ABSTRACT

This study examines the reaction of 1,2-dichloroethane with water vapor. The linear-flow method is utilized, assuming plug flow without axial diffusion. Normal operation is at atmospheric pressure and the reactor is a quartz tube in a thermal region 45 cm in length. Two reactor diameters of 0.4 cm and 1.05 cm are used. Water and 1,2-dichloroethane enter the system in liquid phase via syringe pumps. After vaporizing in heated tubing, they are combined with argon, the reactor carrier gas. The molar ratio of water to 1,2-dichloroethane is 55:1 and varied residence times are achieved by changing the argon flowrate. Reactor products are identified using GC/MS. Product distributions are measured by gas chromatography.

By keeping the molar ratio of water to 1,2-dichloroethane very high (55:1), the rate of decomposition of 1,2-dichloroethane is of the first order. A plot of $\ln(C/C_o)$ versus t results in a straight line through the origin with a slope of k_a. Performing this procedure at more than one temperature allows one to graph $\ln k_a$ versus (1/T). This Arrhenius plot results in a straight line with a slope of $-E_a/R$ and y-intercept of A_a. By utilizing a relationship between the overall rate constant and rate constants for parallel reactions at the reactor wall and in the bulk stream, decoupled activation energies can be determined.

The reaction was studied at three temperatures: 590°C,

630°C, and 680°C. Values of the activation energy for parallel reactions at both the wall and in the bulk stream have been calculated. They were found to be 35.4 kcal/mol and 29.0 kcal/mol, respectively. These results are in close agreement to unimolecular decomposition data in literature.

Methods to correct rate constants in order to account for axial diffusion and wall reactions have been utilized. It was found that these corrections are negligible.

Total decomposition of 1,2-dichloroethane occurs at temperatures greater than 800°C for a residence time range of 0.8 to 1.2 sec. The principle reaction products at temperatures lower than 700°C are vinyl chloride, 1-buten-3-yne, and 2-chloro-1,3-butadiene. At temperatures greater than 800°C, major reaction products include vinyl chloride, acetylene, ethene, benzene, and 1,3-butadiyne.

Identification of variables:

A_a	apparent frequency factor, directly from experimental results (sec^{-1})
C	concentration of unreacted 1,2-dichloroethane
C_o	initial concentration of 1,2-dichloroethane entering reactor
E_a	apparent activation energy, directly from experimental results (kcal/mol)
k_a	apparent first order rate constant, directly from experimental results (sec^{-1})
R	gas constant, 1.987×10^{-3} kcal/mol deg
T	temperature (°K)
t	residence time in reactor (sec)

HIGH TEMPERATURE REACTIONS OF 1,2-DICHLOROETHANE WITH WATER VAPOR IN A TUBULAR REACTOR

by

Charles E. Anderson

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Master of Science in Environmental Engineering
1985

APPROVAL SHEET

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ACKNOWLEDGEMENTS

I would like to express my appreciation to Dr. Joseph W. Bozzelli. Without his patience, guidance, and encouragement, this project would not have been completed.

Thanks also go to my colleagues in the Kinetics Laboratory at New Jersey Institute of Technology. Their assistance and support were invaluable. Special thanks to Ed Ritter who performed GC/MS analyses.

Finally, acknowledgement is made to the U.S. Environmental Protection Agency for partial support of this research under grant number R 81 0014-01.

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I. INTRODUCTION

A. Alternative Methods to Incineration

Microbes have been developed which will break down a multitude of hazardous chemicals including PCBs, creosote, and pentachlorophenol. However, biological treatment is generally applicable only to waste water streams of relatively low concentration pollutants. Composting is a biological method for treating contaminated soil. But its main disadvantage is the extensive time required for effective soil detoxification.

The practice of landfilling toxic wastes has traditionally been the most convenient method for disposal. Many states are finding however, that they are approaching their limit of disposal capacity. Also, serious questions have been raised about the effectiveness of this method as many landfills have been found to leak. The NIMBY (not in my backyard) syndrome has, in the past decade caused the public to strongly resist the siting of new landfills. The Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) was created to clean up the nation´s most dangerous dumps, those which threaten to contaminate water supplies. Under this program however, the wastes from one failed site are often only moved to another landfill which may develop leaks in the future. So the burying of chemical wastes is only considered a temporary solution. The U.S. Environmental Protection Agency (EPA) favors incineration or total destruction as a permament method for disposal. In 1981 the New Jersey Hazardous Waste

Facilities Siting Act was passed in order to promote the development of incinerators in the state.

B. Incinerator Operation

Most hazardous waste incinerator systems consist of two combustion chambers. The primary chamber is where the solid or liquid wastes are introduced, volatilized, and partly oxidized. The combustion process is completed in the secondary chamber [1]. The primary combustion chamber is usually operated fuel rich to prevent nitrogen fixation. By limiting the available oxygen in the high temperature zone, the formation of NO_x is inhibited.

Chlorinated organics are the most common incinerable hazardous material. One source [2] estimates that in 1980 municipal solid waste contained 5 percent plastics by weight, 20 percent of which was polyvinyl chloride (PVC). Industrial waste often contains chlorinated solvents, organo-chlorine pesticides, PCBs, and other similar chemicals. Highly chlorinated materials are noncombustible since the chlorine atom imparts fire retardant qualities. Chlorine-rich waste often has such low caloric value and volatility that it will not burn without the addition of auxiliary fuel [3].

When incinerating chlorinated organic wastes, some provision must be made to hydrolyze the chlorine and to trap it before discharge to the atmosphere. Hydrolysis of the chlorine will result in the formation of HCl which, due to its solubility in water, may be removed by absorption in a packed tower. By keeping an excess of hydrogen to chlorine in the combustion zone, HCl formation is favored. The mole ratio of hydrogen to chlorine is typically kept at about 4 to 1. The source of hydrogen may be the chlorinated organic or the fuel. If there is not enough hydrogen in the waste material and the fuel, steam or water may be added to effect the ratio [3].

If hydrolysis of the chlorine does not occur in the incineration process, caustic scrubbing will be required to remove the chlorine from the gas stream. This is a more expensive process than water scrubbing. The amount of free chlorine exiting the incinerator will vary depending on the operation temperature and the residence time. So secondary scrubbing with caustic usually follows a water scrubber in order to assure removal of free chlorine [4].

The incinerator's operating conditions are more important than pollution control devices in preventing toxic emissions. Insuring that satisfactory combustion takes place in the incinerator is crucial. The basic operation conditions on which this depends include maintenance of a relatively consistent temperature required for oxidation, the complete mixing of combustion gases, adequate retention time, and proper oxygen supply [5].

C. Toxic Emissions From Incinerators

A major problem with present incinerator technology is the emission of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). A wide range of these compounds have been found in incinerator stack and fly ash samples [6-8].

There are many areas of research which may have to be investigated in order to understand the processes by which PCDDs and PCDFs are formed in incinerators. Several mechanisms have been postulated by Shaub and Tsang [9]:

1. Formation from chlorophenol precursors - a proposed mechanism was used by Shaub and Tsang to study PCDD formation under various incinerator combustion conditions through computer simulation. Actual levels of PCDD emissions are higher than those predicted from their model.
2. Survival of PCDDs which were originally present in the input feed streams - this does not account for the significant PCDD emissions from hazardous waste incinerators (PCDDs high in the input stream) where thermal destruction efficiency is very high for PCDDs at the typically achieved flame temperatures of greater than 1500 ^{o}K.
3. Mixing inhomogeneities allow some unburned chlorinated organics to survive the main combustion environment and make it into the post combustion zone. Poor atomization and/or mixing results in pockets of varying fuel mixtures which can reduce destructive efficiencies. The formation of enriched and depleted vapor mixtures (fuel or O_2) as a result of distillation processes result in varying environment temperatures.

4. Temperature fluctuations (thermal transients) result in incomplete thermal stressing due to gas entrapment in cold pockets. This results in transport of unburned or partially combusted fuel to the post combustion zone where PCDD formation might possibly take place at above ambient but below flame temperature conditions.
5. Non-gas-phase or a combination of gas and non-gas-phase reactions are contributing to the production of PCDDs. The enhanced reaction sensitivity of organic species to the presence of reactive surfaces makes surface reactions and/or reactions inside solids strong candidates as potential sources for PCDD and PCDF formation. These reactions may occur on suspended fly ash or on the grate beds of incinerators. Particles may also act as transport agents for passage of unburned toxic precursors to the post combustion zone, where formation of PCDDs and PCDFs may be favored.

Shaub and Tsang conclude that research needs to be conducted in many areas including development of analysis of organics as a function of fly ash particle size and study of fast transient phenomena in incinerators (e.g., cold pockets, mixing inhomogeneities, etc.).

The Midwest Research Institute is presently working on a project which studies the correlation of reactor conditions with production of PCDDs in municipal waste incinerators [10]. Their study will test a hypothesis which relates the formation of carbon monoxide and unburned hydrocarbons to PCDD emissions. They will also investigate the contribution which the presence of polyvinyl chloride may or may not make to the formation of PCDDs.

Christopher Rappe of the University of Umea, Sweden and Ralph Dougherty of Florida State University have conducted tests to determine where chlorinated dioxins come from [11]. These compounds have been found in human adipose tissue samples in studies in the U.S., Canada, Vietnam, and Sweden. Since the exposure is so universal, there must be some major, common source of the dioxins. Rappe and Dougherty feel that the most likely source is combustion of polyvinyl chloride-containing refuse in municipal incinerators. Combustion of PVC in a quartz combustion tube at 800 °C produces PCDDs and PCDFs at a concentration of about 1 ppm. When considering production figures for organochlorine compounds, PCDD and PCDF emissions then become quite significant. Rappe and Dougherty estimate that more than a ton of these compounds are emitted each year by municipal incinerators in the U.S.

D. Toxicology of Emissions

In a University of Amsterdam study, a risk assessment was performed concerning PCDD emissions from municipal incinerators [12]. The calculations were based on concentrations of PCDDs and PCDFs predicted from a dispersion model for a typical incinerator. Their results indicate that inhalation of air in the neighborhood of the incinerator does not cause health problems due to PCDD and PCDF emissions. They did conclude that health problems could result from uptake of contaminated food. The food most affected is milk and milk products from cows which eat contaminated grass.

Epidemiologist Arnold Schecter from the Upstate Medical Center of the State University of New York, Binghampton is working with John J. Ryan of the Canadian government's health protection branch in a study of dioxins and furans in adipose tissue [11]. From animal studies it has been determined that the most toxic member of the dioxin family is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Despite hundreds of millions of dollars spent by the federal government to support research, there has been no clear association between exposure to dioxins and carcinogenesis, teratogenesis, or mutagenesis in man. 2,3,7,8-TCDD has been classified by the EPA as a probable human carcinogen because it has been found to exhibit a carcinogenetic effect in certain animals. Since many cancers have latency periods of 15 years or longer, the absence of cancer so far in human studies may only mean the latency period is not over.

Schecter and Ryan have collected 75 samples of human adipose tissue from the general population of the U.S. and Canada and analyzed them for PCDFs and PCDDs. These compounds accumulate in the highest concentrations in fat, so analysis of fat is the best available method to estimate exposure of PCDDs or PCDFs. Schecter and Ryan found levels of 5 to 10 ppt of 2,3,7,8-TCDD and higher levels of up to 1000 ppt of more chlorinated dioxins. Similar levels of furans were also found. These background levels are lower than levels known to cause health effects in humans. But the long-term effect of these levels in humans are not known.

E. Incinerator Technology Applications

This study may be useful to incinerator technology since it provides an alternate reaction mechanism in the dechlorination of chlorinated organic compounds. The oxidation reactions which occur in incinerators are often inhibited by unfavorable reactor conditions. As a result, incomplete combustion products like PCDDs and PCDFs are found in the emissions from both municipal and hazardous waste incinerators. One reason for these products being formed is because of the lack of readily available hydrogen to react with the liberated chlorine atoms. The unfavorable conditions (e.g., cold pockets, mixing inhomogeneities, presence of fly ash, etc.) increase the likelihood that chlorine atoms will recombine with carbon or they result in an inhibition of the dechlorination process itself. By having excess hydrogen present during the reaction, any liberated chlorine molecules are readily consumed in the formation of HCl since the chlorine molecule´s bond to hydrogen is much more favorable than its bond to carbon. Incinerators which burn chlorine-rich wastes already operate with the mole ratio of hydrogen to chlorine at about 4 to 1 [3]. In this study it is proposed that this ratio be increased at least by a factor of 10. An additional bonus to this method of hydrodechlorination is that the now-dechlorinated hydrocarbons can be recycled to the start of the process as fuel. This would significantly reduce the supplemental fuel demands for the incinerator.

F. Similar Studies

The hydrolysis reactions of chlorinated organics have been investigated only recently. Louw et al. have studied reactions of various chlorocarbons with hydrogen [13 and 14]. Some of the compounds which they have considered include chlorinated benzenes, alkenes, alkanes, and PCBs. There has been at least one previous study on gas phase reactions of chlorinated hydrocarbons with water vapor. Gaisinovich and Ketov used a static quartz cell reactor to examine the hydrolysis of CCl_4 and $COCl_2$ [15]. They studied the reaction in the temperature range of 220 °C to 550°C in order to calculate global activation energies. The reaction products were CO_2 and HCl.

Bose and Senkan have examined the combustion characteristics of chlorinated hydrocarbons [16]. They described a separation of flame zones for highly chlorinated hydrocarbons. In the first zone fast oxidative reactions produce CO, HCl, and Cl_2. In the second zone CO is oxidized with HCl and Cl_2, inhibiting the reaction. Senkan also examined the intermediate zone of a two-stage trichloroethylene-oxygen-nitrogen flame [17]. A kinetic mechanism was combined with a plug-flow model and predictions were found to agree with experimental data. Gupta and Valeiras used burning velocities in a chlorinated hydrocarbon-methane-air flame to calculate the activation energies for various compounds [18]. They noted that as more chlorine is added to the chlorinated hydrocarbon, the flame velocity decreases and the maximum flame velocity is shifted from fuel rich towards fuel lean.

