannot provide an estimate, a priori, of the performance of any incinerator. This is because the combustion of wastes in an incinerator is dependent on a large number of interrelated, complex phenomena: residence time of the fuel, temperature, flow field characteristics, atomization patterns and vaporization rates of the liquid, diffusion of the gases within the incinerator, mass flow rate of the organic compound, overall stoichiometry, as well as the chemical structure and characteristics of the liquid fuel (11, 12).

In an attempt to deal with this complexity, the USEPA has chosen to regulate the incineration of hazardous wastes through a "permit" system (13- 16). This procedure requires trial burns of a proposed hazardous waste incinerator during which each of the following criteria must be met:

1. A destruction and removal efficiency (DRE) of chemical A defined as

$$\text{DRE} = \left[1 - \frac{\text{mass A exhaust}}{\text{mass A inlet}}\right] \text{X } 100 \qquad (1)$$

   must be greater than 99.99 percent for one or more selected components of the waste stream;

2. The particulate emission must be less than 180 milligrams per dry standard cubic meter (0.08 grains per dry standard cubic foot) corrected to 7 percent molecular oxygen in the stack gas;

3. The removal of hydrogen chloride to 1

percent of the uncontrolled emission or
0.505 grams per second (4 lbm per hour),
whichever is greater;

before a permit is granted.

The components of the waste stream whose destruction in the exhaust must be controlled are chosen by the permit writer from a list of priority organic pollutants compiled by the USEPA (the so-called Appendix VIII compounds(13, 14)). The compounds so selected are called the Principal Organic Hazardous Wastes (POHC's) of the particular waste stream. Current USEPA guidelines to permit writers suggest selecting POHC's on the basis of mass fraction, the thermal oxidation stability (TOS) and possible environmental hazard of the compounds in the waste stream (17- 19).

One problem with this system is that there is no universally accepted measure of TOS. The USEPA suggests using heat of combustion (kJ/g) as the ranking criteria, however several other parameters have been proposed:

chemical kinetic considerations such as bond dissociation energy (20, 21);

autoignition temperature (22, 23);

thermal oxidation and thermal decomposition under nonflame conditions (24, 25);

linear regression models based upon autoignition temperature and structural considerations (26, 27);

and toxicity (28).

A second difficulty with a trial burn is the expense and possible environmental damage from a failure. The possibility of failure has produced suggestions to test the DRE of incinerators by using a surrogate compound which is highly stable under incineration conditions, but not hazardous (29, 30).

The problem, therefore, is to develop sufficient understanding of the incineration of hazardous wastes that the public welfare can be protected. As the incineration process is a complex interaction of physical and chemical phenomena it is important to divide the process into smaller parts. One important component of the incineration process is the high-temperature chemical reaction kinetics of the hazardous wastes. Therefore, in order to suggest appropriate operating conditions in existing hazardous waste incinerators, to ensure the effective destruction of hazardous wastes, and to develop additional insight into future incinerator design requirements and research needs, requires among other things, the development of a better understanding of the combustion characteristics of hazardous wastes. The combustion characteristics of hazardous wastes can only be understood if data and theoretical analyses are developed which identify the chemical kinetic pathways for the destruction of hazardous wastes. This information can then be used for the development of combustion models in incineration systems.

One major family of hazardous wastes is the chlorinated hydrocarbons (CHC's), principally used as industrial degreasers and paint removers or feedstocks in the manufacture of refrigerants, pesticides and polymers. Since this family comprises approximately one-third of the organic priority pollutants (22), and most are candidates for incineration, it is important to begin investigating the combustion of these hazardous wastes (22).

One important measure of gas phase oxidative reactivity of a fuel is its ignition delay time, defined as the interval between the initial exposure of a fuel/ oxidizer mixture to a reaction temperature and the occurance of the principal exothermicity of the reactions. This exothermicity is signified by a sudden increase in temperature and pressure. The duration of this ignition delay time is governed by the overall kinetics of the combustion reactions, and measurements of ignition delay time have been useful in determining the combustion characteristics of a wide variety of fuels (31- 33).

Therefore, as one phase of a multi-component research program at Louisiana State University, the ignition delay times of selected $C_1$ and $C_2$ chlorinated hydrocrabons and chlorobenzene have been studied experimentally. These data have been used to develop the first detailed kinetic model, including $C_2$ CHC reactions, of the pre- ignition oxidation of methyl chloride.

# CHAPTER II

# LITERATURE SURVEY

## A. INTRODUCTION

Studies of the gas phase kinetics of chlorinated hydrocarbons (CHC's) have been performed in three significantly different chemical environments. These include pilot plant/full scale incinerators, laboratory high temperature facilities and laboratory room temperature facilities. Each provides a different insight toward developing an understanding of the combustion phenomena.

In full scale/pilot plant incineration experiments, known quantities of CHC's are added to the normal fuel stream of the incinerator. The exhaust gases are then sampled and analyzed to determine the concentration of the reactant CHC and any other CHC which may be formed. This provides a measure of the destruction and removal efficiency (DRE) of the individual incinerator for the particular CHC introduced into the fuel stream. This DRE is actually a measure of the "integrated" effects of all the physical/chemical phenomena which occur within the incinerator.

The laboratory scale moderate and high temperature chemical kinetics of CHC's under pyrolyzing, oxidizing and chemically reducing conditions have been studied in flames, flow reactors and shock tubes. These studies simplify the physical phenomena which occur during the destruction of the CHC and, therefore, provide more detailed information concerning the chemical kinetic parameters which control the destruction of the CHC.

The reactions of CHC's have also been studied in room temperature experiments to examine their influence on the chemistry which controls the removal of the ozone from the troposphere. This work began during the 1960's and 1970's when CHC's were considered the principal cause of the depletion of the ozone layer of the earth. While significantly different from the environment of an incinerator, such studies provide the most complete data on the rates of elementary chemical reactions involving chlorine (Cl), hydrogen (H) and oxygen (O) containing molecules.

The following literature survey is divided into three parts discussing first pilot plant/full scale incineration studies, laboratory scale studies and finally modeling efforts to develop relationships between the laboratory scale and full scale results . The kinetic studies for atmospheric conditions will be considered in the chapter which discusses the development of the chemical kinetic model for the CHC's.

## B. FULL SCALE/PILOT PLANT STUDIES

Until the early 1970's incineration research was limited to programs designed to minimize carbon monoxide

(CO) and smoke emissions in order to fine tune the combustion process and attempt to reduce the emission of odors which offended the public (35, 36). The first series of studies with hazardous wastes in conventional incineration systems was performed by the research divisions of boiler and incinerator manufacturers to determine the performance characteristics of their products (37- 39). These reports were designed to establish that the incineration units could be operated with the wastes as fuel and that the construction materials could survive the high temperature and corrosive environments encountered in the exhaust from the combustion of CHC's. In these studies incinerator performance was determined by measuring the emission of CO and unburnt hydrocarbons (HC's) (38).

As the hazardous nature of the candidates for incineration became apparent, the necessity to identify, measure and control the hazardous components in the exhaust stream was recognized. Therefore, the first task of the United States Environmental Protection Agency (USEPA) was to establish criteria for identifying hazardous chemicals. In 1978 (13) the USEPA released a list of priority organic pollutants which were determined to require control. (This list is included in Appendix VIII of (13) and the hazardous chemicals on the list are often called the Appendix VIII compounds.) To control the incineration of these hazardous materials, the USEPA implemented the permitting procedure described in the introduction. These regulations required the designation of selected chemicals in a fuel stream as Principal Organic Hazardous Components (POHC'S) ( 17). In order to obtain a permit to operate an incinerator for the destruction of hazardous wastes, it is necessary to demonstrate a minimum destruction and removal efficiency (DRE), as defined by equation 1, for each POHC in the waste stream.

Since the enactment of RCRA, the exhaust emissions from numerous boilers, incinerators and cement kilns have been evaluated (40- 46). Generally these studies indicated that under design conditions the wastes were consumed to the required DRE of 99.99 percent. Unfortunately there have also been studies indicating that DRE of POHC's selected from components of the inlet stream may not be the appropriate control parameter. Incinerators and boilers which remove the POHC to a level below 99.99 percent have been shown to emit priority organic compounds formed as intermediates during the combustion, called Products of Incomplete Combustion (PIC's), high levels of soot and polychlorinated- dibenzo-p- dioxins (PCDD's) (47- 51 and references therein).

The formation of PIC's has been documented recently by Castaldini et al (44). In this study, the exhaust gas emissions from eight industrial boilers whose fuel stream had been spiked with a mixture of carbon tetrachloride ($CCL_4$), chlorobenzene ($C_6H_5Cl$) and trichloroethene ($C_2HCl_3$) were analyzed. Under normal operating conditions a DRE greater than 99.99 percent was achieved at almost all of the sites. When low DRE's occurred, they could be correlated with non-design operating conditions such as unsteady operation, burner instability, improper burner settings, instability of feed rate and insufficient combustion air.

These results are encouraging with respect to the destruction of POHC's in industrial furnaces; however, the exhaust gases were reported to contain organic priority pollutants which were not in the original feed stream at levels of one to two orders of magnitude greater than the measured POHC concentration. This demonstrates that a hazardous waste incinerator which is operating legally at a DRE of 99.99 percent with respect to the designated POHC may be emitting significantly larger quantities of one or more PIC which are also regarded as hazardous pollutants.

An additional problem which has been determined in the incineration of chlorinated hydrocarbons is the demonstrated potential of CHC's to promote soot formation (47- 50). This is of special significance because it has been suggested that the formation of PCDD's is controlled by the presence of reactive surfaces such as soot or fly ash (51).

These studies indicate the need for a better understanding of the incineration process. In particular, there are major uncertainties in the identity of the chemical kinetic processes which control the destruction of

CHC's and the formation of PIC's.

## C. LABORATORY STUDIES

### 1. Non-Flame Reactors

The thermal stability both with and without oxygen of CHC's has been reported by the University of Dayton Research Institute, Union Carbide and Environment Canada (24- 26, 52- 62). In all of these studies the reactor vessel was an uncoated quartz capillary column which was coiled in a racetrack configuration inside a high temperature furnace.

In the Dayton studies (24,25, 52- 55, 58- 60, 62) the capillary columns (1 mm nominal diameter) were coiled ( 3.5 turns, 1 meter) within the central zone of a three zone Lindberg furnace. The furnace could be controlled to within ±1 °C from room temperature to 1500K. The effluent from the reactor zone was swept through a heated transfer line to a 30:1 gas phase splitter with the smaller fraction being directed into a gas chromatograph where it was condensed in the first few centimeters of a fused silica capillary column manitained at -30 °C. The analysis of the collected sample was begun when the gas chromatograph oven was temperature programmed and the sample vaporized. The concentration of the test hazardous material was measured by either flame ionization, mass spectrometric or Hall detectors. Solid, liquid and gas phase reactants were studied by using various freeze trapping and heating systems. Following these procedures it was possible to determine the destruction efficiency of each CHC at various temperatures and reaction times.

The experimental studies performed at Union Carbide (26, 56, 57) used an experimental facility similar to that developed by the researchers at Dayton. The reactor column was slightly longer (1.3 m) and the reaction was quenched by a jet of cold air upon exiting the furnace . The cooled reaction gas was then fed into a gas chromatograph equipped with a flame ionization detector through 3mm external diameter tubing.

In order to reduce the possible surface reactions, the Environment Canada study (61) substituted a 2 mm diameter quartz column for the 1 mm reactor column used at Dayton and Union Carbide. They also chose to trap their reactor effluent in methanol. This allowed them to use a liquid syringe for introduction of the sample into a gas chromatograph equipped with a mass spectrometric detector.

A wide range of hazardous wastes has been studied in these facilities and the data reported are usually the temperature required for a DRE of 99.99 percent to occur within a reaction time of 2 seconds, a typical gas residence time within an incinerator. The most recent papers (57, 61, 62) have also reported global rate expressions for the destruction of hazardous materials. A summary of their results for chlorinated hydrocarbons are listed in Table 1. While the temperatures necessary for a DRE of 99.99 percent in a reaction time of 2 seconds is similar for those compounds that were studied by more than one group, the rate parameters vary significantly.

The results of these studies have been criticized for several reasons:

1. The potential for heterogeneous reaction in the small diameter tubes employed as reactors is large.
2. The studies are generally performed at temperatures below those encountered in incinerators.
3. The methods for injection of the reactants into the high temperature furnace do not provide a controlled and known time zero for the reaction, and therefore produce errors in evaluating the overall rate parameters.
4. The global rate parameters are determined assuming first order kinetics with respect to the reactant. Data from experiments with as much as 90 percent reaction are used in these calculations. It is unlikely that the reaction order is the same over this wide range of reactant concentrations.

| Compound | $T_{99.99}$(2s) (K) | $Log_{10}A$ ($s^{-1}$) | E (kJ/mol) | Ref. |
|---|---|---|---|---|
| Methane | 1143 | 9.5 + 0.5 | 200 + 12 | 62 |
| | 1081 | 11.2 | 218 | 26 |
| Methyl Chloride | 1096 | 8.9 | 171 | 26 |
| Dichloromethane | 1053 | 12.8 + 11 | 259 + 220 | 62 |
| Chloroform | 963 | 12.5 + 2.0 | 205 + 33 | 62 |
| Carbon Tetrachloride | 1093 | 5.5 + 0.9 | 108 + 16 | 62 |
| Ethane | 1058 | 5.1 + 1.8 | 100 + 33 | 62 |
| | 993 | 14.8 | 266 | 26 |
| 1,2- Dichloroethane | 907 | 11.7 | 191 | 26 |
| 1,1,1- Trichloroethane | 873 | 8.3 + 1.0 | 134 + 16 | 62 |
| Hexachloroethane | 913 | 7.3 + 1.5 | 126 + 25 | 62 |
| Vinyl Chloride | 995 | 14.6 | 265 | 26 |
| Tetrachloroethene | 1193 | 6.4 + 1.0 | 138 + 20 | 62 |
| Benzene | 1033 | 8.6 + 1.4 | 163 + 25 | 62 |
| | 990 | 21.9 | 401 | 26 |
| Chlorobenzene | 1053 | 4.9 + 3.5 | 96 + 63 | 62 |
| | 1018 | 17.1 | 320 | 26 |
| 1,2- Dichlorobenzene | 1053 | 8.6 + 2.9 | 167 + 54 | 62 |
| 1,2,4- Trichlorobenzene | 1063 | 8.3 + 2.8 | 163 + 54 | 62 |
| 1,2,3,4- Tetrachlorobenzene | 1123 | 6.3 + 3.8 | 125 + 75 | 62 |
| Hexachlorobenzene | 1153 | 8.4 + 4.6 | 171 + 92 | 62 |
| Pentachlorophenol | -- | 0.38 | 9.62 | 61 |
| 2,4,6- Trichlorophenol | -- | 1.90 | 34.3 | 61 |
| 2,3,4,5- Tetrachlorophenol | -- | 2.67 | 49.4 | 61 |
| 2,4,5- Trichlorophenol | -- | 2.82 | 85.9 | 61 |

Table 1. Summary of non- flame studies (24- 26, 52- 62) of chlorinated hydrocarbons.

## 2. Flame Studies

The combustion of CHC's at flame conditions has received relatively limited attention in the past. Early studies were directed primarily toward investigating the inhibition of hydrocarbon/oxygen flames by CHC's (63- 66). These studies have shown that the main effect of inhibition in hydrocarbon flames is caused by chlorine atom (Cl) reaction with hydrogen atom (H), removing them from the pool of reacting species, and thus reducing the rate of the main chain branching reaction

$$H + O_2 = OH + O.$$

Recently there have been several attempts at detailed kinetic modeling of these halogen inhibited flames by Westbrook (67- 69), Schefer and Brown (70) and Galant (71). They have been successful in simulating the inhibition effects on flame speed by adding one halogen decomposition reaction followed by several radical scavenging steps by the halogen atom to the basic hydrocarbon reaction mechanism. In both the modeling and experimental studies, the concentrations of the CHC's were low and hence the flames which were studied maintained the principal characteristics of the non-chlorinated hydrocarbon fuels.

Until the recent interest in the incineration of hazardous compounds the only flame zone studies of pure chlorinated hydrocarbons were those of Kaesche- Krischer (72, 73). In these studies of premixed trichloroethene

($C_2HCl_3$) in oxygen enriched air flames, the flame speed as a function of stoichiometry was reported. A two stage flame zone was also observed. While the presence of Cl-atom was the apparent cause of the phenomena no kinetic explanation for the effect was developed. Additionally, a different definition of stoichiometry for CHC's than that accepted today (11, 47) was used in these studies.

In order to develop a model for this behavior, Bose and Senkan (74, 75) have reexamined the $C_2HCl_3$-air flame. The experiments were performed using an atmospheric pressure premixed laminar flat flame burner with a nitrogen shroud. As in the studies of Kaesche-′Krischer (72, 73) oxygen enriched air was necessary to produce a stable flame. Product distributions as a function of distance from the burner for various equivalence ratios were reported. These investigators also reported a two-stage flame as indicated by several diagnostics: two luminous zones, two rises in temperature and a distinct drop in CO concentration at a particular height above the burner. They presented a basic explanation for the two-stage flame phenomenon based upon the inhibition of the oxidation of carbon monoxide by atomic chlorine. This is consistent with the work of Palmer and Seery (76) and unpublished results in the Combustion Laboratory at Louisiana State University (77).

The burning velocities for the chlorinated methanes, trichloroethene and chlorobenzene have been determined by Valeiras et al (78) and Gupta and Valeiras (79). Direct image photography of a stoichiometric laminar flame supported on a quartz bunsen burner provided a measure of the area of the flame front. When combined with rotameter measurements of the volumetric flow rate of the fuel/ oxidizer mixture the flame velocity could be calculated. The results indicated that CHC flames have significantly lower burning velocities than non-chlorinated hydrocarbon flames.

Product distributions from laminar flat flame studies of several methyl chloride ($CH_3Cl$), $CH_3Cl$/methane ($CH_4$) and dichloromethane ($CH_2Cl_2$)/$CH_4$ mixtures in air have recently been reported by Cundy and Senser (80), Senser and Cundy (81) and Miller et al (82). The premixed flames were stabilized on a water-cooled stainless steel sintered disk type burner with a nitrogen shroud. This assembly is located within a closed Pyrex cross connected to a vacuum exhaust system to contain any hazardous combustion products and allow subatmospheric operation. The experiments were performed for a range of stoichiometries and CHC/HC ratios with the concentration of fuels and major products presented as a function of distance from the burner. These results indicate that more heavily chlorinated compounds which are themselves priority pollutants are formed during the combustion of $CH_3Cl$ and $CH_2Cl_2$. They also measured significantly higher levels of acetylene ($C_2H_2$), which is presumably a precursor to soot formation, in the chlorinated flames. Analysis of the concentration profiles of the reactants corrected for diffusion (80) also indicate that the first order kinetic models of Dellinger (62) are not as conservative at predicting destruction and removal efficiency as they have been assumed to be by furnace modelers (83- 86).

The sooting tendencies of chlorinated hydrocarbons have been examined by Senkan et al (47). Using the same flat flame burner as in (74), they determined soot formation limits for a number of chlorinated methanes, ethanes, ethenes and benzene mixtures in air flames. The formation of soot was observed at lower equivalence ratios as the chlorine content of the fuel was increased. Soot formation also increased as the ratio of CHC/HC on a molar basis increased.

A study of the reactions of droplets of hazardous waste which pass through a flame zone has been performed by Kramlich et al (87). Using a methane-air flat flame into which a simulated hazardous waste stream containing acrylonitrile ($C_3H_3N$), benzene ($C_6H_6$), chlorobenzene ($C_6H_5Cl$) and chloroform ($CHCl_3$) were sprayed, the DRE for each component was determined. Under normal operating conditions a DRE of greater than 99.99 percent was measured for all the species.

The reactor was operated at reduced values of DRE by lowering the flame temperature with the addition of nitrogen for both oxygen rich (10% excess $O_2$) and oxygen poor (0.25 stoichiometric $O_2$) flames. This produced two different destructibility rankings. In environments where no droplet ignition occurs $C_6H_6$ was the most difficult to destroy followed by $C_6H_5Cl$, $CHCl_3$ and $C_3H_3N$; whereas the destructibility of the species ranked $C_6H_6$, $C_6H_5Cl$, $C_3H_3N$ and $CHCl_3$ when droplets did ignite.

A laboratory turbulent flame reactor study performed in conjunction with the droplet study has also shown that under design operating conditions a DRE of 99.99 percent could be achieved for a variety of hazardous materials. Low values of DRE were associated with allowing the flame to impinge on a cold surface, running at high excess air, using widely varying fuel feed rates and changing atomizers. What was also important was that the ranking of DRE changed depending on the failure mode studied.

The results of this study suggest that a single incinerability ranking scale may not be appropriate. Additionally, the rankings obtained in the laboratory should not be strictly applied to incinerators.

### II.C.3. Flow Reactors

The pyrolysis of $CH_3Cl$ has been studied by Shilov and Sabirov (86) in a flow system at temperatures around 1100K and pressures from 10-35 Torr. They concluded that even in the absence of a carrier gas the reaction proceeded as a non-chain process leading to hydrochloric acid (HCl), $CH_4$ and acetylene ($C_2H_2$). They concluded that the decomposition was a second order process initiated by the reaction

$$CH_3Cl + M = CH_3 + Cl + M \qquad R1$$

These data have been analyzed by Holbrook (89) and Forst and St. Laurent (90, 91) to test the Slater and RRKM theories, respectively, of unimolecular reactions. These works were unsuccessful in predicting the second order rate constant by better than within a factor of twenty of the experimental results.

A second experimental study of the pyrolysis of $CH_3Cl$ was performed by LeMoan (92). The experiment was allowed to proceed to greater than 95 percent methyl chloride decomposition at a temperature of 993K. Hydrogen chloride and $CH_4$ were the principal products with moderate quantities of molecular hydrogen ($H_2$), $C_2H_2$, toluene ($C_7H_8$) and soot. Low concentrations of $CH_2Cl_2$, ethane ($C_2H_6$) and ethyl chloride($C_2H_5Cl$) were measured during the initial stages of the reaction.

The most recent study of the decomposition of $CH_3Cl$ was conducted by Weissman and Benson (50). Using a flow system they monitored the product distribution from CH Cl plus additives of ethene ($C_2H_4$), $CH_4$, $C_2H_2$ and $C_2H_6$ at temperatures of 1260 and 1310 K and over the pressure range 180- 370 Torr. Using gas chromatography and mass spectroscopy (GC/MS) techniques they measured $CH_4$, $C_2H_2$, $C_6H_6$ and identified HCl as the major products with lower quantities of aromatic hydrocarbons and soot. These authors also discussed the mechanisms of soot formation from $C_1$ and $C_2$ hydrocarbons.

The destruction of chlorinated chemical warfare agents and solvents in a 3 cm diameter x 30 cm Vycor flow reactor housed within a tube furnace has been studied by Brooks and Parker (93) for the United States Army. Destruction of the reactant and its conversion into intermediates was detected by gas chromatography/mass spectroscopy methods as a function of furnace temperature for a residence time of 2 seconds. Experiments were performed under both pyrolytic and 150% stoichiometric air reaction conditions. They report that in this system a temperature of 1200K is necessary to produce a 99.99 percent DRE for chloroform. At almost all temperatures HCl and $Cl_2$ were the major products for both oxidation and pyrolysis. Low molecular weight CHC's ($CH_3Cl$, $CH_2Cl_2$, $CCl_3$, $C_2H_3Cl$) were formed in the pyrolysis experiments.

The pyrolysis of chloroform has also been studied by Shilov and Sabirov (94), Semeluk and Berstein (95, 96) and Benson and Spokes (97) at low pressures in flow reactors. Over the temperature range studied, 750- 1000 K, all of the authors reported that the principal products were HCl and $C_2Cl_4$. However the results were interpreted differently. Semeluk and Berstein (94) believed that the reaction is a free radical chain, initiated by the Cl-atom elimination, but they admitted to difficulties in describing the early stages of the decomposition. In (94) and (97) it is argued that the decomposition of chloroform is not by a radical chain, but that the elimination of HCl is the initiation step and subsequent recombination of $CCl_2$ radical produces the $C_2Cl_4$. They stated that their results for experiments with $CHCl_3/CCl_4$ mixtures in which no appreciable acceleration of the $CHCl_3$ decomposition occurred confirmed that a radical chain with Cl-atom as the chain carrier was not important.

The reduction of chlorinated hydrocarbons by molecular hydrogen and water has been studied by Bozelli et al. (98, 99) in tubular flow (900-1500K at 1 atm) and microwave induced plasma reactors between 1-10 Torr. In these studies chloroform and 1,1,2 $C_2H_3Cl_3$ were used as candidate CHC's. The main products were the conversion of the reactant to saturated and unsaturated hydrocarbons, but significant quantities of CHC's ( sum $CH_3Cl$, $C_2H_3Cl$, $C_2H_5Cl$ and $CH_2Cl_2$ approximately 10 percent) remained in the products.

## 4. Shock Tube Studies

The shock tube technique has been used in the study of CHC pyrolysis and oxidation. Kondo, Saito and Murakami (100) have studied the decomposition of $CH_3Cl$ behind reflected shock waves over the temperature and total density ranges of 1680-2430 K and $2.0x10^{-6}$ - $3.5x10^{-5}$ mol/cc, respectively. By monitoring the formation of methyl radicals ($CH_3$) produced in R1, they concluded that under their conditions reaction R1 was the principal kinetic initiation and was in the fall-off region.

Both Yano (101) and Shug et al. (102) have studied the decomposition of chloroform in shock tubes. Yano used the single-pulse technique to study the pyrolysis of pure chloroform and mixtures with $D_2$ , $CH_4$ and $CD_4$ over the temperature range 1000- 1200K. In these experiments the total density was $2.4-3.9x10^{-5}$ mol/cc and the dwell time was 1 ms. Using a GC/MS analysis technique a marked shift in the product distribution was noted between the three studies. Based on analysis of the distributions they postulated that the initiation step was the dissociation of the C-Cl bond.

In contrast, Shug (102) postulated the elimination of HCl from the fuel molecule. This was based on a study of the ultraviolet absorption at 230 nm of $C_2Cl_4$ produced in the decomposition over the temperature range 1100- 1400K and total density $3x10^{-6}$ mol/cc. These researchers accepted the arguments of Shilov and Sabirova (94), described above, concerning the identity of the initiation step.

There were two shock tube studies of the decomposition of tetrachloroethene ($C_2Cl_4$), trichloroethene ($C_2HCl_3$) and vinyl chloride ($C_2H_3Cl$) by Zabel (101, 102). In order to study the pressure dependencies of the initiation reactions the experiments in both studies were performed over temperature and pressure ranges 1350- 1900 K and 2- 175 atm, respectively behind reflected shock waves. The progress of the reaction was monitored by ultraviolet absorption measurements of the reactant CHC at wavelengths between 230- 300 nm. For $C_2Cl_4$ and $C_2HCl_3$ the initiation step was reported to be the dissociation of the carbon-chlorine bond; whereas, for $C_2H_3Cl$ the elimination of HCl was the initiation step.

