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Gas-phase reaction of 1,2-dichloroethane with hydrogen in a tubular flow reactor

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ABSTRACT

Title of Thesis: Gas-Phase Reaction of 1,2-Dichloroethane
with Hydrogen in a Tubular Flow Reactor.

Wei-Lian Lee, Master of Science, 1986

Thesis directed by: Dr. J.W. Bozzelli
Professor of Chemistry/Chem. Eng.

We have studied the reaction of 1,2-dichloroethane with H_2 in three tubular flow reactors of different diameters at atmospheric pressure in the temperature range of 550 °C to 1000°C. The kinetic parameters and product distribution were experimentally determined for each size reactor. The wall and bulk reaction rate constants were decoupled via analysis of three different surface to volume reaction data.

The experimental reactor was an isothermal tubular flow reactor that operated within the domain of plug flow region. The reaction was found to follow first-order kinetics with respect to 1,2-dichloroethane when in the presence of excess hydrogen. The resulting rate constants were then used to determine the Arrhenius' plot. Activation energy and frequency factor were determined and put in the form of a reaction rate constant equation. These equations are as follows:

for d = 0.4 cm.ID $k = 4.4 \times 10^{7} \mathrm{Exp}(-32{,}000/RT)$ (1/sec)

for d = 1.05 cm.ID $k = 4.6 \times 10^{7} \mathrm{Exp}(-33{,}000/RT)$ (1/sec)

for d = 1.6 cm.ID $k = 5.0 \times 10^{7} \mathrm{Exp}(-33{,}000/RT)$ (1/sec)

For the case of a reactor with internal diameter of 1.05 cm, the GC analysis showed an appreciable conversion of 1,2-dichloroethane above 550°C. The conversion was found to be proportional to both temperature and residence time. Chlorinated by-products, which all had lesser number of chlorine atoms than the reagent, were observed to increase with temperature from 550°C to 675°C. The major chlorinated products observed were vinyl chloride and chloroethane. Trace amounts of 1,1-dichloroethane and methyl chloride were found by GC/MS analysis. When the temperature reached 700°C, the only chlorinated by-products observed was vinyl chloride. Complete destruction of 1,2-dichloroethane was observed above 850°C for residence time of 1 sec. Benzene was also observed above 800°C in very small amounts. The major products of 1,2-dichloroethane and H_2 reaction were methane, ethane, ethylene, acetylene, vinyl chloride, chloroethane and HCl. The hydrocarbons production increased with temperature.

Applying the Arrhenius' equation to the values of k_b and k_w obtained from the equation derived by Kaufman (1), for each temperature range examined, yielded the following rate constants expressions for wall and bulk reaction:

$k_b = 4.8 \times 10^{7} \mathrm{Exp}(-34{,}000/RT)$ (1/sec)

$k_w = 2.0 \times 10^{6} \mathrm{Exp}(-31{,}000/RT)$ (cm./sec)

GAS-PHASE REACTION OF 1,2-DICHLOROETHANE WITH HYDROGEN IN A TUBULAR FLOW REACTOR

by

Wei-Lian Lee

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
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APPROVAL SHEET

Title of Thesis : Gas-Phase Reaction of 1,2-Dichloroethane with Hydrogen in a Tubular Flow Reactor.

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I also want to thank Dr. Wei-Kuo Lee for giving me the opportunity to study in the United States.

Last but certainly not least, I wish to thank my mother for everything.

DEDICATION

To 'the bird''s beautiful daughter, with whom I once shared dreams by the lake in those fickle Spring mornings, I give these bounded pages of quiet desperation.

And so it goes.....

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I. INTRODUCTION

The decomposition of chlorocarbons has received much attention lately due to their common use as solvents, in plastics and in aerosol propellants. High temperature thermal decomposition to HCl (hydrogen chloride) and hydrocarbons in the presence of hydrogen is a viable alternative to the present incineration method of disposal of such chlorinated compounds. Incomplete combustion of chlorocarbons and possible toxic effluents from combustion are among some of the problems with such incineration methods.

The problems of disposal of these chlorinated hydrocarbons are serious enough for PCBs to be the only group of compounds that were specifically mentioned in the TSCA law enacted in 1976. Many of these chlorinated hydrocarbons previously thought to be safe to use (such as chloroform have now been shown to be toxic and/or carcinogenic. In addition to the disposal problems, the rising cost of energy and raw materials combined with the need to comply with the TSCA and RCRA environmental laws have made the treatment of these hazardous chemicals and possible recycling processes economically feasible.

Presently, many technologies are under consideration for conversion of chlorinated species. Non-thermal methods such as biological treatments using microbes have been developed which can break down many hazardous chemicals including PCB, and pentachlorophenol. However, their application is limited to water treatment with relative low concentration of pollutants. Another popular method that has been used extensively is land filling of toxic waste. This method, however, does not seems to be a permanent solution to the problems in toxic wastes disposal. Due to the possible future occurrence of toxic material leak into ground water, land filling is now receiving strong opposition from people who reject its existence in their community.

Presently, thermal methods such as high temperature incineration are generally considered as the most practical approach to the complete destruction of hazardous wastes (2). Combustion equipment such as high effiency boilers, fluidized bed incineration, rotary kilns, liquid injection burners are already in use. However, this combustion approach can run into problems when halogenated organics are fed into the incinerator, namely, - the formation of toxic byproducts. The observed detection of hazardous species in the product stream would imply the incomplete combustion of halogenated hydrocabons. This phenomena seems to be caused by the persistent existence of halogen-carbon bond of the parent halogenated compound or the formation of halogen-carbon bond in the combustion system where there is no proper reagent to abstract halogen from the halogenated parent compound effectively. Thermal and catalytic reaction in a hydrogen rich atmosphere (3,4,5,6) have been shown as promising alternatives to oxygen rich incineration. In an oxygen rich incinerator, the hydrogen is forced to form more stable H_2O species rather than HCl and therefore the chlorine remains attached to carbon as the most stable adduct.

In the combustion process, toxic wastes such as PCB's, chlorinated solvents, dioxins, etc., are fed to incinerator where the required temperature is $1200^{\circ}C$ with a residence time of 2-4 seconds in the presence of excess oxygen (7). A 99.9% conversion of the parent species is achieved in this process which is supposed to totally oxidize all carbon to CO_2. However, since there is no stable end adduct for the chlorine, partially oxygenated carbon-chlorides and chlorine oxides are formed as end products. These are not acceptable products for discharging to the environment. One desired chloride end product might be hydrogen chloride, which could be easily collected and neutralized.

It is clear that although incineration in an oxidizing environment effectively destroys the initial species it still has a number of unsatisfactory results. An alternative to incineration is a hydro/dechlorination reaction of the folowing type:

$$CH_2ClCH_2Cl + H_2 \text{ -----> } C_2H_4 + 2HCl$$

Hydrogen chloride as an end product for the chlorine is desirable because it can easily be neutralized or collected. Introducing a hydrogen rich environment to chlorocarbons in a thermo-reaction would favor the formation of HCl. Thus all the chlorine could be abstracted from the parent compound by the use of hydrogen under proper conditions. The ideal products would be gaseous hydrocarbons, HCl and carbon. Since the hydrogenation-dechlorination reactions have so far been largely ignored, these experiments would provide needed kinetic data and product distribution information leading to a better understanding of the kinetic mechanism of these reactions.

II. PREVIOUS STUDIES

Although the literature on 1,2-dichloroethane's thermal decomposition is abundant, the literature on reactions of hydrogen with chlorinated halocarbons is not nearly as complete.

A. 1,2-DICHLOROETHANE AND H_2 REACTION.

Relevant studies done in these research laboratories at NJIT are: 1. Chuang (2) studied the reaction of hydrogen with chloroform and 1,1,2-trichloroethane as well as the reaction of water vapor with chloroform. Two papers from Chuang's work have been published (8,9). 2. Another study from Chang (10) in our group on the estimation of wall and bulk rate constants from analysis of laminar flow model has presented data on the reaction of hydrogen with 1,1,1 -trichloroethane. His work on the decoupling of wall and bulk rate constants related to our reactor system has been accepted for publication. 3. Mahmood, who utilized the particular reactor system which this study used, has carefully studied reactions of hydrogen with chloroform and trichloroethylene (11). 4. Additional work done on reactions of water with 1,2-dichloroethane and with chloroform are reported by Anderson(12) and Hwang(13) respectively. Catalytic reactions of hydrogen with 1,2-dichloroethane and with chloroform over various catalysts have been investigated by Yang (14).

B. 1,2-DICHLOROETHANE THERMAL DECOMPOSITION

The thermal decomposition of 1,2-dichloroethane has been previously studied by a number of papers covering a long period of time and indicating continuous interest of researchers in this topic. One possible reason for the popularity of this reaction might be its industrial importance in the production of monomer for PVC polymer. Statistics show that over 83% of the 1,2-dichloroethane produced in the U.S.A. is converted to vinyl chloride monomer through the following pyrolytic reaction:

$$C_2H_4Cl_2 \text{ ------> } C_2H_3Cl + HCl$$

The pyrolysis of 1,2-dichloroethane to vinyl chloride and hydrogen chloride at temperature between 400°C and 500°C is thought to proceed by a radical chain mechanism of following reaction steps(15):

(1) $ClCH_2CH_2Cl \text{ -----> } ClCH_2C.H_2 + Cl.$

(2) $Cl. + ClCH_2CH_2Cl \text{ -----> } ClC.HCH_2Cl + HCl$

(3) $ClC.HCH_2Cl \text{ -----> } CH_2CHCl + Cl.$

(4) $Cl. + ClCH_2C.H_2 \text{ -----> } CH_2CHCl + HCl$

Step (1) is the initiation step where radical Cl. is formed. Steps (2) and (3) are propagation steps and step (4) is the termination step. These steps were first proposed by Howlett to account for the experimentally observed first order kinetics. The kinetics of this reaction has been studied extensively by Barton, Howlett and a number of other workers (16,17,18,19,20). Decomposition near 400°C is characterized by a marked induction period. Once beyond the induction period, the decomposition is observed to obey first-order kinetics with the following rate constant expression :

$$k = 6.5 * 10^{10} \exp(-47,000/RT) \quad (1/sec)$$

The induction period was explained by Howlett (14) in terms of a build-up of the concentration of radical $ClC.HCH_2Cl$ towards a steady state. It should be pointed out that all these results were obtained in an aged static reactor system, where reaction rates were slower than in a clean fresh reactor by a factor of the order of ten, presumably due to wall catalysis by SiO_2 materials in a clean reactor.