II. THEORY

A. Flow Tubes in Combustion Modeling

Plug flow reactors can be used to experimentally study reactions and mechanisms for combustion processes. By maintaining high flow rates, times for diffusion of mass or energy are much longer than residence times. Consequently, there is no need to consider transport effects and this system becomes zero dimensional. In other studies, the flow rates are decreased so that radial diffusion can be used to insure good mixing. The fuel consumption region in a plug flow reactor is more accessable than in other systems like shock tubes and stirred reactors. So it is particularly useful in the study of the elementary reactions of the fuels and intermediate hydrocarbon species in the temperature range of 800 $^{\circ}$K to 1300 $^{\circ}$K.

Simplified reaction mechanisms which predict fuel disappearance can also be developed using plug flow reactors. However the quasi-global approach, which is used in many other systems, has not been used successfully in modeling plug flow reactors [19]. In the quasi-global approach, fuel is assumed to react to CO and H_2. In plug flow systems, oxidation of CO and H_2 is inhibited by the presence of fuel and intermediate species. The quasi-global approach does not provide for this competition. So modeling of plug flow reactors requires that fuel oxidation reactions be treated in better detail.

Flow tube reactors are also useful in determining fast gas-phase reaction data. This data is useful for applications in laser development, atmospheric chemistry, and combustion.

Another technique for studying kinetic data is by flash-photolysis. This technique is more useful at high pressures and heterogeneous reactions do not interfere in the study since the experiment is conducted at the center of a larger reactor, far removed from the walls [20].

Advantages of the flow tube method over flash-photolysis include its lower costs, increased detector versatility, and the possibilities of working with a wider variety of reactants. Flash-photolysis requires a detector with a time resolution that is at least one-tenth the period of the experiment. Since this is in the millisecond range, some detectors like magnetic resonance methods cannot be used. Since the radical reactant must be generated photolytically, some gases like NO_2 and O_3 cannot be used as reactants since they may produce unwanted reactant fragments upon dissociation by the flash radiation.

B. Kinetic Study

This study examines the reaction of 1,2-dichloroethane with water vapor. The linear-flow method is utilized, assuming plug flow without axial diffusion [21]. The molar ratio of water to 1,2-dichloroethane is very high (55:1) and the rate of decomposition of 1,2-dichloroethane is of the first order as the concentration of water remains constant. At one temperature, the amount of unreacted 1,2-dichloroethane exiting the reactor at various residence times is measured. Since the reaction is first order in 1,2-dichloroethane, a plot of $\ln(C/C_o)$ versus t results in a straight line through the origin with a slope of k_a. Performing this procedure at more than one temperature allows one to graph $\ln k_a$ versus T^{-1}. This Arrhenius plot results in a straight line with a slope of $-E_a/R$ and y-intercept of A_a [22]. Values of the rate constants are obtained directly from the Arrhenius plot for subsequent numerical analyses. The reason for this is because the functions in which they will be applied are very sensitive to deviations. So new graphical rate constants, k_g, can be determined at each temperature.

Kaufman and others have shown a relationship between the overall rate constant and rate constants for parallel reactions at the reactor wall and in the bulk stream [23]. This relationship is expressed in the form of the equation:

$$k_g = k_b + (2/r)k_w$$

Using this equation with data from reactors of different diameters will result in the bulk and wall rate constant determination. Arrhenius plots will then result in values for activation energy and frequency factor for reactions at both the wall and in the bulk stream.

C. Deviations From Ideality

The most important assumption made in this study is that of plug flow. This assumption states that all the fluid elements move through the reactor at one bulk velocity and there are no radial concentration gradients. Conditions which are employed to achieve plug flow must give minimum viscous pressure drop, axial diffusion, and wall reactions, along with maximum radial diffusion [24]. Another way in which ideal plug flow is characterized is by a Reynolds number greater than 10^4 and a length to diameter ratio greater than 100 [4].

The pressure gradient along the length of the flow tube can be determined from an equation in Kaufman's paper:

$$\triangle P/\triangle z = 5.9 \times 10^{-3}\,\eta v/r^2$$

Since reaction occurs as the fluid elements move along the tube, there is an axial concentration gradient:

$$dC/dz = -kC/v$$

This concentration gradient results in an additional transport mechanism of the fluid elements as a result of diffusion. According to Fick's first law:

$$J = -D\ dC/dz = v_d C$$

So $v_d = Dk/v$ and the correct transport velocity is $v + v_d$.

Howard developed a method to correct measured rate constants in order to account for axial diffusion [20]:

$$k_c = k_g(1 + k_g D/v^2)$$

He also developed a method to correct for wall reactions which will have an effect on the axial concentration gradient:

$$k_c = k_g[1 + (k_g + 2k_{w'})D/v^2]$$

The $k_{w'}$ in this equation is equal to k_w multiplied by $2/r$. So the actual equation for correcting the rate constant in order to account for wall reactions is:

$$k_c = k_g[1 + (k_g + 4k_w/r)D/v^2]$$

III. EXPERIMENTAL APPARATUS AND PROCEDURE

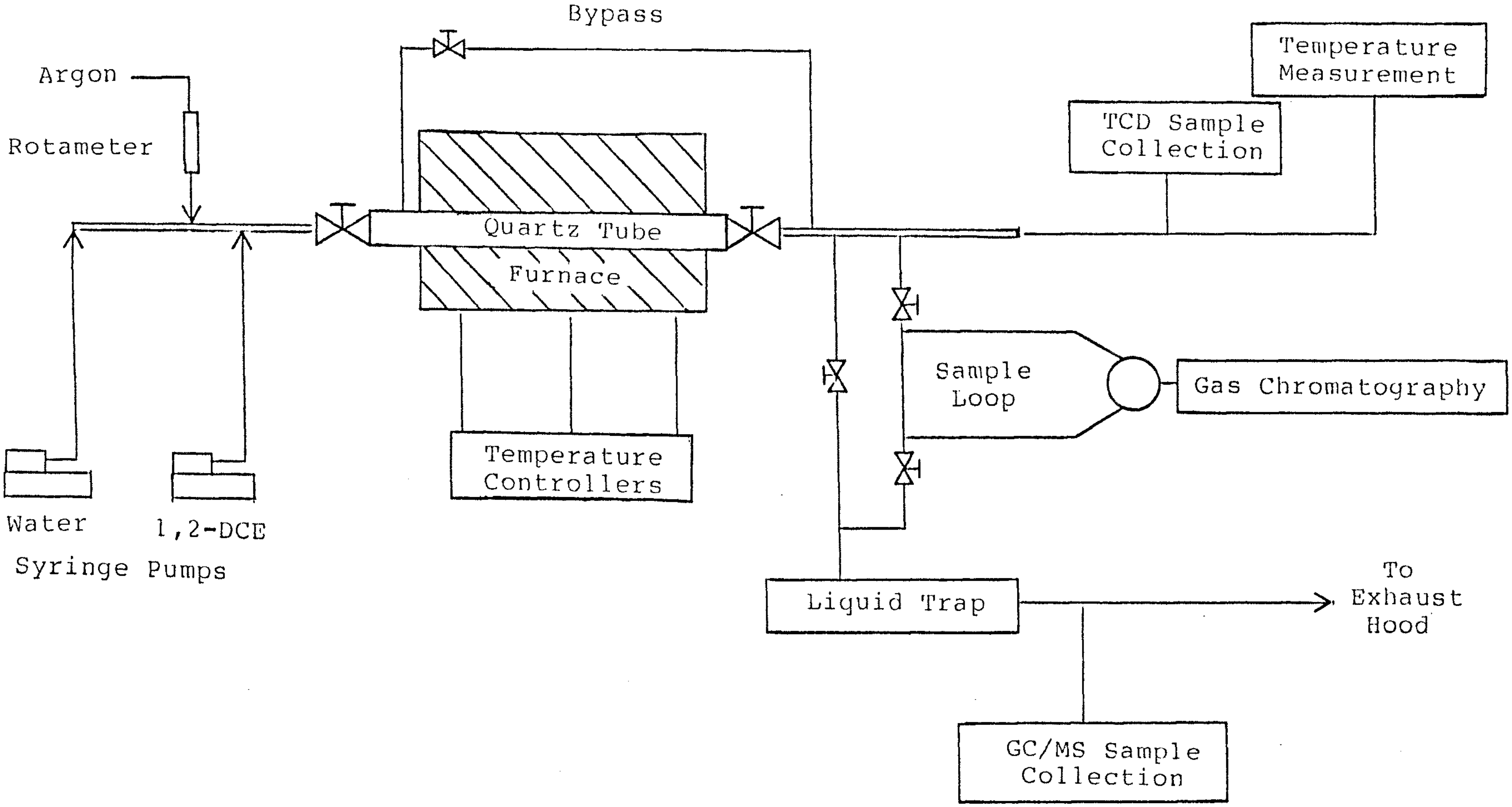
A. Overview of Procedure

This is a study of the pseudo-first order reactions of 1,2-dichloroethane with an excess of water vapor. The temperature range in which 1,2-dichloroethane is only partially reacted is from 500 °C to 700 °C. In this temperature range the change in the amount of reacted 1,2-dichloroethane with reactor diameter, temperature, and residence time can be used to calculate kinetic parameters of the reaction. Product distributions in this temperature range and up to 950 °C are used to gain insight in order to establish a hypothesis for the reaction mechanism. Figure 1 is an illustration of the experimental apparatus.

B. Inlet and Bypass

Water and 1,2-dichloroethane are introduced to the system in liquid phase. Water flow is controlled by a Model 341A syringe pump from Sage Instruments of Cambridge, MA. A Model 600-950 syringe pump by Harvard Apparatus Company of Dover, MA controls the flow of 1,2-dichloroethane. All flow lines throughout the system are wrapped in heater tape and heated to 110 °C to prevent condensation. The vaporized reactants are combined with industrial grade argon, the carrier gas in the reactor. All gases used throughout the system are purchased from MG Scientific of North Branch, NJ. Argon flows through a calibrated Fischer-Porter rotameter. By changing the argon flowrate, various residence times can be effected in the reactor. Generally, the concentration of

Figure 1 EXPERIMENTAL APPARATUS



argon in the reactor is always greater than 10 percent by volume.

By utilizing tubing which bypasses the reactor, the initial concentration of 1,2-dichloroethane can be detected by gas chromatography. For a set flowrate of reactants, this initial concentration will change as a function of the argon flowrate.

C. Thermal Region

The reactor consists of a quartz tube in a furnace which is 18 inches in length. Two reactor tubes with inside diameters of 0.4 cm and 1.05 cm are used. The furnace consists of clam shell-type tubular heaters with inside diameters of 1.25 inches and are supplied by the Mellen Company of Penacook, NH. The heating elements consist of helically coiled nickel chromium wire mounted in a ceramic holder. They are cemented with high purity Al_2O_3 cement and can operate at temperatures up to 1200 ^{o}C. The furnace is divided into three regions: 2 end zones which are 3 inches in length and a center zone 12 inches long. The temperature in each zone is controlled using temperature controllers from the Burling Instruments Company of Chatham, NJ.

The temperature profile in the reactor tube can be determined by insertion of a chromel-alumel thermocouple. The thermocouple is moved along the length of the reactor while argon is flowing at 5 to 10 ml per minute. An Omega temperature indicator Model 650, is used to display the temperature. The thermocouple should be allowed to equilibrate by remaining in position for one minute before recording the temperature. The set temperature on the temperature controller is adjusted until the desired temperature is recorded in the reactor. By this method a flat temperature profile, $\pm 5\ ^{\circ}C$, can be maintained over the central 37 cm of the reactor tube.

D. Outlet and Sampling System

One of the reactor products is HCl which is very corrosive. So all tubing on the outlet side of the reactor is 1/4 inch heavy-walled translucent Teflon^{R} PFA tubing, supplied by the Galtek Corporation of Chaska, MN. The same company supplies Teflon^{R} fittings including male connectors, union tees, and ferrule nuts. A liquid trap in an ice-water bath is used to remove condensables from the gas stream before it reaches an exhaust hood.

The sampling system for flame ionization detector analysis consists of a loop which is isolated from the rest of the system by two fast-action plug valves. The material of construction of each valve is Teflon^{R} PFA and they can operate at temperatures up to 275 $^{\circ}F$. The carrier gas for flame ionization detection in the gas chromatograph is nitrogen. Its flow normally bypasses the sample loop. During sampling, nitrogen flow is diverted through the sampling loop by means of a 1/8 inch bar stock body four-way valve from Conant Controls of Medford, MA. The bar stock body is made of PVC and houses a Teflon^{R} rotor. Its upper temperature limit is 140 $^{\circ}F$.

E. Sample Analyses

Reactor products are identified using a Kratos MS25 magnetic sector gas chromatograph/mass spectrometer. A Kimax 30 ml gas bulb is used for sampling. This item is made from thin-blown glass and has one tube with a lightly-greased stopcock. The gas bulb is evacuated for several minutes by a Duo-Seal vacuum pump from Welch Manufacturing Company of Chicago, IL. By closing the stopcock, a vacuum can be maintained. The evacuated gas balloon tube is then connected to a sample port located downstream from the liquid trap since water is not desired in the sample. The reason for this is because a large water flow will alter the sensitivity of the GC/MS. By opening the stopcock, a sample is drawn into the gas balloon since the reactor system operates at a pressure of 1 atmosphere. Analysis by GC/MS is for the identification of products only and is not quantitative.

The concentrations of chlorinated organic compounds are measured with a Model 1420 Gas Chromatograph from Varian Aerograph of Walnut Creek, CA. A 5 foot long, packed, 1/8 inch column is used to separate the products. The packing materials are Gas-Chrom R, 60/70 mesh (support) from Applied Science Labs of State College, PA and Silicone GE SE-52 (stationary phase) from Alltech Associates of Arlington Heights, IL. Detection is via an accessory flame ionization detector. Operation of the column is isothermal at 80 ^{o}C. The carrier gas through the column is commercial grade nitrogen. The flame in the detector is fueled by industrial grade hydrogen and air from a compressed air line. The nitrogen flows through a Fischer-Porter rotameter at 25 ml per minute. Air (290 ml per minute) and hydrogen (32 ml per minute) both flow through separate Brooks rotameters. The output signal from the flame ionization detector is amplified by a Keithley 416 High-speed Picoammeter. The resulting chromatogram is recorded and integrated by a Varian Model 4270 Integrator.

