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Rate of Initiation of Pyrolysis of Pentachloroethane Using the Toluene Carrier Gas Technique

Teodomiro Cuzcano

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RATE OF INITIATION OF
PYROLYSIS OF PENTACHLOROETHANE
USING THE TOLUENE CARRIER GAS TECHNIQUE

by

Teodomiro Cuzcano

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
December 1973

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Teodomiro Cuzcano

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Western Michigan University, M.A., 1973
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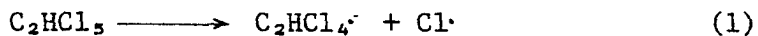
I. INTRODUCTION

The kinetics of the inhibited thermal decomposition of pentachloroethane has been studied in this work by means of the toluene carrier gas technique. The main purpose was to elucidate the rate of initiation of pyrolysis and the mechanistic features of this stage of the decomposition. Pentachloroethane was chosen for this research because the kinetics of the initial step of pyrolysis was uncertain and because in the presence of toluene, a relatively simple mechanism leading to few products was anticipated.

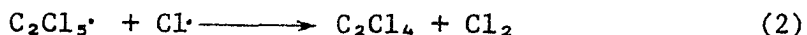
A. Background

The initial research on the pyrolysis of pentachloroethane was carried out by Barton¹ in a flow system with a clean-walled reactor at temperatures up to 450°C. It was found that the only products were tetrachloroethylene and hydrogen chloride, and that the process followed first-order kinetics.

Later work at 407-438°C by Houser and Bernstein² using a carbon coated, stirred-flow reactor with helium as a carrier gas, showed that the pentachloroethane decomposition was not a first-order reaction but was autocatalytic. A radical-chain mechanism with an initiation step involving a C-Cl bond rupture was proposed



It was postulated that the autocatalytic nature of the reaction was due to chlorine formed by the disproportionation



the chlorine formed from reaction (2) then attacks the reactant. The products identified were tetrachloroethylene and hydrogen chloride, and also small amounts of trichloroethylene and chlorine.

Recently, Shvets et al.³ have studied the thermal dehydrochlorination of pentachloroethane in a flow reactor at 396-448°C. Some of the data of this investigation confirmed the findings of Houser and Bernstein.² However, it was postulated, that the absence of a surface effect on the overall reaction coupled with the large accelerating influence of the surface on the inhibited reaction indicated a radical-chain mechanism with initiation on the walls, propagation in the bulk, and termination on the walls from the recombination of chlorine atoms. It was also concluded that the autocatalytic effect of molecular chlorine was much less than that found previously. Further investigation by Shvets et al.⁴ on the chlorine-initiated dehydrochlorination of pentachloroethane in a flow system at 350-425°C confirmed the above observations. However, there are some serious reservations regarding these conclusions because of the limited conditions under which the experiments were carried out; this will be discussed in a later section.

During the last few years many studies⁵⁻¹¹ on the catalytic pyrolysis of pentachloroethane have been carried out, most of them with the aim of improving the yield of trichloroethylene and/or tetrachloroethylene, and of inhibiting the formation of carbonaceous by-products. The catalysts used have been mainly FeCl_2 , FeCl_3 , CuCl , CuCl_2 , CeCl_3 , KCl , SnCl_2 , CuSO_4 , K_2SO_4 , etc., or mixtures of some of these salts.

B. Kinetics in a Flow System

Flow systems may be considered as corresponding to two limiting cases¹², no longitudinal mixing and complete longitudinal mixing.

The derivation of the basic equations for flow systems with no stirring (plug-flow) can be treated by considering a tubular reactor of constant cross-sectional area and steady flow rate of reaction mixture. The change in the number of moles of the component i with time in the volume element dV is expressed by

$$dn_i/dt = r_i dV - udc_i \quad (3)$$

where dV is a small cylindrical volume element, c_i is the concentration of component i , u is the volume rate of flow of the reaction mixture, and r_i is the rate of the chemical reaction. After a time a steady state is reached, such that equation (3) becomes

$$r_i dV = udc_i$$

or

$$r_i = (u/dV)dc_i \quad (4)$$

Equation (4) may be integrated to give

$$V/u = \int_{c_0}^c dc_i/r_i \quad (5)$$

where c_0 is the initial concentration of component i and V is the total volume of the reactor up to the point where i has a concentration c . The use of equation (5) requires a definite expression for the rate r . Under the conditions of constant flow (dV/u) may be replaced by dt (increment of contact time) in equation (4) to give

$$r_i = dc_i/dt \quad (6)$$

which is the familiar closed-system equation.

In a flow system with complete mixing (stirred-flow reactor), the reactant and product compositions are uniform throughout the entire volume of the reactor. Thus, the volume element dV may be replaced by V , and dc_i may be replaced by $(c-c_0)$ in equation (4) which yields at steady-state flow

$$r = (u/V) (c-c_0) \quad (7)$$

This equation can be applied to any component in the system provided the correct expression for r is used. If flow rates are constant, equation (7) may be rewritten as

$$r = (c-c_0) / t \quad (8)$$

where $t = V/u$ is the contact time or the average time of residence of a molecule in the reactor. Equation (8) permits the direct determination of reaction rates without integration. By changing initial concentrations and/or flow rates it is possible to determine the rate equation and the rate constants of a reaction.

For a simple first-order process the reaction rate is given by

$$r = -kc \quad (9)$$

It is possible to combine equations (8) and (9) to give

$$r = (c-c_0) / t = -kc \quad (10)$$

which permits direct calculation of reaction rates, and from these the respective rate constants.

C. The Toluene Carrier Gas Technique

This method¹³ is used to investigate the pyrolysis of compounds which split into two radicals by the breaking of one bond only. If these radicals are formed in the presence of a large excess of toluene,

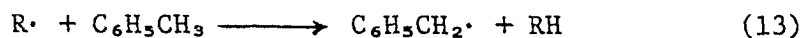
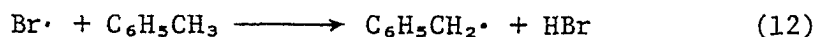
the toluene acts as a very good inhibitor to free radical-chain reactions, making it possible to observe the rate of the initial decomposition. Thus interferences by secondary reactions, and the activity of inhibitors and autocatalytic products are reduced to a minimum.

The most suitable compounds for study by this method are halohydrocarbon derivatives (RX). The successful operation of the method has as a condition the high reactivity of X, which has to be removed rapidly from the system. A limitation of the method is the bond dissociation energy of the compound being investigated which must be smaller than the C-H bond dissociation energy in toluene (77.5 Kcal/mole).

Szwarc and Sehon¹⁴ applied this method to the pyrolysis of methyl bromide and some halogenated bromoethanes. They found that all these decompositions were initiated by the breaking of the R-Br bond



In the presence of an excess of toluene, the bromine atoms and the radical R were removed by the fast reactions



Consequently the rate of the unimolecular process (11) was measured by the rate of formation of HBr. In addition, the formation of dibenzyl in the pyrolyses of these compounds confirmed the mechanism of the overall decomposition.