The kinetics of the reaction in a fresh reactor was first studied by Barton (16) in a flow reactor prior to formation of a gray carbon film on its surface. The reaction was still first order but the reaction rate was sharply higher than that in an aged (carbon coated) reactor. For the pyrolysis of 1,2-dichloroethane, Barton found the following rate constants (in 1/sec):

(in an aged reactors) $k = 6.4 * 10^{10} \exp(-47,000/RT)$

(in a fresh reactor) $k = 1.6 * 10^{6} \exp(-27,100/RT)$

In a similar experimental condition, Kapralova (21) obtained a rate constant (1/sec) of:

(in a fresh reactor) $k = 1 * 10^{8} \exp(-32,000/RT)$

Although these reaction rates on clean surface may also be measured in a static system, precise data are diffcult to obtain since the surface gets covered quickly and reaction rate decreases from run to run. Two hypothesis can explain why the reaction rate is faster on a clean SiO_2 surface: (1) fresh surface acts catalytically but it stops functioning as such after a sufficiently thick film of carbon products has covered the wall; (2) most of the reaction takes place in the bulk and progresses in a radical chain fashion. However, the chains are initiated on the wall surface.

The first hypothesis was ruled out by experiments performed by Barton (16) in a flow reactor at 500 °C. He observed that doubling the surface area with packing only increases the reaction rate by 18%. This seems to indicate that the reaction in the fresh reactor is not a simple catalytic one. The second hypothsis was proved to be the correct one by Kapralova(22) using the technique of differential calorimetry. Kapralova has found evidence that the initiation and possibly the termination of chain in 1,2-dichloroethane pyrolysis occurs on the reaction vessel wall instead of the homogeneous bulk phase. It has also been proposed (23) that the inhibiting effect of propane may be associated with its absorption on the vessel wall causing a reduction in the rate of initiation of chains on the surface. It is suggested here, however, that it is probably the formation of the relatively stable allyl radical that propane inhibits; this action then further inhibits the reaction.

Pyrolysis reaction of 1,2-dichloroethane in a flow type stainless-steel reactor around 500°C at one atm. was studied by Takahashi (24). The reaction was first order and the Arrhenius equation was (in 1/sec):

$$k = 3.3 * 10^{7} \exp(-29{,}100/RT)$$

Notice these values are relatively close to those obtained by Barton and Kapralove in fresh quartz flow reactor under similar condition.

It should also be pointed out that the early investigators such as Barton and Howlett postulated that the radical chain reaction is initiated and terminated in the homogeneous bulk phase. But there are many problems with this interpretation. Consequently, many widely different Arrenius parameters have been reported for the overall rate constant. These discrepancies seem to arise in part from changes in the condition of reactor surface and in part from an autocatalytic effect. The former suggests that the initiation and/or termination may have occured on the surface. The latter autocatalytic effect of the pyrolysis reaction might be caused by chlorine formed on the reactor surface. Holbrook suggests (23) the following schemes:

$C_2H_4Cl_2$ + surface(s) <---->$C_2H_4Cl_2$(s)

$C_2H_4Cl_2$(s) ----> C_2H_4(g) + Cl_2(g)---->Cl_s+Cl(g)

We, however, feel that this is incorrect because it is thermodynamically less favorable than the reaction leading to the formation of HCl and vinyl chloride. Holbrook(23), in a separate paper, has also studied the effect of different carbon films on the reaction. Thermal decomposition of 1,2-dichloroethane catalyzed by 1% of chlorine has been reported by Barton(16). Takahashi et al. (24) and Ashmore et al. (26) later expanded research in this direction and Takahashi, who used a stainless-steel flow reactor, proposed that the chlorine initiated the chain by the surface reaction in the following fashion:

metal + Cl_2 ----> metal---Cl + Cl(g)

Once again, we feel the above explanation neglects the fact that due to the weak Cl-Cl bond, Cl_2 readily dissociates into Cl. + Cl., faster than any C-Cl bond cleavage in this system. Cl., then, can attach to the C-H bonds to form HCl radical, which further undergoes rapid reaction. Ashmore et al. investigated comprehensively the effect of radical chloride on the reaction for both aged and fresh reactors.

III. THEORETICAL CONSIDERATION

A. TUBULAR FLOW REACTOR THEORY

Tubular flow reactors are commonly used for the study of gas-phase high temperature reactions. In order to simplify the interpretation of experimental results from these reactors, reaction conditions are maintained so as to give maximum radial diffusion and minimum axial diffusion, wall reaction and pressure drop. These conditions, pointed out in detail by Kaufman (1), allow the system to be treated as an ideal plug flow reactor. Ideal isothermal tubular flow reactor calculations are often based on plug flow assumption, namely that the flow of fluid through the reactor is orderly with no element of fluid mixing with any other elements behind or ahead. In other words, all fluid elements in a true plug flow reactor have the same residence time inside the reactor and there is no radial concentration gradient. Of course, in reality, these conditions are nearly impossible to meet. In a laboratory scale tubular reactor system, Reynolds number of flow is frequently in the laminar region as opposed to turbulent flow region where the plug flow approximation is known to hold. Here, in the laminar region, radial dispersion helps in mixing concentration across tube diameter, so the plug flow reactor assumption holds. Criteria for checking the validity of plug flow assumption are discussed in the following paragraph, so is the analysis on laminar flow model.

Generally speaking, radial mixing in a tubular reactor is due to molecular diffusion while axial mixing is due to fluid velocity gradients (27). Our flow reactor operates at conditions in which the radial diffusion is often significant due to our reactor size and wall reaction rate while the axial dispersion can be negligible since the gaseous velocity is sufficiently large (28). Therefore, in our experimental conditions, axial diffusion can be assumed to be negligible because the velocity profile has a smaller effect than molecular diffusion.

To estimate the deviation of a tubular flow reactor with axial diffusion from the plug flow assumption, Reman (30) has used Danckwerts solution of a diffential equation which describes a plug flow reactor following first-order kinetics. He found that for D/vl < 0.1 the reactor follows the plug flow assumption, and for D/vl > 2.0 the reactor behaves like a well-mixed one (31). For our reactor, D/vl is below 0.1. This evidence would be sufficient for plug flow assumption to hold true if the Reynolds number were in the upper range of laminar flow where molecular diffusion effects in dispersion are negligible compared to the effect of the velocity profile (28). This is ,however, not true for our experiments.

A more rigorous analysis that is applicable to the our system is the paper by Poirier and Carr (32).They have solved the continuity equations for a tubular flow reactor with radial diffusion following first-order kinetics. Under this condition, they propose that if D/kR^2, where R is the radius of the reactor, is equal to or greater than 0.5, plug flow approximation is satisfied. Our system has a D/kR^2 Values well above 0.5. It is therefore safe to assume that ideal plug flow model is a good approximation for our present reactor.

The reason for all the consideration of plug flow assumption should be obvious for anyone who has done analysis for non-ideal reactor model. The ideal plug flow analysis is far more straight forward than its non-ideal counter part. Therefore, more attention can be paid to experimental results than to worry about the effect of non-ideality. A rigorous laminar flow model (33,34,35) was developed by Chang (5) for our reactor system.

Chang (5,10) has solved analytically a laminar flow model for first-order reaction in a tubular reactor with simultaneous wall and bulk reaction. The appropriate continuity equation is confined to cases of Poiseuille flow with first order kinetics, radial dispersion and both bulk and wall reactions. It is as follows:

$$V_0[1 - (r/R)^2] \frac{\partial C}{\partial z} = \frac{D_{AB}}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C}{\partial r}\right) - k_b C \qquad (1)$$

the boundary conditions are:

1. $C = C_o$ at $z = 0$, (2)

2. C = finite at $r = 0$, and (3)

3. $- D_{AB} \frac{\partial C}{\partial r} = k_w C$ at $r = R$. (4)

The solution of Eq. 1, which is no more than the concentration profile of the laminar model is listed below in its dimensionless form :

$$C(r,z) = \sum_{n=1}^{\infty} B_n \mathrm{Exp}(-w_n z) \mathrm{Exp}(-w_n^{1/2} r^2) \, {}_1F_1[a_n;1;2w_n^{1/2} r^2] \qquad (5)$$

and

$$r = \frac{r}{R}, \quad z = \frac{4D_{AB} z}{v_o R^2}, \quad c = \frac{C}{C_o}, \quad \alpha = \frac{k_b R2}{4D_{AB}},$$

$$\beta = \frac{k_w R}{2D_{AB}} \qquad (6)$$

w is an eigenvalue that can be solved by satisfying the boundary condition at r = 1, and solving Eq. 7 for its roots:

$$f(w) = (\beta - w^{1/2}) \, {}_1F_1[a;1;2w^{1/2}] + 2aw^{1/2} \, {}_1F_1[a+1;2;2w^{1/2}] \qquad (7)$$

Coeffecient B_n can be solved by satisfying the boundary condition at z = 0 and using the orthonornality of the eigen functions.

$$B_n = \frac{\int_0^1 r(1 - r^2)\mathrm{Exp}(-w_n^{1/2} r^2)\,{}_1F_1[a_n;1;2w_n^{1/2} r^2]\,dr}{\int_0^1 r(1 - r^2)\{\mathrm{Exp}(-w_n^{1/2} r^2)\,{}_1F_1[a_n;1;2w_n^{1/2} r^2]\}^2\,dr} \qquad (8)$$

With these expressions, c, α, and β can be calculated. Comparision of values obtained from the numerical solution of the continuity equation derived from the laminar flow model with that derived from the plug flow model proves that the plug flow assumption was correct for the condition our experiments were performed. A specific comparision analysis between the laminar and plug flow model was done by Mahmood (11) for the laboratory tubular reactor used for this study. Our assumption of ideal plug flow model for our laminar flow reactor is justified.

B. WALL AND BULK REACTION

Mahmood (11) and Chuang (3) have shown that the decomposition of chlorinated hydrocarbons is not only a function of the temperature and concentration but also of the radius of the reactor. High temperature thermal decomposition of many organic substances as well as chlorinated hydrocarbons occured via both bulk and wall reactions. The overall reaction rate constant is therefore the combined reaction rate of these two different mechanisms. When wall reaction is significant, kinetic parameters for the wall reaction will have to be considered. Therefore, a method that can evaluate both the wall and the bulk reactions is needed for our study.

When a species undergoes both wall and bulk reaction, it is difficult to determine their separate kinetic parameters simultaneously since the bulk and wall reactions proceed in parallel and the rate constants for these parallel reactions are coupled. Fortunately, a simple relationship between these two parameters have been derived by Kaufman (1) for a first order reaction in an ideal plug-flow reactor. When a chemical reaction consists of both bulk and wall reactions, it can be considered as a special case of two parallel reactions. The relative contribution of the bulk reaction is a function of the reactor volume whereas the relative contribution of the wall reaction is a function of the reactor surface. Then, the ratio of the relative contribution of the wall reaction to the bulk reaction is a function of the surface to volume ratio 2/R. The relative importance of surface reaction will be more pronounced in a smaller reactor tube than in a larger one. For a first order reaction under plug flow conditions, Kaufman (1) has shown the following relationship to be valid:

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

Therefore, using reactors of different radii i.e., of different surface to volume ratios, keeping all other reaction conditions the same, kinetic parameters for both wall and bulk can be found. By simply ploting k_{expt} vs. 2/R from the above quation, we can decouple the wall rate constant, " k_w ", from the bulk rate constant " k_b ". With these values, activation energies and frequency factors for the wall and the bulk reactions can be calculated from the Arrhenius equation.