The soot formation of chlorinated methanes and ethenes has been studied recently behind reflected shock over the temperature range 1600- 2800 K for a constant carbon atom density of $5x10^{+17}$ C-atoms/cc (48). At temperatures below 2000K the amount of soot formed from $CH_2Cl_2$ and the dichloroethenes is an order of magnitude larger than that of other reactants tested, actually reaching the levels of soot formation in aromatic hydrocarbons (105, 106). These observations were explained based on the lower C-Cl bond energy compared to the C-H bond energy in methane and the catalyzed formation of $C_2H_2$ by Cl abstraction of H-atom. Further conjecture was presented concerning a possible high temperature soot formation mechanism because of an increase in soot formation at high temperatures.

## D. MODELING STUDIES

There has been a major effort to develop methods and models to predict, a priori, the performance of an incinerator processing hazardous waste streams. These efforts are motivated by the time and costs required to perform the USEPA trial burn/ permit procedure.

The simplest models have been those which attempt to develop a ranking scale for the incinerability of hazardous wastes. These scales would then be used to imply that one test burn of the most difficult compound to incinerate would be sufficient for all the compounds in the waste stream. As mentioned above many ranking scales have been suggested and none have received universal acceptance.

The next level of complexity has involved coupling a furnace heat transfer/ fluid flow model with simple, but necessarily, conservative chemical kinetics. Such a model has been used by Wolbach (83- 85) to place "lower" limits on the possible DRE of an incinerator. The most recent effort (85) included a relatively detailed heat transfer/ fluid flow model of the post flame region of an incinerator including processes occuring in the boundary layers at the incinerator walls. The chemical kinetics used were taken from the work of Lee et al. (26) and Dellinger et al. (62).

This model was designed to be conservative as it does not account for flame zone destruction. The waste is assumed to be delivered to the incinerator as a gas at the region of highest temperature. When compared with experimental data using carbon tetrachloride in a pilot scale furnace, the model underpredicted the actual DRE as anticipated and predicted the result of non-design operating conditions reasonably well.

Unfortunately, the model has several difficulties, which the authors discuss:

1. It does not account for liquid fuel vaporization which may disturb the energy balance equations and therefore the temperatures used in the global kinetics expresssions.
2. There is no attempt to model the atomization and trajectory of fuel droplets even though they do comment that 98 percent of the waste which reaches the boundary layers on the walls are not destroyed.
3. The model is shown to be sensitive to the parameters in the global kinetic expressions, 20 percent changes in values resulting in three orders of magnitude changes in the prediction of DRE.

While prediction of DRE based on this model must be questioned, the model is useful in examining the effects of off-design operating conditions on performance.

A similar approach using detailed heat transfer/ fluid flow models has been taken by Clark et al. (86). This model was not identical to that of Wolbach, using different methods to calculate radiative heat transfer, but suffers from the same problems listed above. However, this model did account for the possibility of poor atomization by allowing the initial waste concentration to be inserted into any of the incinerator zones. Additional differences between the models are that the Clark model uses empirical correlations of atomizer performance to provide initial estimates of the spatial distribution of waste within the incinerator and it also allows the waste to be processed in the flame zone. In comparisons with experimental data for $C_6H_5Cl$, $CH_2Cl_2$, $CHCl_3$ and $CCl_4$, the model predicts $C_6H_5Cl$ and $CCl_4$ exhaust concentrations well but underpredicts $CH_2Cl_2$ and $CHCl_3$. The most probable explanation for this descrepancy was the use of the non-flame kinetics in a flame zone which has been shown to be non-conservative (80).

Senkan (107) has recently reported the results of detailed modeling of the moist oxidation of CO in the presence of HCl and molecular chlorine ($Cl_2$). In this work he suggests that inhibition has two aspects. At low concentrations Cl competes for H-atom with the chain branching reaction

$$H + O_2 = OH + O ;$$

reducing the concentration of hydroxyl radical (OH), which is available for oxidizing the CO by its predominant oxidation path

$$CO + OH = CO_2 + H.$$

At high concentrations of Cl- atom, the hydroxyl radical concentration is so severely reduced that the CO oxidation mechanism changes and occurs primarily by the much slower reaction

$$CO + O_2 = CO_2 + O.$$

## II.E. CONCLUSIONS

The literature cited above indicates the complexity of the problems associated with the incineration of hazardous compounds. Studies under varying operating conditions with the same hazardous materials produce differing results. This is caused by a lack of a basic understanding of the chemical kinetics of the high temperature reactions of CHC's. To begin resolution of this issue, a study of the pyrolysis and oxidation of the $C_1$ and $C_2$ families of CHC's was undertaken.

# CHAPTER III

# EXPERIMENTAL FACILITIES

## A. INTRODUCTION

The experimental work was performed in the Combustion Laboratories of the College of Engineering of Louisiana State University . The laboratory facilities used include a conventional shock tube and a single-pulse shock tube with their associated electronics and reaction monitoring equipment. Two gas chromatographs were employed to analyze the quenched reactants and products obtained from the single-pulse experiments.

## B. SHOCK TUBE LABORATORY

A shock tube is a device which uses the adiabatic compression of a normal shock wave to produce conditions of high temperature and pressure in an experimental, usually gas phase, test mixture. The "step" function increases in temperature and pressure produced by the passage of the shock wave can be used to study chemical reactions and/or fluid mechanics of high speed flows. One method of producing the shock wave is to allow a high pressure gas to expand into a low pressure gas. In this mode of operation the shock tube is divided into two sections; a high pressure section called the driver and a low pressure experimental section called the driven section. These two sections are initially separated by a diaphragm; when the diaphragm is removed the expansion of the driver gas into the low pressure region creates a normal shock wave which propogates within the tube into the experimental section. The progress of the reaction can be monitored by several optical techniques and/or dynamic pressure measurements. In a slightly modified configuration, a gas sample can be heated for a short period of time, then quenched and analyzed by any chemical technique.

The principal advantages of the shock tube technique are three-fold (108- 112).

1. Any gas phase compound can be studied; including pure compounds, with or without oxidizer.
2. The passage of the shock wave through the experimental gas is equivalent to moving the gas from a reactor at room temperature to another reactor at a specified temperature in a time on the order of 1E-10 seconds.
3. The typical reaction time in a shock tube (approximately 2 milliseconds) is far shorter than the time for chemical species to diffuse to the walls and hence wall effects are negligible.

To determine the experimental conditions produced by the passage of the shock wave, the speed of the shock is measured. From this measurement the ratios of shocked to unshocked density, pressure and temperature can be calculated by iteratively solving the conservation equations of mass, energy and momentum simultaneously with a mechanical equation of state, and a caloric equation of state.

### 1. Conventional Shock Tube Facility

Experiments measuring pressure and/or spectroscopic emission versus time were conducted in a 7.6 cm diameter stainless steel conventional shock tube (CST), schematically shown in Figure 1. The driven section of the tube is 7.3 m long and the driver is 3 m in length. The driven and driver sections of the tube are separated by two diaphragms. This "double" diaphragm system allows for better reproducibility of driven/driver pressure ratios. In order to produce a clean reaction vessel the shock tube is fitted with an Edwards "Speedivac" E06 oil diffusion vacuum pump system which can evacuate the tube and associated gas mixture manifold to a pressure of 2E-05 Torr (measured near the end cap of the driven section of the shock tube).

The incident shock velocity was measured, see Figure 2, using the voltage signal generated by Atlantic Research LD-25 pressure pulse transducers to trigger the start and stop channels of an interval timer purchased from the Chemistry Department of the University of Texas, Austin (UT). The transducer voltage was preprocessed by an amplifier and a comparator latch circuit obtained from UT and subsequently modified at LSU. The timer is driven by a

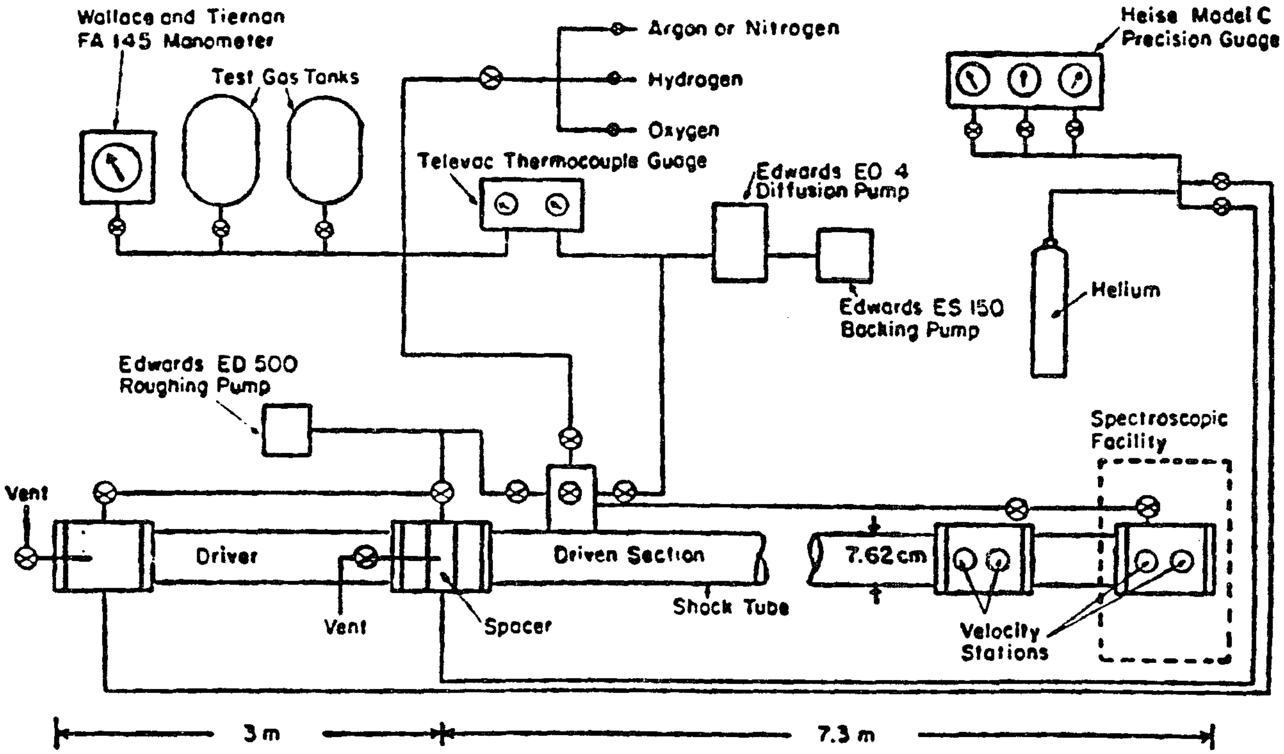

Figure 1. Schematic diagram of the conventional shock tube facility.

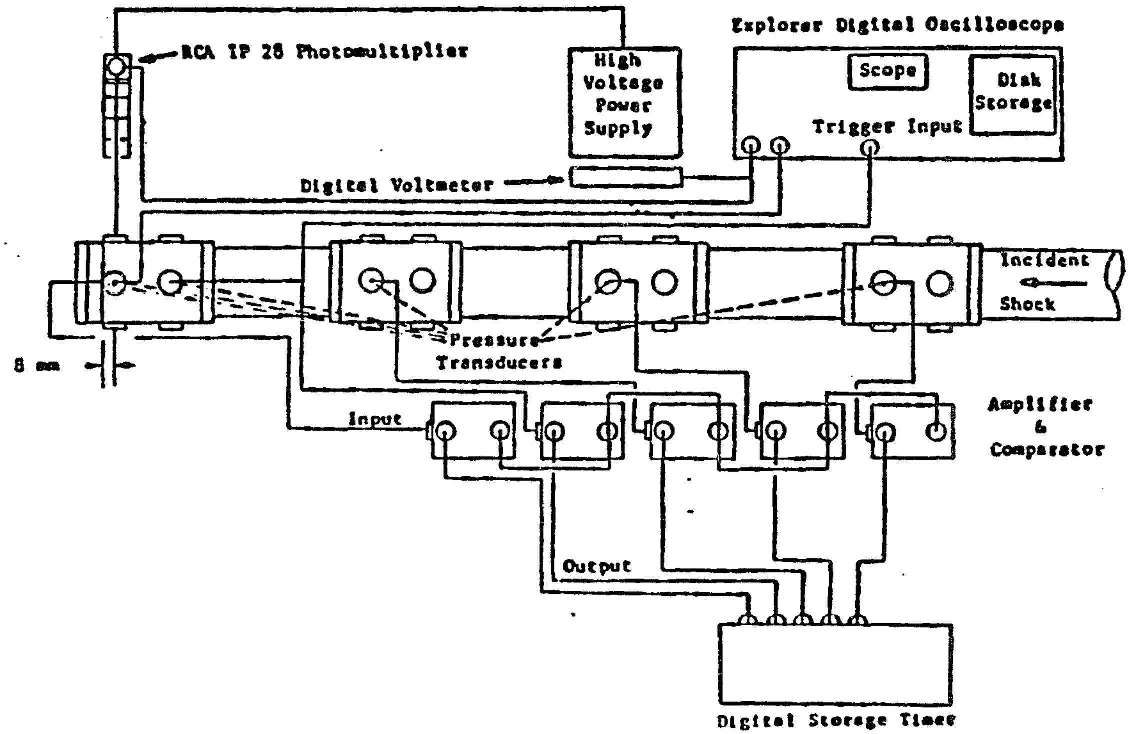

Figure 2. Schematic diagram of the conventional shock tube electronics.

10 MHz crystal oscillator and has a storage delay of less than 300 nanoseconds. This results in a net accuracy within 1 microsecond ($\mu$s) for the transit times between transducer stations which corresponds to a ± 15 K uncertainty in reaction temperature. To account for shock wave deceleration caused by boundary layer growth and viscous drag between the shock wave and the walls of the shock tubes, the measured velocity is extrapolated to the end wall of the shock tube using a linear extrapolation developed by Cheong (113).

### 2. Reaction monitoring system

The progress of the reaction in the conventional shock tube could be monitored with both absolute pressure measurements and spectroscopic emission measurements at several wavelengths in the ultraviolet and infrared regions of the electromagnetic spectrum. Figure 2 depicts the reaction monitoring system.

A PCB model 113A piezoelectric pressure transducer was mounted in a specially designed end plate of the shock tube in order to monitor the pressure of the reacting gas mixture behind the reflected shock wave. The signal generated by the transducer was amplified by a Kistler type 504A Charge Amplifier.

The ultraviolet measurements were made approximately 1.5 cm from the end plate of the shock tube and a prism monochromator, Perkin-Elmer model 99, was used to define the wavelength, and a photomultiplier tube (PMT), EMI type 9785B, as detector. With a typical gain of five million over its effective operating range of 185 to 830 nanometers, the PMT provided a signal to noise ratio of greater than 5 for the experimental conditions of this study. An accelerating potential of 800 volts (V) was applied to the PMT by a Power Design Pacific, model HV-1547, 1-3000 V power supply.

Two different infrared optical systems were available which could monitor two regions of the infrared spectrum simultaneously. One system included a Texas Instruments indium antimonide (InSb) detector operated in the photoconductive mode using a Perry Model 720 preamplifier. The preamplifier has a gain of 100 and bandwidth in excess of 0.5 MHz. This produced a combined detector/amplifier time constant of approximately 2 $\mu$s. The second system consisted of an Infrared Industries InSb detector with a matched preamplifier ( model PPA- 15-1S). The time constant of this combination is 1.5 $\mu$s.

The detectors which were located 1.5 cm from the endwall of the shock tube were aligned to "look" at each other through the shock tube. The spectral bandpass for each detector was defined by narrow bandpass interference filters purchased from OCLI, Inc. The field of view was defined by two 1.5 mm pinholes located 5 cm apart.

### 3. Single-Pulse Shock Tube (SPST) Facility

A 2.54 cm diameter single-pulse or chemical shock tube (SPST) shown in Figure 3, was used to determine quenched product and reactant distributions from pyrolysis and oxidation experiments with selected chlorinated methanes. The driver was constructed of stainless steel. The length of the driver could be adjusted from 0.3 to 1.52 m in increments of 5 cm by the insertion of appropriate plugs. A 2.9 m driven section was constructed primarily of Pyrex conical piping with three stainless steel sections located in the final 0.70 m. The stainless steel sections contained piezoelectric transducers, a sampling port, and a ball valve which served to isolate a test sample in the end of the shock tube. A single diaphragm of Mylar separated the driver and driven sections of the tube.

The shock tube was fitted with an Edwards "Speedivac" E02 oil diffusion pump system that was capable of evacuating the driven section to less than 2E-04 Torr, measured at the inlet to the diffusion pump. As in the conventional shock tube, incident shock velocity was measured with Atlantic Research LD-25 piezoelectric pressure transducers which were used to trigger a three channel interval timer, designed and constructed at Louisiana State University, with a resolution of 0.1 $\mu$s. Experimental dwell times and quenching rates were determined from measurements of the voltage trace produced by a Kistler 603A piezoelectric pressure transducer located

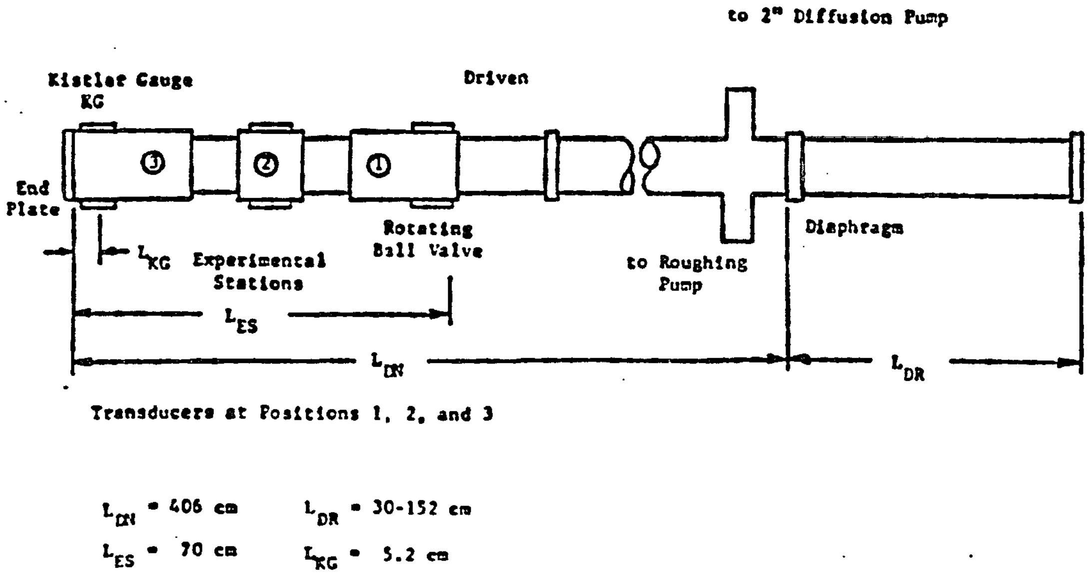

Figure 3. Schematic diagram of the single-pulse shock tube facility.

approximately 5 cm from the end wall of the shock tube, see Figure 4.

### 4. Quenched Products Analysis

After quenching, the partially consumed reactants and reaction products were drawn into a previously evacuated 100 cubic centimeter Pyrex sampling bulb. The contents of the bulb were subsequently analyzed by gas chromatographic techniques. Both flame ionization and thermal conductivity detectors (FID and TCD, respectively) were employed to obtain maximum sensitivity for the hydrocarbons, chlorinated hydrocarbons (CHC's) and fixed gases produced during the reactions. An overview of gas chromatographic techniques is given by McNair and Bonelli (114) and Thompson (115) and the gas chromatographic methods used in this study are described below.

During the initial stages of the study, experiments involving methane and methyl chloride the stable species analyses of the quenched samples were performed with a single Varian VISTA 6000 GC equipped with both a TCD and an FID. Peak areas were calculated with a VISTA 402 Data Analyzer. Carrier flow for both detectors was helium at 30 cc/min. Temperature programming was used to reduce analysis time. An initial temperature of 35 C was held for 3 minutes, followed by a linear temperature ramp of 15 C/min was applied until 170 C was reached. The temperature was held constant at 170 C for the remainder of the

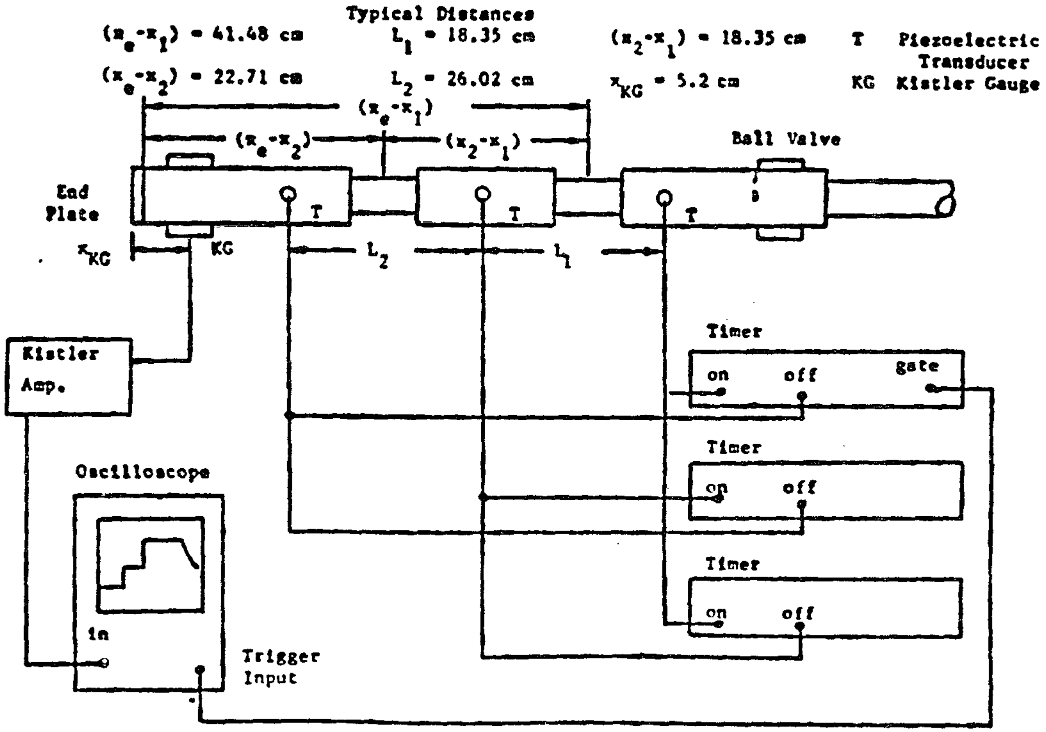

Figure 4. Schematic diagram of the single-pulse shock tube driven section.

analysis.

During an analysis, a single sample bottle was coupled to a stainless steel sampling manifold which was connected into a Valco 10 port gas sampling valve (GSV) with two 5 cc sample loops. The manifold and GSV were evacuated to less than 20 microns and then the sample was expanded into the sample loops of the valve. The contents of loops were then simultaneously injected into the columns of each detector.

For the FID 2m x 3mm columns of Porapak N and Porapak Q were arranged in series to provide separation of the hydrocarbons and CHC's. The analysis of the fixed gases required a more complicated column arrangement. In the main oven of the GC a 2m x 3mm Porapak N was connected in series to a 2m x 3mm Molecular Sieve 5A. The outlet of this combination was fed into a Valco 6 port GSV. This GSV was connected so as to switch the flow between a direct line to the TCD and a second set of columns mounted in an ice bath outside the GC and then into the TCD. The external columns were 4m x 3mm MS 5A and 4m x 3mm MS 13X which are necessary to separate argon from oxygen. During the measurements the carrier flow is initially routed through the external columns. After 6.7 minutes $Ar/O_2$ have flowed into these columns and they are isolated from the flow by actuation of the valve. The components N , CH and carbon monoxide (CO) elute from the internal columns through a restricter and into the detector. After the CO peak has been measured (approximately 13 minutes) the flow is again routed through the external columns for detection of the separated Ar/O peaks. Following the oxygen peak the external columns are again isolated. The total analysis time is 55 minutes per sample.

For the dichloromethane study a second Varian 6000 gas chromatograph was available. This GC is configured with the column used in USEPA Method 601 (116) (8' x 1/8", 1% SP-1000 on Carbopak B, 40 cc/min helium flow rate) to separate chlorinated hydrocarbons. For detection an FID is used because the Hall detector also mounted on the GC did not produce reproducible results. In order to provide a second check on $C_1$ and $C_2$ hydrocarbon concentrations, the initial temperature of the oven is lowered to 35 C from the 45 C suggested by the USEPA method and programmed after a 2 minute hold to 220 C at 10 C/min. For analysis of carbon dioxide a 12' x 1/8" column packed with Porapak Q was installed in the oven of the second GC and connected to the TCD. Helium flowing at 30 cc/min was used for the TCD carrier gas.

Peak identification is accomplished by injecting pure gas phases and recording the retention volume. Confirmation of identity of species within a sample is performed on each analysis by matching the retention volumes on different GC columns. Species partial pressures are determined by comparison with the electronically integrated areas of known pressures of the species contained in calibration mixtures.

The compounds which can be identified and those which can be measured are listed in Table 2. A calibration mixture containing all the $C_1$ hydrocarbons and CHC's was run prior to and after each series of experiments.

## C. DATA ACQUISITION

The signal from both the pressure and the spectroscopic measurements were digitized and displayed on a Nicolet 2090-3 digital oscilloscope. This oscilloscope has the capability of sampling two voltage inputs. Each channel of information can store 2048 data points. The sweep time of the scope can be selected from 500 nanoseconds per point to 200 seconds per point. The oscilloscope has 12 bit voltage resolution. Depending on the levels encountered the scope could be set at full scale voltage levels from 200 mV to 40 V in a 1, 2 and 4 sequence. The data can be permanently stored on magnetic diskettes for future analysis.

## D. CALCULATION OF EXPERIMENTAL CONDITIONS

In order to determine the experimental conditions in the shock tubes it is necessary to solve the conservation equations for the propogation of a normal shock wave into a gas. Several programs (117, 118) are available in the laboratory to iteratively solve these equations using the measured shock speed linearly extrapolated to the end wall of the shock tubes. It is assumed that there is no

|  | Chemical Compounds |  |
|---|---|---|
|  | Measureable | Identifiable |
| Fixed Gases: | $O_2$, $N_2$, CO, $CO_2$, Ar |  |
| Hydrocarbons: | $CH_4$, $C_2H_2$, $C_2H_4$, | $CH_3OH$, $C_2H_5OH$ |
|  | $C_2H_6$, $C_3$'s |  |
| Chlorinated Hydrocarbons : | $CH_3Cl$, $CH_2Cl_2$ | $CHCl_3$, $CCl_4$ |
|  | $C_2H_3Cl$, 1,2- $C_2H_2Cl_2$, | $C_2Cl_2$, $C_2Cl_4$, |
|  | $C_2HCl_3$, $C_2H_5Cl$, 1,2- $C_2H_4Cl_2$ | 1,1- $C_2H_2Cl_2$, |
|  | 1,1- $C_2H_4Cl_2$ | 1,1,1- $C_2H_3Cl_3$ |

Table 2. Gas chromatographic capabilities.

reaction behind the incident shock wave and that the specific heat of the test gases are functions of temperature. Another program (119) can be used to calculate the temperature and pressure assuming chemical equilibrium occurs behind either or both the incident shock wave and the reflected shock wave.