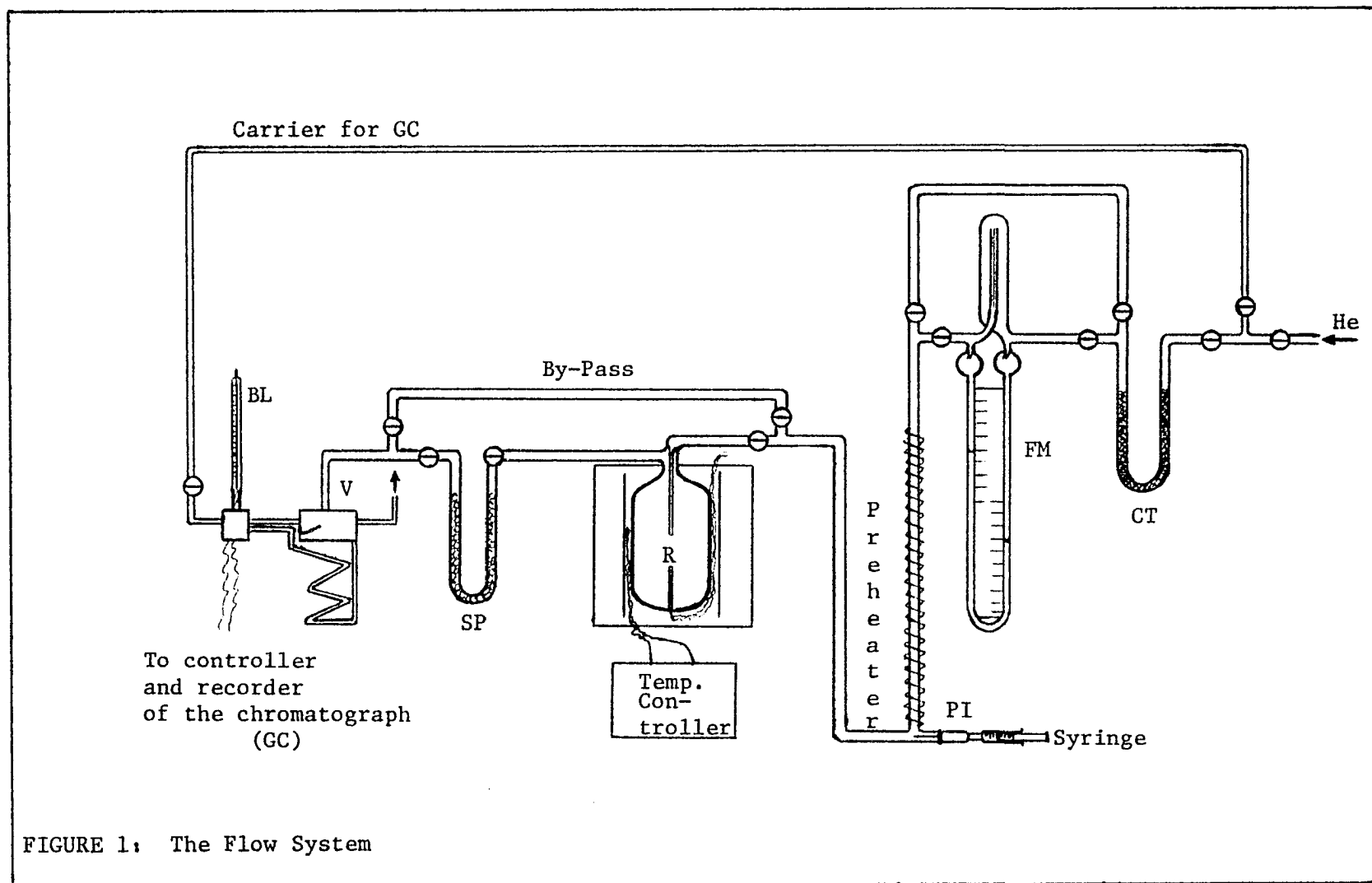
II. EXPERIMENTAL

A. Apparatus

The flow system¹⁵ used for the experiments in this study is schematically represented in Figure 1. The complete flow-line was made of Pyrex glass tubing, except the reactor which was constructed of Vycor to permit temperatures as high as 1200°C. The traps of the system were joined to the line by 18/9 ball joint unions which allow rapid changes and cleaning.

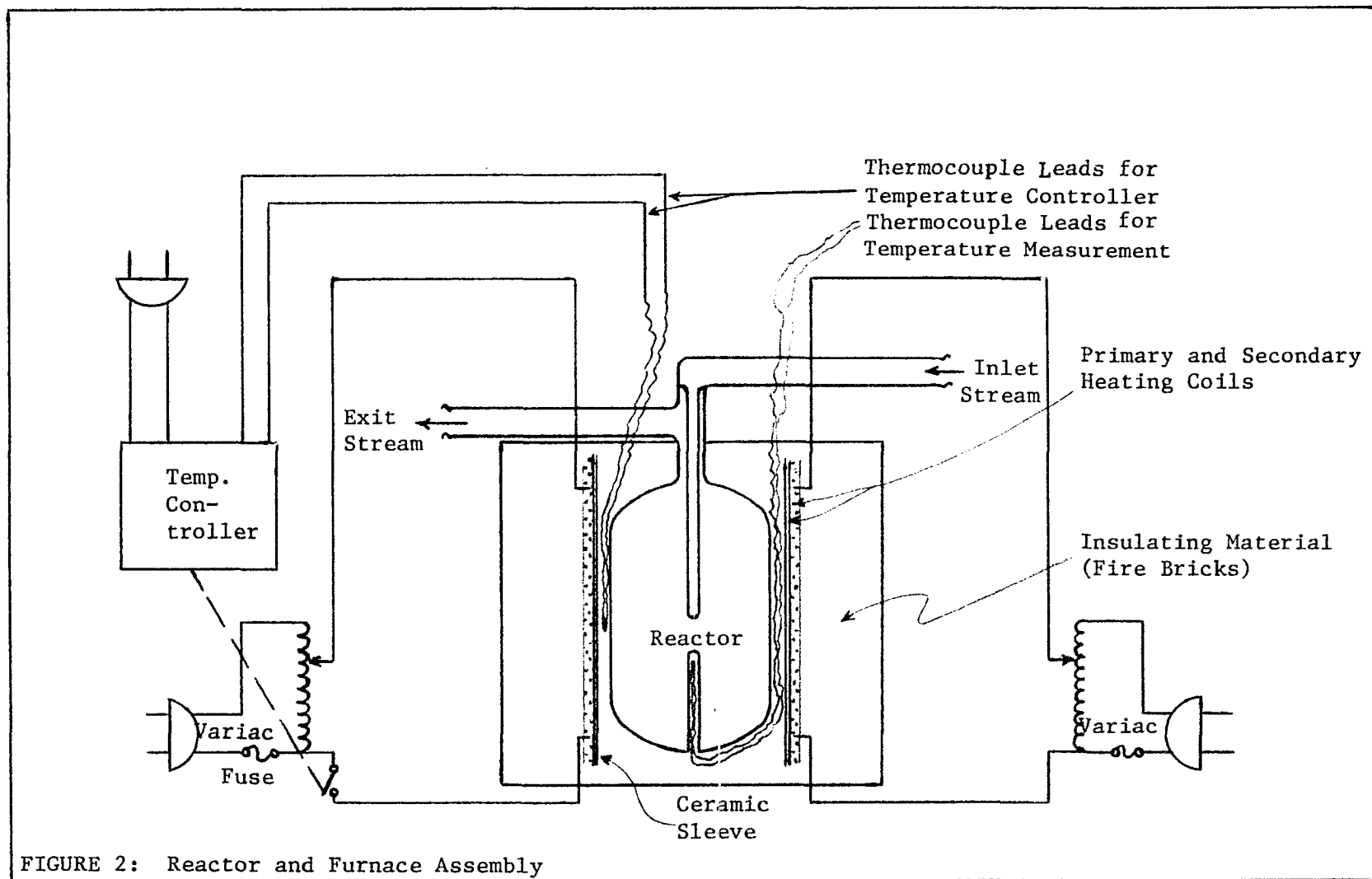
The only gas used for dilution was helium. It was purified in the flow system by passing through about 1 longitudinal foot of charcoal in a ''U'' trap (CT) at room temperature. The flow of helium was set with a pressure-regulator needle valve combination, and then measured by a capillary flowmeter (FM) which used dibutylphthalate as the manometric liquid. Two sizes of capillary tubing were used for the flowmeter, and each was calibrated (see data in Appendix B) with a ''Precision'' wet test meter by measuring pressure drops (in mm) against flow rates (in cc/sec) at room temperature. It was found that the pressure drop was a linear function of the flow rate for capillary No. 1, of smaller diameter, but for capillary No. 2, a small curvature was found.

To vaporize the reacting solution, the helium was heated to about 85-90°C by a 15 inch long preheater section consisting of 10 mm Pyrex tubing wrapped with 22 B and S gauge chromel resistance wire insulated by asbestos.



A solution of pentachloroethane in toluene was injected into the helium gas stream at point PI, using a Sage, Model 237-2, Serial 1801, motor driven syringe. A 1.0, 2.0 or 5.0 ml tuberculin syringe was joined to a hypodermic needle which had been silver soldered to a metal ball joint for connecting the assembly to the flow system. The rate of injection was determined by the dial setting for a given syringe whose delivery had been previously calibrated (see data in Appendix B) by injecting dibutyl phthalate into weighed vials. Injection was started and stopped manually.