IV. EXPERIMENTAL METHODS

A high temperature tubular flow reactor, operated isothermally and at atmospheric pressure was used for this study. A constant temperature profile within 5°C deviation was maintained within the reaction zone of 40 cm. Residence times between 0.25 sec to 2.5 sec were maintained in clean quartz tubes of various internal diameters (0.5, 1.05 and 1.6 cm). Hydrogen gas, which acted both as reagent and carrier, was passed through a two-stage saturation bubbler where it picked up the 1,2-dichloroethane. The bubbler was maintained at 0°C in an ice bath. Before entering the reactor, the H_2 and 1,2-dichloroethane mixture was preheated to prevent cooling at the reactor's entrance. The reactor was heated by a three zone Mellen clamshell furnace. The quartz tubes were cleaned after each series of runs to prevent any carbon from accumulating on the wall of the reactor. The reactor effluent was monitored using an on-line gas chromatograph equipped with a FID (Flame Ionization Detector) in addition to an ECD (Electron Capture Detector). The quantitative output of FID was measured by a Varian CDS III integrator while the ECD's output was used for qualitative identification of chlorinated hydrocarbons species. Samples of the reactor effluent were also analyzed using a Kratos GC/Mass Spectrometer for positive identification.

A. EXPERIMENTAL APPARATUS

The 1,2-dichloroethane used was 99% pure and purchased from Aldrich Chemical Company INC.. Clean Quartz tubes with interal diameters 0.4, 1.05, 1.6 cm. were used for the kinetic studies. Reactor tubes were cleaned after each temperature run. A diagram of the experimental apparatus is shown in Figure 1. Hydrogen was used both as a carrier and as a reagent gas. Calibrated rotameters were used to control the flow of hydrogen through two tubes which were connected together by a tee before inlet to the reactor. One part of the hydrogen flow was passed through a series of two bubblers to become saturated with the compound under study. The bubbler system was maintained at zero degrees C. by submerging it in a ice-water bath. Hydrogen flow from the second bubbler was used to achieve the desired molar ratio between hydrogen and chlorinated hydrocarbon. The 1,2-dichloroethane/hydrogen vapor was then preheated to about 300 °C before being passed through the reactor. Previous experiments have shown that no reaction takes place below 350°C in the space times used for our experiment. The temperature of the product gases from the outlet of the reactor was maintained at about 100°C to prevent vaporous products from condensation.

The reactor furnaces were made of clamshell type heating elements from Mellen Co. New Hampshires. The oven consisted of three heating zones. A 230 volts 12 inches

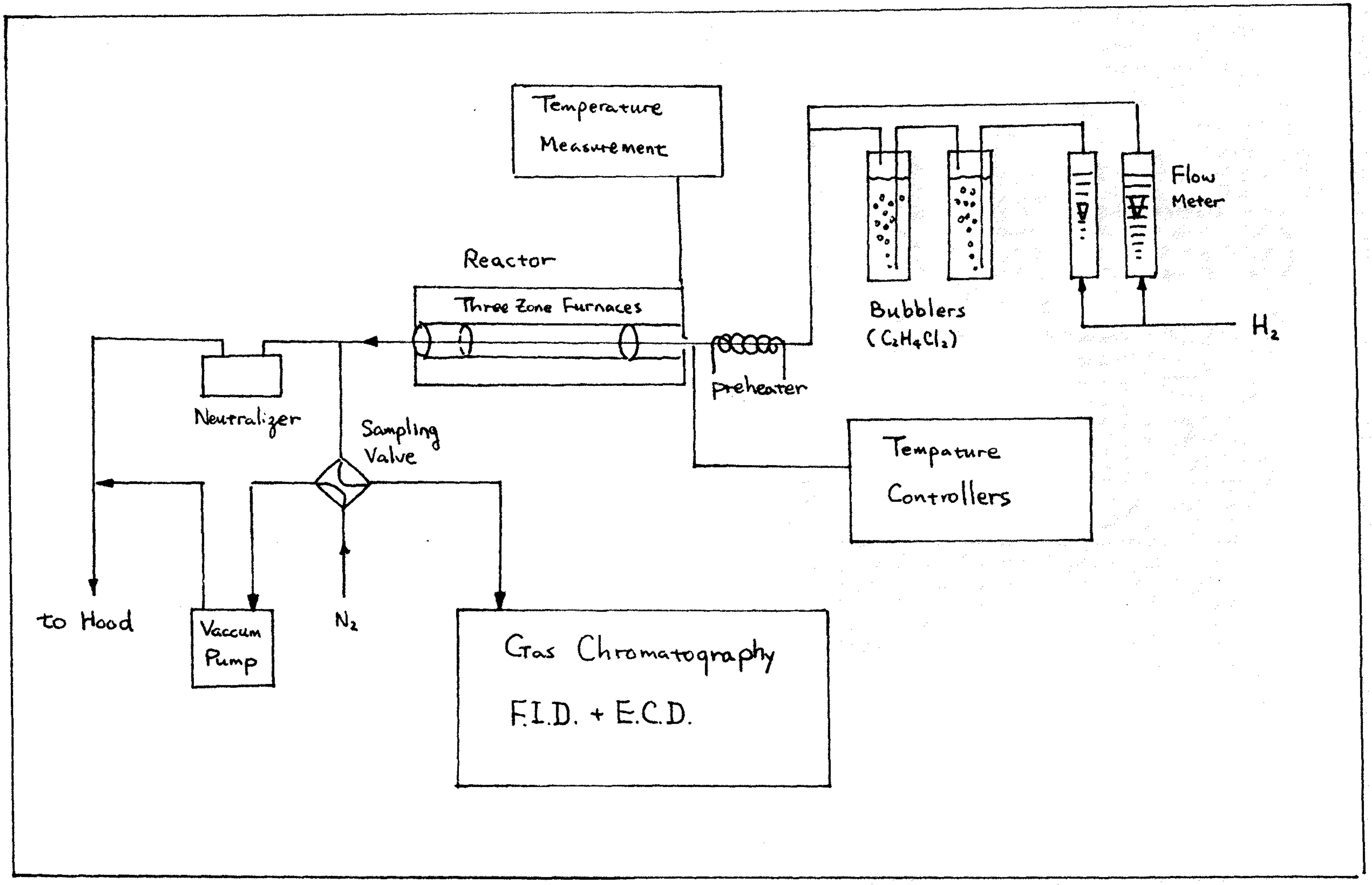


Figure 1. Experimental Set Up

section was connected with two 120 volts 3 inches end zone sections, one on each side. The shorter sections provided greater control over the heat dissipation effects of the end zone sections. The furnace temperature was controlled by three OMEGA CN300K time proportioal type temperature controllers. The furnance was insulated and enclosed in a LINGBERG HEVI-DUTY furnace enclosure.

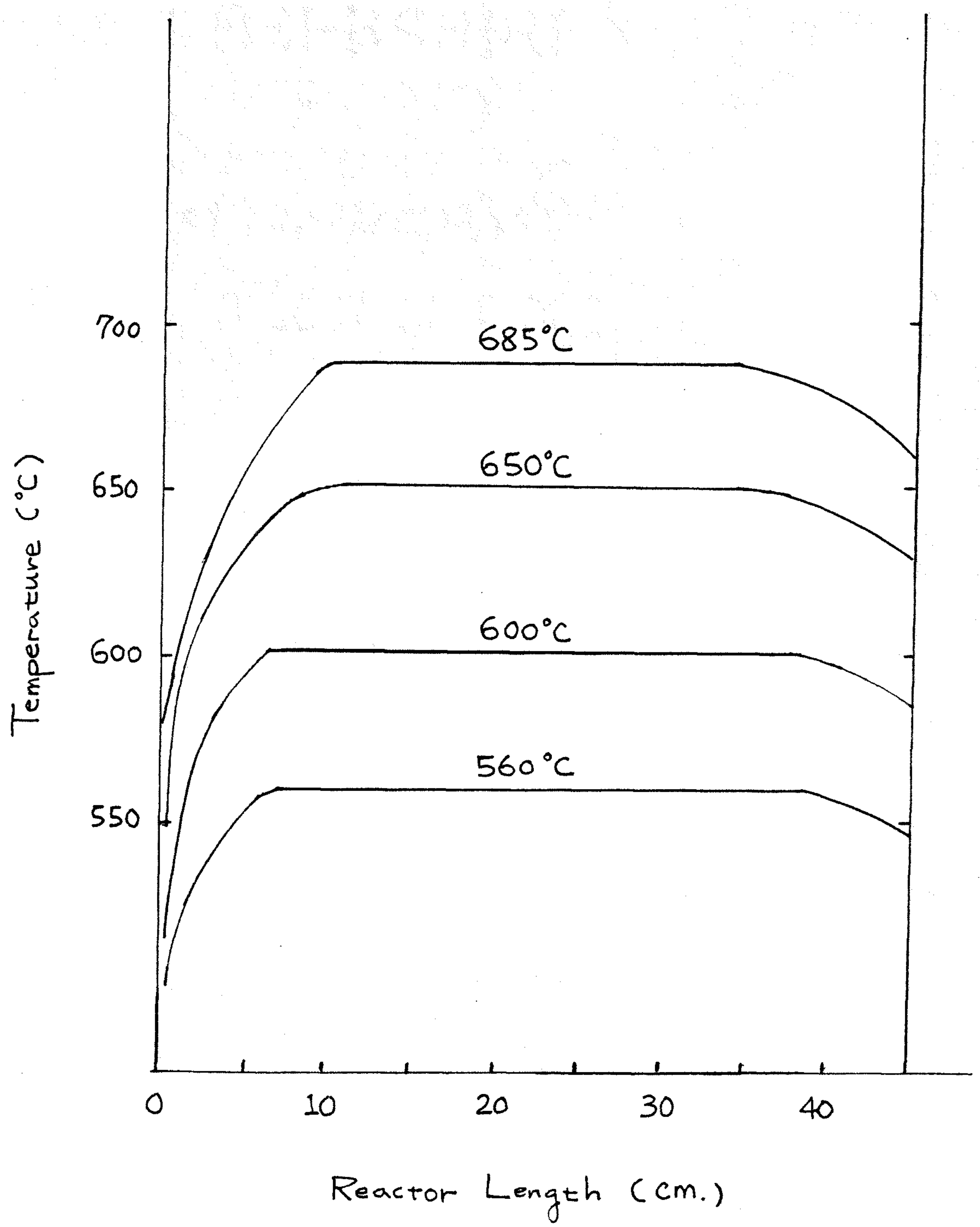
Outlet gases from the reactor were passed through a glass tube loosely packed with glass wool to trap any entrained solid carbon particles. This packed section also served as a mixing zone for the outlet gases. Less than one-fifth of the minimum volumetric flow rate was allowed through a six port Valco Model CV-6hpax gas sampling valve installed inside a Tracor 550 Gas Chromatograph, with the help of needle valve vacuum control. The remainder of the outlet gases were passed through a sodium-bicarbonate flask before being released to the atmosphere via a laboratory hood.