The Varian 1420 gas chromatograph is also used to analyze CO and CO_2. A packed column, 8 feet in length, is used to separate the compounds. The packing material is Porapak Q. The detector for this analysis is a thermal conductivity detector. The carrier gas through the column is industrial grade argon which flows at 40 ml per minute. To facilitate separation of CO and CO_2 within a reasonable length of time, the column is temperature programmed. Normal operation is at 60 ^{o}C for one minute, the temperature is increased at 20 C^{o} per minute, and the final temperature of the column is 175 ^{o}C. The resulting chromatogram is recorded by a Model 1005 Ten-Inch Laboratory Potentiometric Recorder from Beckman Instruments of Fullerton, CA. The signal is integrated by the Varian Model 4270 Integrator.

F. Choosing Operating Conditions

The operating temperature range for collecting kinetic data for this reaction system is between 500 ^{o}C and 700 ^{o}C. The goal is to obtain a wide range of conversions while keeping the range of residence times between 0.1 sec and 1.5

sec. The flowrates of water and 1,2-dichloroethane are held constant while the argon flowrate is varied to effect different residence times. Gross adjustments to the reactants flowrates can be made when the reactor diameter is changed. This is done to obtain meaningful residence times.

At temperatures of 500°C to 600°C, the conversion of 1,2-dichloroethane to products will be low. The controlling factor which determines the lowest operation temperature is that at the shortest residence time, the 1,2-dichloroethane conversion should be approximately 10 percent. At temperatures of 650°C to 700°C, the conversion of 1,2-dichloroethane will be high. The controlling factor which determines the highest operation temperature is that at the longest residence time, the 1,2-dichloroethane conversion should be approximately 90 percent.

IV. RESULTS AND DISCUSSION

A. Kinetics

Data for establishing kinetic parameters is collected by operating the reactor at 590 ^{o}C, 630 ^{o}C, and 680^{o}C. Figures 2 and 3 show plots of $-\ln(C/C_o)$ versus t. Each point on the graphs represents an average of two values of $-\ln(C/C_o)$ at each residence time for which data is collected. The two values must agree to within 10 percent. Actually, most of the duplicate values (about 80 percent of them) agree to within 5 percent.

As described in the theory section, plots of $-\ln(C/C_o)$ versus t can be used to calculate values for first order rate constants. Arrhenius plots are graphs of $\ln k_a$ versus T^{-1} which are illustrated in Figure 4. A straight line is drawn through the data points for one reactor diameter. Subsequent numerical analyses are sensitive to deviations from this linear relationship. So values for the rate constants are obtained directly from the Arrhenius plots. Table 1 lists values of rate constants, residence time ranges, and ranges of percent conversion of 1,2-dichloroethane for each reactor diameter.

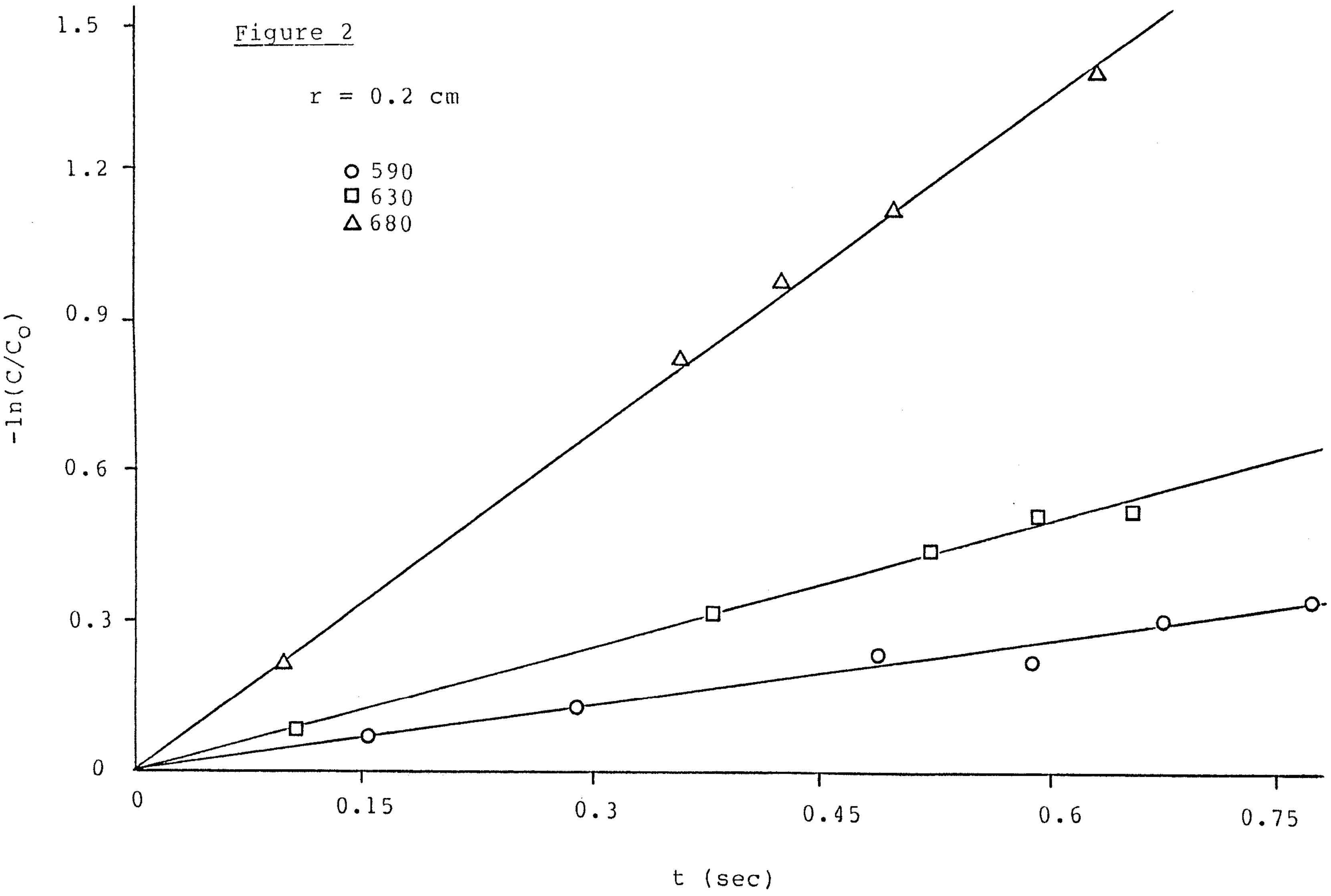


Figure 2

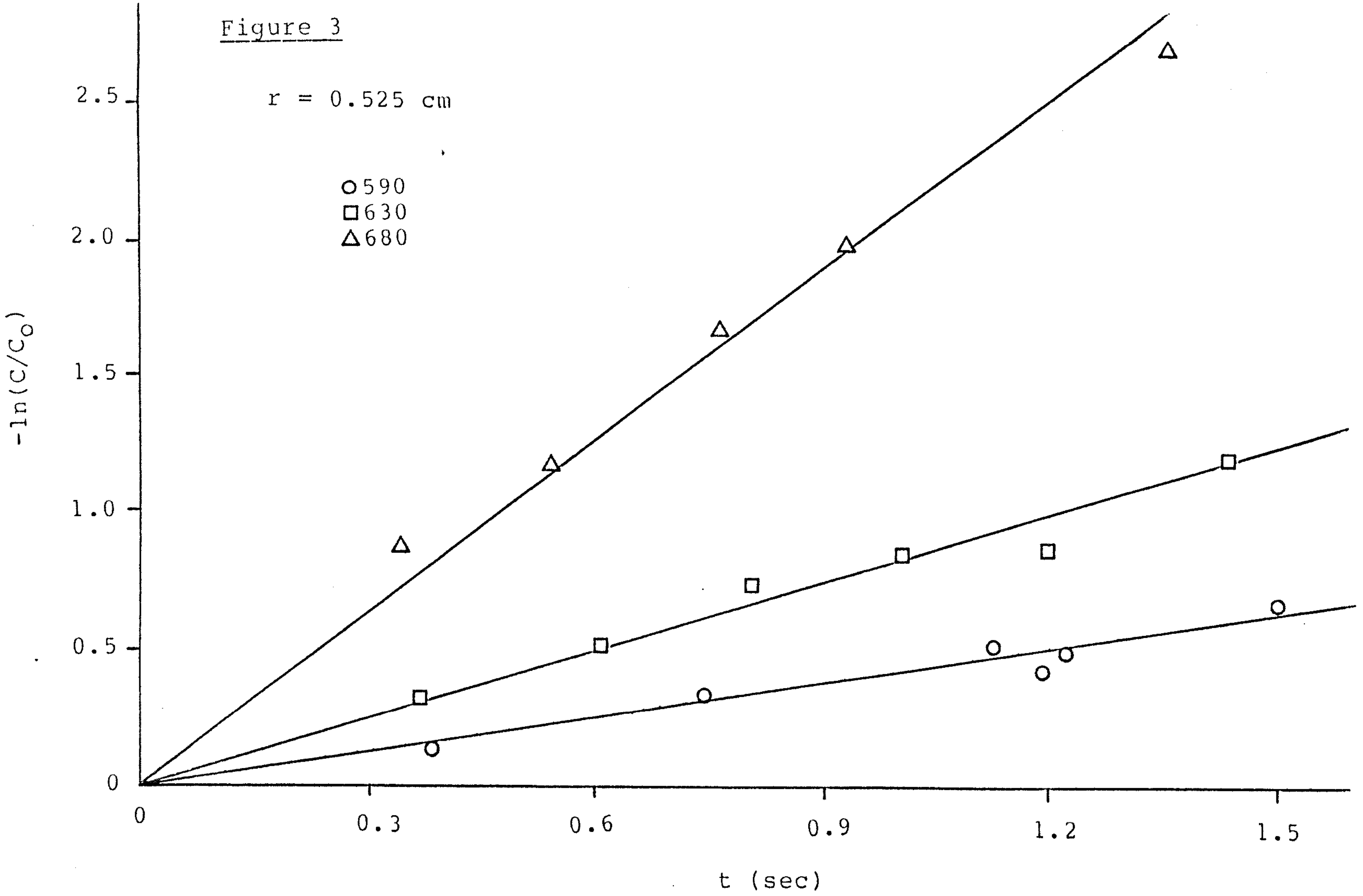


Figure 3

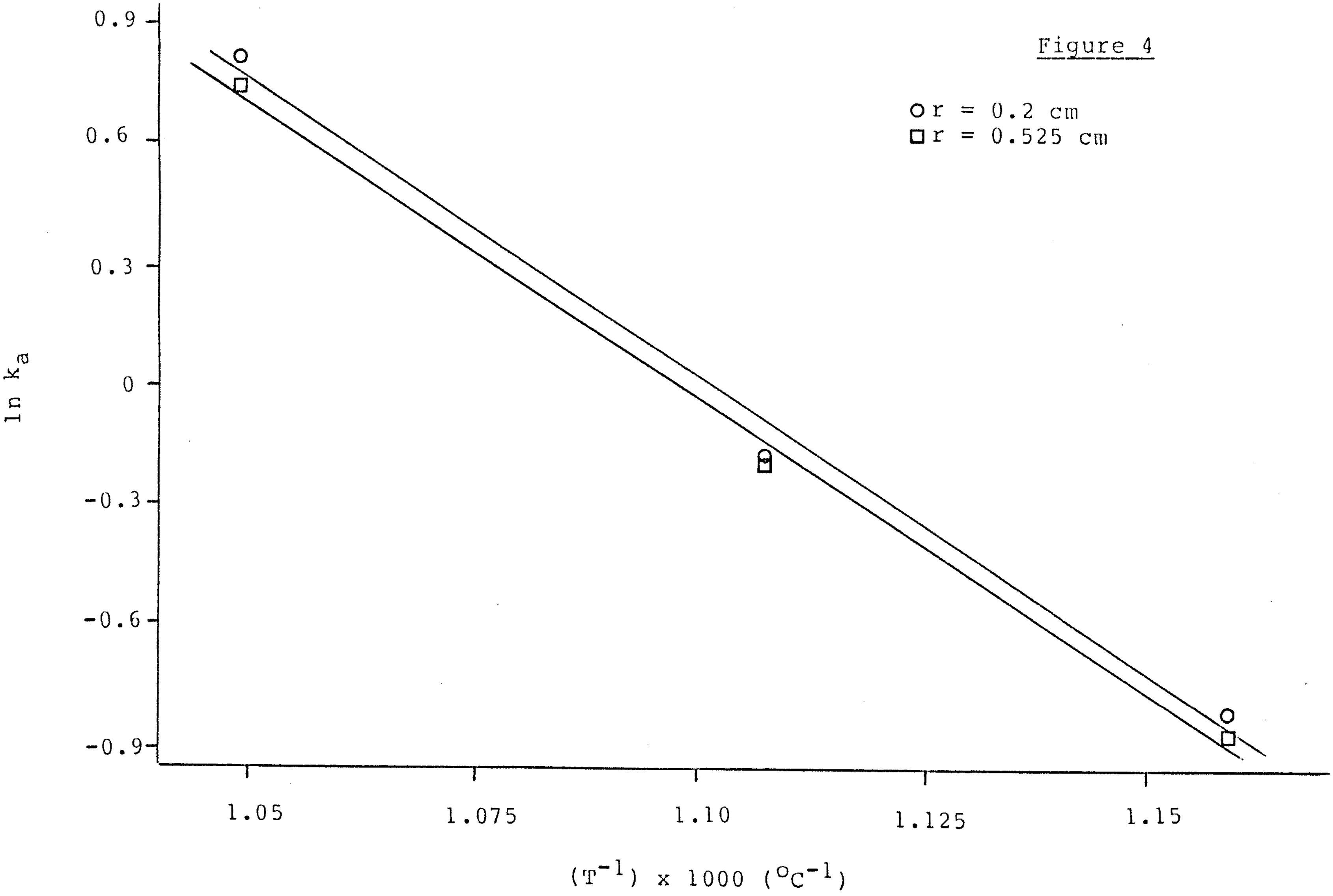


Figure 4

○ r = 0.2 cm
□ r = 0.525 cm
ln k_a
0.9
0.6
0.3
0
-0.3
-0.6
-0.9
1.05
1.075
1.10
1.125
1.15
$(T^{-1}) \times 1000\ (^{\circ}C^{-1})$

Table 1 - Rate Constants, Residence Time Ranges, and Percent Conversions

r = 0.2 cm

$T(^{o}C)$	$k_a(sec^{-1})$	$k_g(sec^{-1})$	t(sec)	%Reaction
590	0.447	0.427	0.15 - 0.77	7 - 30
630	0.840	0.916	0.11 - 0.66	8 - 41
680	2.26	2.17	0.10 - 0.63	19 - 75

r = 0.525 cm

$T(^{o}C)$	$k_a(sec^{-1})$	$k_g(sec^{-1})$	t(sec)	%Reaction
590	0.442	0.410	0.38 - 1.5	13 - 49
630	0.827	0.872	0.37 - 1.4	27 - 70
680	2.10	2.05	0.34 - 1.4	59 - 93

By utilizing the relationship reported by Kaufman [23], the overall rate constant can be decoupled to calculate rate constants for parallel reactions at the reactor wall and in the bulk stream. Figure 5 shows plots for k_g versus 2/r. New values for k_w and k_b can be determined from these plots as described in the theory section. Table 2 lists the resulting values of the decoupled rate constants at each temperature.