The gaseous mixture of pentachloroethane, toluene and helium was assumed homogeneous at the entrance to the reactor, a distance of about 3 feet including three 90° bends, from the point of injection. Two types of reactors (R) were used for experimentation in this study. Reactor No. 1, schematically shown in Figure 2, was 3.47 in. high and 1.765 in. diameter, and had an effective volume of 78.3[±] 1.5 cc. To induce stirring, the reactor entrance had a centered 4 mm tube with pin holes at the end near the center of the reactor. The gaseous mixture entered through this inlet and jetted inside the reactor. To serve as a thermocouple well for temperature measurement the reactor had another centered 4 mm tube extending from the bottom to about one third the height of the reactor. The outlet and inlet of the reactor were concentric. To obtain an explicit determination of differential rate data from this system, it was necessary that the reactor design assure complete mixing of the reacting species, i.e. that the concentrations of the gaseous species in the reactor and in the exit stream were equal. Sullivan and Houser¹⁶ proved



that this assumption was valid for the type of reactor here described. Reactor No. 2 was very much the same as reactor No. 1, but with the following distinctions: it was joined to the flow line by 18/9 ball joint unions making its position five 90° bends from the point of injection; it was 3.49 in. high and 1.753 in. in diameter and had an effective volume of 76.8 ± 3.0 cc; its entrance tubing had a cut end (no pin holes); the length of the reactor outlet was shorter but wider in diameter causing a lower effective temperature in the reactor.

Reactor No. 1 was used for the conventional rate experiments of this study, reactor No. 2 was exclusively used to determine the effects of the surface on the reaction rate. To carry out these experiments, the surface to volume ratio (S/V) was increased from 1.43 cm^{-1} , corresponding to the empty reactor, to a value of 9.45 cm^{-1} by filling the reactor with about 440 cylindrical Vycor pieces of 10 mm length and 2.6 mm diameter.

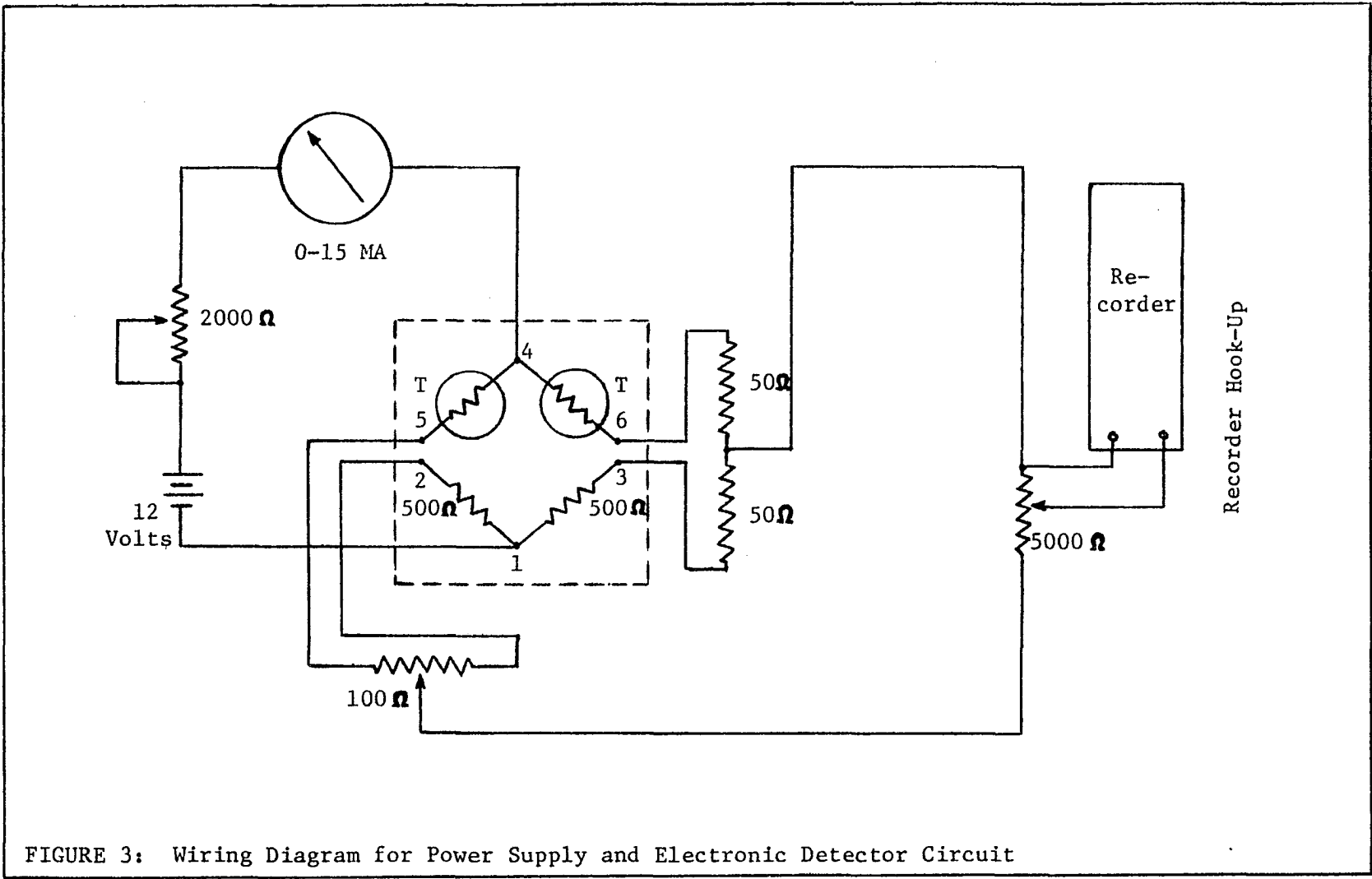
The reactor was heated by an electric furnace, the heating element of which was constructed by wrapping a 2 in. diameter (I.D.) by 1/8 in. thick Norton-Mullite ceramic sleeve with two concentric windings of 18 B and S gauge nichrome resistance wire the full length of the sleeve; each was about 10 ohms. Sheets of asbestos were used as insulating material around the windings. The inner concentric winding was powered by a 1 KVA variac actuated ON-OFF by a Honeywell type K 200-1200°C, Model MS2, temperature controller. The outer winding was powered by a 1 KVA variac directly connected to a 115 volts 60 cps power line. As a temperature detector for the

controller, a chromel-alumel thermocouple was placed between the reactor and the furnace wall. An additional standardized chromel-alumel thermocouple placed in the thermocouple well of the reactor was used for potentiometric temperature measurement. The insulation of the furnace was constructed of seven, $9 \times 4 \frac{1}{2} \times 2 \frac{1}{2}$ in. fire bricks arranged as a cubical housing and held together by steel pins through holes in the bricks.

The gaseous reaction products leaving the reactor were passed through a 'U' trap (SP) filled with 6 mm glass beads to increase the surface area and thus remove the solid products at room temperature. Other products and noncondensable gasses passed to a Beckman gas sampling valve (V), where samples were taken for chromatographic analysis; the valve was equipped with two loops with a total capacity of about 45 cc.

In order to obtain samples for chromatographic analysis of the reacting species before they reached the reactor, a by-pass line connecting a point before the reactor entrance to another point after the 'U' trap filled with beads was constructed as part of the flow system.

The gas chromatograph (GC) used was composed of a GOW-MAC thermistor detector, a column heated by an oil bath to about 75°C, a homemade power supply and electronic detector circuit (Figure 3), and a Bristol Dynamaster, Model 1PH760-51, recorder. The solid phase of the chromatographic column was acid washed Chromosorb-W, the liquid phase was 10% dinonyl phthalate. The carrier gas for the chromatograph was helium; the flow was measured by a calibrated



(see Appendix B) flow meter (BL).

B. Procedure and Sample Calculations

Run No. 19 is described as an example of the technique used for the experimental procedure followed in all runs.

The desired reactor temperature for this run was 578°C. To determine the temperature, the output potential of the thermocouple in the thermocouple well of the reactor was measured with a Honeywell, Model 2732, portable potentiometer. Since this reading corresponded to the number of degrees above room temperature, a thermocouple output equivalent to $578 - 27 = 551^\circ\text{C}$ or 22.79 mV^{17} was necessary. Thus, the ON-OFF temperature controller was adjusted until the desired out-put potential was attained (the reading of the temperature controller was not a reliable indication of the reactor temperature). The placement of the temperature controller detector in the annular space between the reactor and the furnace wall enhanced controller sensitivity to temperature changes and relative consistency; thus, the temperature cycling never exceeded $\pm 1^\circ\text{C}$.

The helium gas pressure downstream from the flowmeter was considered to be that of the laboratory, 740 mm Hg, which was measured with a mercury barometer.