B. TEMPERATURE MEASUREMENT

Omega Model 650 Temperature Indicator connected to an Omega chromel-alumel (K type) thermocouple was used for measuring the temperature profile of the reactor.

Temperature measurements were carried out with steady flow rate of hydrogen gas through the reactor. Temperature readings were taken every 5 cm. and care was taken to ensure that steady state was obtained for every point along the length of the reactor. The profile obtained as shown in Figure 2 was isothermal to within +/- 5°C for about 80% of the reactor length.

Figure 2. Temperature Profiles



C. DATA COLLECTION

An on line Tracor Model 550 Gas Chromatograph with Flame- Ionization and Electron Capture detection was used for product distribution analysis. Steady state conditions were allowed before each sample was injected into the on line Gas Chromatograph. A tube filled with glass wool packing installed at the outlet of the reactor broke the laminar flow profile and mixed the outlet gases for a well mixed product sample. Each sample analysis by the chromatograph took about 20 minutes. During this period of waiting, low flow rate of pure hydrogen was passed through the reaction zone to prevent the build up of a carbon layer on the reactor's surface and to maintain a constant temperature profile. Measurement of hydrogen chloride concentration was performed by passing the outlet gases for a small number of runs through a fixed quantity of NaOH solution of known normality. The time required to bring this solution to the phenopthalien end point was measured for each run. The amount of HCl required to bring the fixed quantity of solution to the phenopthalien end point was found separately and is equal to the amount of HCl in the outlet gases. Since the time required to reach this end point was measured and the flow rate of gases for the run was known, the rate of HCl production could then be calculated.

Integration of the Flame Ionization Detector output was performed by a Varian Model CDS 111 Integrator. The Electron Capture Detector was used mainly to qualilitatively identify chlorinated hydrocarbons.

The gas chromotography column used for separating reaction products was a two meter long, 1/8 inch O.D., stainless steel tube packed with D.C. 200, 30 % on chromompak column . It was kept at 50°C. for 2.5 minutes and then raised to 180 degrees at the rate of 20 degrees per minute. Elution of all products occured in about 10 minutes total time. Another 10 minutes was required for cooling the oven and simultaneously preparing the reactor for another sample. The flame ionization detector was operated optimally with 30 cc per minute hydrogen fuel gas, 250 cc per minute air. Nitrogen at the rate of 30 cc per minute was used as the carrier gas.

Calibration for the flame ionization detector has been performed by Chuang (3), by injecting known quantities of the relevant compounds such as ethane,1,2-dichloroethane vinyl chloride, etc., and then comparing the corresponding response area. The response factor for C_1 chlorocarbons are close to one and are about half as much as the C_2 compounds. These results are in general agreement with the principle of flame ionization detectors which are known as carbon counters. The relative response factors can thus be considered as corresponding to the number of carbon atoms present in the molecule and the effect of the chlorine present can be ignored for quantitative analysis.

A Kratos MS-25 magnetic sector GC/Mass Spectrometer was used for qualitative identification of the products. Samples were collected in evacuated Pyrex bulbs.

Identification of the lighter hydrocarbon gases was done with a Varian GC fitted with a flame ionization detector and a two meter, 1/16 inch O.D., stainless steel column packed with spherocarb. With this column methane, acetylene+ethylene, and ethane could be identified and measured. Samples of five cc were injected into the column which was kept at 100°C. No elution of heavier products was observed.

V. RESULT AND DISCUSSION

A. REACTION OF $C_2H_4Cl_2$ WITH H_2

The reaction of 1,2-dichloroethane with hydrogen gas was studied in a high temperature tubular flow reactor operated within the domain of the plug flow model (5). The reaction was found to be first-order with respect to 1,2-dichloroethane in the presence of excess hydrogen (33:1 mole ratio H_2:DCE). The conversion of 1,2-dichloroethane was experimentally observed to follow the first order kinetic model ($\ln(C/Co)=-kt$) as shown on figure 3. The experimental conditions of the reaction of 1,2-dichloroethane with hydrogen are listed below:

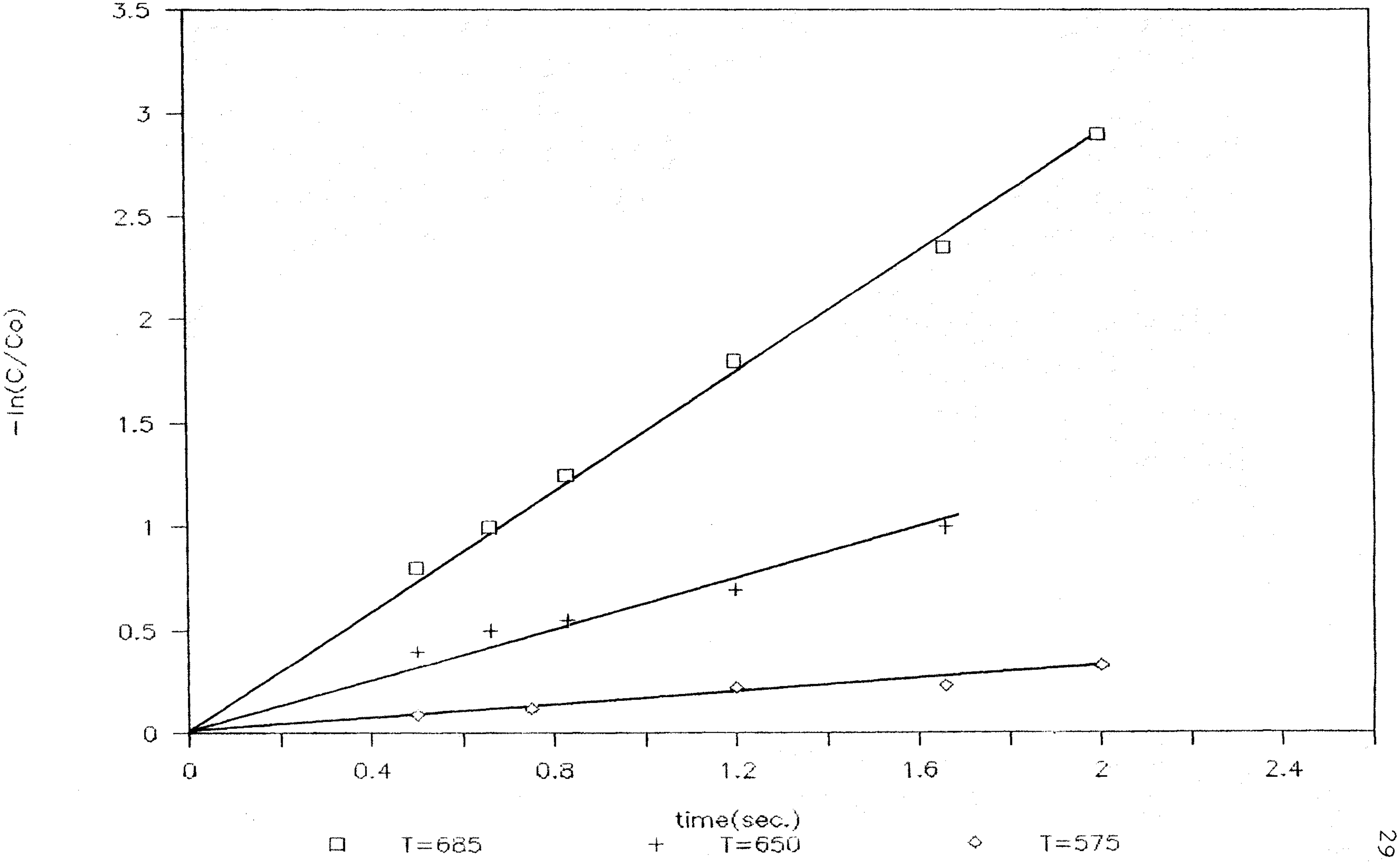
Temperatures (°C): 575, 595, 650, 685, 700, 850 ,900
Reactor Length(cm.): 45
Reactor Diameters(cm.): 0.4, 1.05, 1.6
Reactant Ratios between $C_2H_4Cl_2$ and H_2 : 1:33, 1:58
Residence Time Range: 0.1 - 1.3 sec.(d=0.4 cm.)
0.4 - 2.5 sec.(d=1.05 cm.)
0.5 - 2.5 sec.(d=1.6 cm.)

All figures mentioned below are for the reactor diameter of 1.05 cm. and the concentration ratio of 1:33 between $C_2H_4Cl_2$ and H_2.

Data from runs at temperatures 575, 660 and 685 °C were used for estimating kinetic parameters because of the

Figure 3: 1st. Order Plot

1,2-DCE + H2 RXN. D=1.05 cm.



high conversion initiation achived by this reaction. The conversion of 1,2-dichloroethane at these temperature range and residence time of 2.0 sec. are 30%, 55% and 85% respectively. At higher temperatures, the conversion becomes too high for meaningful kinetic study.

First order integrated rate equation plots of reagent conversion vs. resident time ln(C/Co)=-kt show high correlation. A sample of this plot at three different temperatures 575°C, 650°C, and 685°C respectively is shown on figure 3. Plots such as figure 3 yield the global rate constants " k_{expt}", from the slopes of the straight lines.

Data from runs at other temperatures and from the other two reactor diameters also fit first order integrated rate equation. However, slight discrepancy between the data and the straight line fit does occur at low residence times, (high linear velocities) and high temperatures. This discrepancy is probably due to greater non-linerarity in the temperature profile as a result of higher flow velocity and reactor temperature. Another reason for this difference may be the incomplete saturation of hydrogen gas with 1,2-dichloroethane vapor in the bubbler due to high flow velocity.

