THE GAMMA-RADIOLYSIS OF HCL-C_2H_4 MIXTURES

THE GAMMA-RADIOLYSIS OF HCL-C_2H_4 MIXTURES
AND OTHER RELATED TOPICS

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SCOPE AND CONTENTS:

The gamma-radiation induced reactions occuring in the three vapour phase systems; CH_4-$TiCl_4$, C_2H_4-$TiCl_4$ and C_2H_4-HCl, have been studied. A solid product was obtained in the first system, which has been identified as a mixture of $TiCl_3$ and chlorinated organic polymer. Low molecular weight chlorinated hydrocarbons were observed to form in the other two systems. The reaction taking place in the C_2H_4-HCl system has been shown to be a chain reaction, the chain propagator being a chlorine atom. A reaction mechanism has been devised, which gives kinetic expressions governing the rates of formation of the chlorinated products, which is in agreement with the experimental data.

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GENERAL INTRODUCTION

The industrial use of ionizing radiation as a means of initiating chemical reactions has been limited by the cost involved in producing irradiation facilities. The only reactions which have proven to be of commercial value are those which are difficult to initiate by more conventional means and which yield a large amount of product per unit of radiation. In actual fact, only one process, that of the production of ethyl bromide, from ethylene and hydrogen bromide, is currently being carried out on an industrial scale. Power reactors, however, should be able to provide low cost radiation. The reactor could be initially designed so that the gamma radiation would be absorbed by reactants contained in a vessel surrounding the core. It was with a view to finding a reaction which could conceivably be used in this type of application that this study was undertaken.

The presence of free radicals, as well as other highly reactive species, in hydrocarbons which are exposed to a radiation field has long been known (1). It was postulated that the reduction of a substance like titanium tetrachloride, when in the presence of a hydrocarbon, might be possible with the aid of the reactive species produced by the radiation.

Titanium metal has qualities which make it an excellent structural material. Its use has been limited to special applications due to its high cost of production. The oxide is fairly easily converted to the tetrachloride and it was thought that if radiolysis of $TiCl_4$ - hydrocarbon mixtures led to reduction of the titanium, this could prove important.

When mixtures of $TiCl_4$ and CH_4 were irradiated in the reactor (1a), a brown solid product of considerable bulk was formed. It was shown that this solid was a mixture of $TiCl_3$ and chlorinated organic polymer. The gaseous products of the reaction revealed no detectable chlorinated hydrocarbons. The notable feature of these studies was the fact that the formation of the regular radiolysis products of methane was largely inhibited by the presence of the $TiCl_4$ vapour.

A further reaction between $TiCl_4$ and C_2H_4 was studied in three different ways. Samples, sealed in quartz tubes, were irradiated in the core of the reactor, in the same way as was done in the case of the $TiCl_4$ - CH_4 system. Secondly, a continuous flow system was constructed whereby a mixture of known concentration could be passed through copper tubing to a quartz reaction vessel located close to the reactor core. Separation of the products from the reactants was carried out at the exit end of the flow system. This system proved to be particularly useful in the identification of the chlorinated hydrocarbons produced in the reaction, since milligram quantities of the products could be collected using this device. The chlorinated hydrocarbon products were ethyl chloride, 1-chlorobutane, 2-chlorobutane and 1,2-dichloroethane.

Kinetic studies on the rate of disappearance of $TiCl_4$ were carried out using this apparatus. This was done by measuring the amount of $TiCl_4$ remaining in the gas phase after radiolysis. The results indicated that the reaction rate was less than linearly dependent on the $TiCl_4$ concentration.

The third way in which this reaction was studied was by means of static irradiations using a 5 kilocurie cobalt-60 source. This setup proved useful in the observation of the rates of formation of the chlorinated hydrocarbons. The irradiation of relatively large samples was possible in this case and as a result, sufficient quantities of products could be obtained for quantitative analysis for a small percentage consumption of $TiCl_4$.

Variation of the surface to volume ratio of the irradiation vessels was accomplished by the addition of carefully cleaned glass wool. These experiments showed that the rate of production of 1,2-dichloroethane was markedly enhanced by the increased surface area.

Lack of reproducibility of the results obtained in the $TiCl_4$ - C_2H_4 experiments, particularly when dealing with large surface areas, was traced to the presence of small quantities of adsorbed water in the system. This water, on reaction with $TiCl_4$, yielded HCl which underwent a radiation induced reaction with the ethylene. This discovery led to the study which is the main contribution of the thesis, namely the study of the radiolysis of the HCl - C_2H_4 system. The CH_4 - $TiCl_4$ and C_2H_4 - $TiCl_4$ systems have by no means been exhaustively investigated nor have the results obtained led to a complete understanding of the reactions taking place. These sections have been included in the thesis, to give a complete picture of the work which was carried out.

The reaction which was observed to occur between HCl and C_2H_4, was a chain reaction, initiated by the addition of a chlorine atom to an ethylene molecule. Studies were made on systems wherein the parameters such as HCl pressure, ethylene pressure, surface to volume ratio and radiation intensity were varied. The rates of formation of the chlorinated hydrocarbons were observed in each case. A reaction mechanism has been postulated which gives kinetic expressions for the rates of formation of these products in agreement with the experimental data.

Since many of the fundamental processes occuring in radiation chemistry are far from being fully understood, it was considered worthwhile to do some experiments which might conceivably establish the mode of formation of the chlorine atom. A comparison of the yields of products formed during irradiation with and without an applied electric field has shown that excited molecules play some part in the formation of the chlorine atoms.

Experiments using nitric oxide to scavenge the chlorine atoms produced in irradiated HCl, have given a measure of the rate of formation of chlorine atoms, and ion chamber studies have given the rate of production of ions in the system. These measurements indicate that about half of the gamma ray energy absorbed by the HCl in the system leads to the formation of chlorine atoms, which in turn lead to the observed products. The energy absorbed by the ethylene has been shown to be unimportant in this system.

The information obtained concerning the reactions between HCl and C_2H_4 has led to an understanding which has seldom been realized in other radiation induced reactions of comparable complexity.

HISTORICAL INTRODUCTION

A. Early Work

The discovery of X-rays by Roentgen in 1895 (2) along with that of radioactivity by Becquerel in the following year (3), opened up the new field of radiation chemistry. For the most part, the papers dealing with this subject which appeared in the literature at the turn of the century, were notes by workers who were studying radioactivity. These papers described, without explanation, various phenomena they had observed. For example, in 1899 Marie and Pierre Curie (4) reported finding ozone when a sample of air was exposed to the radiations from radium. They also described how the glass vessels containing radium salts became coloured. Becquerel (5) in 1901 substantiated the claims of the Curies and noted that white phosphorous was transformed to red under the influence of the rays from radium. He also noted that the reduction of $HgCl_2$ by oxalic acid was enhanced by radiation and prolonged irradiation prevented the germination of grain.

The systematic study of the radiolysis of gaseous hydrocarbons was started almost simultaneously by two groups in the middle 1920's. In 1924, Lind and Bardwell (6) published a paper describing experiments wherein C_2H_4 was mixed with radon. Droplets of liquid were observed on the inside of the vessel after several days, indicating the formation of higher hydrocarbons. The following year the same workers (7) reported experiments carried out on other hydrocarbons, namely CH_4, C_3H_8, C_2H_4 and C_2H_2. In the same year Mund and Koch (8) published results showing pressure changes which occured during the radiolysis of CH_4, C_2H_6, C_2H_4 and C_2H_2.

The mechanisms leading to the formation of the products found when substances are irradiated has been the subject of much investigation.

The first theory to explain the phenomena observed in the radiolysis of gaseous hydrocarbons was put forward by Lind (6), in connection with his work on the radiolysis of ethane. This theory, known as the ion cluster theory, proposed that neutral molecules clustered around the ion formed by the radiation. The products were formed when this cluster was neutralized by an electron or an ion cluster of opposite charge. For example, the formation of C_2H_6 from CH_4 could be explained by the reaction:

$$(CH_4^+) \quad (CH_4) + e^- \longrightarrow C_2H_6 + H_2$$

One point in favour of this theory was its ability to explain the fact that quite often the number of product molecules exceeded the number of ion pairs formed. A serious short-coming of the mechanism lay in its inability to adequately explain the formation of polymer. For example, to form polymer from acetylene necessitated the postulation of a great many acetylene molecules clustered around a single ion.

In 1936, a free radical mechanism was postulated by Eyring, Hirschfelder and Taylor (9) to explain the radiation induced conversion of para to ortho hydrogen. A similar type of mechanism had been proposed much earlier by Debierne (10) in connection with the radiolysis of water. However, it had been largely ignored. Eyring et al. proposed that this type of mechanism could be applied to many radiation systems, the high yields of some reactions being explained by the decomposition of excited molecules.

The results of mass spectrometric studies by Schissler and Stevenson, published in 1956 (11), gave evidence for the occurrence of reactions between positive ions and neutral molecules. This has given rise to a number of mechanisms, based on ion-molecule reactions, which explain the formation of radiolysis products.

B. Radiation Chemistry of Methane

Tracing the advances made in the understanding of the processes occuring in the radiolysis of methane, will illustrate the general progress made by researchers in radiation chemistry.

The radiolysis of CH_4, along with low concentrations of the free radical scavenger I_2, by Gevantman and Williams in 1952 (12), indicated that reactions other than free radical were occuring in the system. The formation of C_2H_5I as well as the expected CH_3I and CH_2I_2 suggested that ethyl radicals were being formed from non-free radical species.

Three reactions had been previously postulated to account for the formation of ethyl radicals.

$$\begin{array}{lll}
(1) & CH_3^{\bullet} + {}^{\bullet}CH_2^{\bullet} \longrightarrow & C_2H_5^{\bullet} \\
(2) & CH_3^{\bullet} + CH_4 \longrightarrow & C_2H_5^{\bullet} + H_2 \\
(3) & CH_3^{+} + CH_4 \longrightarrow & C_2H_5^{+} + H_2 \\
 & & \quad \searrow e^{-} \\
 & & \qquad C_2H_5^{\bullet} \text{ or } C_2H_4 + H^{\bullet}
\end{array}$$

The first reaction could not take place in the presence of a free radical scavenger and the second reaction has a high energy of activation and can be ruled out. The third reaction is a likely one since CH_3^+ has been shown to be present in the mass spectrum of methane (13). Later mass spectrometric work by Wegler and Jesse (14) has also shown the existence of $C_2H_5^+$ and CH_5^+ in the mass spectrum of methane.

Experiments by Ausloos et al. (15, 16) have indicated that both $C_2H_5^+$ and CH_5^+ react with higher hydrocarbons. The former extracts a hydide ion from the hydrocarbon while the latter transfers a proton. This means that earlier workers, investigating the radiolysis of methane, did not observe the true reactions of CH_5^+ and $C_2H_5^+$ since, for the major portion of the radiolysis, these ions were being scavenged by the higher hydrocarbon reaction products.

It is now generally accepted that both ion - molecule and free radical reactions contribute to the formation of the observed radiolysis products of methane. A method whereby these two types of mechanisms can be distinguished was developed by Ausloos et al. (17). This consisted of the application of a potential across the irradiation chamber. As the potential is varied between the current saturation voltage and that required to cause secondary ionization, the yields of products arising from ion - molecule reactions will not be affected while those of products coming from the decomposition of excited molecules should be increased. The results they obtained by irradiating CH_4 - C_3D_8 mixtures confirmed this. The yield of C_2H_6 produced by means of an excited molecule mechanism was increased fifty-fold while that of C_2H_5D, produced by the reaction of $C_2H_5^+$ with C_3D_8 was unchanged.

C. Radiation Chemistry of Ethylene

Only three papers dealing with the radiolysis of ethylene, appeared in the literature before the middle 1950's. In 1925 Mund and Koch (8) reported observing a drop in pressure and the formation of a condensed phase when ethylene was irradiated. The following year, Lind, Bardwell and Perry (18) noted that CH_4 and C_2H_6 were also products of the reaction. McLennen and Patrick (19) in 1931 were the first to find acetylene among the reaction products.

Accounts of investigations into the feasibility of using radiation to initiate the polymerization of ethylene, appeared in the literature in 1954. Lewis, et al. (20) irradiated ethylene at fairly high pressures (17-109 atm.) and observed the formation of white solid polyethylene with a G $(-C_2H_4)$ as high as 2000. Hayward and Bretton (21) studied the reaction at lower pressures, limiting their observations to pressure changes taking place during the reaction. They found the polymerization to be strongly inhibited by oxygen.

With the advent of vapour phase chromatography, more complete identification of reaction products became possible. In 1958, Mikhailov et al. (22) reported finding hydrogen, methane, ethane, acetylene, butane and butene in the gas phase as well as C-6 and C-8 aliphatic, aromatic and olefinic hydrocarbons in the liquid phase. The following year, work by Lampe (23) confirmed the presence of the gas phase products found by Mikhailov et al while adding propene, propane, and n-pentane. G values for the 12 products identified were determined at 75 mm. and 150 mm. initial ethylene pressure. It was also noted that only about one-third of the ethylene which had reacted could be accounted for by the gaseous products.

The mode of formation of hydrogen in the radiolysis of ethylene has received some attention. Studies by Ausloos and Gordon (24) using CD_2CD_2, CHDCHD, and C_2H_4 - C_2D_4 mixtures, indicate that the hydrogen is formed by two different molecular elimination processes. One mechanism requires that a hydrogen comes from each carbon while the other requires that both hydrogen come from the same carbon. The $\overset{\cdot}{\underset{\cdot}{C}}\ CH_2$ species resulting from the latter mechanism is thought to rearrange to CH CH. The work done by these authors was in close agreement with earlier work done by Sauer and Dorfman (25).

D. Addition of HBr to Ethylene

Studies of the photo-induced addition of HBr to olefins were reported in 1942 by Vaughan, Rust and Evans (26). This work was primarily undertaken to give proof to the free radical theory of abnormal addition of hydrogen bromide to the ethylenic double bond. They found that the reaction between HBr and propylene was extremely rapid, even at -78°C, providing the wavelength of light used was short enough to cause the dissociation of the hydrogen bromide.

Later work by Armstrong and Spinks (27) using a 90 curie Co^{60} source to initiate the chain reaction between hydrogen bromide and ethylene, showed the only detectable product to be ethyl bromide. The observation of pressure changes occuring during the radiolysis was used to find the rate dependence on ethylene concentration, HBr concentration and radiation intensity. It was concluded that when HBr was in great excess, termination by the reaction Br + wall $\longrightarrow \frac{1}{2}$ Br_2 predominated. For other concentration ranges no conclusions regarding the mode of termination could be made. It was postulated that the propagation was by means of the $\cdot Br$ and $\cdot C_2H_4Br$ radicals.

E. Radiolysis of HCl

In 1963 Lee and Armstrong (28) reported γ-radiolysis studies carried out on pure HCl in the gas phase. The prime objective of this work was to determine the mode of formation of H_2. By using Br_2 and Cl_2 to scavenge hydrogen atoms, they concluded that the hydrogen was formed by two different types of processes. One of these involved the reaction of a "hot" hydrogen atom with an HCl molecule, the other involved thermal hydrogen atoms. The "hot" hydrogen atoms were thought to arise from the dissociation of electronically excited HCl molecules. The thermal hydrogen atoms were considered to originate from an ion-molecule reaction followed by an ion recombination;

$$HCl^+ + HCl \longrightarrow H_2Cl^+ + Cl$$

$$H_2Cl^+ + e^- \longrightarrow H + HCl + \text{energy}$$

F. Photolysis of HCl - C_2H_4

The vapour phase photo-induced addition of HCl to ethylene and other olefins was reported in 1948 by Raley, Rust and Vaughan (29). They found the reaction could be induced by means of di-t-butyl peroxide as well as photochemically. The only product detected when equimolar amounts of ethylene and HCl were irradiated with a hydrogen lamp, was ethyl chloride. The following mechanism was proposed without kinetic verification:

$$\mathrm{HCl} \xrightarrow{h\nu} \mathrm{H}^{\bullet} + \mathrm{Cl}^{\bullet} \qquad (1)$$

Initiation

$$\mathrm{H}^{\bullet} + \mathrm{C_2H_4} \longrightarrow {}^{\bullet}\mathrm{C_2H_5} \xrightarrow{\mathrm{HCl}} \mathrm{C_2H_6} + \mathrm{Cl}^{\bullet} \qquad (2)$$

$$\mathrm{H}^{\bullet} + \mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{Cl}^{\bullet} \qquad (3)$$

$$\mathrm{Cl}^{\bullet} + \mathrm{C_2H_4} \longrightarrow {}^{\bullet}\mathrm{C_2H_4Cl} \qquad (4)$$

Propagation

$${}^{\bullet}\mathrm{C_2H_4Cl} + \mathrm{HCl} \longrightarrow \mathrm{C_2H_5Cl} + \mathrm{Cl}^{\bullet} \qquad (5)$$

From the yields of C_2H_6 and H_2 formed in reactions (2) and (3), and the yield of C_2H_5Cl formed in reaction (5), a chain length of about 30 was estimated. The relative yields of H_2 and C_2H_6 were not given.

No studies have appeared in the literature dealing with the γ-ray initiated reaction between HCl and C_2H_4.

PART I

$TiCl_4$ - CH_4 SYSTEM

CHAPTER 1

EXPERIMENTAL TECHNIQUES

A. Preparation of Samples for Irradiation

(a) Irradiation vessels

Irradiations were carried out, first in small quartz capsules, 4 mm. in diameter and 3 cm. long, and later in quartz tubes 20 mm. in diameter and 25 cm. long, having a volume of about 50 c.c. In order to make the irradiation of the larger capsules possible, an aluminum irradiation can was constructed as well as a lead castle for its transportation.