These "shock" programs, as well as the kinetics programs used below, require expressions for the thermochemistry (e.g. specific heat, enthalpy and entropy) of the reactants as a function of temperature. At present the dual temperature range, seven term polynomial suggested by the Lewis Research Center of the National Aeronautics and Space Administration (NASA) is used for this thermochemical information. A program, PAC 3 (120) has been obtained from NASA to calculate and/or fit thermochemistry from several sources:

1. Calculate thermochemical values directly from statistical mechanical expressions, which requires spectroscopic data, such as principal moments of inertia, fundamental vibration frequencies, rotational symmetry numbers, etc. as input.
2. Fit the NASA format polynomials to tabulated data such as JANAF Thermochemical Tables (121), API-44 (122) or data from Duff and Bauer (123).

## CHAPTER IV

## EXPERIMENTAL RESULTS/OBSERVATIONS

### A. INTRODUCTION

The ignition delay times of selected chlorinated $C_1$ and $C_2$ hydrocarbons and stoichiometric oxygen mixtures were measured in a conventional shock tube facility of the Combustion Laboratory of Louisiana State University. Such studies have been useful in determining the combustion characteristics of a wide variety of hydrocarbon fuels (31-34).

To further study the combustion of CHC's, single-pulse shock tube experiments were performed for the pyrolysis and stoichiometric oxidation of methane, methyl chloride and dichloromethane. These experiments were designed to identify important stable intermediate products formed during the reaction.

### B. STOICHIOMETRY OF THE CHLORINATED HYDROCARBONS

When studying chlorinated hydrocarbons which contain chlorine (Cl), hydrogen (H) and carbon (C), it is necessary to define a methodology for determining the stoichiometric oxygen required for complete combustion of the compound. The equilibrium between water, oxygen, molecular chlorine and hydrogen chloride is controlled by the overall reaction

$$H_2O + Cl_2 = 2HCl + 1/2\ O_2$$

which is known as the Deacon reaction. Above 1000K the equilibrium constant favors the production of HCl and O by more than a factor of 10. Incineration temperatures are generally high enough to favor the conversion of almost all of the H-atoms and Cl-atoms in the CHC to hydrogen chloride (HCl). This indicates that when determining the stoichiometric oxygen requirements for the chlorinated hydrocarbons it should be assumed that maximum conversion of available H-atom and Cl-atom to HCl occurs. Any remaining Cl-atom is assumed to form molecular chlorine ($Cl_2$) and any remaining H-atom is assumed to form water ($H_2O$). Based on this reasoning the stoichiometric rection equation for methyl chloride ($CH_3Cl$) with molecular oxygen ($O_2$) is given by

$$CH_3Cl + 1.5\ O_2 = CO_2 + HCl + H_2O.$$

This definition of stoichiometry was used to determine the test mixture compositions for all the compounds studied.

## C. EXPERIMENTAL MIXTURES

The liquid CHC's were purified by bulb-to- bulb distillation. In this procedure the first portion of the liquid to distill is discarded because it may contain impurities with lower boiling points than the desired CHC.

The liquid CHC to be purified is not allowed to boil completely as this last portion may contain impurities with higher boiling points than the desired CHC. The vapor from the purified liquids collected during the middle fraction of the distillation procedure was used to prepare the mixtures. The $CH_4$, $CH_3Cl$, $C_2H_4$ and $C_2H_6$ were Matheson CP grade gases and the Ar and O. were Matheson pre-purified grade gases.

Test mixtures and gas chromatographic calibration mixtures were made following standard manometric procedures. Approximately 20- 40 ml of the liquid CHC's were poured into a Pyrex thimble which was then emersed in a liquid nitrogen bath. After the liquid CHC had frozen the non-condensibles were evacuated with a diffusion pump. The liquids were then allowed to thaw and return to room temperature. The freeze/ evacuate/ thaw cycle was repeated twice. After the liquid thawed from the second cycle the mixture was made. In all cases the partial pressure of the liquid in a mixture was kept below 50 percent of the vapor pressure at 20 °C to ensure no condensation occurred on the walls of the tanks. The mixtures were stored in stainless steel tanks at approximately 1.1 atm and allowed to mix for a minimum of 36 hours before use.

## D. IGNITION DELAY STUDIES

### 1. Ignition Delay Diagnostics

Ignition delay is defined as the interval between the initial exposure of the fuel/oxidizer mixture to a step function change in temperature and the occurance of the principal exothermicity of the reaction, which is signified by a sudden increase in temperature and pressure. The ignition delay is determined by the overall kinetics of the combustion reactions.

Several diagnostics have been used to identify the onset of ignition. These include the maximum curvature in the pressure trace due to the rapid increase in temperature and pressure produced by the ignition,the emission and/or absorption from the hydroxyl radical in the ultraviolet region of the electromagnetic spectrum ( 306.4 nm and 308.0 nm, respectively), the chemiluminescence at 270.0 nm produced by the reaction

$$CO + O = CO_2 + h\nu$$

and the infrared emision at 4.24 microns of carbon dioxide. Each method was considered during the initial stages of the reseach program. Spectroscopic measurements of OH were eliminated because in the limit of maximum Cl-atom substitution for H-atom there should be no OH radical present in the systems of interest. The chemiluminescence at 270.0 nm was eliminated because of an interference from chlorinated compounds. Emission from carbon dioxide was considered inappropriate because of the proposed inhibition of the oxidation of CO to $CO_2$ in the presence of Cl- atom

(75, 76). Therefore, pressure was chosen to characterize the ignition delay time. A typical pressure trace for a mixture undergoing ignition is depicted in Figure 5.

## 2. Experimental Design

In order to compare the ignition delay times and thereby the combustion mechanism of selected CHC's with their hydrocarbon analogs, stoichiometric fuel- oxygen mixtures, diluted with argon (Ar), using methane and its chlorinated derivatives, ethane, 1,1,1- trichloroethane, and 1,2- dichloroethane, ethene, vinyl chloride and trichloroethene and benzene and monochlorobenzene were shock heated over the temperature ranges listed in Table 3. Additional studies with mixtures of CHC/ hydrocarbons/ $O_2$ were also performed (Table 4) to examine the synergistic effects upon the ignition delay time.

A useful correlation equation for ignition delay time data is of the form (31- 34):

$$\tau = A\, T^{B} \exp(E_a/ RT)\, [\mathrm{fuel}]^{a}\, [O_2]^{b}\, [\mathrm{Ar}]^{c} \qquad (2)$$

where,

$\tau$ = ignition delay time, ($\mu$s)

T = initial post- shock temperature, (K)

R = universal gas constant, (kJ/ mol/ K)

[ ] = initial concentration, (mol/ cc)

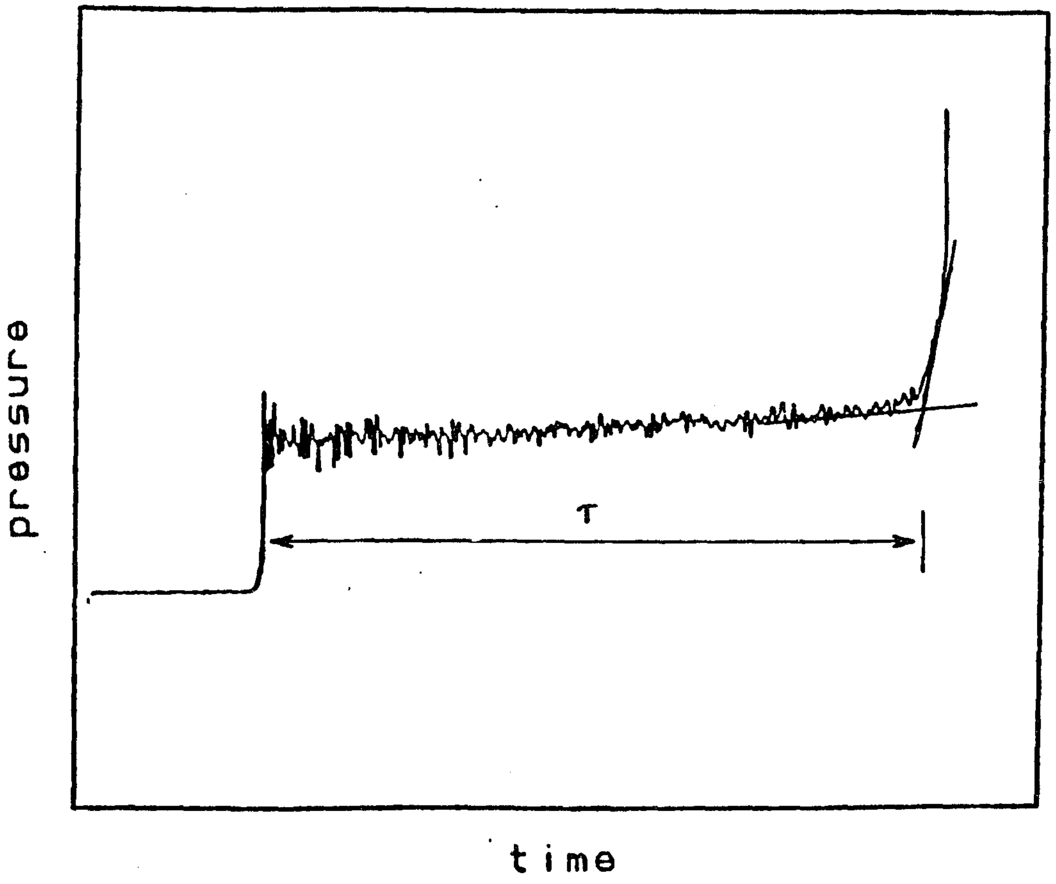

Figure 5. Typical pressure trace from the ignition delay studies.

| Test Mixture | P (atm) | T Range (K) | ln A[a] (μs) | E/R × $10^{-3}$ (K) |
|---|---|---|---|---|
| 10% $CH_4$ + 20% $O_2$ + Ar | 2.0 | 1330- 1544 | -4.05 ± 1.4 | 15.7 ± 1.8 |
| 10% $CF_3Cl$ + 15% $O_2$ + Ar | 2.0 | 1280- 1570 | - 5.3 ± 0.9 | 17.9 ± 1.8 |
| 10% $CH_2Cl$ + 10% $O_2$ + Ar | 2.0 | 1220- 1398 | - 9.0 ± 2.0 | 19.7 ± 2.9 |
| 10% $CHCl_3$ + 10% $O_2$ + Ar | 2.1 | 1277- 1470 | ------------ | ---------- |
| 10% $CCl_4$ + 10% $O_2$ + Ar | 2.1 | 1313- 1441 | ------------ | ---------- |
| | | | | |
| 5% $C_2H_6$ + 17.5% $O_2$ + Ar | 1.7 | 1155- 1287 | - 7.8 ± 3.7 | 17.4 ± 4.4 |
| 5% 1,2- $C_2H_4Cl_2$ + 12.5% $O_2$ + Ar | 1.8 | 1188- 1540 | - 6.0 ± 0.4 | 15.0 ± 0.5 |
| 5% 1,1,1- $C_2H_3Cl_3$ + 10% $O_2$ + Ar | 2.3 | 1288- 1618 | -0.02 ± 1.2 | 9.5 ± 1.7 |
| | | | | |
| 5% $C_2F_4$ + 15% $O_2$ + Ar | 1.6 | 1103- 1307 | -10.4 ± 3.2 | 19.0 ± 3.6 |
| 5% $C_2HCl_3$ + 12.5% $O_2$ + Ar | 1.7 | 1080- 1284 | ------------ | ---------- |
| 2.3% $C_2F_3Cl$ + 5.77% $O_2$ + Ar | 3.8 | 1100- 1700 | - 5.4 ± 0.5 | 14.3 ± 0.7 |
| | | | | |
| 1.67% $C_6F_6$ + 12.5% $O_2$ + Ar | 1.8 | 1196- 1604 | - 6.7 ± 1.1 | 16.8 ± 1.2 |
| 1.67% $C_6H_5Cl$ + 11.7% $O_2$ + Ar | 1.7 | 1179- 1552 | - 6.9 ± 0.9 | 16.6 ± 1.2 |

[a] Ignition delay times fit to the relation: $\ln t = \ln A + E/R \times 1.0/T$

Table 3. Test gas mixtures for ignition delay studies of pure compounds.

| Test Mixture | P (atm) | T Range (K) | ln A[a] ($\mu$s) | E/R x $10^{-3}$ (K) |
|---|---|---|---|---|
| 5% $H_2$ + 2.5% $O_2$ + Ar | 1.6 | 900- 1344 | - 2.8 ± 1.7 | 9.4 ± 1.8 |
| 2.5% $C_2H_4$ + 5% $CH_3Cl$ + 15% $O_2$ + Ar | 2.0 | 1250- 1500 | - 4.9 ± 0.9 | 15.8 ± 1.2 |
| 2.5% $C_2H_4$ + 2.5% 1,1,1- $C_2H_3Cl_3$ + 12.5% $O_2$ + Ar | 1.8 | 1050- 1325 | - 7.6 ± 1.0 | 15.3 ± 1.2 |
| 1% $H_2$ + 10% $CH_3Cl$ + 15.5% $O_2$ + Ar | 2.2 | 1300- 1690 | - 5.7 ± 0.9 | 18.2 ± 1.4 |

a. Ignition delay times fit to the relation: ln t = ln A + E/ R x 1.0/ T

Table 4. Test gas mixtures for ignition delay studies for mixtures

A,B,E,a,b,c = empirical constants.

This equation provides a means of comparing shock tube data, but is not directly applicable to real combustion systems since the $O_2$ and Ar dependencies must be replaced with an air dependence. A correlation equation of this nature is also derivable from a reaction mechanism (32).

Many experimental data points are required to determine the six empirical constants in Equation 2 for each fuel of interest. A simpler scheme for comparison of ignition delay time data is employed in this study (124). Initial test gas compositions were carefully chosen to allow a direct comparison of the apparent activation energies of the fuels studied without having to explicitly determine the concentration dependencies a, b, c. In these experiments stoichiometric CHC- oxygen mixtures, diluted in argon, with approximately equal carbon atom concentrations were studied. The pressure behind the reflected shock wave was held nearly constant at 2.0 atm for all experiments. Within these limitations, the measured ignition delay times and apparent activation energies for the fuels studied may be compared directly.

## 3. Ignition Delay Times of Pure Reactants

The natural logarithms of the measured ignition delay times vs. the reciprocal of the initial experimental temperature for the $C_1$, parafinic $C_2$, olefinic $C_2$ and $C_6$

reactants are plotted in Figures 6- 9, respectively. Where possible, the data were fit by least squares analysis to an expression of the form

$$\ln t = \ln A + E/T$$

where

$t$ = ignition delay time, ($\mu$s)
$T$ = initial experimental temperature, (K)
$A,E$ = empirical constants calculated by least squares.

The least square lines are also shown in the figures. The reflected shock pressure, the apparent activation energies divided by the universal gas constant, fuel/ oxidizer compositions, and the temperature range for each set of data are also listed in Table 3.

Examination of Figure 6 indicates that $CH_4$ and $CH_3Cl$ have similar ignition delay times and that dichloromethane ($CH_2Cl_2$) is more easily ignited. Data for chloroform ($CHCl_3$) and carbon tetrachloride ($CCl_4$) exhibit considerable scatter, but they tend to cluster between the results for $CH_4$ and $CH_2Cl_2$.

Inspection of Figure 7 indicates that ethane ($C_2H_6$) and the doubly chlorinated 1,2- dichloroethane have similar ignition delay behavior. In contrast, the triply chlorinated 1,1,1- trichloroethane has an ignition delay

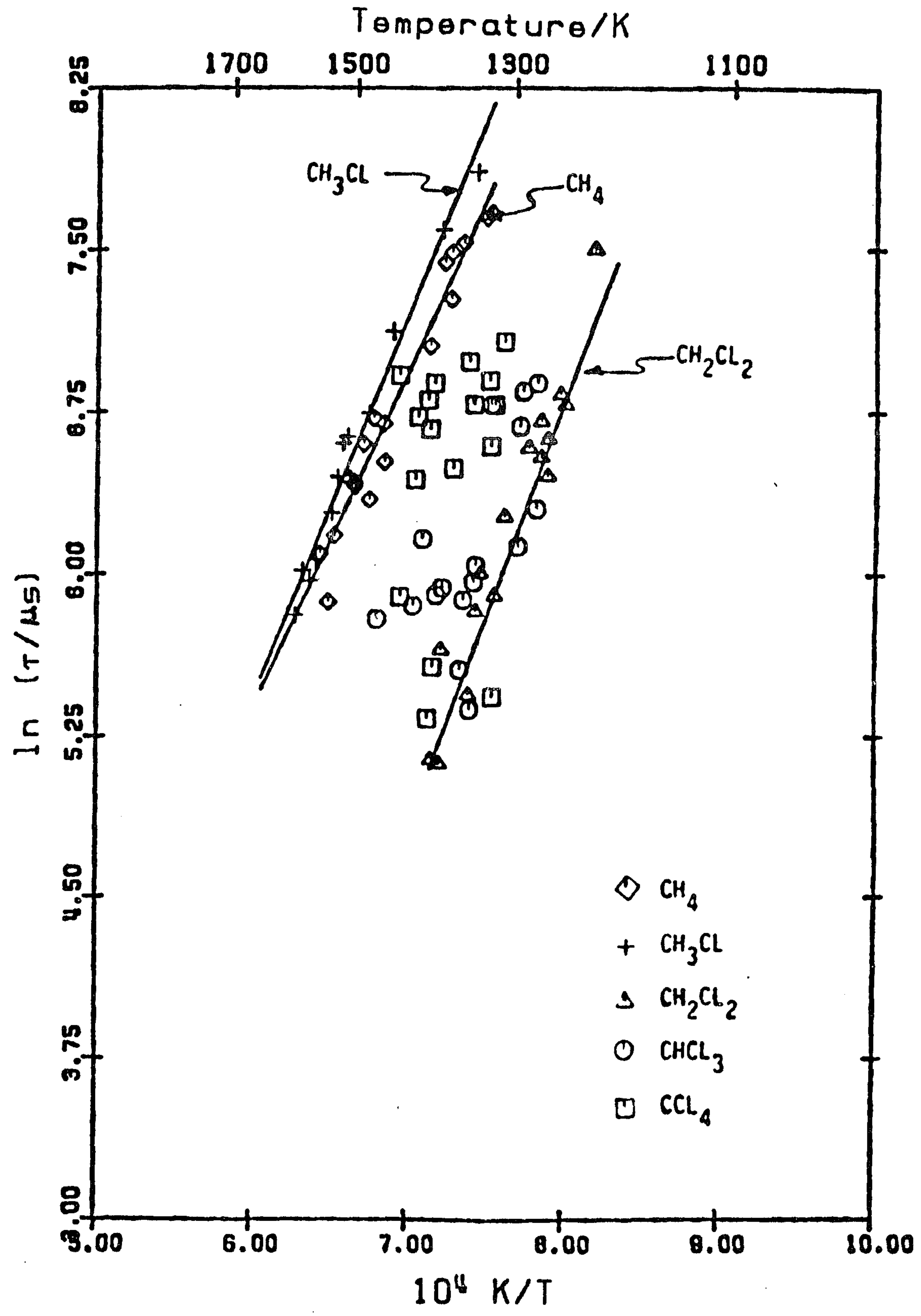

Figure 6. Ignition delay time of the chlorinated methanes versus reciprocal temperature.

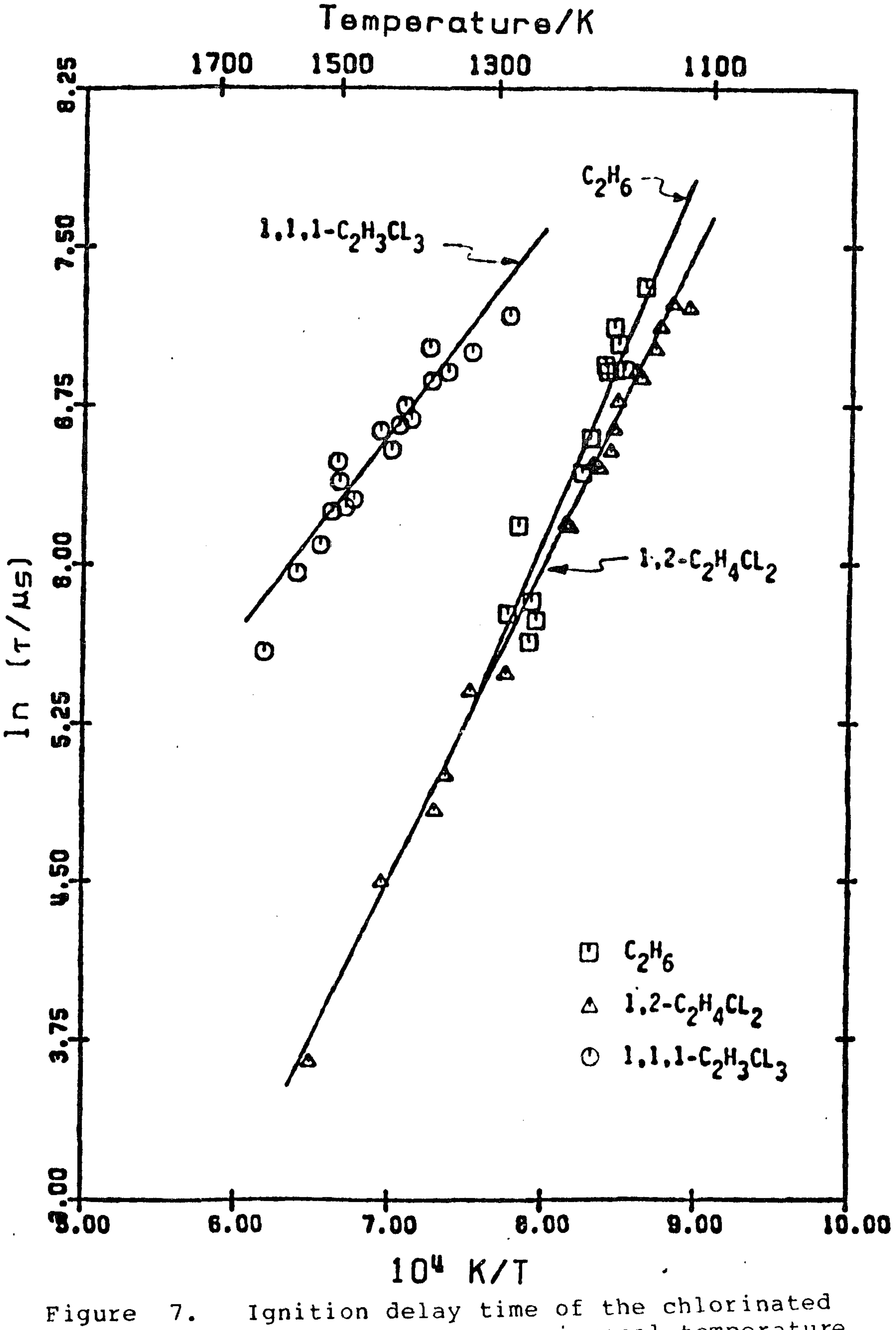

Figure 7. Ignition delay time of the chlorinated ethanes versus reciprocal temperature.

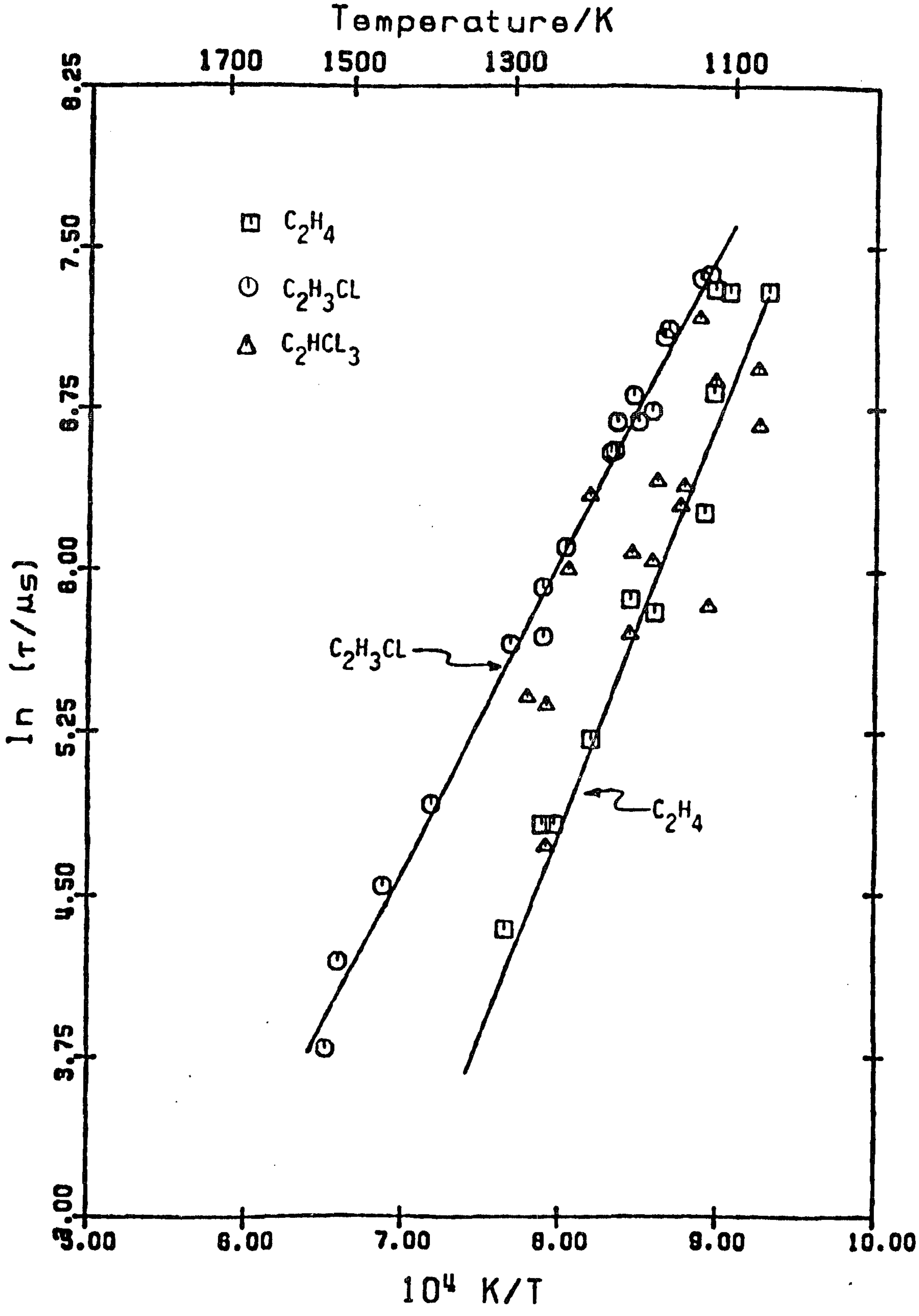

Figure 8. Ignition delay time of the chlorinated ethenes versus reciprocal temperature.