According to the conditions for run No. 19 the flow rate of helium was chosen to be 12.64 cc/sec, which corresponded to a ΔP value of 190 mm with capillary No. 1. Using a 2.0 ml syringe, a dial setting of 16.0 gave a rate of injection of $0.885 \times 10^{-3} \text{ cc/sec}$ of liquid solution of 10.16 mole % pentachloroethane in toluene. The

flow and injection rates selected would give the contact time and concentration that were needed.

The factors which limited the concentration range for the reactant were the vapor pressures of toluene and pentachloroethane at room temperature and the sensitivity of the GC cells. At these injection and flow rates a vapor concentration of less than 2 mole % of toluene in the helium stream was obtained; the maximum vapor concentration of toluene at room temperature is about 4 mole %. The flow line was carefully checked to insure that the appropriate rate of injection was used and did not cause any condensation of the reactants on the walls of the tubing before the reactor.

After having established the conditions to give the desired reactant concentration and contact time, the succeeding steps were followed: Before connecting the syringe to the flow system, helium was allowed to flow through the complete system for a few minutes to flush out oxygen, remove any previously deposited volatile material and warm up the stream by the preheater. The solution of pentachloroethane in toluene of the concentration to be used was freshly prepared (density of 0.9577 g/cc for the 10.16 mole % solution, see Appendix B). After carefully filling the syringe and removing any air in the syringe and hypodermic needle, the system for injection was assembled and jointed to the flow system. With the helium flow properly adjusted the syringe drive motor was actuated and the gaseous mixture produced was directed through the by-pass line and finally vented to the room. After about 25-30 minutes to establish steady-state flow, the first sample for relative quantitative chromatographic analysis was

taken using the Beckman valve. The time for sampling was 15 seconds because both loops were combined for one sample and the time was needed to fill the second loop. After about 7 minutes a second sample was taken and these established the zero percent reaction peak heights. Next, the syringe was refilled and again run under the same conditions, but the reactant mixture was directed through the reactor. After about 30 minutes to allow the establishment of the steady-state condition, two samples for chromatographic analysis were taken, following the same technique. Since the injection and flow rates were known, the initial concentration of the reactant mixture could be calculated, which corresponded to the peaks of the chromatogram for the run through the by-pass. Similarly, the peaks of the chromatogram obtained for the run through the reactor corresponded to the final concentrations of the reactant mixture after pyrolysis.

It was found that for a given run the width of the chromatographic peaks for pentachloroethane from the by-pass or from the reactor did not differ significantly, and that the baseline was quite stable. Because of this, it was possible to use the height ratio of the moderately broad peaks to determine the extent of reaction of pentachloroethane instead of the area ratio. The sensitivities used for the chromatograms were 70-90% of maximum for pentachloroethane, and 3-5% of maximum for toluene (power supply settings were 12 volts and 8.0 mA). Toluene had a retention time of about 2 minutes (for a helium flow of about 3.7 cc/sec), while pentachloroethane had one of about 17 minutes, thus there was no interference.

The following information was known for experimental run No. 19:

flow rate of helium at 27°C, 12.64 cc/sec; rate of injection of reactant solution, 0.885×10^{-3} cc/sec; pentachloroethane concentration of the solution, 10.16 mole % in toluene; density of the solution, 0.9577 g/cc; molecular weights, 202.30 g/mole for pentachloroethane, and 92.14 g/mole for toluene; room temperature, 27°C; reactor temperature above room temperature, 551°C; reactor volume, 78.3 ± 1.5 cc; barometric pressure, 740 mm Hg; and, molar volume of a gas at the laboratory conditions, 25.3×10^3 cc/mole. Assuming ideal behavior it was possible to determine the following:

Volume of vapor injected at 27°C

$$= \frac{0.885 \times 10^{-3} \text{ cc/sec} \times 0.9577 \text{ g/cc} \times 25.3 \times 10^3 \text{ cc/mole}}{(92.14 \times 0.8984 + 202.30 \times 0.1016) \text{ g/mole}}$$

$$= 0.21 \text{ cc/sec.}$$

Rate of pentachloroethane injected at 27°C

$$= \frac{0.885 \times 10^{-3} \text{ cc/sec} \times 0.1016 \times 0.9577 \text{ g/cc}}{(92.14 \times 0.8984 + 202.30 \times 0.1016) \text{ g/mole}}$$

$$= 0.833 \times 10^{-6} \text{ mole/sec}$$

Total flow rate at 27°C

$$= 12.64 + 0.21 = 12.85 \text{ cc/sec}$$

Initial concentration of pentachloroethane at the reactor entrance

$$= \frac{0.833 \times 10^{-6} \text{ mole/sec} \times 1000 \text{ cc/l}}{12.85 \text{ cc/sec} \times 851 \text{ K}/300 \text{ K}}$$

$$= 2.285 \times 10^{-5} \text{ mole/l}$$

Contact time

$$= \frac{78.3 \text{ cc}}{12.85 \text{ cc/sec} \times 851 \text{ K}/300 \text{ K}}$$

$$= 2.15 \text{ sec.}$$

By comparison of the height of the chromatographic peaks of pentachloroethane obtained from samples taken from the by-pass and from the reactor, it was possible to calculate the extent of the reaction.

$$\begin{aligned}\text{Extent of reaction} &= \left(1 - \frac{\text{Height Peak Reactor}}{\text{Height Peak By-Pass}}\right) \times 100 \\ &= \left(1 - \frac{6.75}{9.15}\right) \times 100 = 29.5\%\end{aligned}$$

Because of the low concentration of the reactant, the change in the number of moles of the reactant mixture during pyrolysis did not significantly affect the total flow rate.

Run No. 19 is again used as an example for the calculation of the reaction rate and rate constant. Making the reasonable assumption that the reaction is first-order with respect to pentachloroethane, equations (8) and (9) can be combined to give the following rate expression:

$$-\text{rate} = (c_0 - c)/t = X/t = kc \quad (14)$$

where X is the change in concentration of reactant $(c_0 - c)$, c_0 is the initial concentration of reactant, c is the concentration of reactant at time t , and t is the contact time.

The change in concentration,

$$\begin{aligned}X &= (c_0 - c) = 2.285 \times 10^{-5} \text{ mole/l} \times 0.295 \\ &= 0.673 \times 10^{-5} \text{ mole/l}\end{aligned}$$

Concentration at time t ,

$$\begin{aligned}c &= (c_0 - X) = (2.285 - 0.673) \times 10^{-5} \text{ mole/l} \\ &= 1.612 \times 10^{-5} \text{ mole/l}\end{aligned}$$

Hence,

The rate of reaction,

$$r = \frac{X}{t} = 0.673 \times 10^{-5} \text{ mole-l}^{-1}/2.15 \text{ sec}$$

$$= 0.315 \times 10^{-5} \text{ mole-l}^{-1}\text{-sec}^{-1}$$

and

The apparent rate constant,

$$k_a = \frac{X}{ct} = \frac{0.315 \times 10^{-5} \text{ mole-l}^{-1}\text{-sec}^{-1}}{1.612 \times 10^{-5} \text{ mole-l}^{-1}} = 0.194 \text{ sec}^{-1}$$

The first-order assumption was validated by the relative consistency of the values obtained for k.

C. Materials

Aldrich pentachloroethane practical reagent grade, 96% purity and refractive index $\eta_D^{20} = 1.5033$ was used after it was purified by fractional distillation at low pressure and at a constant boiling point of 47°C; after distillation it was stored in a dark flask. The toluene used was 'Baker Analyzed' Reagent, spectrophotometric grade and boiling point 110.6°C, without further purification.

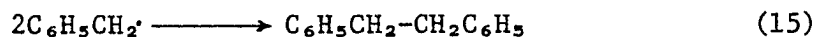
III. RESULTS AND DISCUSSION

A. Reaction Products

The major volatile products of the inhibited pyrolysis of pentachloroethane were hydrogen chloride and trichloroethylene. The first was quantitatively determined by acid-base titration. The second was qualitatively determined by the comparison of the retention times of chromatographic peaks observed during the regular runs of pentachloroethane in toluene through the reactor with that obtained for the pure trichloroethylene, through the by-pass line. In addition, the size of the peak indicated that it was the major organic product. Trichloroethylene was also checked by running pentachloroethane alone through the reactor. In this case, it is known^{2,3} that tetrachloroethylene is the major organic product, and trichloroethylene is a minor product. Two chromatographic peaks were obtained: a small peak at the same retention time as that already found for trichloroethylene (which confirmed the above determination), and a large peak at the same retention time as that regularly found for toluene. It was concluded (by odor) that this second peak corresponded to tetrachloroethylene.