(b) Introduction of $TiCl_4$

The introduction of a known amount of $TiCl_4$ was accomplished by vacuum distilling a few milligrams of $TiCl_4$ into glass ampoules (Fig.1). These ampoules could be broken open under vacuum, as shown in Fig. 2, and their contents distilled into the irradiation vessel. This operation was accomplished by placing the bent tip of the $TiCl_4$ container through the hole in the glass rod A. The other end of the glass rod was sealed to the inside of the manifold. The flattened end of the container fitted snugly into the "pinched" tip of the outside standard joint B. A twist of the standard joint caused the container

Figure 1. TiCl$_4$ Container Used to Introduce a Known Amount of TiCl$_4$ into the Irradiation Vessel

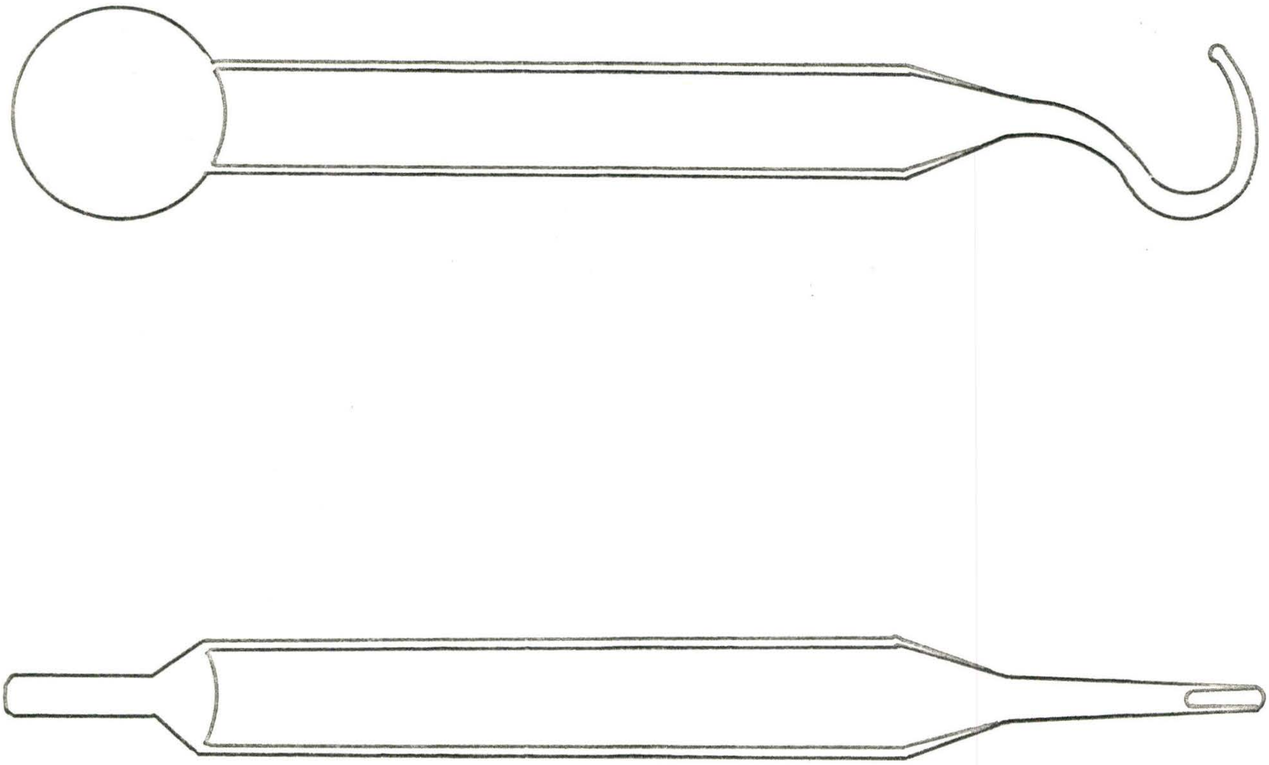
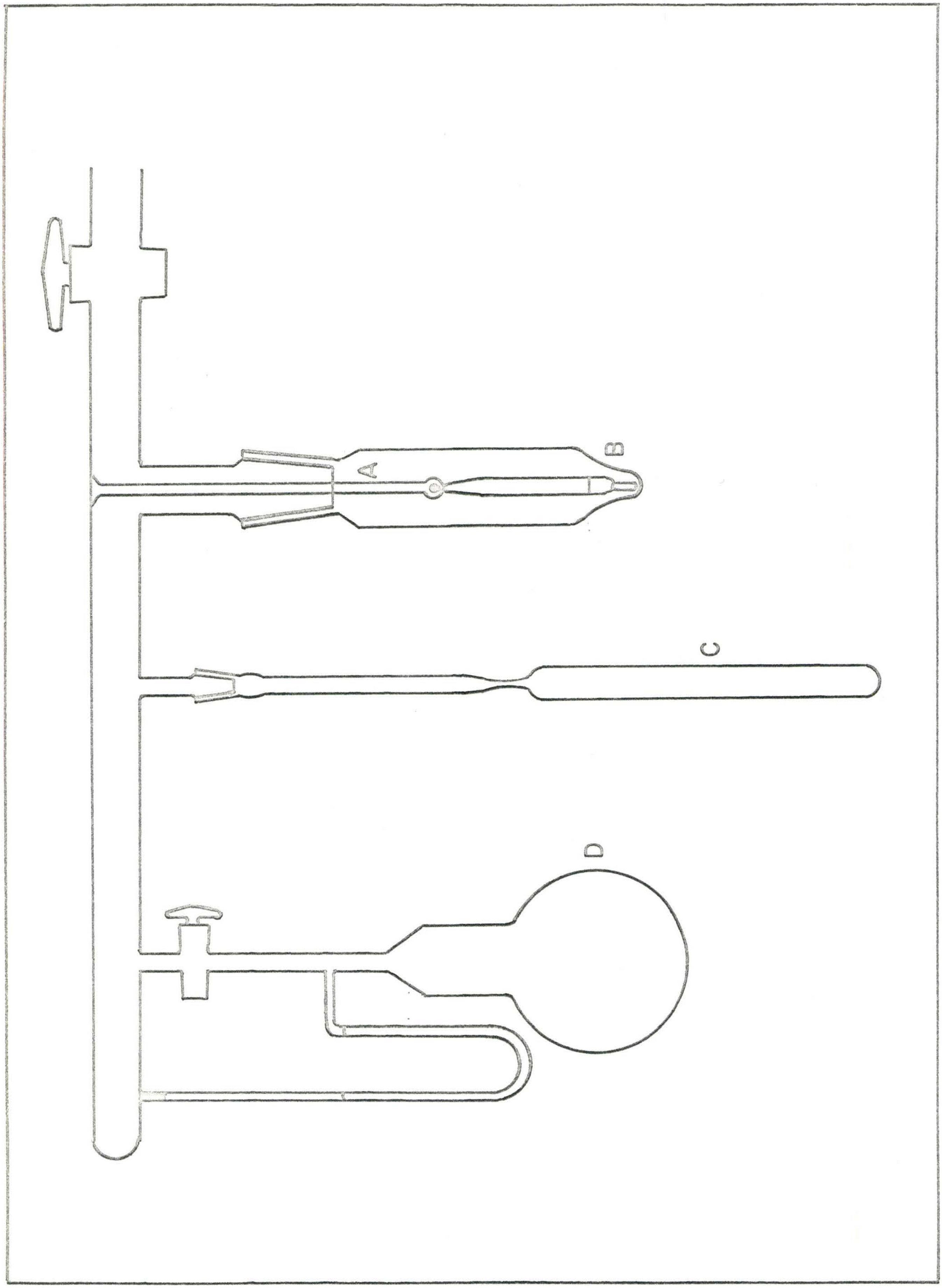


Figure 2. Apparatus for the Quantitative Introduction of $TiCl_4$ and CH_4 into the Irradiation Vessel



to be broken open and the $TiCl_4$ was distilled into the irradiation vessel by cooling it with liquid air. It was found to be advisable to freeze the $TiCl_4$ before breaking the container open. This eliminated the possibility of glass fragments being swept out of the standard joint by the surge of $TiCl_4$ vapour. The amount of $TiCl_4$ added to the irradiation vessel was determined from the weight of the capsule before opening and the weight of the capsule and fragments after opening.

The purified grade $TiCl_4$ used in this study was obtained from the Fisher Scientific Company. It was subjected to several trap-to-trap vacuum distillations before use. Reagent quality methane was obtained from the Matheson Company and was used without further purification.

(c) Introduction of methane

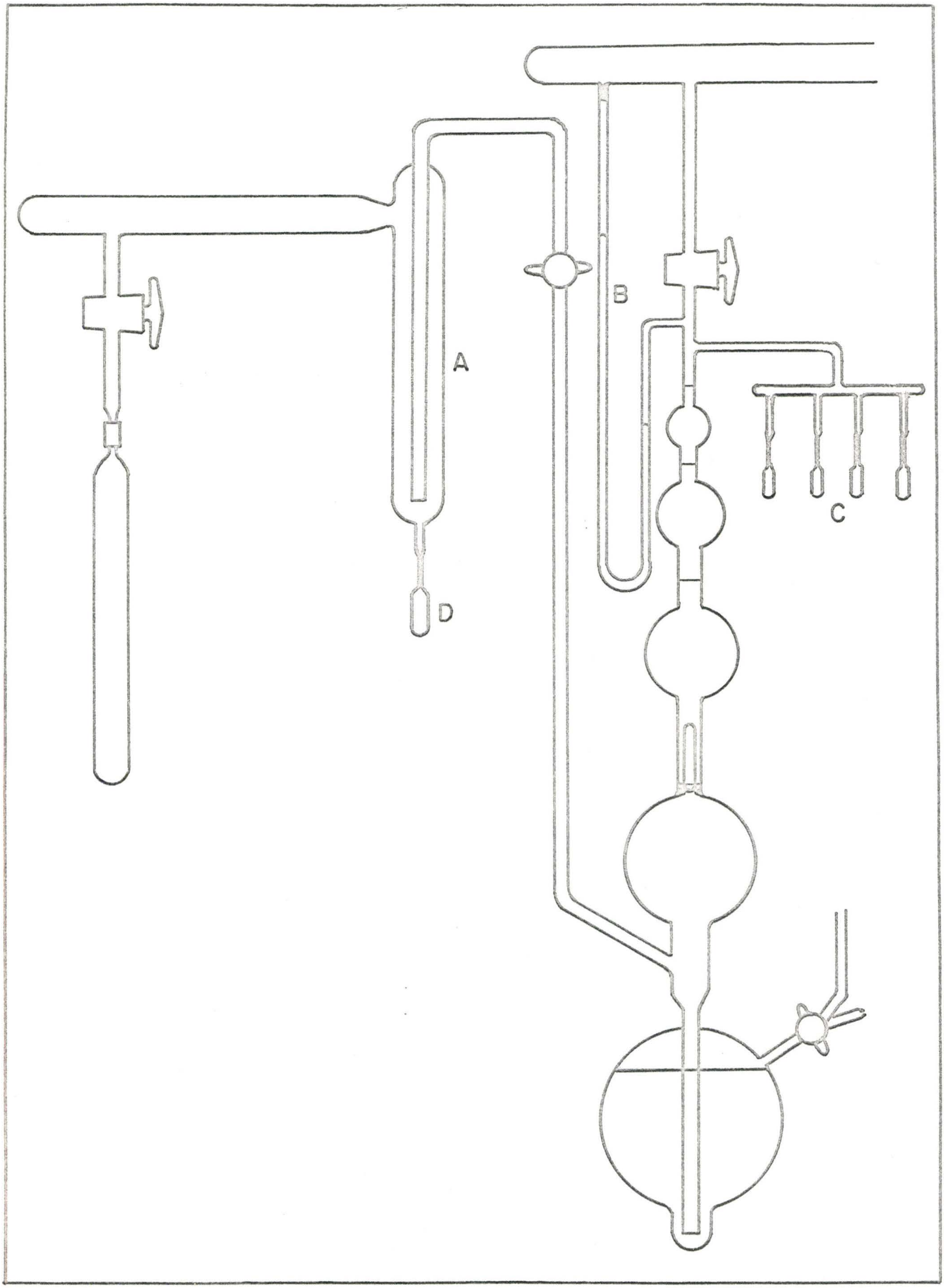
Methane was introduced quantitatively into the liquid air cooled irradiation vessel from the calibrated volume D (Fig. 2). This bulb had been filled, prior to the opening of the $TiCl_4$ container, to a pressure such that the final pressure in the irradiation vessel, after it had been drawn off and come to room temperature, would be about 76 cm. Hg.

B. Analytical Procedures

(a) Separation and analysis of gaseous products

The opening of the reaction vessel was accomplished by making a short connection with tygon tubing from the tip of the quartz reaction tube to the vacuum line as shown in Fig. 3. After evacuating

Figure 3. Apparatus for the Separation of Gaseous $TiCl_4$ Reaction Products



the line, the tip of the quartz vessel was broken with pliers. The gases were toeplered from the reaction vessel through the liquid air trap A. By this procedure it was possible to separate CH_4 and H_2 from the rest of the gases. The mixture of H_2 and CH_4 was then forced into a known volume, and the pressure, as shown by manometer B, recorded. Samples were removed by drawing off two previously prepared glass ampoules C. The thin-walled constrictions connecting these ampoules to the vacuum line enabled the drawing off to be accomplished without appreciable heat decomposition of the contents. The ampoules were designed to fit into a length of rubber tubing situated in the gas inlet line of the gas chromatograph and were sufficiently thin-walled to facilitate their fracture, by means of pliers, at the appropriate time.

The analysis of these samples was carried out using a 1-meter charcoal column at 25 C., CO_2 carrier gas.

The next step in the separation of the gaseous products was to replace the liquid air around trap A by a CO_2 - acetone bath. This allowed the next fraction of hydrocarbons to be toeplered into another known volume, the pressure recorded and the samples drawn off as before. This fraction was analysed using a 2-meter silica gel column at 25 C., helium carrier gas.

The final step in the separation procedure consisted of the application of liquid air to the glass ampoule at the base of trap A. This caused any unreacted $TiCl_4$ along with reaction products with negligible vapour pressures at -78 C. to distill into ampoule D which was subsequently drawn off. The analysis of this sample was carried out on a 2-meter silicone oil (DC 200) column at 40 °C., helium carrier.

(b) Neutron activation analysis

Polyethylene capsules containing mixtures of TiO_2 and KCl in various proportions were prepared as standards for use in the neutron activation analysis of the solid irradiation product. The TiO_2 and KCl were weighed to the nearest microgram on a Cahn electrobalance. Samples of the brown solid were obtained in a container suitable for irradiation by transferring the solid from a reaction vessel to polyethylene tubes which were then heat sealed. This operation had to be carried out in a dry nitrogen atmosphere as the solid was reactive toward oxygen and water vapour.

The samples of the solid reaction product along with the standards were irradiated in the rabbit facility of the nuclear reactor. One minute irradiation times were used for the majority of the experiments. The γ-ray spectra of the irradiated samples were observed by means of an RCL 256-channel analyser, the detector of which consisted of a 3" x 3" NaI (Tl) scintillation crystal. The analysis was carried out in two parts. First, the titanium ^{51} peak was observed at 0.323 MeV. To enable this peak to be clearly observed, the gain of the amplifier had to be adjusted to a value such that the chlorine peak in question could not be simultaneously observed. After a reasonable number of counts had been obtained, (a live-time count of 1 min. proved sufficient), the clock time and the count were recorded. The gain was then adjusted to bring the 2.15 MeV gamma ray of Cl^{38} in range. This isotope has a half life of 37.5 min. as compared with 8.5 min. for

Ti^{51}. A second count was taken to get the chlorine activity at a definite time after the irradiation. The results were then plotted and the areas under the peaks obtained.

Since the proportions of titanium and chlorine in the standards were known and the ratios of the counts in their photopeaks measured, the ratios of the counts in the photopeaks of the unknowns could be used to obtain their proportions of titanium and chlorine.

(c) Carbon-hydrogen combustion analyses

Carbon-hydrogen micro analyses were carried out using a Sargeant micro combustion unit. A similar apparatus is described in reference 30. A weighed sample of the brown powder was introduced into the combustion tube, care being taken to prevent the powder from coming into contact with water vapour and oxygen. After the combustion, the absorption tubes were removed and weighed on a micro balance. The weights of water and carbon dioxide absorbed by the respective tubes gave a value for the hydrogen-carbon ratio.

CHAPTER 2

EXPERIMENTAL RESULTS

A. Gaseous Products

(a) Comparison of gaseous radiolysis products of CH_4, with and without added $TiCl_4$

Twenty-five hour irradiations of capsules containing about 0.2 c.c. methane at atmospheric pressure, as well as capsules containing the same amount of methane in the presence of about 1 mg. of $TiCl_4$ yielded the peaks given in Table I, upon gas chromatographic analysis. The tentative assignment of the major peaks has been effected by comparing the retention times with the vapour pressures of the radiolysis products of methane. (cf 31) Those with no assignment are probably unsaturates.

It can be seen from Table I that the regular irradiation products of methane are markedly inhibited by the presence of $TiCl_4$. The retention times of the most volatile chlorinated hydrocarbons CH_3Cl, C_2H_5Cl and CH_2Cl_2 showed that the peak at 2.9 min. was not one of these and hence it is probably not a chlorinated species.

TABLE I

Comparison of chromatograms of irradiated CH_4 and CH_4 - $TiCl_4$ mixtures for a total dose of 1.4×10^9 rads

Retention Time (min.)	Assignment	Peak Height CH_4	 CH_4 - $TiCl_4$
1.6	CH_4	915	915
2.3	C_2H_6	26	---
2.9		---	0.5
3.1	C_3H_8*	4.1	---
3.8	iso-C_4H_{10}*	5.4	---
4.1	n-C_4H_{10}*	2.0	---
6.5	neo-C_5H_{12}*	1.8	---
8.1		0.3	---
10.9	n-C_5H_{12}*	1.3	0.2
12.4		0.3	---
14.5		0.3	---
16.2		0.2	---
20.9	iso-hexane*	1.9	0.7
32.0	n-hexane*	3.6	1.2

* Tentative Assignment

(b) Quantitative analysis of gaseous products

The rates of formation of hydrogen and products non-condensable at -78° C. for three separate irradiations are given in Table II.

TABLE II

Rates of formation of H_2 and products non-condensable at -78° C.

Sample Number	Irradiation Time (hr.)	Initial STP vol. CH_4 (c.c.)	Initial $TiCl_4$ weight (mg.)
1	21.7	43.0	33.9
2	27.2	43.8	35.8
3	28.2	39.9	30.0

Sample Number	STP Vol. H_2 (c.c.)	G (H_2)	STP Vol. non-cond. -78° C. (c.c.)	G (products non-cond. -78° C.)
1	4.6	0.04	1.3	0.01
2	6.4	0.05	1.6	0.01
3	7.2	0.05	1.7	0.01

B. Solid Reaction Products

The $TiCl_4$ - CH_4 system was found to produce a considerable quantity of brown solid material of rather low density. The irradiation of a sample of $TiCl_4$ alone, produced no observed effect.

(a) General reactivity of solid product

(i) Reaction with N_2, O_2 and H_2O

A reaction vessel containing several milligrams of the solid product was connected to the vacuum line and the gaseous products pumped off. Helium was then expanded into the reaction flask from a small bulb attached to the vacuum line, the pressure being recorded before and after the expansion. Helium was used to calibrate the system since it was assumed that it would not react with the solid. Nitrogen and oxygen were similarly expanded into the vessel. Nitrogen showed no signs of reaction, while oxygen was observed to react very slowly. The reaction could not be detected by means of the pressure measurements but rather was discernable through a colour change to a lighter brown which occured in the solid. The reaction with water vapour was very rapid, being easily observed by a reduction in pressure and a colour change from brown to violet.

(ii) Solubility in various media

The brown powder was found to dissolve readily in acetone, provided prior contact with water vapour or oxygen had not been made. It did not dissolve to any appreciable extent in hydrochloric, nitric or sulfuric acids but was partially soluble in benzene.

When placed in water, the separation into two components could be observed. Part of the solid could be seen to dissolve while the rest remained suspended in the water as a flaky precipitate. When this precipitate was filtered off, it was found to be soluble in acetone, chloroform and benzene but insoluble in aqueous HCl. The aqueous solution was violet in colour and upon evapouration yielded dark violet crystals. Tests for Ti and Cl on the aqueous solution were positive.

(b) Melting Point Determination

A melting point determination carried out on a few milligrams of the solid gave a melting range of 189 - 193°C.

(c) Neutron activation analyses

(i) Standard samples

The composition of five standards is given in Table III.

TABLE III

Composition of Standard Samples

Sample No.	Weight TiO_2 (mg.)	Weight KCl (mg.)	Cl atoms to Ti atoms
1	0.844	3.107	3.96
2	0.782	2.335	3.20
3	0.859	2.301	2.86
4	0.842	1.503	1.92
5	0.883	1.522	1.85

The chlorine to titanium ratios found by activation analysis for the standards are shown in Table IV. The values given are the averages of six separate determinations.

TABLE IV

Average experimental Cl/Ti ratios for standards

Sample No.	Average Cl/Ti found	Known Cl/Ti	per cent deviation
1	3.97 ± 0.19	3.96	0.25
2	3.19 ± 0.17	3.20	0.31
3	2.94 ± 0.11	2.86	2.6
4	1.91 ± 0.03	1.92	0.52

(iii) Hydrogen-carbon ratios

The experimentally observed hydrogen-carbon ratios are given in Table VI.

TABLE VI

Carbon-hydrogen ratios

Run	Sample Number	H/C Ratio
(a)	1	1.35
(b)	1	1.36
(c)	1	1.44
(d)	1	1.46
(a)	2	1.39
(b)	2	1.46
(a)	3	1.53
(b)	3	1.61
(a)	4	1.32
(b)	4	1.37

CHAPTER 3

DISCUSSION AND CONCLUSIONS

A. Gas Phase Products

Since the regular radiolysis products of methane are strongly inhibited by the presence of $TiCl_4$ while at the same time, no detectable amounts of gaseous chlorinated hydrocarbons are formed, it follows that the reactive species are leading to the formation of the brown solid. This must be occuring by means of some polymerization reaction which has not been elucidated by this work. Since the product has been shown to be highly unsaturated, the rate of formation of hydrogen should be a measure of the rate of formation of solid. The low G value for hydrogen indicates that the reaction leading to solid product is not a chain reaction.

B. Solid Phase Products

(a) Evidence for $TiCl_3$

The reasonably small melting range of four centigrade degrees of the solid reaction product would seem to indicate a compound of moderate purity. There were, however, strong indications that the solid product contained $TiCl_3$ and since it was also shown to contain organic material, it was probably a mixture. Anhydrous $TiCl_3$ is known (32) to decompose slowly at room temperature to give $TiCl_2$ and $TiCl_4$. It was observed that when samples of the brown solid were thoroughly evacuated, to remove any unreacted $TiCl_4$, and then stored for several days, fumes were formed when they were reopened. This indicated the presence of $TiCl_4$ produced by the disproportionation of $TiCl_3$.

