ABSTRACT

Title of Thesis: Reactions of Hydrogen with Chloroform and
Trichloroethylene at High Temperatures

Burhan Mahmood, Master of Science in Chemical Engineering,
1985

Thesis Directed by: Dr. Joseph W. Bozzelli,
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The reactions of chloroform and trichloroethylene with hydrogen in the temperature range 550 to 1000°C were studied using tubular flow reactors of varying diameters. The residence time range was from 0.05 to 3.0 seconds.Two different concentrations of the chlorinated species were used, each with hydrogen in large excess. Flat temperature profiles (+/- 5°C) were achieved over 80 to 85 per cent of the 45 cm long reaction zone, with inlet gases preheated to about 400°C.

No chlorinated hydrocarbons, products or reactants were observed at /above 850°C. The major products at these temperatures were C_2H_2, C_2H_4, CH_4, HCL and benzene.

The first order plug flow model was used for analysis of the experimental data. A comparison of these results with a more rigorous laminar flow model is also shown. Wall and homogeneous phase rate constants were evaluated using Kaufman's method. The following rate equations were found to fit the data:

a) Chloroform

$k = 3.86 * 10^{12} e^{(-35.3/RT)}$ sec^{-1}, gas phase.

$k = 3.24 * 10^{14} e^{(-43.4/RT)}$ sec^{-1}, at the wall

b) Trichloroethylene

$k = 4.54 * 10^{12} e^{(-35.0/RT)}$ sec^{-1}, gas phase.

$k = 9.6 * 10^{10} e^{(-31.2/RT)}$ sec^{-1}, at the wall.

REACTIONS OF HYDROGEN WITH CHLOROFORM AND TRICHLOROETHYLENE AT HIGH TEMPERATURES

by

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1. INTRODUCTION

1.1 GENERAL

The disposal of chlorinated organics has generated much interest in recent years possibly because PCBs were the only group of compounds specifically mentioned in the TSCA law enacted in 1976, and because many of the chlorinated hyrdocarbons have now been shown to be toxic and/or carcinogenic. Moreover the rising cost of raw materials and the need to conserve resources and energy combined with the need to comply with the TSCA and RCRA environmental laws have made the treatment of hazardous wastes, and possible reutilization economically feasible.

Many technologies are in various stages of development. Non-thermal methods include carbon adsorption, chlorinolysis, Na-based dechlorination, photolytic and microwave plasma destruction, catalyzed wet air oxidation, activated sludge, trickling filters and other bacterial methods.

Of all these processes for the destruction of PCBs, only the Na-based dechlorination method is commercially available (1). The process however cannot tolerate free water and is very expensive when pure PCBs are treated. Biological degradation studies indicate that individual isomers are not equally destroyed by microorganisms. Catalytic dehydrochlorination may lead to a moderate cost process with greater than 90% waste destruction (1).

At present incineration remains the main method used to destroy chlorinated organics. Combustion equipment varies from rotary kilns, cement kilns, high effiency boilers, fluidized bed incineration and molten salt incineration to liquid injection burners without the release of chlorinated by-products to the atmosphere.

The oxygen rich environvment of the combustion process, where the temperature is 1200°C with a dwell time of 2-4 seconds in the combustion zone (2) is supposed to totally oxidize all carbon to CO_2, but there is no stable end adduct for the chlorine. Chlorine oxides and CL_2 are not acceptable products for discharge to the atmosphere.

Some polychlorinated dibenzo-p-dioxin (TCDD) isomers, including 2,3,7,8-TCDD, the most toxic of these compounds, were found in ash samples from the incineration of trichlorophenol (TCP), which is widely used as a starting material for some herbicides and bactericidies; and from the incineration of pentachlorophenol (PCP) which is used in wood preserving processes (3). The other chlorine products are usually smaller chlorinated hydrocarbons such as chloromethane, chlorobenzenes, chlorinated ethylenes, fragments of the initial reactants which may be toxic and chlorinated aldehydes and acids.

1.2 BASIS OF PRESENT RESEARCH

It is clear that incineration in an oxidizing environment effectively destroys the initial species but has a number of attendant unsatisfactory results.

An alternative to incineration is detoxication by reductive reactions of the type :

$$CHCL_3 + 3H_2 \dashrightarrow CH_4 + 3HCL$$

Hydrogen chloride as an end product for the chlorine is desirable because it can easily be neutralized or collected. CH_4 is a useful gas which can be recyled as fuel.

Introducing a hydrogen (reductive) rich environment would favor the formation of HCL, possibly uptaking all the chlorine under proper conditions. Other products that can be expected are gaseous hydrocarbons and carbon. Thus, detoxication would be achieved with the additional benefit of producing usable fuel gas and HCl.

Since these reducing reactions have so far been largely ignored, these experiments would also provide much-needed kinetic parameters and reaction product information leading to a better understanding of the chemistry of these species.

The choice of pure hydrogen in this work is based on the conviction that it leads to less complex chemical systems compared to other hydrogen sources. It also provides a fundamental and more readily interpreted series of reactions. It is felt that this more straight forward reaction will yield important kinetic data and permit later calculation on the thermodynamic equilibrium and the extent to which equilibrium achieved in the reactor. The kinetic and thermodynamic information as well as the data on the reaction product distribution will serve as an important reference source for other hyrogen sources such as less expensive natural gas, hyrdazine or water vapor.

2. PREVIOUS STUDIES

Beyond the results of the work done in the laboratories of NJIT, under the guidance of Dr. Bozzelli, a thorough search of published literature has not revealed any report on the reactions of hydrogen with chlorinated halocarbons. Nor has any reaction kinetic parameters for the reaction of hydrogen with the halocarbons of interest in this research been found.

The only relevant studies, mentioned above, are those of Chuang (4) who 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 accepted for publication. Chang (5) in his work on the estimation of homogenous and wall rate constants from laminar flow anlysis has presented data on the reaction of hydrogen with 1,1,1 trichloroethane. This work has just been submitted for publication.

The thermal decomposition of pure chlorinated hydrocarbons has been studied to some degree. A number of reports were found on the thermal decomposition of chloroform and trichloroethylene.

2.1 CHLOROFORM

Verhoek (6) studied the thermal decomposition of chloroform identifying only HCL as a product. Semeluk and

Bernstein (7,8) studied the products and the kinetics of chloroform in a flow reactor. They suggested a rupture of the carbon-chlorine bond as the primary step (7), and found that the reaction was inhibited by HCL (8). Shilov and Sabirova (9,10) proposed that the initial step is the formation of dichlorocarbene and HCL in the pressure range of1.18 to 35.9 mm.Hg. Other studies include that of Lemoan (11), and of Vacherot and Parant (12), who studied the thermal decomposition of chloroform over silica.

The reaction of chloroform with atomic hydrogen was studied by Clark and Tedder (13) in a flow system. They proposed a decomposition by the carbene route at low temperatures.

Murgulescu and Wiessmann (14,15) have studied the influence of methane on the thermal decomposition of chloroform. They rationalized their results using the mechanism proposed by Shilov and Sabirova (10).

All reports agree on a unimolecular decomposition as the initial step.

2.2 TRICHLOROETHYLENE

The pyrolysis of trichloroethylene was investigated by Goodwall and Howlett (16). They proposed a bimolecular initial step in the pressure range of 17 to 42 mm.Hg. The step proposed was :

$$2C_2HCL_3 \text{ -----> } CL + C_2HCL_2 + C_2HCL_3$$

$$\text{or -----> } HCL + C_2HCL_2 + C_2CL_3$$

They found that the reaction was inihibited strongly by propylene and n-hexane. An activation energy of 35.4 kcal/mol was found for this reaction.

Harding (17) studied the kinetics of the reaction of trichloroethylene with cyclopentane at high pressures assuming the initial step to be unimolecular. The unimolecular decomposition step proposed was :

$$C_2HCL_3 \text{------>} C_2HCL_2 + CL$$

The activation energy found for this step was 61.2 kcal/mol. The temperature range of their study was 250 to 360^{o}C. In this temperature range the decomposition of trichloroethylene is extremely slow and thermal initiation periods of 20 to 100 minutes were used. The activation energy for thermally initiated reactions was found to be 35.4 kcal/mol.

Zabel (18) investigated the thermal decomposition oftrichloroethylene at high pressures between 2 and 175 atmospheres behind reflected shock waves. He applied unimolecular reaction rate theories for calculating the limiting low and high pressure rate equations as well. The experimentally found activation energy for the unimolecular decomposition first step was 84 +/- 3 kcal/mol. According to his analysis the mode of decomposition was suggested to follow the following route :

$$C_2HCL_3 \text{------->} CL + C_2HCL_2$$

2.3 OTHER COMPOUNDS OF INTEREST

Some work has been done on the reaction of atomic hydrogen with chlorinated halocarbons. Arnold and Shelling (19,20) have reported on the flame production and characterized the emission spectra from atomic hydrogen with halocarbons in a low pressure flow reactor. Costes et al (21) have utilized reactions of hydrogen atoms with CCL_4 showing the production of carbon atoms in low pressure reactors. According to their study, the initial reaction is thought to be the slow abstraction of chlorine to form HCL and a free radical carbon species with subsequent fast chain branching and termination reactions resulting in a flame and the final products.

A number of studies have been reported on the oxidation of hazardous organic halocarbons such as CCL_4, DDT, PCB, etc., to carbon dioxide and other carbon-chlorine adducts . Roberts and Sawyers (22) have reported the degradation of several halocarbon chemicals to carbonates using superoxide ions in solution. Pytlewski et al (23) have effectively decomposed PCBs in liquid polyethyleneglycol solutions of suspended sodium, and Botre et al. (24) have examined the degradation of dioxins (TCDD) using chloroiodines produced in a mixture of chlorine, iodine, and quartenary ammonium salt surfactants.

Rubey and Duvall (25) have shown thermal decomposition of PCBs in a flow reactor where smaller chlorinated species like hexachlorobenzene were produced.

The use catalysts for the destruction of these halocarbons has also been studied to some extent. An extensive list of references on this subject may be found in Chuang´s (4) work.

3. THEORY

3.1 THE FIRST STEP

Reaction between hydrogen and the chlorinated species, is initiated in the present study, by thermal decomposition of the chlorinated species.

The decomposition behavior of halogenated hydrocarbons may generally be related to the strengths of the carbon-halogen bonds. Rupture of the carbon-carbon bonds occur in compounds of flourine, where the carbon-flourine bond is the strongest. In other halogen compounds the initial rupture of the carbon-halogen bond is much more likely, as the carbon-halogen bond is a weaker bond than the carbon-carbon bond. As a result many decompositions are free-radical in nature. Some of these compounds decompose by unimolecular mechanisms as well . Thermally induced unimolecular reactions of these species include dehydrohalogenation and isomerization. In many cases both modes of decomposition may be operative at the same time.

The decomposition of most chlorinated hydrocarbons is believed to be free-radical in nature. All the reports cited previously for chloroform (4-15) and trichloroethylene (16- 18) confirm the general acceptance of this mechanism of decomposition for the two compounds studied in this work.

The first step in the free-radical mode of decomposition is generally unimolecular (27). The thermal decomposition of chloroform has been rationalised to be unimolecular in all the above mentioned reports. This is true for trichloroethylene too. Interestingly, Goodwall and Howlett (16) have attempted to verify the reversion of first order kinetics to second order at low pressures as predicted by unimolecular theory, by using trichloroethylene. They report second order behavior at pressures below 50 mm.Hg. The mechanism proposed for the homogenous non-chain mode of reaction was bimolecular.

3.2 UNIMOLECULAR REACTION THEORY

The Lindemann theory explains the unimolecular mechanism for the class of reactions represented by :

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

which are most often found to be first order. He showed how activation by collision could lead to first order kinetics under certain circumstances. The more generally accepted Hinshelwood modification (27) of the Lindemann mechanism is presented below :

$$A + M \underset{k_d}{\overset{k_a}{\longleftrightarrow}} A^* + M \qquad (1)$$

$$A^* \xrightarrow[k_p]{A\#} P \text{ (Products)} \qquad (2)$$

where M can be A itself or any foreign gas molecule like a product or inert gas. A* is an energized molecule and A# is an activated complex.

In this model an energized molecule is one which has sufficient energy to smoothly pass into the activated complex without the acquisition of additional energy. The transformation involves vibrational changes and localization of energy only.

Applying steady-state theory to the above mechanism where the concentration of A* is constant, we get

Rate of formation of $A^* = 0 = k_a[A][M] - k_d[A^*][M] - k_p[A^*]$

leading to

$$[A^*] = \frac{k_a[A][M]}{k_d[M] + k_p} \qquad (3)$$

Therefore the rate of formation of product f is :

$$f = k_p[A^*] = \frac{k_a k_p[A][M]}{k_d[M] + k_p} \qquad (4)$$

If [M] is approximately constant as in a pseudo-first order reaction, k can be defined as :

$$k = \frac{k_a k_p[M]}{k_d[M] + k_p} \qquad (5)$$

This gives

$$f = k[A] \qquad (6)$$

Here k is the observed first order global rate constant. Its limiting values are :

(a) for high pressures, $k_d[M] >> k_p$ giving

$$k = k_{\infty} = \frac{k_a k_p}{k_d} \tag{7}$$

(b) for low pressures, $k_d[M] << k_p$ giving

$$k = k_o = k[M] \tag{8}$$

In the high pressure region as is the case in this study, the rate limiting step is the formation of products from the activated complex. This is shown by using the inequality $k_d[M] >> k_p$ in the equation for the rate of formation of A*, which gives :

$$k_a[A][M] = k_d[A^*][M]$$

This shows that the rate of activation is equal to the rate of deactivation. Since $k_d[M][A^*] >> k_p[A]$, the rate of the equation (2) is much less than for the equation (1) and thus the equilibrium concentration of A* controls the rate of the reaction.

3.3 CHEMICAL REACTOR THEORY

Ideal tubular reactor analysis for isothermal systems is based on plug flow conditions, where all elements of the fluid have the same residence time in the reactor. There is no axial or radial diffusion as well. These conditions are nearly impossible to meet in a practical system. Quite frequently flow conditions are in the laminar flow range as opposed to turbulent flow where the plug flow approximation is known to hold. Consideration of methods for dealing with deviation from isothermality will be discussed later in this section. All quantitative analysis will be found in the Results and Discussion section.

In tubular flow reactors in general, radial mixing is due to molecular diffusion and axial mixing is due to fluid velocity gradients (28). The mechanism of dispersion that may be assumed (29,30) for low range Reynolds numbers, which is the range of this study, is : In the low range the velocity profile has a smaller effect than molecular diffusion. Thus, in the present study axial diffusion is assumed to be negligible.

Reman (31) has used Danckwerts solution for the differential equation of first-order reactions in tubular reactors with plug flow and axial diffusion to present a general plot of the deviation of a reactor with axial diffusion from a mixed or plug flow reactor in the case of a first order reaction. From his data it appears that for D/vl < 0.1 the reactor behaves as an ideal tubular reactor, and for D/vl > 2.0 the reactor behaves like a well-mixed one (32). In this study D/vl is well below 0.1 .

This evidence would be sufficient for plug flow assumption 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 (29,30). This is not true for the experiments carried out in the present study.

A more rigorous analysis that is closely applicable to the system in the present study is the report by Poirier and Carr (33).They have numerically solved the continuity equations for first-order reactions considering radial diffusion. For first order reactions they propose that if D/kR, where R is the radius of the reactor, is equal or greater than 0.5, plug flow approximation is probably satisfactory. Values of D/kR found for this study are well above 0.5

It is therefore assumed that ideal tubular flow model is a good approximation for this work.

A comparision of the kinetic values found by plug flow analysis with values obtained by applying the numerical solution of the continuity equation for first order kinetics with laminar flow done by Chang (5), is shown in the Results and Discussion section. The comparison turns out to be favourable to the plug flow assumption.

3.4 ANALYSIS OF NON-ISOTHERMAL SYSTEMS

The longitudinal temperature profiles obtained for the kinetic study runs are shown in Figure 1. End effects could not be eliminated and non-isothermality exists to a certain degree. Non-isothermal data can be treated as isothermal after appropiate correction are made according to the method outlined by Hougen and Watson (34). The method utilizes the concept of equivalent reactor volume V_r, which at the reference temperature T_1 and the reference total pressure P_1 would give the same conversion as the actual reactor, with its non flat temperature profile.

The experiments were carried out at one atmosphere and negligible pressure drop. The pressure is thus considered to be constant. The equation for the equivalent volume for first order reactions becomes :

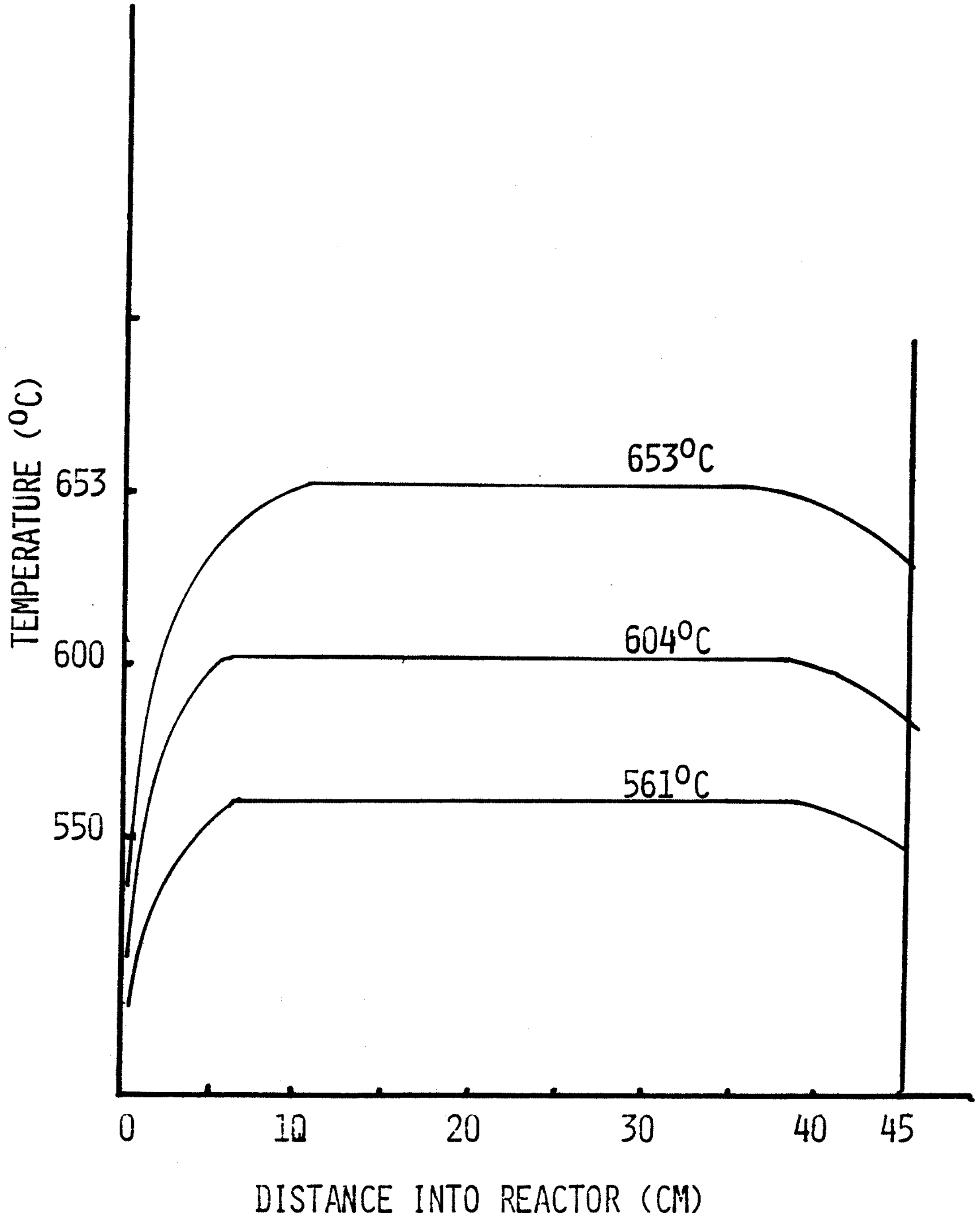
$$V_r = \int_0^V \frac{T_1}{T} \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right) dv \qquad (9)$$

Since the activation energy E is not known, a first estimate can be made by the equal conversion method of Froment and Bischoff (35). An example of the required plot is shown as Figure 2. Equation 9 is numerically solved by Simpson´s method.