The Arrehenius' law ln(k) = ln(Ao) + (-E/RT) expresses the temperature-dependence of the reaction rate constant k. Ao, the frequency factor, is an indicator for the ratio of successful collisions, and E is the activation energy. By plotting k_{expt} vs. 1/T, we can obtain values for E/R from the slopes and Ao from the intercepts. An Arrehenius' plot for the reactor diameter of 1.05 cm. is shown on figure 4. Similar Arrhenius' plots for diameter of 0.4 cm. and 1.6 cm. were also done, activation energy and frequency factor were determined and put in the form of a reaction rate constant equation. These equations are as follow:

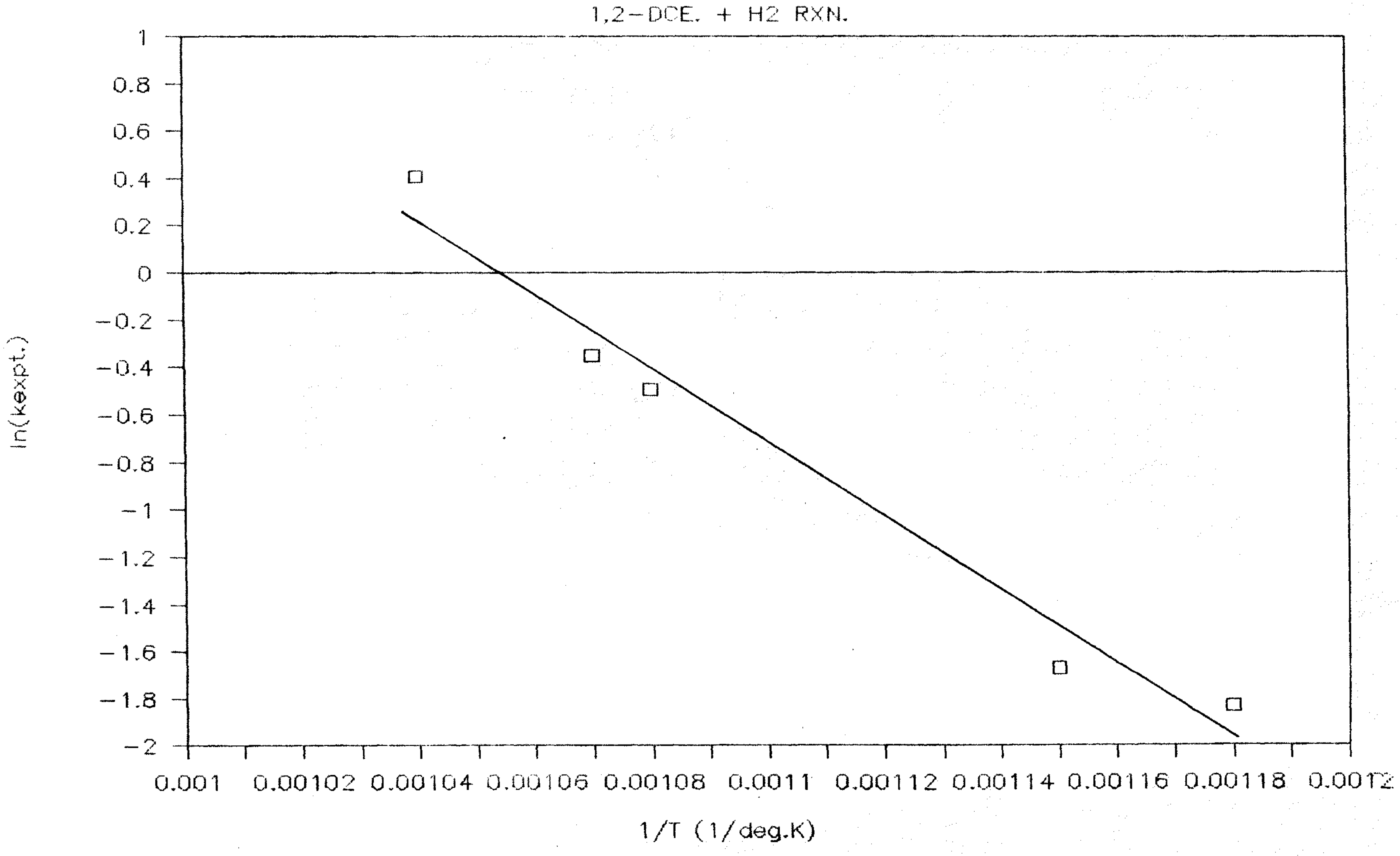
for 0.4 cm $k = 4.4 \times 10^{7} \mathrm{Exp}(-32,000/RT)$ (1/sec)
for 1.05 cm $k = 4.6 \times 10^{7} \mathrm{Exp}(-33,000/RT)$ (1/sec)
for 1.6 cm $k = 5.0 \times 10^{7} \mathrm{Exp}(-33,000/RT)$ (1/sec)

These rate equations yield values close to those obtained by Barton (16) and Kaprolova (21) for the simple pyrolysis of 1,2-dichloroethane in clean quartz flow reactors and Takahashi er al.(24) in a stainless-tube flow reactor. Their results are:

Barton $k = 1.59 * 10^{6} \mathrm{Exp}(-27,000/RT)$
Kapralova $k = 10^{8} \mathrm{Exp}(-32,000/RT)$
Takahashi $k = 3.3 * 10^{7} \mathrm{Exp}(-29,000/RT)$

The similarity of these kinetic parameters and ours seems to indicate that the experimental data is in general agreement and that the initial step of the reaction is unimolecular in nature.

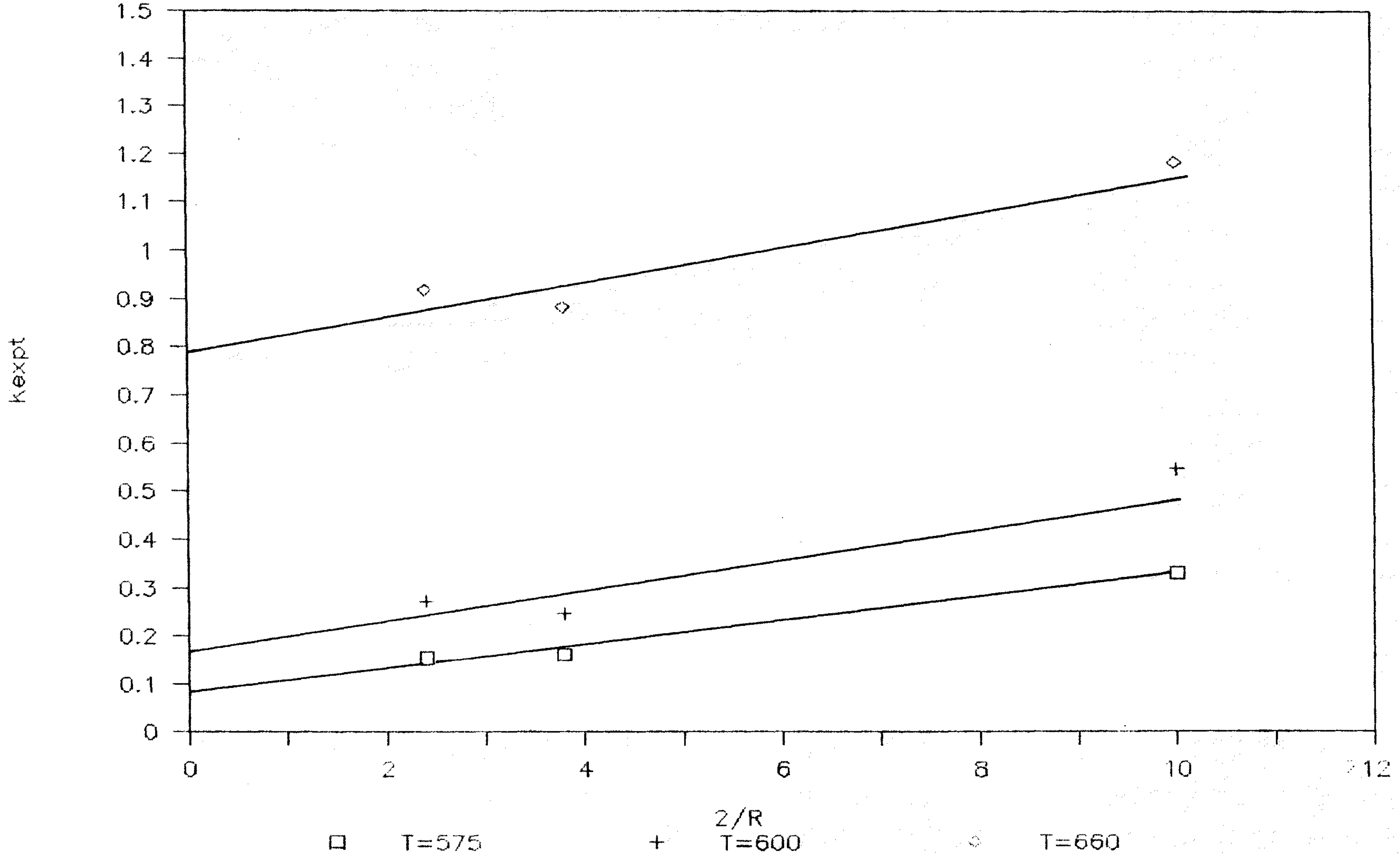
Figure 4: Arrehenius Plot for d=1.05cm.



The rate of 1,2-dicholoroethane decomposition is known to be affected by the nature of the surface and the S/V (surface to volume ratio) of the reactor (1,25). With these factors in mind, our experiments were always carried out in clean quartz tubes with intention of discerning the effect of surface to volume ratio upon the reaction rate and thus determining the bulk kinetic parameters more accurately. At constant temperature, our experimental results showed slight increase in the rate of reaction with increasing surface to volume ratio. This points out the existence of a wall reaction that has the effect of accelerating the overall reaction. In order to distinguish the relative importance of the wall reaction from the bulk reaction, Kaufman's equation in the form of $k = k_b + (2/R)k_w$ (1) was used. This is valid in the domain of plug flow model in which we operated. The series of experiments with all reaction conditions held constant except the surface to volume ratio, allowed us to decouple these reaction rates from the observed overall rate. Plots of experimental rate constants k_{expt}, versus the surface to volume ratio 2/R, where R is the radius of the reacter in cm. resulted in a straight line with slope k_w and intercept k_b. These plots are shown on figure 5. for three different diameters of 0.4 cm., 1.05 cm. and 1.6 cm. at three different temperatures: 575 °C, 600°C and 660°C. The resulting values of k_b and k_w are listed in table 1. for each of the temperatures. Applying the Arrhenius' law to the values of k_b and k_w

Figure 5: Kexpt. vs. 2/R

1,2-DCE. + H2 Rxn.



obtained for each temperature examined gave the following rate constants:

$$k_b = 4.8 \times 10^7 \mathrm{Exp}(-34{,}000/RT) \qquad (1/\mathrm{sec})$$

$$k_w = 2.0 \times 10^6 \mathrm{Exp}(-31{,}000/RT) \qquad (\mathrm{cm./sec})$$

The above expressions are found from Arrenhius plots such as Figure 6 and 7 where activation energies for the wall and bulk rate constants are determined from the slopes of the line and the frequency factors are determined from the intercepts. The values found for all the parameters discussed above are listed in Table 1. The results for the 1,2-dichloroethane to hydrogen ratios of 1:33, and 1:58 are also shown on table 1. Whereas the concentration of the 1,2-dichloroethane changes by a factor of almost two, the concentration of hydrogen does not change much. The fact that doubling the hydrogen concentration does not significantly alter the kinetic parameters indicates that our assumption of pseudo-first order kinetic is valid. In other words, experimental results would have varied significantly if the dependence of the experimental rate constants on the concentration of hydrogen were other than the assumed first order. Also shown on table 1. is that at temperatures below 700°C the wall reaction has a slightly lower activation energy than the bulk indicating that the reaction is probably initiated on the wall as well as occuring in the bulk phase.