The formation of violet coloured solution when water was added to the brown solid, which yielded dark violet crystals when evapourated to dryness, gave further evidence to the initial presence of anhydrous $TiCl_3$, since $TiCl_3$-$6H_2O$ is known (32) to be dark violet and to dissolve to give a violet coloured aqueous solution.

Although a qualitative analysis for titanium and chlorine was carried out, a quantitative analysis was not undertaken because of the very small amounts of product being dealt with.

Nuclear magnetic resonance measurements made on an acetone solution of the brown solid yielded one broad peak which could be explained as being due to paramagnetic Ti (III).

The colour change observed to take place in the product upon the introduction of water vapour into the reaction tube indicated the presence of $TiCl_3$. Anhydrous $TiCl_3$ is known to exist in two monotropic crystalline modifications, one brown, the other violet (32). The brown form is evidently produced during the irradiation and the introduction of water vapour leads to violet hydrated $TiCl_3$.

(b) Neutron activation analyses.

The data obtained from the neutron irradiation of standard mixtures of KCl and TiO_2 were reproducible to within five per cent. The chlorine to titanium ratios for samples of solid product obtained from two different irradiations were found to be 3.8 and 4.2. This is far from the value of 3 which would be expected if $TiCl_3$ were the only chlorinated species present. In fact, if all the $TiCl_4$ reacts to form $TiCl_3$ and chlorinated polymeric hydrocarbon, the chlorine to titanium ratio of the solid products would be 4. Since the observed ratio is close to 4, this is further confirmation of the fact that no gaseous chlorinated hydrocarbons are produced.

(c) Carbon-hydrogen analyses

The hydrogen to carbon ratios, obtained by combustion analyses, show a trend to higher values with each attempt to duplicate a given analysis. Since the product is known to be highly reactive toward water vapour, it is possible that between analyses a small amount of water came into contact with the solid, despite the efforts made to prevent this. On this basis, the hydrogen to carbon ratio would be expected to increase toward the value obtained for sample 3 which was purposely allowed to react with water vapour. This suggests that the true value is about 1.35 or 4 hydrogens to 3 carbons. This is very similar to the value obtained for the material from which the water soluble portion had been removed and gives further confirmation to the suggestion that the solid product is a mixture of $TiCl_3$ and chlorinated unsaturated polymeric organic material.

The information obtained concerning the CH_4 - $TiCl_4$ system is far from being sufficient to devise a mechanism which can explain the processes occurring. These processes were obviously so complicated that it seemed advisable to turn to another system in the hopes that the reactions occurring could be understood. An understanding of the simpler system would possibly enable the more difficult one to be elucidated. A study of the C_2H_4 - $TiCl_4$ system was thus undertaken.

PART II

$TICL_4$ - C_2H_4 SYSTEM

CHAPTER 1

EXPERIMENTAL TECHNIQUES

A. Static Irradiations in the Reactor

A few runs were carried out with C_2H_4 - $TiCl_4$ mixtures using irradiation vessels similar to those described for the CH_4 - $TiCl_4$ experiments. The filling procedure was somewhat simplified due to the fact that the vapour pressure of ethylene at liquid air temperatures is very low in contrast to that of methane which is about 10 mm. Hg. This meant that only one pressure reading was needed to give a quantitative measure of the C_2H_4 used.

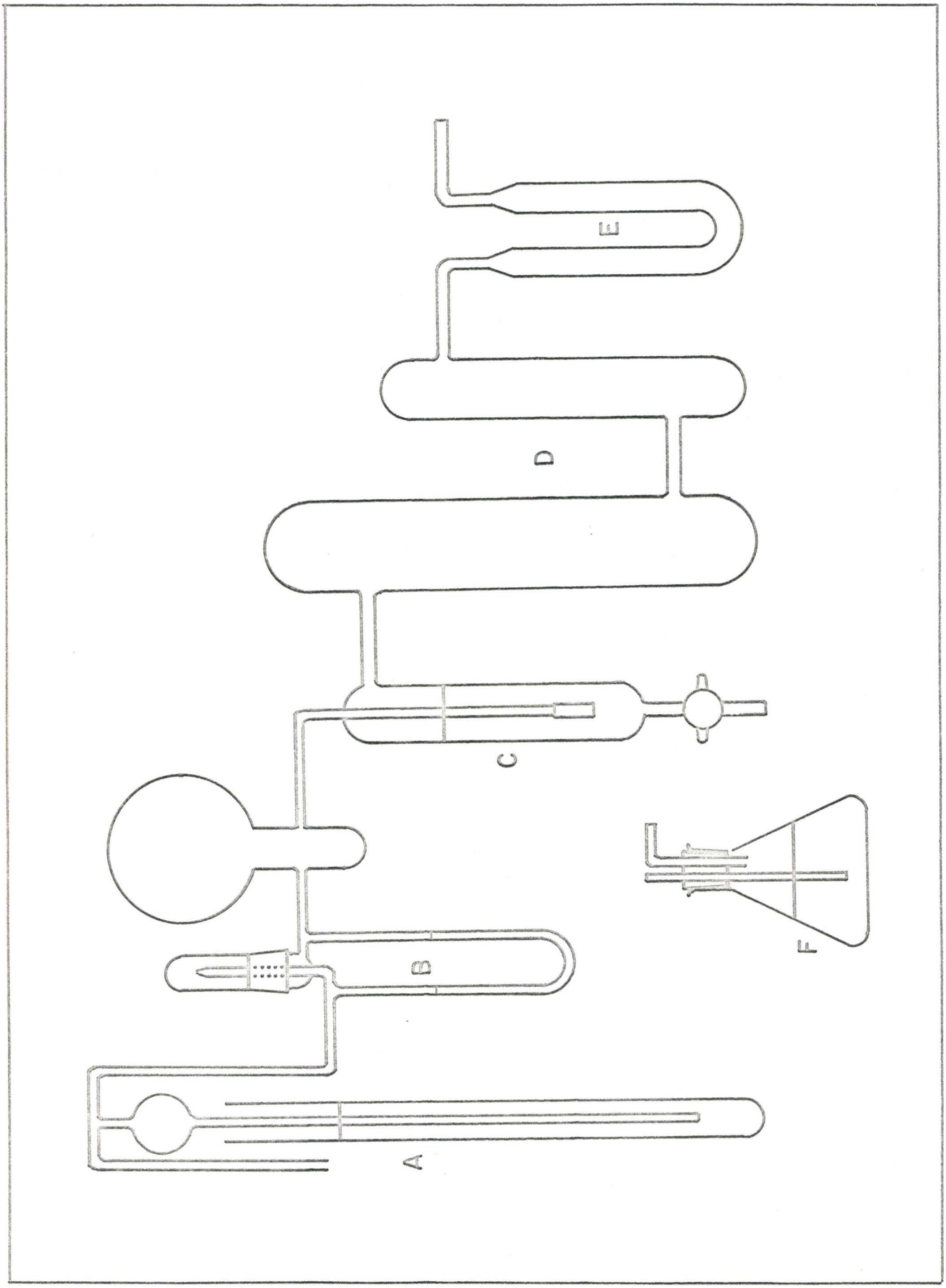
B. Continuous Flow Apparatus

A continuous flow apparatus was designed and constructed. The main components of this apparatus consisted of the inlet gas train, reaction vessel and exit gas train.

(a) Inlet gas train

The gas inlet side of the continuous flow apparatus is shown in Fig. 4. Matheson CP grade ethylene was passed from the cylinder to the flow regulator A. The flow through the system was varied by

Figure 4. Inlet Gas Train of Continuous Flow Apparatus



raising or lowering the tube containing liquid paraffin at A. During operation, the ethylene was allowed to bubble out through the liquid paraffin at a slow rate. From A, the ethylene passed through the flowmeter B and then through a damping volume to a purification train consisting of C, D and E. The damping volume was needed to smooth out the pressure fluctuations caused by the bubbler C, facilitating flowmeter readings. C was filled with Fieser's solution, prepared by dissolving 20 g. of KOH, 15 g. of sodium hydrosulfite and 2 g. of sodium anthraquinone-β-sulfonate in 100 ml. of water. This solution reacted with any oxygen in the ethylene to give a non-volatile product. The stopcock at the base of C was included to enable changes of the solution to be carried out without dismantling the line. After the old solution had been forced out of C, new solution was admitted by connecting F to C and applying a pressure to the bent tube of F. This operation had to be carried out fairly often as the oxidation product, being a solid, tended to block the flow of ethylene through the glass frit of the bubbler.

The next part of the purification train consisted of a two unit drying section D. The first tube was filled with anhydrous $CaSO_4$ and the second with a 50-50 mixture of P_2O_5 and glass microspheres. The latter component of the mixture was added to prevent the hydrolysis products of P_2O_5 from blocking the tube. Following the drying unit was a U-tube, E, filled with degassed activated charcoal. This unit, the contents of which were replenished periodically was used to remove any organic impurities having molecular weights higher than ethylene. During operation, this trap was maintained at -78° C.

(b) $TiCl_4$ bubbler

The purified ethylene was passed to the $TiCl_4$ bubbler setup illustrated in Fig. 5. During operation, stopcocks a and b were open, thus the ethylene passed through bubbler A which was at room temperature. From A, the gases passed through bubbler B and glass wool-filled trap C. These latter two were surrounded by a constant temperature water bath which was maintained below room temperature. Since the ethylene was saturated with $TiCl_4$ below room temperature, the possibility of condensation in the line was ruled out. The vessel D was added to eliminate the necessity of lengthy refilling operations and also to provide a means of keeping the level of $TiCl_4$ in A approximately constant. $TiCl_4$ was added to A from the reservoir D by closing stopcock a and opening stopcocks c and d. The ethylene pressure in the line was then increased to force $TiCl_4$ from D to A. The stopcocks shown in the diagram were all 2 mm. bore teflon plug, pyrex shell stopcocks. Ordinary stopcocks could not be used due to the high reactivity of $TiCl_4$ towards stopcock grease.

(c) Filling of $TiCl_4$ bubbler

The filling of the $TiCl_4$ bubbler setup was carried out in two parts. The reservoir D was separated from the rest of the system at x and y, (Fig. 5) and attached to the vacuum line as shown in Fig. 6. With stopcocks c and d closed, the $TiCl_4$ in E was degassed by the conventional freeze-thaw technique, after which stopcock e was closed,

Figure 5. $TiCl_4$ Bubbler Apparatus for Continuous Flow System

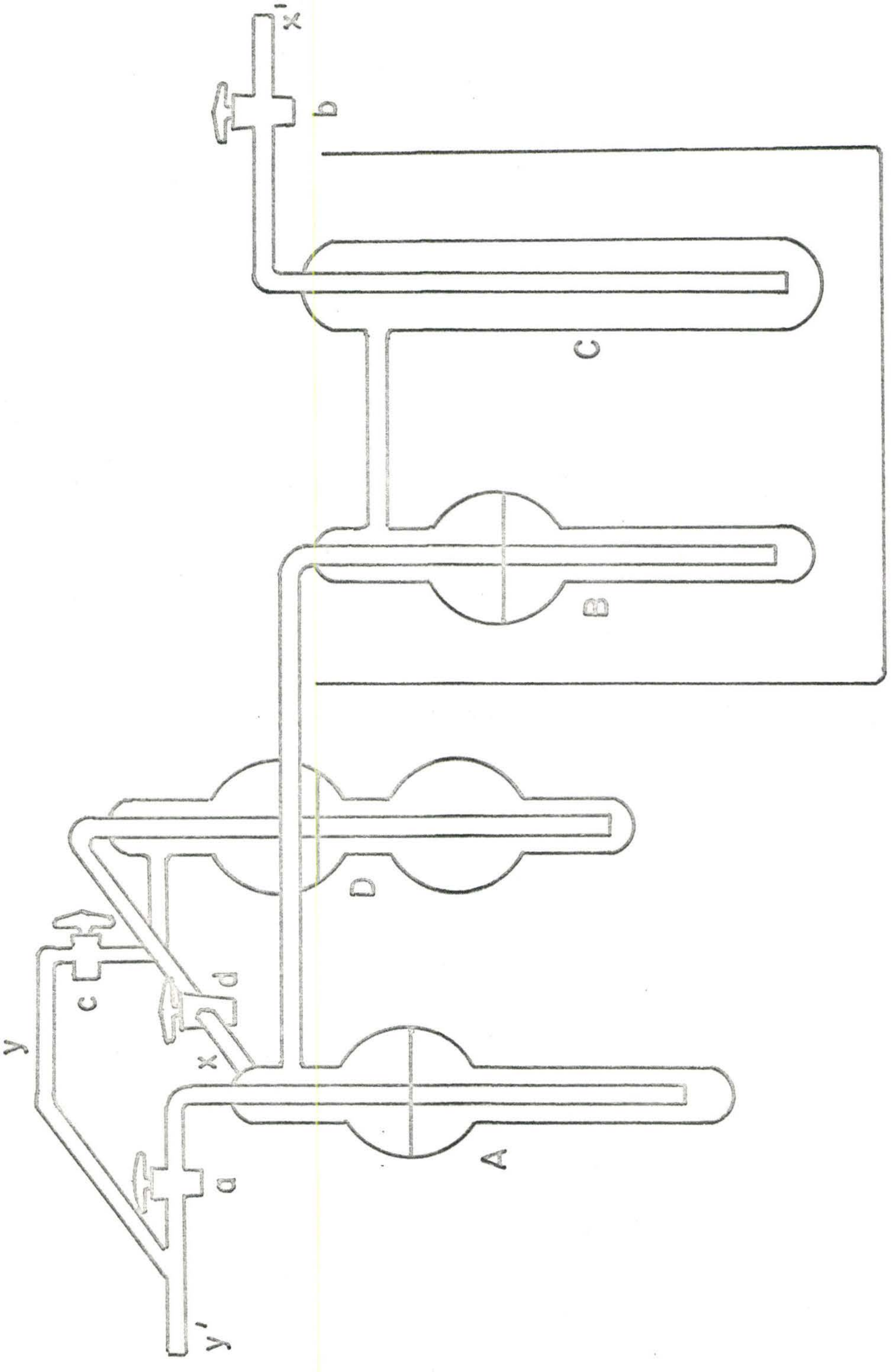
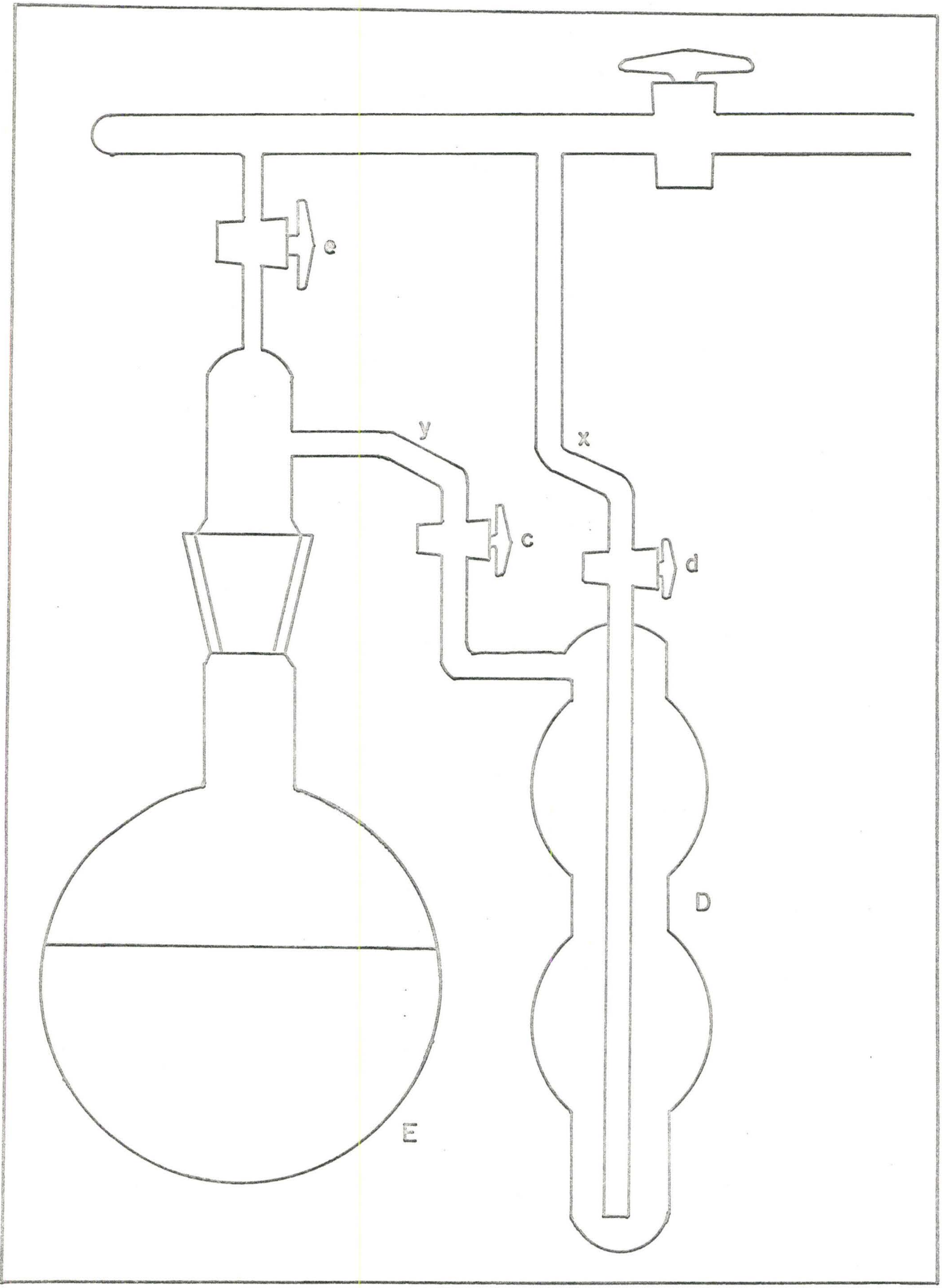


Figure 6. Filling of $TiCl_4$ Reservoir for Continuous Flow System

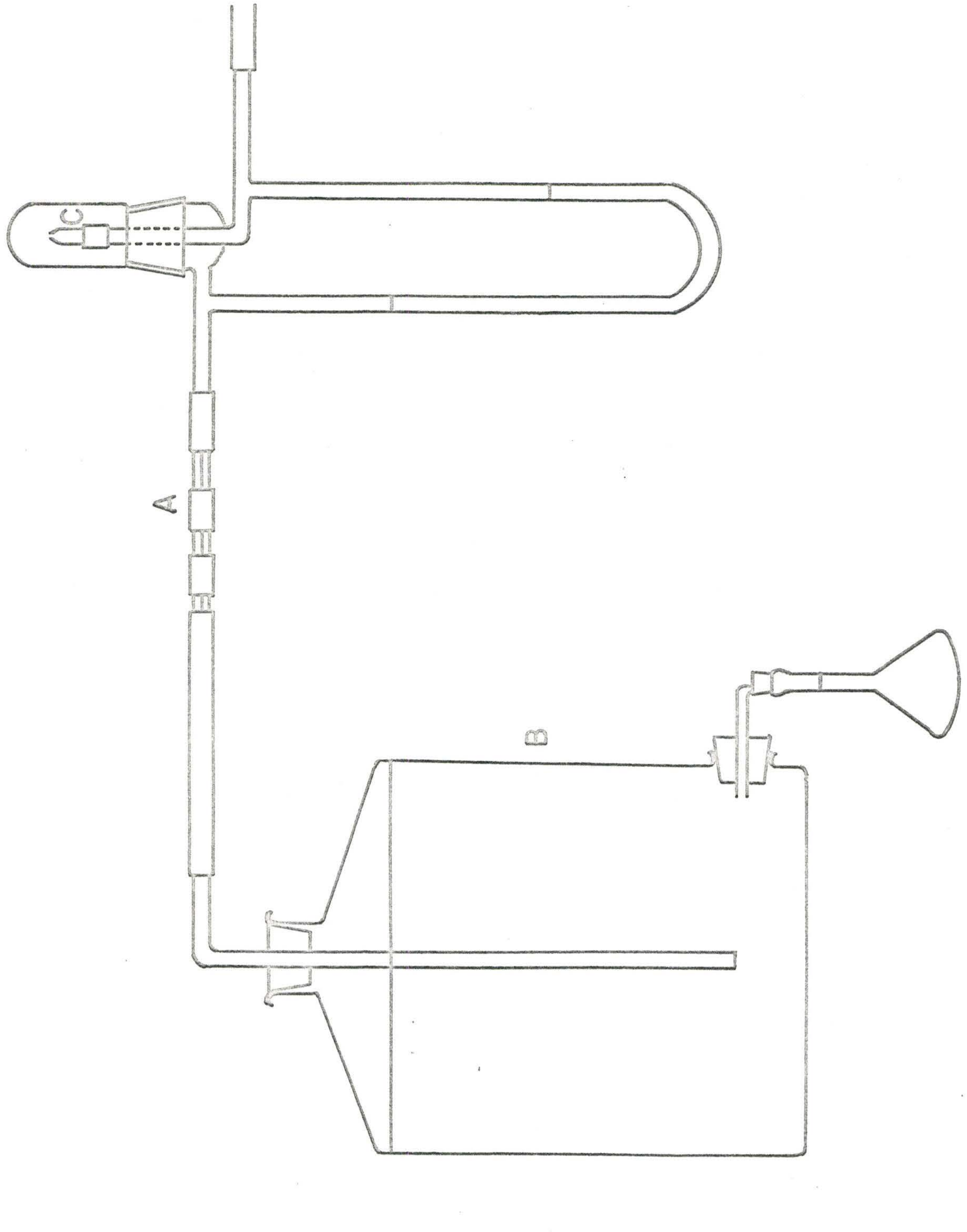


d opened and the vessel to be filled evacuated. A CO_2-acetone bath was then placed around D, the surface of the liquid in the bath being adjusted to the level of the lowest bulb of the vessel. With stopcock d left open, stopcock c was opened and the $TiCl_4$ vapour was condensed as a solid on the walls of the lowest enlargement, leaving a passage open to the high vacuum. When the amount of condensed $TiCl_4$ had increased to the point where this passage was in danger of being closed off, the cold bath was raised to cause condensation to take place in the upper bulb. The distillation was continued as long as the passage to the high vacuum remained open. The reasons for this passage were two-fold. The teflon stopcocks, while giving a moderately good vacuum could not produce a high vacuum, thus the small amount of air leaking into the system was continually being pumped out. Secondly, it was necessary to pump on the system during distillation to remove any traces of HCl which might be present. The possibility of the presence of HCl also excluded the use of liquid air as a cooling medium as it would have condensed the HCl along with the $TiCl_4$. After the distillation was complete, the reservoir was filled with ethylene, removed from the vacuum line and glass blown back onto the $TiCl_4$ bubbler system. The whole operation was then repeated in order to fill bubbler A (Fig. 5) x^1 being attached to the $TiCl_4$ reservoir E and y^1 to the high vacuum.