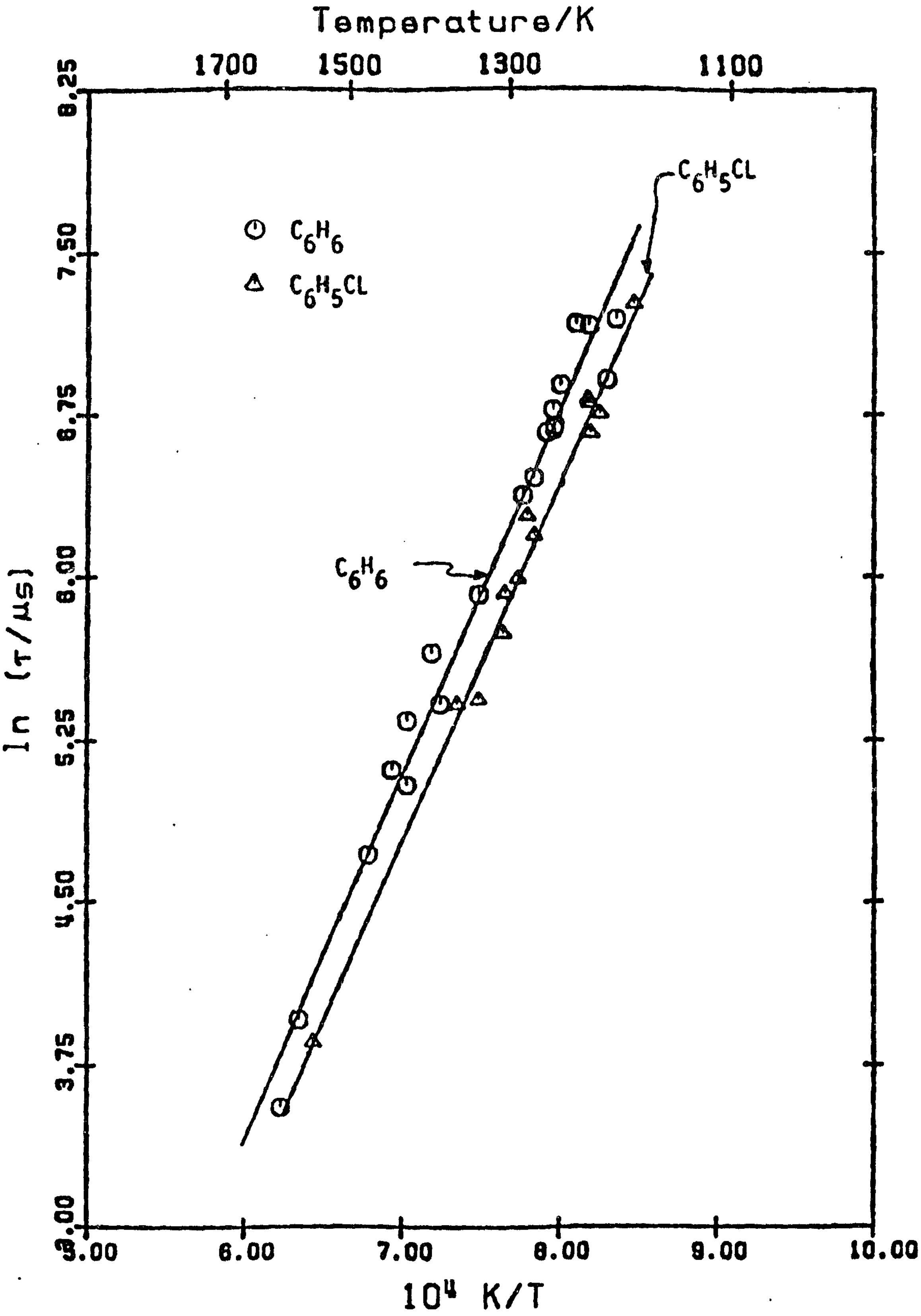

Figure 9. Ignition delay time of the chlorobenzene versus reciprocal temperature.

time approximately one order of magnitude longer.

For the olefinic $C_2$ hydrocarbons, ethene has the shortest ignition delay time. Vinyl Chloride has a longer ignition delay time than ethene by a factor of approximately 7 over the temperature range. The data for trichloroethene ($C_2HCl_3$) are too scattered to obtain good least square parameters; however, they tend to scatter around the $C_2H_4$ results.

The measured ignition delays for benzene ($C_6H_6$) and chlorobenzene ($C_6H_5Cl$), Figure 9, are nearly identical.

## 4. Discussion

The present results indicate that it is not universally more difficult to ignite the chlorinated hydrocarbons which were studied than their analogous hydrocarbons. Some of the CHC's ignite more easily than the HC's and some do not. This appears to be in contradiction with conventional wisdom which reports that all chlorinated hydrocarbons are difficult to effectively ignite within an incinerator.

A possible explanation for this difference is that there is a large difference in the "strength" of the ignition between hydrocarbons and progressively more substituted chlorinated hydrocarbons. Once an ignition occurs in the hydrocarbons the reactions are exothermic enough to increase the temperature and completely destroy the fuel; whereas, in contrast, the less exothermic CHC ignition may not provide sufficient temperature rise to produce total destruction.

Actually, a comparison of the C-H and C-Cl bond dissociation energies, 435 kJ/mol and 358 kJ/mol, respectively, indicates it may be reasonable to expect that the chlorinated compounds will more readily decompose to produce the radical pool required to initiate ignition. This may partially explain the relative ignition delay times of the compounds studied. In addition, recent results obtained near room temperature (125) indicate that the rate of hydroxyl radical attack on $CH_2Cl_2$ is faster than similar attacks on the other chlorinated methanes or on methane.

However, too much emphasis should not be placed on the rate of initiation. The initiation is just the first step in a sequence of chemical processes which determine the ignition behavior of the reactant. For instance, a rapid initiation step which results in a relatively stable, unreactive radical would not produce short ignition delay times.

### 5. Ignition Delay Times of Mixtures

To investigate the synergistic effect of HC's on the ignition delay times of CHC's, experiments were conducted with mixtures of the species with short ignition delay times and those with long ignition delay times. The natural logarithms of the measured ignition delay times versus the reciprocal of the initial experimental temperature for these experiments are plotted in Figure 10. The compositions of the tested mixtures and least square parameters to equation 2 are listed in Table 4. The dashed line in the figure is the correlation for the ignition delay time of a $H_2/O_2$ mixture measured in the shock-tube facility of the Combustion Laboratory of Louisiana State University extrapolated into the temperature range of CHC ignition delays. These studies indicate that if sufficient hydrocarbon is available the mixture will ignite with the delay time of the hydrocarbon, note, for example, the data for the "pure" 1,1,1- $C_2H_3Cl_3$, $C_2H_4$ compared with the data for $C_2H_4$/1,1,1- $C_2H_3Cl_3$ mixtures and for the $C_2H_4$/ $CH_3Cl$ mixures.

### 6. Ignition Delay Data Summary

The results of the ignition delay study can be summarized:

1. The most difficult compounds to ignite were methyl chloride and methane.
2. The easiest to ignite were ethylene and trichloroethene.
3 Measured ignition delay times at 1300K vary by a factor of approximately 15.
4. There is no simple relationship between ignition delay times and the number of Cl-atoms within an homologous hydrocarbon series. For example, the addition of one

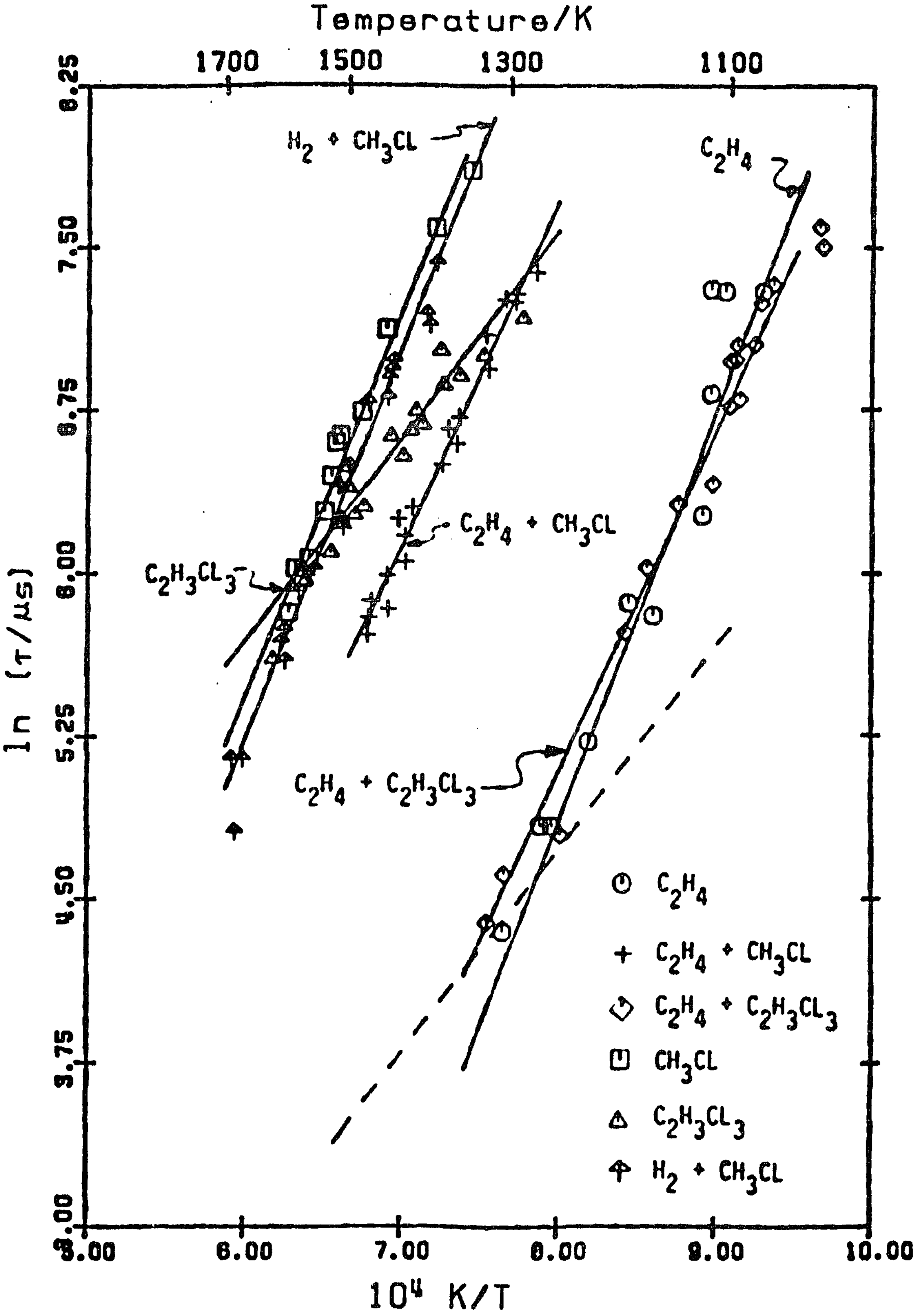

Figure 10. Ignition delay time of the mixtures of chlorinated hydrocarbons / hydrocarbons versus reciprocal temperature.

Cl- atom to the methane has little or no effect; whereas, the addition of a second Cl- atom significantly reduces the ignition delay time. This must indicate that a markedly more reactive intermediate is formed from $CH_2Cl_2$ than from $CH_3Cl$ The differences in ingition behavior within the homologous series of the ethanes and ethenes may be explained by similar reasoning.

5. The addition of readily ignitable compounds to chlorocarbons reduces the ignition delay time as compared to the parent CHC.

The kinetic pathways which control this interesting ignition behavior of the CHC's are investigated in the product distribution study and modeling effort described below.

## E. QUENCHED PRODUCT ANALYSIS

### 1. Experimental Design

The pyrolysis and preignition stoichiometric oxidation of $CH_4$ , $CH_3Cl$ and $CH_2Cl_2$ were studied behind reflected shocks over the temperature ranges 1200- 2600K and 1200-1600 K, respectively. The percentage of fuel reacted and the product distribution were measured over the temperature range at a constant initial density and reaction time.

In these experiments the initial test mixures were 3% fuel/ zero or stoichiometric $O_2$/ 10% $N_2$, used as a tracer, in argon. These levels of reactants were chosen to be certain that sufficient concentrations of the products were available in the quenched sample for gas chromatographic analysis. This is important in the SPST because in a typical experiment 50 Torr of test mixture is shock heated. After the experiment the helium driver gas expands into the driven section of the tube and the entire shock tube reaches a uniform pressure. Typically, this pressure is approximately 1 atm. Therefore, if there were no reaction, the test mixture would have been diluted by a factor of approximately 15. It is necessary to use concentrations of the reactants high enough that they are still detectable after the reaction and dilution.

These test mixtures were shock heated so that at the carbon atom concentration of the fuel was kept constant at 7.5 ± 0.5 x 10-7 mol/ cc. The combination of temperature and density were chosen so that at the end of an experiment the pressure in the shock tube was above atmospheric so that leaks of tramp air were minimized. The reaction time was 500 + 50 $\mu$s.

The percentage of the initial fuel which was reacted as a function of the initial temperature for both pyrolysis and stoichiometric oxidation conditions behind the reflected shock is shown in Figure 11. Pyrolysis and pre-ignition oxidation product distributions are plotted versus temperature in Figures 12- 17. In order to account for the dilution effect which occurs in single pulse shock tubes between the quenching of the reaction and sampling, all concentrations are normalized with respect to nitrogen, which was used as a non-reactive tracer in all of the experiments. In addition to the chemical species plotted in Figures 14 and 15 $C_2H_5Cl$ and $C_2H_3Cl$ were identified during both the pyrolysis and oxidation of $CH_3Cl$.

### 2. Discussion of Percentage Reacted Data

The pyrolysis data from the shock tube shown in Figure 11 indicate that in the reaction time of these experiments, 50 percent depletion of the initial $CH_4$ does not occur until the temperature reaches 2300K. In contrast, 50 percent of the $CH_3Cl$ reacts at a temperature of 1800K and for $CH_2Cl_2$ the temperature for 50 percent reaction is only 1500K. The difference between the methane and chlorinated methanes reflects reflects the bond dissociation energies, the C-H bond strength in $CH_4$ (435 kJ/mol) and the C-Cl bond strength in $CH_3Cl$ and $CH_2Cl_2$ (358 kJ/mol and 347 kJ/mol, respectively). The increased reactivity of $CH_2Cl_2$ over CH.Cl must be explained by the formation of more reactive intermediates or more rapid radical- $CH_2Cl_2$ reactions (125).

The oxidation experiments confirm that ignition, indicated by the rapid decrease in concentration of $CH_4$ and $CH_3Cl$, occurs at approximately the same temperature (1450K)

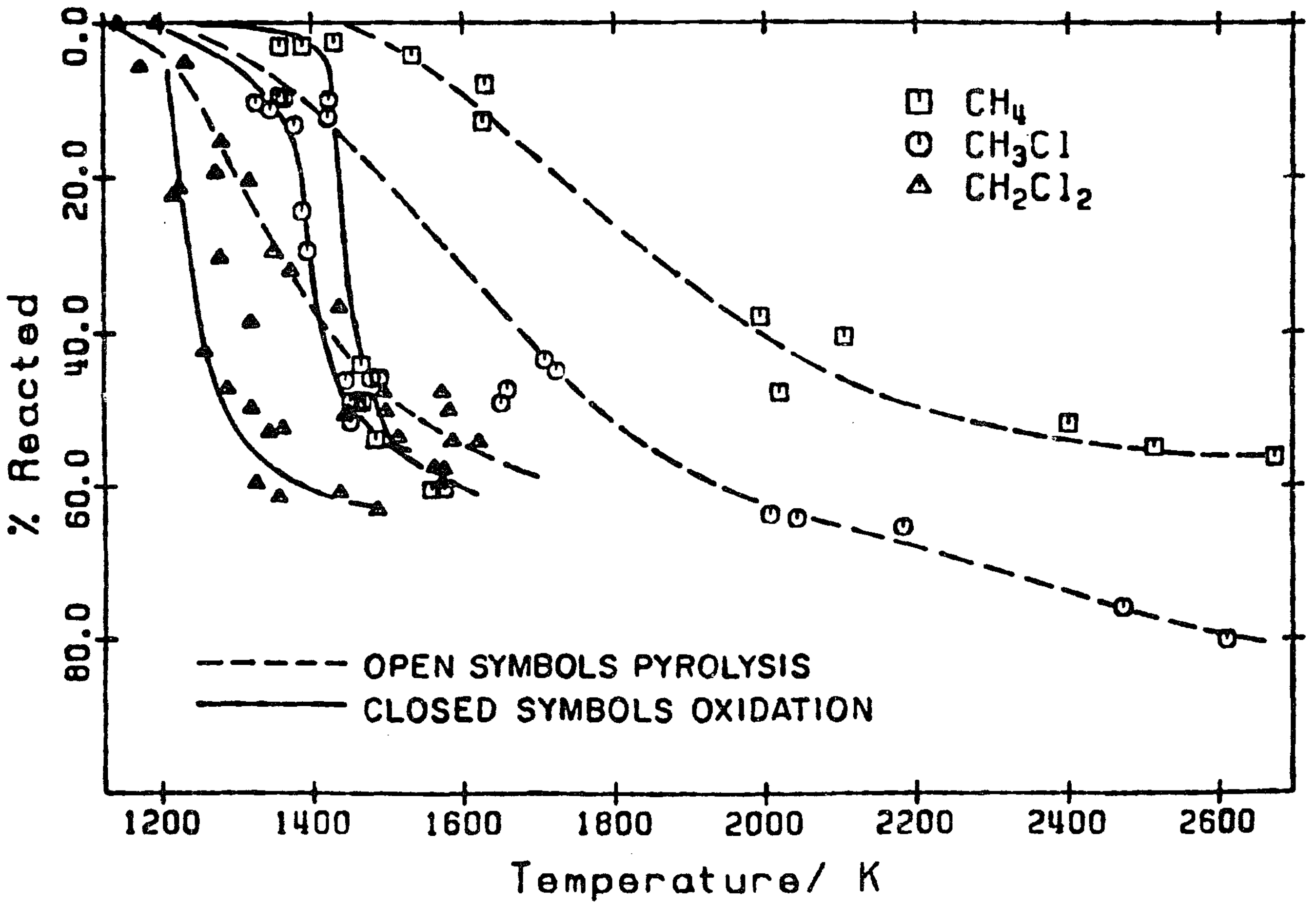

Figure 11. Comparison of methane, methyl chloride and dichloromethane percentage reacted during pyrolysis and stoichiometric oxidation.

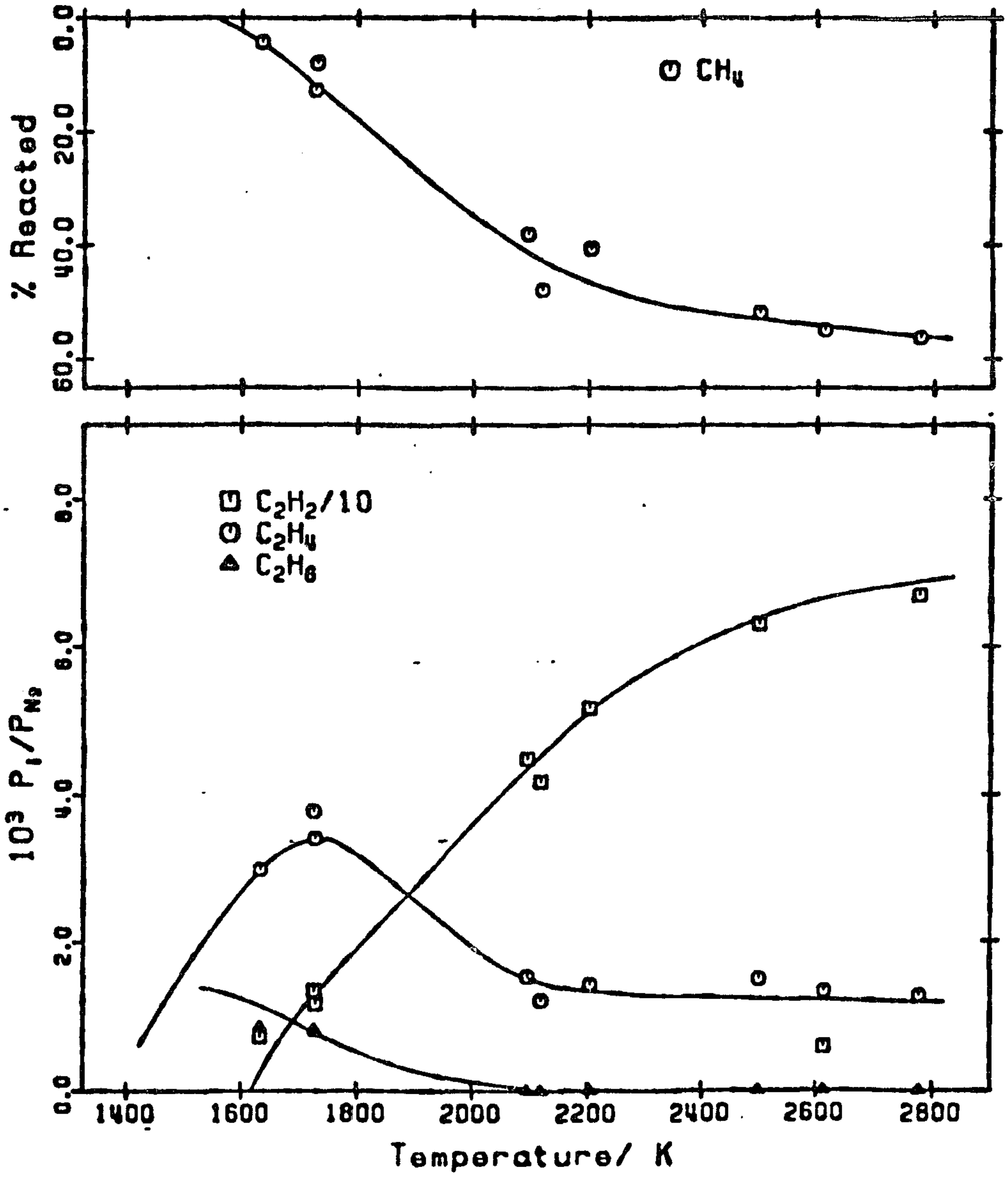

Figure 12. Percentage methane reacted and quenched product distribution during pyrolysis. Reaction time = 500 μs.

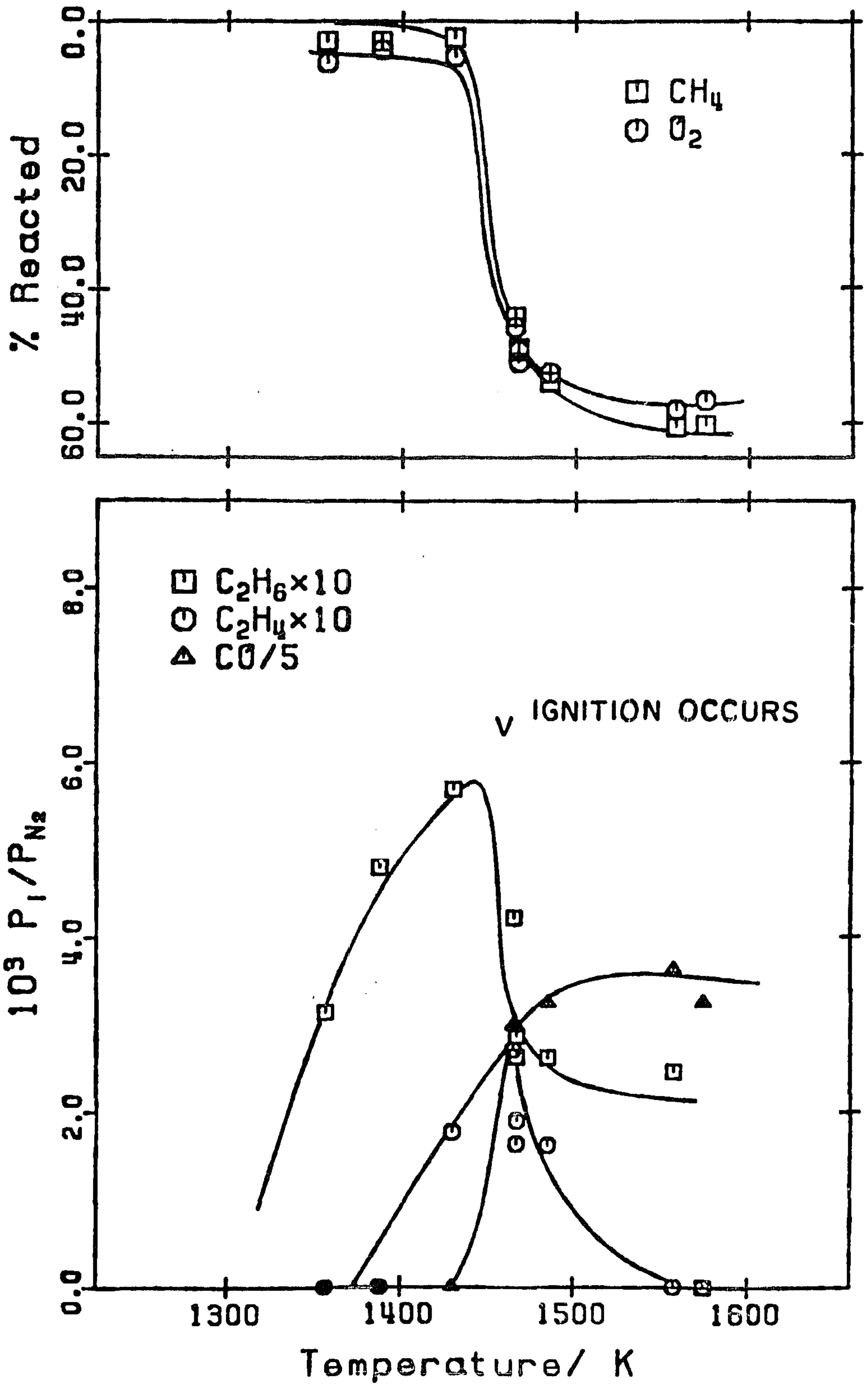

Figure 13. Percentage methane/oxygen reacted and quenched product distribution during stoichiometric oxidation. Reaction time = 500 μs

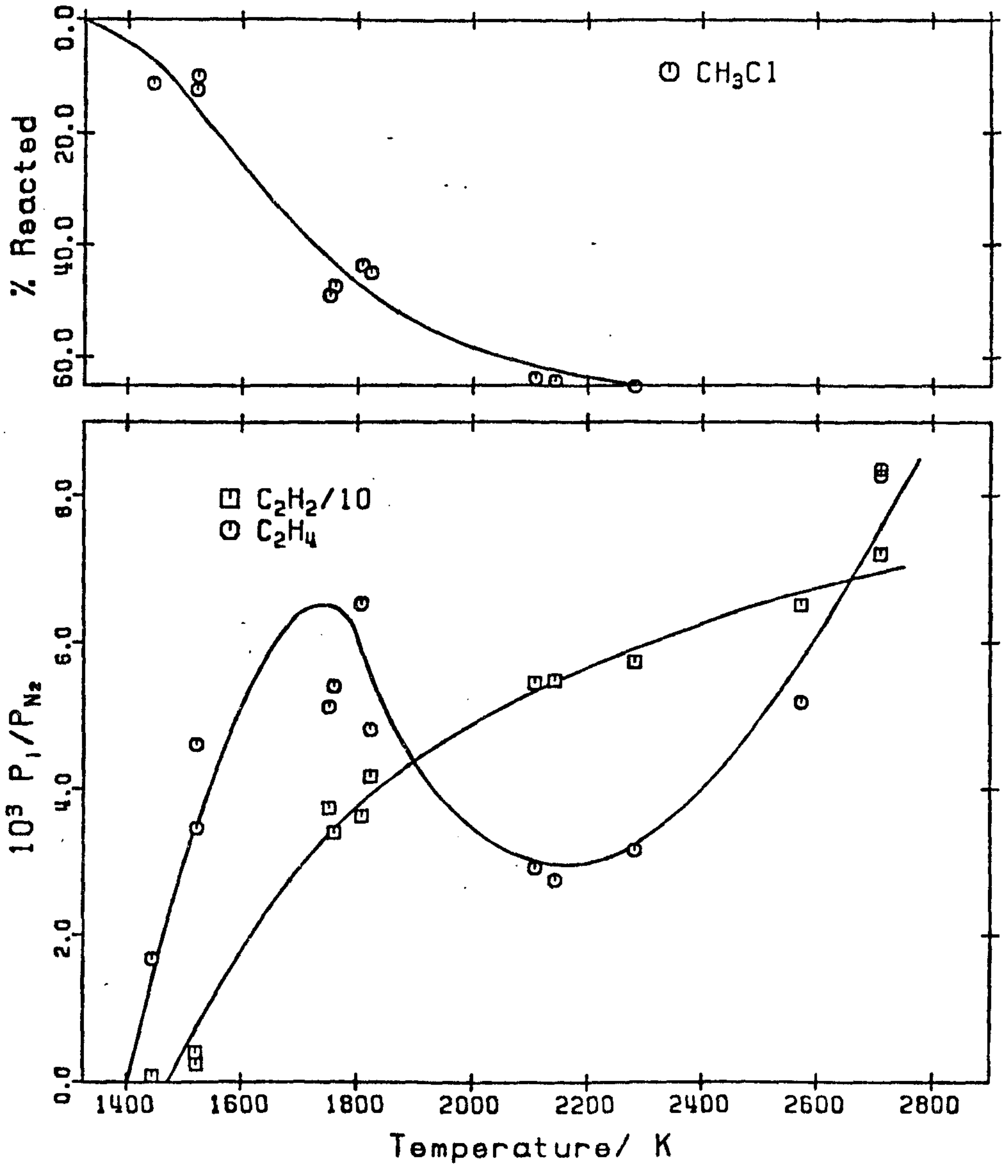

Figure 14. Percentage methyl chloride reacted and quenched product distribution during pyrolysis Reaction time = 500 $\mu$s.