A non-volatile, yellow product of the reaction coated the walls of the reactor exit line and part of the SP "'U'" trap. Most of this residue was readily soluble in carbon tetrachloride, ethanol, acetone and carbon disulfide. It had been previously reported ¹³⁻¹⁴ that the main component of this residue is dibenzyl which is formed by dimer-

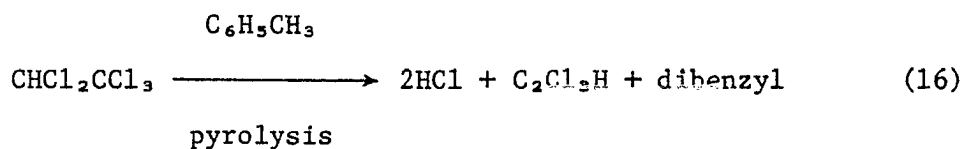
ization of the benzyl radicals in the exit stream of the reactor



Other carbonaceous by-products completed the residue and gave it the yellow color. Dibenzyl was qualitatively characterized by running a chromatographic analysis of a sample of the yellow material, which gave a peak at a certain retention time; a second sample with pure dibenzyl added, gave the same peak, but increased in size, which indicated the presence of dibenzyl. For this analysis, an F and M, Model 720, gas chromatograph was used.

In order to verify the stoichiometry of the reaction, quantitative analysis of hydrogen chloride was carried out. To accomplish this, several runs were made using reactor No. 1 at 851 and 865 K and contact times of 2.15 and 5.00 seconds respectively with a procedure similar to that described earlier (Chapter 2, Section B). However, the "'U'" trap (SP) following at the exit of the reactor was immersed in a dry-ice bath (to condense all volatile materials, except HCl) and the exit stream from the reactor was bubbled through a basic solution. Table I shows the results obtained, and Appendix D presents the procedure used.

It was concluded that the decomposition of pentachloroethane in the presence of toluene follows the stoichiometry



It should be pointed out that under the experimental conditions employed, decomposition of toluene¹⁸ was not observed in the absence

TABLE I

Results of the Hydrogen Chloride Analysis

Exp. No.	Temp., K	Contact time, sec	Pentachloroethane		HCl Moles x 10 ⁴ ^c	HCl/ ^d PCE
			Moles x 10 ⁴ ^a	X/c ₀ ^b		
1	851	2.15	2.435	0.237	1.123	1.95
2			2.435	0.237	1.265	2.19
3			3.653	0.237	1.590	1.84
4			4.871	0.237	2.143	1.86
5	865	5.00	1.592	0.574	1.591	1.74
6			1.592	0.574	1.684	1.84

^a Moles injected. ^b Mole fraction decomposed according to the quantitative chromatographic analysis carried out under the same flow conditions as for the HCl analysis. ^c Moles produced as detected by titration. ^d Moles of HCl produced per mole of pentachloroethane (PCE) decomposed.

of pentachloroethane.

B. Kinetics Results

The results obtained for the inhibited pyrolysis of pentachloroethane by flow experiments using reactor No. 1 at 548, 563, 578 and 592°C are tabulated in Appendix A. Determinations at four different contact times for each temperature were carried out (three for 563°C). Furthermore, at 578°C three different initial concentrations were used to establish the order of the reaction rate with respect to pentachloroethane.

The rate was found to be first-order, thus equation (14) was used to represent the data

$$-r = X/t = k_1 c$$

where r is the rate expressed in $\text{mole-l}^{-1}\text{-sec}^{-1}$, k_1 is a first-order rate constant in sec^{-1} , X is the change in reactant concentration due to decomposition in mole-l^{-1} , and c is the pentachloroethane concentration in the reactor in mole-l^{-1} .

Table II presents a summary of the rate constants obtained with reactor No. 1 at the four different temperatures. Appendix C presents the uncertainties in the individual measurements and their effects on the final results.

Figure 4 is the Arrhenius plot for the flow experiments using reactor No. 1. A least-squares analysis of these results gives the following expression

$$k_1 = 10^{11.56 \pm 0.67} e^{-(48,200 \pm 2,600)/RT}, \text{ sec}^{-1} \quad (17)$$

TABLE II
Summary of Kinetic Results

<u>T, K</u>	<u>1/T x 10³</u>	<u>k₁, sec⁻¹ x 10</u>		<u>-log k₁ (Obs.)</u>
		<u>Obs.</u>	<u>Calc.</u>	
821	1.218	0.543 \pm 0.026 ^a	0.533	1.265
836	1.196	0.948 \pm 0.046	0.905	1.023
851	1.175	1.43 \pm 0.04	1.51	0.8447
865	1.156	2.53 \pm 0.08	2.41	0.5969

^aStandard deviation of the mean. ^bCalculated from equation (17).

The results found using reactor No. 2 at 578°C to study the effects of the surface on the reaction rate are summarized in Table III and are tabulated in Appendix A also. Four and three contact times for the empty and packed reactor, respectively, were used.

TABLE III
Surface Effects on the Rate at 851 K

<u>Reactor No. 2</u>	<u>k₁, sec⁻¹ x 10^a</u>
Empty	0.518 \pm 0.023 ^b
Filled	0.444 \pm 0.020

^aThe apparent decrease in k₁ was due to a different temperature distribution with reactor No. 2 in comparison to reactor No. 1 for the same temperature. ^bStandard deviation of the mean.