Once the equivalent reactor volume is found, the analysis continues according to the ideal plug flow model.

FIGURE 1

TEMPERATURE PROFILE



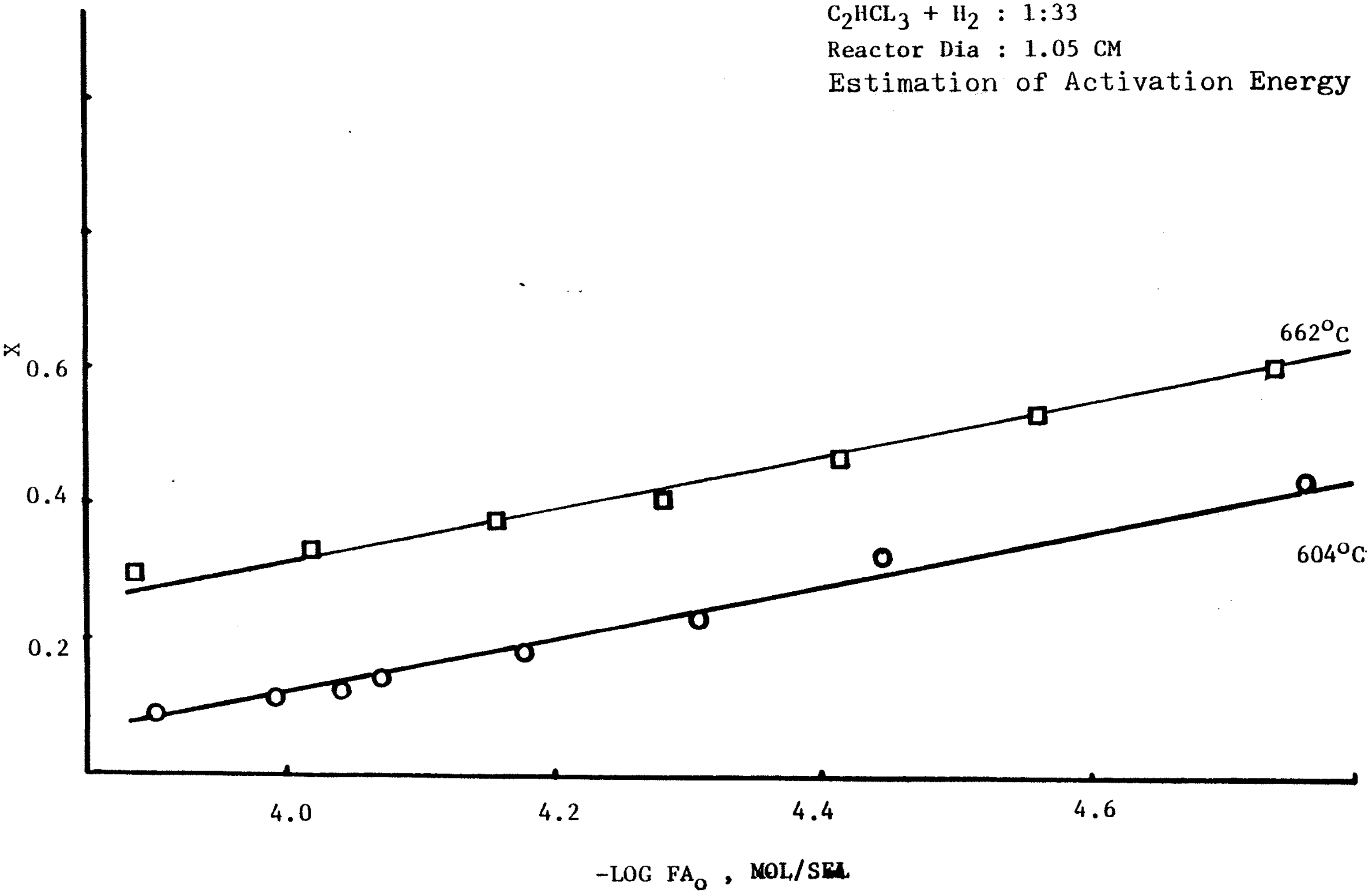


Figure 2
$C_2HCL_3 + H_2$: 1:33
Reactor Dia : 1.05 CM
Estimation of Activation Energy

In this study one of the reactants (hydrogen) is added in large excess, leading to pseudo-first order kinetics for the chlorinated species.

3.5 WALL AND HOMOGENOUS RATE CONSTANTS

The results obtained by Chuang (4) show that the decomposition of chlorinated hydrocarbons is a function of the radius of the reactor as well as of the temperature and concentration. When wall removal is appreciable kinetic parameters for the reaction at the wall in addition to the bulk or homogenous reaction need to be evaluated.

The system consisting of homogenous and wall reactions is a special case of two parallel reactions. The relative contribution of the homogenous phase is a function of the reactor volume whereas the contribution of the wall depends on the surface area of the reactor. The ratio of the wall to the homogenous phase reaction is a function of the surface to volume ratio 2/R.

For plug flow reactor conditions Kaufman (36) has shown the following relationship to be applicable :

$$k_{(expt)} = k_h + (2/R)k_w \tag{10}$$

By running reactions with reactors of different diameters i.e., of different surface to volume ratios, keeping all other conditions same the differences in the reactions parameter values can be found. A plot of equation 10 then provides a method of decoupling the wall rate constant, " k_w ", from the homogenous phase rate constant " k_h ". With these values separate activation energies for the wall and homogenous phase reactions can be calculated.

4. EXPERIMENTAL

An isobaric flow system was designed for operation in the plug flow regime. Near isothermal temperature profile for the reaction zone were achieved for temperatures in the range of 550 to about 1000$_o$C. Space time ranged from 0.05 to 3.0 seconds in a reaction zone of 45 cm., in flow tubes of varying diameter.

4.1 MATERIALS AND APPARATUS

The chloroform used was 99.9% pure´Baker Analysed´, HPLC reagent grade. The trichloroethylene (Stabilized) used was 100.0 % pure ´Baker Analysed´, epichlorohydrin free, reagent grade.

Vycor or Quartz tubes of interal diameters 0.4, 1.05, 1.6 cm. were used for the kinetic studies.

A schematic diagram of the experimental apparatus is shown in Figure 3. Hydrogen was used as both a carrierand reagent gas. Calibrated rotameters were used to controlthe 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 a ice-water bath. The other part of the hydrogen flow was used to achieve the desired molar ratio between hydrogen and chlorinated hydrocarbon. The mixed vapors were then

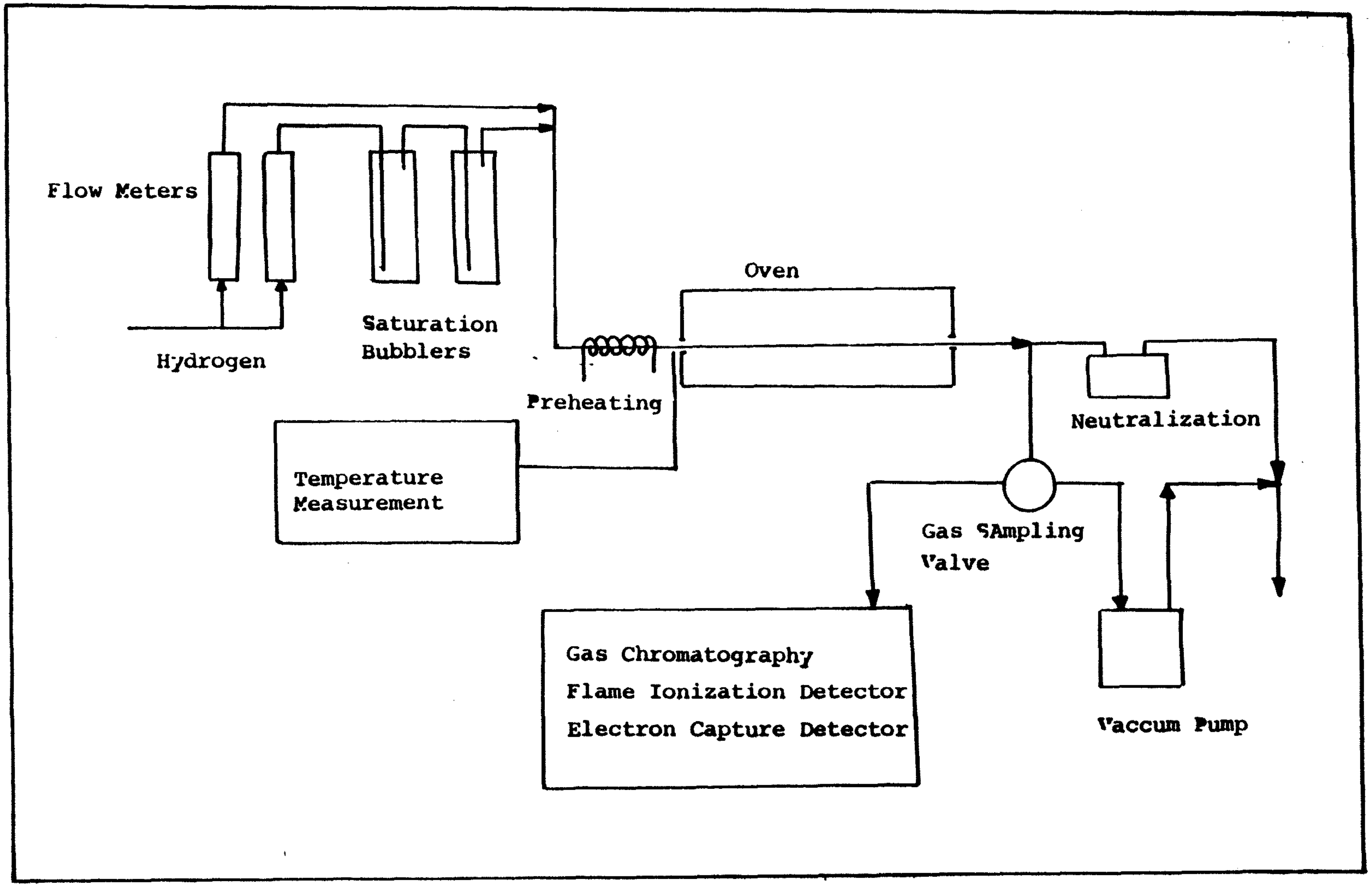


FIGURE 3. EXPERIMENTAL SET UP

preheated to about 400^{o}C. before passing through the actual reaction zone. It has previously been determined that no reaction takes place below 450^{o}C in the space times used for this work. The reactor outlet is maintained at about 100^{o}C to prevent product condensation.

Mellen clamshell type furnaces were used fot the reactor oven. The oven consisted of three heating zones. A 12 inch 230 volt section was flanked by a 3 inch 120 volt section on each side. The smaller sections provided greater control over the end zone effects. The furnace temperature was controlled by variacs. Bricks were used for insulation.

The reactor outlet gases were passed through a loosely packed plug of glass wool before going through a mixing zone to trap any entrained solids like carbon. Less than one- fifth of the minimum flow rate was routed through a six port Valco Model CV-6hpax sampling valve installed in a Tracor 550 Gas Chromatograph, with the help of a vacuum pump and needle vacuum control. The remainder of the outlet gases were passed through a sodium-bicarbonate solution bubbler before being released to the atmosphere via a hood.

4.2 TEMPERATURE MEASUREMENT

Omega chromel-alumel thermocouples linked with a Omega Model 650 Microprocessor Controlled Temperature Indicator were used for measuring the temperature profile of the reactor. Thermocouple linearization, cold junction compensation gain and off-set error correction were automatically performed by the internal firmware in the indicator.

Temperature measurements were carried out with a very dilute mixture of the compound under study and hydrogen flowing through the reactor at a median flow rate. Excessive carbon deposits were observed on the stainless steel sheathing material of the thermocouple. Readings were taken every 5 cm. along the length of the reactor, taking care to observe that steady state was reached for every point.

The profile obtained as shown in Figure 1 was isothermal within +/- 5^{o}C for between 80 to 85 % of the reactor length. The analysis of non-isothermal systems has been discussed in the Theory section.

4.3 DATA COLLECTION AND ANALYSIS

Before each sample was injected to an on line Tracor Model 550 Gas Chromatograph modified for Flame-Ionization as well as Electron Capture detection, steady state conditions were allowed to be reached in the reactor. An irregularly shaped outlet tube as well as the glass wool packing installed in it helped to break the laminarflow profile and mix the outlet gases for obtaining a well mixed sample. Each sample analysis by the chromatograph took about 20 minutes. During this period pure hydrogen was passed through the reaction zone. This prevented the build up of any carbon layer on the reaction surface and the consequent suppression of the wall reaction. Hydrogen chloride measurement 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 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.

A two meter long, 1/8 inch O.D., stainless steel tube packed with D.C. 200, 30 % on citrompak column was used for separation of reaction products. It was kept at 50_{o}C. for 2.5 minutes and then raised to 120 degrees at the rate of 20 degrees per minute. Elution of all products occured in about 10 minutes total time. Another 10 minutes were 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 (4), by injecting known quantities of the revelant compounds such as chloroform, dichlorometane, carbontetrachloride, etc., and then comparing the corresponding responce area. The relative factor was determined for the four compounds shown in Table 1. 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 (26).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.

Qualitative analysis of the products was done with the help of a GC/Mass Spectrometer. Samples were collected in evacuated Pyrex bulbs. The GC/MS used was a 60 meter OV 101 WCOT fused silica capillary column, electron impact ionization, and a dual disc Varian microcomputer data system.

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 propylene could be identified and measured.Samples of five cc were injected into the column which was kept at 110_{o}C. No elution of heavier products was observed.

TABLE 1

RESPONSE FACTORS OF SEVERAL CHLOROCARBONS*

Component	Response Factors		
	Run 1	Run 2	Average
CH_2CL_2	1	1	1
$CHCL_3$	0.938	1.03	0.984
CCL_4	1.058	1.31	1.18
1,1,2-$C_2H_3CL_3$	1.881	2.33	2.105

* Data is from Chuang (4). Normalization based on mole numbers of 0.2 µl liquid.

5. RESULTS AND DISCUSSION

5.1 REACTION OF $CHCL_3$ WITH H_2

The reaction parameter values for the study of the reactionof chloroform with hydrogen are listed below :

Temperatures (^oC) : 561, 604, 653, 748, 835, 982.
Reactor Length : 45 cm.
Reactor Diameters (cm) : 0.4, 1.05, 1.6
Reactant Ratios : $CHCL_3$: H_2 :: 1:9, 1:17
Residence Time Range: 0.05 - 1.2 sec.(0.4 cm Diam. Reactor)
0.2 - 2.5 sec.(1.05 cm Diam. Reactor)
0.5 - 2.5 sec.(1.6 cm Diam. Reactor)

All Figures mentioned below are for the 1.05 cm diameter reactor and data are from the runs at the concentration ratio of 1:9.

Data from runs at temperatures 561, 604 and 653 ^oC were used for estimating kinetic parameters. The data for the conversion chloroform at these temperatures are shown in Figure 4. The plot shows that conversions upto 25%, 50% and 90% are achieved at 561, 604 and 653^oC respectively. At higher temperatures the conversion is too high for reliable kinetic analysis.

Integrated rate equations plots for the conversion of chloroform for half order, first order and second order rate equations are shown in Figure 5. The data indicates that the reaction closely follows the first order decay plot, with the half order plot also showing a reasonable fit. Plots with data from runs at other temperatures and from the two other size reactors also show that the data best fits the integrated first order rate equation. The first order plots for chloroform at different temperatures are shown in Figure 6. The global rate constants " k´ ", are obtained from such plots. The data at low residence times, high linear velocities, tends not to follow the lines for high temperatures. This discrepency is probably due greater non-uniformity in the temperature profile from the combined effects of higher temperatures and velocity. Another reason may be the incomplete saturation of the hydrogen with chloroform due to high velocity.

Kaufman´s (36) equation is used to find the homogenous and wall rate constants, " k_h ", and " k_w ", respectively. This is done by plotting k´ against 2/R, where R is the radius of the reactor in centimeters. Two such plots are shown in Figure 7. The slope is k_w and the intercept is k_h.

The activation energies are found from Arrenhius plots such as those shown in Figure 8., and Figure 9. Activation energies for the wall and homogenous rate constants as well as the global rate constants are found.

The values found for all the parameters discussed above are listed in Table 2 and Table 3. Table 2 lists the results without application of the corrected reactor volume method.

FIGURE 4

$CHCL_3 + H_2$ :: 1:9

REACTOR DIA. 1.05CM.