(d) Calibration of flowmeter

The apparatus used to calibrate the flowmeter is shown in Fig. 7. Ethylene was passed through the flowmeter, through the variable resistance A and into the 2000 c.c. Mariotte bottle B. The

Figure 7. Apparatus for Calibration of Flowmeter

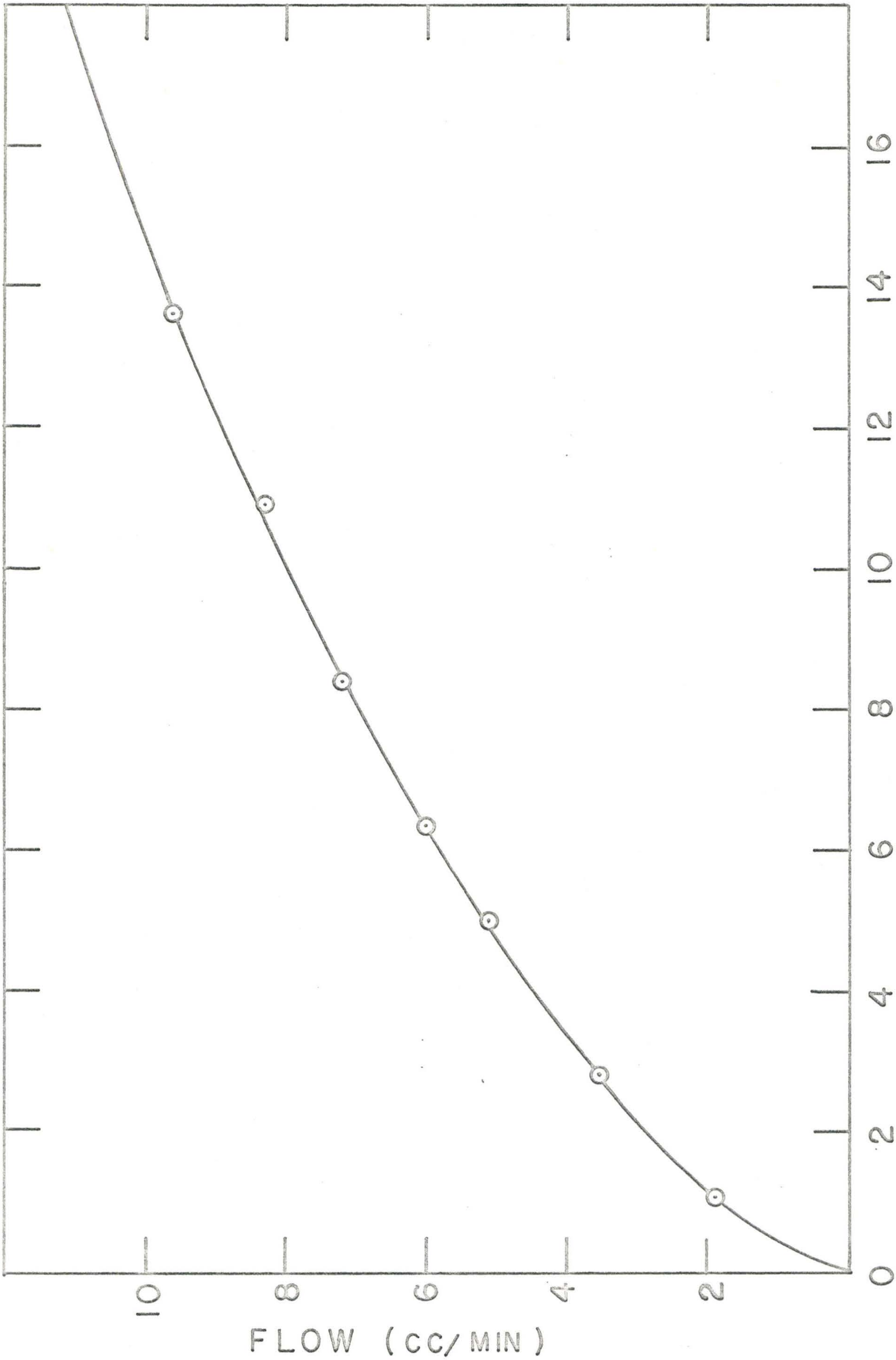


time taken for 100 ml. of water to be collected was noted for various flow rates. The absolute flow rate was calculated from the data, allowance being made for the vapour pressure of water in the ethylene above the water in the bottle as well as for the variations in the volume of water displaced at different Mariotte bottle heads. The water used in the Mariotte bottle was saturated with ethylene before any readings were taken. The size of the opening in C was adjusted to obtain a suitable reading on the flowmeter for the particular range of flow rates to be used. A typical calibration curve is shown in Fig. 8.

(e) Tubing of continuous flow apparatus

Various types of material were tried for the tubing which carried the gases to and from the reaction vessel. Polyethylene, being quite resistant to radiation as well as easily obtainable was the first choice. After a number of experiments, the polyethylene tubing began to show some evidence of reaction with the $TiCl_4$ vapour and as a result was replaced by teflon tubing. The continued persistence of HCl in the exit gases, even in the absence of a radiation field, led to the conclusion that water was finding its way through the teflon, either at the connections or by diffusion through the walls of the tubing. The teflon tubing was thus replaced by 1/8" OD copper tubing. Connections, both to the reaction vessel itself and to the entrance and exit gas trains were made by means of kovar, glass to metal seals. This arrangement eliminated the hydrolysis problem.

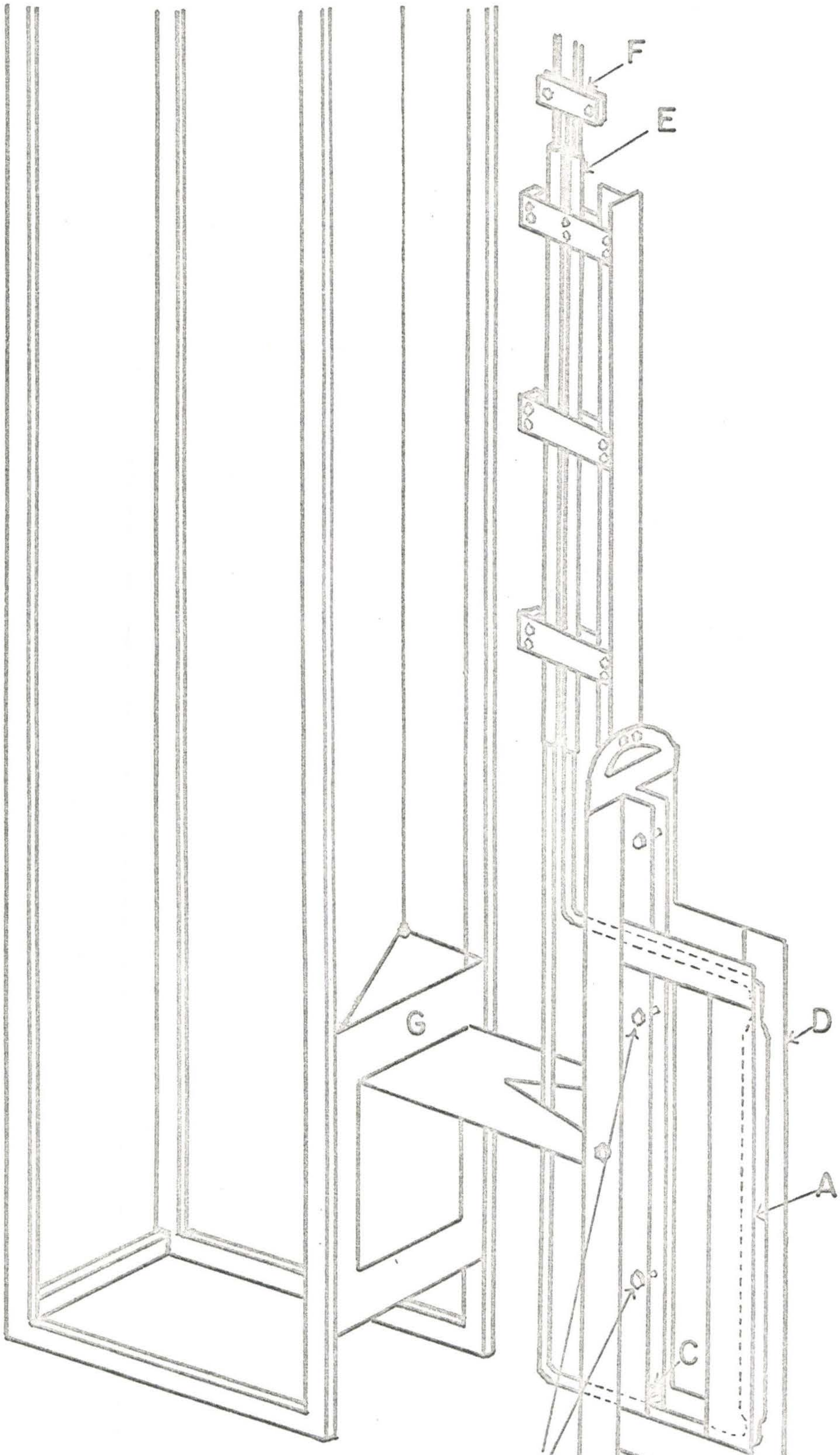
Figure 8. Typical Flowmeter Calibration Curve



(f) Reaction vessel and holder

The cadmium-wrapped quartz reaction vessel along with the aluminum holder which was constructed to position it near the core, is shown in Fig. 9. The main chamber of the irradiation vessel A was constructed from 20 mm. quartz tubing while the inlet and outlet quartz tubes were 10 mm. in diameter. The vessel was clamped in position by tightening the aluminum bolts B. The major force of the clamp was taken by four aluminum blocks, the only one visible designated as C in the diagram. These blocks had to be of a size such that when the clamp was tightened, the quartz would be held firmly but not crushed. To enable this condition to be more easily met, layers of polyethylene film, 2 layers per side, were placed between the quartz and the clamp. The aluminum shield D, constructed from 1/4" aluminum plate, was necessary to protect the vessel during handling. Further structural strength was added to the apparatus by clamping the inlet and outlet tubing inside the aluminum tubes E. Inside these tubes, near the reaction vessel end, the quartz tubes were joined to glass tubing by means of quartz to pyrex graded seals. The two glass tubes were in turn joined to kovar pyrex to metal seals. Each kovar seal was silver soldered to one end of a brass connector, the other end being silver soldered to the copper tubing. In order to keep the copper tubing from acidentally being bent at a sharp angle, it was run through 1/4" polyethylene tubing, this tubing being connected to the brass adapter and coupled to the aluminum tubes by means of swagelock connectors. The polyethylene tubing which was securely clamped at F, also eliminated the danger of copper dissolving in the pool water. The reaction vessel was wrapped with a section of

Figure 9. Reaction Vessel and Holder for Continuous Flow Apparatus



1/16" cadmium sheet. This absorbed the thermal neutrons and kept the activity of the chlorinated products to a minumum.

To irradiate, the apparatus was placed on trolley G (31a) associated with the instrument bridge of the reactor pool. The trolley was lowered to a reproducible level and the instrument bridge was moved to position the irradiation vessel about 2 inches from the face of the core. A measurement of the distance between the instrument bridge and the reactor bridge made it possible to place the vessel in the same position from run to run.

(g) Exit gas train

The exit train of the continuous flow system was initially set up to collect milligram quantities of the chlorinated hydrocarbons produced by the radiation. Such relatively large amounts of these products would facilitate their identification. This train consisted of a trap containing hydrated copper sulfate to pick up the unreacted $TiCl_4$, followed by a trap filled with $CaSO_4$ to collect any water expelled from the first trap. Next was a trap maintained at dry ice temperature containing detergent as an adsorbent for chlorinated hydrocarbons. The adsorbent was prepared by heating "Tide" brand household detergent for several hours at approximately 150° C. This was necessary to drive off any volatile substances such as perfumes. This trap was followed by a liquid air trap to prevent any active compounds from escaping into the air.

C. Collection, Separation and Identification of Chlorinated Hydrocarbons

(a) Collection

Products were collected in the detergent trap for several hours after which the trap was removed from the train and attached to a vacuum line equipped with a further trap similar to A in Fig. 3. The majority of the ethylene was pumped out of the detergent trap, which was maintained at -78° C. Liquid air was then placed around the trap with the sample bulb attached, the dry ice-acetone bath removed from the detergent trap and replaced by one of water at about 90° C. After the chlorinated hydrocarbons had been desorbed from the detergent trap and collected in the liquid air trap, the latter was isolated from the high vacuum pump as well as from the detergent trap. Since a fraction of the chlorinated hydrocarbons contained radioactive chlorine^{38}, their progress from trap to trap could be easily followed with the aid of a Geiger counter. The dewar containing the liquid air was then lowered until just the tip of the sample bulb was under the surface of the liquid air. After essentially all the activity was found to be located in the sample bulb, it was drawn off with the aid of a flame.

(b) Separation

The separation of the various chlorinated hydrocarbons was accomplished by introducing the sample, collected as described above, into the vapour phase fractometer in the usual manner. The chromotographic column used in this operation was a 3-meter detergent column. To prepare this column, 40-60 mesh detergent, heated as described above, was funnelled into a three-meter length of 1/4" OD copper tubing. The exit gases from the chromatograph were passed through a liquid air trap, which was replaced with a new trap after each successive compound had passed through the detector system. Each liquid air trap was then placed on the vacuum line and the collected product transferred to a glass ampoule. As this procedure failed to give complete separation in one step, it was found necessary to carry out the operation twice for the first fraction and three times for the other two.

(c) Identification

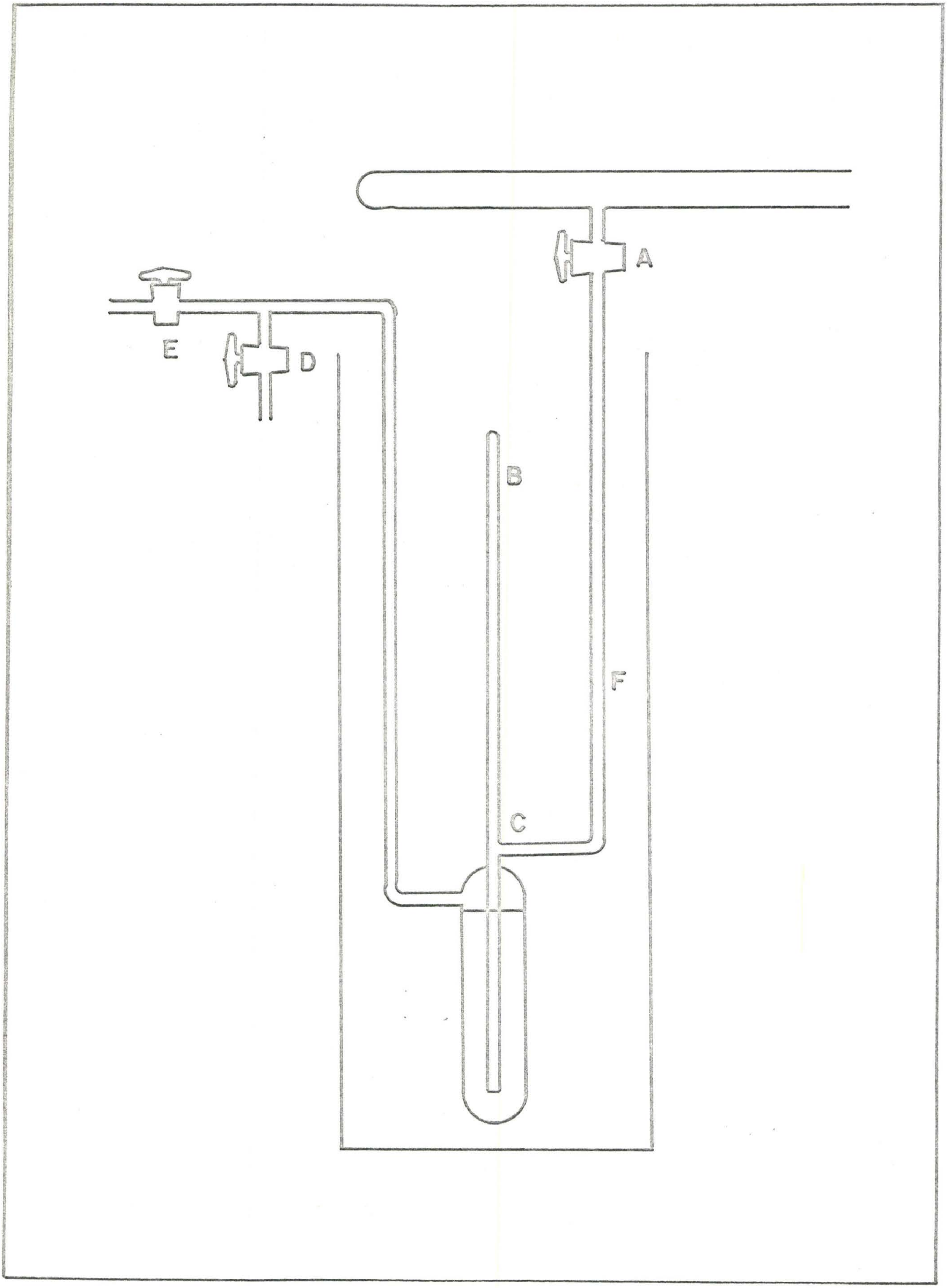
(i) Infrared measurements

The purified compounds were examined by means of a Perkin-Elmer model 21 infrared spectrophotometer. The ampoule containing the sample to be analysed was placed in a short section of tygon tubing which was connected to an infrared gas cell equipped with NaCl windows. After the open end of the tygon tubing had been securely clamped shut, the glass ampoule was broken, the stopcock to the gas cell opened and the vapour of the unknown compound allowed to enter the cell. The spectrum of the compound was recorded between 800 and 4000 cm.$^{-1}$. This operation was repeated for each of the unknowns, and their spectra compared with known chlorinated hydrocarbons.