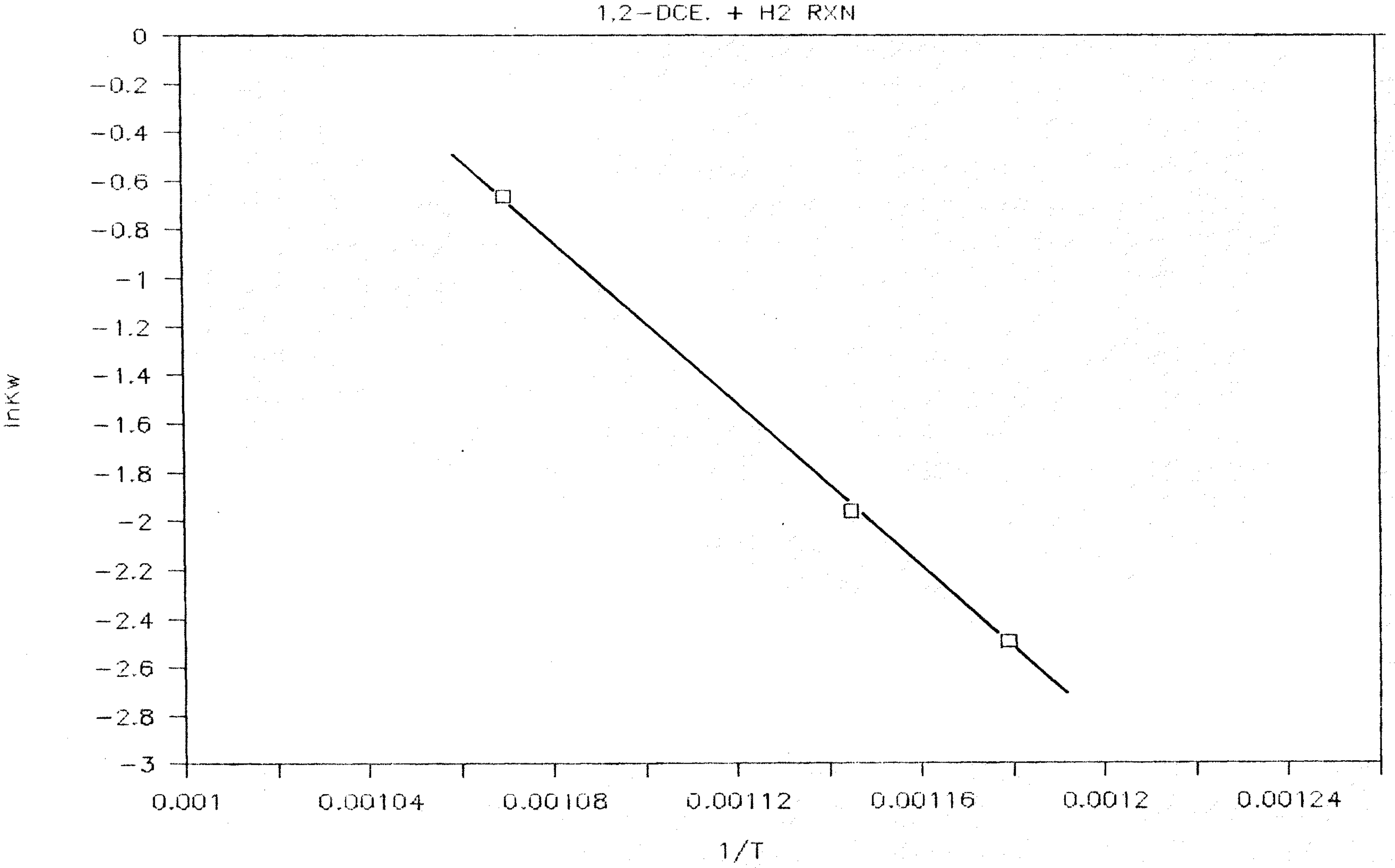


Figure 6:Arrehenius Plot for Kb

Figure 7: Arrehenius Plot for Kw

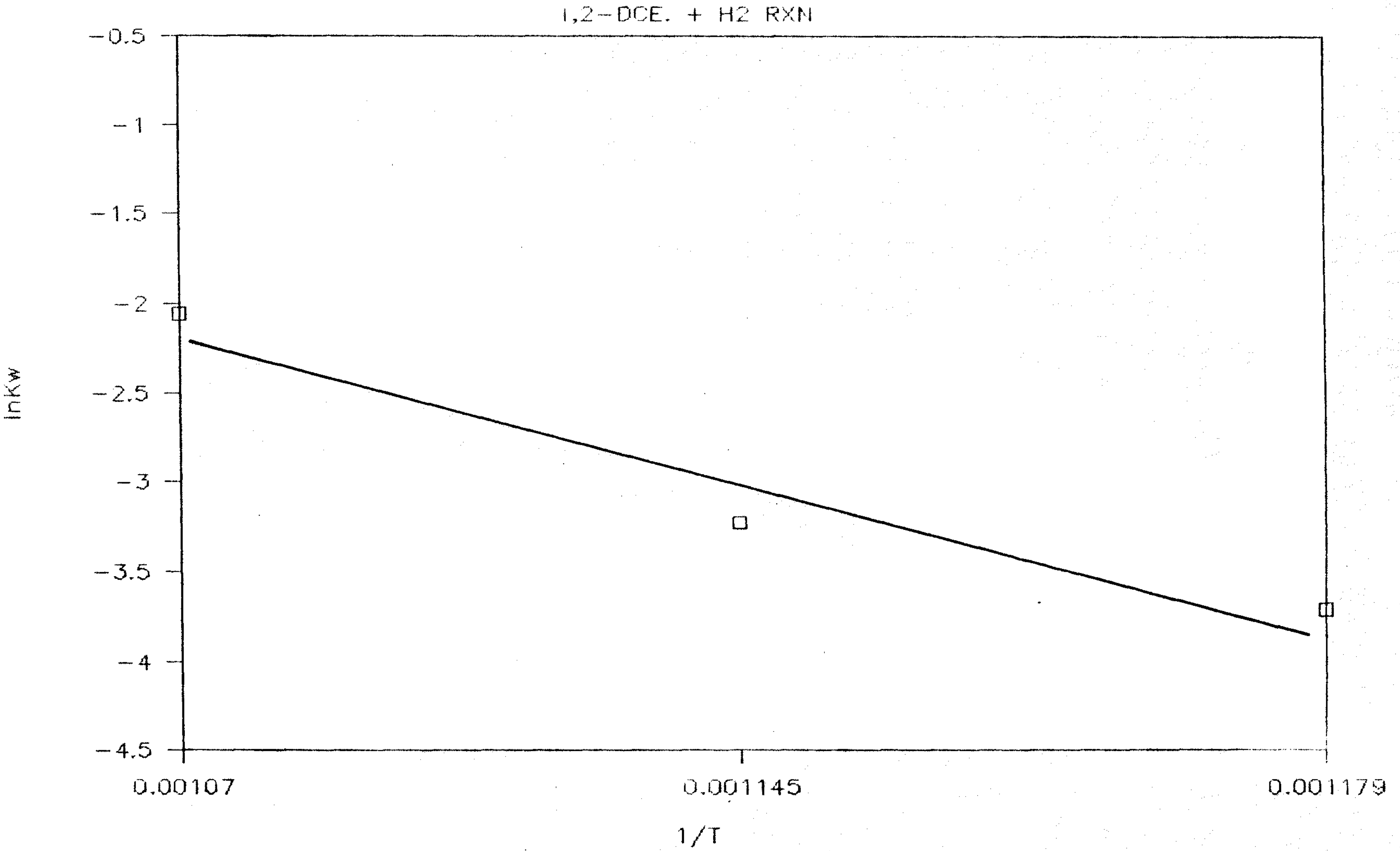


TABLE I.

RATE CONSTANTS FOR $C_2H_4Cl_2 + H_2$

$C_2H_4Cl_2 : H_2 :: 1 : 33$

Dia.(cm.)	0.4	1.05	1.6	k_b	k_w
Temp.(C)					
575	0.33	0.16	0.154	0.083	0.024
600	0.546	0.247	0.273	0.141	0.039
660	1.82	0.88	0.918	0.515	0.128
E(kcal/mol)	31.5	33.04	33.03	34.03	30.76
A(1/sec.)	4.35×10^7	3.16×10^7	5.01×10^7	4.78×10^7	2.04×10^6

$C_2H_4Cl_2 : H_2 :: 1 : 58$

575	---	0.15	0.1
600	---	0.25	0.3
660	---	0.9	0.93
E(kcal/mol)	---	33.0	33.0

B. PRODUCT DISTRIBUTION FOR 1,2-DCE AND H2 RXN.

The major products observed were C_2H_4, C_2H_2, CH_4 C_2H_6,C_2H_3Cl, C_2H_5Cl,HCl with minor product of C_6H_6, C_3H_6, CH_3Cl and trace amounts of 1,1-dichloroethane.

Product distribution as a function of time for the reactions at 595°C, 650°C and 685°C are shown on figures 8, 9 and 10, respectively. These plots indicate that the major hydrocarbon products below 700°C are ethylene, acetylene, ethane and methane and the major chlorinated hydrocarbons are vinyl chloride and chloroethane. These plots show that the production of hydrocarbons seems to increase monotonically with residence time while the vinyl chloride increases for a mid-range residence time and subsequently levels off. The concentration profile of chloroethane stays relatively insensitive to residence time changes.