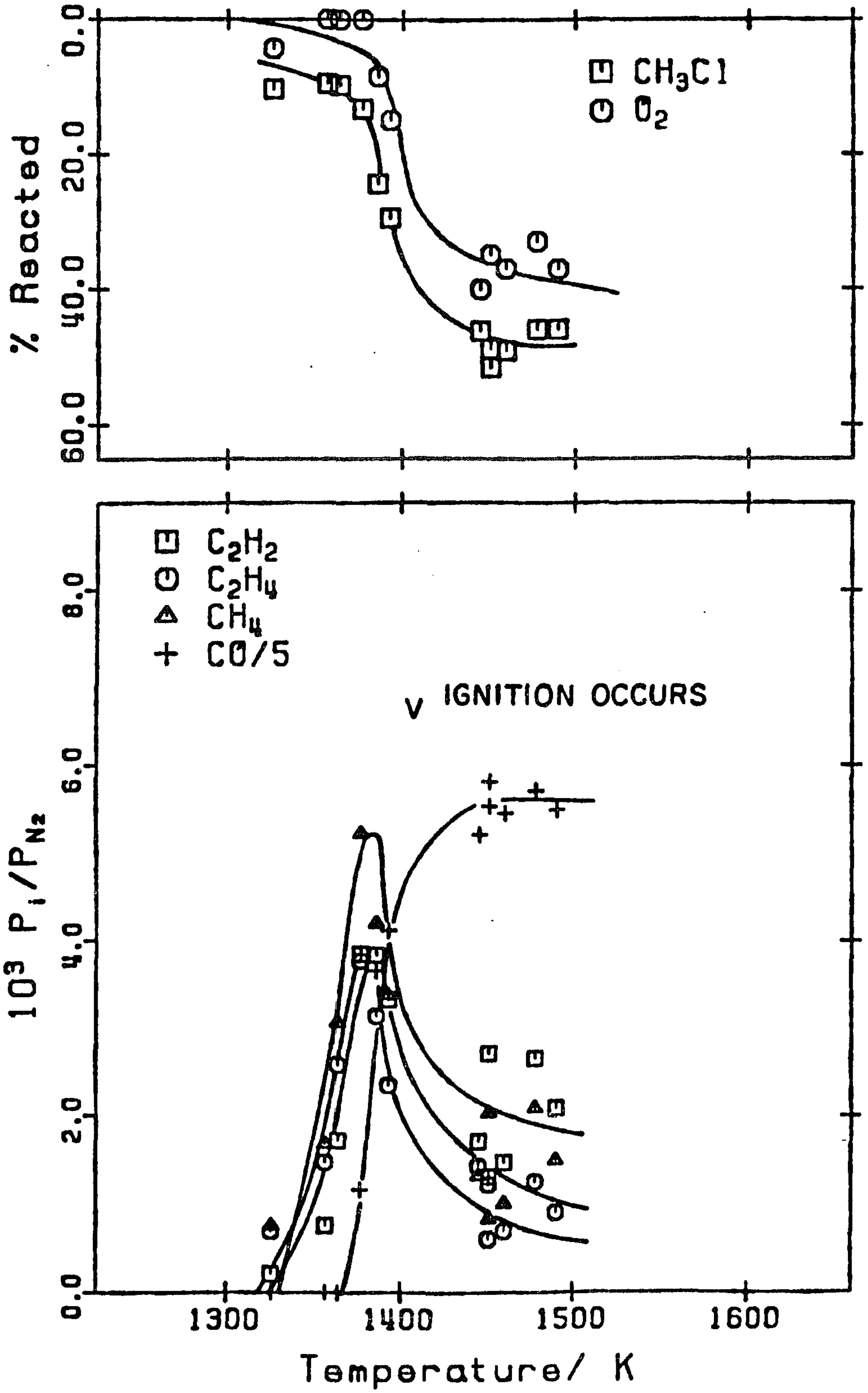

Figure 15. Percentage methyl chloride/ oxygen reacted and quenched product distribution during stoichiometric oxidation. Reaction time = 500 μs.

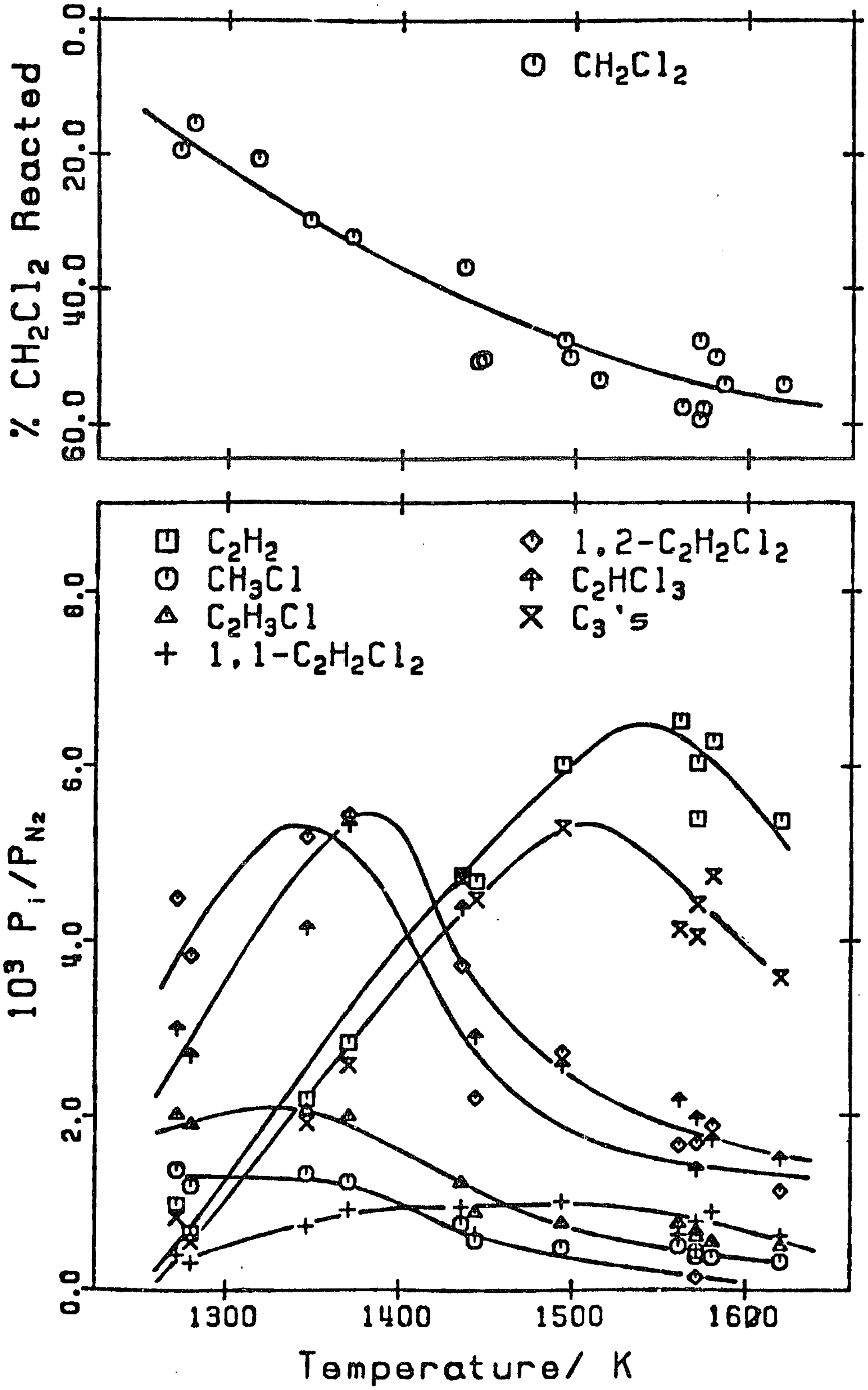

Figure 16. Percentage dichloromethane reacted and quenched product distribution during pyrolysis. Reaction time = 500 μs.

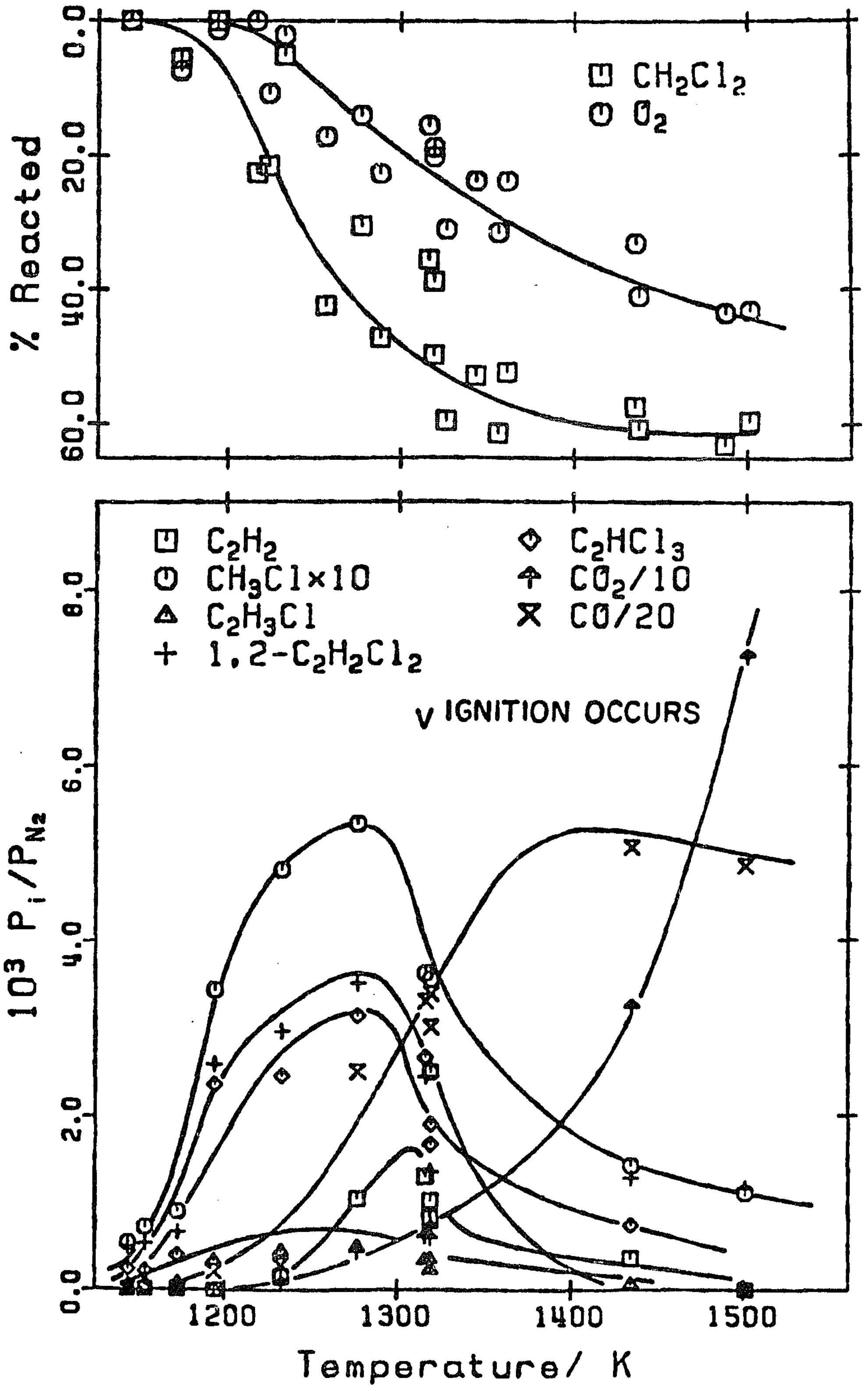

Figure 17. Percentage dichloromethane/ oxygen reacted and quenched product distribution during stoichiometric oxidation. Reaction time = 500 μs.

and that $CH_2Cl_2$ ignites at lower temperatures (1250K). While methane is virtually unreactive before ignition methyl chloride exhibits a 10 percent decomposition in its preignition regime. There is also a small preignition decomposition of the dichloromethane. The level of this preignition decomposition for both $CH_3Cl$ and $CH_2Cl_2$ is similar to the pyrolytic decomposition of these CHC's. This indicates that, as with most hydrocarbons, the principal effect of oxygen is not to react directly with the "fuel" but rather with the decomposition fragments of the fuel in chain branching reactions. These reactions produce reactive radicals and when a critical concentration of these radicals is produced, they react rapidly with the "fuel", producing ignition.

## 3. Discussion of Product Distribution Data

The product distribution from experiments in pyrolysis and oxidation of the three fuels studied are plotted in Figures 12- 17. Not plotted on these figures is the fact that during the pyrolysis experiments with $CH_2Cl_2$ soot was collected in the sample bulb; whereas no soot was collected during the pyrolysis of $CH_4$ or $CH_3Cl$.

Qualitatively the most important observation is that non-reactant CHC's were observed in the products (though not quantitively measured in the case of $CH_3Cl$) of both pyrolysis and oxidation of $CH_3Cl$ and $CH_2Cl_2$. This includes some species which are more heavily chlorinated than the reactant molecule.

No ethane was measured in either of the sets of experiments with $CH_3Cl$ or $CH_2Cl_2$. Weissman and Benson (50) explained this by a radical process in which the Cl-atom reactions with $C_2H_6$ rapidly consume $C_2H_6$ to produce $C_2H_4$ and similarly attack $C_2H_4$ to produce $C_2H_2$. This rapid pathway to the formation of $C_2H_2$, which is postulated (50) as an important step in the soot formation process, may explain the propensity of CHC's to produce soot.

For more heavily chlorinated hydrocarbons the concentration of carbon monoxide in the final products is higher than for lightly chlorinated hydrocarbons. This would seem to confirm that some mechanism for inhibiting the oxidation of CO to form $CO_2$ is occurring during the oxidation of CHC's.

High concentrations of the combined cis- and trans-1,2 $C_2H_2Cl_2$ were measured in the $CH_2Cl_2$ experiments. This could indicate the identity of the initiation step for the decomposition of $CH_2Cl_2$. However, such references concerning initiation processes based upon product distributions are inappropriate. The dichloroethenes may be formed by rapid H-atom or Cl-atom abstraction reactions from another $C_2$ CHC.

These data confirm the fact that the combustion of chlorinated hydrocarbons can produce equally hazardous chlorinated hydrocarbons. In the regions of an incinerator with poor fuel/ oxidizer which are approximately pyrolytic in nature, significant quantities of PIC's, both gaseous priority organic conpounds and soot, are more readily produced as the Cl-atom/ H-atom ratio increases.

# CHAPTER V

# DEVELOPMENT OF A CHEMICAL KINETIC MODEL FOR THE IGNITION OF CHLORINATED HYDROCARBONS

## A. INTRODUCTION

The use of models in the analysis of hazardous waste incinerators was discussed in Chapter II. Presently the more advanced incinerator models (85, 86) perform detailed heat transfer/ fluid mechanical calculations, but use simple, usually single step, expressions for the chemistry of the combustion. These expressions are applied to conditions of temperature, pressure and concentration far removed from the experimental environment where they were developed.

Recently, there have been efforts to develop better models for the chemistry which occurs within flames which consist primarily of chlorinated hydrocarbons (CHC's). Senkan et al. (74, 75) have used semi- global models which combine a one step global expression for the conversion of the CHC (in this case trichloroethene) to non- chlorinated intermediates, hydrogen chloride and carbon monoxide (CO) followed by a detailed model for the oxidation of CO. This has been fairly successful in matching the experimental flame data measured in the post flame zone. Cundy and Senser (80) are developing models which include several irreversible chemical steps involving the reactant CHC and the major CHC intermediates for $C_1$ chlorinated compounds. These types of chemical models should be more appropriate for use in incinerator models than those presently in use as they were developed from flame environment data.

With the increased computational capabilities available to the technical community, complex numerical models for reacting flows which combine detailed chemistry and fluid mechanics have become common (126- 129). An important facet of these models is the use of large sets of elementary, reversible chemical reactions. These models, which include 30- 500 reactions, have several advantages over global and quasi- global models:

1. Use of elementary, reversible chemical reactions, places the model on rigorous theoretical and experimental foundations.
2. Inclusion of all possible chemical events hypothetically allows the model to be used for any set of conditions.
3. Analysis of the simulations provides insight into the relative importance of individual species and reaction paths. This information is often unavailable experimentally. These computational results can then be used to guide future experimental and theoretical

research.

However, there are problems with the development of these detailed models:

1. Omission of a reaction or set of reactions may cause erroneous interpretation of results.
2. Use of unrealistic or obsolete rate parameters may also produce misinterpretations.
3. Approximation of the reaction rate constants for many reactions is necessary.

If these problems are overcome, the detailed chemical kinetic model can provide insight into the chemistry which occurs in a reaction system. Therefore, the development of a detailed chemical kinetic model for the ignition delay behavior of chlorinated hydrocarbons was begun. The initial effort was to assemble a model for the simplest CHC, methyl chloride ($CH_3Cl$). The model would be used to identify the primary kinetic steps through which CH Cl proceeds during pre- ignition oxidation.

## B. ASSEMBLING THE DETAILED MODEL

### 1.. Ignition Model for Methane/ Oxygen Mixtures

A recently published detailed chemical kinetic model for the ignition delay of methane ($CH_4$) and oxygen ($O_2$) mixtures (34) was chosen as a starting point for the development of the model for the oxidation of methyl chloride. Since the publication of the $CH_4/O_2$ model, several new studies (130, 131) have suggested modifications to rate constants and the deletion of certain reactions from the mechanism. Therefore, it was necessary to update the reaction mechanism.

While modifying the mechanism, it was decided to change the kinetics program to account for the pressure dependence of reactions known to exhibit unimolecular behavior. The correction is based on a Rice- Ramsperger- Kassel (RRK) development suggested by Warnatz (130).

The modified $CH_4/O_2$ mechanism is listed as the first 121 reactions in the Appendix. The updated mechanism differs from that published in (34) in three areas:

1. The original mechanism had three methyl radical recombination reactions

$$CH_3 + CH_3 = C_2H_6 \qquad R$$

$$CH_3 + CH_3 = C_2H_5 + H \qquad Ra$$

$$CH_3 + CH_3 = C_2H_4 + H_2 \qquad Rb$$

A shock-tube study by Kiefer (131) has determined that Ra and Rb probably do not occur, and if they do, their rates are much less than R. Therefore Rb has been omitted from the reaction set and the rate of Ra reduced to that suggested by Kiefer.

2. Sensitivity analysis during the previous $CH_4/O_2$ study (34) indicated the importance of the reaction of propene during the ignition of methane. Therefore, the reaction

$$(M +)\ C_3H_6 = CH_3 + C_2H_3\ (+ M)$$

has been added with the rate parameters suggested by Burcat (132).

3. The rate parameters of the reactions which are denoted by a star have been updated according to Warnatz (130) and recent work presented at the Twentieth Symposium on Combustion.

To check whether the conclusions of reference remained valid the ignition delay times for the 9 cases (IC1- IC9) in (34) were recalculated with the revised model. During these numerical experiments the ordinary differential equations in the species concentrations and the temperature arising from the application of the rate laws to the system of reactions were solved assuming a constant density control volume. The use of the constant density approximation has been suggested for simulating conditions behind reflected shocks (133). As problems of this type are often numerically stiff, the packages LSODE and LSODES (134) were used to solve the differential equations.

The revised methane ignition delay mechanism predicted shorter ignition delay times than did the old mechanism. To tune the mechanism into agreement with the data the rate of the reaction

$$CH_3 + O_2 = CH_2O + O \qquad \mathrm{RN}$$

was reduced by 30 percent from that used previously. This is still a factor of 1.75 greater than the value suggested by Hsu et al. (135). The comparison of the old results, new results and experiment data is listed in Table 5. To further investigate the performance of this revised mechanism, sensitivity analysis using a saturated design (136) was performed on the 11 reactions with the highest rate constant sensitivity as listed in Table 4 of (34). The ranking of the sensitivities between the old and new mechanism were nearly identical. This indicated that the mechanistic conclusions of (34) need not be modified.

| Exp. Nos. | Computed $\tau$ ($\mu$s) | | Experimental $\tau$ ($\mu$s) |
|---|---|---|---|
| (reference 34) | (reference 34) | revised | (reference 34) |
| IC1 | 201 | 222 | 268 |
| IC2 | 45.2 | 40. | 45.8 |
| IC3 | 13.9 | 14. | 17.9 |
| IC4 | 380 | 417 | 436 |
| IC5 | 79.5 | 84 | 99 |
| IC6 | 74.2 | 73 | 99 |
| IC7 | 1450 | 1340 | 1512 |
| IC8 | 508 | 508 | 549 |
| IC9 | 210 | 227 | 226 |

Table 5. Comparison of methane mechanism of Frenklach (34) with the revised mechanism.

### 2. Additional Reactions for the Chlorinated Hydrocarbon System

The expansion of the methane/ oxygen reaction set into a reaction set valid for methyl chloride requires the addition of four groups of reactions. The first group includes reactions between chlorine and oxygen. These reactions R315, R318 - R344 were taken from the review of Baulch et al. (137). Reactions which involve hydrogen and chlorine comprise the second additional group (R302- R314, R316- R317). This group of reactions has recently been reviewed by Shum and Benson during an investigation of the oxidation of hydrogen chloride (138).

The third set of reactions involves radicals unique to the chlorinated hydrocarbon system, such as OCl, Cl, ClOO, CHCl, $CHCl_2$, etc. reacting with the hydrocarbons. Reactions between chlorinated hydrocarbons comprise the fourth set of additional reactions which must be added to the methane mechanism.

After assembling the reaction set there were 432 elementary reactions. All were considered reversible except those marked with an I in the Appendix. These reactions actually proceed through a stable intermediate and should not be considered reversible. For the majority of the reactions the reverse rate constants were calculated from the forward rate and a logarithm fit to the equilibrium constant with respect to pressure, $K_p$.

There were 59 chemical species involved in the reactions. The thermochemistry of approximately 15 species was not available in the literature and had to be calculated during the course of the study (139).

## 3. Evaluation of the Rate Constants

For the first two subsets of reactions which were added to the methane mechanism the rate constants were available from references 137, 138. Unfortunately, many of the reactions in sets three and four have not been studied. The rate constants for the chlorination reactions of C. and C. hydrocarbons have been reviewed by Chiltz et al. (140) and their rate constants were adopted. Certain other reactions have also been studied and the reference for their rate parameters is given in the Appendix.

For the remaining reactions approximations were necessary. The reactions can be divided into five groups.

1. Reactions of O, $O_2$ and OH with the single carbon CHC's. Rate parameters of these reactions were set equal to the reactions with the analogous single carbon hydrocarbons.
2. Reactions of $C_2$ CHC's involving HCl elimination. Those which had not been studied were given rate constants of

   $$k = 1.E+13 \exp(-27700/T)$$

   which is the typical rate for this type of reaction found in Benson (141) and Benson and O'Neal (142).

3. Reactions involving radical recombination-disproportionation, such as

   $CH_2Cl + CHCl = 1,2\text{-} C_2H_2Cl_2 + H$

   were written as two reactions

   $CH_2Cl + CHCl = 1,2\text{-} C_2H_3Cl_2$ kd

   $H + 1,2\text{-} C_2H_3Cl_2 = 1,2\text{-} C_2H_2Cl_2$ ke

   with rates of kd = 1.0E+13 and ke = 1.0E+12.