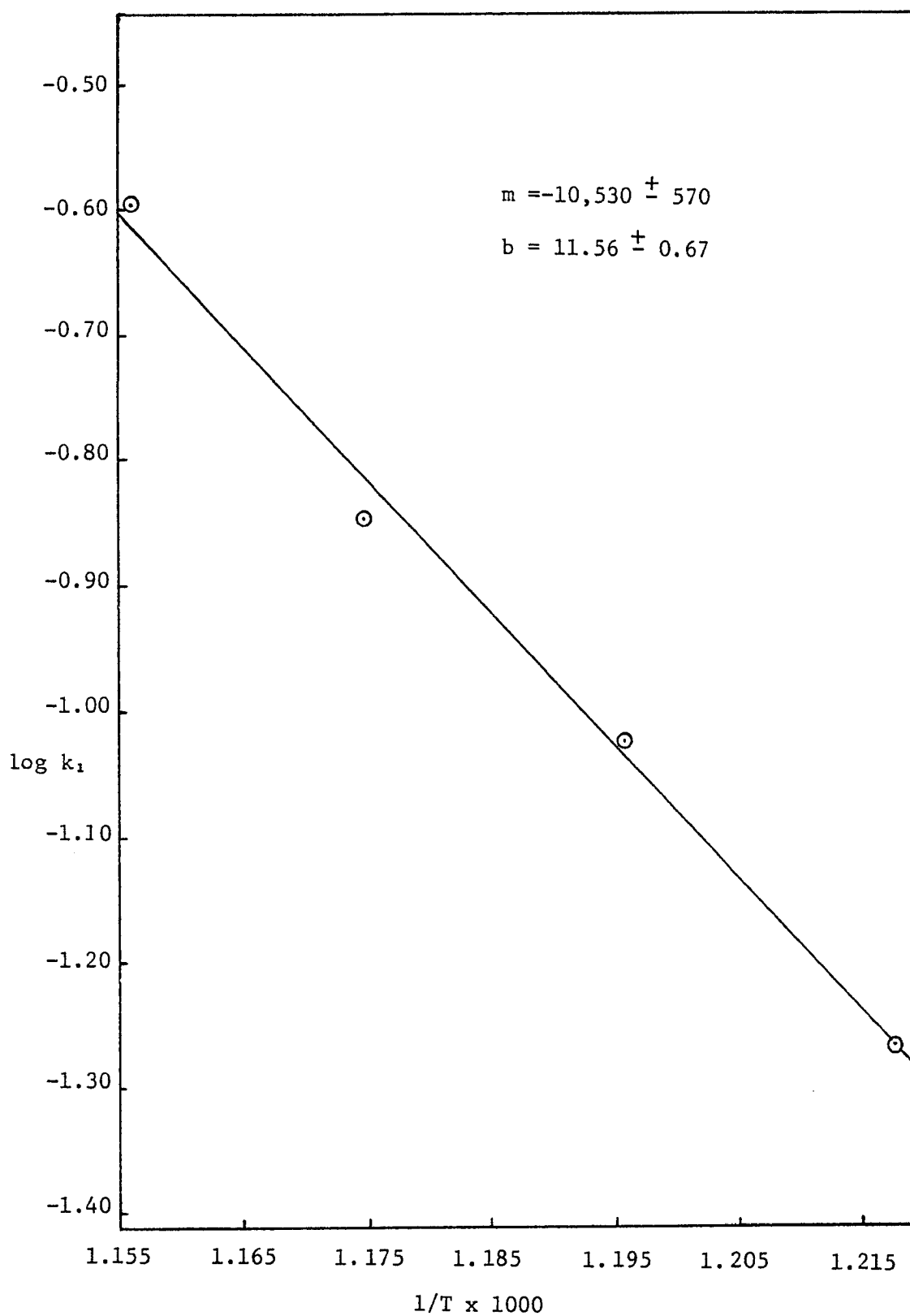


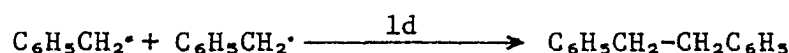
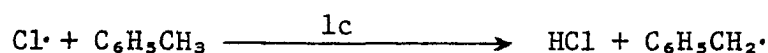
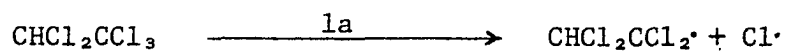
FIGURE 4: Arrhenius Plot

C. Calculation of the $\text{CHCl}_2\text{CCl}_2\text{-Cl}$ Bond Dissociation Energy

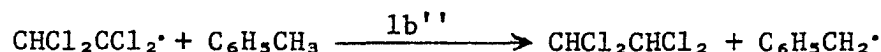
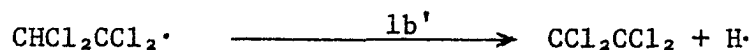
There is no reported value for this bond dissociation energy based on direct kinetic data. An estimation value of 72 Kcal/mole was reported by Houser and Bernstein² for the activation energy of the initiation step of their mechanism. Calculations based on thermochemical data and an estimation from group property additivity rules by Franklin and Huybrechts¹⁹, give in both cases a value of 70 Kcal/mole (at 25°C and 1 atm) for the C-Cl bond dissociation energy in pentachloroethane. The activation energy calculated from the results of this study is 48.2 Kcal/mole which can be directly equated to the $\text{CHCl}_2\text{CCl}_2\text{-Cl}$ bond dissociation energy. The disagreement with the former values is unresolved at this time.

D. Mechanism of Reaction

Taking into account the stoichiometry of the reaction, the observed first-order rate law, the activation energy, and the results on the surface effects (see below), the following simple mechanism is proposed for the pyrolysis of pentachloroethane inhibited by toluene,



A few other variations were considered such as:



but these were ruled out as major contributors to the mechanism due to energetic considerations ($E_a = 21.4$ Kcal/mole for lb and $E_a = 42.6$ for lb')¹⁹, and because tetrachloroethylene and tetrachloroethane were not observed as significant products. In addition, since two moles of HCl were produced for each mole of $\text{CHCl}_2\text{CCl}_3$ decomposed, a Cl elimination step like lb is necessary.

The results on the effects of the surface clearly revealed that the initial process of pyrolysis is homogeneous, since increasing the surface area/volume of the reactor by a factor of 6.6 did not show a significant change on the reaction rate. This contradicts the findings of Shvets et al.³, who have reported a factor of 2.5 increase in the rate of the inhibited decomposition when the surface area/volume was increased by a factor of 3.14. It should be noted that these authors used n-hexane at low concentrations (about 1 mole %) as the inhibitor, worked with a Pyrex tubular reactor at temperatures more than 100°C below those of this study, and did not use a carrier gas; it is possible that these changes in conditions account for the difference.

The low values for the rate constant obtained with reactor No. 2 at 851 K, compared with those obtained with reactor No. 1 for the same temperature, were mainly due to reactor design which did not permit an efficient heating of the upper end of reactor No. 2. In spite of that, the results on the effects of the surface on the reaction rate are valid because the same heating was provided for the reactor in both cases, empty and filled. One last consideration, from the carbonaceous deposits on the reactor and packing it did

not appear that significant channeling took place to offset possible rate increases due to a larger surface area.

The overall mechanism for the pyrolysis of pentachloroethane proposed by Shvets et al.³ appears reasonable, with the exception of the heterogeneity of the initiation and termination steps. Reevaluation of the kinetic data of Houser²⁰ in accordance with the rate equation obtained from their mechanism leads to the conclusion that the data and mechanism are consistent.

APPENDIX A

Kinetics Data

Symbols:

% conc = mole percent of pentachloroethane in toluene

c_0 = initial concentration of pentachloroethane at reactor conditions, $\text{mole-l}^{-1} \times 10^5$

t = contact time, sec

X = concentration of pentachloroethane reacted, $\text{mole-l}^{-1} \times 10^5$

X/c_0 = fraction of pentachloroethane decomposed

c = concentration of pentachloroethane at time t , $\text{mole-l}^{-1} \times 10^5$

$r = X/t$ = rate of reaction, $\text{mole-l}^{-1}\text{-sec}^{-1} \times 10^6$

$k = r/c$ = rate constant, $\text{sec}^{-1} \times 10$

Data at 548°C (821 K), Reactor No. 1

<u>Run No.</u>	<u>% conc.</u>	<u>c_0</u>	<u>t</u>	<u>X/c_0</u>	<u>c</u>	<u>r</u>	<u>k</u>
1	5.077	1.127	3.00	0.162	0.9443	0.540	0.572
2				0.120	0.9912	0.401	0.405
3	5.156	1.123	5.01	0.228	0.8665	0.512	0.591
4				0.247	0.8457	0.554	0.655
5				0.234	0.8600	0.525	0.611
6	5.077	1.132	7.00	0.233	0.8676	0.377	0.435
7				0.289	0.8051	0.466	0.579
8	5.156	1.124	9.99	0.347	0.7340	0.390	0.532
9				0.314	0.7707	0.354	0.459
10				0.372	0.7054	0.419	0.594

Data at 563°C (836 K), Reactor No. 1

<u>Run No.</u>	<u>% conc.</u>	<u>c₀</u>	<u>t</u>	<u>X/c₀</u>	<u>c</u>	<u>r</u>	<u>k</u>
11	5.065	1.115	3.01	0.196	0.8964	0.727	0.811
12				0.179	0.9158	0.663	0.723
13	5.136	1.103	4.92	0.348	0.7197	0.779	1.083
14				0.323	0.7469	0.724	0.969
15				0.311	0.7599	0.697	0.918
16	5.136	1.104	9.81	0.512	0.5393	0.576	1.067
17				0.484	0.5695	0.545	0.957
18				0.508	0.5431	0.572	1.053

Data at 578°C (851 K), Reactor No. 1

<u>Run No.</u>	<u>% conc.</u>	<u>c₀</u>	<u>t</u>	<u>X/c₀</u>	<u>c</u>	<u>r</u>	<u>k</u>
19	10.16	2.285	2.15	0.295	1.612	3.13	1.94
20				0.253	1.707	2.69	1.58
21	10.09	2.255	3.40	0.281	1.621	1.87	1.15
22				0.392	1.371	2.60	1.90
23				0.358	1.443	2.37	1.64
24				0.365	1.433	2.42	1.69
25	10.09	2.252	6.80	0.471	1.191	1.56	1.31
26				0.542	1.004	1.80	1.79
27				0.430	1.283	1.43	1.11
28				0.515	1.093	1.70	1.56
29				0.451	1.236	1.49	1.21
30				0.467	1.201	1.55	1.29
31	10.09	2.367	12.5	0.636	0.8623	1.20	1.40
32				0.615	0.9115	1.16	1.28
33	5.105	1.234	0.98	0.105	1.104	1.32	1.20
34				0.139	1.063	1.74	1.64
35	5.156	1.114	2.15	0.296	0.7845	1.37	1.75
36				0.222	0.8662	1.03	1.19
37				0.221	0.8674	1.03	1.19
38				0.240	0.8461	1.24	1.47
39				0.230	0.8575	1.19	1.39
40				0.223	0.8653	1.16	1.34
41	4.980	1.114	3.40	0.367	0.7055	1.20	1.70
42				0.296	0.7839	0.971	1.24
43				0.284	0.7972	0.932	1.17
44	4.980	1.113	6.80	0.476	0.5835	0.779	1.34
45				0.458	0.6034	0.749	1.24
46				0.476	0.5830	0.779	1.34