Table 2 - Rate Constants for Reactions at the Wall and in the Bulk Stream

$T\ (^{o}C)$	$k_w(cm/sec)$	$k_b(sec^{-1})$
590	0.00275	0.400
630	0.00711	0.845
680	0.0194	1.98

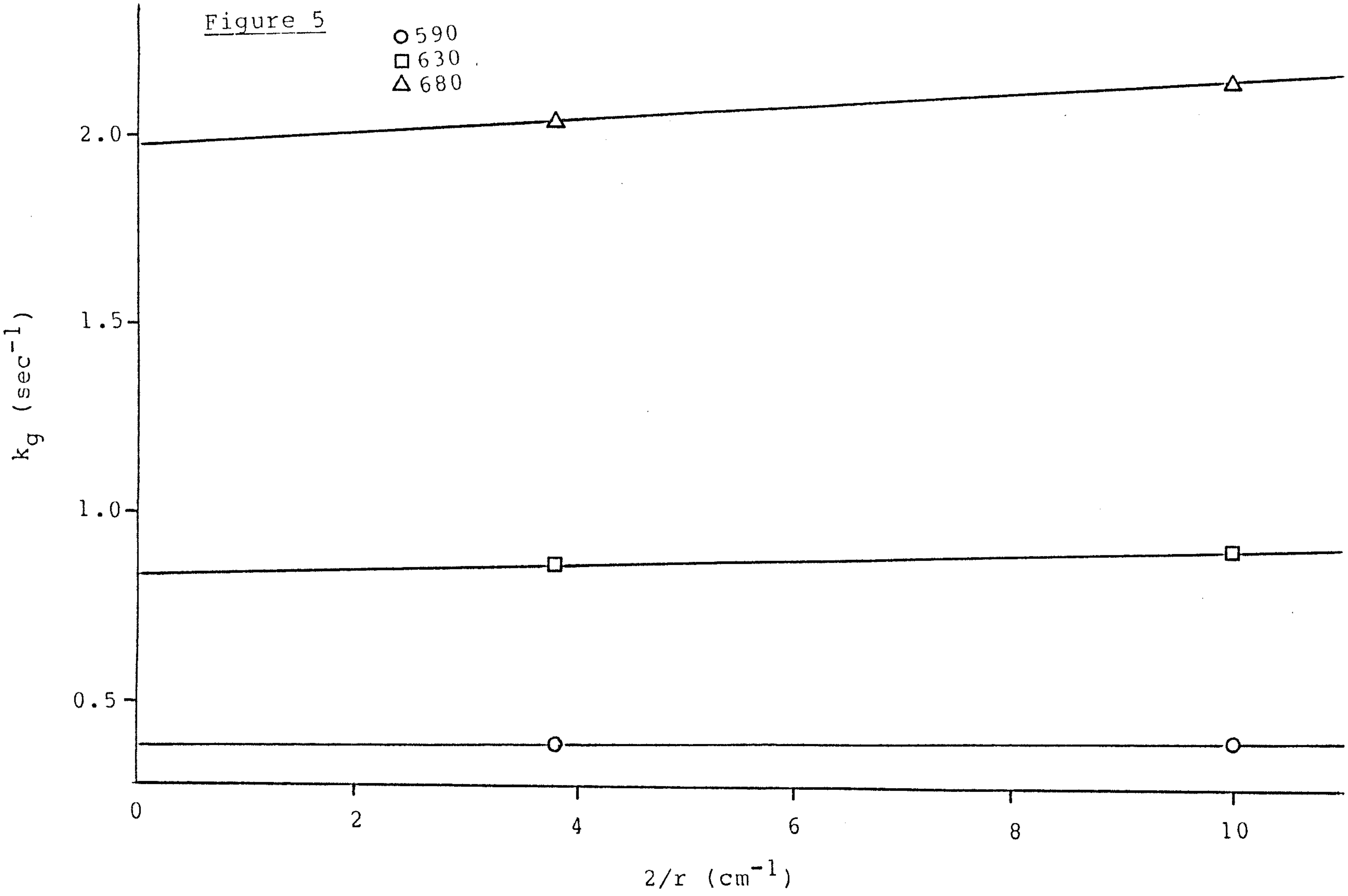


Figure 5

Values of the decoupled rate constants can be applied in an Arrhenius plot in order to calculate values for the activation energies and the frequency factors. This is illustrated in Figures 6 and 7. The following values result:

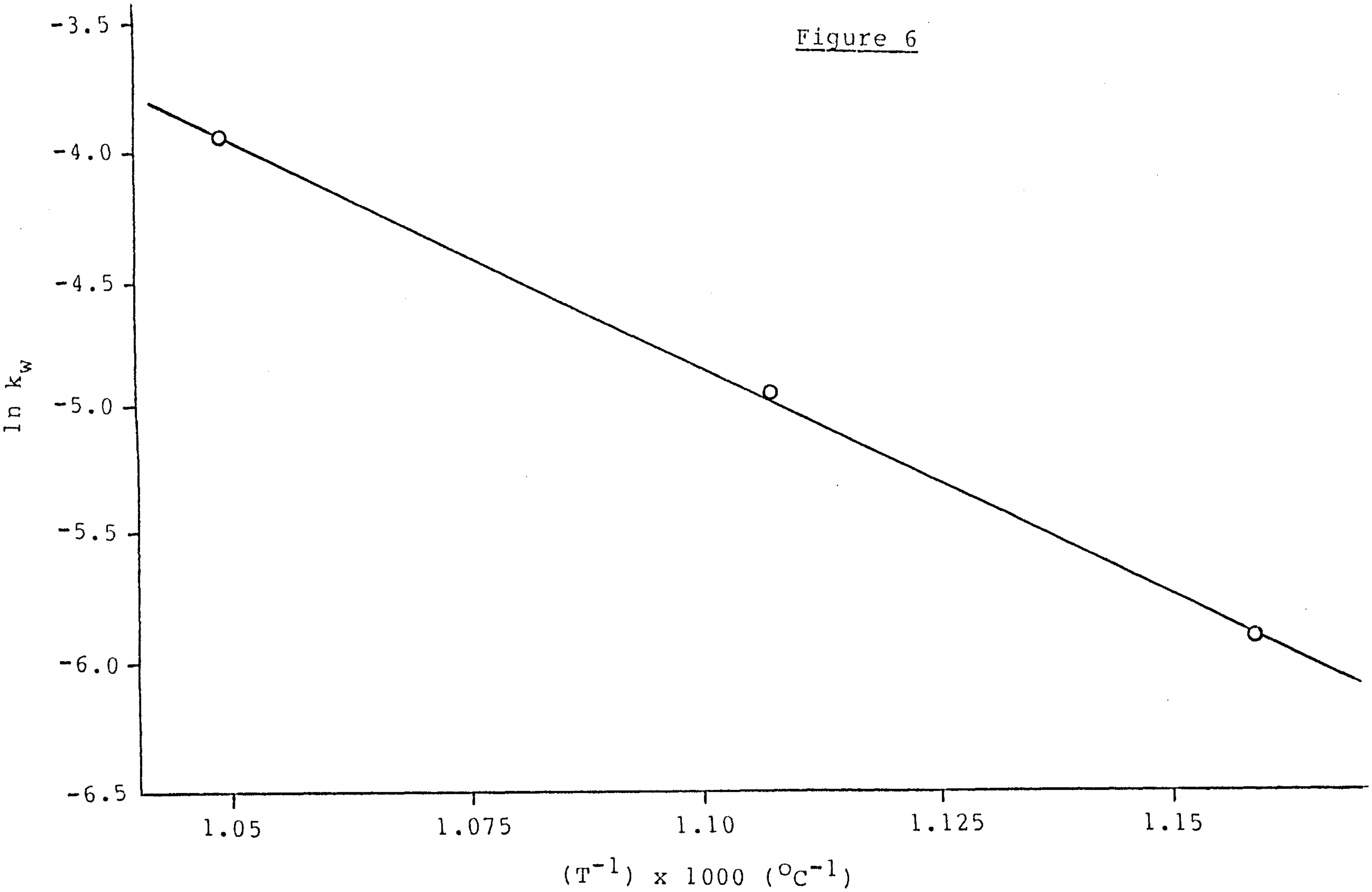
E_w= 35.4 kcal/mol E_b= 29.0 kcal/mol

A_w= 2.65 x 10^6 cm/sec A_b= 9.06 x 10^6 sec^{-1}

These activation energy values are in close agreement with unimolecular decomposition data in literature. In a pyrolysis study of 1,2-dichloroethane in a static system, the activation energy was determined to be 33.0 kcal/mol [25].

Figures 8 and 9 show the decomposition of 1,2-dichloroethane versus residence time for various temperatures in the different reactors. The results show that in the same residence time range, the amount of unreacted 1,2-dichloroethane is lower in the large diameter reactor compared to the small diameter reactor. This result is also shown in Figure 10 which is a plot of conversion of 1,2-dichloroethane versus temperature for different reactor diameters. The relative rates of reactions at the wall compared to reactions in the bulk stream are illustrated in Table 2. The bulk stream rate constants are on the order of 100 times those for reactions at the wall. The surface to volume ratio of the small diameter reactor is 2.6 times that of the large reactor. An activated 1,2-dichloroethane molecule has a higher probability of colliding with the wall in the smaller reactor rather than the larger one. A stabilizing effect results as the activated molecule loses some of its excess energy upon collision with the wall and has less chance of reacting with some other radical.

Figure 6



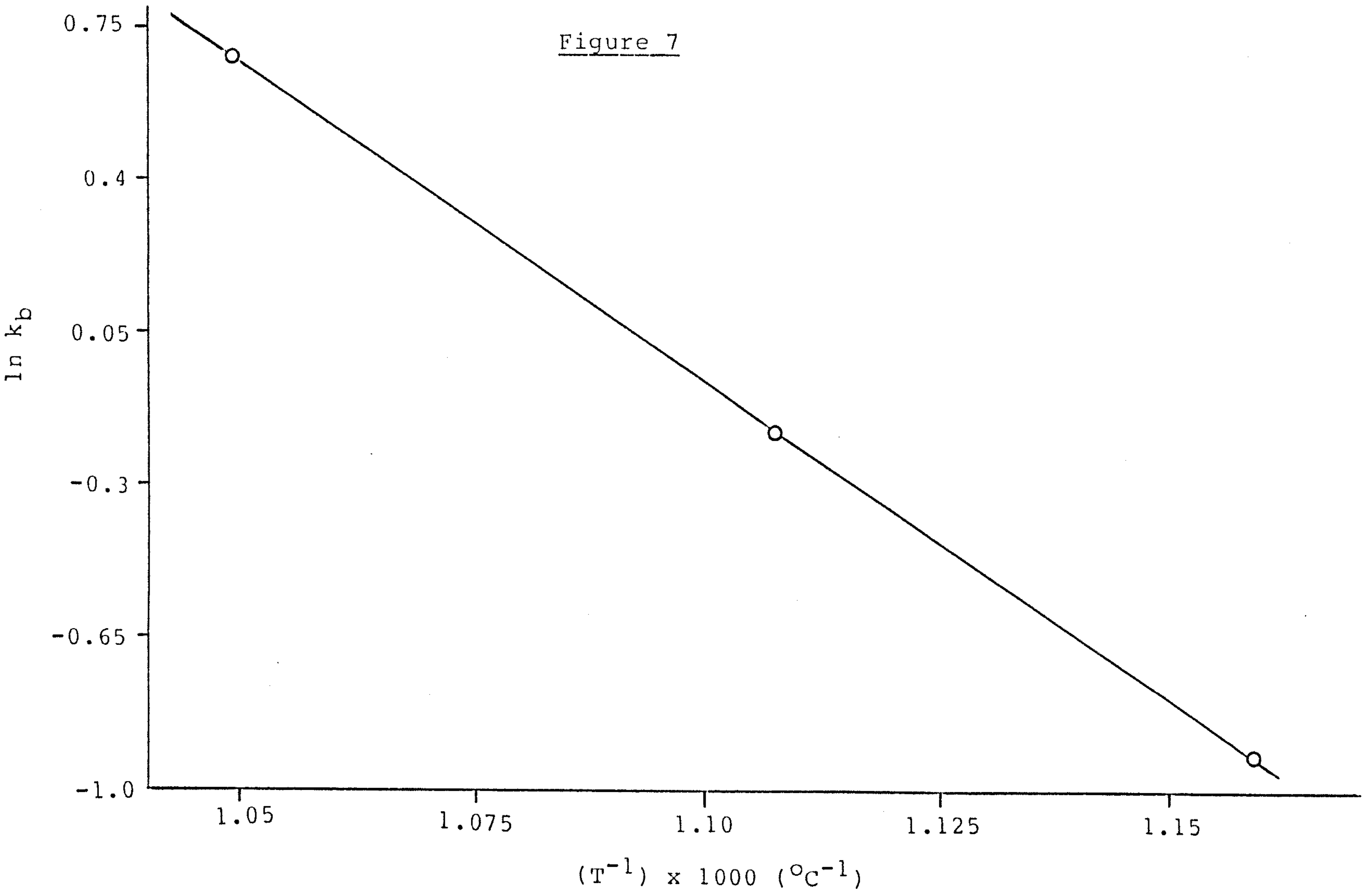


Figure 7

0.75
0.4
0.05
-0.3
-0.65
-1.0
ln k_b
1.05
1.075
1.10
1.125
1.15
$(T^{-1}) \times 1000$ ($^{o}C^{-1}$)