4. Reactions involving molecule- radical combination and disproportionation such as

   $CH_3Cl + CH_3 = C_2H_5Cl + H$ kf

   were set to kf = 1.0E13exp(-6000/T). The activation energy is required to distort the electron cloud around the molecule in order to allow the formation of the C-C bond.

5. All of the remaining reactions were written in the exothermic direction. This allows the assumption that the activation energy, $E_a$, is equal to zero as a first approximation. The frequency factors for these reaction were set according to the system presented in Table 6. These values are suggested by examination of the frequency factors for similar reactions tabulated by Benson (141) and the discussion in a recent paper by Golden (143). Detailed transition state analysis suggests that the larger the mass and more complicated the structure of two reactants the lower the

| Radical Reaction Partners | $\text{Log}_{10}$ A Factor |
|---|---|
| H- atom | 14.0 |
| O- atom | 13.5 |
| Cl-atom, OH, CH | 13.25 |
| OCl, CCl, CH | 12.75 |
| OHCl, CHCl | 12.50 |
| Heavy and Complex Structures | 11.00 |

UNITS: mol, cm**3, s

Table 6. Frequency factors of the estimated rate constants.

> frequency factor for their reaction. This is because there is a larger change in entropy from the unreactive state during the formation of the transition state when the six rotational degrees of freedom of large reactants are converted into the 3 rotational degrees of freedom of the activated complex than when smaller reactants form the activated complex.

As all the required data are not available for this relatively unknown reaction system, it is premature to apply the rigorous, powerful but complicated methods of Transition State Theory and Bond-Order Bond-Energy correlations to approximate rate parameters.

## C. COMPARISON OF MODEL RESULTS TO EXPERIMENTAL DATA

The $CH_3Cl$/ $O_2$ ignition delay mechanism was integrated using the constant density assumption suggested above for conditions at the extremes of the experimental temperature range, 1400 and 1600K at P= 1.8 atm. The comparison of the calculated ignition delays and the expermental values is plotted Figure 18. Without modifying any of the estimated rate parameters, the model is within a factor of two of the experimental data. A better fit could be obtained by adjusting rate parameters within the model, but that is not justified without a more detailed examination of the behavior of the model.

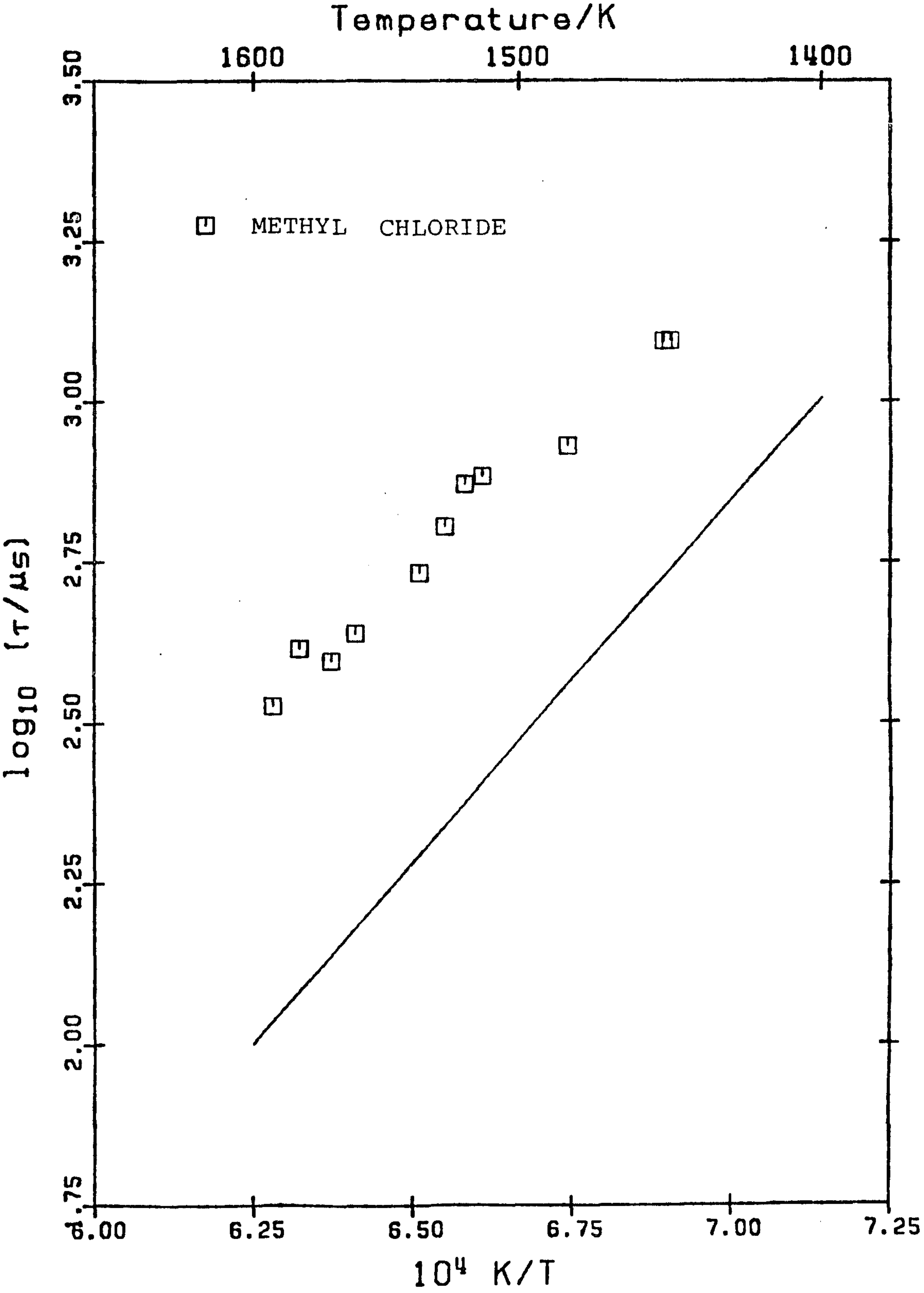

Figure 18. Comparison of experimental ignition delay time for methyl chloride with the model predictions.

The next step in the analysis of the model was to remove those reactions which did not contribute to the calculation of ignition delay times. This reduction of the reaction mechanism is important for two reasons:

1. There is no justification to keep reactions in the mechanism which are not important in simulating the measured parameter, in this case ignition delay time. However, it must be emphasized that for purposes other than ignition delay time calculations the full mechanism must be used as the starting point.
2. Understanding the behavior of the model is easier, the fewer reactions there are.

The reduction of reaction was accomplished by using the pR spectrum (144, 145). For reaction j

$$pR = \text{sign}*\log_{10} |R_f - R_r| / \text{molecule-cm}^{-3}\text{-s}^{-1}$$

where

$R_f$, $R_r$ are the forward and reverse rates, respectively;

sign is the sign of $(R_f - R_r)$

The pR value of each reaction was examined near the beginning, the middle and the end of the ignition delay time for both the high and low temperature numerical experiments. Any reaction whose $pR < 0.001\ pR_{max}$ and was not nearing equilibrium was eliminated. This reduced the mechanism to 131 reactions and 46 species. The reduced mechanism performs to within 1 percent of the complete mechanism.

## D. IDENTIFICATION OF THE PRINCIPAL KINETIC PATHWAYS

One tool to determine the major kinetic paths during the ignition is to identify the reactions through which the most reaction species flux is occurring. These reactions are those with the largest reaction rate, pR, defined above. Table 7 lists the reaction which at the midpoint of the high temperature ignition delay time are undergoing the highest reaction flux. Table 8 contains a similar list for the low temperature computation. Examination of these two tables indicates that the stoichiometric oxidation of $CH_3Cl$ is considerably different from that of methane. In methane the major reactions during stoichiometric oxidation involve the methyl radical ($CH_3$) and molecular oxygen and hydroperoxyl radical

$$CH_3 + O_2 = CH_3O + O$$

$$CH_3 + HO_2 = CH_3O + OH$$

and the subsequent sequence of reactions beginning with the methoxy radical ($CH_3O$) decomposiiton to produce

| | Reaction | pR |
|---|---|---|
| 1. | $Cl + CH_3Cl == HCl + CH_3Cl$ | 21.72 |
| 2. | $CH_3Cl == CH_3 + Cl$ | 21.35 |
| 3. | $C_2H_3 == H + C_2H_2$ | 21.27 |
| 4. | $CH_2Cl + CH_2Cl ==$ 1,2- $C_2H_4Cl$ | 21.25 |
| 5. | 1,2- $C_2H_4Cl == HCl + C_2H_3Cl$ | 21.08 |
| 6. | $Cl + CH_4 == CH_3 + HCl$ | -21.07 |
| 7. | $C_2H_5Cl == C_2H_4 + HCl$ | 21.06 |
| 8. | $CH_3 + CH_2Cl == C_2H_5Cl$ | 21.05 |
| 9. | $CH_2Cl + C_2H_4 == C_2H_3 + CH_3Cl$ | 21.02 |
| 10. | $Cl + C_2H_2 == C_2H_2Cl$ | -20.98 |
| 11. | $OH + CH_3Cl == H_2O + CH_2Cl$ | 20.96 |
| 12. | $H + CH_3Cl == CH_3 + HCl$ | 20.89 |
| 13. | $H + CH_3Cl == H_2 + CH_2Cl$ | 20.86 |
| 14. | $M + HCO == H + CO + M$ | 20.86 |
| 15. | $O + HCl == OH + Cl$ | 20.85 |
| 16. | $H + C_2H_3Cl == H + C_2H_2Cl$ | 20.70 |
| 17. | $H + C_2H_3Cl == HCl + C_2H_3$ | 20.70 |
| 18. | $H + O_2 == OH + O$ | 20.69 |
| 19. | $CHClO == CO + HCl$ | 20.68 |
| 20. | $Cl + C_2H_3Cl ==$ 1,2- $C_2H_3Cl_2$ | -20.57 |
| 21. | $CH_2O + CH_2Cl == HCO + CH_3Cl$ | 20.50 |
| 22. | $O_2 + CHCl == O + CHClO$ | 20.43 |
| 23. | $O_2 + C_2H == O + C_2HO$ | 20.40 |
| 24. | $O_2 + CH_2 == H + OH + CO$ | 20.39 |
| 25. | $O + C_2H_2 == CH_2 + CO$ | 20.34 |

Table 7. The twenty- five reactions with the highest pR at one- half the calculated ignition delay time for the 1600K case.

| | Reaction | pR |
|---|---|---|
| 1. | Cl + $CH_3Cl$ == HCl + $CH_2Cl$ | 20.64 |
| 2. | $CH_2Cl$ + $CH_2Cl$ == 1,2- $C_2H_4Cl_2$ | 20.26 |
| 3. | $CH_3Cl$ == $CH_3$ + Cl | 20.10 |
| 4. | 1,2- $C_2H_4Cl_2$ == HCl + $C_2H_3Cl$ | 20.08 |
| 5. | OH + $CH_3Cl$ == $H_2O$ + $CH_2Cl$ | 20.06 |
| 6. | Cl + $C_2H_2$ == $C_2H_2Cl$ | -19.97 |
| 7. | Cl + $CH_4$ == $CH_3$ + HCl | -19.98 |
| 8. | $C_2H_3$ == H + $C_2H_2$ | 19.89 |
| 9. | M + HCO == H + CO + M | 19.75 |
| 10. | Cl + $C_2H_3Cl$ == 1,2- $C_2H_3Cl_2$ | -19.70 |
| 11. | $CH_2O$ + $CH_2Cl$ == HCO + $CH_3Cl$ | 19.69 |
| 12. | $CH_2Cl$ + $C_2H_4$ == $C_2H_3$ + $CH_3Cl$ | 19.66 |
| 13. | O + HCl == OH + Cl | 19.65 |
| 14. | CHClO == CO + HCl | 19.62 |
| 15. | $C_2H_5Cl$ == $C_2H_4$ + HCl | 19.61 |
| 16. | H + $CH_3Cl$ == $CH_3$ + HCl | 19.59 |
| 17. | H + $C_2H_3Cl$ == H + C H Cl | 19.59 |
| 18. | H + C $H_3Cl$ == HCl + C $H_3$ | 19.59 |
| 19. | CH Cl + 1,2- C H Cl == CH Cl + 1,2- C $H_3Cl$ | 19.57 |
| 20. | H + $CH_3Cl$ == $H_2$ + $CH_2Cl$ | 19.56 |
| 21. | OH + $C_2H_2$ == H + $C_2H_2O$ | 19.54 |
| 22. | O + $C_2H_2$ == H + $C_2HO$ | 19.52 |
| 23. | CH + $C_2H_3Cl$ == $CH_4$ + $C_2H_2Cl$ | 19.52 |
| 24. | OH + $C_2H_3Cl$ == $H_2O$ + $C_2H_2Cl$ | 19.52 |
| 25. | Cl + $C_2H_4$ == $CH_2CH_2Cl$ | -19.47 |

Table 8. The twenty- five reactions with the highest pR at one- half the calculated ignition delay time for the 1400K case.

formaldehyde which reactants to form formyl radical which is the source of carbon monoxide.

In contrast for the methyl chloride system after the initiation

$$CH_3Cl \quad = \quad CH_3 \quad + \quad Cl$$

which is the dominant route in these conditions, Cl-atom reacts with the CH Cl abstracting an H-atom

$$Cl \quad + \quad CH_3Cl \quad = \quad CH_2Cl \quad + HCl$$

The methyl and chloromethyl ($CH_2Cl$) radicals combine to form the $C_2$ CHC's, ethyl chloride and 1,2 dichloroethane. These two $C_2$'s then quickly decompose by elimination of HCl to produce the unsaturated $C_2$ chloro- and hydrocarbons, vinyl chloride ($C_2H_3Cl$) and ethene ($C_2H_4$). These compounds also decompose quickly to produce acetylene which oxidizes to form carbon monoxide. The process is depicted in Figure 19. This suggests that under these experimental conditions the large quantities of acetylene and ethylene which are measured in the CHC experiments may not be from the Cl-atom catalyzed decomposition of ethane as suggested by Weissman and Benson (50). Instead the first $C_2$ species formed is not the $C_2$ hydrocarbon but the $C_2$ CHC's.

The HCl which is formed during these eliminations from the $C_2$ CHC's serves as an important chain carrier in the

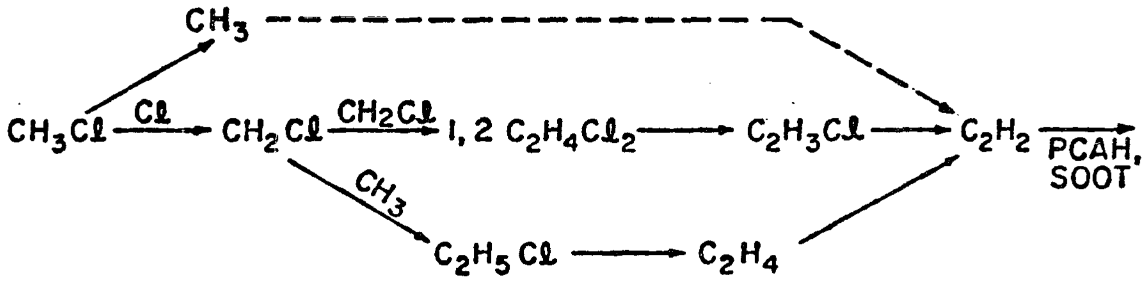

Figure 19. Representation of the major kinetic pathways to the ignition of methyl chloride.

reaction. Through radical reactions they serve as a source for replenishing the Cl- atom concentration.

## E. CONCLUSIONS

The first detailed chemical kinetic mechanism composed primarily of CHC reactions has been used to analyze the ignition delay times of methyl chloride. This mechanism can serve as a starting point for developing reaction models for more heavily chlorinated compounds. Initial analysis of the model has allowed the postulation of the kinetic paths which are important to the stoichiometric pre- ignition oxidation of methyl chloride.

## CHAPTER VI

## CONCLUSIONS AND RECOMMENDATIONS

Developing an understanding of the combustion processes occurring during the incineration of chlorinated hydrocarbons is important in the proper design and safe operation of hazardous waste incinerators. The data gathered and the analysis performed during this study have provided the following information:

1. Contrary to conventional wisdom, chlorinated hydrocarbons are not universally more difficult to ignite than their analogous hydrocarbons.
2. There is no simple relationship between ignition delay times and the number of Cl-atoms within an homologous hydrocarbon series.
3. The stability to thermal decomposition ranks methane > methyl chloride > dichloromethane, in parallel with the lowest bond dissociation energies of each compound.
4. Products of Incomplete Combustion, polycyclic aromatic hydrocarbons (PCAH's), soot, and priority organic compounds are produced at higher levels as Cl-atom/ H-atom ratio increases.
5. The levels of carbon monoxide which persist during the oxidation of CHC's increases as the Cl-atom/

H-atom ratio increases, which confirms the inhibition of carbon monoxide by Cl-atom.

6. The chemical kinetic pathways important in the oxidation of methyl chloride are considerably different from those for methane. Methyl Chloride is quickly converted into $C_2$ CHC's which rapidly decompose via $\alpha,\beta$ HCl elimination, thereby contributing to the reactive pool of radicals. This is different from methane in that the $C_2H_6$ which forms is relatively stable and does not contribute to the radical pool.

Further study is recommended on the following issues:

1. A complete sensitivity analysis of the $CH_3Cl/ O_2$ mechanism to determine the rate parameters which have the most effect on the computed ignition delay time and species concentration. This would allow small modifications of the literature values and/ or approximated values to bring the model into better agreement with the experimental data. It would also identify reactions for which more rigorous rate constant approximations would be justified and for which experimental measurements would be advised.
2. Expansion of the mechanism through the calculation

of the necessary thermochemistry and postulation of additional reactions to investigate the oxidation of dichloromethane, which has a very short ignition delay time.

3. Combination of the mechanism with the soot formation mechanism recently developed (115) to simulate the sooting behavior of chlorinated hydrocarbons.
4. Application of the mechanism to flame codes for comparison with data from flat flame burners.
5. The extension of the product distribution data for the pyrolysis of chlorinated hydrocarbons to higher temperatures so that it would more closely complement the soot formation studies.
6. Develop experimental techniques to study individual reactions important to chlorinated hydrocarbon combustion.
7. The development of a computer software package which would organize and automate the tedious and error producing steps in the analysis of the reaction mechanism
   a. Automatic removal of reactions designated by the user; either by reaction number or by typing the reaction in at the terminal.
   b. Automatic sorting and listing of the reactions according to pR at each time step.

c. Automatic partition of the reactions according to pR powers of ten.

# LIST OF ABBREVIATIONS

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| | |
|---|---|
| API | American Petroleum Institute |
| CERCLA | Comprehensive Environmental Response, Compensation and Liability Act, 1980 |
| CHC | Chlorinated Hydrocarbon |
| CST | Conventional Shock Tube |
| DRE | Destruction and Removal Efficiency |
| FID | Flame Ionization Detector for a gas chromatograph |
| GC | Gas Chromatograph |
| GSV | Gas Sample Valve for a gas chromatograph |
| HC | Hydrocarbon |
| JANAF | Joint Army Navy Air Force Commission on Thermochemistry |
| LSODE(S) | Livermore Solver of Ordinary Differential Equations (Sparse) |
| LSU | Louisiana State University |
| MS | Mass Spectrometer |
| NASA | National Aeronautical and Space Administration |
| PCB | Polychlorinated Biphenyl |
| PCDD | Polychlorinated- dibenzo- p- dioxins |
| PIC | Product of Incomplete Combustion |
| PMT | Photomultiplier Tube |
| POHC | Principal Organic Hazardous Component |
| RCRA | Resource Conservation and Recovery Act, 1976 |
| RRK | Rice- Ramsparger- Kassel theory of unimolecular reactions |

| | |
|---|---|
| RRKM | Rice- Ramsparger- Kassel- Marcus theory of unimolecular reactions |
| SPST | Single- Pulse Shock Tube |
| TCD | Thermal Conductivity Detector on a gas chromatograph |
| TOS | Thermal Oxidation Stability |
| USEPA | United States Environmental Protection Agency |
| UT | University of Texas |

| | |
|---|---|
| cc | cubic centimeter |
| k | rate constant for a reaction |

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# APPENDIX

The appendix contains a listing of the detailed chemical reaction mechanism developed during this research.

| REACTION | LG10A | N | EACT[a,b] (kJ/mol) | DEHR[c] (kJ/mol) | NOTE[d] | REF[e] |
|---|---|---|---|---|---|---|
| ( 1) CH4 => CH3 + H | 15.00 | 0.00 | 419.99 | 453.3 | ■ | 130 |
| ( 2) CH4 + O2 => CH3 + HO2 | 13.92 | 0.00 | 234.30 | 226.4 | ■ | 34 |
| ( 3) CH4 + H => CH3 + H2 | 7.74 | 1.97 | 46.89 | 3.6 | ■ | 146 |
| ( 4) CH4 + OH => CH3 + H2O | 6.20 | 2.10 | 10.30 | -59.2 | ■ | 34 |
| ( 5) CH4 + O => CH3 + OH | 6.33 | 2.21 | 27.11 | 11.7 | ■ | 130 |
| ( 6) CH4 + HO2 => CH3 + H2O2 | 13.30 | 0.00 | 75.31 | 90.0 |  | 34 |
| ( 7) CH4 + CH3 => H + C2H6 | 12.90 | 0.00 | 173.64 | 74.6 |  | 34 |
| ( 8) CH4 + CH3 => H2 + C2H5 | 12.00 | 0.00 | 100.42 | 40.9 |  | 146 |
| ( 9) CH4 + CH2 => CH3 + CH3 | 13.00 | 0.00 | 0.00 | -15.2 | ■ | 146 |
| ( 10) CH3 + M => H + CH2 + M | 16.00 | 0.00 | 379.00 | 468.4 |  | 146 |
| ( 11) CH3 + O2 => O + CH3O | 34.58 | -5.94 | 176.98 | 121.4 | ■ | 34 |
| ( 12) CH3 + O2 => OH + CH2O | 13.72 | 0.00 | 150.62 | -225.6 |  | 34 |
| ( 13) CH3 + O2 => HO2 + CH2 | 13.90 | 0.00 | 234.30 | 241.6 |  | 34 |
| ( 14) CH3 + H => H2 + CH2 | 14.26 | 0.00 | 63.18 | 18.8 |  | 34 |
| ( 15) CH3 + OH => H2 + CH2O | 12.90 | 0.00 | 0.00 | -300.4 | ■ | 34 |
| ( 16) CH3 + OH => H2O + CH2 | 6.19 | 2.13 | 10.04 | -44.0 | ■ | 34 |
| ( 17) CH3 + OH => H + CH3O | 15.10 | 0.00 | 115.06 | 54.6 | ■ | 34 |
| ( 18) CH3 + O => H + CH2O | 13.84 | 0.00 | 0.00 | -292.4 | ■ | 130 |
| ( 19) CH3 + O => OH + CH2 | 14.61 | 0.00 | 58.58 | 26.8 |  | 34 |
| ( 20) CH3 + HO2 => OH + CH3O | 13.20 | 0.00 | 0.00 | -93.3 |  | 34 |