DECOMPOSITION CURVES

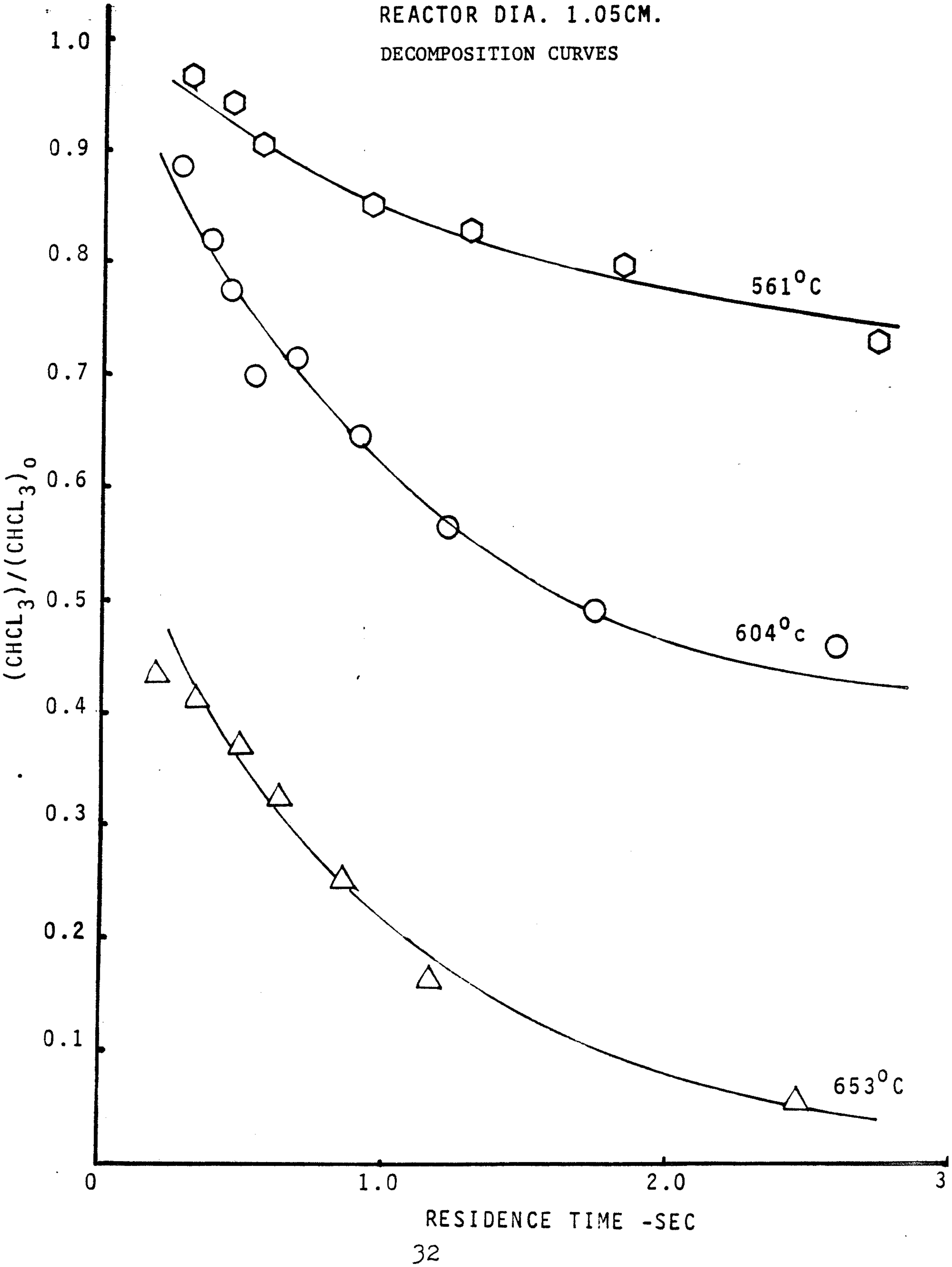
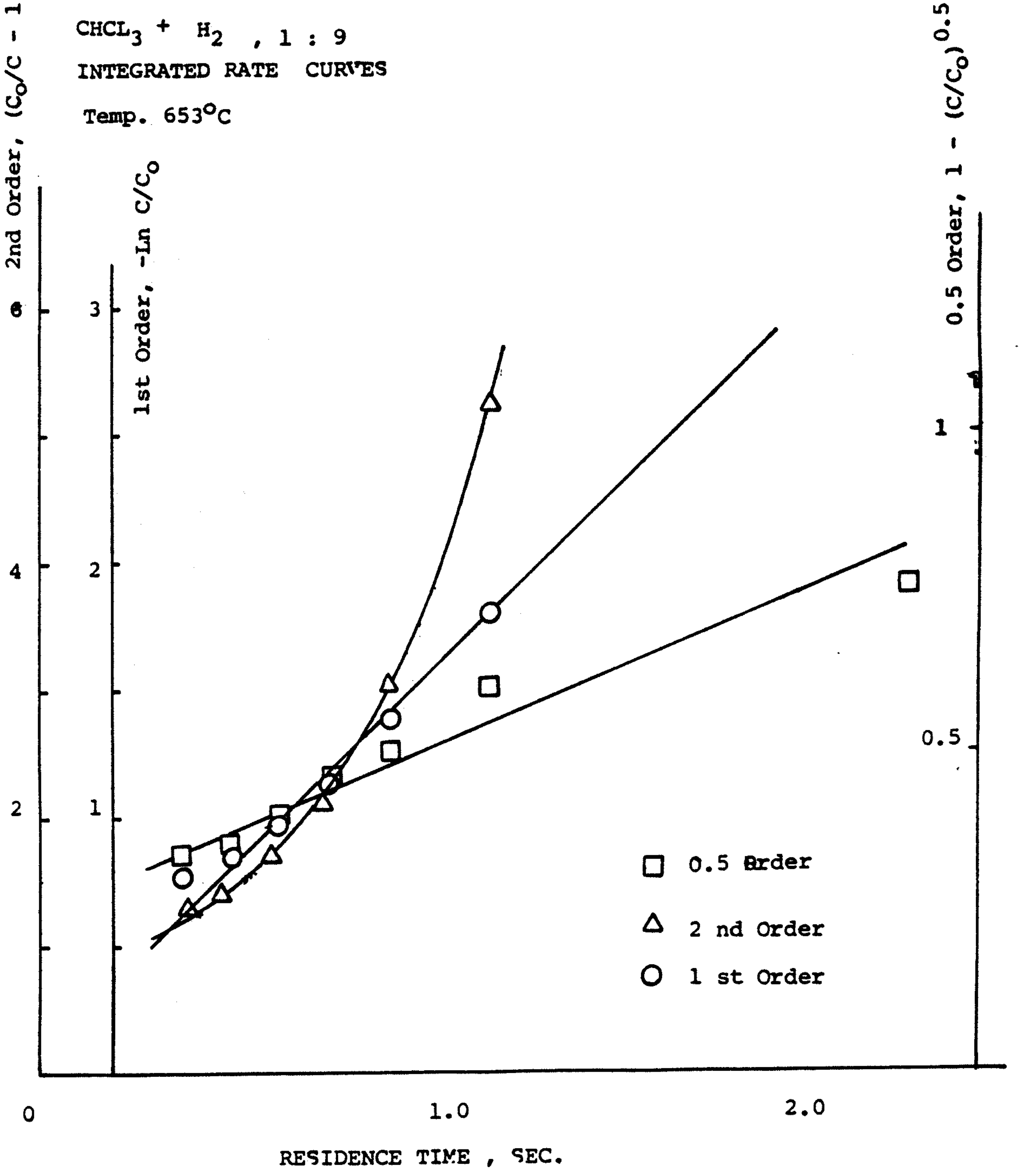


FIGURE 5

$CHCL_3 + H_2$, 1 : 9

INTEGRATED RATE CURVES

Temp. 653°C



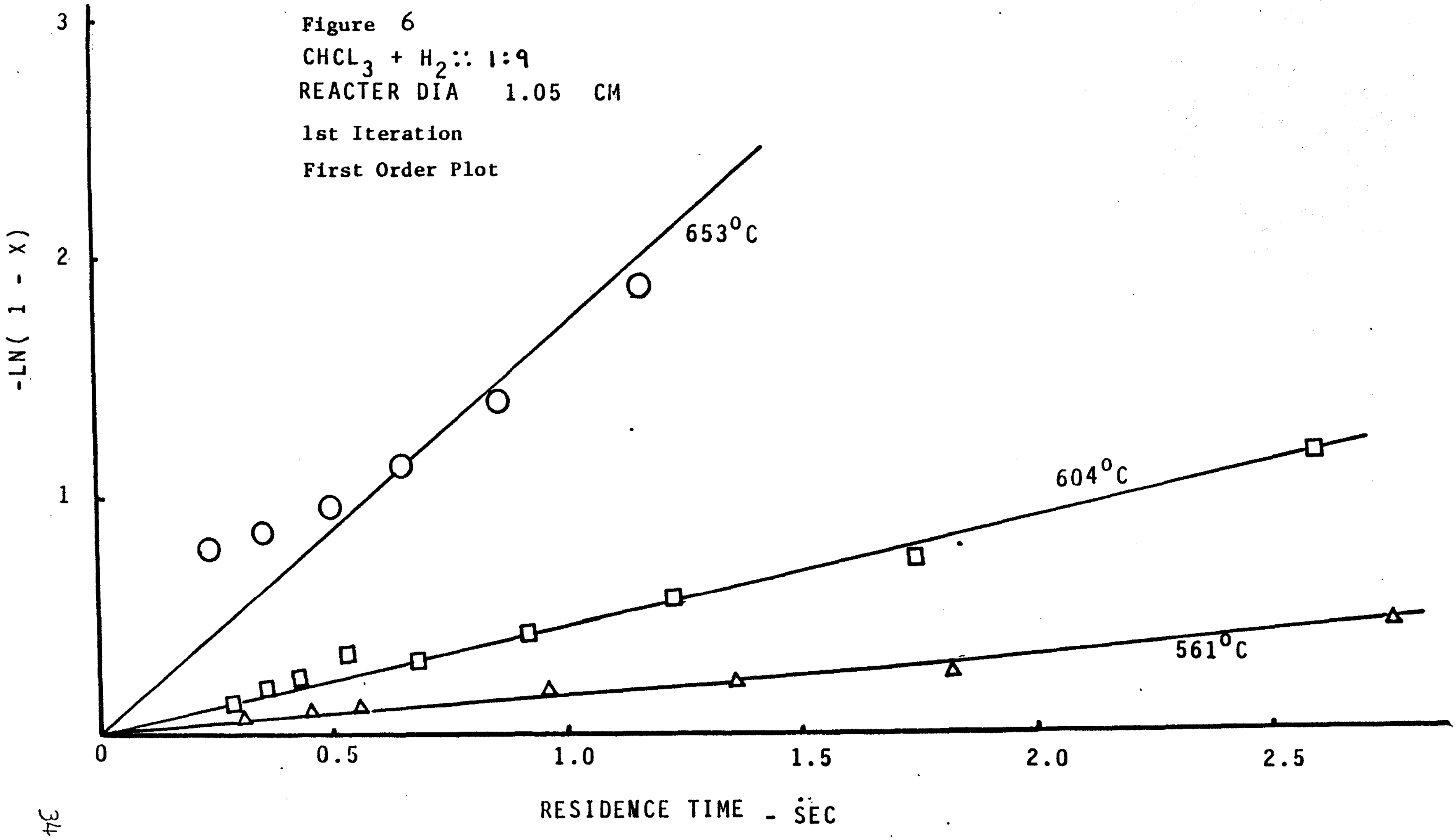


Figure 6
$CHCL_3 + H_2$ :: 1:9
REACTER DIA 1.05 CM
1st Iteration
First Order Plot

FIGURE 7
$CHCL_3 + H_2$ :: 1:9
1st ITERATION
K' vs 2/R PLOT

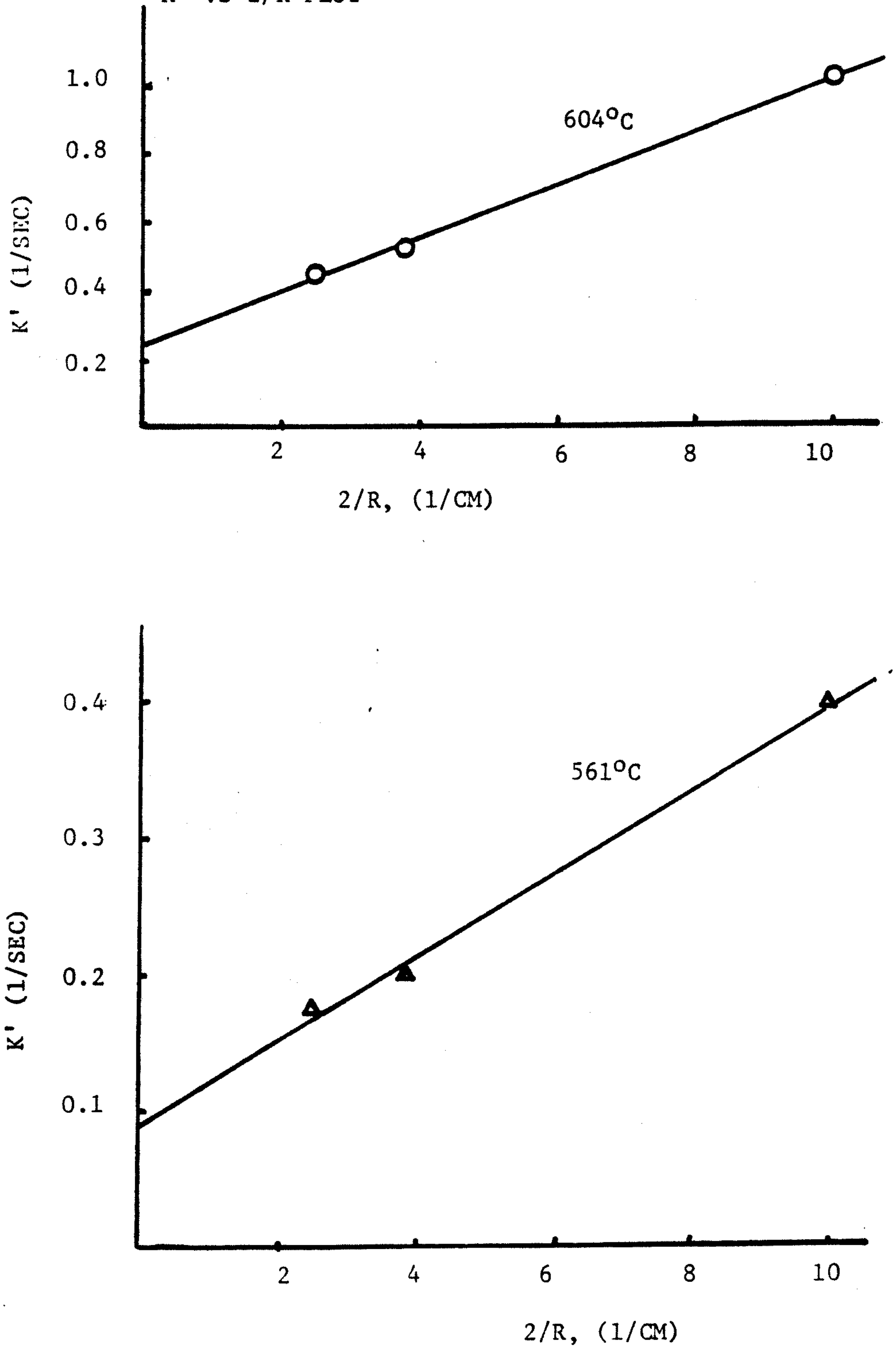


Figure 8
$CHCL_3 + H_2$

REACTOR DIA. 1.05CM.
1st Iteration
Arrenhius Plot

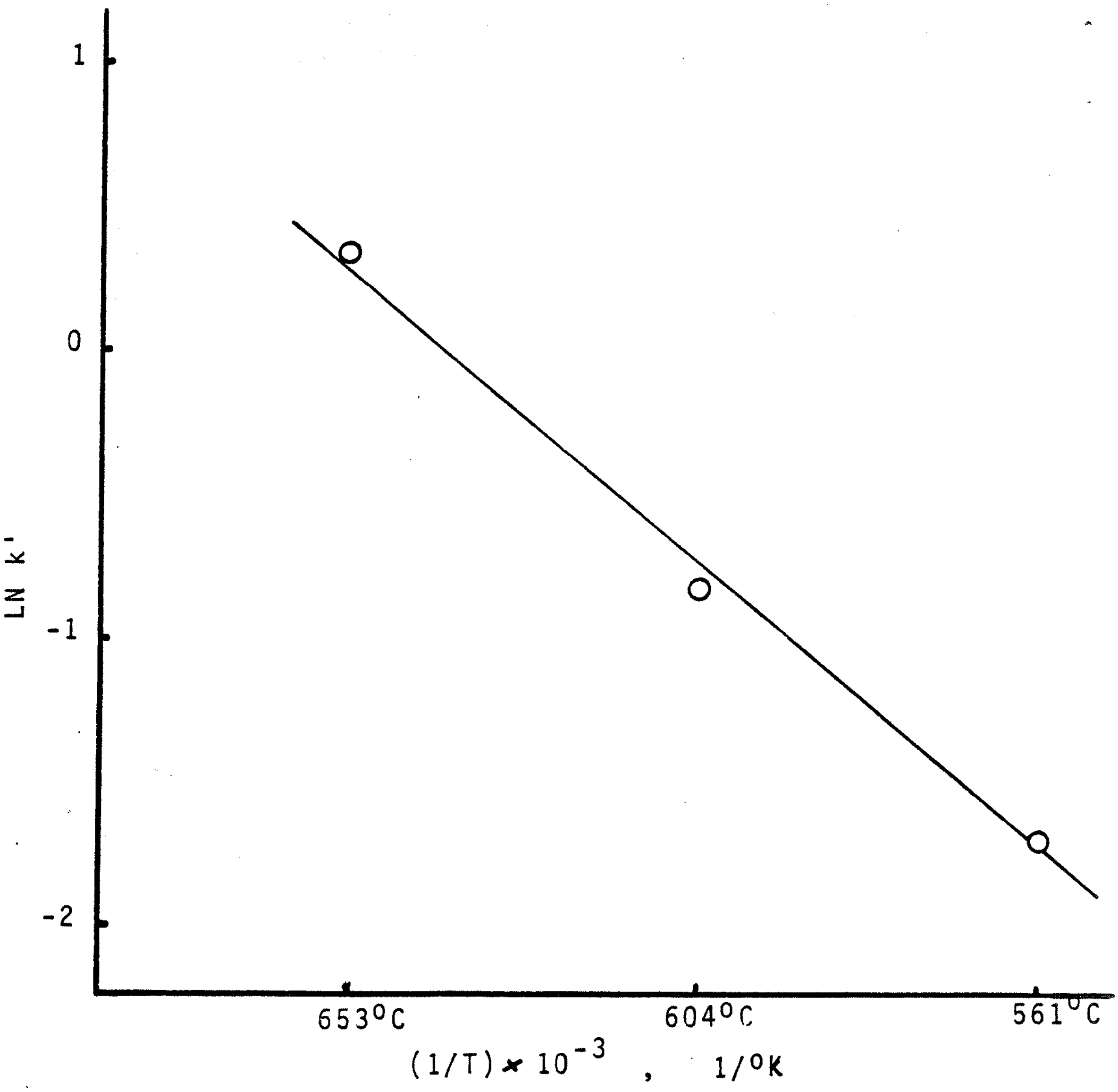


Figure 9
$CHCL_3 + H_2$ :: 1:9
1st Iteration
Arrhenius Plot

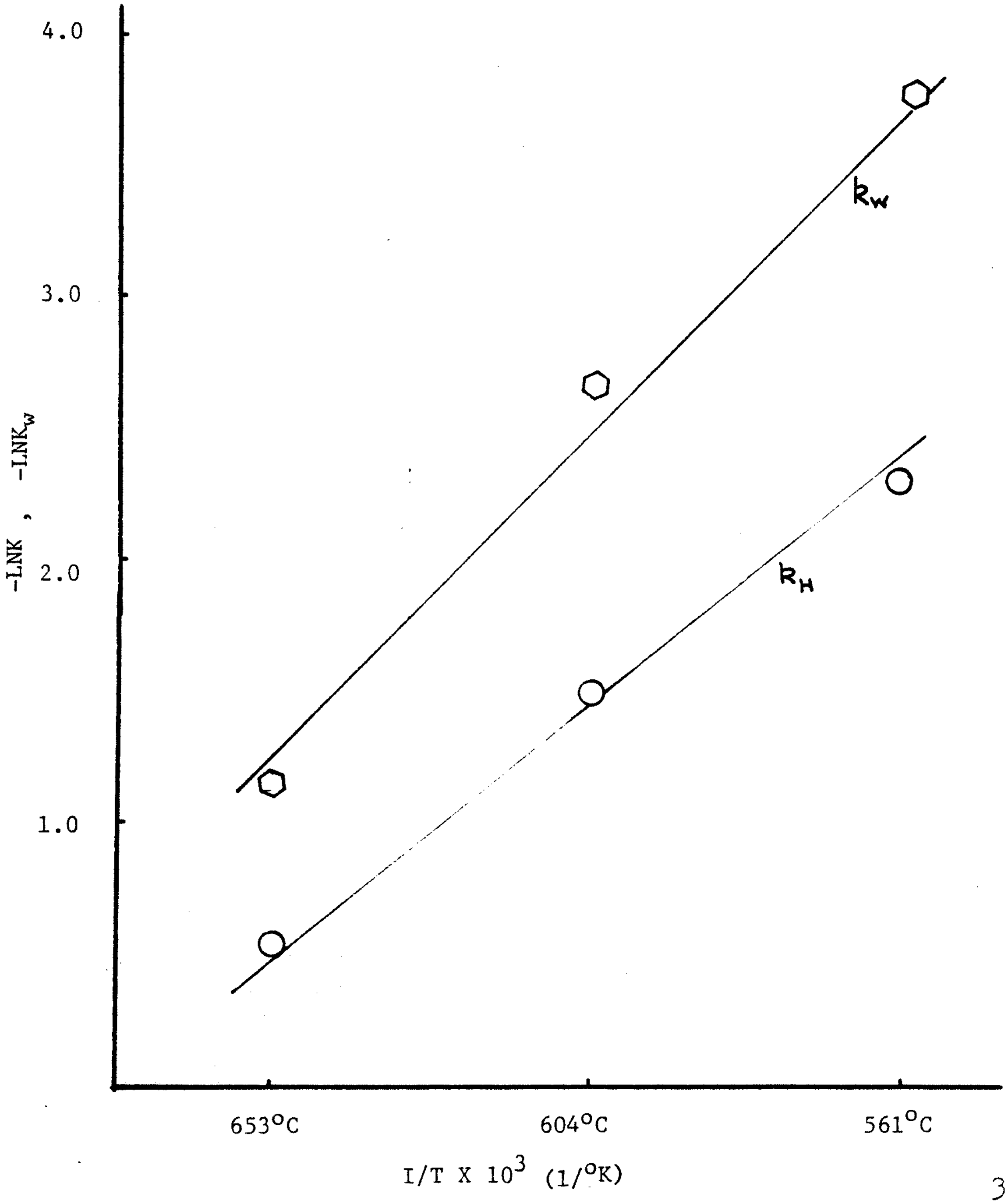


Table 3 lists the results after correction.