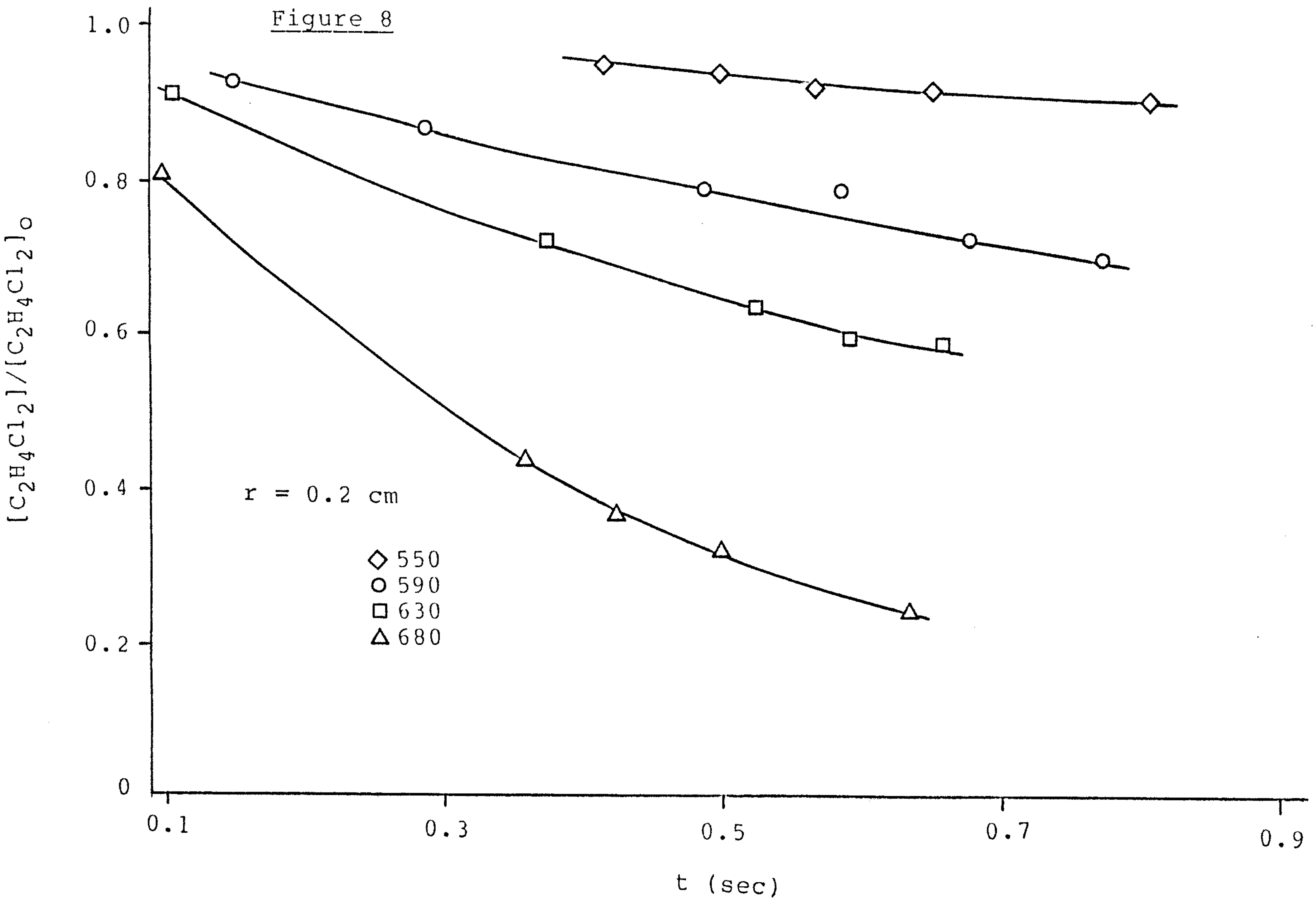


Figure 8

1.0
0.8
0.6
0.4
0.2
0
$[C_2H_4Cl_2]/[C_2H_4Cl_2]_o$
0.1
0.3
0.5
0.7
0.9
t (sec)
r = 0.2 cm
◇ 550
○ 590
□ 630
△ 680

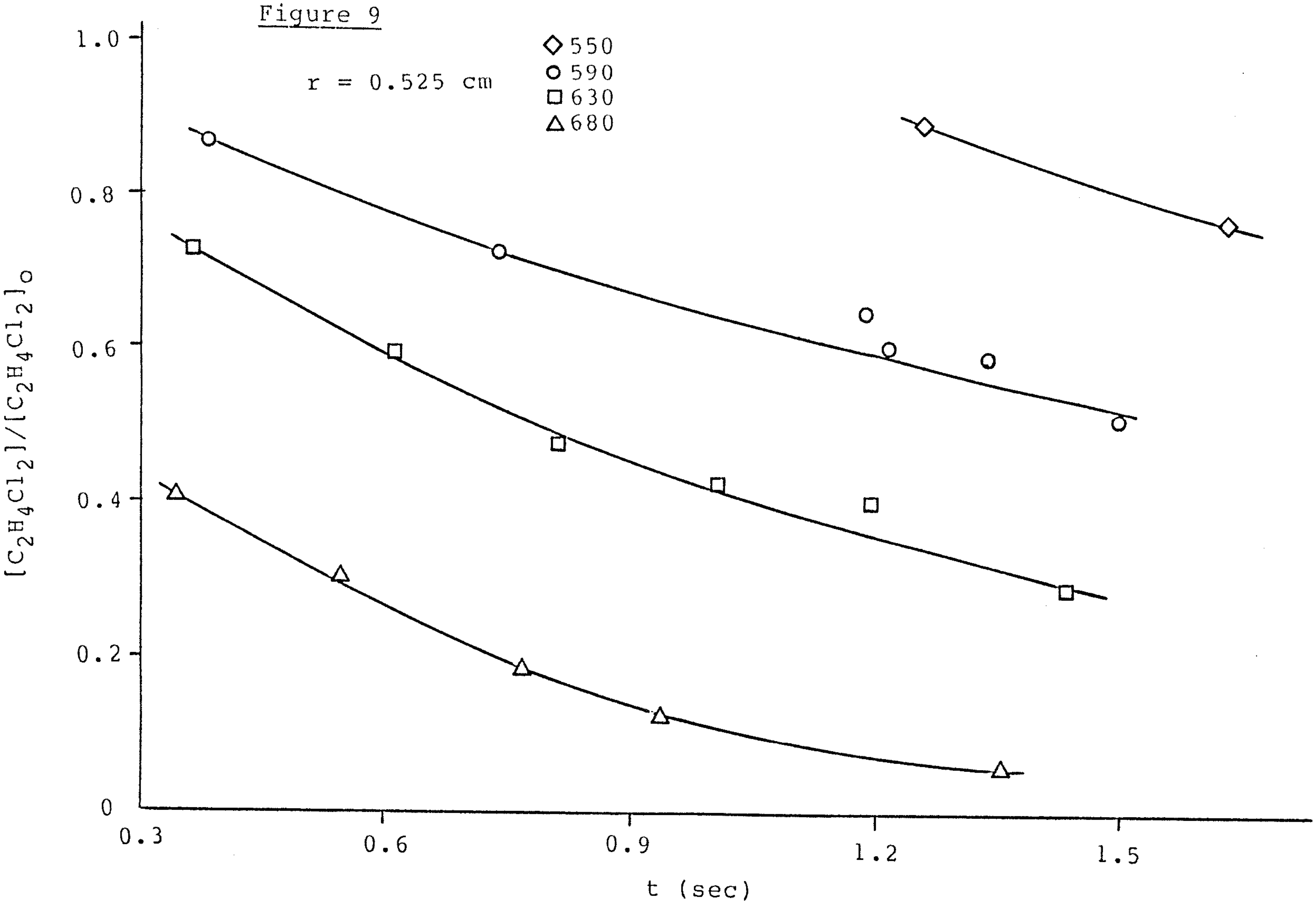


Figure 9

r = 0.525 cm
◇ 550
○ 590
□ 630
△ 680
$[C_2H_4Cl_2]/[C_2H_4Cl_2]_o$
1.0
0.8
0.6
0.4
0.2
0
0.3
0.6
0.9
1.2
1.5
t (sec)

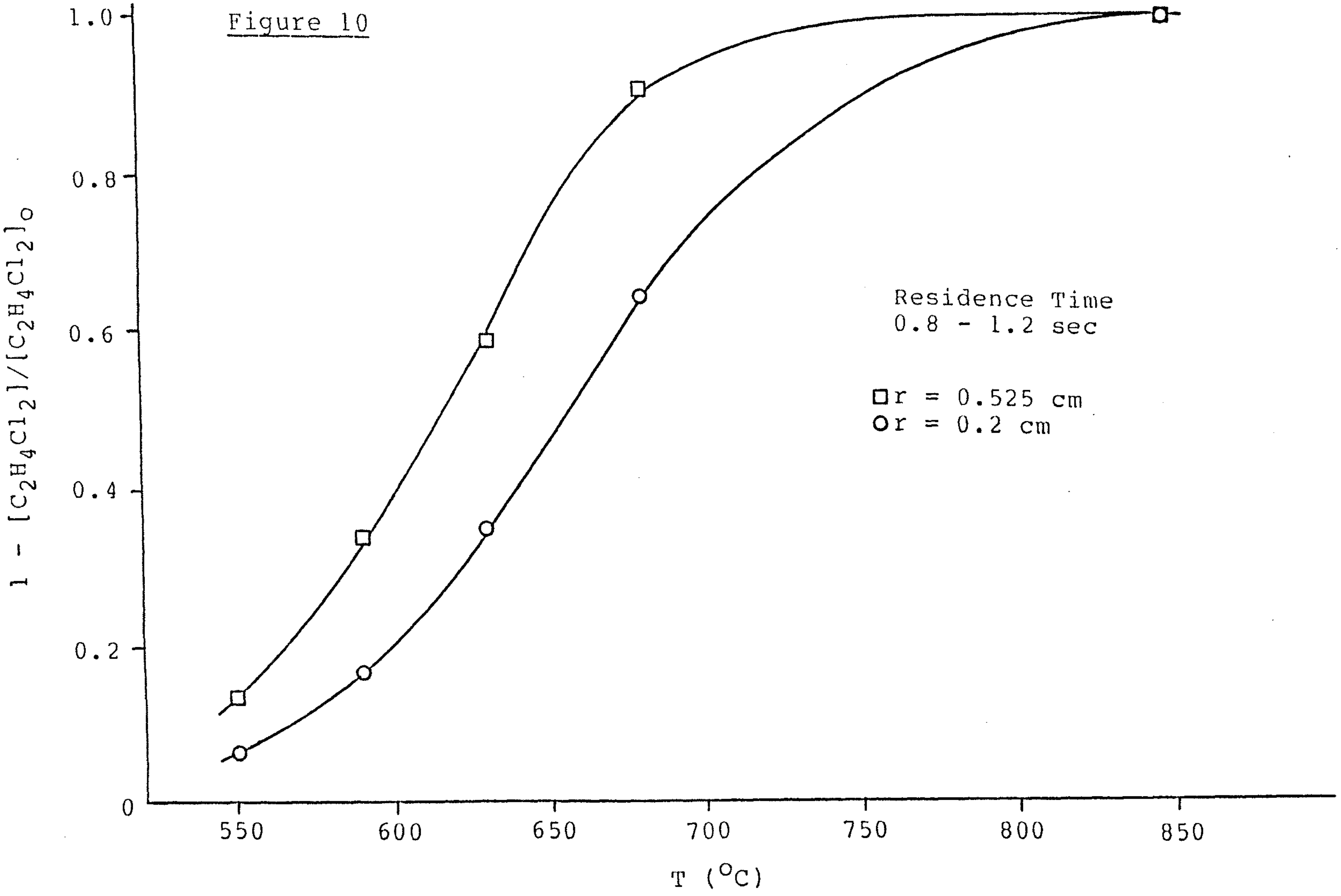


Figure 10

1.0
0.8
0.6
0.4
0.2
0
550
600
650
700
750
800
850
T (^oC)
1 - $[C_2H_4Cl_2]/[C_2H_4Cl_2]_o$
Residence Time
0.8 - 1.2 sec
□ r = 0.525 cm
○ r = 0.2 cm

B. Deviations From Ideality

Values for the pressure drop over the length of the flow tube are greatest for the tube with the smaller diameter, 0.4 cm. They are also found to increase with decreasing residence time (higher flow rates) and increasing temperature. At 680 °C the pressure drop ranges from 0.18 to 0.37 atmosphere in the small flow tube. The largest pressure drop across the 1.05 cm diameter flow tube is 0.076 atmosphere.