(ii) Vapour pressure studies

Vapour pressure measurements were made on samples of the unknowns, which had been purified as described above. A vapour pressure measuring apparatus was designed and constructed as shown in Fig. 10. The apparatus was surrounded by a water bath to enable measurements to be made at ice temperature as well as room temperature.

Figure 10. Vapour Pressure Measuring Apparatus



The purified sample was admitted to the previously evacuated system through stopcock A and condensed in tube B. The mercury was then allowed to rise above the level C by letting air in through stopcock D, E being closed. The sample was then allowed to vapourize in tube B, thus depressing the mercury in the tube. When some visible liquid was present, the difference between the heights of the two columns of mercury in B and F gave a measure of the vapour pressure of the liquid.

(iii) Activation analysis

The isolated products were identified as chlorinated species by means of activation analysis. Samples of purified products were sealed in glass ampoules in the usual way and these were then placed in polyethylene containers suitable for rabbit irradiations. After the irradiation, each sample was introduced into the gas chromatograph and the effluent gases were directed through a length of teflon tubing which was coiled around the probe of a Geiger counter. The signal from the counter was sent to an Esterline-Angus recorder. By comparing the trace made by the gas chromatograph with that of the Esterline-Angus recorder it was possible to determine which of the substances were radioactive. The time lag between the gas chromatographic detector and the Geiger counter detector was calculated to be of the order of 3 or 4 seconds.

(iv) Identified products

By these techniques, the products were identified as 1-chlorobutane, 2-chlorobutane and 1,2-dichloroethane. The more volatile ethyl chloride could not be efficiently collected using the continuous flow apparatus. It was identified on the basis of its gas chromatographic retention time.

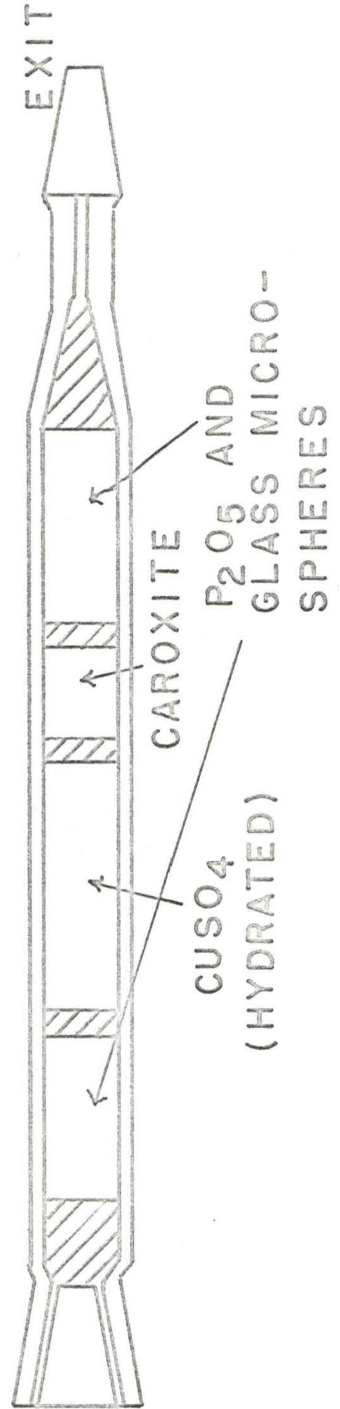
D. Measurement of the Rate of Disappearance of $TiCl_4$

Quantitative measurements using the continuous flow apparatus described earlier, were limited to the observation of the rate of disappearance of $TiCl_4$ at various relative $TiCl_4$-C_2H_4 concentrations.

(a) Quantitative analysis of $TiCl_4$

It was found that $TiCl_4$ could be quantitatively removed from the ethylene stream by means of hydrated copper sulfate, all other gases present passing through. Absorption tubes similar to those used in the micro-combustion work described earlier were filled as shown in Fig. 11. This diagram illustrates an absorption tube designed to be used on a vacuum line. The filling is the same as for those used on the continuous flow apparatus. The layer of P_2O_5 mixed with glass microspheres was necessary to prevent the loss of water vapour. The caroxite layer was added to react with any HCl formed by the hydrolysis of $TiCl_4$, which was not absorbed by the copper sulfate. Caroxite is an alkali hydroxide suspended on an inert medium with an added dye to indicate percent comsumption. It was found that the $CuSO_4 \cdot 5H_2O$ not only reacted with the $TiCl_4$ but also retained the bulk of the HCl produced in this reaction. Analar grade 40-60 mesh $CuSO_4 . 5H_2O$

Figure 11. $TiCl_4$ Absorption Tube

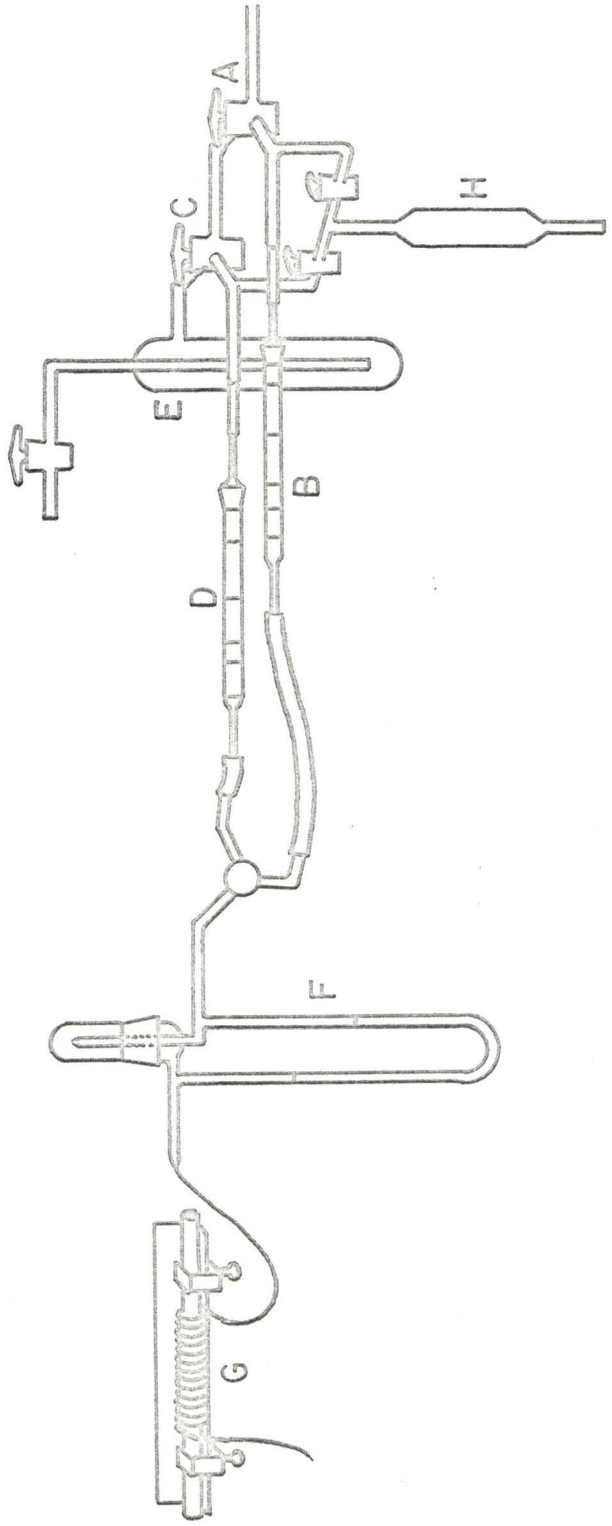


was used. The P_2O_5 layer at the entrance end of the tube was found to be necessary to keep the water vapour from diffusing out to the capilliary entrance where a reaction with the incoming $TiCl_4$ would cause the entrance to become blocked. Glass wool was used to separate the various layers, as well as to prevent any solid material from escaping through the entrance or exit holes.

(b) Exit gas train

The exit gas train was designed and constructed as shown in Fig. 12. The gases from the irradiation cell arrived at the three way teflon stopcock A. From this point the gases could be directed through either absorption tube B or to three way stopcock C. From C the gases could be sent through absorption tube D or through the equilibration trap E. After the $TiCl_4$ had been removed from the gas stream, either by the absorption tubes or by trap E, which was maintained at -78° C. during operation, the gases were passed through flowmeter F and then through a coil of tygon tubing approximately 1/32" in diameter G. The coil was wrapped around a short length of aluminum rod which was clamped, by means of a boss-head at either end, to a length of 1" angle iron. This arrangement gave a very sensitive control of the flow rate. Since very low flow rates were employed in the majority of the experiments, (of the order of 5 to 10 cc./min.), and since the resistances of the two absorption tubes were not the same, this flow control was necessary. From G, the gases were passed through a trap at -78° C. to remove the chlorinated hydrocarbons.

Figure 12. Exit End of Continuous Flow Apparatus for the Quantitative Determination of $TiCl_4$



(c) Absorption procedure for $TiCl_4$

In making a quantitative study of the amount of $TiCl_4$ used in the reaction, the gain in weight of the absorption tubes was determined in the absence of a radiation field for various temperatures of the constant temperature water bath, ie., at various concentrations of $TiCl_4$ in the ethylene. The procedure was then repeated with the reaction chamber near the core. The system was allowed to come to equilibrium by maintaining a constant flow rate for several hours. During the equilibration time, the exit gases were passed through the cold trap E (Fig. 12). When equilibrium was reached, the gases were directed through one of the absorption tubes, these having been previously flushed with pure ethylene and weighed to the nearest 0.01 mg. The absorption tubes were connected to the gas exit apparatus by means of a short section of teflon tubing.

After the gases had passed through the absorption tube for a certain period of time, (20 to 30 minutes was usual), the flow was diverted to pass through the other absorption tube, adjustment being made if necessary on G to keep the flow rate constant. The first absorption tube was then flushed with pure ethylene from an ethylene cylinder separate from the main ethylene supply. This ethylene was passed through a P_2O_5 and glass beads trap, H. While the second absorption tube was collecting $TiCl_4$, the first absorption tube was weighed and returned to its position in the line ready for its next absorption. In this way continuous operation could be maintained.

E. Static Cobalt-60 Irradiations

(a) The source

The irradiation facility used in these experiments was a 5 kilocurie cobalt-60 source housed in a hot cell equipped with manipulators, and leaded glass viewing window. This source consisted of 12 cobalt-60 rods positioned to form a cage with a central cylindrical cavity (31b). This cage could be lowered, by means of a crane, into a water-filled hole in the floor of the hot cell.

(b) Irradiation vessels and holder

Irradiation vessels having a volume of about 600 c.c. were constructed from 50 mm. pyrex glass tubing. These vessels were individually calibrated to the nearest cc., their relatively large size providing ample quantities of products for quantitative analysis when about 10% of the $TiCl_4$ was consumed.

The irradiation vessel was held in position by an aluminum stand which consisted of a length of 6.5 cm. inside diameter aluminum pipe, slightly longer than the main body of the irradiation vessel. This pipe was bolted in an upright position to a square piece of 1/2" aluminum plate. The filling tube and break seal at the top of the irradiation vessel were protected by a strip of 1/4" aluminum plate, bent in the shape of a U, the rounded part of which protruded above the level of the glass tubes.

(c) Filling of the reaction vessels

The vessels were attached to the vacuum line for filling as shown in Fig. 13. Teflon stopcocks were used because of the high reactivity of $TiCl_4$ towards various available types of stopcock grease.

With the break seal F intact, the vessels were pumped out through B to a pressure of approximately 10^{-5} mm. Hg. and thoroughly flamed. B was then collapsed by means of a flame, as were the large diameter vessel pump-out tubes at the places denoted by arrows in the diagram. During the foregoing operation, the $TiCl_4$-C_2H_4 mixture had been brought to equilibrium by passing purified ethylene through the $TiCl_4$ bubbler and equilibration volume C and from there to the manostat which kept the pressure at the desired level.

The manostat is shown in Fig. 14. This regulated the pressure in the following manner: When the pressure in the system rose above a preset value, electrical contact at A was broken. This activated electromagnet B which opened the spring loaded clamp C, allowing gas to flow through rubber tube D. The resulting pressure drop, caused contact at A followed by closure of C. The system could be adjusted to give an insignificantly small pressure fluctuation. The large bulb E was periodically evacuated as shown to be necessary by manometer F. A bypass G and a damping volume H were found to be necessary. The former was used during the equilibration operation along with the manostatic tube B as it was not practical to have the full flow go through B. The pressure at which the manostat operated could be varied by changing the amount of mercury in I, extra mercury being stored in J.

After the irradiation vessels had been evacuated and sealed off from the high vacuum system, the section of the filling line, between

Figure 13. Apparatus for Filling Irradiation Vessels with C_2H_4-$TiCl_4$ Mixtures

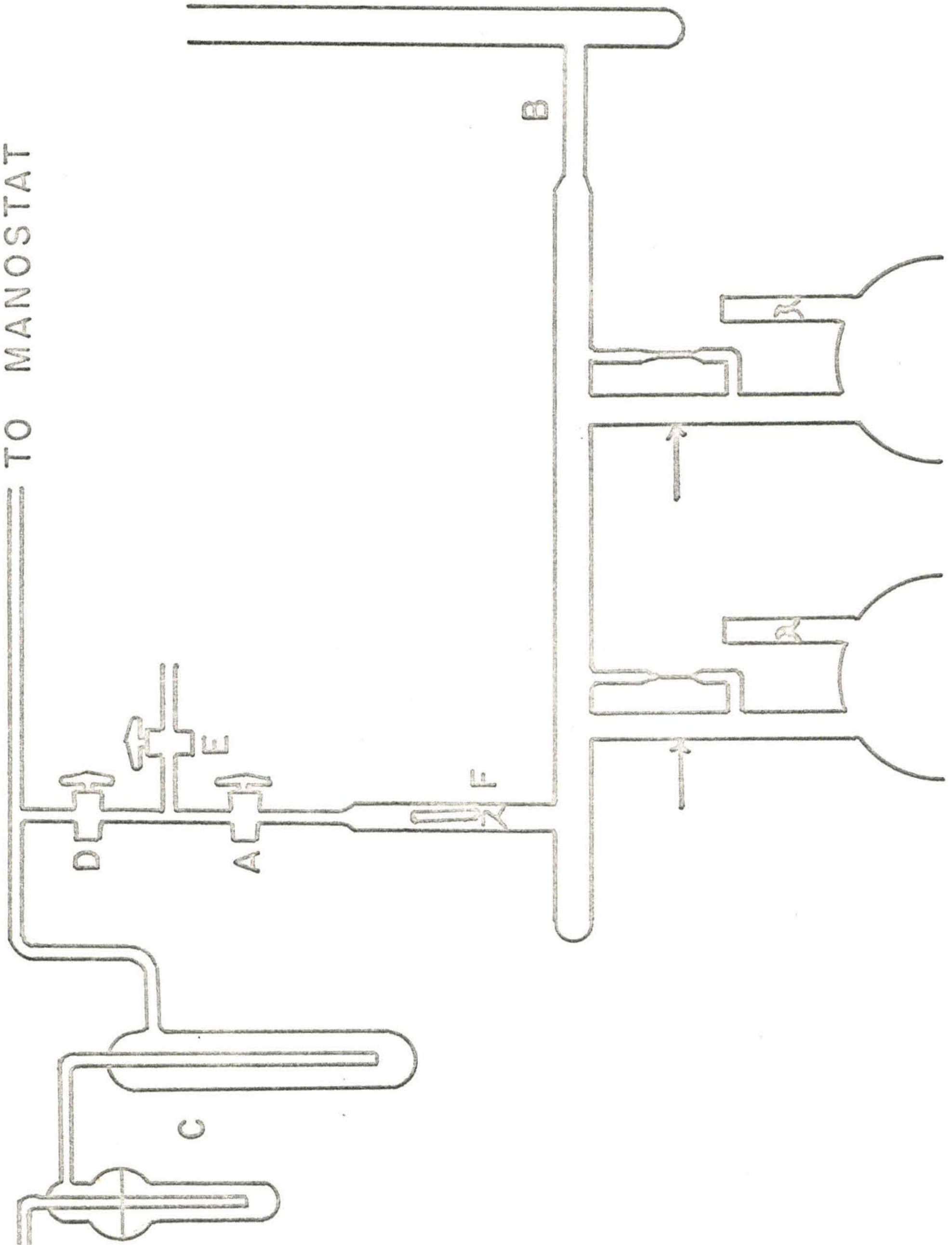
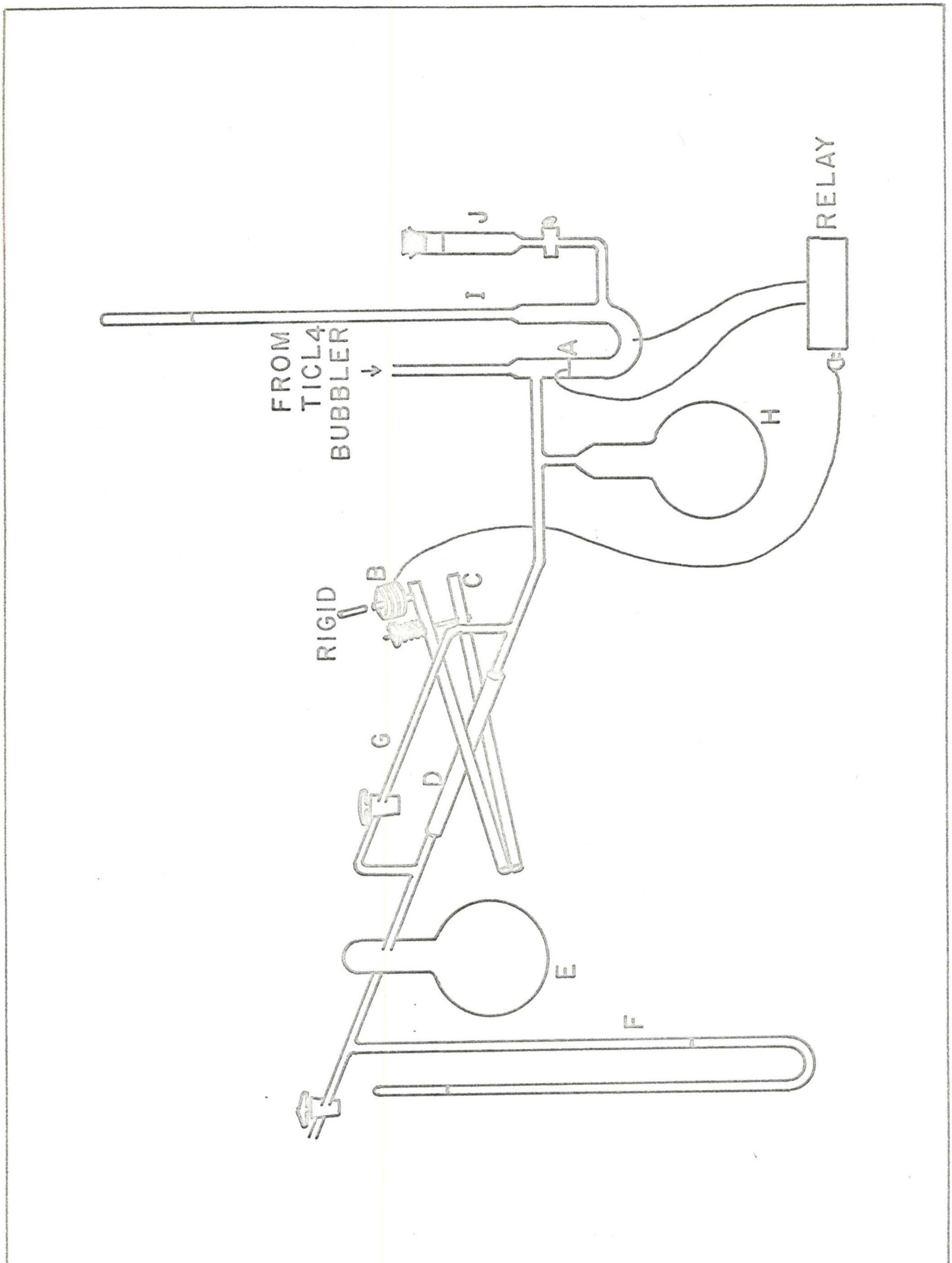


Figure 14. Manostat Associated with C_2H_4-$TiCl_4$ Filling Apparatus



stopcock D (Fig. 13) and the break seal F, was evacuated. Following this step, stopcock E was closed and D opened slowly. To fill the vessels, A was closed, the break seal F broken and A adjusted so that the rate of flow into the vessels was slow enough not to upset the equilibrium. When the flow through the manostat indicated that the vessels were filled, A was closed and each vessel isolated by heating the thin walled constrictions with a small hot flame. The amount of decomposition brought about by this step was considered to be negligible as the volume of gas affected was a very small fraction of the total. The final pressure was slightly below atmospheric to make the collapsing of the thin-walled constrictions possible.