The results for the chloroform to hydrogen ratios of 1:9, and 1:17 are shown. Whereas the concentration of the chloroform changes by a factor of almost two the concentration of hydrogen does not change significantly. The actual concentrations are

$CHCL_3 : H_2$

1 : 9 $(1.2188*10^{-3})*1/T : 10.97*10^{-3}*1/T \quad \frac{Mol\,^{\underline{o}}k}{cm^3}$

1 : 17 $(0.6816*10^{-3})*1/T : 11.578*10^{-3}*1/T$ "

The two sets of results would have varied significantly if the dependency of the global rate constants on the concentration of chloroform were other than the assumed first order.Table 3. shows that at temperatures below 700° the wall reaction has a higher activation energy than the homogenous reaction indicating that the wall tends to stabilize the reaction. The vapor phase value of 35.3 +/- 1.7 kcal/mol. for the activation energy is in fairly close agreement with the value found by Semeluk and Bernstein (6) for the unimolecular decomposition of chloroform. However Shilov and Sabirova (7) have found a much higher activation energy of about 47 kcal/mol.

Attempts to establish the order of hydrogen by use of the Arrenhius type equation $k' = k_o * e^{-E/RT} * [H_2]$ failed to provide reliable results due to the close proximity of the two hydrogen concentrations.

Taking $k_o*[H_2]^a$ = A to be the frequency factor for this analysis where the order of the hydrogen depenendcy "a" is unknown Table 4 is constructed. An average value of E = 39040 cal/mol is used in those calculations involving k', and actual values of E from Table 3 are used for calculations involving k_h and k_w.

Table 5 gives the values of " k_o ", when " a " is assumed to be one. Since the data for the concentration ratio between chloroform and hydrogen of 1 : 9 is more reliable due to the comparatively higher concentration of chloroform, the average value of k_o is calculated from this set of data, giving :

$k_h = 3.86*10^{12}e^{-35.3/RT}$ $(sec.)^{-1}$ for the gas phase reaction

$k_w = 3.24 * 10^{14}e^{-43.4/RT}$ $(sec.)^{-1}$ for the wall reaction.

Data for the probability of reaction due to wall collisions is shown in Appendix 1.

5.2 PRODUCT DISTRIBUTION FOR CHLOROFORM

The major products observed were C_2H_4, C_2H_2, CH_4 CH_2CL_2, C_2HCL_3, C_6H_6, C_3H_4, $C_2H_2CL_2$, CH_3CL and HCL Product distribution as a function of time for the reactions at 561, 604, 653°C are shown in Figures 10, 11 and 12. These plots indicate that the major product below 700°C is methylene chloride with ethane, ethylene, acetylene and methane as the other major products. Chloromethane, a product found in earlier studies is observed only above 600°C and as can be seen in Figure 13 is not found at all above 750°C.

Plots of stable products versus temperature of reaction at residence times between 0.5-0.6 seconds are shown in Figures 13 and 14. Figure 13 shows that benzene production is less than 2.5 % of the parent chloroform. Complete conversion of chloroform to benzene which would utilize six carbons or six chloroform molecules would result in 16.6 % of the parent chloroform. The Figure also shows that $CHCL_3$ and $C_2H_2CL_3$ are not observed above 850°C .Figure 14 shows that the combination of acetylene, ethylene and methane production accounts for more than above 90 % of the parent chloroform for temperatures higher than 800°C. All chlorinated products as well as chloroform are destroyed above 850°C.

A material balance for 100 moles of carbon (100 moles of chloroform) at different temperatures in the residence time range of 0.5 to 0.6 seconds is shown in Table 6. The Table shows that at temperatures above 800°C all carbon is accounted for. This indicates that no free carbon is deposited at these temperatures and no other products other than those listed are formed.

Small quantities of vinyl chloride, chlorobenzene, and toluene were detected at lower temperatures as well as the other products. Table 7 is the material balance for 300 moles of chlorine (100 moles of chloroform). Unaccounted for chlorine at temperatures below 700°C is small showing that very little higher chlorinated products are formed. For temperatures above 700^{o}C the larger fractions the unaccounted chlorine is probably due to reaction of HCL with either the metal of the valves in the outlet lines or with the material of the plastic tubing.

TABLE 2

FIRST ITERATION RATE CONSTANTS FOR $CHCL_3 + H_2$ *

$CHCL_3 : H_2 :: 1 : 9$

Dia.(cm.)	0.4	1.05	1.6	k_h	k_w
Temp.(^{o}C)					
561	0.365	0.175	0.164	0.10	0.023
604	0.962	0.473	0.42	0.23	0.072
653	5.78	1.714	1.385	0.56	0.334
E cal/mol	38000	35000	41000	33000	41000

$CHCL_3 : H_2 :: 1 : 17$

561	0.355	0.213	0.148	0.07	0.026
604	1.09	0.746	0.575	0.34	0.084
653	6.67	1.93	1.85	0.72	0.452
E cal/mol	44000	36000	42000	35000	43000

* Units for rate constants are (sec.)$^{-1}$

TABLE 3

SECOND ITERATION RATE CONSTANTS FOR CHLOROFORM*

$CHCL_3 : H_2 :: 1 : 9$

Dia.(cm.	0.4	1.05	1.6	k_h	k_w
Temp.(°)					
561	0.399	0.191	0.179	0.088	0.030
604	1.028	0.505	0.449	0.258	0.077
653	6.53	1.937	1.565	0.56	0.334
E cal/mol	38000	37600	36200	33600	43000

$CHCL_3 : H_2 :: 1 : 17$

Dia.(cm.)	0.4	1.05	1.6	k_h	k_w
Temp.(°C)					
561	0.388	0.233	0.182	0.115	0.031
604	1.26	0.797	0.614	0.39	0.082
653	7.54	2.18	2.09	0.83	0.477
E cal/mol	42800	38000	41600	37000	43800

* Units for rate constants are $(sec.)^{-1}$

TABLE 4

FREQUENCY FACTOR $A*10^{-9}$

$CHCL_3$: H_2 :: 1 : 9

Dia.(cm.) Temp.(°C)	0.4	1.05	1.6	k_h	k_w
561	5.828 *	2.792 *	2.616 *	0.049#	4.709+
604	4.767	2.341	2.083	0.054	3.415
653	9.325	2.341	2.083	0.042	4.048
$CHCL_3$: H_2 :: 1 : 17					
561	5.673	3.41	2.661	0.495**	7.86##
604	5.846	3.70	2.848	0.565	5.738
653	10.77	3.113	2.985	0.394	8.905

Value of Activation Energy used :

* E = 39040 cal/mol (average value from global rate constants)

\# E = 33600 cal/mol

\+ E = 43000 cal/mol

** E = 37000 cal/mol

\## E = 43800 cal/mol

The frequency factor A has units of $(sec.)^{-1}$

TABLE 5

FREQUENCY FACTOR K_o

$CHCL_3 : H_2 :: 1 : 9$

Temp. (°C)	GAS PHASE	WALL
561	$3.725 * 10^{12}$	$3.58 * 10^{14}$
604	$4.317 * 10^{12}$	$2.73 * 10^{14}$
653	$3.545 * 10^{12}$	$3.417 * 10^{14}$

$CHCL_3 : H_2 :: 1 : 17$

561	$3.565 * 10^{13}$	$5.662 * 10^{14}$
604	$4.28 * 10^{13}$	$4.346 * 10^{14}$
653	$7.121 * 10^{13}$	$7.121 * 10^{14}$

The frequency factor k_o has units of $cm^3/mol.\ sec.$

TABLE 6 *

MATERIAL BALANCE FOR 100 MOLES CARBON FOR $CHCL_3 : H_2 :: 1 : 9$

REACTOR DIAMETER 1.05 CM.

TEMP°C	561	604	653	748	835	982
CH_4	0.2	0.34	1.02	4.0	5.64	13.21
C_2H_2 + C_2H_4	0.49	1.27	10.13	53.12	82.32	71.40
C_2H_6	0.9	2.48	4.24	6.68	2.48	-----
C_3H_4	----	0.14	4.65	4.72	-----	-----
CH_3CL	----	0.03	1.47	----	-----	-----
CH_2CL_2	5.98	13.74	21.85	14.07	0.19	-----
$C_2H_2CL_2$	0.05	0.51	1.63	0.34	-----	-----
C_6H_6	----	0.29	2.26	9.98	10.18	15.39
C_2HCL_3	3.62	6.38	6.63	1.54	-----	-----
$CHCL_3$	84.67	69.8	32.0	0.13	-----	-----
TOTAL	95.91	94.98	85.86	94.58	101.3	100
RES.TIME (sec.)	0.52	0.50	0.58	0.6	0.57	0.56

*Based on carbon detected by flame ionization detector.

TABLE 7

MATERIAL BALANCE FOR 300 MOLES CHLORINE

$CHCL_3 : H_2 :: 1 : 9$

REACTOR DIAMETER 1.05 CM.

TEMP^oC	561	604	653	748	835	982
CH_3CL	---	0.03	1.47	---	---	---
CH_2CL_2	11.96	27.48	43.7	28.14	0.38	---
$C_2H_2CL_2$	0.05	0.51	1.63	0.34	----	---
C_2HCL_3	5.41	9.57	9.95	2.31	----	---
$CHCL_3$	254	247	163	31.2	0.38	---
HCL	N.A.	47.5	129	184	211	258
TOTAL	271.4	294.1	281.7	215.2	211.4	258
RES.TIME (sec)	0.52	0.50	0.58	0.6	0.57	0.58

N.A. = Not available.

MECHANISM FOR THE REACTION OF CHLOROFORM WITH HYDROGEN

A simple mechanism which explains the stable products and kinetics observed is shown below. It is not meant to be exhaustive and is only one of many possible sets of reaction steps.

$$CHCL_3 \text{ -----> } CHCL_2 + CL$$

$$CL + H_2 \text{ <------> } HCL + H$$

$$H_2 + CHCL_2 \text{ -----> } H + CH_2CL_2$$

$$H + CHCL_2 + M \text{ ------> } M + CH_2CL_2$$

$$CHCL_2 + CHCL_2 \text{ <------> } C_2H_2CL_4$$

$$C_2H_2CL_4 \text{ -----> } C_2HCL_3 + HCL$$

$$C_2HCL_3 \text{ -----> } C_2CL_2 + HCL$$

$$C_2CL_2 + H_2 \text{ -----> } C_2H_2CL_2$$

$$C_2H_2CL_2 \text{ ------> } C_2HCL + HCL$$

$$C_2HCL + H_2 \text{ -----> } C_2H_3CL$$

$$C_2H_3CL \text{ -------> } C_2H_2 + HCL$$

$$C_2H_2 + H_2 \text{ -----> } C_2H_4$$

Figure 10

$CHCL_3 + H_2$ :: 1:9

REACTOR DIA. 1.05CM.

TEMP. 561°C

Product Distribution

1st Iteration

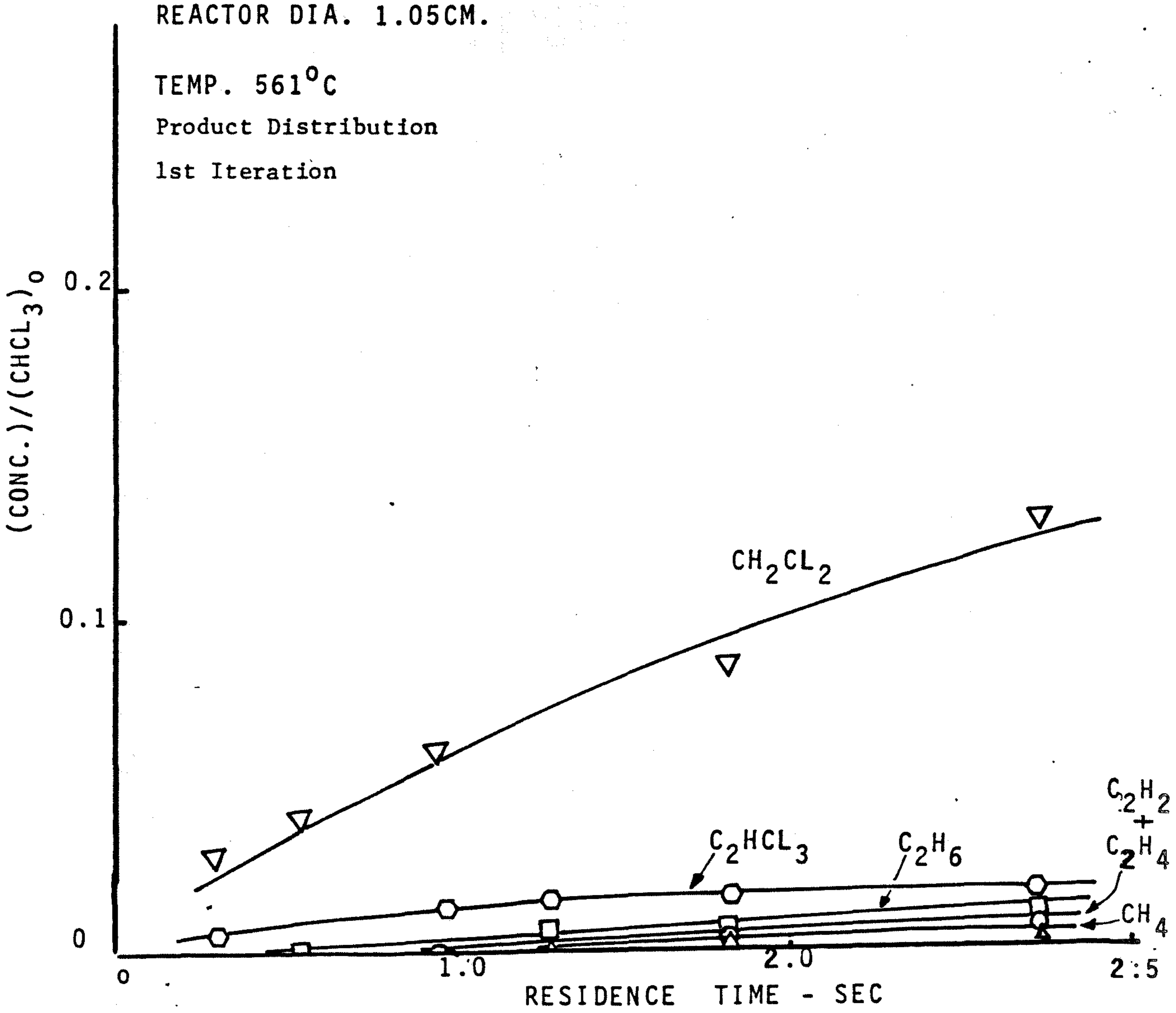


Figure 11

$CHCL_3 + H_2$

REACTOR DIA. 1.05CM.