In Howard's equation to correct values of rate constants in order to account for axial diffusion, the additive correction factor (CF_a) is equal to $k_g D/v^2$. The correction factor for considering wall reactions (CF_w) is equal to $(k_g + 4k_w/r)D/v^2$ [20]. Values of these correction factors are shown in Table 3.

Table 3 - Correction Factors for First Order Rate Constants

r = 0.2 cm

T (°C)	CF_a	CF_w
590	1.82×10^{-4}	2.05×10^{-4}
630	3.76×10^{-4}	4.35×10^{-4}
680	8.96×10^{-4}	1.06×10^{-3}

T (°C)	CF_a	CF_w
590	6.87×10^{-4}	7.22×10^{-4}
630	1.40×10^{-3}	1.49×10^{-3}
680	3.23×10^{-3}	3.47×10^{-3}

These values show that axial diffusion and wall reactions have very small or insignificant influence on the results of calculated first order rate constants.

C. Reaction Products and Mechanism Analysis

Table 4 - Reaction Products

vinyl chloride	C_2H_3Cl
2-chloro-1,3-butadiene	C_4H_5Cl
carbon dioxide	CO_2
hydrogen chloride	HCl
chloroethane	C_2H_5Cl
ethane	C_2H_6
1,1-dichloroethene	$C_2H_2Cl_2$
acetylene	C_2H_2
trichloroethene	C_2HCl_3
1-buten-3-yne	C_4H_4
propyne	C_3H_4
benzene	C_6H_6 (ring)
chloromethane	CH_3Cl
1,3-butadiyne	C_4H_2
ethene	C_2H_4

Figure 11 shows the changes in product distributions as a function of temperature. Peaks for acetylene and ethene are not separable by the gas chromatography system used in this study, so both compounds are represented by one peak. Figures 12 through 17 show the relationship between product distributions and residence times in each reactor at temperatures between 590 °C and 680 °C.

A comparison between the list of reaction products in

Table 4 and the products shown in Figures 11 through 17 points out the sensitivity differences between the analyses used. Many more compounds are identified by GC/MS analysis than are detected by gas chromatography with flame ionization detection. This problem is most unfortunate regarding CO_2 since this is the product of total oxidation. As mentioned in Section III, the thermal conductivity detector is used for this analysis and its lowest detection limit is 10 ppm. The concentration of 1,2-dichloroethane in the reactant stream is on the order of 1000 ppm. Concentrations of CO_2 in the product streams were found to be undetectable by gas chromatography, or less than 10 ppm. This indicates that less than 0.5 percent of the 1,2-dichloroethane carbon is converted to CO_2.

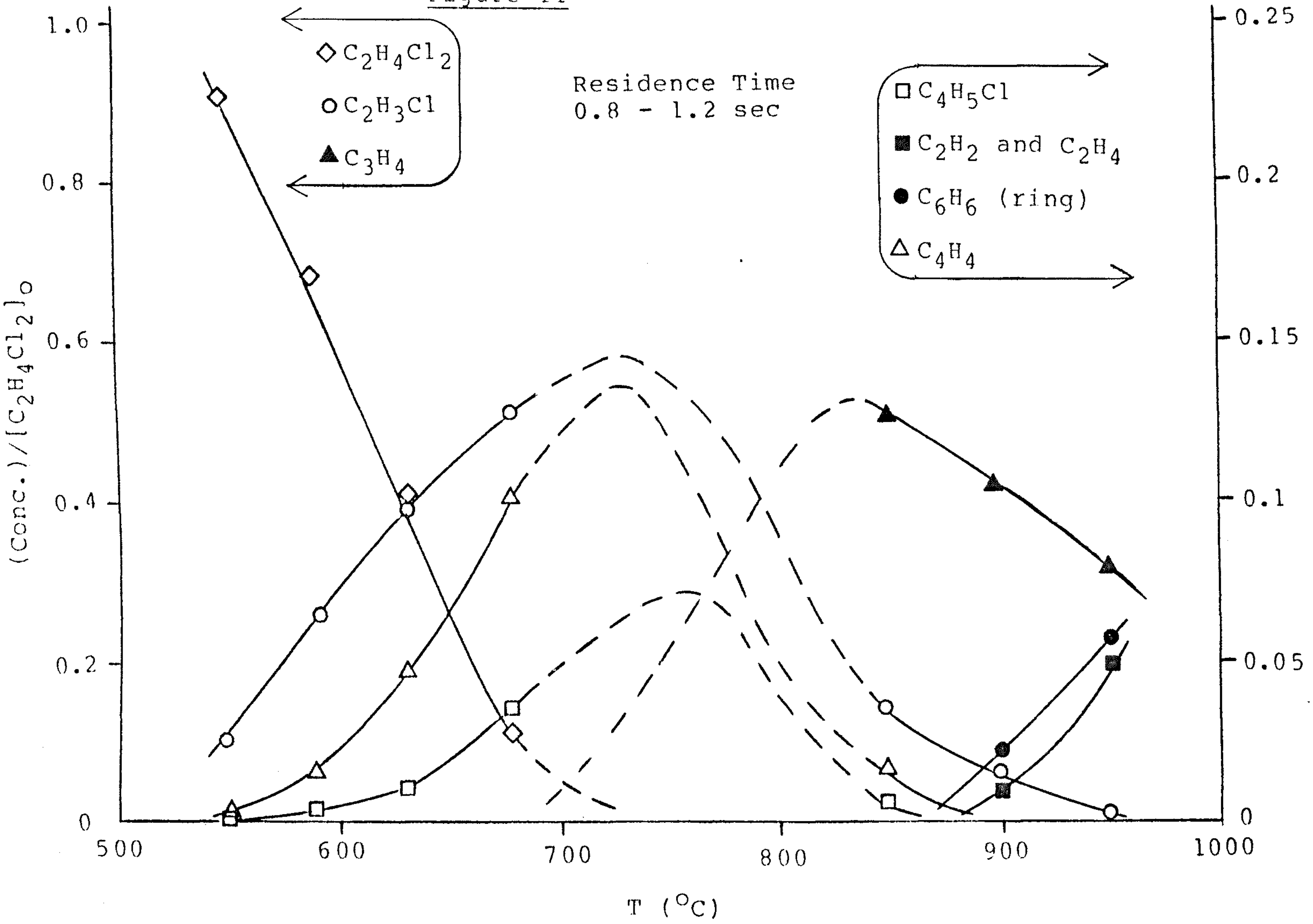
The low levels of CO_2 and lack of CO in the product stream indicates that water is a poor hydrogen donor in this system. The only reagent attacking water is Cl which reacts with water through O_2 channels such as:

$$OH + OH \longrightarrow H_2O + O$$

$$O + OH \longrightarrow HO_2$$

$$Cl + HO_2 \longrightarrow HCl + O_2$$

Figure 11



◇ $C_2H_4Cl_2$
○ C_2H_3Cl
▲ C_3H_4
Residence Time
0.8 - 1.2 sec
□ C_4H_5Cl
■ C_2H_2 and C_2H_4
● C_6H_6 (ring)
△ C_4H_4
(Conc.)/$[C_2H_4Cl_2]_o$
1.0
0.8
0.6
0.4
0.2
0
0.25
0.2
0.15
0.1
0.05
0
500
600
700
800
900
1000
T (^oC)

Figure 12

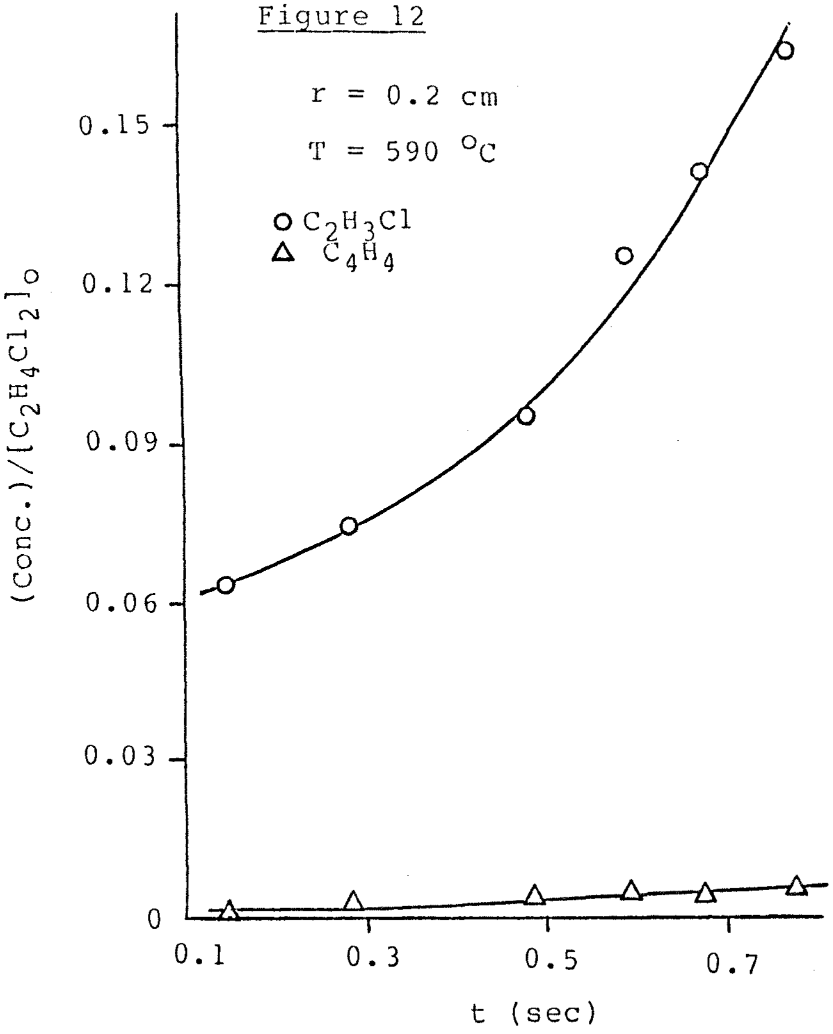
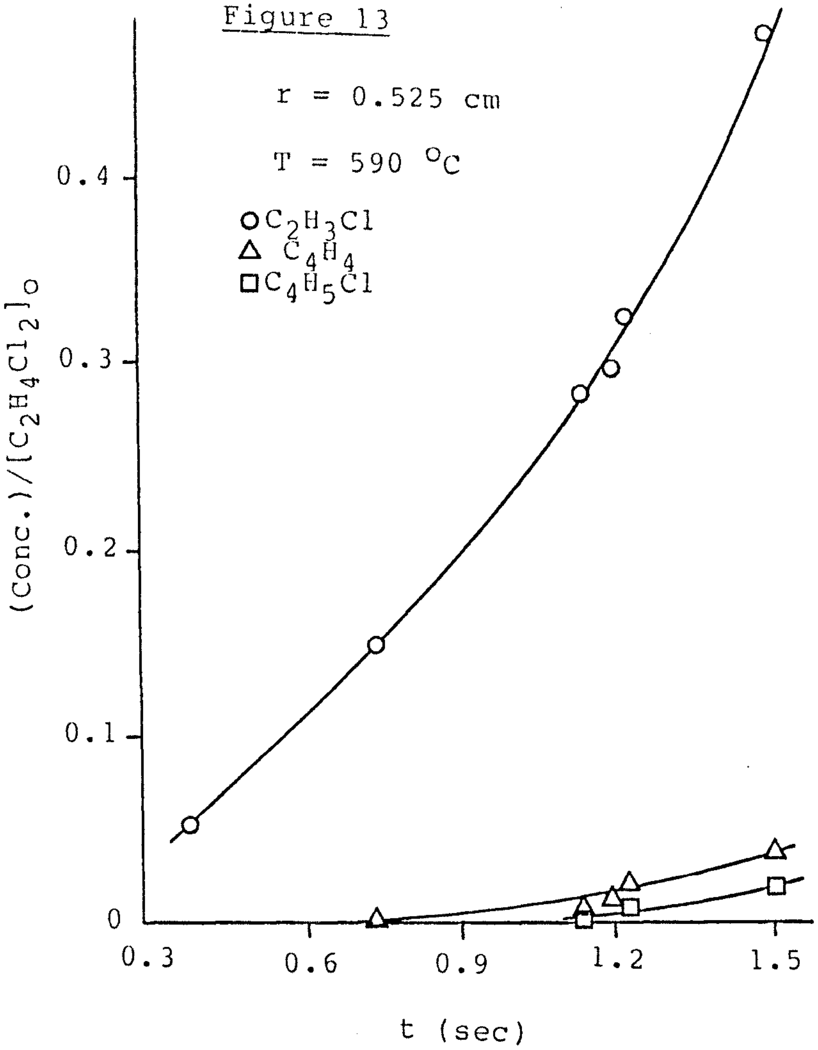