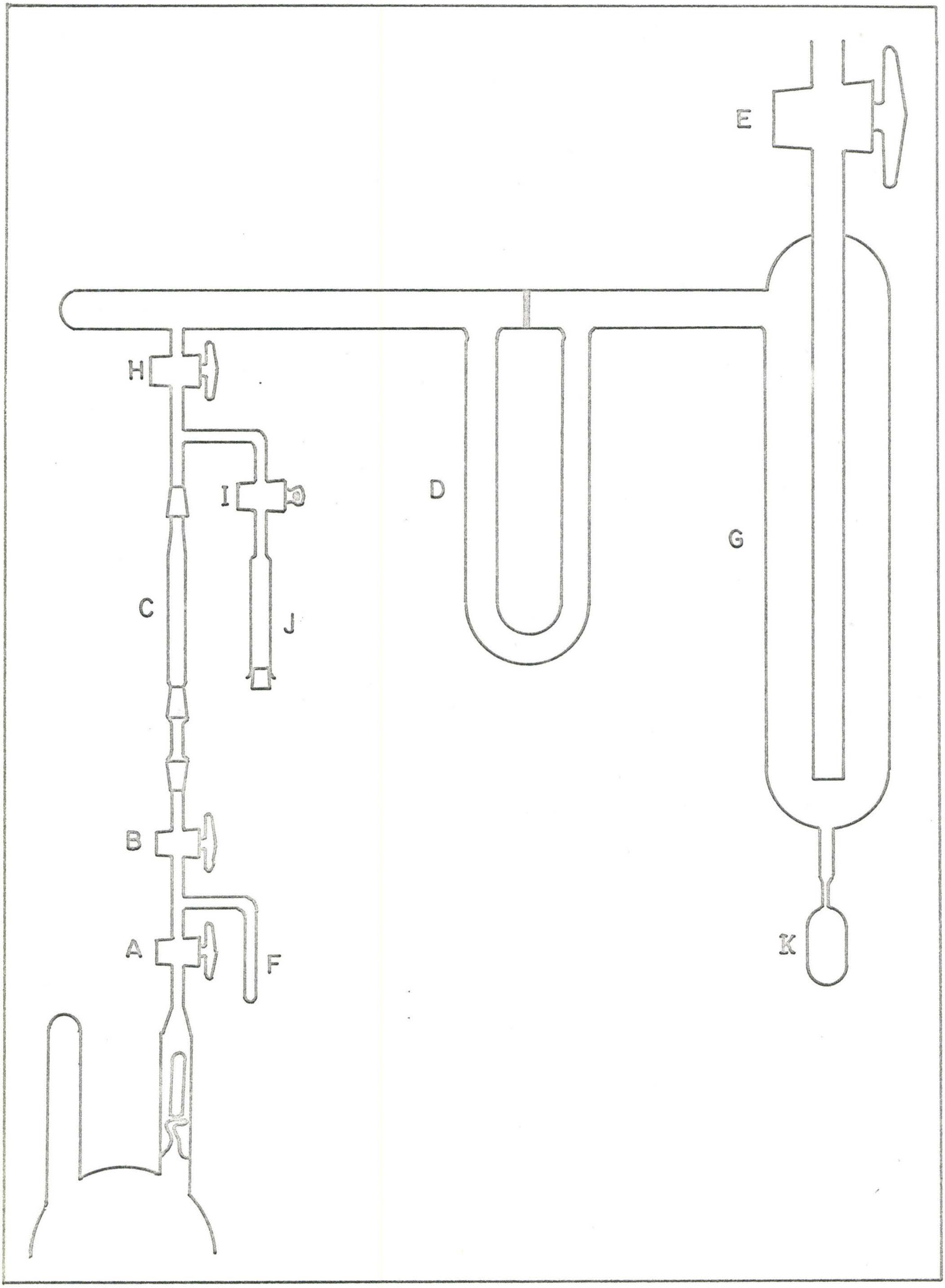
(d) Variation of surface to volume ratio

The variation of the surface to volume ratio of the irradiation vessels was effected by the addition of weighed amounts of pyrex glass wool, the fibres of which had an approximate diameter of 6×10^{-4} cm. From a knowledge of the density of the glass, it was possible to calculate the approximate surface area per gram of the glass wool. Before insertion into the irradiation vessels, the glass wool was thoroughly washed with carbon tetrachloride. This was carried out in a soxhlet extractor, extraction being continued for several hours. The washing of the glass wool was found to be necessary to remove the layer of oil applied during the manufacturing process. The reactants were introduced into the glass wool filled vessels as previously described except that the heating of the vessels during evacuation was more intensive. Instead of applying a flame to the vessels, electrical heaters were constructed to fit snugly around them. The vessels were pumped on overnight while being heated to a temperature of about 120° C.

(e) Analytical procedure

The analytical apparatus for the static irradiations is shown in Fig. 15. After the system had been evacuated, stopcock A was closed, and the break seal broken. Stopcocks A and B were solid plug 2 mm. bore high vacuum stopcocks greased at the ends only. The gases were pumped out of the irradiation vessel, the rate being regulated by stopcock A. After two or three minutes of restricted flow, A was opened full. It was found that if A was opened full from the start, there was danger of the more volatile products being swept through the cold trap. The gases passed from the irradiation vessel through the absorption tube C. This tube, illustrated in Fig. 11, removed the $TiCl_4$ from the gases while allowing the radiolysis products to proceed to trap D which was a detergent filled trap kept at dry ice temperature. The ethylene along with low molecular weight radiolysis products such as ethane, acetylene, hydrogen etc. passed through D and were pumped off. Pumping was continued for five minutes whereupon stopcocks E and B were closed, and liquid air was applied to tube F so that the major fraction of the gases remaining in the irradiation vessel would be condensed in this tube. With A closed and B open, F was allowed to come to room temperature after which E was opened for one minute. This operation was repeated until nothing could be observed to condense in F which was usually found to be the case after three such operations. The use of tube F was necessary since it

Figure 15. Apparatus for the Collection of $TiCl_4$ and the Chlorinated Hydrocarbons from Irradiated C_2H_4-$TiCl_4$ Mixtures



shortened the time needed to remove the gases from the irradiation vessel. Prolonged pumping resulted in losses of ethyl chloride, the most volatile of the chlorinated hydrocarbons. With E open and B closed, liquid air was applied to G and the dry ice bath removed from D. Water at roughly 90° C. was placed around trap D to speed up the desorption of the chlorinated hydrocarbons. During this desorption, H was closed and I opened, allowing dry air to enter the absorption tube through the P_2O_5 filled tube J. The absorption tube was then removed, thoroughly wiped to remove the stopcock grease and weighed on a semi-micro balance. The difference between this weight and that of the tube before the analysis gave a measure of the unreacted $TiCl_4$.

With stopcock E closed, the chlorinated hydrocarbons, now in trap G, were transferred to bulb K by lowering the liquid air. K was subsequently drawn off. The products were then analysed gas chromatographically, using a 3-meter detergent column at 25° C., helium carrier.

The relation between chromatographic peak area and number of moles of material was established by introducing measured quantities of the substances of interest. This was done by means of a Hamilton No. 701-N microliter syringe.

CHAPTER 2

EXPERIMENTAL RESULTS

A. Continuous Flow System

(a) Vapour pressure measurements

The results obtained from the vapour pressure studies are summarized in Table VII.

TABLE VII

Vapour pressure measurements on chlorinated hydrocarbons

Compound	Temperature (° C.)	Experimental vapour pressure (cm. Hg.)	Identified as	Known Vapour Pressure (cm. Hg.)
1	22.7	14.6	2-C_4H_9Cl	15.0
1	0.4	5.1		4.8
2	19.2	7.4	1-C_4H_9Cl	7.8
2	0.6	2.7		3.2
3	22.8	6.8	1,2-$C_2H_4Cl_2$	7.1
3	0.6	2.2		2.2

(b) Infrared data

The peaks appearing in the infrared analyses of samples of unknowns 1, 2 and 3, along with those of the corresponding standards are shown in Tables VIII, IX and X respectively.

TABLE VIII

Infrared data for 2-C_4H_9Cl and compound 1

Compound 1		2-C_4H_9Cl	
Frequency (cm.$^{-1}$)	Strength	Frequency (cm.$^{-1}$)	Strength
2914	S	2918	S
2825	M	2830	M
1450	M		
1440	M	1430	S
1375	M	1362	S
1283	M	1278	M
1230	M	1228	M
1155	W	1148	W
1145	W	1140	W
1110	W	1108	W
1060	W	1060	W
990	W	988	W
950	W	950	W
845	W	840	W
835	W	830	W
787	W	780	W
738	W	730	W

TABLE IX

Infrared data for 1-C_4H_9Cl and compound 2

Compound 2		1-C_4H_9Cl	
Frequency (cm.$^{-1}$)	Strength	Frequency (cm.$^{-1}$)	Strength
2920	S	2912	S
2840	M	2830	M
1450	M	1445	M
		1390	W
1280	M	1280	M
1232	W	1228	W
870	W	860	W
		810	W
740	W	740	W

TABLE X

Infrared data for 1,2-$C_2H_4Cl_2$ and compound 3

Compound 3		1,2-$C_2H_4Cl_2$	
Frequency (cm.$^{-1}$)	Strength	Frequency (cm.$^{-1}$)	Strength
2915	M	2920	M
2830	W	2825	W
1450	W	1450	W
1440	W	1440	W
1280	M	1285	M
1228	M	1228	M
1218	M	1218	M
		960	W
722	M	719	M
712	M	712	M

In the above three tables, S, M and W stand for strong, medium and weak. The three extra weak peaks appearing in the standard spectra in Tables IX and X were probably not observed for the unknowns because the amount of unknown was lower than that of standard. The 1440 - 1450 cm.$^{-1}$ doublet in the spectrum of compound 1 appeared as a singlet in the standard spectrum. This has not been explained.

(c) Determination of $TiCl_4$ reacted in continuous flow system

The amount of $TiCl_4$ collected at various flow rates and for various bubbler temperatures in the absence of an irradiation field is given in Table XI.

TABLE XI

Weight $TiCl_4$ collected at various flow rates and saturation temperatures

Flow rate (cc./min.)	Bath Temperature (° C.)	Weight $TiCl_4$ collected/min. (mg.)
3.6	18.0	0.27
4.7	18.0	0.35
8.2	18.0	0.62
8.5	10.0	0.35
8.6	0.1	0.20

A summary of the results obtained when the vessel was in the irradiation position is given in Table XII.

TABLE XII

Rate of reaction of $TiCl_4$ with C_2H_4 at various $TiCl_4$ concentrations (30° C.)

Run	Bath Temp. (° C.)	$TiCl_4$ conc. before irr. (mg/cc x 10^2)	$TiCl_4$ conc. after irr. (mg/cc x 10^2)	Ave. $TiCl_4$ conc. (mg/cc x 10^2)	Log. $TiCl_4$ reacted	Log. ave. $TiCl_4$ conc.
(i)	20.1	8.5	6.4	7.5	-1.692	-1.128
(ii)	18.0	7.5	5.9	6.7	-1.774	-1.173
(iii)	15.0	6.2	4.5	5.4	-1.782	-1.272
(iv)	10.0	4.4	3.2	3.8	-1.921	-1.416
(v)	0.1	2.1	1.5	1.8	-2.214	-1.735

A plot of log $TiCl_4$ reacted vs. log average $TiCl_4$ concentration is given in Fig. 16. The slope of this curve gives the reaction order of 0.85 for the disappearance of $TiCl_4$.

(d) Adsorbed $TiCl_4$ in continuous flow system

The volume of the continuous flow system was estimated to be 350 cc. When the partial pressure of $TiCl_4$ in the system was 6.7 mm. it should have contained 26 mg. of $TiCl_4$. The actual weight of $TiCl_4$ collected when the system was flushed with several thousand cubic centimeters of pure ethylene was 61 mg. It was therefore concluded that 35 mg. of $TiCl_4$ were adsorbed on the walls of the system for the reactor pool temperature of 30° C.

(e) Purity of ethylene

The chromatogram obtained when a sample of purified ethylene was run on the gas chromatograph showed seven peaks in all. The ethylene peak represented 99.97% of the total peak area, the other six components combining to make up the other 0.03%. Impurities in this concentration range were considered relatively unimportant and no positive identification was attempted.

B. Static Irradiations

(a) Variation of dose

The rate of disappearance of $TiCl_4$ and the rates of formation of the chlorinated hydrocarbons at various total doses is given in Table XIII.

Figure 16. Rate of Reaction of $TiCl_4$ with C_2H_4 at Various $TiCl_4$ Concentrations, (Continuous Flow Apparatus)

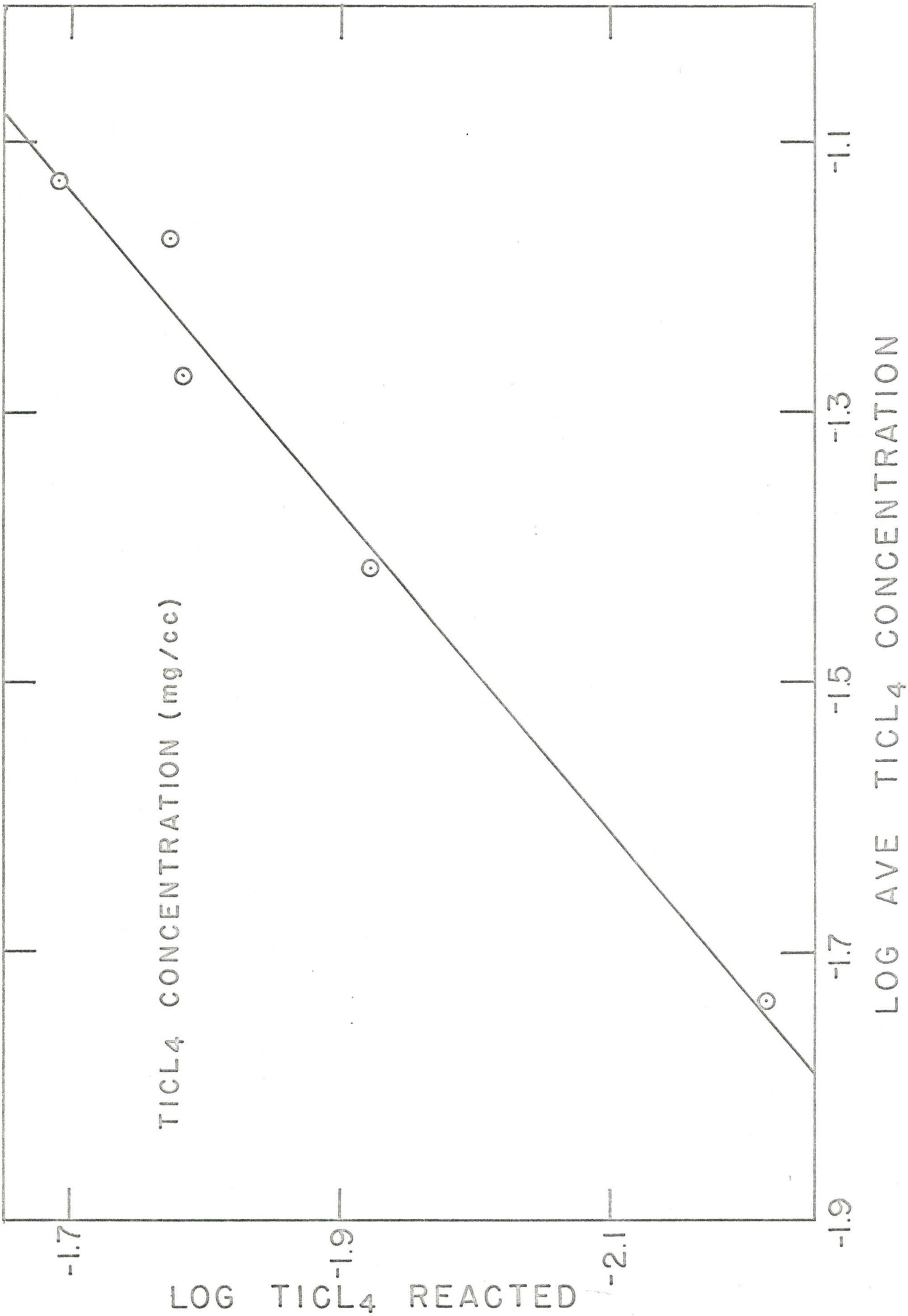


TABLE XIII

Rates of disappearance of $TiCl_4$ and rates of formation of chlorinated hydrocarbons at various doses and 30° C.

Run	$TiCl_4$ conc. (mg./cc.)	Dose (rads x 10^{-5})	Rate of disappearance of $TiCl_4$ (mg/cc/rad x 10^8)	Rate of formation moles/1/rad x 10^{12}			
				C_2H_5Cl	2-C_4H_9Cl	1-C_4H_9Cl	1,2-$C_2H_4Cl_2$
(i)	0.08	4.3	-	3.2	0.09	1.0	1.7
(ii)	0.08	4.3	2.8	2.3	0.31	3.9	5.7
(iii)	0.08	8.7	2.9	9.3	0.11	3.6	4.7
(iv)	0.08	8.7	2.0	1.3	0.12	2.6	3.0
(v)	0.08	17	1.5	10.4	0.04	1.1	1.2
(vi)	0.08	17	1.1	7.4	0.09	3.3	3.2
(vii)	0.08	26	0.95	5.9	0.07	2.0	2.2
(viii)	0.08	26	1.1	9.6	0.07	1.8	2.4
(ix)	0.08	35	0.85	10.0	0.10	5.1	5.5
(x)	0.08	35	0.85	7.9	0.04	3.0	2.8

These results illustrate the lack of reproducibility which was obtained. No trends can be seen to take place as the dose is increased except for the rate of disappearance of $TiCl_4$.

(b) Surface to volume variation

The rate of disappearance of $TiCl_4$ and the rates of formation of the chlorinated hydrocarbons for two different surface areas are given in Table XIV. All runs were made at an initial $TiCl_4$ concentration of 0.08 mg./cc.

TABLE XIV

Rate of disappearance of $TiCl_4$ and rates of formation of chlorinated hydrocarbons at two different surface areas and 30° C.

Run	Surface Area (m^2)	Dose (rads x 10^{-6})	Rate of Disappearance of $TiCl_4$ (mg/cc/rad x 10^8)	Rate of formation moles/l/rad x 10^{12}			
				C_2H_5Cl	2-C_4H_9Cl	1-C_4H_9Cl	1,2-$C_2H_4Cl_2$
(i)	0.4	10.4	0.23	1.7	0.35	1.7	0.07
(ii)	0.4	10.4	0.24	1.7	0.35	1.7	0.09
(iii)	3.0	2.6	0.95	5.9	0.072	2.0	2.2
(iv)	3.0	2.6	1.1	9.6	0.073	1.8	2.4

(c) Non-irradiated $TiCl_4$ determination

The weights of $TiCl_4$ recovered from irradiation vessels filled with various amounts of glass wool are listed in Table XV.

TABLE XV

Weight of $TiCl_4$ recovered, with no irradiation, from vessels containing various amounts of glass wool

Weight glass wool (g)	Weight $TiCl_4$ Recovered (mg)
0	44.2
5	42.5
15	37.0
25	32.9

CHAPTER 3

DISCUSSION AND CONCLUSIONS

A. Continuous Flow Apparatus

The presence of adsorbed $TiCl_4$ in the continuous flow apparatus led to a lack of reproducibility in the results obtained when the amount of $TiCl_4$ in the exit gases was quantitatively determined. A slight change in pool temperature could cause a large change in the amount of adsorbed $TiCl_4$ and therefore a large error in the weight of $TiCl_4$ collected. This experimental uncertainty, along with the fact that the solid reaction products were difficult to remove from the reaction vessel, largely limited the usefulness of the continuous flow system to its ability to produce milligram quantities of gaseous products.