TEMP. 605°C

1st Iteration

Product Distribution

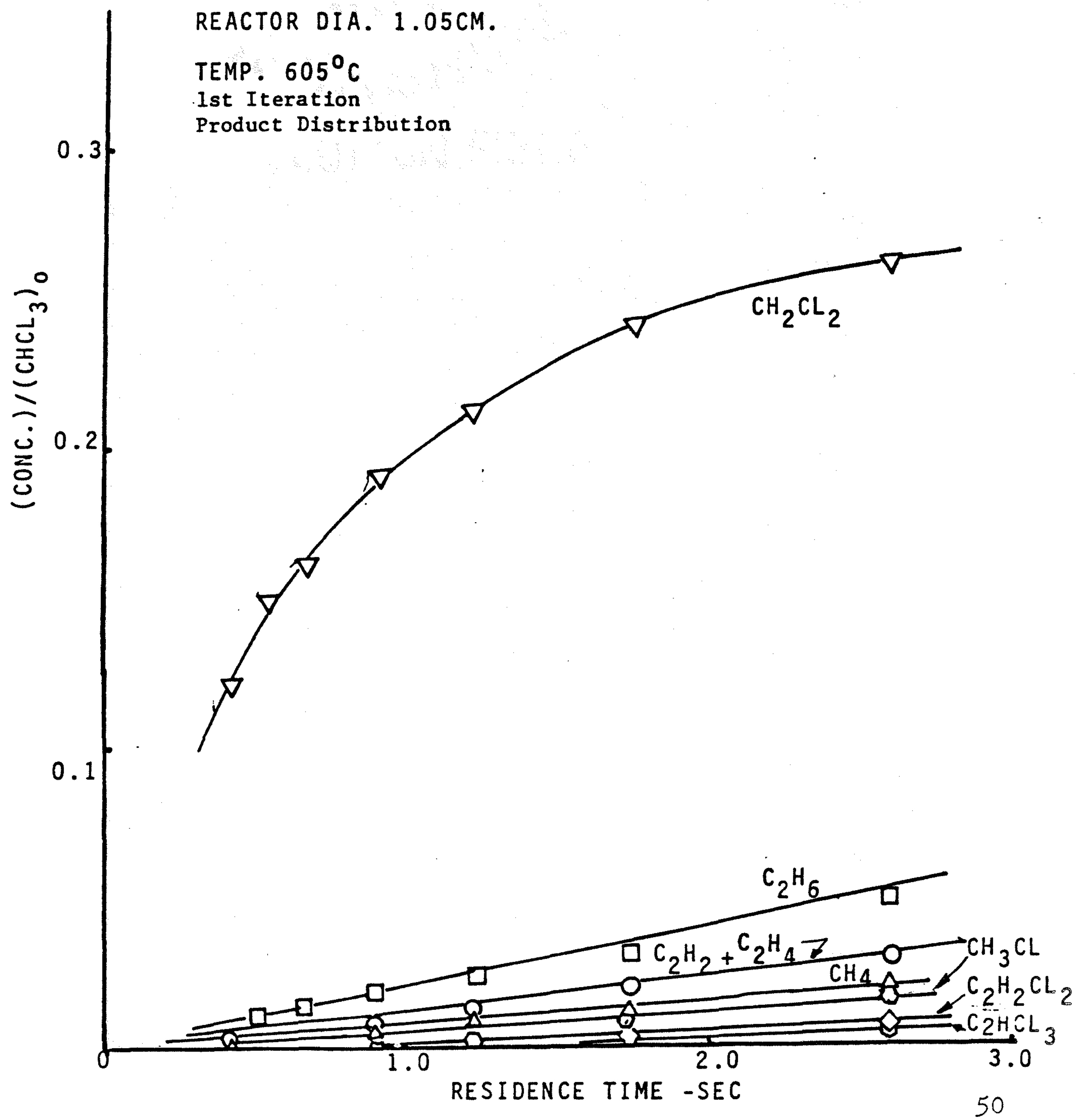


Figure 12
$CHCL_3 + H_2$
REACTOR DIA. 1.05CM
TEMP. 653°C
1st Iteration
Product Distribution

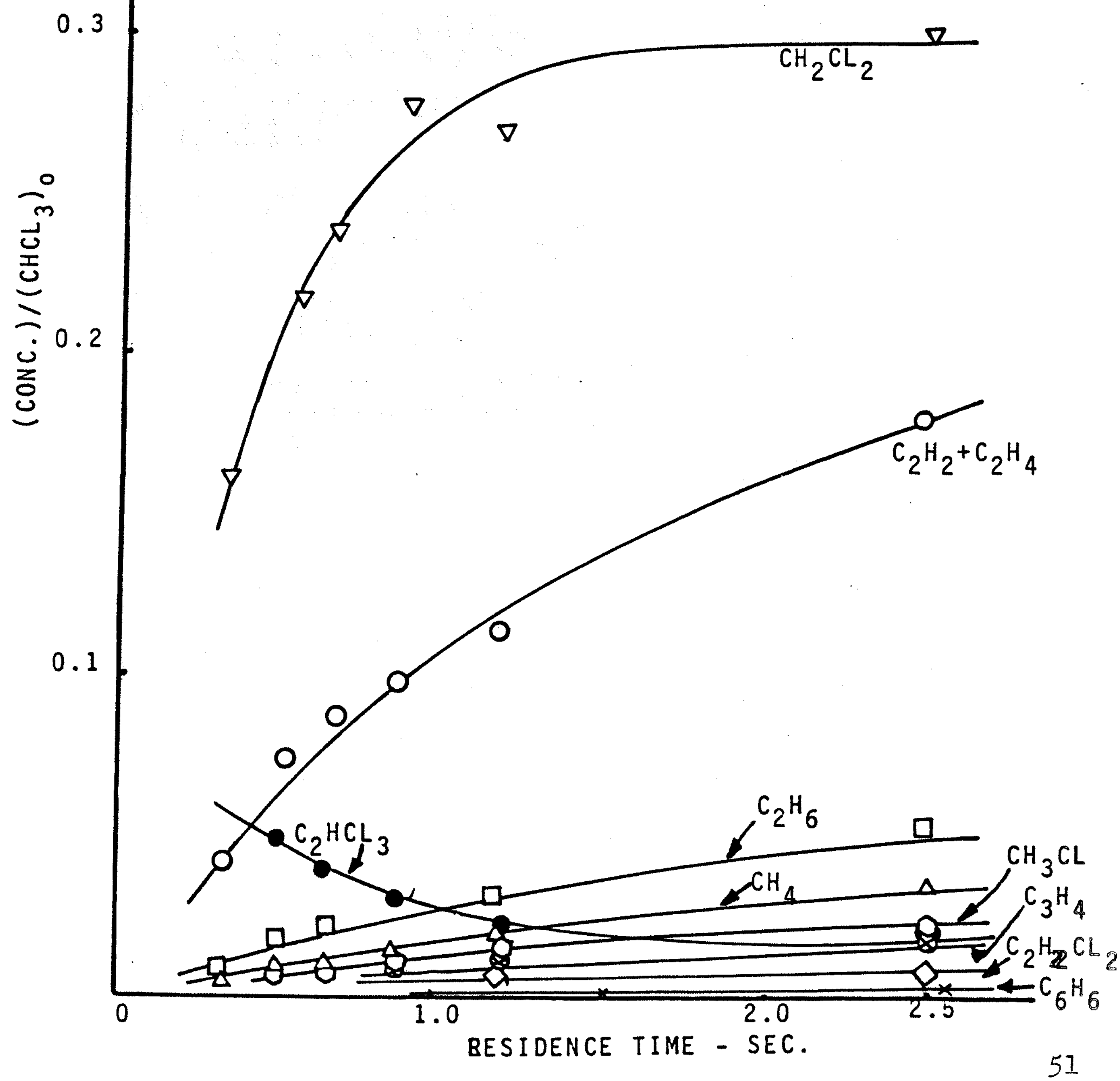


FIGURE 13

$CHCL_3 + H_2$

REACTOR DIA. 1.05CM.

RESIDENCE TIME 0.5-0.6 SEC.

PRODUCT DISTRIBUTION

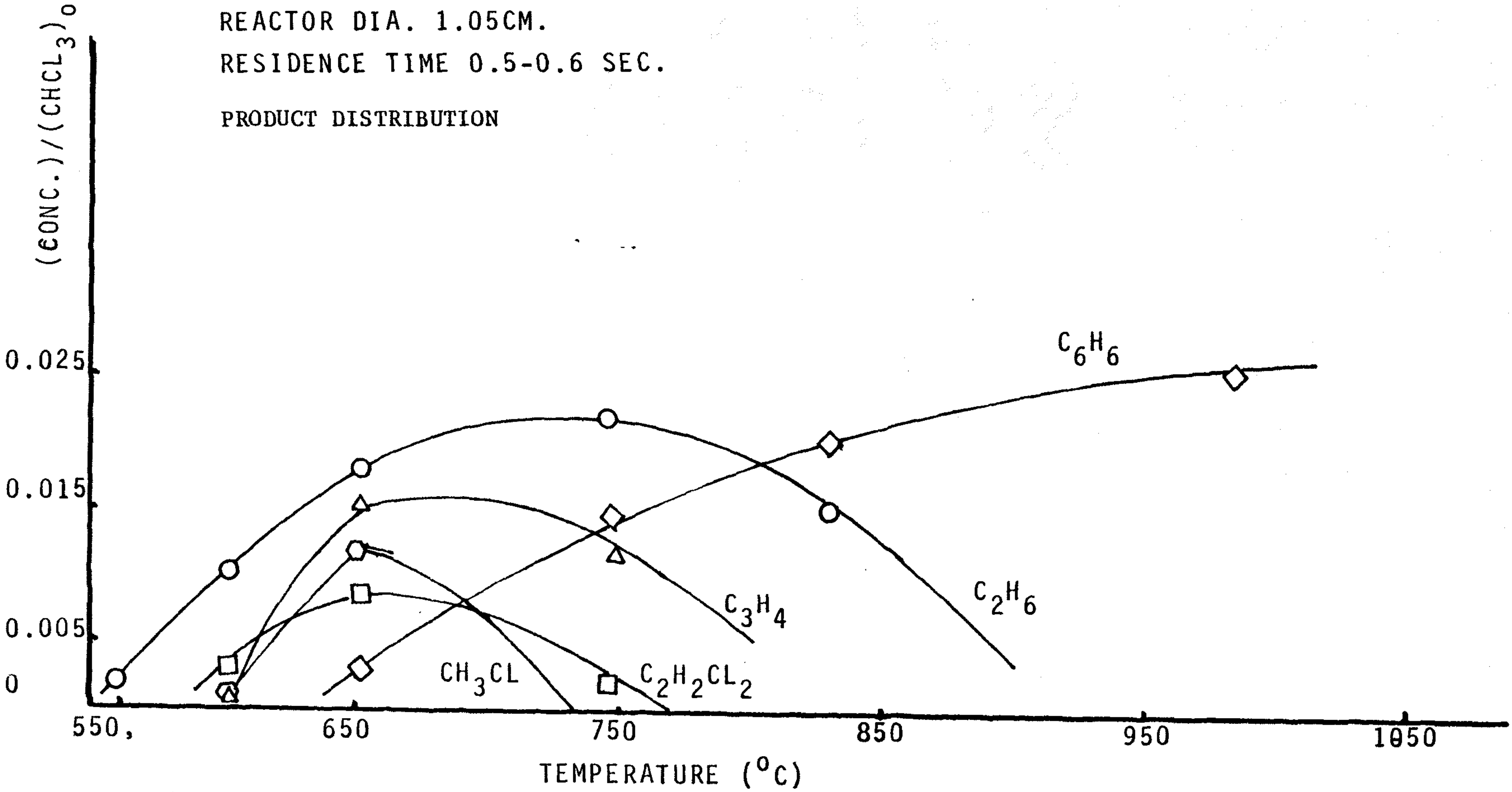


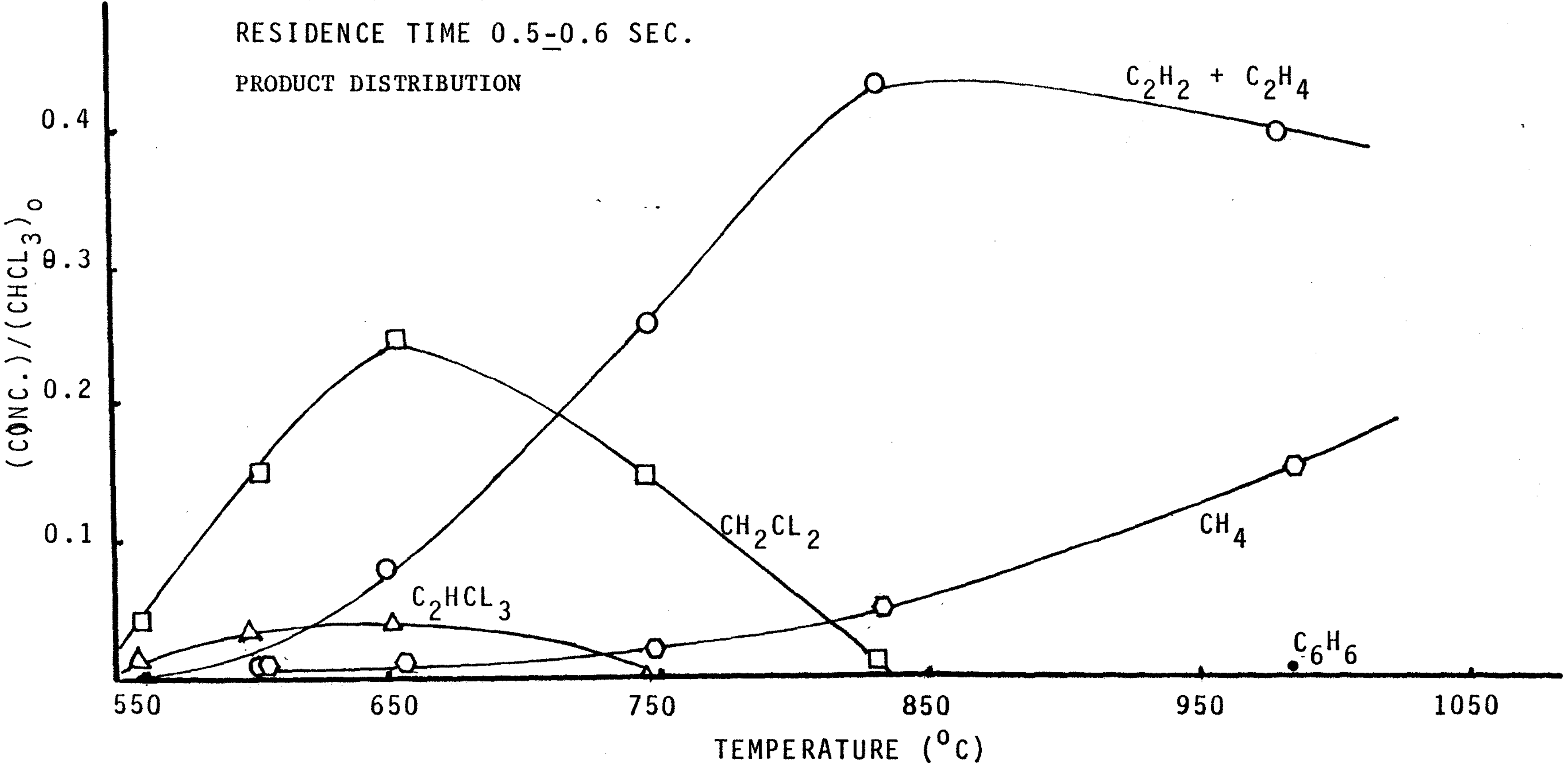
FIGURE 14

$CHCL_3 + H_2$

REACTOR DIA. 1.05CM.

RESIDENCE TIME 0.5-0.6 SEC.

PRODUCT DISTRIBUTION



5.3 REACTION OF C_2HCL_3 WITH H_2

The reaction variables for the study of the reaction of trichloroethylene with hydrogen are listed below:

Temperatures (°C): 604, 662, 698, 748, 853, 982
Reactor Length : 45 CM.
Reactor Diameters(cm) : 0.4, 1.05, 1.6
Reactant Ratios : C_2HCL_3 : H_2 :: 1:33, 1:58
Residence Time Range: 0.05 - 1.2 sec.(0.4 cm Diam. Reactor)
0.2 - 2.5 sec.(1.05 cm Diam. Reactor)
0.5 - 2.5 sec.(1.6 cm Diam. Reactor)

All Figures mentioned below are for the 1.05 cm. diameter reactor and data are from the runs at the concentration ratio of 1:33.

Data from runs at temperatures 604, 662 and 698 °C were used for estimating kinetic parameters. The conversion of trichloroethylene at these temperatures are shown in Figure 15. The plot shows that conversions upto 30%, 60% and 85% are achieved at 561, 604 and 653°C respectively. At higher temperatures the conversion is too high for reliable kinetic analysis.

Integrated rate equations plots of the conversion of trichloroethylene for half order, first order and second order rate equations are shown in Figure 16. The data indicates that the reaction closely follows the first order decay plot, with the half order plot also showing a reasonable fit. Plots with data from runs at other temperatures and from the two other size reactors also show that the data best fits the integrated first order rate equation. The first order plots for trichloroethylene at different temperatures are shown in Figure 17. The global rate constants " k´ ", are obtained from such plots. The data at low residence times, high linear velocities, tends not to follow the lines for high temperatures. This discrepency is probably due greater non- uniformity in the temperature profile from the combined effects of higher temperatures and velocity. Another reason may be the incomplete saturation of the hydrogen with trichloroethylene due to high velocity.

Kaufman´s(36) equation is used to find the homogenous and wall rate constants, " k_h ", and " k_w ", respectively. This is done by plotting k´ against 2/R, where R is the radius of the reactor in centimeters. These plots are shown in Figure 18. The slope is k_w and the intercept is k_h.

The activation energies are found from Arrenhius plots such as Figure 19. Activation energies for the wall and homogenous rate constants as well as the global rate constants are found.

The values found for all the parameters discussed above are listed in Table 8 . The values listed in this table are those calculated after correction for volume.