Figure 13



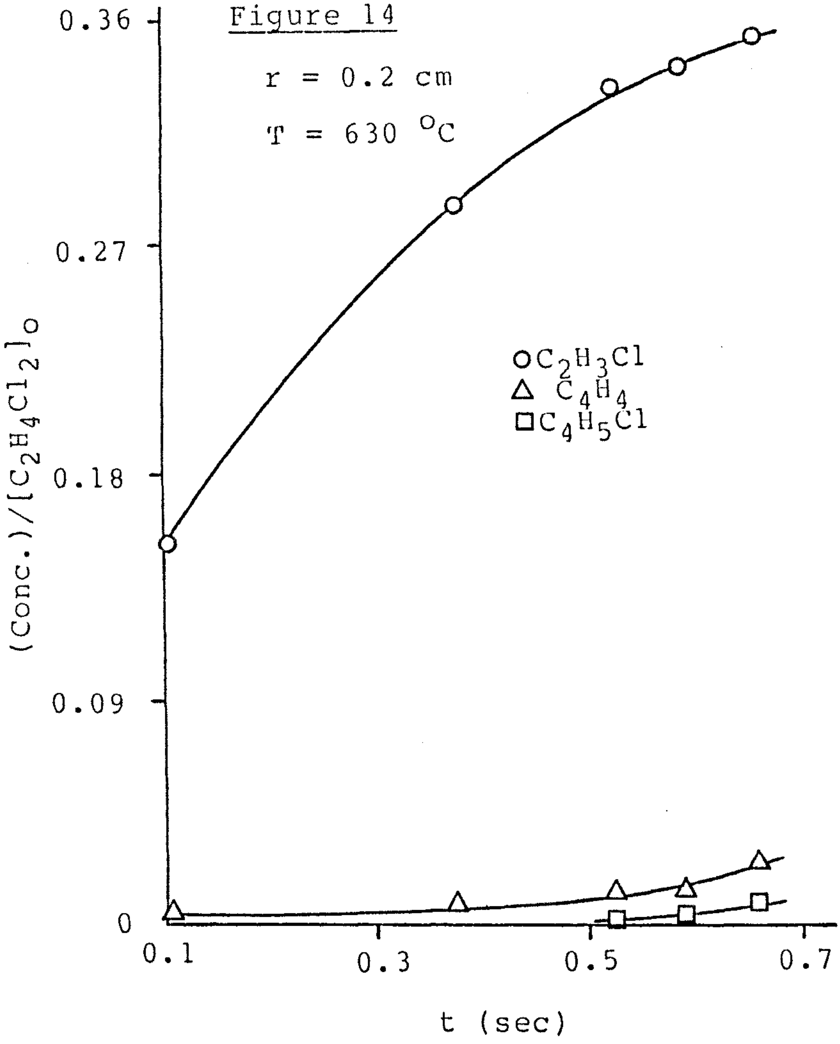


Figure 14

r = 0.2 cm

T = 630 °C

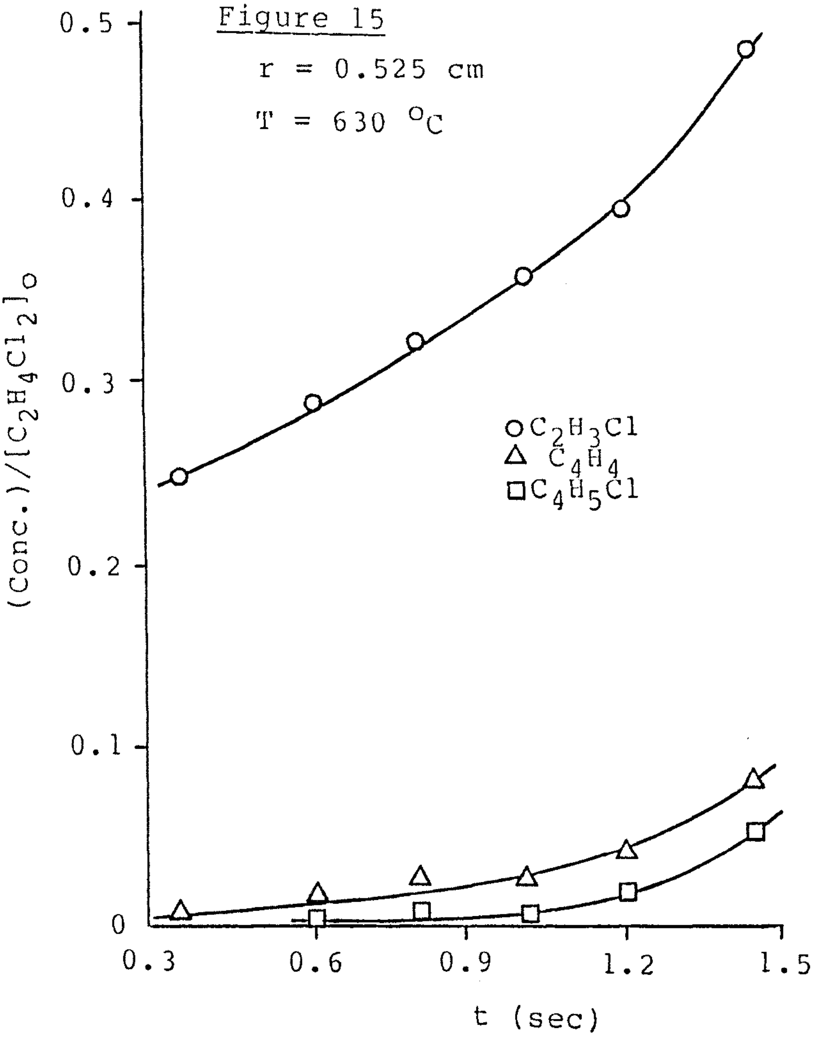


Figure 15

r = 0.525 cm

T = 630 °C

Figure 16

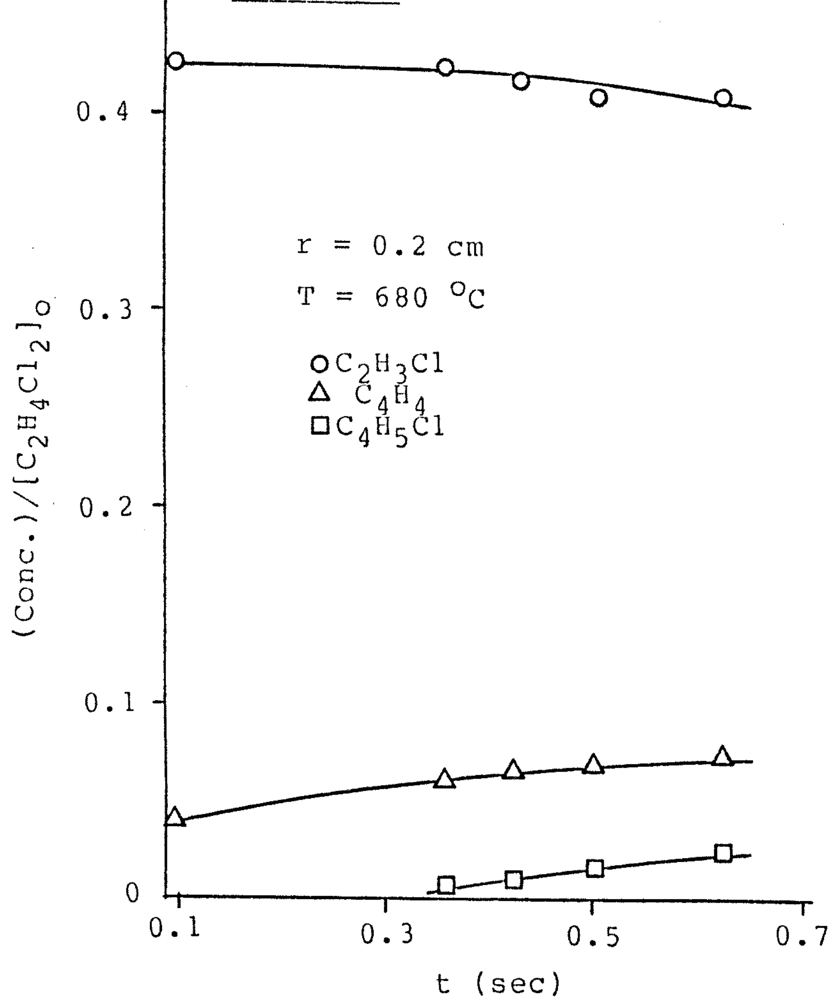
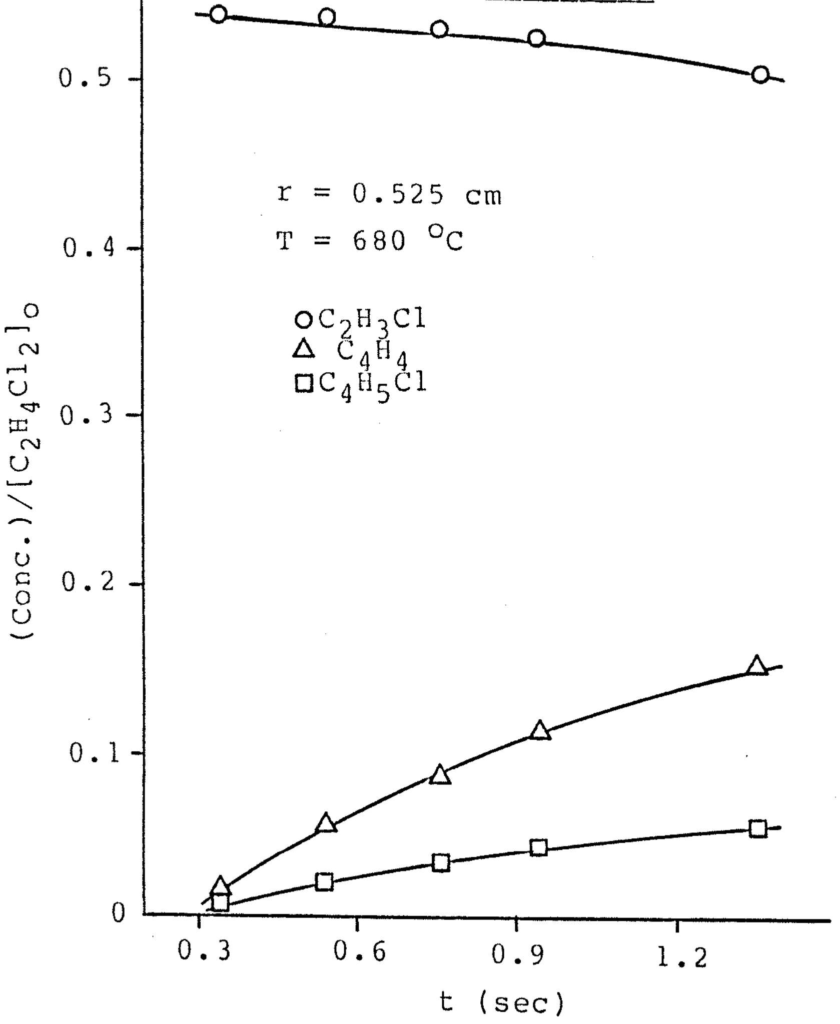


Figure 17



The reaction appears to proceed by way of a free radical chain mechanism with the first step involving unimolecular decomposition of the parent 1,2-dichloroethane.

$$\begin{array}{lll} C_2H_4Cl_2 & \longrightarrow & C_2H_4Cl^{\cdot} + Cl^{\cdot} \\ & & \quad\text{or} \\ & & C_2H_3Cl + HCl \end{array}$$

Subsequent reactions include:

Initial Chain Branching Reactions:

$$\begin{array}{lllllll}
C_2H_4Cl^{\cdot} & + H_2O & \longleftrightarrow & C_2H_5Cl & + OH^{\cdot} & & * \\
C_2H_3Cl & + H_2O & \longleftrightarrow & C_2H_4Cl^{\cdot} & + OH^{\cdot} & & * \\
C_2H_4Cl^{\cdot} & + OH^{\cdot} & \longleftrightarrow & C_2H_5Cl & + O: & & \\
C_2H_3Cl & + OH^{\cdot} & \longleftrightarrow & C_2H_2Cl^{\cdot} & + H_2O & & \\
C_2H_4Cl_2 & + OH^{\cdot} & \longleftrightarrow & C_2H_3Cl_2^{\cdot} & + H_2O & & \\
OH^{\cdot} & + OH^{\cdot} & \longleftrightarrow & H_2O & + O: & & \\
Cl^{\cdot} & + H_2O & \longleftrightarrow & HCl & + OH^{\cdot} & & * \\
O: & + OH^{\cdot} & \longleftrightarrow & O_2 & + H^{\cdot} & & \\
H^{\cdot} & + H_2O & \longleftrightarrow & H_2 & + OH^{\cdot} & & * \\
H_2 & + Cl^{\cdot} & \longleftrightarrow & HCl & + H^{\cdot} & & \\
C_2H_3Cl & + H_2 & \longleftrightarrow & C_2H_5Cl^{\cdot} & & & \\
C_2H_4Cl^{\cdot} & + H_2 & \longleftrightarrow & C_2H_5Cl & + H^{\cdot} & & \\
C_2H_4Cl^{\cdot} & & \longleftrightarrow & C_2H_4 & + Cl^{\cdot} & & \\
C_2H_3Cl_2^{\cdot} & & \longleftrightarrow & C_2H_3Cl & + Cl^{\cdot} & & \\
C_2H_4Cl_2 & + Cl^{\cdot} & \longleftrightarrow & C_2H_3Cl_2^{\cdot} & + HCl & &
\end{array}$$

* Slightly endothermic but shifted in forward direction by very high concentrations of H_2O.