Plots of stable products distribution versus temperature of reaction at residence times of 1 second are shown in Figures 11. From this figure, we see that vinyl chloride is not observed above 825°C and that chloroethane, which is never present in significant quantity, disappeares around 760°C.It is interesting to note that for a residence time of one second the only chlorinated products observed above 850 °C in any quantity is HCl. At the higher temperature, the major products are all hydrocarbons: methane, acetylene, ethylene, ethane and some benzene. The

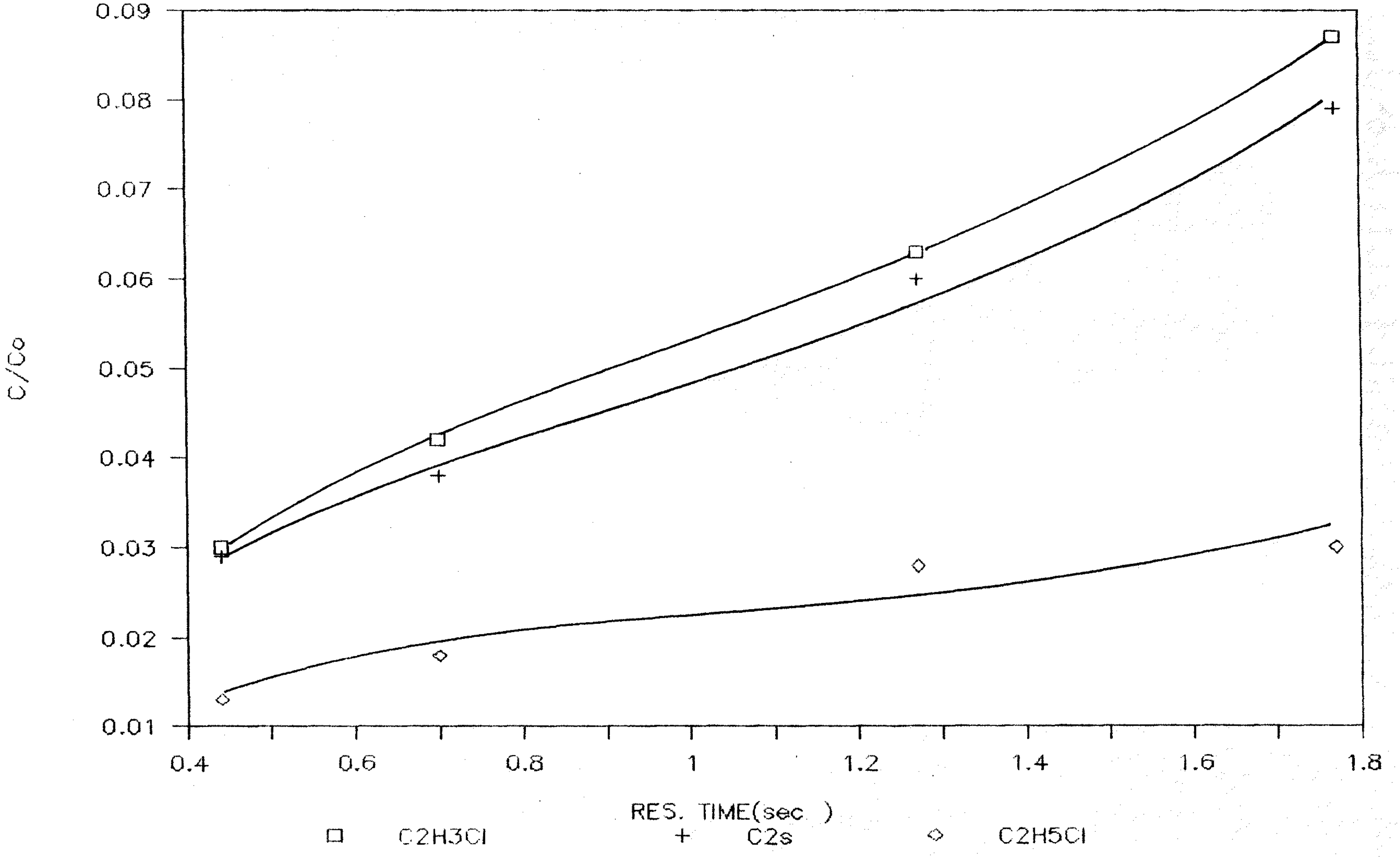


Figure 8: Prod. Dis. vs. Res.Time.