<u>Run No.</u>	<u>% conc.</u>	<u>c_o</u>	<u>t</u>	<u>X/c_o</u>	<u>c</u>	<u>r</u>	<u>k</u>
47	2.555	0.6118	1.00	0.0976	0.5521	0.599	1.08
48				1.110	0.5446	0.674	1.24
49				1.128	0.5337	0.784	1.47
50	2.537	0.6193	2.95	0.284	0.4433	0.597	1.35
51				0.300	0.4335	0.630	1.45
52				0.250	0.4645	0.525	1.13
53	2.537	0.6145	5.12	0.423	0.3545	0.508	1.43
54				0.415	0.3597	0.498	1.38
55				0.368	0.3885	0.441	1.14
56	2.537	0.6070	9.88	0.652	0.2111	0.401	1.90
57				0.652	0.2111	0.401	1.90
58				0.607	0.2385	0.373	1.56

Data at 592°C (865 K), Reactor No. 1

<u>Run No.</u>	<u>% conc.</u>	<u>c_o</u>	<u>t</u>	<u>X/c_o</u>	<u>c</u>	<u>r</u>	<u>k</u>
59	5.102	1.114	1.00	0.185	0.9080	2.06	2.26
60				0.234	0.8530	2.61	3.06
61				0.179	0.9140	2.00	2.18
62	5.065	1.106	1.00	0.195	0.8900	2.16	2.42
63				0.174	0.9131	1.93	2.11
64	5.077	1.131	2.00	0.286	0.8080	1.62	2.00
65				0.299	0.7926	1.69	2.14
66				0.331	0.7569	1.87	2.47
67	5.156	1.130	3.03	0.438	0.6356	1.63	2.57
68				0.435	0.6390	1.62	2.54
69				0.421	0.6538	1.57	2.40
70	5.102	1.114	5.00	0.607	0.4381	1.35	3.08
71				0.600	0.4455	1.34	2.99
72	5.065	1.106	5.00	0.578	0.4670	1.28	2.74
73				0.584	0.4596	1.29	2.81
74				0.553	0.4943	1.22	2.47
75				0.573	0.4719	1.27	2.69

Data at 578°C (851 K), Reactor No. 2, Empty

<u>Run No.</u>	<u>% conc.</u>	<u>c₀</u>	<u>t</u>	<u>X/c₀</u>	<u>c</u>	<u>r</u>	<u>k</u>
76	5.762	0.9945	1.49	0.0645	0.9303	0.431	0.463
77				0.0705	0.9244	0.471	0.509
78	5.762	0.9985	2.99	0.153	0.8459	0.510	0.603
79				0.129	0.8694	0.432	0.497
80				0.154	0.8448	0.514	0.609
81	5.762	0.9952	5.00	0.238	0.7587	0.473	0.624
82				0.192	0.8048	0.381	0.474
83				0.217	0.7796	0.432	0.554
84	5.762	1.026	7.02	0.258	0.7617	0.377	0.495
85				0.257	0.7619	0.376	0.494
86				0.206	0.8145	0.301	0.370

Data at 578°C (851 K), Reactor No. 2, Filled

<u>Run No.</u>	<u>% conc.</u>	<u>c₀</u>	<u>t</u>	<u>X/c₀</u>	<u>c</u>	<u>r</u>	<u>k</u>
87	5.169	0.9962	1.50	0.0643	0.9321	0.427	0.458
88				0.0546	0.9419	0.362	0.385
89				0.0524	0.9440	0.348	0.368
90				0.0707	0.9258	0.469	0.507
91	5.169	1.001	3.00	0.101	0.9000	0.338	0.375
92				0.131	0.8698	0.438	0.504
93				0.111	0.8900	0.371	0.417
94				0.146	0.8545	0.488	0.572
95				0.128	0.8730	0.428	0.490
96				0.113	0.8880	0.378	0.425
97	5.169	1.000	4.99	0.192	0.8084	0.385	0.475
98				0.149	0.8515	0.298	0.350

APPENDIX B

Calibration Data

Flow Rate of Helium:

Capillary No. 1 (smaller Diameter)		Capillary No. 2	
<u>Pressure drop, mm</u>	<u>Flow rate, cc/sec^a</u>	<u>Pressure drop, mm</u>	<u>Flow rate, cc/sec^a</u>
16.0	1.15	17.0	4.64
31.3	2.20	33.5	9.00
60.0	4.12	55.2	14.20
89.7	6.20	91.0	22.57
124.0	8.43	117.3	28.40
164.5	11.06	154.2	36.11
208.5	13.75	203.1	45.13
221.5	14.62	221.0	48.61

^a Flow rates of helium were calibrated at $27 \pm 2^\circ\text{C}$ and 740 mm Hg total pressure.

Rate of Injection:

<u>Dial setting for the syringe drive</u>	<u>Rate of injection, cc/sec x 10³</u>		
	<u>1.0 ml syringe</u>	<u>2.0 ml syringe</u>	<u>5.0 ml syringe</u>
10.0	0.172	0.569	
15.0			1.541
20.0		1.125	
30.0	0.484	1.678	3.017
40.0		2.205	
45.0			4.575
50.0	0.825	2.757	
60.0		3.288	6.118
70.0	1.166	3.839	
75.0			7.791
90.0	1.481		9.076

The volume flow rates were determined using dibutyl phthalate (1.043 g/cc density) at a temperature of $27 \pm 2^\circ\text{C}$.

Flow Rate of Helium for the Gas Chromatograph:

<u>Height level of ball, mm</u>	<u>Flow rate, cc/sec</u>
27.0	0.984
53.0	3.050
63.0	4.000
74.5	4.874

This calibration and those for the capillaries were made using a "Precision" wet test meter at room temperature of $27 \pm 2^\circ\text{C}$ and 740 mm Hg total pressure.

Solutions of pentachloroethane in toluene

The desired concentrations were prepared by pouring into small weighed dark flasks (each of about 60 cc capacity), the desired volumes of pentachloroethane and toluene, and each respectively weighed using a Mettler, Type H15, electric balance. The density of each solution was determined using a 5.00 ml volumetric flask. The room temperature was $27 \pm 2^\circ\text{C}$.

APPENDIX C

Error Analysis

The uncertainties in the individual measurements and their effects on the final results were analyzed in the following way:

1) The uncertainty in the flow rate of helium depended on the magnitude of the pressure drop (ΔP) which could be read to ± 1 mm. The highest reading was 190 mm; the lowest reading was 35 mm (both with capillary No. 1 for the flowmeter). These gave the minimum uncertainty of $1/190 \times 100 = 0.5\%$ and the maximum uncertainty of $1/35 \times 100 = 3.0\%$, respectively. Consequently, maximum uncertainty appeared at relatively long contact times.

2) The uncertainties in the concentration of pentachloroethane solutions were estimated to be 10.16 ± 0.01 mole % for the highest concentration and 2.537 ± 0.003 mole % for the lowest concentration. Thus, the uncertainty was about 0.1% for both cases.

3) The uncertainty in the amount of pentachloroethane injected was based on the rate of injection, which was limited by its reproducibility estimated to be $\pm 0.002 \times 10^{-3}$ cc/sec. Hence, the largest uncertainty appeared at the lowest concentration of pentachloroethane solution (2.537 mole %) and the respective longest contact time (9.88 sec.) where the rate was 0.205×10^{-3} cc/sec. For this, the uncertainty was 1.0%. The smallest uncertainty was about 0.1% when the rate of injection was 2.080×10^{-3} cc/sec of 5.105 mole % pentachloroethane solution.

4) The volume of reactor No. 1 was measured to ± 1.5 cc, and its

total volume was 78.3 cc, which gave an uncertainty of $1.5/78.3 \times 100 = 1.9\%$. Reactor No. 2 was measured to ± 3.0 cc, and its total volume was 76.8 cc, which produced an uncertainty of $3.0/76.8 \times 100 = 3.9\%$. The source of uncertainty for either reactor was systematic and therefore did not contribute to the random behavior of the individual values, but was added to the final uncertainty in the rate constant. Volume variations due to temperature changes were considered negligible (because of the very low thermal expansion coefficient of Vycor).