The results for the trichloroethylene to hydrogen

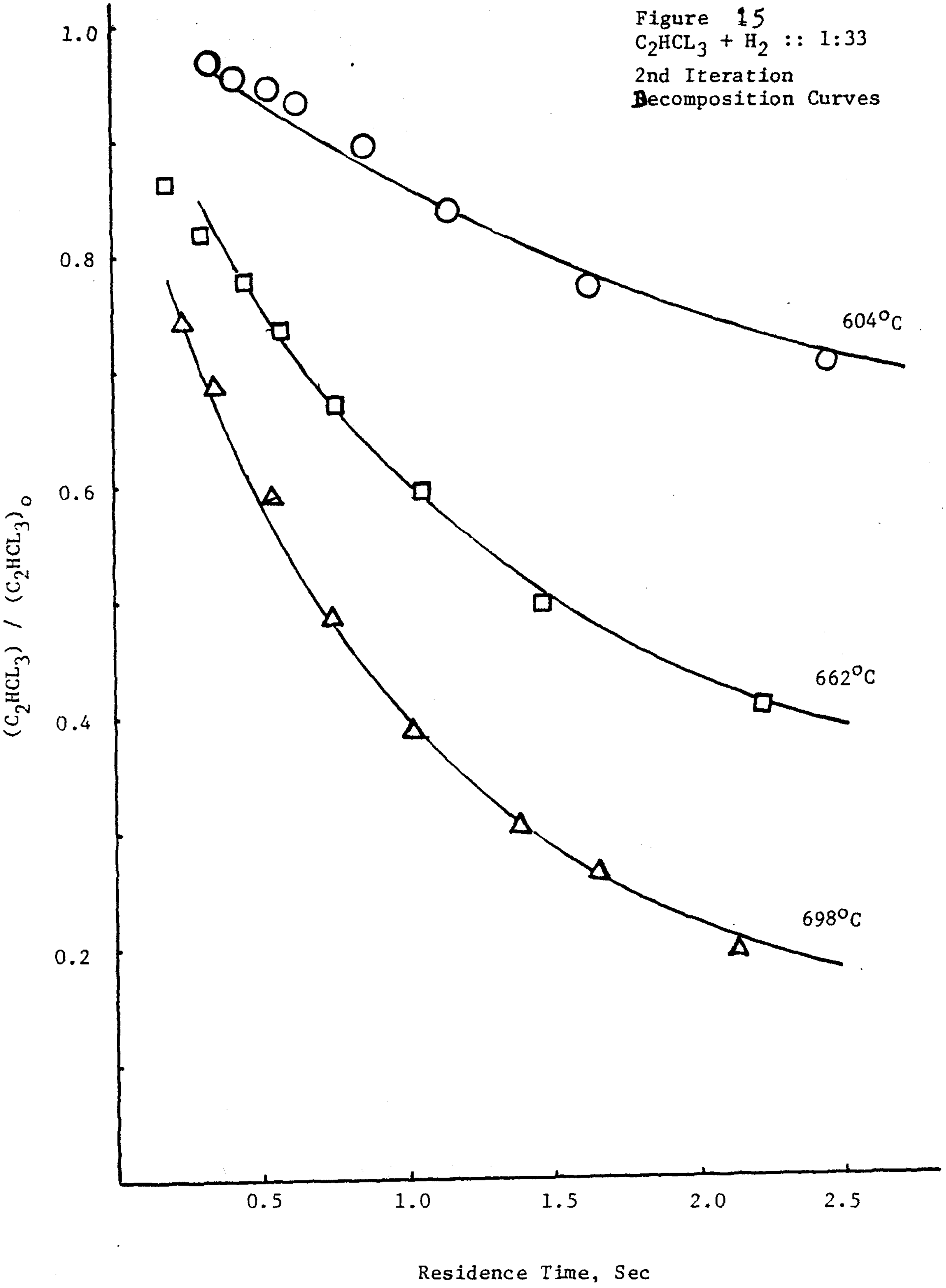


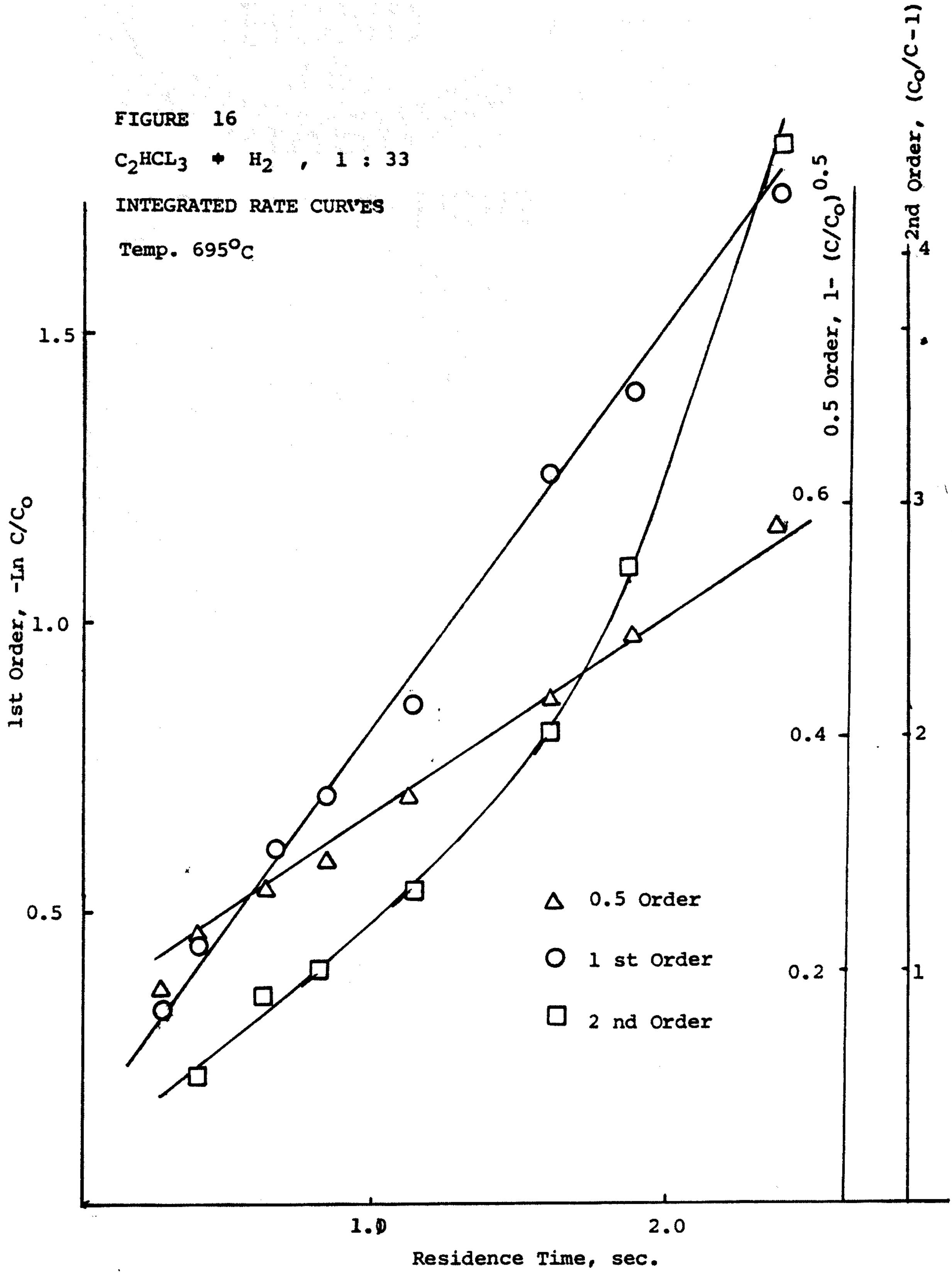
Figure 15
$C_2HCL_3 + H_2$ :: 1:33
2nd Iteration
Decomposition Curves

FIGURE 16

C_2HCL_3 + H_2 , 1 : 33

INTEGRATED RATE CURVES

Temp. 695°C



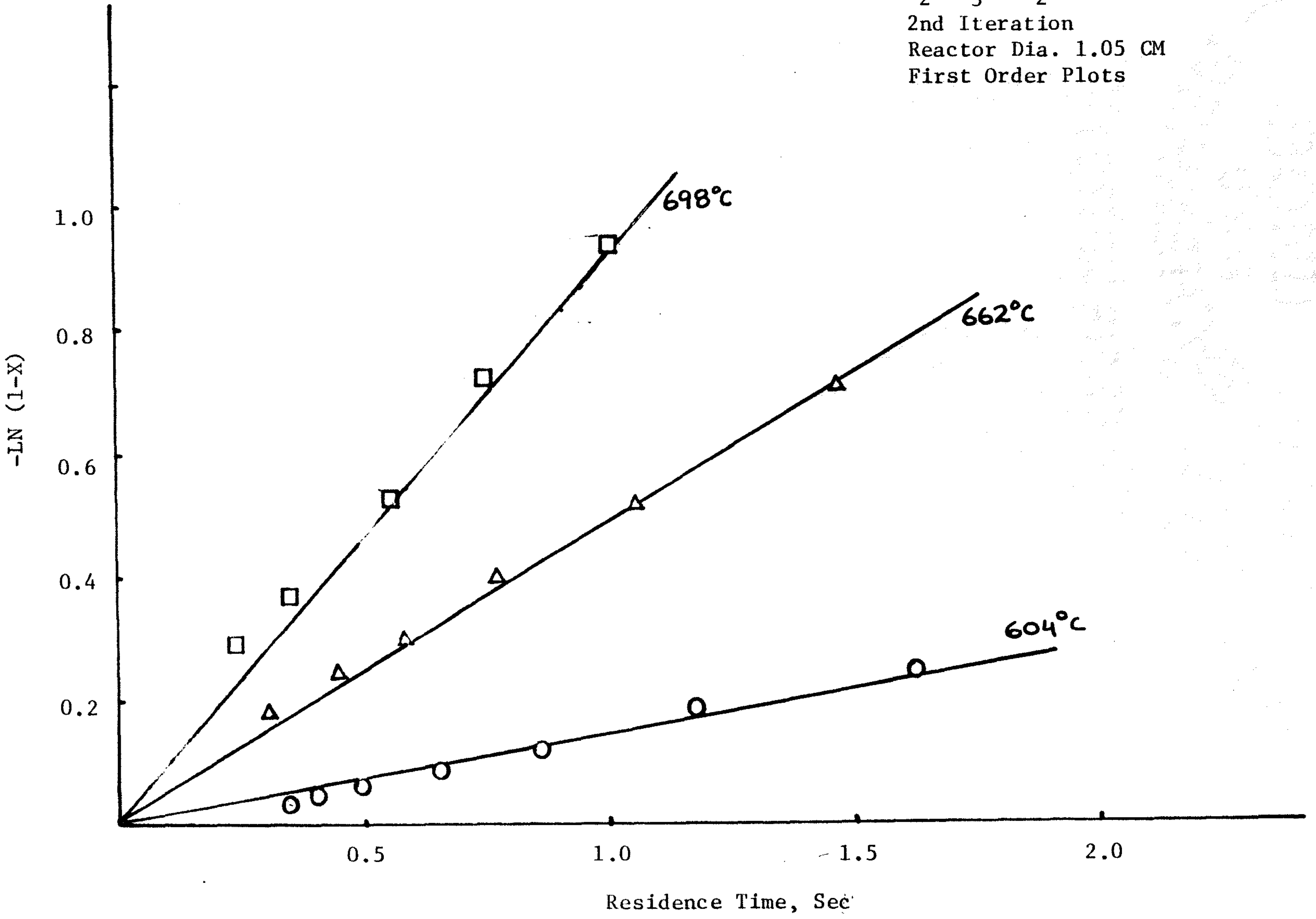


Figure 17
$C_2HCL_3 + H_2$ :: 1:33
2nd Iteration
Reactor Dia. 1.05 CM
First Order Plots

Figure 18

$C_2HCL_3 + H_2$ :: 1:33

K' vs 2/R Plot

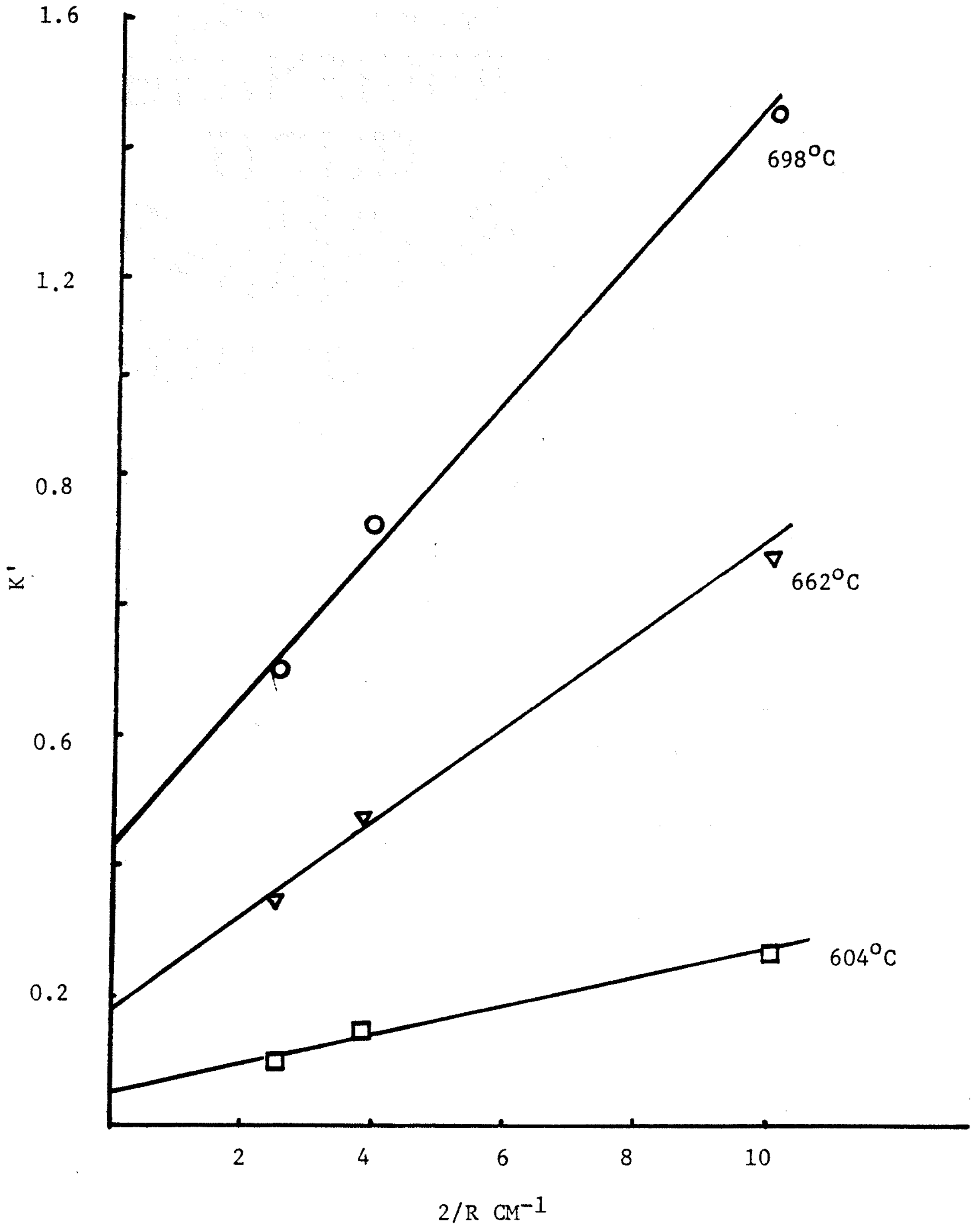
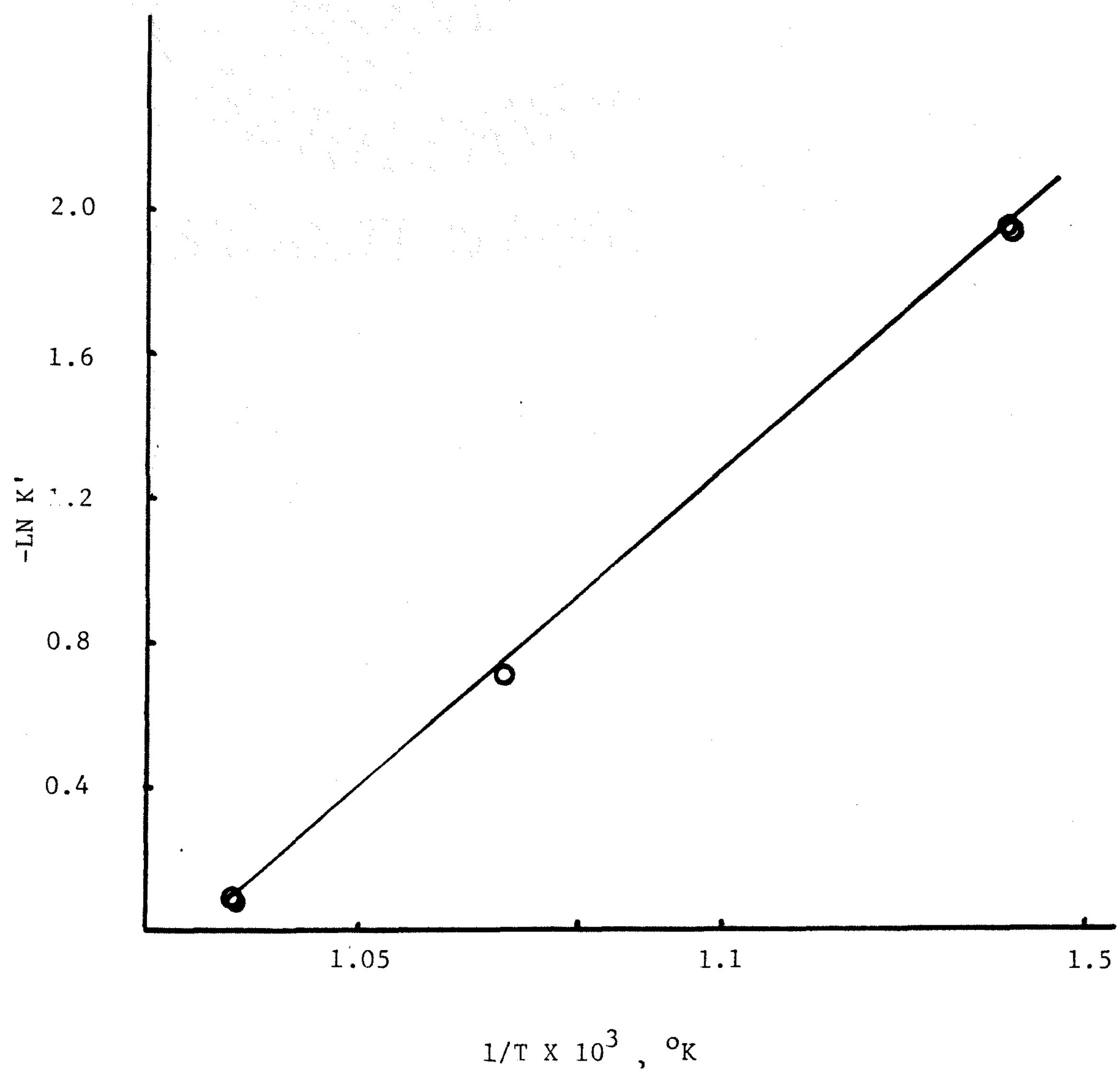


Figure 19
$C_2HCL_3 + H_2$ :: 1:33
Reactor Dia: 1.05 CM
2nd Iteration
Arrhenius Plot



ratios of 1:33, and 1:58 are shown. Whereas the concentration of the trichloroethylene changes by a factor of almost two the concentration of hydrogen does not change significantly. The actual concentrations are :

C_2HCL_3 : H_2

1 : 33 $(3.528 * 10^{-4}) * 1/T$: $10.97 * 10^{-3} * 1/T$ $\frac{Mol\,^{o}k}{cm^3}$

1 : 58 $(2.007 * 10^{-4}) * 1/T$: $11.578 * 10^{-3} * 1/T$ "

The two sets of results would have varied significantly if the dependency of the global rate constants on the concentration of trichloroethylene were other than the assumed first order.

Table 8. shows that at temperatures below 700°C the wall reaction has slightly a lower activation energy than the homogenous reaction indicating that the reaction is probably initiated at the wall, as well as occuring in the vapor phase.

The vapor phase value of $E = 35.0 +/- 1.0$ kcal/mol. for the vapor phase reaction is in close agreement with the value found by Hardwick (15) in his study of thermally and radiation initiated reaction between trichloroethylene and cyclopentane. In thermally initiated experiments he found the activation energy for trichloroethylene to be 35.4 kcal/mol, with a 3/2 order reaction for trichloroethylene and zero order for cyclopentane. He calculated an activation energy of 61.2 kcal/mol for the unimolecular decomposition of trichloroethylene which was the first step in the reactions.

Goodall and Howlett (14) have proposed that the pyrolytic decomposition of trichloroethylene at low pressures (below 50 mm Hg.) proceeds with bimolecular mechanisms, and that the homogeneous non-chain mode of reaction is second order. They have also suggested that the chain part of the decomposition is second order as well. For reactions maximally inhibited by propylene the reaction was proposed to be independent of the surface to volume ratio and non-chain in character. An activation energy of 42 kcal/mol was found for trichloethylene for this reaction. They propose that maximum inhibition is reached at 2 mm pressure of proplyne. In the present study the pressures of the product propylene at about 0.5 second residence time are

604°C --------	0.09 mm Hg
653°C --------	1.38 mm Hg
698°C --------	1.49 mm Hg

Maximum inhibition is thus not reached. However the inihibition effect of the propylene may have affected the values of the rate constants reported in Table 8.

Goodwall and Howlett found that the reaction was inhibited by the product HCL, and the activation energy for this was found to be 35.4 kcal/mol. which is very close to the values shown in Table 8 of this report.

Zabel (16) has found an activation energy of 84 kcal/mol for the unimolecular decomposition of trichloroethylene at high pressures. His theoritical analysis for the reaction initiated by the first step

$$C_2HCL_3 \text{ -----> } C_2HCL_2 + CL$$

gave an activation energy of 82 +/- 5 kcal/mol . His experimental results therefore suggest that the decomposition follows the above route. A separate theoritical analysis also shown is for the route C_2HCL_3 --- C_2CL_2 + HCL, which gives an activation energy of 48 +/- 3 + # kcal/mol. This route is more probable in our case and is further supported by the observation of dichloroethylene as a major product.