| REACTION | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|
| ( 21) CH3 | + CH3 | => H | + C2H5 | | 11.89 | 0.00 | 54.50 | 37.2 | | 131 |
| ( 22) CH3 | + HCO | => CH4 | + CO | | 11.50 | 0.50 | 0.00 | -380.0 | | 34 |
| ( 23) CH3 | + CH2O | => CH4 | + HCO | | 10.00 | 0.50 | 25.10 | -64.6 | | 34 |
| ( 24) CH3 | + CH2 | => H | + C2H4 | | 13.60 | 0.00 | 0.00 | -255.0 | | 130 |
| ( 25) H | + CH2 | => H2 | + CH | | 12.84 | 0.00 | 0.00 | -12.7 | | 147 |
| ( 26) OH | + CH2 | => H2O | + CH | | 11.43 | 0.67 | 107.53 | -75.5 | | 34 |
| ( 27) O | + CH2 | => OH | + CH | | 14.48 | 0.00 | 49.90 | -4.7 | | 147 |
| ( 28) CH2 | + CH2 | => H2 | + C2H2 | | 13.50 | 0.00 | 0.00 | -536.8 | | 34 |
| ( 29) O2 | + CH | => OH | + CO | | 13.30 | 0.00 | 0.00 | -669.1 | | 130 |
| ( 30) CH4O | + M | => CH3 | + OH | + M | 42.71 | -7.08 | 376.56 | 392.2 | ■ | 148 |
| ( 31) CH3O | + M | => H | + CH2O | + M | 14.00 | 0.00 | 105.00 | 94.6 | ■ | 130 |
| ( 32) O2 | + CH3O | => HO2 | + CH2O | | 12.00 | 0.00 | 25.10 | -132.3 | ■ | 130 |
| ( 33) CH2O | + M | => H | + HCO | + M | 16.70 | 0.00 | 320.00 | 388.7 | | 130 |
| ( 34) CH2O | + M | => H2 | + CO | + M | 15.91 | 0.00 | 291.21 | 12.2 | I | 34 |
| ( 35) O2 | + CH2O | => HO2 | + HCO | | 11.00 | 0.00 | 167.36 | 161.8 | | 34 |
| ( 36) H | + CH2O | => H2 | + HCO | | 9.40 | 1.27 | 11.05 | -61.0 | ■ | 34 |
| ( 37) OH | + CH2O | => H2O | + HCO | | 4.84 | 2.65 | -7.95 | -123.8 | ■ | 34 |
| ( 38) O | + CH2O | => OH | + HCO | | 6.23 | 2.32 | 6.19 | -53.0 | ■ | 34 |
| ( 39) HO2 | + CH2O | => H2O2 | + HCO | | 12.00 | 0.00 | 33.47 | 25.4 | | 34 |
| ( 40) HCO | + M | => H | + CO | + M | 14.40 | 0.00 | 70.30 | 73.2 | ■ | 130 |
| ( 41) O2 | + HCO | => HO2 | + CO | | 12.48 | 0.00 | 0.00 | -153.6 | ■ | 130 |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| ( 42) H + HCO => H2 + CO | 14.30 | 0.00 | 0.00 | -376.4 | | 130 |
| ( 43) OH + HCO => H2O + CO | 13.70 | 0.00 | 0.00 | -439.2 | | 130 |
| ( 44) O + HCO => OH + CO | 13.48 | 0.00 | 0.00 | -368.4 | | 130 |
| ( 45) O2 + CO => O + CO2 | 13.70 | 0.00 | 264.30 | -26.2 | | 149 |
| ( 46) OH + CO => H + CO2 | 6.64 | 1.50 | -3.13 | -93.0 | ■ | 130 |
| ( 47) O + CO + M => CO2 + M | 13.72 | 0.00 | -19.00 | -534.6 | | 130 |
| ( 48) HO2 + CO => OH + CO2 | 14.18 | 0.00 | 98.92 | -241.0 | ■ | 34 |
| ( 49) O2 + M => O + O + M | 14.08 | 0.00 | 451.00 | 508.4 | | 130 |
| ( 50) H2 + M => H + H + M | 12.35 | 0.50 | 387.44 | 449.6 | | 34 |
| ( 51) H + O2 => OH + O | 17.09 | -0.91 | 69.45 | 66.8 | | 130 |
| ( 52) H2 + O => H + OH | 7.18 | 2.00 | 31.60 | 8.0 | ■ | 130 |
| ( 53) HO2 + H2 => OH + H2O | 11.86 | 0.00 | 78.24 | -210.8 | | 34 |
| ( 54) H2O + O => OH + OH | 13.83 | 0.00 | 76.99 | 70.8 | | 34 |
| ( 55) H2 + OH => H + H2O | 13.72 | 0.00 | 27.00 | -62.8 | ■ | 150 |
| ( 56) OH + H2O2 => HO2 + H2O | 12.84 | 0.00 | 6.00 | -149.2 | | 130 |
| ( 57) H + OH + M => H2O + M | 23.15 | -2.00 | 0.00 | -512.4 | | 34 |
| ( 58) H + O2 + M => HO2 + M | 17.84 | -0.80 | 0.00 | -226.9 | | 130 |
| ( 59) HO2 + O => O2 + OH | 13.70 | 0.00 | 4.14 | -214.7 | | 34 |
| ( 60) H + HO2 => OH + OH | 14.40 | 0.00 | 7.61 | -148.0 | ■ | 34 |
| ( 61) H + HO2 => O2 + H2 | 13.40 | 0.00 | 2.93 | -222.8 | | 34 |
| ( 62) HO2 + OH => O2 + H2O | 13.30 | 0.00 | 0.00 | -285.6 | | 34 |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| ( 63) O2 + H2O2 => HO2 + HO2 | 13.60 | 0.00 | 178.24 | 136.4 | | 34 |
| ( 64) H2O2 + M => OH + OH + M | 16.20 | 0.00 | 190.37 | 215.3 | ■ | 34 |
| ( 65) H + H2O2 => HO2 + H2 | 12.23 | 0.00 | 15.90 | -86.4 | | 34 |
| ( 66) C2H6 => CH3 + CH3 | 16.40 | 0.00 | 366.00 | 378.6 | ■ | 130 |
| ( 67) H + C2H6 => H2 + C2H5 | 2.73 | 3.50 | 21.76 | -33.7 | | 130 |
| ( 68) OH + C2H6 => H2O + C2H5 | 7.34 | 1.90 | 4.74 | -96.6 | | 153 |
| ( 69) O + C2H6 => OH + C2H5 | 7.48 | 2.00 | 21.40 | -25.7 | | 130 |
| ( 70) CH3 + C2H6 => CH4 + C2H5 | 0.55 | 4.00 | 34.70 | -37.4 | ■ | 130 |
| ( 71) C2H5 => H + C2H4 | 13.30 | 0.00 | 166.00 | 176.2 | ■ | 130 |
| ( 72) O2 + C2H5 => HO2 + C2H4 | 12.30 | 0.00 | 20.33 | -50.7 | ■ | 130 |
| ( 73) H + C2H5 => H2 + C2H4 | 12.27 | 0.00 | 0.00 | -273.5 | ■ | 34 |
| ( 74) C2H5 + C2H3 => C2H4 + C2H4 | 17.50 | 0.00 | 148.95 | -258.0 | | 34 |
| ( 75) C2H4 + M => H2 + C2H2 + M | 17.41 | 0.00 | 331.79 | 186.7 | | 34 |
| ( 76) C2H4 + M => H + C2H3 + M | 17.42 | 0.00 | 404.00 | 434.2 | | 34 |
| ( 77) H + C2H4 => H2 + C2H3 | 14.18 | 0.00 | 43.03 | -15.5 | ■ | 130 |
| ( 78) OH + C2H4 => H2O + C2H3 | 13.71 | 0.00 | 12.50 | -78.3 | ■ | 34 |
| ( 79) OH + C2H4 => CH3 + CH2O | 13.28 | 0.00 | 12.50 | -64.2 | ■ | 34 |
| ( 80) O + C2H4 => CH2 + CH2O | 8.92 | 1.20 | 3.10 | -37.4 | ■ | 34 |
| ( 81) O + C2H4 => CH3 + HCO | 8.88 | 1.20 | 3.10 | -117.2 | | 34 |
| ( 82) CH3 + C2H4 => CH4 + C2H3 | 11.62 | 0.00 | 46.50 | -19.1 | | 130 |
| ( 83) C2H3 => H + C2H2 | 14.22 | 0.00 | 158.99 | 202.1 | | 130 |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| ( 84) H + $C_2H_3$ => $H_2$ + $C_2H_2$ | 13.30 | 0.00 | 0.00 | -247.5 |  | 130 |
| ( 85) $C_2H_2$ + M => H + $C_2H$ + M | 16.60 | 0.00 | 446.85 | 474.0 |  | 130 |
| ( 86) OH + $C_2H_2$ => $H_2O$ + $C_2H$ | 14.43 | 0.00 | 62.76 | -38.4 | ■ | 150 |
| ( 87) O + $C_2H_2$ => $CH_2$ + CO | 8.61 | 1.50 | 7.10 | -211.8 | ■ | 130 |
| ( 88) O + $C_2H_2$ => H + $C_2HO$ | 14.63 | 0.00 | 51.04 | -242.1 | ■ | 150 |
| ( 89) $C_2H_2$ + $C_2H_2$ => H + $C_4H_3$ | 13.00 | 0.00 | 188.28 | 197.6 |  | 34 |
| ( 90) $C_2H_2$ + $C_2H$ => H + $C_4H_2$ | 13.60 | 0.00 | 0.00 | -2.9 | ■ | 34 |
| ( 91) $C_4H_3$ + M => H + $C_4H_2$ + M | 15.93 | 0.00 | 251.04 | 273.5 |  | 34 |
| ( 92) $C_4H_2$ + M => H + $C_4H$ + M | 17.54 | 0.00 | 334.72 | 397.6 |  | 34 |
| ( 93) $H_2$ + $C_2H$ => H + $C_2H_2$ | 12.90 | 0.00 | 11.00 | -24.4 | ■ | 150 |
| ( 94) H + $C_2HO$ => $CH_2$ + CO | 12.84 | 0.00 | 0.00 | 30.3 | ■ | 150 |
| ( 95) O + $C_2HO$ => HCO + CO | 12.08 | 0.00 | 0.00 | -341.8 |  | 150 |
| ( 96) $C_3H_6$ + M => $CH_3$ + $C_2H_3$ + M | 18.00 | 0.00 | 309.20 | 381.9 |  | 34 |
| ( 97) OH + $C_2H_3$ => $H_2O$ + $C_2H_2$ | 13.30 | 0.00 | 0.00 | -310.3 |  | 130 |
| ( 98) O + $C_2H_3$ => OH + $C_2H_2$ | 13.48 | 0.00 | 0.00 | -239.5 |  | 130 |
| ( 99) $CH_3$ + $C_2H_3$ => $CH_4$ + $C_2H_2$ | 13.08 | 0.00 | 0.00 | -251.1 |  | A |
| (100) $CH_2$ + $C_2H_3$ => $CH_3$ + $C_2H_2$ | 13.06 | 0.00 | 0.00 | -266.3 |  | A |
| (101) CH + $C_2H_3$ => $CH_2$ + $C_2H_2$ | 13.05 | 0.00 | 0.00 | -234.8 |  | A |
| (102) $C_2H_5$ + $C_2H_3$ => $C_2H_6$ + $C_2H_2$ | 13.15 | 0.00 | 0.00 | -213.8 |  | A |
| (103) $C_2H_3$ + $C_2H$ => $C_2H_2$ + $C_2H_2$ | 13.13 | 0.00 | 0.00 | -271.9 |  | A |
| (104) OH + $C_2H_2$ => H + $C_2H_2O$ | 14.00 | 0.00 | 48.12 | -94.2 | ■ | 150 |

| REACTION | | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (105) CH3 | + CH | => CH2 | + CH2 | | | 13.00 | 0.00 | 0.00 | 31.5 | | A |
| (106) CH4 | + CH | => CH3 | + CH2 | | | 13.00 | 0.00 | 0.00 | 16.3 | | A |
| (107) O | + HCO | => H | + CO2 | | | 13.48 | 0.00 | 0.00 | -461.4 | | 150 |
| (108) O2 | + C2H | => O | + C2HO | | | 13.00 | 0.00 | 0.00 | -207.8 | * | 150 |
| (109) C2H2O | + M | => CH2 | + CO | + M | | 15.56 | 0.00 | 248.11 | 324.0 | | 150 |
| (110) O | + C2H2O | => HCO | + HCO | | | 13.00 | 0.00 | 25.10 | -121.4 | | 150 |
| (111) CH2 | + CH2 | => H | + C2H3 | | | 13.90 | 0.00 | 0.00 | -289.3 | | 150 |
| (112) OH | + C2H2O | => H2O | + C2HO | | | 13.00 | 0.00 | 11.30 | -218.8 | * | 150 |
| (113) H | + C2H2O | => H2 | + C2HO | | | 13.48 | 0.00 | 35.56 | -156.0 | | 150 |
| (114) O2 | + C2H3 | => CH2O | + HCO | | | 12.78 | 0.00 | 0.00 | -335.3 | * | 150 |
| (115) HCO | + HCO | => CH2O | + CO | | | 13.30 | 0.00 | 0.00 | -315.4 | | 150 |
| (116) O2 | + CH2 | => H | + OH | + CO | | 13.11 | 0.00 | 6.28 | -232.2 | *,I | 150 |
| (117) O | + CH | => H | + CO | | | 13.60 | 0.00 | 0.00 | -735.9 | | 150 |
| (118) O | + CH2 | => H | + H | + CO | | 13.48 | 0.00 | 0.00 | -299.0 | I | 150 |
| (119) O | + CH2 | => H2 | + CO | | | 13.70 | 0.00 | 0.00 | -748.6 | | 150 |
| (120) CH3 | + C2H5 | => CH4 | + C2H4 | | | 13.00 | 0.00 | 0.00 | -277.1 | | A |
| (121) C2H6 | + CH2 | => CH3 | + C2H5 | | | 13.00 | 0.00 | 0.00 | -52.6 | | A |
| (122) CH4 | + CL | => CH3 | + HCL | | | 13.70 | 0.00 | 16.32 | 7.4 | * | 140 |
| (123) CH3 | + CLHO | => CH4 | + OCL | | | 12.00 | 0.00 | 0.00 | -29.8 | | B |
| (124) CH3 | + CH3CL | => CH4 | + CH2CL | | | 12.10 | 0.00 | 48.53 | -20.1 | * | 151 |
| (125) CH3 | + CH2CL | => CH4 | + CHCL | | | 12.10 | 0.00 | 48.53 | -35.9 | | B |

| REACTION | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|
| (126) CH3 | + CHCL | => CH4 | + CCL | 12.10 | 0.00 | 48.53 | -29.9 | | B |
| (127) CH3 | + CHCLO | => CH4 | + CCLO | 12.00 | 0.00 | 0.00 | -112.9 | | B |
| (128) CH3 | + CHCL2 | => CH4 | + CCL2 | 12.00 | 0.00 | 0.00 | -60.2 | | B |
| (129) CH3 | + CH2CL2 | => CH4 | + CHCL2 | 11.80 | 0.00 | 37.66 | -54.2 | | 151 |
| (130) CH3 | + CL | => CH2 | + HCL | 13.70 | 0.00 | 16.32 | 22.6 | * | 140 |
| (131) CH2 | + CLHO | => CH3 | + OCL | 12.75 | 0.00 | 0.00 | -45.0 | | B |
| (132) CH2 | + CH2CL | => CH3 | + CHCL | 12.75 | 0.00 | 0.00 | -51.1 | | B |
| (133) CH | + CH3CL | => CH3 | + CHCL | 13.25 | 0.00 | 0.00 | -54.9 | | B |
| (134) CH3 | + CL2 | => CL | + CH3CL | 12.90 | 0.00 | 9.62 | -109.1 | | 140 |
| (135) CH3 | + CHCL | => CH3CHCL | | 13.00 | 0.00 | 0.00 | -367.4 | | B |
| (136) C2H4 | + CL | => CH2CH2CL | | 12.00 | 0.00 | 0.00 | -85.6 | | B |
| (137) H | + C2H3CL | => CH3CHCL | | 12.00 | 0.00 | 0.00 | -179.5 | * | B |
| (138) H | + C2H3CL | => CH2CH2CL | | 12.00 | 0.00 | 0.00 | -174.1 | | B |
| (139) CH2 | + CH2CL | => CH2CH2CL | | 13.00 | 0.00 | 0.00 | -413.1 | | B |
| (140) CH3 | + OCL | => CH3O | + CL | 12.75 | 0.00 | 0.00 | -109.0 | | B |
| (141) CH2 | + CHCLO | => CH3 | + CCLO | 12.50 | 0.00 | 0.00 | -128.1 | | B |
| (142) CH3 | + CCLO | => CO | + CH3CL | 12.00 | 0.00 | 0.00 | -284.7 | | B |
| (143) CH2 | + CHCL2 | => CH3 | + CCL2 | 12.50 | 0.00 | 0.00 | -75.4 | | B |
| (144) CH3CL | + CCL | => CH3 | + CCL2 | 12.75 | 0.00 | 0.00 | -25.1 | | B |
| (145) CH2 | + CHCL | => CH3 | + CCL | 12.50 | 0.00 | 0.00 | -45.1 | | B |
| (146) CH2 | + CL | => CH | + HCL | 13.25 | 0.00 | 0.00 | -8.9 | | B |

| REACTION | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|
| (147) | CH | + CLHO | => CH2 | + OCL | 13.25 | 0.00 | 0.00 | -13.5 | | B |
| (148) | CH2 | + OCL | => CH2O | + CL | 12.75 | 0.00 | 0.00 | -482.8 | | B |
| (149) | CH2 | + OCL | => O | + CH2CL | 12.75 | 0.00 | 0.00 | -118.0 | | B |
| (150) | CH | + CHCL2 | => CH2 | + CCL2 | 13.25 | 0.00 | 0.00 | -43.9 | | B |
| (151) | CH2 | + CCL2 | => CH2CL | + CCL | 12.75 | 0.00 | 0.00 | -10.1 | | B |
| (152) | CH2 | + CCLO | => CO | + CH2CL | 12.75 | 0.00 | 0.00 | -319.9 | | B |
| (153) | CH | + CHCLO | => CH2 | + CCLO | 13.25 | 0.00 | 0.00 | -96.6 | | B |
| (154) | CH2O | + CL | => HCO | + HCL | 13.68 | 0.00 | 0.28 | -57.2 | ■ | 137 |
| (155) | CH2O | + OCL | => HCO | + CLHO | 8.78 | 0.00 | 0.00 | -34.8 | | 137 |
| (156) | CH2O | + CH2CL | => HCO | + CH3CL | 12.50 | 0.00 | 0.00 | -44.6 | ■ | B |
| (157) | CH2O | + CHCL | => HCO | + CH2CL | 12.50 | 0.00 | 0.00 | -28.7 | | B |
| (158) | CH2O | + CCL | => HCO | + CHCL | 12.75 | 0.00 | 0.00 | -34.7 | | B |
| (159) | CH2O | + CCL2 | => HCO | + CHCL2 | 11.00 | 0.00 | 0.00 | -4.4 | | B |
| (160) | HCO | + CHCLO | => CH2O | + CCLO | 11.00 | 0.00 | 0.00 | -48.3 | | B |
| (161) | HCO | + CL | => CO | + HCL | 13.50 | 0.00 | 0.00 | -372.6 | | B |
| (162) | CH | + OCL | => HCO | + CL | 13.25 | 0.00 | 0.00 | -531.1 | | B |
| (163) | HCO | + OCL | => CO | + CLHO | 12.75 | 0.00 | 0.00 | -350.3 | | B |
| (164) | CH | + OCLO | => HCO | + OCL | 12.75 | 0.00 | 0.00 | -558.9 | | B |
| (165) | HCO | + CH2CL | => CO | + CH3CL | 12.50 | 0.00 | 0.00 | -360.0 | | B |
| (166) | HCO | + CHCL | => CO | + CH2CL | 12.50 | 0.00 | 0.00 | -344.1 | | B |
| (167) | HCO | + CCL | => CO | + CHCL | 12.50 | 0.00 | 0.00 | -350.1 | | B |

| REACTION | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|
| (168) HCO | + CCL2 | => CO | + CHCL2 | 11.00 | 0.00 | 0.00 | -319.8 | | B |
| (169) HCO | + CCLO | => CO | + CHCLO | 11.00 | 0.00 | 0.00 | -267.1 | | B |
| (170) C2H6 | + CL | => C2H5 | + HCL | 14.00 | 0.00 | 4.18 | -30.0 | ■ | 140 |
| (171) C2H6 | + OCL | => C2H5 | + CLHO | 12.75 | 0.00 | 0.00 | -7.6 | | B |
| (172) C2H6 | + CH2CL | => C2H5 | + CH3CL | 12.50 | 0.00 | 0.00 | -17.3 | ■ | B |
| (173) C2H6 | + CHCL | => C2H5 | + CH2CL | 12.50 | 0.00 | 0.00 | -1.4 | | B |
| (174) C2H5 | + CH2CL2 | => C2H6 | + CHCL2 | 11.00 | 0.00 | 0.00 | -16.8 | | B |
| (175) C2H5 | + CHCL2 | => C2H6 | + CCL2 | 11.00 | 0.00 | 0.00 | -22.8 | | B |
| (176) C2H5 | + CHCLO | => C2H6 | + CCLO | 11.00 | 0.00 | 0.00 | -75.5 | | B |
| (177) CH3 | + C2H5CL | => C2H5 | + CH3CL | 12.00 | 0.00 | 0.00 | -23.2 | ■ | B |
| (178) C2H5 | + CH2CL | => C2H4 | + CH3CL | 12.50 | 0.00 | 0.00 | -257.0 | | B |
| (179) CH2 | + C2H5CL | => C2H5 | + CH2CL | 12.75 | 0.00 | 0.00 | -58.4 | | B |
| (180) C2H5 | + CHCL | => C2H4 | + CH2CL | 12.50 | 0.00 | 0.00 | -241.2 | | B |
| (181) CH | + C2H5CL | => C2H5 | + CHCL | 12.75 | 0.00 | 0.00 | -78.1 | | B |
| (182) C2H6 | + CCL | => C2H5 | + CHCL | 12.75 | 0.00 | 0.00 | -7.5 | | B |
| (183) C2H5 | + CCL | => C2H4 | + CHCL | 12.75 | 0.00 | 0.00 | -247.2 | | B |
| (184) C2H5 | + CL | => C2H4 | + HCL | 14.30 | 0.00 | 0.00 | -269.7 | ■ | 140 |
| (185) C2H5 | + OCL | => C2H4 | + CLHO | 12.75 | 0.00 | 0.00 | -247.3 | | B |
| (186) C2H5 | + HCL | => H | + C2H5CL | 13.78 | 0.00 | 152.76 | 108.2 | | 137 |
| (187) C2H5 | + CL2 | => CL | + C2H5CL | 13.10 | 0.00 | 4.18 | -85.9 | | 140 |
| (188) C2H5 | + CCL2 | => C2H4 | + CHCL2 | 11.00 | 0.00 | 0.00 | -216.9 | | B |

| REACTION | | | | | LC10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|
| (189) CCL | + C2H5CL | => | C2H5 | + CCL2 | 12.75 | 0.00 | 0.00 | -48.3 | | B |
| (190) C2H5 | + CCLO | => | C2H4 | + CHCLO | 11.00 | 0.00 | 0.00 | -164.2 | | B |
| (191) C2H5 | + CCLO | => | CO | + C2H5CL | 11.00 | 0.00 | 0.00 | -261.5 | | B |
| (192) C2H4 | + CH2CL | => | C2H3 | + CH3CL | 12.50 | 0.00 | 0.00 | 1.0 | * | B |
| (193) C2H3 | + CH2CL | => | C2H4 | + CHCL | 12.50 | 0.00 | 0.00 | -16.8 | * | B |
| (194) C2H3 | + CHCL | => | C2H4 | + CCL | 12.50 | 0.00 | 0.00 | -10.8 | | B |
| (195) C2H4 | + CL | => | C2H3 | + HCL | 14.00 | 0.00 | 29.29 | -11.7 | * | 149 |
| (196) C2H3 | + CLHO | => | C2H4 | + OCL | 12.50 | 0.00 | 0.00 | -10.7 | | B |
| (197) C2H3 | + CHCL2 | => | C2H4 | + CCL2 | 11.00 | 0.00 | 0.00 | -41.1 | | B |
| (198) C2H3 | + CHCLO | => | C2H4 | + CCLO | 11.00 | 0.00 | 0.00 | -93.8 | | B |
| (199) C2H3 | + CH2CL | => | C2H2 | + CH3CL | 12.50 | 0.00 | 0.00 | -231.1 | | B |
| (200) CH2 | + C2H3CL | => | C2H3 | + CH2CL | 13.25 | 0.00 | 0.00 | -50.3 | | B |
| (201) CH | + C2H3CL | => | C2H3 | + CHCL | 13.25 | 0.00 | 0.00 | -69.9 | | B |
| (202) C2H3 | + CCL | => | C2H2 | + CHCL | 12.75 | 0.00 | 0.00 | -221.2 | | B |
| (203) C2H3 | + CL | => | C2H2 | + HCL | 13.25 | 0.00 | 0.00 | -243.7 | | B |
| (204) C2H3 | + OCL | => | C2H2 | + CLHO | 12.75 | 0.00 | 0.00 | -221.4 | | B |
| (205) C2H3 | + CCL2 | => | C2H2 | + CHCL2 | 11.00 | 0.00 | 0.00 | -190.9 | | B |
| (206) CCL | + C2H3CL | => | C2H3 | + CCL2 | 12.75 | 0.00 | 0.00 | -40.2 | | B |
| (207) C2H3 | + CCLO | => | CO | + C2H3CL | 11.00 | 0.00 | 0.00 | -269.6 | | B |
| (208) C2H3 | + CCLO | => | C2H2 | + CHCLO | 11.00 | 0.00 | 0.00 | -138.2 | | B |
| (209) C2H3 | + CL2 | => | CL | + C2H3CL | 13.10 | 0.00 | 0.00 | -94.1 | | 137 |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (210) C2H2 + CL => C2H + HCL | 14.20 | 0.00 | 70.71 | 28.2 | ■ | 140 |
| (211) C2H + CLHO => C2H2 + OCL | 12.75 | 0.00 | 0.00 | -50.5 | | B |
| (212) C2H + CH3CL => C2H2 + CH2CL | 12.75 | 0.00 | 0.00 | -40.8 | ■ | B |
| (213) C2H + CH2CL => C2H2 + CHCL | 12.75 | 0.00 | 0.00 | -56.7 | ■ | B |
| (214) C2H + CHCL => C2H2 + CCL | 12.75 | 0.00 | 0.00 | -50.7 | | B |
| (215) C2H + CH3CL => CH3 + C2HCL | 12.75 | 0.00 | 0.00 | -24.5 | | B |
| (216) CH2 + C2HCL => C2H + CH2CL | 12.75 | 0.00 | 0.00 | -10.7 | | B |
| (217) CH + C2HCL => C2H + CHCL | 13.25 | 0.00 | 0.00 | -30.3 | | B |
| (218) C2H + CHCL2 => C2H2 + CCL2 | 12.75 | 0.00 | 0.00 | -81.0 | | B |
| (219) C2H + CHCLO => C2H2 + CCLO | 12.75 | 0.00 | 0.00 | -133.7 | | B |
| (220) CH3CL => CH3 + CL | 15.40 | 0.00 | 366.10 | 360.8 | ■ | 50 |
| (221) CH3CL => H + CH2CL | 15.40 | 0.00 | 430.95 | 433.2 | ■ | B |
| (222) CH3CL => CH2 + HCL | 13.50 | 0.00 | 418.40 | 383.4 | ■ | B |
| (223) H + CH3CL => CH3 + HCL | 7.74 | 1.97 | 46.86 | -85.0 | ■ | B |
| (224) H + CH3CL => H2 + CH2CL | 7.74 | 1.97 | 46.86 | -16.4 | ■ | B |
| (225) H + CH3CL => CH4 + CL | 10.00 | 0.00 | 0.00 | -92.4 | | B |
| (226) CH3 + CLHO => OH + CH3CL | 12.50 | 0.00 | 0.00 | -100.9 | ■ | B |
| (227) OH + CH3CL => H2O + CH2CL | 6.20 | 2.10 | 10.29 | -79.2 | ■ | 125 |
| (228) CH3 + OCL => O + CH3CL | 12.75 | 0.00 | 0.00 | -82.8 | ■ | B |
| (229) O + CH3CL => OH + CH2CL | 13.02 | 0.00 | 28.45 | -8.4 | ■ | 152 |
| (230) CH3 + CH3CL => C2H6 + CL | 11.00 | 0.00 | 50.21 | -17.8 | ■ | B |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (231) CH2 + CH3CL => CH3 + CH2CL | 12.75 | 0.00 | 0.00 | -35.2 | * | B |
| (232) HO2 + CH3CL => H2O2 + CH2CL | 13.30 | 0.00 | 75.31 | 69.9 | * | B |
| (233) O2 + CH3CL => CH3 + CLOO | 13.92 | 0.00 | 234.30 | 333.1 | * | B |
| (234) O2 + CH3CL => HO2 + CH2CL | 13.92 | 0.00 | 234.30 | 206.3 | * | B |
| (235) CL + CH3CL => HCL + CH2CL | 13.54 | 0.00 | 12.97 | -12.6 | * | 151 |
| (236) CH3 + CL2O => OCL + CH3CL | 11.00 | 0.00 | 0.00 | -222.9 |  | B |
| (237) CLHO + CH2CL => OCL + CH3CL | 12.50 | 0.00 | 0.00 | -9.7 | * | B |
| (238) CH3CL + CH2CL => CL + C2H5CL | 11.00 | 0.00 | 50.21 | -11.9 | * | B |
| (239) H + 12C2H4CL2 => CH3CL + CH2CL | 12.00 | 0.00 | 0.00 | -74.4 |  | B |
| (240) CH2CL + CH2CL => CH3CL + CHCL | 12.50 | 0.00 | 0.00 | -15.9 |  | B |
| (241) CH2CL + CHCL => CH3CL + CCL | 12.50 | 0.00 | 0.00 | -9.8 |  | B |
| (242) H + 12C2H3CL2 => 12C2H4CL2 | 12.00 | 0.00 | 0.00 | -420.8 |  | B |
| (243) CL + CH2CH2CL => 12C2H4CL2 | 12.00 | 0.00 | 0.00 | -341.8 | * | B |
| (244) CH3 + CHCL2 => CH3CL + CHCL | 11.00 | 0.00 | 0.00 | -5.2 | * | B |
| (245) CH2CL + CHCL2 => CH3CL + CCL2 | 11.00 | 0.00 | 0.00 | -40.2 |  | B |
| (246) CH2CL + CHCLO => CH3CL + CCLO | 11.00 | 0.00 | 0.00 | -92.8 |  | B |
| (247) CH3 + CCL2O => CH3CL + CCLO | 11.00 | 0.00 | 0.00 | -81.6 |  | B |
| (248) CH + CH3CL => CH2 + CH2CL | 13.25 | 0.00 | 0.00 | -3.7 |  | B |
| (249) CH2CL => CH2 + CL | 15.40 | 0.00 | 396.22 | 396.1 | * | B |
| (250) CH2CL => H + CHCL | 15.40 | 0.00 | 417.14 | 417.3 | * | B |
| (251) CH2CL => CH + HCL | 13.50 | 0.00 | 418.40 | 387.2 |  | B |