The length of time required to bring the system to equilibrium after the reaction vessel was moved into the irradiation position was found to be of the order of six hours. This long equilibration time was disadvantageous since it meant the buildup of considerable quantities of solid irradiation products, as well as causing the aluminum holder and cadmium shield to become highly radioactive, making it hazardous to dismantle for cleaning.

The results obtained for the rate of disappearance of $TiCl_4$ at various $TiCl_4$ concentrations shown graphically in Fig. 16

are fairly reliable since several determinations were made to obtain the average values plotted. The slope of the line in Fig. 16 is 0.85, although values of 0.75 and 1.0 are probably within the limits of error. Without further studies giving the order with respect to ethylene concentration and radiation intensity it is not possible to establish the mechanism for the reaction.

B. Static Irradiations

The first objective of the static irradiations, using the cobalt-60 gamma source, was to determine the effect of variations in the surface to volume ratio of the reaction vessels on the rates of formation of the gaseous chlorinated hydrocarbons. When the amount of surface was increased by the addition of glass wool, the results became quite irreproducible. This was at first thought to be due to inefficient removal of the reaction products from the vessels. To check this theory, two vessels, one of which contained glass wool, were filled with equal quantities of 1,2-dichloroethane. The amount of 1,2-dichloroethane added was roughly what would be produced in a typical experiment. 1,2-dichloroethane was chosen since it is the least volatile of the products and hence would probably be most strongly adsorbed on the glass wool. The analyses, carried out in the usual way, showed that the lack of reproducibility was not due to this cause.

The amount of $TiCl_4$, recoverable from unirradiated samples was found to be proportional to the amount of glass wool in the vessel. Water is known to be adsorbed on glass surfaces up to temperatures as high as 350° centigrade (33). The reaction vessels, as well as the glass wool, would be expected to have a monolayer of adsorbed water even though pumped on for several hours and heated to over 100° C. Upon introduction of the reactants some of the $TiCl_4$ would be hydrolysed to give HCl and $TiCl_3OH$. If this were indeed occuring, vessels containing glass wool should yield less recoverable $TiCl_4$ than those with no glass wool, when filled with equal amounts of $TiCl_4$ and analysed without irradiation. The experimental results shown in Table XV bear this out.

The formation of HCl in the reaction between $TiCl_4$ and the adsorbed water in the system is postulated as being the major cause of the lack of reproducibility. The reaction between C_2H_4 and HCl in the presence of ionizing radiation, as is shown later in this work, proceeds by a chain mechanism. The gaseous chlorinated reaction products are the same as those observed to be formed in the radiolysis of the $TiCl_4$-C_2H_4 system. The observed products cannot all arise from the reaction between the HCl and C_2H_4. If this were the case, the rates of formation of the chlorinated hydrocarbons would be expected to drop off rapidly with total dose since the HCl would be largely consumed at relatively small doses. This is not observed.

The variation of surface to volume ratio has a marked effect on the rate of formation of 1,2-dichloroethane. Its rate is increased by thirty-fold when the surface is increased by eight-fold. The rates of formation of the other three chlorinated products are also increased, the increase being much less than that observed for 1,2-dichloroethane. The increase for these three products can be considered to result from the presence of a higher concentration of HCl in the gas phase. The much larger increase in the rate of formation of 1,2-dichloroethane is probably due to the adsorption of some of the HCl on the surface of the glass. As will be shown later, when HCl and C_2H_4 undergo a radiation induced reaction, 1,2-dichloroethane is formed by means of a heterogeneous reaction between HCl adsorbed on a surface and the chloroethyl radicals produced when chlorine atoms add to ethylene. If the amount of adsorbed HCl was greater than the amount of HCl in the gas phase, the increase in the rate of formation of 1,2-dichloroethane due to an increase in surface would be expected to be greater than that for the other products which are produced homogeneously in the gas phase.

The realization that a significant portion of the reaction being observed in this system was due to traces of HCl present, prompted the study of the HCl-C_2H_4 system which is the main contribution of the thesis.

PART III

HCL-C_2H_4 SYSTEM

CHAPTER 1

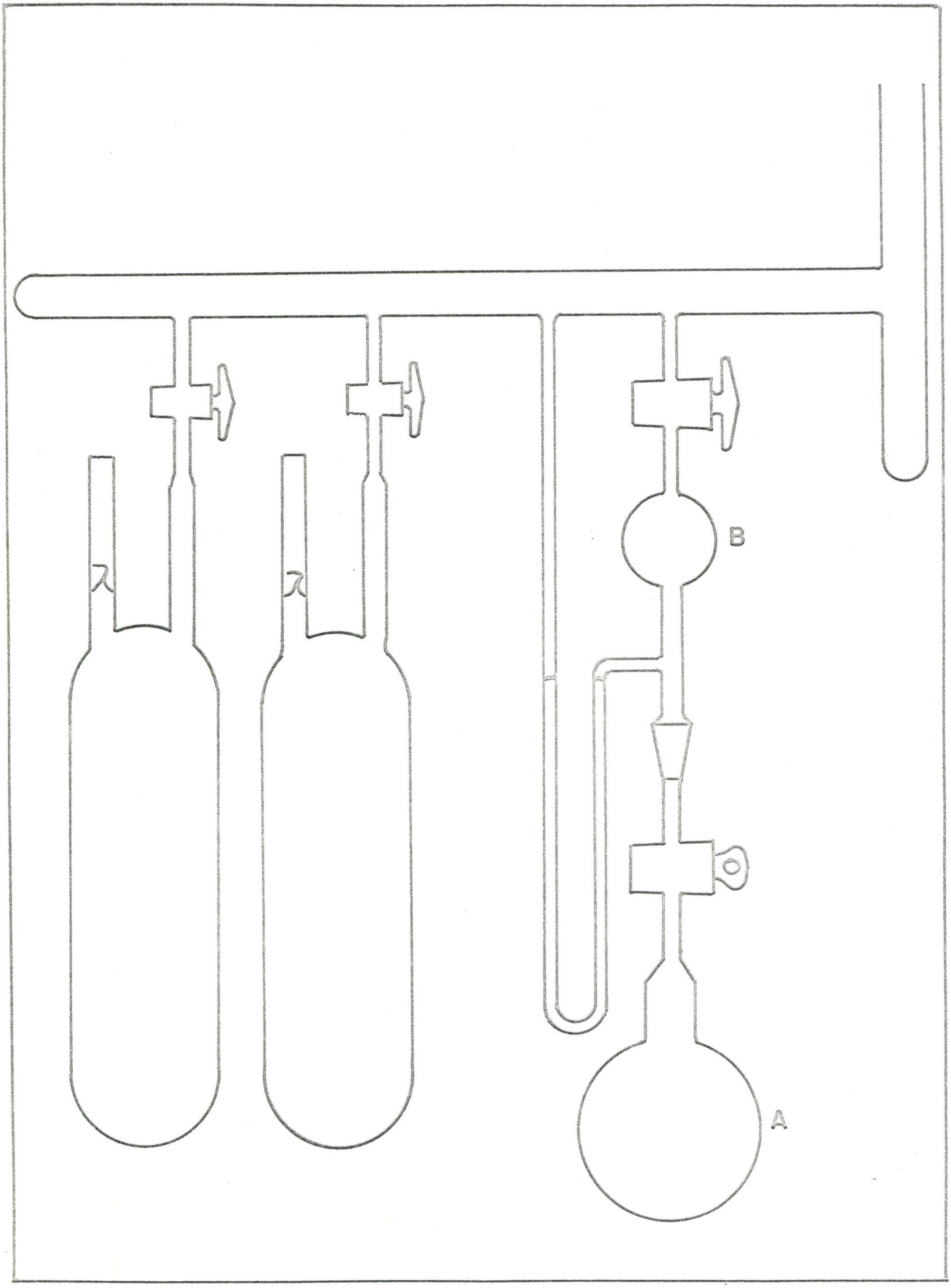
EXPERIMENTAL TECHNIQUES

A. Filling of Irradiation Vessels

The filling apparatus for this system is shown in Fig. 17. Anhydrous HCl, supplied by the Dow Chemical Company having a stated minimum purity of 99%, was purified by trap to trap vacuum distillation and stored in bulb A. The addition of small amounts of HCl to the irradiation vessels was accomplished by first establishing the volume relationships between bulb B and the various vessels to be filled. When this had been done, B was filled with HCl to a measured pressure, after which an expansion into the vessel to be filled yielded the appropriate HCl pressure. For very low HCl concentrations, two expansions were used. After the vessels were filled with HCl, ethylene was added to make the total pressure slightly above atmospheric. Liquid air was then applied to the vessels and they were drawn off with the aid of a flame.

The Matheson CP grade ethylene used in these experiments was purified, first by passing it through a charcoal trap and then by

Figure 17. Apparatus for Filling Irradiation Vessels with $HCl-C_2H_4$ Mixtures (Static Irradiations)



trap to trap vacuum distillation. It was stored in a 5 liter storage bulb at a pressure of about 50 cm. Hg. above atmospheric.

B. Analytical Procedures

The analytical procedures used were identical to those used for the $TiCl_4$-C_2H_4 except that the gain in weight of the absorption tube gave a measure of the unreacted HCl instead of the unreacted $TiCl_4$.

C. Dosimetry

The dose absorbed by the system in question was calculated from the values obtained when Fricke dosimetry solutions were irradiated in identical vessels and under identical conditions. The water used to prepare the dosimetry solutions was distilled from alkaline permanganate to remove any organic impurities. Reagent grade ferrous ammonium sulfate and reagent grade sulfuric acid were used to prepare the solutions which were 10^{-3} M ferrous ammonium sulfate in 0.1N sulfuric acid. Solutions containing 10^{-3} molar sodium chloride along with the other constituents were also prepared. The results obtained with this latter solution, when compared with those obtained from the regular solutions served as a check on the purity of the reagents. If the two solutions yielded similar results, the absence of impurities could be assumed. (1)

The irradiation times for the dosimetry experiments were of the order of two minutes. For a short irradiation time such as this, the way in which the source is brought up to and removed from the sample is important. Since the HCl-ethylene irradiation times were also short, being four minutes in most cases, a standardized procedure was used. Dosimetry irradiation times were varied so that the measurement of the dose received by the sample during the advance and withdrawal of the source could be made.

Spectrophotometric measurements were carried out on the irradiated solutions using a Perkin Elmer-Hitaschi UV-visible spectrophotometer. Absorption was measured at 604 mμ using 1 cm. cuvettes. In each case the instrument was set at 100% transmission with a sample of unirradiated solution in the light beam. The measured optical density was related to absorbed dose by the expression given in reference 1.

D. Measurement of the Rate of Production of Ion Pairs in Irradiated HCl and Air

A measurement of the rate of production of ion pairs in irradiated HCl was obtained by determining the saturation ionization current produced by the radiation field. The rate of deposition of energy in the system was determined by measuring the saturation current in air under identical conditions. This was accomplished by applying a potential across an irradiation cell which had been silvered as shown in Fig. 18(a), the resulting current being measured by means of a vibrating reed electrometer.

The preparation of the ion chamber was as follows: Platinum electrodes were sealed through the glass at the base of the two tubes of the vessel, each electrode making contact with the two silver

Figure 18(a). Silvered Irradiation Vessel used to Measure Ion Currents in Air and HCl

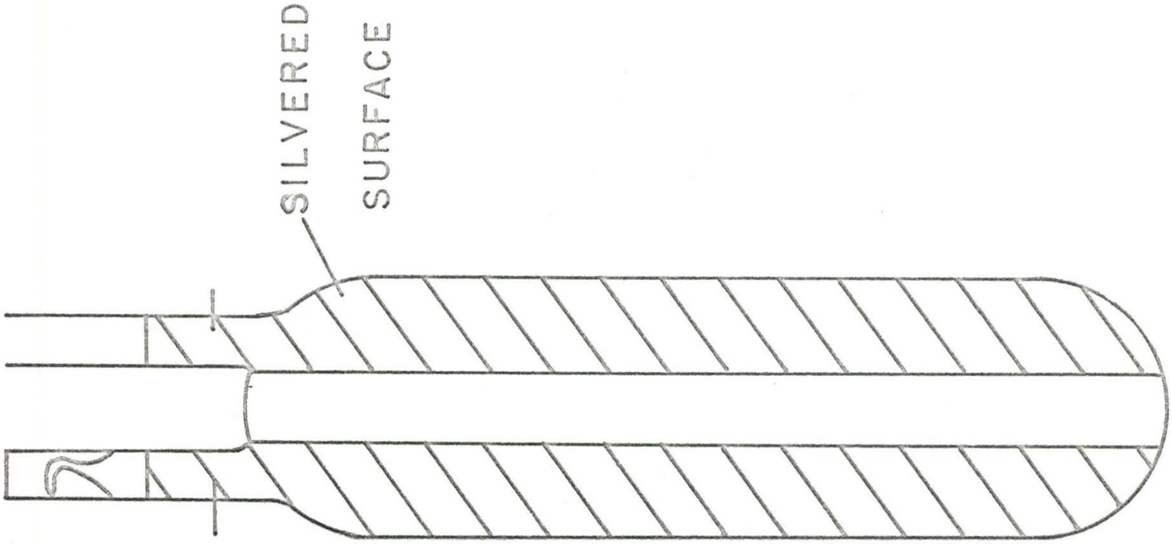
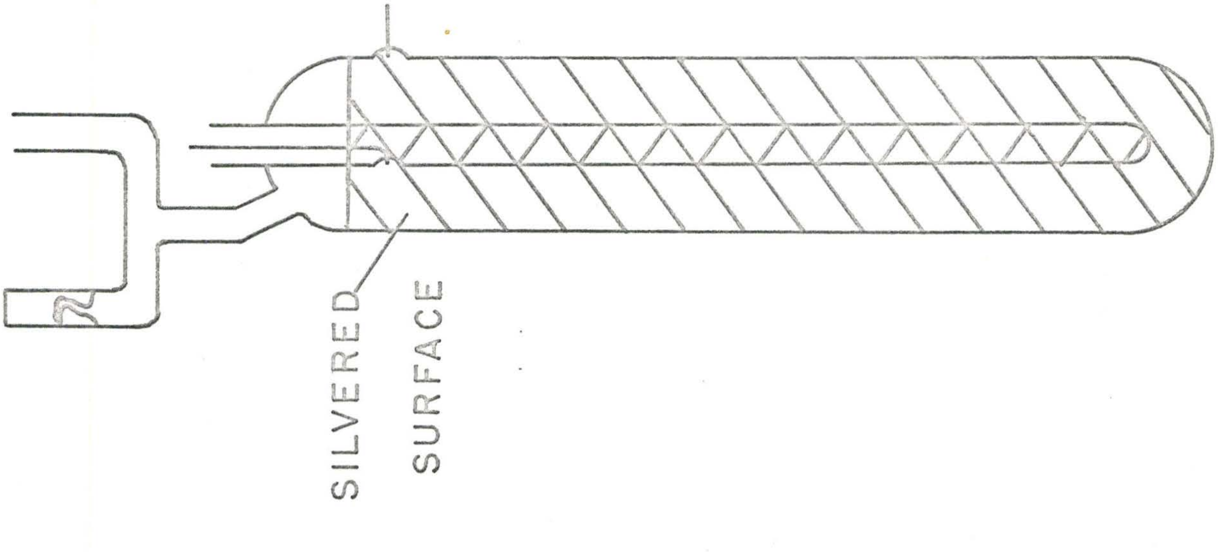


Figure 18(b). Ionization Chamber for Irradiation of $HCl-C_2H_4$ Mixtures



surfaces which had been deposited on opposite inner faces of the vessel. The silvering operation was carried out using Brashear's process (34). The contact between the two silver coatings and their respective platinum electrodes was checked as was the resistance between the two plates. If these tests proved satisfactory, the vessel was attached to the vacuum line and evacuated. As platinum doesn't make a reliable vacuum tight seal with glass, the areas around the electrodes were given a coating of black wax. After evacuation, the vessel was filled with a known amount of HCl and removed from the vacuum line. Shielded cables were connected to the electrodes and the system placed in the irradiation stand in the hot cell. The cables were brought out under the door of the hot cell, one being connected to a high voltage supply, the other to the signal input of the vibrating reed electrometer. The shields of the two cables were connected at the irradiation cell and grounded. The voltage was increased in 80 volt increments between 0 and 1500 volts, the current flowing across the cell being measured at each voltage. A plot of current vs. volts gave a value for the saturation current in HCl produced by the radiation. A similar measurement was carried out with air in the cell. Since the energy required to produce an ion pair in air is known with a reasonable amount of accuracy, this allows a calculation of the rate of deposition of energy in the HCl to be made.

E. Adsorption of HCl on Glass

An experiment was performed to check the extent of adsorption of HCl on glass. Radioactive HCl^{38} was prepared by irradiating, in the reactor rabbit irradiation facility, a few tenths of a gram of polyvinylidene chloride (trade name Saran). The radioactive film was placed in a tube on the vacuum line and after evacuation the tube was heated, thus decomposing the polyvinylidene chloride to HCl and carbon. The radioactive HCl, which had been collected in a liquid air trap, was allowed to enter a 500 c.c. glass bulb filled with glass wool. The stopcock leading to the glass bulb was shut and the excess HCl was pumped out of the manifold to a trap some distance from the bulb. A Geiger-Mueller probe, connected to a scaler unit, was clamped a few inches away from the HCl filled vessel. The count rate was recorded for various HCl pressures.

A plot of count rate vs. HCl pressure was made after the observed count rate had been corrected for dead-time losses and for radioactive decay of Cl^{38}.

F. HCl - NO Irradiations

In order to obtain a measure of the rate of initiation of the HCl - C_2H_4 chain reaction, HCl was irradiated in the presence of a small percentage of nitric oxide. The nitric oxide served as scavenger for the chlorine atoms produced by the action of the radiation on the HCl molecules.

Irradiation vessels were filled to a pressure of 3 cm. Hg. of NO and 74 cm. Hg. of HCl. These samples were irradiated for 5, 10 and 15 hour periods, using the Co^{60} source. After irradiation, the vessels were attached to the vacuum line and the NOCl which was formed during the irradiation was separated from the unreacted HCl and NO. This separation was carried out by slowly pumping the gases through a U-tube filled with glass beads which was immersed in a bath of methyl cyclohexane, maintained at its freezing point of -126° C. Pumping was continued for about an hour after which the stopcock to the high vacuum was closed and liquid air placed around a trap adjacent to the glass beads trap, the latter being equipped with a sample bulb at its base. The methyl cyclohexane was removed from the glass beads trap, the nitrosyl chloride was allowed to distill into the liquid air trap and subsequently isolated in the sample bulb. Small amounts of HCl could be detected by the bright red colour it exhibited at liquid air temperatures when in the presence of traces of NO. A pumping time of an hour was found to be sufficient to give no evidence of this red colour.

The glass ampoule containing the NOCl was broken at the bottom of a 20 cm. tube filled with water, brought to a pH of about 10 by the addition of dilute NaOH solution. The amount of chloride ion produced by hydrolysis of the NOCl was established by precipitation as AgCl.

G. Ion Chamber Irradiations

Irradiations of HCl - C_2H_4 mixtures were carried out in an ionization chamber as shown in Fig. 18 (b). The central anode of the chamber was about one centimeter from the cathode. The leads through the glass were made of tungsten and were recessed to prevent high local field gradients. Contact between the tungsten leads and the silver coating was made with the aid of silver contact paint. The purpose of these experiments was to irradiate samples in which the number of excited HCl molecules was increased by the presence of the electric field, while the number of HCl^+ ions was not.

In an effort to establish the appropriate voltage which should be applied across the cell, the vessel was filled to a particular pressure and connected to the high voltage power supply and vibrating reed electrometer. With a small Co^{60} source near the vessel, current vs. voltage measurements were made to find the proportional region. Irradiations were carried out with the applied voltage slightly below the proportional region.

CHAPTER 2

EXPERIMENTAL RESULTS

A. Percent Consumption of Reactants for Standard Conditions

Preliminary experiments showed that an irradiation time of 4 minutes at an intensity of 8.3×10^5 rads/hr. and 30°C. resulted in about a 10 percent consumption of HCl, the minor constituent. These conditions of time, intensity and temperature were used for all of the experiments unless otherwise stated.

B. Variation of HCl Concentration

The rates of formation of the chlorinated hydrocarbons at various HCl concentrations are tabulated in Table XVI.