Attempts to establish the order of hydrogen by use of the Arrenhius type equation $k' = k_o * e^{-E/RT} * [H_2]$ failed to provide reliable results due to the close proximity of the two hydrogen concentrations. Taking $k_o * [H_2]^a = A$ to be the frequency factor for this analysis where the order of the hydrogen dependency "a" is unknown Table 9 is constructed. An average value of E = 33340 cal/mol is used in those calculations involving k′, and actual values of E from Table 8 are used for calculations involving k_h and k_w.

The frequency factor k_o is calculated by assuming "a" to be one. The set of data for the trichloroethylene to hydrogen ratio 1 : 33 is more reliable since this concentration is relatively larger and was easier to maintain experimentally. Table 10 shows the values of k_o obtained. The above mentioned set of data gives :

$k_h = 4.54 * 10^{12}e^{-35000/RT}$ (sec)$^{-1}$ for the vapor phase

$k_\omega = 9.6 * 10^{10}e^{-31200/RT}$ (sec.)$^{-1}$ for the wall reaction.

Data for the probability of reaction due to wall collisions is shown in Appendix 1.

5.4 PRODUCT DISTRIBUTION FOR TRICHLOROETHYLENE

The major products observed were C_2H_4, C_2H_2, CH_4 $C_2H_2CL_2$, C_6H_6, C_3H_6, and HCL.

Product distribution as a function of time for the reactions at 604, 662, 698° are shown in Figures 20, 21 and 22. These plots indicate that the major product below 700°C is dichloroethylene with ethylene, acetylene and methane as the other major products. It is interesting to note that the only chlorinated product observed above 850° in any significant quantity is HCL.

Plots of stable products versus temperature of reaction at residence times between 0.5-0.6 seconds are shown in Figures 23. Figure 23 shows that dichloroethylene is not observed above 900°C and that the major product at higher temperatures are the species listed above. Benzene production starts above 800°C reaching a maximum of about 2% of the parent trichloroethylene. It can be noted that the maximum possible conversion to benzene is about 33% of the parent trichloroethylene. Methane, acetylene,and ethylene constitute more than 95 % of the product near 1000°C.

A material balance for 100 moles of carbon (50 moles of trichloroethylene) at different temperatures in the residence time range of 0.5 to 0.6 seconds is shown in Table 11. The Table shows that at temperatures above 800°C no other compounds than those followed in this experiment were observed. Small quantities of methylene chloride were also observed.

Table12 is the material balance for 300 moles of chlorine (100 moles of trichloroethylene). Unaccounted for chlorine for temperatures below 700°C is very small showing that very little higher chlorinated products are formed. For temperatures above 700°C the larger fractions for the unaccounted chlorine is possibly due to the reaction of HCL with the material of the outlet tubing and valves before the gases reach the measuring equipment.

Figure 20
$C_2HCL_3 + H_2$ :: 1:33
2nd Iteration
Product Distribution
At 604°C
Reactor Dia. 105 CM

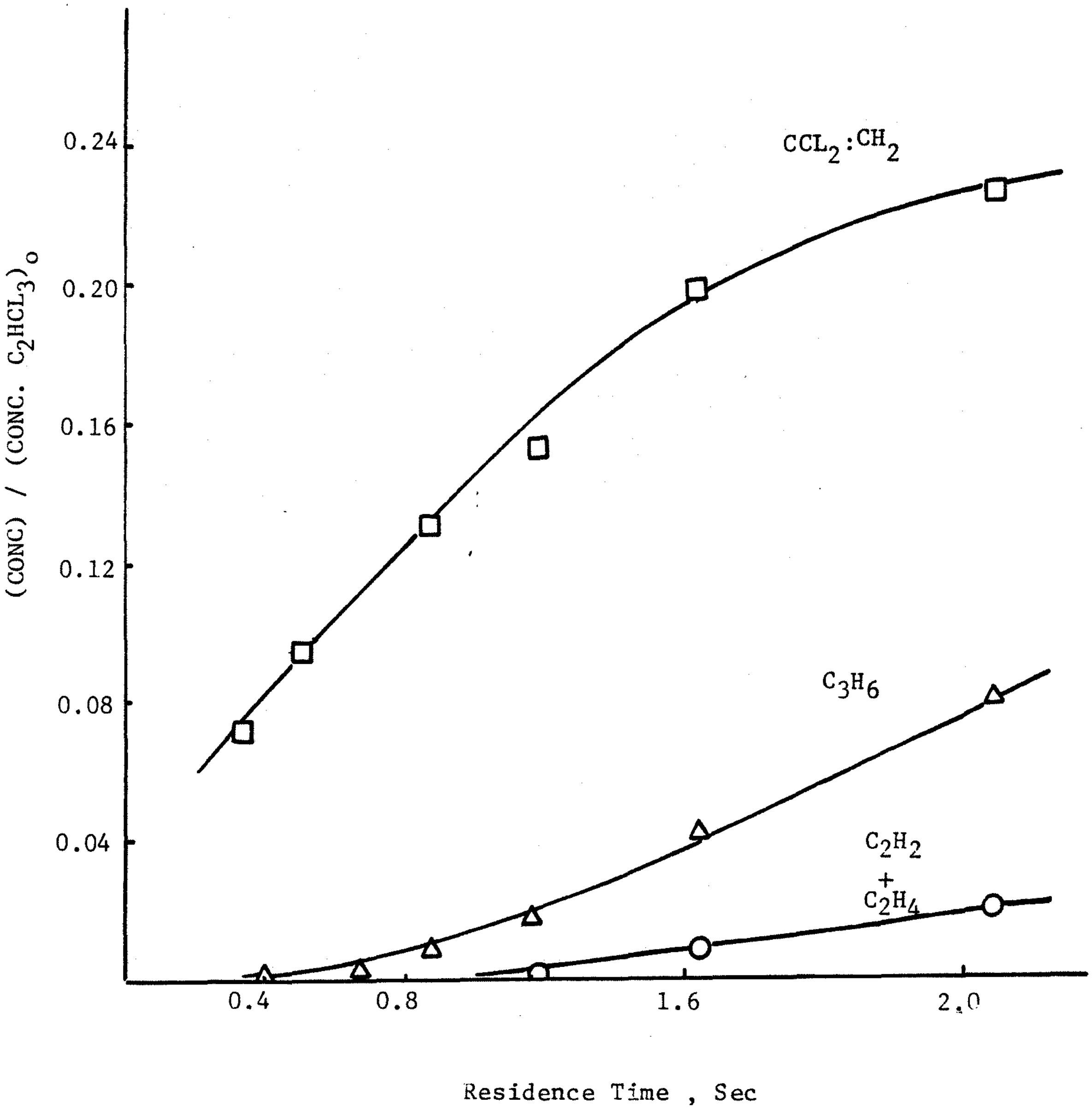
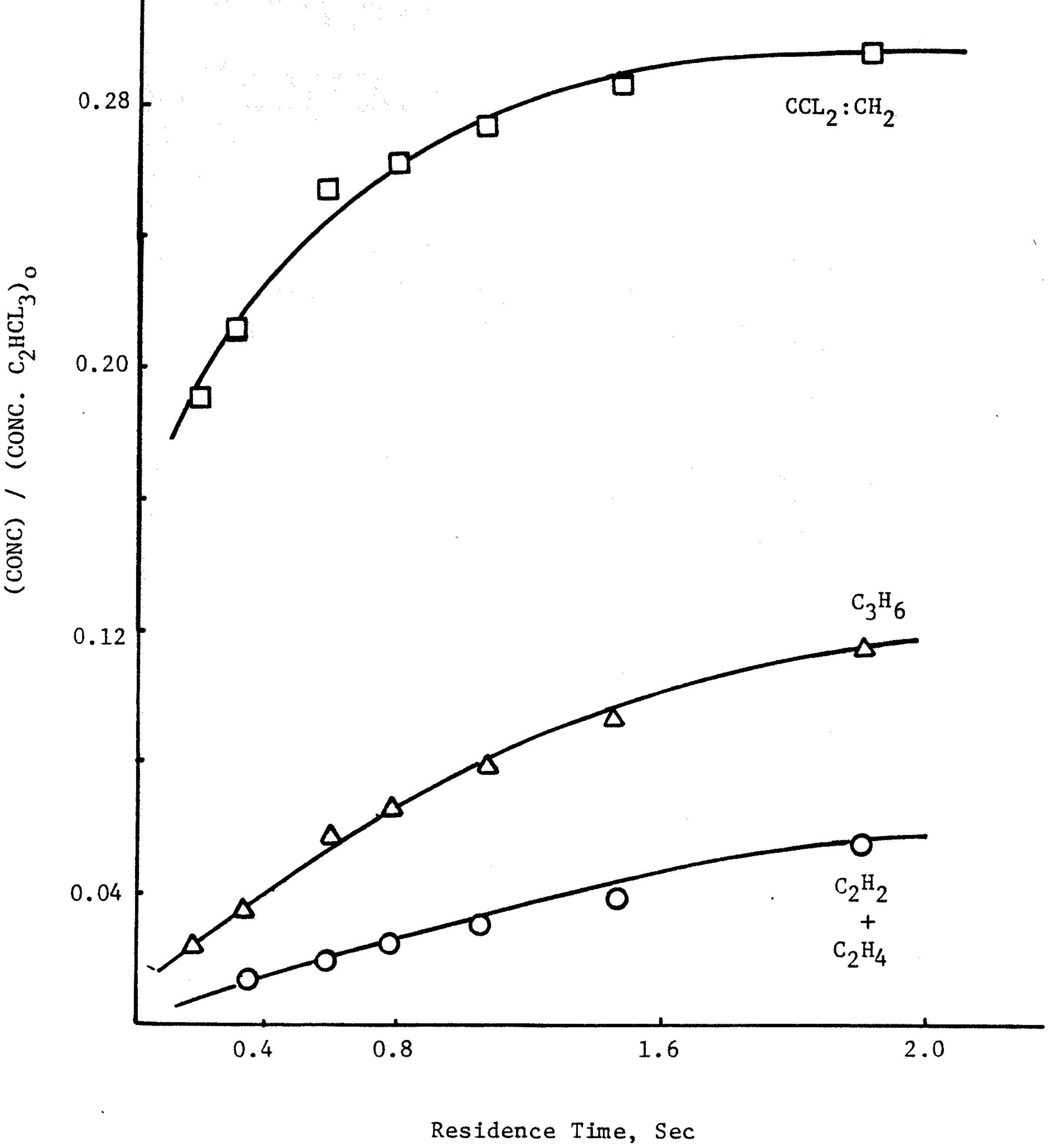


Figure 21
$C_2HCL_3+H_2$ :: 1:33
2nd Iteration
Product Distribution
At 662°C
Reactor Dia. 1.05 CM



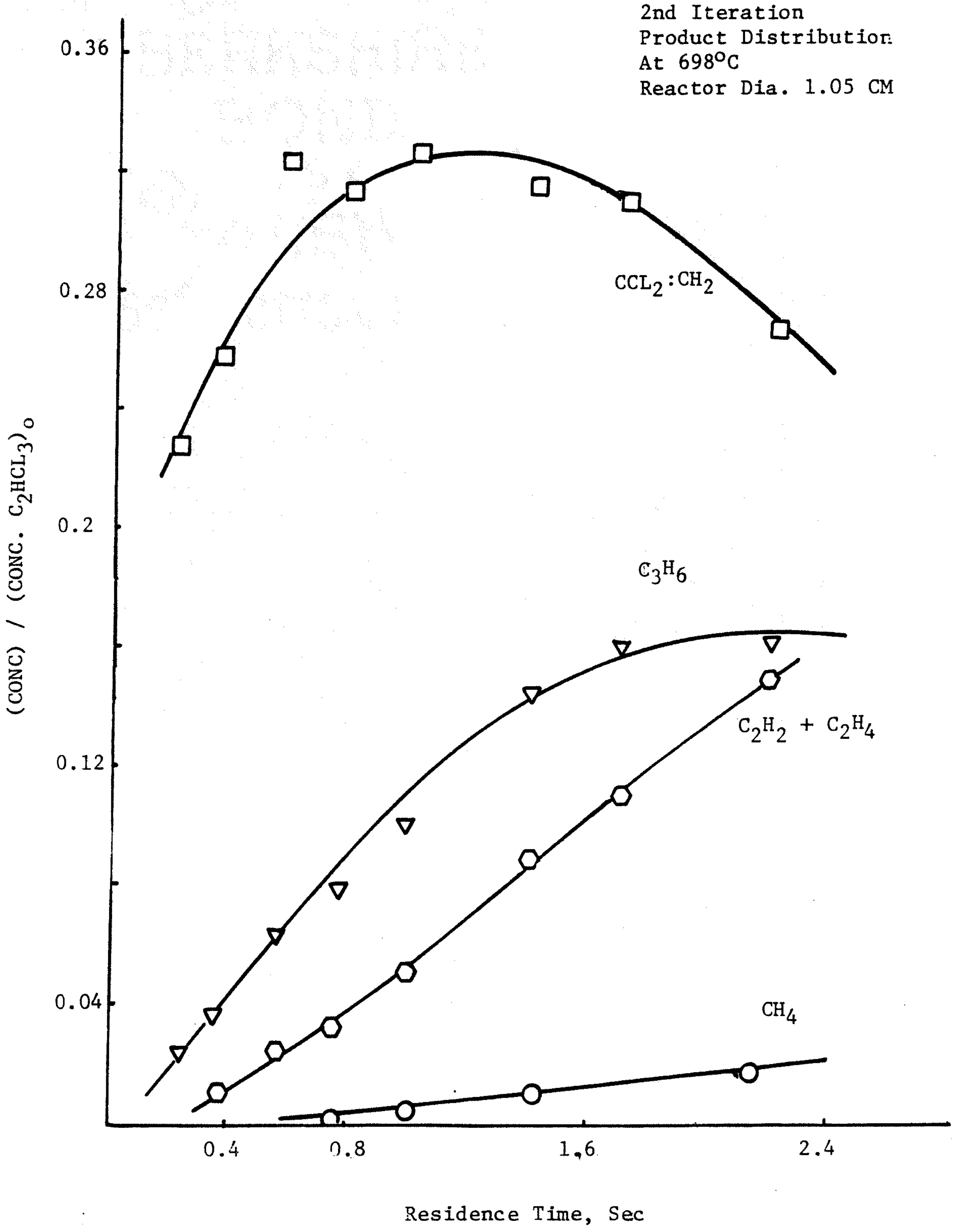


Figure 22
$C_2HCL_3 + H_2$ :: 1:33
2nd Iteration
Product Distribution
At 698°C
Reactor Dia. 1.05 CM

FIGURE 23

$C_2HCL_3 + H_2$ :: 1:33

Product Distribution

Residence Time: 0.5 - 0.6

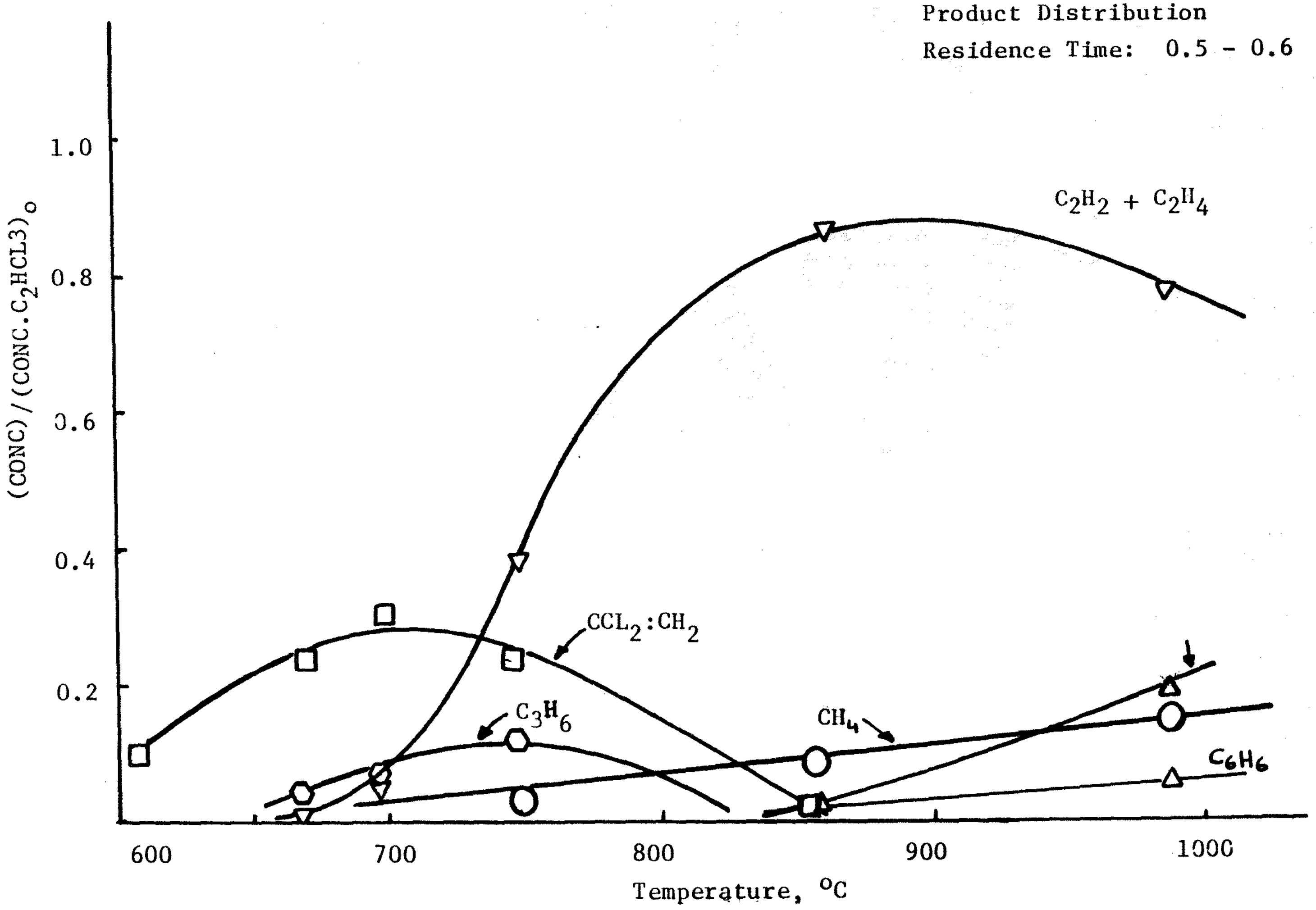


TABLE 8

SECOND ITERATION RATE CONSTANTS FOR $C_2HCL_3 + H_2$

$C_2HCL_3 : H_2 :: 1 : 33$

Dia.(cm.)	0.4	1.05	1.6	k_h	k_w
Temp.(°)					
604	0.262	0.145	0.094	0.061	0.02
662	0.912	0.49	0.332	0.189	0.073
698	1.55	0.92	0.655	0.432	0.115
E cal/mol	34000	34800	35800	36200	31200

$C_2HCL_3 : H_2 :: 1 : 58$

604	0.296	0.193	0.115	0.092	0.02
662	0.964	0.55	0.433	0.278	0.07
698	1.68	0.98	0.688	0.55	0.113
E cal/mol	31200	31000	33200	34000	31200

The rate constants have units of $(sec)^{-1}$

TABLE 9

FREQUENCY FACTOR $A*10^{-9}$

$C_2HCL_3 : H_2 :: 1 : 33$

Dia.(cm.)	0.4	1.05	1.6	k_h	k_w
Temp.(^oK)					
604	0.047*	0.026*	0.017*	0.056#	0.0010+
662	0.050	0.027	0.018	0.048	0.0013
698	0.047	0.028	0.020	0.057	0.0011

$C_2HCL_3 : H_2 :: 1 : 58$

604	0.053	0.035	0.021	0.024@	0.0010##
662	0.053	0.030	0.024	0.022	0.0012
698	0.050	0.029	0.021	0.023	0.0011

Value of Activation Energy used :

* E = 33340 cal/mol (average value from global rate constants)

\# E = 36200 cal/mol

\+ E = 31200 cal/mol

@ E = 34000 cal/mol

\#\# E = 31200 cal/mol

Units for frequency factor A are $(sec.)^{-1}$

TABLE 10

FREQUENCY FACTOR k_o

C_2HCL_3 : H_2 :: 1 :33

Temp.°	GAS PHASE (k_o * 10^{-12})	WALL (k_o * 10^{-10})
604	4.477	7.995
662	4.091	11.08
698	5.045	9.737

C_2HCL_3 : H_2 :: 1 : 58

604	1.818	7.575
662	1.777	9.691
698	1.981	9.47

The units of k_o are cm^3/mol.sec.