| REACTION | | | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (252) | H | + CH2CL | => H2 | + CHCL | | | 14.26 | 0.00 | 63.18 | -32.3 | * | B |
| (253) | H | + CH2CL | => CH2 | + HCL | | | 14.26 | 0.00 | 63.18 | -49.8 | * | B |
| (254) | CH2 | + CLHO | => OH | + CH2CL | | | 12.50 | 0.00 | 0.00 | -136.2 | | B |
| (255) | OH | + CH2CL | => H2O | + CHCL | | | 6.19 | 2.13 | 35.15 | -95.1 | | B |
| (256) | CH3 | + CH2CL | => C2H5CL | | | | 13.00 | 0.00 | 0.00 | -372.8 | * | B |
| (257) | H | + CH3CHCL | => C2H5CL | | | | 12.00 | 0.00 | 0.00 | -422.7 | | B |
| (258) | H | + CH2CH2CL | => C2H5CL | | | | 12.00 | 0.00 | 0.00 | -428.2 | | B |
| (259) | C2H5 | + CL | => C2H5CL | | | | 12.00 | 0.00 | 0.00 | -337.6 | | B |
| (260) | O | + CH2CL | => OH | + CHCL | | | 14.61 | 0.00 | 58.58 | -24.3 | * | B |
| (261) | O2 | + CH2CL | => O | + CH2O | + CL | | 34.58 | -5.94 | 176.98 | 143.6 | *,I | B |
| (262) | O2 | + CH2CL | => H | + O | + CHCLO | | 34.58 | -5.94 | 176.98 | 189.0 | *,I | B |
| (263) | CH2 | + CLOO | => O2 | + CH2CL | | | 12.00 | 0.00 | 0.00 | -368.3 | | B |
| (264) | O2 | + CH2CL | => HO2 | + CHCL | | | 13.90 | 0.00 | 234.30 | 190.5 | * | B |
| (265) | O2 | + CH2CL | => CH2O | + OCL | | | 13.72 | 0.00 | 150.62 | -134.4 | * | B |
| (266) | O2 | + CH2CL | => OH | + CHCLO | | | 13.72 | 0.00 | 150.62 | -252.6 | | B |
| (267) | CH2 | + CH2CL | => C2H4 | + CL | | | 12.50 | 0.00 | 0.00 | -327.4 | | B |
| (268) | CH2 | + CL2 | => CL | + CH2CL | | | 12.50 | 0.00 | 0.00 | -144.4 | | B |
| (269) | CL | + CH2CL | => HCL | + CHCL | | | 13.25 | 0.00 | 0.00 | -28.5 | * | B |
| (270) | CH2 | + CL2O | => OCL | + CH2CL | | | 11.00 | 0.00 | 0.00 | -258.1 | | B |
| (271) | OCL | + CH2CL | => CLHO | + CHCL | | | 12.50 | 0.00 | 0.00 | -6.2 | | B |
| (272) | CH2CL | + CH2CL | => 12C2H4CL2 | | | | 13.00 | 0.00 | 0.00 | -358.8 | * | B |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (273) 12C2H4CL2 => HCL + C2H3CL | 13.10 | 0.00 | 230.12 | 70.0 | * | B |
| (274) CH + CH2CL => CH2 + CHCL | 12.00 | 0.00 | 0.00 | -19.6 | | B |
| (275) CH2 + CHCL2 => CH2CL + CHCL | 11.00 | 0.00 | 0.00 | -40.4 | | B |
| (276) CH2CL + CHCL => 12C2H3CL2 | 13.00 | 0.00 | 0.00 | -355.4 | * | B |
| (277) H + 12C2H2CL2 => 12C2H3CL2 | 12.00 | 0.00 | 0.00 | -169.7 | | B |
| (278) CL + C2H3CL => 12C2H3CL2 | 12.00 | 0.00 | 0.00 | -95.1 | * | B |
| (279) 12C2H3CL2 => HCL + C2H2CL | 13.10 | 0.00 | 230.12 | 89.6 | | B |
| (280) HO2 + CH2CL => H2O2 + CHCL | 13.30 | 0.00 | 75.31 | 54.1 | | B |
| (281) CL + CH2CL => CH2CL2 | 12.00 | 0.00 | 0.00 | -337.4 | | B |
| (282) CHCL + CHCL2 => CH2CL + CCL2 | 11.00 | 0.00 | 0.00 | -24.3 | | B |
| (283) CHCL + CHCLO => CH2CL + CCLO | 11.00 | 0.00 | 0.00 | -77.0 | | B |
| (284) CH2 + CCL2O => CH2CL + CCLO | 11.00 | 0.00 | 0.00 | -116.9 | | B |
| (285) OH + CHCL => H2O + CCL | 11.43 | 0.67 | 107.53 | -89.1 | | B |
| (286) CH + CLHO => OH + CHCL | 13.25 | 0.00 | 0.00 | -155.8 | | B |
| (287) H2O2 + CCL => HO2 + CHCL | 11.00 | 0.00 | 0.00 | -60.1 | | B |
| (288) CH + CLOO => O2 + CHCL | 11.00 | 0.00 | 0.00 | -387.9 | | B |
| (289) HO2 + CCL => O2 + CHCL | 11.00 | 0.00 | 0.00 | -196.5 | | B |
| (290) O + CHCL => CO + HCL | 13.50 | 0.00 | 0.00 | -766.1 | | B |
| (291) O + CHCL => OH + CCL | 14.48 | 0.00 | 49.92 | -18.2 | | B |
| (292) CH + OCL => O + CHCL | 12.75 | 0.00 | 0.00 | -137.7 | | B |
| (293) H + CHCL => CH + HCL | 14.00 | 0.00 | 0.00 | -30.2 | | B |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (294) H + CHCL => H2 + CCL | 14.00 | 0.00 | 0.00 | -26.3 | | B |
| (295) CHCL + CL2 => CL + CHCL2 | 12.75 | 0.00 | 0.00 | -103.9 | | B |
| (296) CL + CHCL => HCL + CCL | 13.50 | 0.00 | 0.00 | -22.5 | | B |
| (297) CH + CL2 => CL + CHCL | 12.75 | 0.00 | 0.00 | -164.0 | | B |
| (298) CCL + CHCL2 => CHCL + CCL2 | 12.50 | 0.00 | 0.00 | -30.3 | | B |
| (299) CCL + CHCLO => CHCL + CCLO | 12.75 | 0.00 | 0.00 | -83.0 | | B |
| (300) CH + CCL2O => CHCL + CCLO | 13.25 | 0.00 | 0.00 | -136.5 | | B |
| (301) CH + CHCL => CH2 + CCL | 13.25 | 0.00 | 0.00 | -13.6 | | B |
| (302) HO2 + OCL => O2 + CLHO | 12.75 | 0.00 | 0.00 | -196.6 | | 138 |
| (303) OH + CLOO => O2 + CLHO | 13.25 | 0.00 | 0.00 | -232.1 | | 138 |
| (304) HO2 + CL => O2 + HCL | 13.25 | 0.00 | 0.00 | -219.0 | | 138 |
| (305) O + CLHO => O2 + HCL | 13.50 | 0.00 | 0.00 | -252.7 | | 138 |
| (306) H + CLOO => O2 + HCL | 14.00 | 0.00 | 0.00 | -418.1 | | 138 |
| (307) O + CLHO => OH + OCL | 13.50 | 0.00 | 0.00 | -18.1 | | 138 |
| (308) OH + OCL => HO2 + CL | 13.25 | 0.00 | 0.00 | -15.6 | * | 138 |
| (309) HO2 + HCL => H2O2 + CL | 12.78 | 0.00 | 7.95 | 82.6 | * | 138 |
| (310) OH + HCL => H2O + CL | 12.26 | 0.00 | 3.35 | -66.6 | * | 138 |
| (311) HCL + OCL => CL + CLHO | 13.00 | 0.00 | 8.37 | 22.4 | * | 138 |
| (312) CL + OCL => O + CL2 | 12.80 | 0.00 | 39.33 | 26.3 | | 138 |
| (313) CL + CLHO => OH + CL2 | 13.10 | 0.00 | 25.10 | 8.2 | | 138 |
| (314) CLHO + M => OH + CL + M | 8.80 | 0.00 | 213.38 | 259.9 | | 138 |

| REACTION | | | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (315) | H | + CL | + M | => HCL | + M | | 12.00 | 0.00 | -152.91 | -445.8 | | 137 |
| (316) | O | + HCL | | => OH | + CL | | 13.54 | 0.00 | 13.81 | 4.2 | | 138 |
| (317) | H | + HCL | | => H2 | + CL | | 12.70 | 0.00 | 13.39 | -3.8 | | 138 |
| (318) | CL2 | + M | | => CL | + CL | + M | 13.15 | 0.00 | 197.48 | 251.7 | | 137 |
| (319) | H | + CL2 | | => CL | + HCL | | 14.57 | 0.00 | 7.53 | -194.2 | | 137 |
| (320) | O2 | + CL2 | | => CL | + CLOO | | 13.90 | 0.00 | 104.60 | 223.9 | | 137 |
| (321) | O2 | + CL | | => O | + OCL | | 14.75 | 0.00 | 115.90 | 230.4 | ■ | 137 |
| (322) | O2 | + CCL2O | | => CCLO | + CLOO | | 11.00 | 0.00 | 168.20 | 251.4 | | 137 |
| (323) | CCL2O | + M | | => CL | + CCLO | + M | 16.26 | 0.00 | 128.45 | 279.2 | | 137 |
| (324) | CCL2O | + M | | => CO | + CL2 | + M | 15.00 | 0.00 | 104.60 | 103.6 | | 137 |
| (325) | O | + CCL2O | | => CO2 | + CL | + CL | 5.54 | 2.42 | 5.69 | -179.3 | | 137 |
| (326) | O | + CCL2O | | => OCL | + CCLO | | 6.23 | 2.32 | 6.28 | 1.2 | | 137 |
| (327) | CLOO | + CCL2O | | => OCL | + OCL | + CCLO | 12.00 | 0.00 | 33.47 | 259.3 | | 137 |
| (328) | OCL | + CCL2O | | => CCLO | + CL2O | | 4.84 | 2.65 | -7.53 | 141.2 | | 137 |
| (329) | CL | + CCL2O | | => CCLO | + CL2 | | 9.40 | 1.27 | 10.88 | 27.5 | | 137 |
| (330) | CCLO | + M | | => CO | + CL | + M | 11.60 | 0.00 | 26.36 | 76.1 | | 137 |
| (331) | O2 | + CCLO | | => CO | + CLOO | | 12.50 | 0.00 | 29.29 | 48.4 | | 137 |
| (332) | O | + CCLO | | => CO | + OCL | | 13.48 | 0.00 | 0.00 | -201.9 | | 137 |
| (333) | O | + CCLO | | => CO2 | + CL | | 13.48 | 0.00 | 0.00 | -458.5 | | 137 |
| (334) | CL | + CCLO | | => CO | + CL2 | | 15.11 | 0.00 | 13.93 | -175.5 | | 137 |
| (335) | OCL | + CCLO | | => CO | + CL2O | | 13.48 | 0.00 | 0.00 | -61.8 | | 137 |

| REACTION | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|
| (336) O | + CL2O | => OCL | + OCL | | 13.10 | 0.00 | 4.60 | -140.1 | | 137 |
| (337) CL | + CL2O | => OCL | + CL2 | | 11.50 | 0.00 | 0.00 | -113.7 | | 137 |
| (338) CLOO | + M | => O2 | + CL | + M | 15.12 | 0.00 | 33.47 | 27.8 | ■ | 137 |
| (339) O | + OCLO | => O2 | + OCL | | 11.50 | 0.00 | 0.00 | -258.2 | | 137 |
| (340) O | + CLOO | => O2 | + OCL | | 13.70 | 0.00 | 41.84 | -250.3 | | 137 |
| (341) CL | + CLOO | => OCL | + OCL | | 12.48 | 0.00 | 0.00 | -19.9 | | 137 |
| (342) CL | + OCLO | => OCL | + OCL | | 13.55 | 0.00 | 0.00 | -27.8 | | 137 |
| (343) O2 | + CCL | => CO | + OCL | | 11.13 | 0.67 | 107.95 | -513.2 | | 137 |
| (344) CO | + OCL | => CO2 | + CL | | 11.78 | 0.00 | 0.00 | -256.6 | | 137 |
| (345) C2H5CL | => C2H4 | + HCL | | | 13.50 | 0.00 | 236.81 | 68.0 | ■ | 141 |
| (346) CH2 | + CHCL | => C2H3CL | | | 13.00 | 0.00 | 0.00 | -656.3 | | B |
| (347) C2H3CL | => C2H2 | + HCL | | | 13.50 | 0.00 | 290.37 | 102.0 | | 104 |
| (348) HO2 | + 12C2H3CL2 | => O2 | + 12C2H4CL2 | | 11.00 | 0.00 | 0.00 | -193.9 | | B |
| (349) CH2CH2CL | + CLOO | => O2 | + 12C2H4CL2 | | 11.00 | 0.00 | 0.00 | -314.1 | | B |
| (350) O | + 12C2H4CL2 | => OH | + 12C2H3CL2 | | 13.50 | 0.00 | 0.00 | -20.8 | ■ | B |
| (351) OCL | + CH2CH2CL | => O | + 12C2H4CL2 | | 12.75 | 0.00 | 0.00 | -63.8 | | B |
| (352) H | + 12C2H4CL2 | => H2 | + 12C2H3CL2 | | 14.00 | 0.00 | 0.00 | -28.9 | ■ | B |
| (353) H | + 12C2H4CL2 | => HCL | + CH3CHCL | | 14.00 | 0.00 | 0.00 | -109.5 | ■ | B |
| (354) H | + 12C2H4CL2 | => HCL | + CH2CH2CL | | 14.00 | 0.00 | 0.00 | -104.0 | ■ | B |
| (355) OH | + 12C2H4CL2 | => H2O | + 12C2H3CL2 | | 13.25 | 0.00 | 0.00 | -91.7 | ■ | B |
| (356) CLHO | + CH2CH2CL | => OH | + 12C2H4CL2 | | 12.50 | 0.00 | 0.00 | -81.9 | | B |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (357) CH3 + 12C2H4CL2 => CH4 + 12C2H3CL2 | 12.00 | 0.00 | 0.00 | -32.5 | * | B |
| (358) CH3 + 12C2H4CL2 => CH3CL + CH2CH2CL | 12.00 | 0.00 | 0.00 | -19.0 | * | B |
| (359) CL + 12C2H4CL2 => HCL + 12C2H3CL2 | 13.50 | 0.00 | 0.00 | -25.1 | * | B |
| (360) CL2 + CH2CH2CL => CL + 12C2H4CL2 | 12.75 | 0.00 | 0.00 | -90.1 |  | B |
| (361) OCL + 12C2H4CL2 => CLHO + 12C2H3CL2 | 12.75 | 0.00 | 0.00 | -2.7 |  | B |
| (362) CH2CH2CL + CL2O => OCL + 12C2H4CL2 | 11.00 | 0.00 | 0.00 | -203.9 |  | B |
| (363) CH2 + 12C2H4CL2 => CH3 + 12C2H3CL2 | 12.75 | 0.00 | 0.00 | -47.7 |  | B |
| (364) CH2 + 12C2H4CL2 => CH2CL + CH2CH2CL | 12.75 | 0.00 | 0.00 | -54.2 |  | B |
| (365) CH + 12C2H4CL2 => CH2 + 12C2H3CL2 | 13.25 | 0.00 | 0.00 | -16.2 |  | B |
| (366) CH + 12C2H4CL2 => CHCL + CH2CH2CL | 13.25 | 0.00 | 0.00 | -73.9 |  | B |
| (367) CH2CL + 12C2H4CL2 => CH3CL + 12C2H3CL2 | 12.50 | 0.00 | 0.00 | -12.4 | * | B |
| (368) CH2CL2 + CH2CH2CL => CH2CL + 12C2H4CL2 | 11.00 | 0.00 | 0.00 | -4.5 |  | B |
| (369) CH2CL + 12C2H3CL2 => CHCL + 12C2H4CL2 | 12.50 | 0.00 | 0.00 | -3.4 |  | B |
| (370) CHCL + 12C2H4CL2 => CHCL2 + CH2CH2CL | 12.50 | 0.00 | 0.00 | -13.8 |  | B |
| (371) CCL + 12C2H4CL2 => CHCL + 12C2H3CL2 | 12.75 | 0.00 | 0.00 | -2.6 |  | B |
| (372) CCL + 12C2H4CL2 => CCL2 + CH2CH2CL | 12.75 | 0.00 | 0.00 | -44.1 |  | B |
| (373) CHCL + CHCL => 12C2H2CL2 | 13.00 | 0.00 | 0.00 | -603.0 |  | B |
| (374) 12C2H2CL2 => HCL + C2HCL | 13.10 | 0.00 | 236.81 | 116.2 |  | B |
| (375) H + 12C2HCL2 => 12C2H2CL2 | 12.00 | 0.00 | 0.00 | -428.7 |  | B |
| (376) CL + C2H2CL => 12C2H2CL2 | 12.00 | 0.00 | 0.00 | -365.8 |  | B |
| (377) O2 + CHCL => O + CHCLO | 12.50 | 0.00 | 0.00 | -228.4 | * | B |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (378) HCO + CL2 => CL + CHCLO | 12.50 | 0.00 | 0.00 | -91.6 |  | B |
| (379) CHCLO => CO + HCL | 13.00 | 0.00 | 0.00 | -29.3 | ■ | B |
| (380) CL + CHCLO => HCL + CCLO | 13.50 | 0.00 | 0.00 | -105.5 |  | B |
| (381) C2H3 + OCL => O + C2H3CL | 12.75 | 0.00 | 0.00 | -67.7 |  | B |
| (382) O + C2H3CL => OH + C2H2CL | 13.50 | 0.00 | 0.00 | -1.2 | ■ | B |
| (383) H + C2H3CL => H2 + C2H2CL | 14.00 | 0.00 | 0.00 | -9.3 | ■ | B |
| (384) H + C2H3CL => C2H3 + HCL | 14.00 | 0.00 | 0.00 | -100.1 | ■ | B |
| (385) OH + C2H3CL => H2O + C2H2CL | 13.25 | 0.00 | 0.00 | -72.1 | ■ | B |
| (386) C2H3 + CLHO => OH + C2H3CL | 13.25 | 0.00 | 0.00 | -85.9 |  | B |
| (387) H2O2 + C2H2CL => HO2 + C2H3CL | 11.00 | 0.00 | 0.00 | -77.1 |  | B |
| (388) CH3 + C2H3CL => CH4 + C2H2CL | 12.00 | 0.00 | 0.00 | -12.9 | ■ | B |
| (389) CH3 + C2H3CL => C2H3 + CH3CL | 12.00 | 0.00 | 0.00 | -15.1 | ■ | B |
| (390) CH2 + C2H3CL => CH3 + C2H2CL | 13.25 | 0.00 | 0.00 | -28.1 |  | B |
| (391) CH + C2H3CL => CH2 + C2H2CL | 12.50 | 0.00 | 0.00 | 3.4 |  | B |
| (392) CH3CL + C2H2CL => CH2CL + C2H3CL | 11.00 | 0.00 | 0.00 | -7.2 |  | B |
| (393) C2H3 + CH2CL2 => CH2CL + C2H3CL | 11.00 | 0.00 | 0.00 | -8.4 |  | B |
| (394) CH2CL + C2H2CL => CHCL + C2H3CL | 12.50 | 0.00 | 0.00 | -23.0 |  | B |
| (395) CHCL + C2H3CL => C2H3 + CHCL2 | 12.50 | 0.00 | 0.00 | -9.9 |  | B |
| (396) CHCL + C2H2CL => CCL + C2H3CL | 12.50 | 0.00 | 0.00 | -17.0 |  | B |
| (397) CL + C2H3CL => HCL + C2H2CL | 13.25 | 0.00 | 0.00 | -5.5 | ■ | B |
| (398) CLHO + C2H2CL => OCL + C2H3CL | 12.50 | 0.00 | 0.00 | -16.9 |  | B |

| REACTION | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|
| (399) C2H3 + CL2O => OCL + C2H3CL | 11.00 | 0.00 | 0.00 | -207.8 | | B |
| (400) OCL + C2H2CL => O + 12C2H2CL2 | 12.75 | 0.00 | 0.00 | -87.8 | | B |
| (401) O + 12C2H2CL2 => OH + 12C2HCL2 | 13.50 | 0.00 | 0.00 | -12.9 | | B |
| (402) H + 12C2H2CL2 => H2 + 12C2HCL2 | 14.00 | 0.00 | 0.00 | -20.9 | | B |
| (403) H + 12C2H2CL2 => HCL + C2H2CL | 14.00 | 0.00 | 0.00 | -80.0 | | B |
| (404) OH + 12C2H2CL2 => H2O + 12C2HCL2 | 13.25 | 0.00 | 0.00 | -83.8 | | B |
| (405) CLHO + C2H2CL => OH + 12C2H2CL2 | 12.50 | 0.00 | 0.00 | -105.9 | | B |
| (406) H2O2 + 12C2HCL2 => HO2 + 12C2H2CL2 | 11.00 | 0.00 | 0.00 | -65.4 | | B |
| (407) CH3 + 12C2H2CL2 => CH4 + 12C2HCL2 | 12.00 | 0.00 | 0.00 | -24.6 | | B |
| (408) CH3CL + C2H2CL => CH3 + 12C2H2CL2 | 11.00 | 0.00 | 0.00 | -5.0 | | B |
| (409) CH2 + 12C2H2CL2 => CH3 + 12C2HCL2 | 12.75 | 0.00 | 0.00 | -39.8 | | B |
| (410) CH2 + 12C2H2CL2 => CH2CL + C2H2CL | 12.75 | 0.00 | 0.00 | -30.2 | | B |
| (411) CH + 12C2H2CL2 => CH2 + 12C2HCL2 | 13.25 | 0.00 | 0.00 | -8.3 | | B |
| (412) CH + 12C2H2CL2 => CHCL + C2H2CL | 13.25 | 0.00 | 0.00 | -49.9 | | B |
| (413) CH2CL + 12C2H2CL2 => CH3CL + 12C2HCL2 | 12.50 | 0.00 | 0.00 | -4.5 | | B |
| (414) CH2CL2 + C2H2CL => CH2CL + 12C2H2CL2 | 11.00 | 0.00 | 0.00 | -28.4 | | B |
| (415) CHCL + 12C2HCL2 => CH2CL + C2HCL | 12.50 | 0.00 | 0.00 | -189.1 | | B |
| (416) CHCL2 + C2H2CL => CHCL + 12C2H2CL2 | 11.00 | 0.00 | 0.00 | -10.2 | | B |
| (417) CHCL + 12C2HCL2 => CCL + 12C2H2CL2 | 12.50 | 0.00 | 0.00 | -5.3 | | B |
| (418) CCL + 12C2H2CL2 => CCL2 + C2H2CL | 12.75 | 0.00 | 0.00 | -20.1 | | B |
| (419) CL + 12C2H2CL2 => HCL + 12C2HCL2 | 13.25 | 0.00 | 0.00 | -17.2 | | B |

| REACTION | | | | | | LG10A | N | EACT (kJ/mol) | DEHR (kJ/mol) | NOTE | REF |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (420) | CL2 | + C2H2CL | => CL | + 12C2H2CL2 | | 12.75 | 0.00 | 0.00 | -114.1 | | B |
| (421) | CLHO | + 12C2HCL2 | => OCL | + 12C2H2CL2 | | 12.50 | 0.00 | 0.00 | -5.2 | | B |
| (422) | CL2O | + C2H2CL | => OCL | + 12C2H2CL2 | | 11.00 | 0.00 | 0.00 | -227.9 | | B |
| (423) | HCO | + CLOO | => OH | + CO | + OCL | 12.00 | 0.00 | 0.00 | -110.3 | I | B |
| (424) | C2H5 | + CLOO | => OH | + C2H4 | + OCL | 11.00 | 0.00 | 0.00 | -7.3 | I | B |
| (425) | C2H3 | + CLOO | => OH | + C2H2 | + OCL | 11.00 | 0.00 | 0.00 | 18.6 | I | B |
| (426) | CHCL | + CLOO | => OH | + OCL | + CCL | 11.00 | 0.00 | 0.00 | 239.9 | I | B |
| (427) | CHCL | + CCL | => 12C2HCL2 | | | 13.00 | 0.00 | 0.00 | -597.7 | | B |
| (428) | CL | + C2HCL | => 12C2HCL2 | | | 12.00 | 0.00 | 0.00 | -133.3 | | B |
| (429) | H | + C2CL2 | => 12C2HCL2 | | | 12.00 | 0.00 | 0.00 | -234.0 | * | B |
| (430) | CH | + CHCL | => C2H2CL | | | 12.00 | 0.00 | 0.00 | -652.9 | | B |
| (431) | H | + C2HCL | => C2H2CL | | | 12.00 | 0.00 | 0.00 | -196.2 | | B |
| (432) | C2H2 | + CL | => C2H2CL | | | 12.00 | 0.00 | 0.00 | -107.5 | * | B |

a. The rate constants have the form : k = A x T**N x exp( -EACT/ R/ T)
b. Units are : kJ, mol, s, cm**3
c. Heat of Reaction at 1500 K
d. If I: The reaction is irreversible
*: Denotes a member of the reduced mechanism
e. Reference numbers refer to List of References
A: Estimated by collision theory
B: Estimated as explained in Chapter V

# VITA

David Leslie Miller was born on October 26, 1954 in Granite City, Illinois. He has lived most of his life in Louisiana, New Orleans, Metairie and Baton Rouge. After graduating from East Jefferson High School in 1972 as valedictorian of his class, he attended Louisiana State University. He has been there ever since, earning a Bachelor of Science in Mechanical Engineering magna cum laude in 1976 and a Master of Science in Mechanical Engineering in 1979.

Upon completion of his PhD, fall 1984, David will continue at Louisiana State University as a Post-Doctoral Research Associate, while searching for a permanent academic position.

# EXAMINATION AND THESIS REPORT

**Candidate:** David Leslie Miller

**Major Field:** Mechanical Engineering

**Title of Thesis:** High Temperature Combustion of Selected Chlorinated Hydrocarbons

**Approved:**

Richard A. Matula

Major Professor and Chairman

Dean of the Graduate School

**EXAMINING COMMITTEE:**

Frank A. Cartledge

M. Frenklach

Vic A. Cundy

**Date of Examination:**

December 6, 1984