Formation of Some Specific Compounds

C_2H_3Cl formation:

$$C_2H_4Cl_2 \longleftrightarrow C_2H_3Cl + HCl$$

C_2H_6 and C_2H_2 formation:

$$C_2H_3Cl \longleftrightarrow C_2H_2 + HCl$$

$$C_2H_4Cl^{\cdot} + H^{\cdot} \longleftrightarrow C_2H_4{:} + HCl$$

$$C_2H_4{:} \longleftrightarrow C_2H_4$$

$$C_2H_4 \longleftrightarrow C_2H_3^{\cdot} + H^{\cdot}$$

$$C_2H_3^{\cdot} \longleftrightarrow C_2H_2 + H^{\cdot}$$

$$C_2H_4{:} + H^{\cdot} \longleftrightarrow C_2H_5^{\cdot}$$

$$C_2H_5^{\cdot} + H^{\cdot} \longleftrightarrow C_2H_6$$

$C_2H_2Cl_2$ Formation:

$$C_2H_2Cl^{\cdot} + Cl^{\cdot} \longleftrightarrow C_2H_2Cl_2$$

$$C_2H_2Cl^{\cdot} + HCl \longleftrightarrow C_2H_2Cl_2 + H^{\cdot}$$

C_2HCl_3 Formation:

$$C_2H_2Cl_2 \longleftrightarrow C_2HCl_2^{\cdot} + H^{\cdot}$$

$$C_2HCl_2^{\cdot} + Cl^{\cdot} \longleftrightarrow C_2HCl_3$$

CO_2 Formation:

$$HCO^{\cdot} + OH^{\cdot} \longleftrightarrow CO_2 + 2H^{\cdot}$$

$$CO + O{:} \longleftrightarrow CO_2$$

C_4H_5Cl Formation, carbon chain growth:

$$C_2H_3Cl \longleftrightarrow C_2H_2Cl^{\cdot} + H^{\cdot}$$

$$C_2H_4 \longleftrightarrow C_2H_3^{\cdot} + H^{\cdot}$$

$$C_2H_2Cl^{\cdot} + C_2H_3^{\cdot} \longleftrightarrow C_4H_5Cl$$

Another reaction product is solid carbon as evident by the observation of coke deposition in the reactor. The degree of carbon buildup is directly related to the temperature. It occurs the most at temperatures greater than 700°C. The solid carbon reaches noticeable levels only after it is allowed to accumulate by operating the system for at least 5 days at a temperature greater than 700°C. Gay et al. [26] proposed a mechanism for the formation of coke during the pyrolysis of acetylene in a shock tube. Virk et al. [27] related coke formation to the decomposition of benzene during pyrolysis. The most likely mechanism which applies to this system is similar to one proposed by Froment et al. [28]. As heavy products condense on the tube, hydrogen is gradually lost until a carbonaceous material is left. The detection of 1,3-butadiyne reinforces the hypothesis that carbon chain growth with successive loss of hydrogen is the primary mechanism of carbon solid formation.

Observation of solid carbon is another indication that the H_2O does not react to any significant degree with the carbon fragments to produce CO or CO_2. Facile production of CO and CO_2 would eliminate the solid carbon formation.

V. CONCLUSION

The reactions of 1,2-dichloroethane with water vapor have been studied in a tubular reactor at atmospheric pressure and in the temperature range of 550 °C to 950°C. The study has proven to be useful in order to better understand the high temperature reactions of chlorinated organic compounds and their possible detoxification.

Rate constants have been determined for two reactor diameters and decoupled by a method from Kaufman [23] with the following results:

	r = 0.2 cm	r = 0.525 cm		
T (°C)	k_g(sec^{-1})	k_g(sec^{-1})	k_w(cm/sec)	k_b(sec^{-1})
590	0.427	0.410	0.00275	0.400
630	0.916	0.827	0.00711	0.845
680	2.17	2.05	0.0194	1.98

From Arrhenius plots, values of the activation energy for parallel reactions occuring at both the wall and in the bulk stream have been calculated. They are:

$$E_w = 35.4 \text{ kcal/mol} \qquad E_b = 29.0 \text{ kcal/mol}$$

This study is the first time that activation energies have been determined for both bulk stream and wall reactions. The results are in close agreement to unimolecular decomposition data in literature which report an activation energy of 33.0 kcal/mol [25].

Deviations from ideality have been investigated in regards to pressure drops along the reactor length and corrections to rate constants for axial diffusion and wall reactions. The pressure drop is significant in flow tubes of small diameter. So lower residence times should be avoided in small diameter tubes. Howard's method of correcting rate constants [20] shows that axial diffusion and wall reactions have an insignificant influence on the results.

Total decomposition of 1,2-dichloroethane occurs at temperatures greater than 800 °C for a residence time range of 0.8 to 1.2 sec. The principle reaction products at temperatures lower than 700 °C are vinyl chloride, 1-buten-3-yne, and 2-chloro-1,3-butadiene. At temperatures greater than 800 °C, principle reaction products include vinyl chloride, acetylene, ethene, benzene, and 1,3-butadiyne.

APPENDIX A - Sample Calculations

A. Calculation of Residence Time

Reactants are introduced in the liquid phase by syringe pumps. Their flowrates in the reactor can be calculated by:

$$q_g = q_l \rho\, 22.414(1000)T/M(60)273$$

For water which is injected into a 590 $^{\circ}$C reactor at 0.1 ml/min:

$$q_w = \frac{0.1\ \mathrm{ml/min}(0.99843\ \mathrm{g/ml})22.414\ \mathrm{l/gmol}(1000\ \mathrm{ml/l})863\ ^{\circ}\mathrm{K}}{18.015\ \mathrm{g/gmol}(60\ \mathrm{sec/min})273\ ^{\circ}\mathrm{K}}$$

$$= 6.5448\ \mathrm{ml/sec}$$

For 1,2-dichloroethane injected into the same reactor at 0.0079 ml/min:

$$q_d = \frac{0.0079\ \mathrm{ml/min}(1.254\ \mathrm{g/ml})22.414\ \mathrm{l/gmol}(1000\ \mathrm{ml/l})863\ ^{\circ}\mathrm{K}}{98.9576\ \mathrm{g/gmol}(60\ \mathrm{sec/min})273\ ^{\circ}\mathrm{K}}$$

$$= 0.1182\ \mathrm{ml/sec}$$

Argon is introduced in the gas phase through a rotameter which is calibrated at ambient conditions. When the aluminum float is at 10 on the rotameter scale:

$$q_a = q_c\ T/298(60)$$

$$= \frac{16.2\ \mathrm{ml/min}(863\ ^{\circ}\mathrm{K})}{298\ ^{\circ}\mathrm{K}(60\ \mathrm{sec/min})}$$

$$= 0.7189\ \mathrm{ml/sec}$$

The residence time can be calculated from:

$$t = \pi r^2 l/(q_w + q_d + q_a)$$

$$= \frac{\pi(0.2\ \mathrm{cm})^2 18\ \mathrm{in}(2.54\ \mathrm{cm/in})}{(6.5448 + 1.1182 + 0.7819)\ \mathrm{ml/sec}}$$

$$= 0.772\ \mathrm{sec}$$

B. Calculation of Pressure Drop

The pressure gradient along the length of the flow tube can be determined from an equation in Kaufman's paper [23]:

$$\triangle P/\triangle z = 5.9 \times 10^{-3}\,\eta v/r^2$$

where P is in torrs.

The viscosity of the gas stream is estimated by treating it as a binary mixture of water vapor and argon. From the kinetic theory of Chapman-Enskog [29]:

$$\eta_m = \sum_{i=1}^{n} [y_i\eta_i/(\sum_{j=1}^{n} y_i\phi_{ij})]$$

The Wilke method is used to calculate ϕ_{ij}:

$$\phi_{ij} = \frac{[1 + (\eta_i/\eta_j)^{0.5}(M_j/M_i)^{0.25}]^2}{[8(1 + M_i/M_j)]^{0.5}}$$

$$\phi_{ji} = \frac{\eta_j}{\eta_i}\,\frac{M_i}{M_j}\,\phi_{ij}$$

Data for the viscosities of the pure components is found in reference 30. Let 1 refer to water and 2 to argon. $M_1 = 18.015$ and $M_2 = 39.948$. At 590 $^{\circ}$C, $\eta_1 = 313.8$ mP and $\eta_2 = 509.9$ mP.

$$\phi_{21} = \frac{[1 + (509.9/313.8)^{0.25}(18.015/39.948)^{0.25}]^2}{[8(1 + (39.948/18.015))]^{0.5}}$$

$$= 1.5768$$

$$\phi_{12} = (313.8/509.9)(39.948/18.015)1.5768$$

$$= 2.1519$$

As the argon flow rate is changed, y, η_m, t, and v also change. The following calculations are for the flow tube with r = 0.525 cm, and T = 590 $^{\circ}$C. When the stainless steel float is at 23.7 on the rotameter scale:

$$y_2 = F_2/(F_1 + F_2)$$

$F_1 = q_w\rho(60)/M_1$

$= [0.25\ \text{ml/min}(0.99843\ \text{g/ml})60\ \text{min/hr}]/(18.015\ \text{g/gmol})$

$= 0.8313$ gmol/hr

$$F_2 = q_a\ (60)273/1000(22.414)298$$

$$= \frac{1792\ \text{ml/min}(60\ \text{min/hr})273\ ^{\circ}\text{K}}{1000\ \text{ml/l}(22.424\ \text{l/gmol})298\ ^{\circ}\text{K}}$$

$$= 4.3946\ \text{gmol/hr}$$

$$y_2 = 4.3946/(4.3946 + 0.8313)$$

$$= 0.8409$$

$$y_1 = 1 - 0.8409 = 0.1591$$

$$\eta_m = \frac{0.1591(313.8)}{0.1591 + 0.8409(2.1519)} + \frac{0.8409(509.9)}{0.8409 + 0.1591(1.5768)}$$

$$= 418.1\ \text{mP}$$

$$v = l/t = 18\ \text{in}(2.54\ \text{cm/in})/0.384\ \text{sec} = 119.1\ \text{cm/sec}$$

The pressure drop over the length of the reactor can be calculated from:

$$\triangle P = 5.9 \times 10^{-3}\, \eta v l/r^2$$

$$= 5.9 \times 10^{-3}(418.1\ \text{mP})119.1\ \text{cm/sec}(18\ \text{in})2.54\ \text{cm/in} \times (0.001316\ \text{atm/torr})/(1000\ \text{mP/P})(0.525\ \text{cm})^2$$

$$= 0.0641\ \text{atm}$$

C. Corrections to Rate Constants

In order to calculate Howard's corrected first order rate constants, the diffusion coefficients must be determined. As in the case of estimating the viscosity, the gas stream is treated as a binary mixture of water vapor and argon. From the Chapman-Enskog equation [30]:

$$D = 1.858 \times 10^{-3} T^{1.5} \frac{[(M_A + M_B)/M_A M_B]^{0.5}}{P \sigma_{AB}^2 \Omega_D}$$

where P is in atmospheres.

$$D = \frac{A}{T^{*B}} + \frac{C}{\exp DT^*} + \frac{E}{\exp FT^*} + \frac{G}{\exp HT^*}$$

where $T^* = kT/\epsilon_{AB}$ $A = 1.06036$ $B = 0.15610$

$C = 0.19300$ $D = 0.47635$ $E = 1.03587$

$$F = 1.52996 \quad G = 1.76474 \quad H = 3.89411$$

From Appendix C of reference 29:

	σ (Å)	ϵ/k (°K)
argon	3.542	93.3
water	2.641	809.1

$$(\epsilon/k)_{AB} = [(\epsilon/k)_A(\epsilon/k)_B]^{0.5}$$

$$= [93.3(809.1)]^{0.5} = 274.8\ ^{\circ}\mathrm{K}$$

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2$$

$$= (3.542 + 2.641)/2 = 3.092\ \text{Å}$$

When $T = 590\ ^{\circ}\mathrm{C}$:

$$T^* = kT/\epsilon = 863/274.1 = 3.141$$

$$\text{and } \Omega_D = 0.939$$

$$D = 1.858 \times 10^{-3}(863)^{1.5}\frac{[(18.015+39.948)/18.015(30.948)]^{0.5}}{1(3.092)^2 0.939}$$

$$= 1.490\ \mathrm{cm}^2/\mathrm{sec}$$

Howard's equation to correct measured rate constants in order to account for axial diffusion is:

$$k_c = k_g(1 + k_gD/v^2)$$

When $r = 0.525$ cm and the stainless steel float is at 4.9 on the rotameter scale, $v = 29.82$ cm/sec.

$$k_gD/v^2 = 0.410\ \mathrm{sec}^{-1}(1.490\ \mathrm{cm}^2/\mathrm{sec})/(29.82\ \mathrm{cm/sec})^2$$

$$= 6.87 \times 10^{-4}$$

Howard's equation to correct measured rate constants in order to account for wall reactions is:

$$k_c = k_g[1 + (k_g + 4k_w/r)D/v^2]$$

$$(k_g + 4k_w/r)D/v^2 = [0.410\ \mathrm{sec}^{-1} + 4(0.00275\ \mathrm{cm/sec}) \times (0.525\mathrm{cm})^{-1}](1.490\ \mathrm{cm}^2/\mathrm{sec})/(29.82\ \mathrm{cm/sec})^2 = 7.22 \times 10^{-4}$$

APPENDIX B - Identification of Variables

A_a	apparent frequency factor, directly from experimental results (sec^{-1})
A_b	frequency factor for reactions in the bulk stream (sec^{-1})
A_w	frequency factor for reactions at the wall (cm/sec)
C	concentration of unreacted 1,2-dichloroethane
C_o	initial concentration of 1,2-dichloroethane entering reactor
CF_a	Howard's correction factor for axial diffusion, k_gD/v^2
CF_w	Howard's correction factor for wall reactions, $(k_g + 4k_w/r)D/v^2$
D	diffusion coefficient (cm^2/sec)
E_a	apparent activation energy, directly from experimental results (kcal/mol)
E_b	activation energy for reactions in bulk stream (kcal/mol)
E_w	activation energy for wall reactions (kcal/mol)
F	molar flow rate (gmol/hr)
J	flux (molecules/cm^2 sec)
k	first order rate constant (sec^{-1})
k_a	apparent first order rate constant, directly from experimental results (sec^{-1})
k_b	first order rate constant for reactions in bulk stream (sec^{-1})
k_c	corrected first order rate constant (sec^{-1})
k_g	apparent first order rate constant, graphical value from Arrhenius plot (sec^{-1})
k_w	first order rate constant for reactions at the wall (cm/sec)
l	reactor length, 18 inches
M	molecular weight (g/gmol)
m	mass flow rate (g/sec)

P	pressure (torr or atm)
q	volumetric flow rate (ml/min)
R	gas constant, 1.987×10^{-3} kcal/mol deg
r	radius of reactor (cm)
T	temperature (^{o}K)
t	residence time in reactor (sec)
v	flow velocity (cm/sec)
v_d	velocity due to diffusion (cm/sec)
y	mole fraction in gas phase (dimensionless)
z	distance along length of flow tube (cm)
ϵ	characteristic energy parameter (dimensionless)
η	gas viscosity (g/cm sec)
ρ	liquid density (g/ml)
σ	characteristic length (Å)
ϕ	mixture viscosity parameter (dimensionless)
Ω_D	diffusion collision integral (dimensionless)

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