TABLE 11. *

MATERIAL BALANCE FOR 100 MOLES CARBON

FOR C_2HCL_3 : H_2 :: 1 : 33

REACTOR DIAMETER 1.05 CM.

TEMP^{oC}	604	662	698	748	853	982
CH_4	---	----	1.02	7.5	9.1	11.98
C_2H_2 + C_2H_4	0.06	2.06	2.37	37.7	86.8	82.45
C_2H_6	0.23	0.11	0.1	----	-----	-----
C_3H_6	0.55	8.80	9.84	18.7	-----	-----
$CL_2C:CH_2$	9.55	25.4	32.55	23.24	1.55	-----
$CL_CH:HC_CL$	1.23	1.7	1.03	1.3	-----	-----
C_6H_6	----	0.03	0.08	1.54	1.56	5.77
C_2HCL_3	87.55	59.64	51.73	7.38	0.22	-----
TOTAL	99.17	97.74	98.3	97.33	99.23	100
RES.TIME (sec.)	0.51	0.58	0.56	0.57	0.54	0.61

*Based on carbon detected by flame ionization detector.

TABLE 12

MATERIAL BALANCE FOR 300 MOLES CHLORINE

$C_2HCL_3 : H_2 :: 1 : 33$

REACTOR DIAMETER 1.05 CM.

TEMP^{o}C	604	662	698	748	853	982
$CL_2C:CH_2$	19.1	50.8	65.1	46.48	3.10	---
CLCH:HCCL	2.46	3.4	2.06	2.61	----	---
HCL	14.3	59.32	65.7	206	N.A.	277
TOTAL	298.5	292.3	288.5	277.0	N.A.	300
RES.TIME (sec)	0.51	0.58	0.56	0.56	0.54	0.61

N.A. = Not available.

MECHANISM FOR THE REACTION OF TRICHLOROETHYLENE WITH HYDROGEN

A simple mechanism which explains the stable products and kinetics observed is shown below. It is not meant to be exhaustive and is only one many possible sets of reaction steps.

$C_2HCL_3 + H_2 \longleftrightarrow C_2H_3CL_3$ (fast, equilibrium)

$C_2H_3CL_3 \longrightarrow HCL + C_2H_2CL_2$

$C_2H_2CL_2 + H_2 \longrightarrow C_2H_4CL_2$

$C_2H_4CL_2 \longrightarrow HCL + C_2H_3CL$

$C_2H_3CL + H_2 \longrightarrow C_2H_5CL$

$C_2H_5CL \longrightarrow HCL + C_2H_4$

$C_2H_4 \longleftrightarrow H_2 + C_2H_2$

5.5 COMPARISON WITH LAMINAR FLOW MODEL

Chang (5) has shown that plug flow analysis for reaction conditions similar to those of the present study closely matches the results obtained by the more rigourous laminar flow model.

His work provides a way of obtaining true valuesof the wall and homogeneous phase rate constants from experimental data by numerically solving the continuity equation for first order reactions under laminar flow conditions. A comparison using his method for the experimental data of this study provides a more relevant test of the assumption of plug flow in this study.

Data from the runs for the chloroform to hydrogen ratio of 1 : 9, and trichloroethylene to hydrogen ratio of 1 : 33 at three different temperatures and three different reactor diameters were used.

Theoritically for every run at a particular temperature and reactor diameter an infinite number of optimum values for the two rate constants can be found. However for runs at a particular temperature and different reactor diameters the plots for the optimum values of the rate constants for each diameter must intersect at a common point which gives the true values of the constants.

Two such plots, Figures 24 and 25, show that the calculated plug flow values are very close to the centre of the triangle made by the intersection of the three lines, which according to Chang's analysis are the true values. The prediction is that the three lines intersect at a single common point. The degree to which they do not do so is a measure of the variance of the experimental data used.

Table 13 shows the values for the comparison performed.

TABLE 13

$CHCL_3 : H_2 :: 1 : 9$

	Plug flow model		Laminar flow model	
°C	k_h	k_w	k_h	k_w
561	0.088	0.030	0.078	0.035
604	0.258	0.077	0.256	0.079
653	0.56	0.334	0.51	0.55

$C_2HCL_3 : H_2 :: 1 : 33$

	Plug flow model		Laminar flow model	
°C	k_h	k_w	k_h	k_w
604	0.061	0.02	0.076	0.017
662	0.189	0.073	0.186	0.075
695	0.432	0.115	0.445	0.119

The units for the rate constants are $(\text{sec.})^{-1}$

Figure 24
$C_2HCL_3 + H_2$ :: 1:33
Temp. 662°C
Comparison of Kw & K Values
From Laminar Model and Plug Flow Model

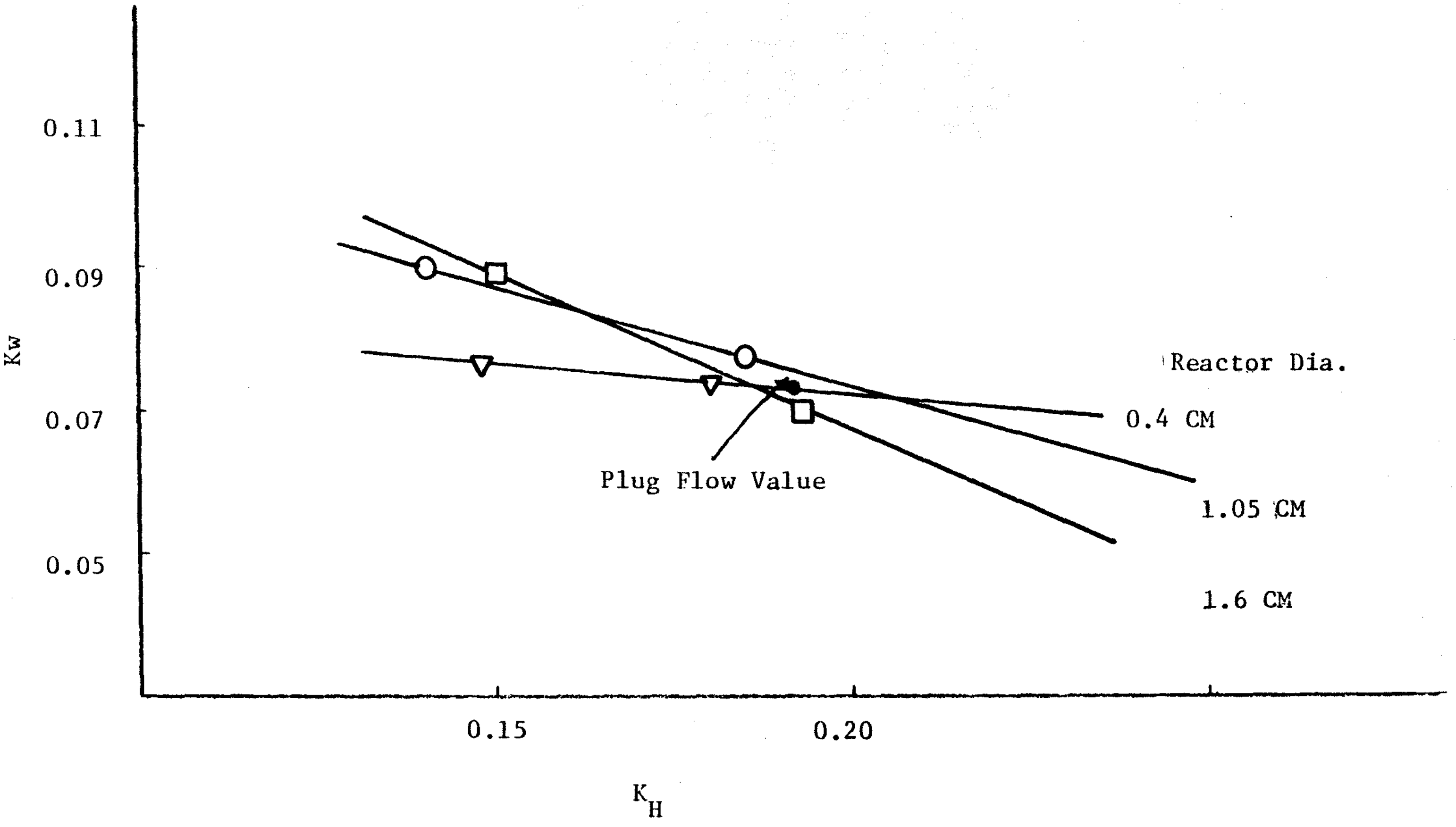
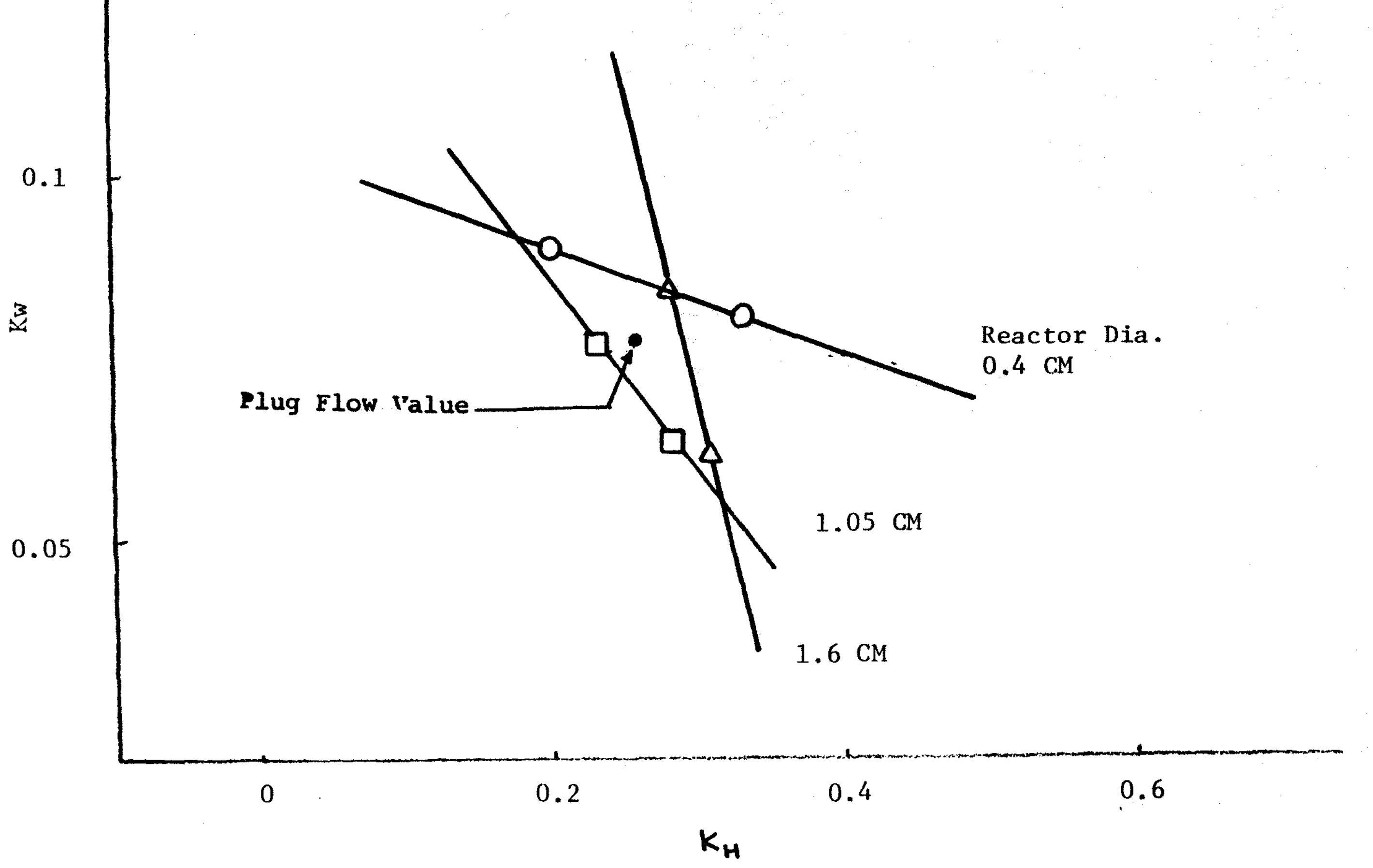


Figure 25
$CHCL_3 + H_2$ :: 1:9

Comparison of KH&K Values With Plug Flow



6. CONCLUSION

The reactions of chloroform and trichloroethylene with hydrogen in the temperature range 550 to 1000°C were studied using tubular flow reactors of varying diameters. Kinetic parameter values reported in the present study are from the data from the three lowest temperatures for each chlorinated species. For chloroform these temperatures were 561, 604, and 653°C where the conversions upto 25, 50 and 90 percent respectively were observed. For trichloroethylene, data from runs at 604, 662 and 698°C with conversions upto 30, 60 and 90 per cent respectively, were used for kinetic analysis. Above these temperatures the conversion of the respective chlorinated species was too high for accurate kinetic study. The reactor diameters used were 0.4, 1.05 and 1.6 cm, giving surface to volume ratios of 2.5, 3.8 and 10 $(cm)^{-1}$, respectively.

Flat temperature profiles (+/- 5°C) were achieved over 80 to 85 per cent of the 45 cm reaction zone. This required the inlet gases to be preheated to about 400°C. It had previously been determined that no reaction occurs below 450°C in the residence time range of the present study.

The residence time range for the the present study was from 0.05 to 3.0 seconds. Two different concentrations of the chlorinated species were used, each with hydrogen in large excess. The chloroform to hydrogen molar ratios used were 1 : 9 and 1 : 17 ; and the trichloroethylene to hydrogen molar ratios were 1 : 33 and 1 : 58. The large excess of hydrogen lead to the application of pseudo-first order kinetic analysis.

The experimental data seemed to reasonably fit he first order plug flow model. Kaufman's formula (36) for this type of reactions was sucessfully applied and the rate constants for the wall and homogeneous phase reactions were found. These are :

a) Chloroform

$k = 3.86 * 10^{12} e^{(-35.3/RT)}$ sec^{-1}, gas phase.

and

$k = 3.24 * 10^{14} e^{(-43.4/RT)}$ sec^{-1}, at the wall.

b) Trichloroethylene

$k = 4.54 * 10^{12} e^{(-35.0/RT)}$ sec^{-1}, gas phase.

and

$k = 9.6 * 10^{10} e^{-31.2/RT)}$ sec^{-1} sec, at the wall.

The small change in the concentration of hydrogen did not allow accurate prediction for the order of reaction for hydrogen and was assumed to be one for the reactions in the present study.

All chlorinated species, reactants and products were completely destroyed at/or above 850°C. The major products at these temperatures were CH_4, C_2H_2, C_2H_4, HCL and benzene. The important observation is that all chlorine from the chlorinated species is converted into hydrogen chloride, and the gases produced are useable as fuel or chemical feed-stock. Thus, this type of reactions are shown to be an alternative to incineration that merits further study.

It is hoped that future studies will find the results of the present study relevant and useful.

APPENDIX 1. REACTIONS ON THE WALL

The first order rate constant at the wall can be related to the fraction of wall collisions that result in reaction (37,38) by the equation :

$$k_w = \gamma \omega/(2R) \quad (\mathrm{sec})^{-1}$$

where

k_w = first order rate constant at wall

γ = wall reaction coefficient, (i.e. the fraction of collisions with the wall that results in reaction).

ω = average molecular speed

R = radius of cylindrical reactor

Obviously γ must be less than one. It is shown in Tables 14 and 15 that γ is of the order of one per 10^6 collisions.

The average molecular speed, " ", is calculated from the Maxwell distribution law and is:

$$\omega = (8RT/\pi M)^{0.5} \quad \mathrm{cm/sec}$$

where

R = Gas Constant

= $8.3143 * 10^7$ ergs/(mole $^{\circ}$K)

M = Molecular Weight, grams/mole

T = Temperature, $^{\circ}$K

ω = Average Molecular Speed, $(\mathrm{ergs/grams})^{0.5}$ = (cm/sec)

TABLE 14

WALL REACTION COEFFICIENT - CHLOROFORM

$CHCL_3 : H_2 = 1 : 9$

Diam(cm)	0.4	1.05	1.6
Temp(^{o}C)			
561	$3.12*10^{-8}$	$0.82*10^{-6}$	$1.25*10^{-6}$
604	$7.81*10^{-8}$	$2.05*10^{-6}$	$3.12*10^{-6}$
653	$33.0*10^{-8}$	$8.65*10^{-6}$	$13.2*10^{-6}$

$CHCL_3 : H_2 = 1 : 9$

561	$3.22*10^{-8}$	$0.85*10^{-6}$	$1.29*10^{-6}$
604	$8.32*10^{-8}$	$2.18*10^{-6}$	$3.33*10^{-6}$
653	$47.1*10^{-8}$	$12.5*10^{-6}$	$18.8*10^{-6}$

TABLE 15

WALL REACTION COEFFICIENT - TRICHLOROETHYLENE

$C_2HCL_3 : H_2 = 1 : 33$

Diam(cm)	0.4	1.05	1.6
Temp($^{\circ}$C)			
604	$2.12*10^{-8}$	$0.56*10^{-6}$	$0.85*10^{-6}$
662	$7.52*10^{-8}$	$1.98*10^{-6}$	$3.01*10^{-6}$
698	$11.6*10^{-8}$	$3.05*10^{-6}$	$4.65*10^{-6}$

$C_2HCL_3 : H_2 = 1 : 58$

604	$2.12*10^{-8}$	$0.56*10^{-6}$	$0.85*10^{-6}$
662	$7.21*10^{-8}$	$1.89*10^{-6}$	$2.89*10^{-6}$
698	$11.4*10^{-8}$	$3.00*10^{-6}$	$4.57*10^{-6}$

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