5) The uncertainty in the relative quantitative gas chromatographic determination of pentachloroethane originated mainly from instrumental factors which resulted in irreproducibility. Thus, the uncertainty in the determination of samples from the by-pass line was $0.10/6.00 \times 100 = 1.7\%$, and the uncertainty of samples from the reactor was $0.10/4.00 \times 100 = 2.5\%$, both on the average. It should be pointed out that a systematic source of uncertainty was involved in any sampling produced by possible disturbances in the inherent steady-state flow or by the sampling valve itself. Since this uncertainty is not random, it could not be added to the individual determinations, but would appear in the final uncertainty in the rate constant. Uncertainty in the time of sampling was estimated to be negligible.

6) The uncertainties in the initial concentration were from (1), (2) and (3) and those in the final concentration originated from (1), (2), (3) and (5).

The uncertainty in the initial concentration was,

$$\text{Maximum: } (3.0^2 + 0.1^2 + 1.0^2)^{\frac{1}{2}} = 3.2\%$$

$$\text{Minimum: } (0.5^2 + 0.1^2 + 0.1^2)^{\frac{1}{2}} = 0.5\%$$

The uncertainty in the final concentration was,

$$\text{Maximum: } (3.0^2 + 0.1^2 + 1.0^2 + 1.7^2 + 2.5^2)^{\frac{1}{2}} = 4.4\%$$

$$\text{Minimum: } (0.5^2 + 0.1^2 + 0.1^2 + 1.7^2 + 2.5^2)^{\frac{1}{2}} = 3.1\%$$

7) The uncertainties in contact time arose mainly from the uncertainties in the flow rate of helium, whose limits were 0.5 and 3.0%. Minor contributions from uncertainties in the rate of injection and in any gas volume change due to pyrolysis, were considered negligible. If pyrolysis caused any gas formation with the consequence of volume increment, the formation of non-volatile residue with the consumption of some gas mixture component produced a volume decrease, which gave a net result of approximately no gas volume change.

The uncertainty in contact time was,

$$\text{Maximum: } 3.0\%$$

$$\text{Minimum: } 0.5\%$$

8) The uncertainty in the rate constant resulted from the total uncertainty in the difference between the initial and the final concentrations which had a high dependence on the extent of reaction. As illustration, the following examples are presented:

(a) Run No. 48. The data are, initial concentration, $c_0 = 0.6118 \times 10^{-5}$ mole/l; final concentration, $c = 0.5446 \times 10^{-5}$ mole/l; contact time, $t = 1.00$ sec; and, temperature, $T = 851$ K. For this run the minimum concentration uncertainty was applicable because the contact time was low, being at the high flow rate.

$$\begin{aligned}
 X = c_o - c &= (0.6118 - 0.5446) \times 10^{-5} \pm \left[(0.6118 \times 0.005)^2 \right. \\
 &\quad \left. + (0.5446 \times 0.031)^2 \right]^{\frac{1}{2}} \times 10^{-5} \\
 &= 0.0672 \times 10^{-5} \pm \left[(0.0031)^2 + (0.0169)^2 \right]^{\frac{1}{2}} \times 10^{-5} \\
 &= (0.0672 \pm 0.0172) \times 10^{-5}
 \end{aligned}$$

Thus, the uncertainty in X was $\pm 0.0172/0.0672 \times 100 = \pm 26\%$.

(b) Run No. 32. The data are, initial concentration, $c_o = 2.367 \times 10^{-5}$ mole/l; final concentration, $c = 0.9115 \times 10^{-5}$ mole/l; contact time, $t = 12.5$ sec; and, temperature, $T = 851$ K. For this example, a concentration uncertainty greater than minimum but less than maximum was applicable because the contact time was long but the concentration was high.

$$\begin{aligned}
 X = c_o - c &= (2.367 - 0.9115) \times 10^{-5} \pm \left[(2.367 \times 0.022)^2 \right. \\
 &\quad \left. + (0.9115 \times 0.030)^2 \right]^{\frac{1}{2}} \times 10^{-5} \\
 &= 1.456 \times 10^{-5} \pm \left[(0.0521)^2 + (0.0274)^2 \right]^{\frac{1}{2}} \times 10^{-5} \\
 &= (1.456 \pm 0.059) \times 10^{-5}
 \end{aligned}$$

Thus, the uncertainty in X was $\pm 0.059/1.456 \times 100 = \pm 4.1\%$

(c) Run No. 70. The data are, initial concentration, $c_o = 1.114 \times 10^{-5}$ mole/l; final concentration, $c = 0.4381 \times 10^{-5}$ mole/l; contact time, $t = 5.00$ sec; and, temperature, $T = 865$ K. For this case an intermediate uncertainty concentration was applicable because the contact time and concentration were intermediate.

$$\begin{aligned}
 X = c_o - c &= (1.114 - 0.431) \times 10^{-5} \pm \left[(1.114 \times 0.018)^2 \right. \\
 &\quad \left. + (0.4381 \times 0.026)^2 \right]^{\frac{1}{2}} \times 10^{-5} \\
 &= 0.676 \times 10^{-5} \pm \left[(0.0201)^2 + (0.0114)^2 \right]^{\frac{1}{2}} \times 10^{-5} \\
 &= (0.676 \pm 0.023) \times 10^{-5}
 \end{aligned}$$

Thus the uncertainty in X was $\pm 0.023/0.676 \times 100 = \pm 3.4\%$.

For runs of low contact time and low extent of reaction the uncertainty in the calculated rate (X/t) gave,

$$(26^2 + 0.5^2)^{\frac{1}{2}} = 26\%$$

Long contact time and high extent of reaction gave an uncertainty in the rate of

$$(4.1^2 + 3^2)^{\frac{1}{2}} = 5.1\%$$

And for an intermediate value of contact time and a high extent of reaction, the uncertainty in the rate was,

$$(3.4^2 + 3^2)^{\frac{1}{2}} = 4.5\%$$

It can be seen that there was a leveling effect because high flow rates which gave low uncertainty in concentrations and produced low extents of reaction, resulted in high rate uncertainties as a consequence of the small values of X , and viceversa. Nevertheless, the above examples showed that the uncertainty in X was always more significant than that in contact time.

9) According to the above examples, the maximum deviation from the mean that the rate constants can have under a specific set of conditions, fall within the range of the deviations found experimentally, but indeed are not very reliable. Tabulated below are the mean values for the rate constants, shown together with the observed standard deviations of a sample, which are felt to be more reliable than the predicted maximum deviations from the analysis of uncertainties.

<u>Temperature</u>	<u>Mean value</u>	<u>Observed (std.) deviation</u>
<u>K</u>	<u>k_1, sec^{-1}</u>	
821	0.0543	± 0.0079 (15%)
836	0.0948	± 0.0120 (13%)
851	0.143	± 0.0245 (17%)
865	0.253	± 0.0324 (13%)
851 ^a	0.0518	± 0.0072 (14%)
851 ^b	0.0444	± 0.0065 (15%)

^aReactor No. 2, empty. ^bReactor No. 2, filled

APPENDIX D

Procedure for Determining the Hydrogen Chloride in the Exit Stream

As mentioned earlier (Results Section), a simple acid-base titration was used to determine the HCl in the exit stream from the reactor. The following procedure was used:

By means of a pipette, 10.0 ml NaOH solution freshly prepared was poured into a gas bubbler flask of about 300 ml capacity. Then, three drops of phenolphthalein indicator solution and enough distilled water (about 30 ml) to cover the tip of the bubbler were added. Next, the bubbler flask was connected to the exit stream from the reactor using a teflon tubing, and the gases leaving the "U" trap (SP) immersed in a dry-ice bath were permitted to bubble through the basic solution for a certain time. Finally, the bubbler flask was removed and the excess of NaOH was titrated with a hydrochloric acid solution using a 50.0 ml buret.

The tabulation below summarizes the data for the analysis of HCl in the exit stream from the reactor.

<u>Exp. No.</u>	<u>T, K</u>	<u>PCE^a, x 10⁷</u>	<u>Time^b, min.</u>	<u>10.0 ml NaOH solution, N</u>	<u>HCl sol., N</u>	<u>ml HCl sol. for exc. NaOH</u>
1	851	4.059	10.0	0.07112	0.07130	8.40
2		4.059	10.0	0.07112	0.07130	8.20
3		4.059	15.0	0.07674	0.09218	6.60
4		4.059	20.0	0.07674	0.09218	6.00
5	865	1.769	15.0	0.07537	0.09218	6.45
6		1.769	15.0	0.07537	0.09218	6.35

^aRate of injection of pentachloroethane (PCE) to the reactor in moles/sec x 10⁷. ^bTime of bubbling through the NaOH solution.

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