1,2-DCE + H2 RXN @ 575 deg. C

Figure 9: Prod. Dis. vs. Res. Time

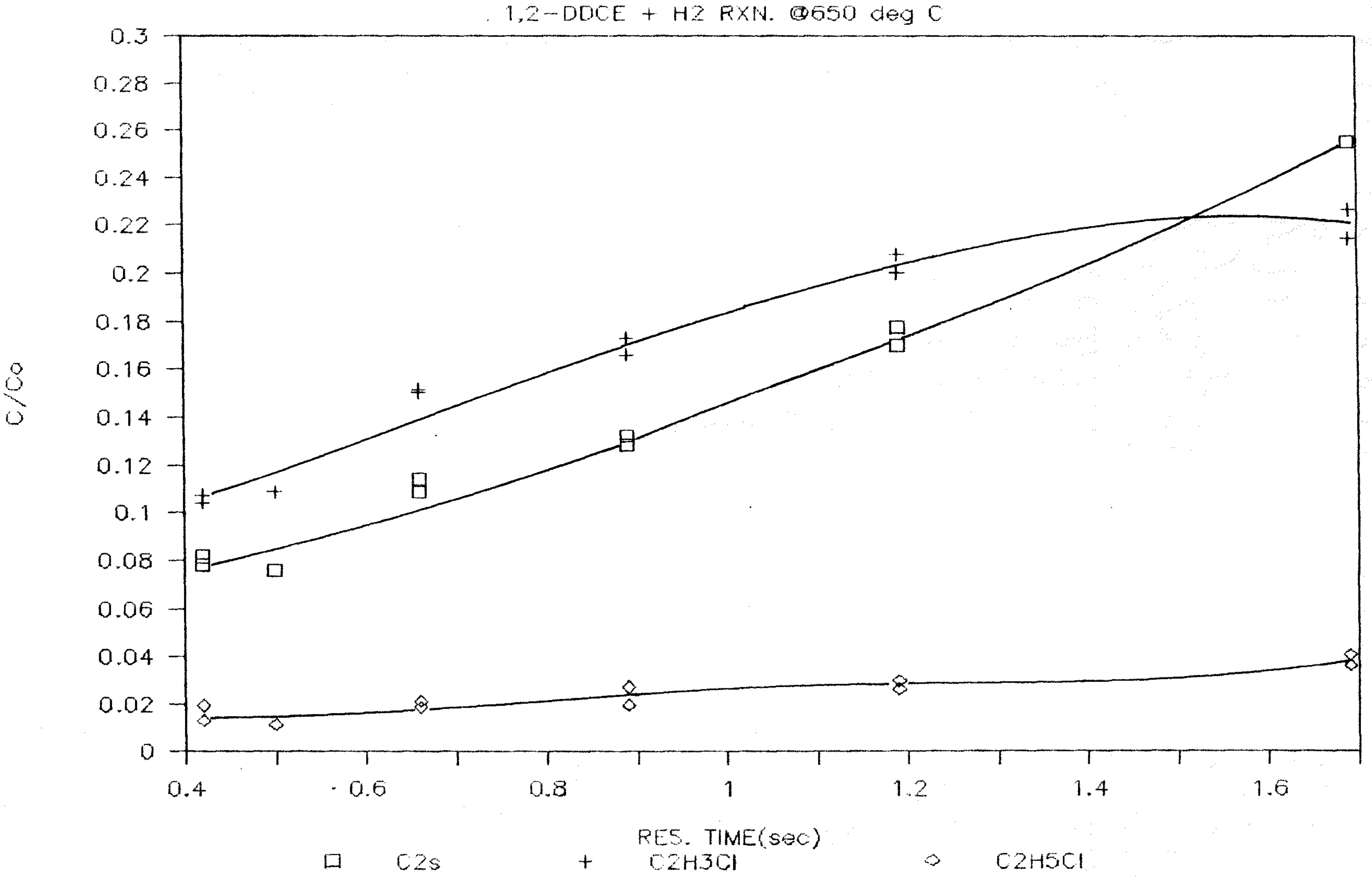


Figure 10: Prod. Dis. vs. Res. Time

1,2-DCE. + H2 RXN. @685 deg. C

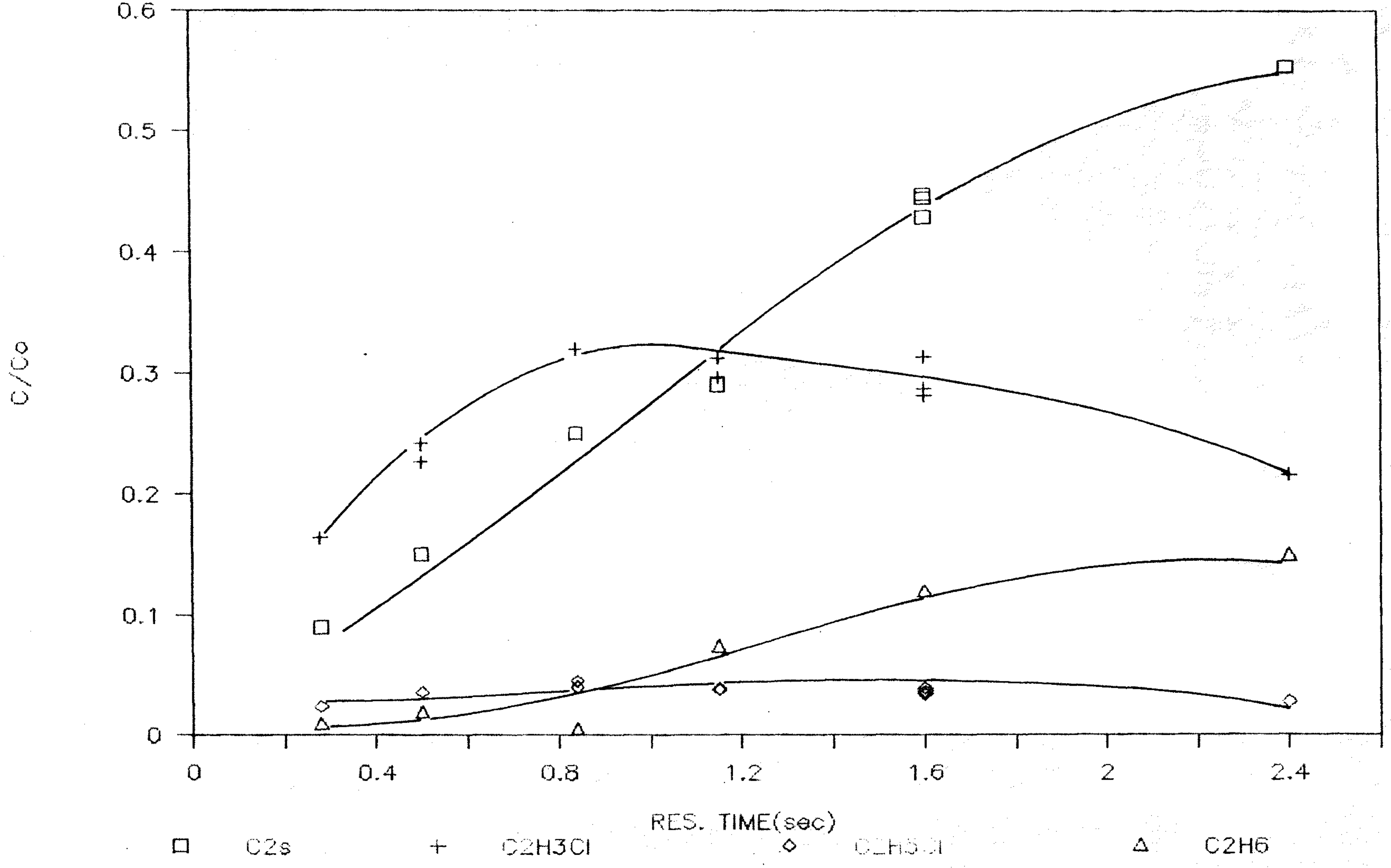
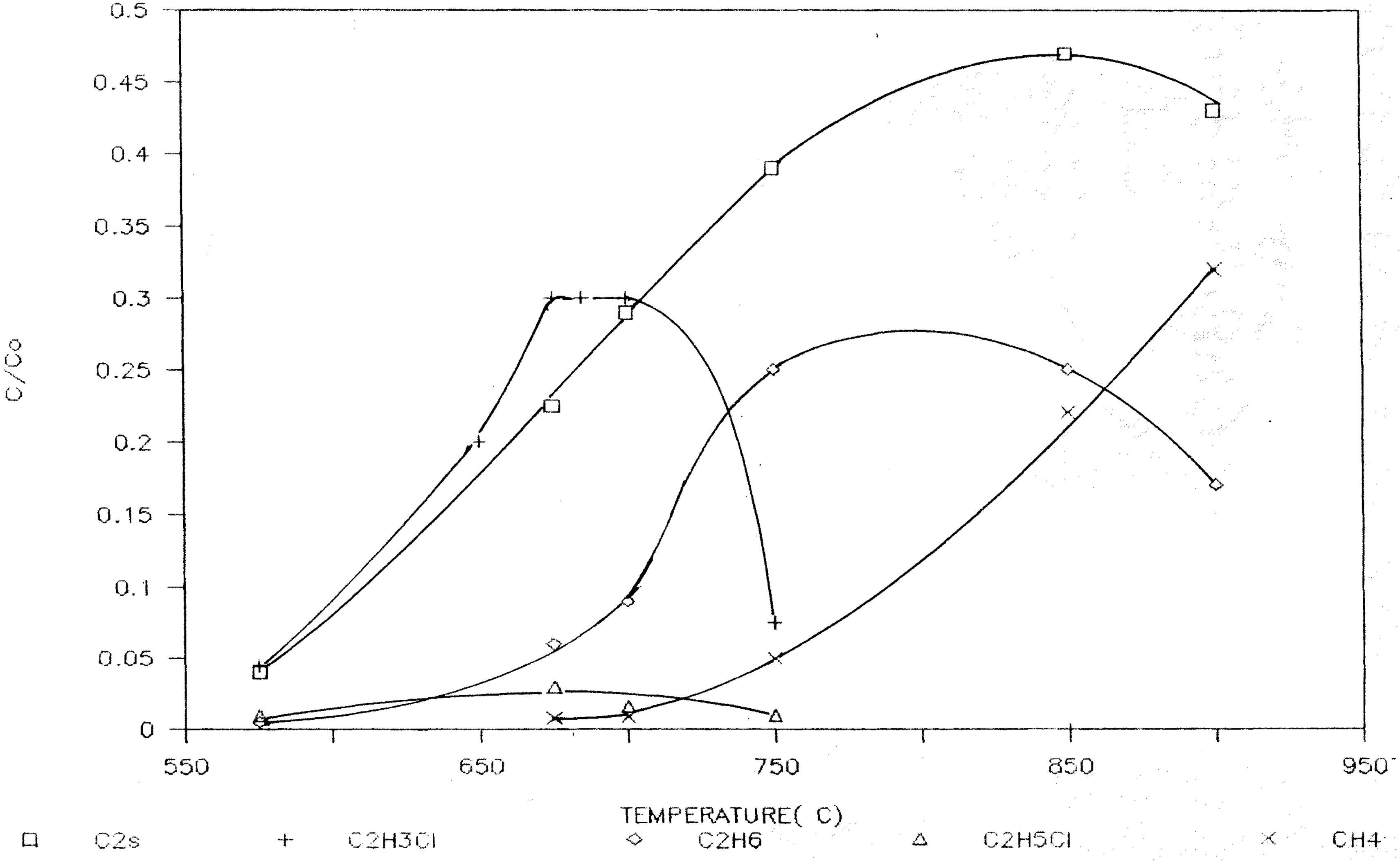


Figure 11: Prod. Dis. vs. Temp.

1,2-DCE + H2 RXN. d=1.05cm.



acetylene and ethylene production rises continuously with temperature through the whole temperature range until about 850°C at which it starts falling. Following the same kind of profile acetylene and ethylene have, ethane rises to about 790°C and then starts to drop in production. Methane, on the other hand, is a late product. It does not become a significant product until 750°C. then it rises steadily with temperature. Benzene is only produced in small quantities - about 1.5% of the total products- at 900°C and residence time of one second. A very interesting aspect of figure 11 is the decrease in acetylene, ethylene, and ethane concentration profiles coincides with the increase in production of methane concentration.

The vinyl chloride production rises with temperature in the range of 575-675°C; it reaches a plateau around 680-690 °C and then starts to fall off quickly above 700 ° C to practically nothing at 800°C. It is interesting to notice that as the vinyl chloride concentration falls off between the temperature range of 690°C and 760°C, the production of ethane rises drastically over the same temperature range. This seems to indicate that the disappearance of vinyl chloride is partially responsible for the increasing concentration of ethane. Of course, there is another phenomena that could be the cause of this steady increase in the production of methane - that is the unimolecular decomposition of the carbon-carbon bond in ethane. Since the increase in methane does coincide with the decrease in ethane concentration profile, it is safe to assume the high temperature gives ethane molecule enough kinetic energy to break the carbon-carbon bond. Another possible CH_4 production route could be the reaction between H. and C_2H_5. to form a $(C_2H_6)^*$ complex, which then dissociates into CH_3. and CH_3.. CH_3. then react with H_2 to form methane.

A material balance for 100 moles of carbon (50 moles of 1,2-dichloroethane) at different temperatures for a residence time of about one second is shown in Table 2. The Table also shown that at temperatures above 800°C, no other compounds than those found in this experiment were observed. Trace quantities of 1,1-dichloroethane, methyl chloride and butene were also observed on the GC/MS analysis. Each column in this table represents a temperature run. The sum of all the species in the column sometime do not add up to a hundred percent. This loss is probably due to carbon films coated on the reactor wall surface. Although cares were taken in keeping the reactor wall as clean as possible (reactor wall wes cleaned after each temperature run), the coating of carbon on the wall was nevertheless obverved toward the end of each run. The material balance seem to show that the loss was most severe in the 650-750° C temperature range.

TABLE II.
MATERIAL BALANCE FOR 100 MOLES CARBON

FOR $C_2H_4Cl_2$: H_2 :: 1 : 33

REACTOR DIAMETER 1.05 CM.

TEMP °C	575	675	700	750	850	900
CH_4	---	1	1	5	22	32.5
C_2H_2 + C_2H_4	4	22.5	30	40	47.5	40.5
C_2H_6	1	6	8	25	25	17
C_2H_3Cl	4	30	30	7	0.25	0.21
C_6H_6	----	----	----	----	----	1.47
C_2H_5Cl	1	2.5	2.5	1	---	0.2
C_2H_4Cl	90.4	30	18	9	----	----
TOTAL	99.4	95.0	89.5	87	94.75	98.8

C. MECHANISM FOR THE 1,2-DICHLOROETHANE + HYDROGEN RXN.

A simple mechanism which explains the stable products observed is shown below. It is not meant to be comprehensive.

$$
\begin{array}{lcl}
C_2H_4CL_2 & \longleftrightarrow & C_2H_3Cl + HCl \\
C_2H_3Cl & \longrightarrow & C_2H_2 + HCl \\
C_2H_3Cl + H_2 & \longrightarrow & C_2H_5Cl \\
C_2H_3Cl + H_2 & \longrightarrow & C_2H_4 + HCl \\
C_2H_4Cl_2 & \longrightarrow & 2(CH_2Cl.) \\
2(CH_2Cl.) + 3(H_2) & \longrightarrow & 2CH_4 + 2HCl \\
C_2H_4Cl_2 + H_2 & \longrightarrow & C_2H_5Cl + HCl \\
C_2H_5Cl & \longrightarrow & C_2H_4 + HCl \\
C_2H_5Cl + H_2 & \longrightarrow & C_2H_6 + HCl \\
C_2H_4 & \longleftrightarrow & H_2 + C_2H_2 \\
C_2H_6 & \longleftrightarrow & CH_3. + CH_3. \\
CH_3. + H_2 & \longrightarrow & CH_4 + H.
\end{array}
$$

VI. CONCLUSIONS

The reaction of 1,2-dichloroethane with hydrogen gas was studied in a tubular flow reactor. It was experimentaliy determined to follow the first order kinetic model (ln(C/Co)=-kt). Using Arrehenius'plot, activation energy and frequency factor were found and put in the form of a reaction rate constant equation as follow:

for 0.4 cm $k = 4.4 \times 10 \mathrm{Exp}(-32{,}000/RT)$ (1/sec)
for 1.05 cm $k = 4.6 \times 10 \mathrm{Exp}(-33{,}000/RT)$ (1/sec)
for 1.6 cm $k = 5.0 \times 10 \mathrm{Exp}(-33{,}000/RT)$ (1/sec)

Equation derived by Kaufman was used to decouple expressions for the wall and bulk constants:

$k_b = 4.8 \times 10 \mathrm{Exp}(-34{,}000/RT)$ (1/sec)
$k_w = 2.0 \times 10 \mathrm{Exp}(-31{,}000/RT)$ (cm./sec)

The major products were methane, acetylene+ethylene, ethane, vinyl chloride and chloroethane. The minor products were butene and benzene. Trace amounts of methyl chloride and 1,1-dichloriethane were found too. Since the complete conversion of all chlorinated hydrocarbons occured above 760 C and at one second, it appeared that the hydrogen was very effective in the this type of reaction. Our study acheived our goal of collecting kinetic parameters for the elucidation of chlorinated hydrocarbons and hydrogen reaction. Kinetic mechanism study based on our results will further our knowledges of this fascinating reaction.

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