Ethylene was added to each of the mixtures to make the total pressure 760 mm. In determining reaction orders, it has been assumed that the ethylene concentration remained constant.

A log-log plot of the rate of formation of ethyl chloride vs. average HCl pressure is given in Fig. 19. The line in the graph has a slope of 1.01, determined by a least squares fit of the data. The mechanism discussed in Chapter 3 indicates that the rate of formation should fall off more rapidly than linearly at lower HCl concentrations. Possible explanations as to why this is not being observed will be dealt with in Chapter 3 when the experimental results for C_2H_5Cl and 1-C_4H_9Cl are compared with the theoretical curve.

TABLE XVI

Rates of formation of chlorinated hydrocarbons at various HCl concentrations

Ave. HCl pressure (mm.)	Rate of formation (moles/l/rad x 10^{12})			
	C_2H_5Cl	$1-C_4H_9Cl$	$2-C_4H_9Cl$	$1,2-C_2H_4Cl_2$
0.2	11.4	10.1		
0.5		24.2		
0.5	23.6	25.0	0.5	0.23
1.0	62.7	34.6	1.2	0.34
1.9	118	31.6	1.2	0.63
3.8	216		1.2	0.63
5.0	319	48.0		0.42
6.0	321	41.3	1.8	0.60
9.5	625	48.8	3.6	0.70
11.5		50.0	2.5	0.59
14.5	786	47.5	3.7	0.59
18.3	1120		1.9	
30.7	1720	40.9		

A plot of the rates of formation of the other three products at various HCl concentrations is given in Fig. 20. The curve for $1-C_4H_9Cl$ was drawn by inspection, the other two were drawn to have a functional form similar to that for the $1-C_4H_9Cl$ as required by the mechanism outlined in Chapter 3.

Figure 19. Rate of formation of C_2H_5Cl at Various Concentrations of HCl in C_2H_4

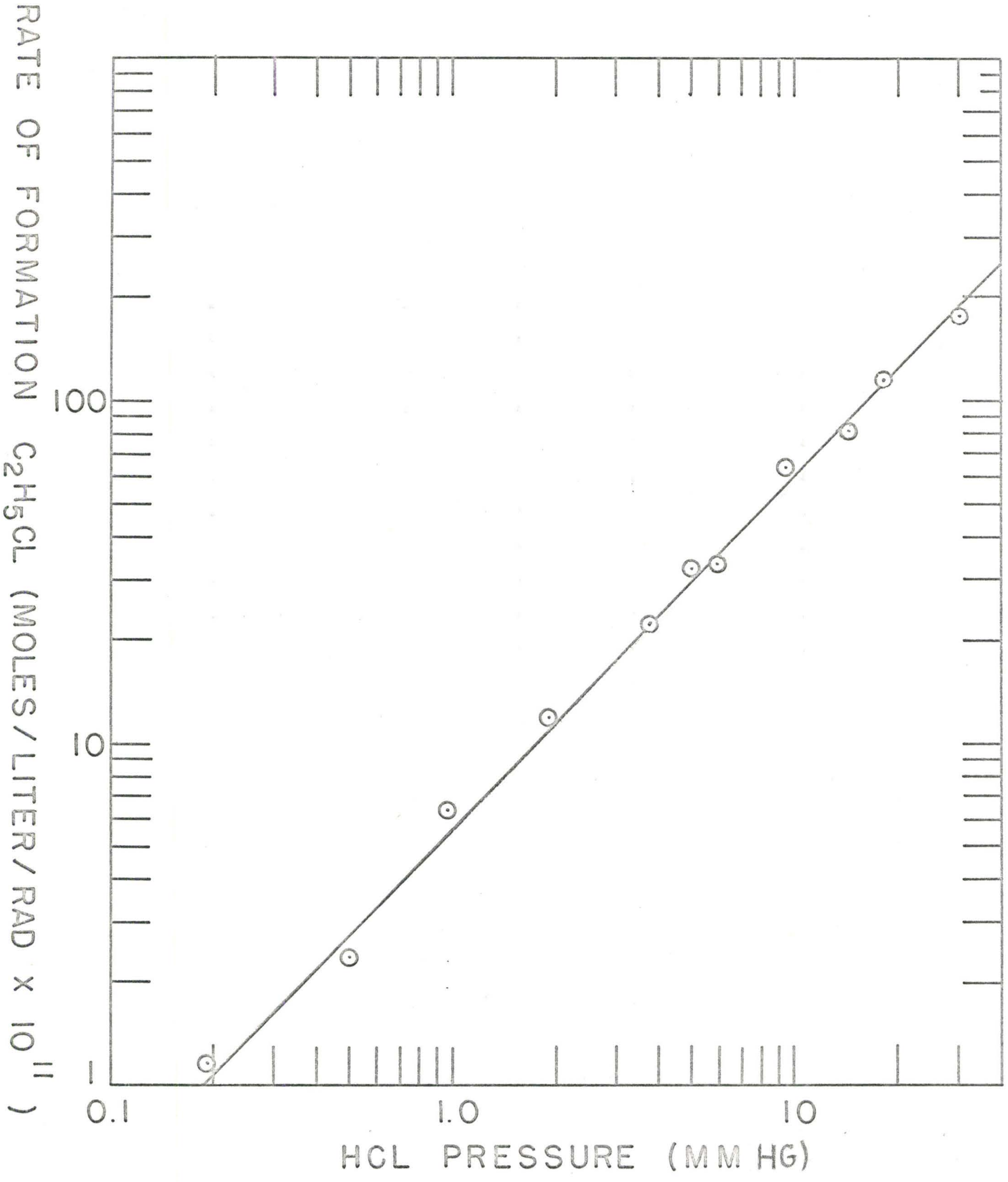
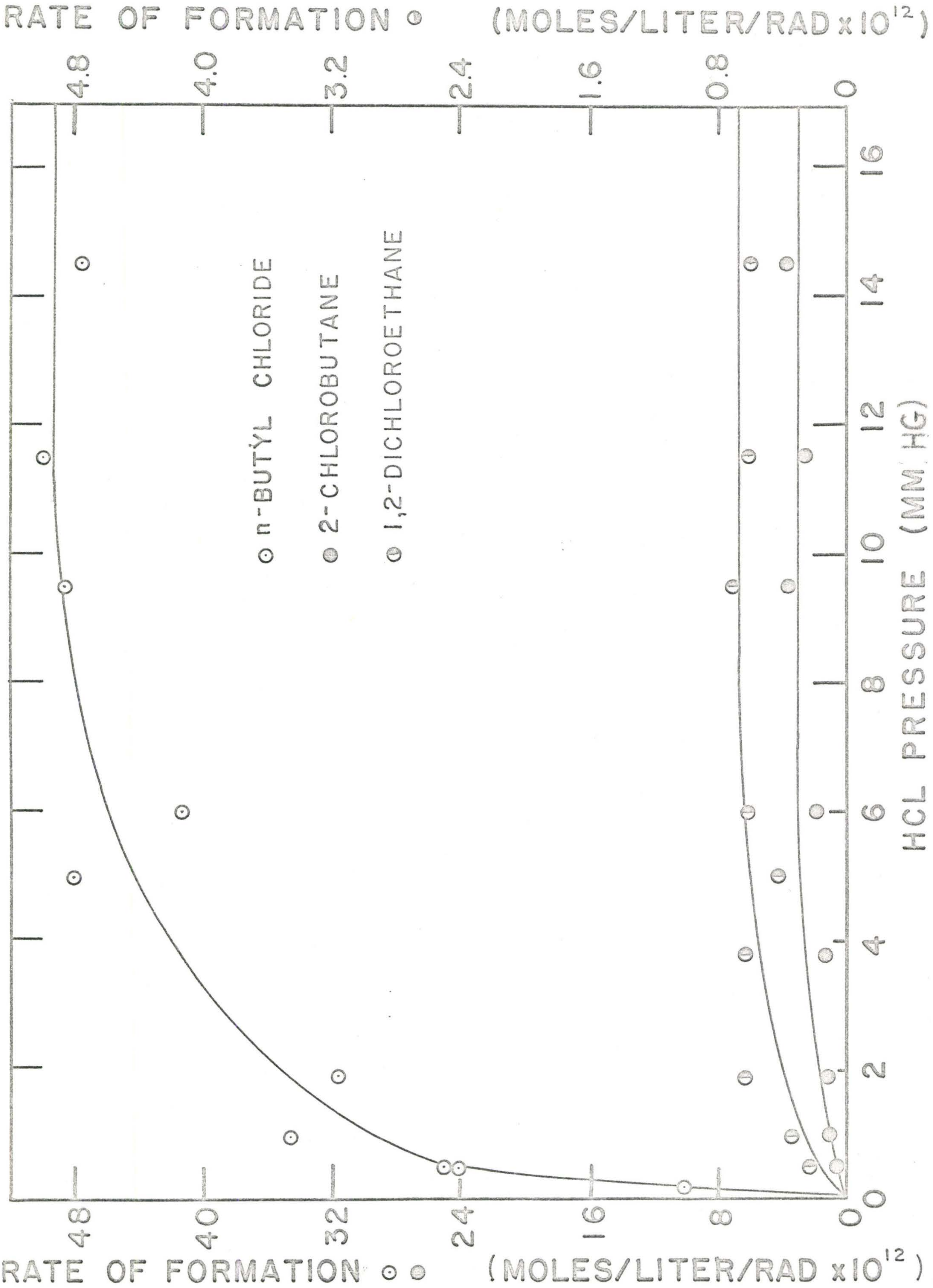


Figure 20. Rates of Formation of Chlorinated Products vs. HCl Conc.



C. Variation of C_2H_4 Concentration

Irradiations were carried out at four different C_2H_4 concentrations, the rates of formation of C_2H_5Cl and 1-C_4H_9Cl being observed in each case. The results are shown in Table XVII.

TABLE XVII

Rates of formation of C_2H_5Cl and 1-C_4H_9Cl at various C_2H_4 concentrations *

C_2H_4 pressure (atm.)	Rate of formation (moles/1/rad x 10^{11})	
	C_2H_5Cl	1-C_4H_9Cl
1.00	62	4.7
0.75	54	2.8
0.50	53	1.4
0.25	33	0.53

* HCl pressure 1.0 cm.

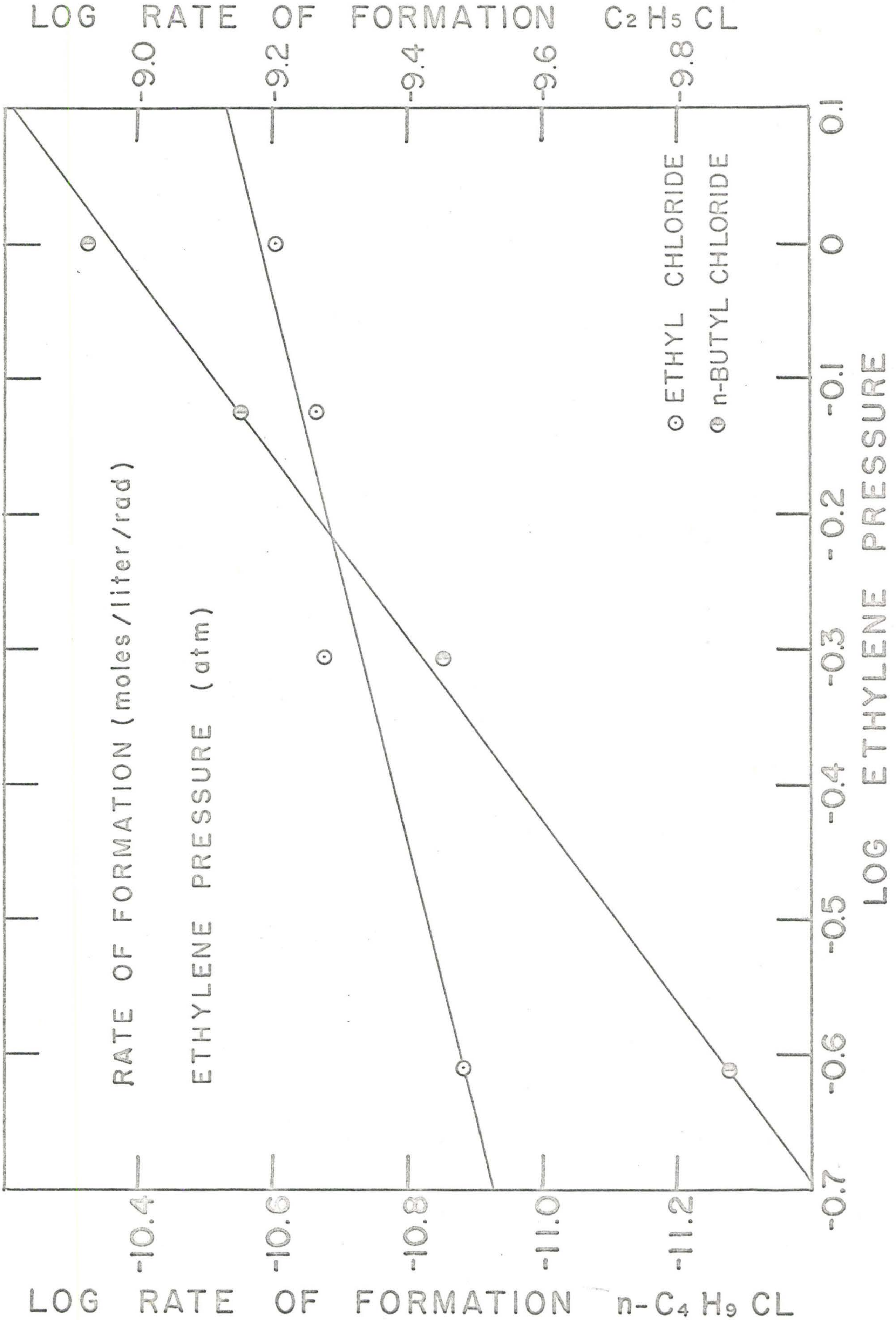
A plot of log C_2H_4 pressure vs. log rate of formation for the two products is given in Fig. 21.

The slopes of the lines for ethyl chloride and 1-chlorobutane are 1/2 and 3/2 respectively. These are not necessarily the best fitting lines but are lines having slopes predicted by the mechanism to be discussed in chapter 3. The amounts of 2-C_4H_9Cl and 1,2-$C_2H_4Cl_2$ formed at the lower C_2H_4 pressures were too small to permit quantitative determination.

D. Variation of Surface Area

The rates of formation of C_2H_5Cl, 1-C_4H_9Cl and 1,2-$C_2H_4Cl_2$ were

Figure 21. Rates of Formation of C_2H_5Cl and $1\text{-}C_4H_9Cl$ at Various C_2H_4 Concentrations



determined for various surface areas. Table XVIII summarizes the data obtained.

TABLE XVIII

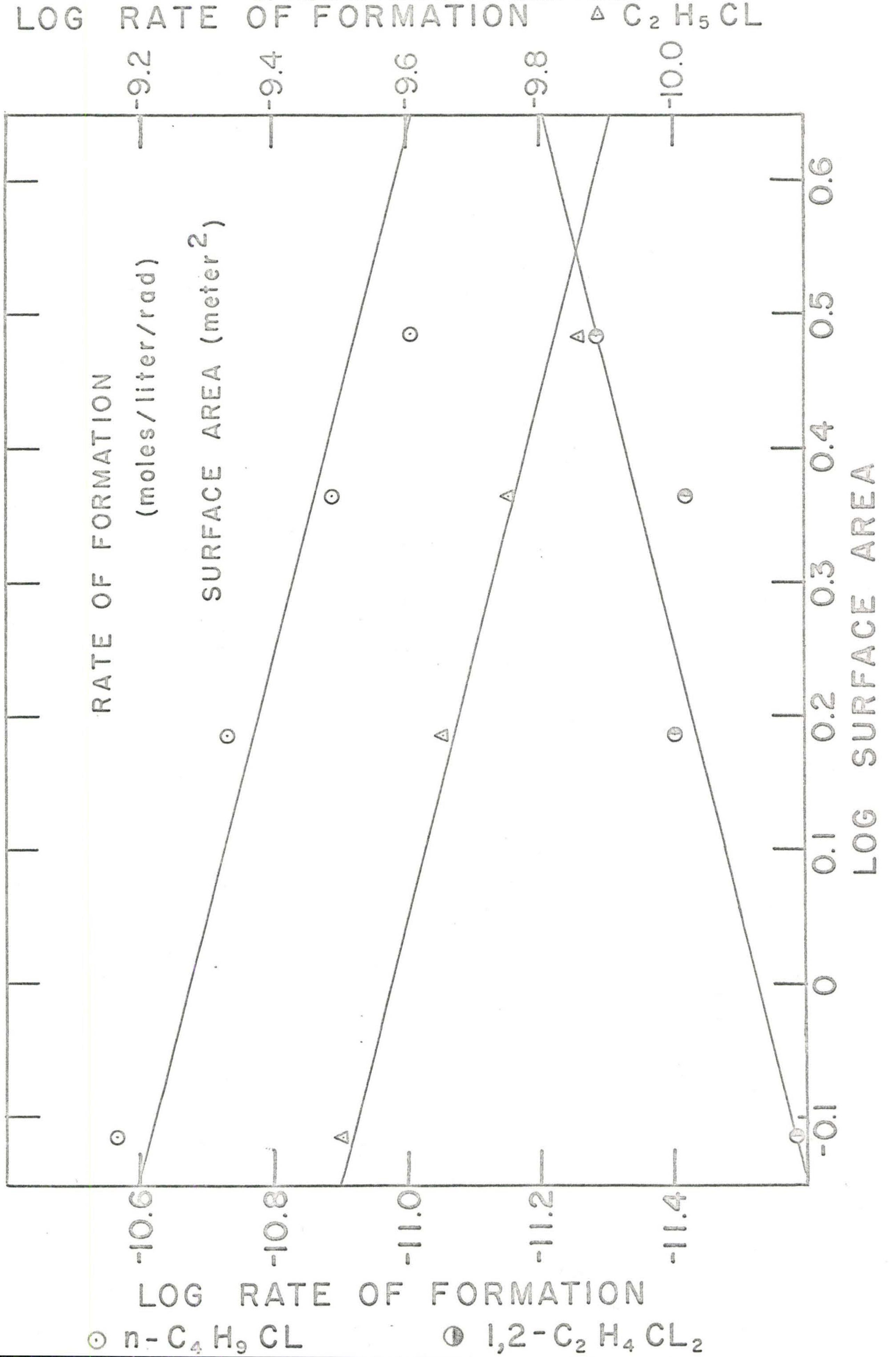
Rates of formation of C_2H_5Cl, 1-C_4H_9Cl and 1,2-$C_2H_4Cl_2$ for various surface areas

Surface Area (m^2)	Rate of formation (moles/l/rad x 10^{12})		
	C_2H_5Cl	1-C_4H_9Cl	1,2-$C_2H_4Cl_2$
0.8	310	27	2.6
1.5	220	19	4.0
2.3	180	13	3.8
3.0	140	9.1	5.2

In the above experiments, the HCl pressure was 1 cm. and the C_2H_4 pressure 75 cm. Plots of log rates of formation vs. log surface area are given in Fig. 22.

The slopes of the lines in the diagram are -1/2, -1/2 and + 1/2 for ethyl chloride, 1-chlorobutane and 1,2-dichloroethane respectively. Again the choice of slopes for the lines was governed by the value predicted by the reaction mechanism to be discussed later. The decrease in the rates of formation of the first two has been considered to be as a result of an increase in the efficiency of the termination reactions. The increase in the rate of formation of the third product indicates that it is being formed by a heterogeneous reaction taking place at the surface. The major portion of the 1,2-dichloroethane observed cannot be coming from a termination reaction

Figure 22. Rates of Formation of C_2H_5Cl, $1\text{-}C_4H_9Cl$ and $1,2\text{-}C_2H_4Cl_2$ at Various Surface to Volume Ratios



as its rate of formation would not level off at higher HCl concentrations.

E. Variation of Radiation Intensity

The results found for experiments carried out at two different dose rates are given in Table XIX.

TABLE XIX

Rates of formation of C_2H_5Cl and $1\text{-}C_4H_9Cl$ at two radiation intensities *

Relative Intensity	Rate of formation (moles/l/sec x 10^9)	
	C_2H_5Cl	$1\text{-}C_4H_9Cl$
1.00	140	12
0.31	79	5.6

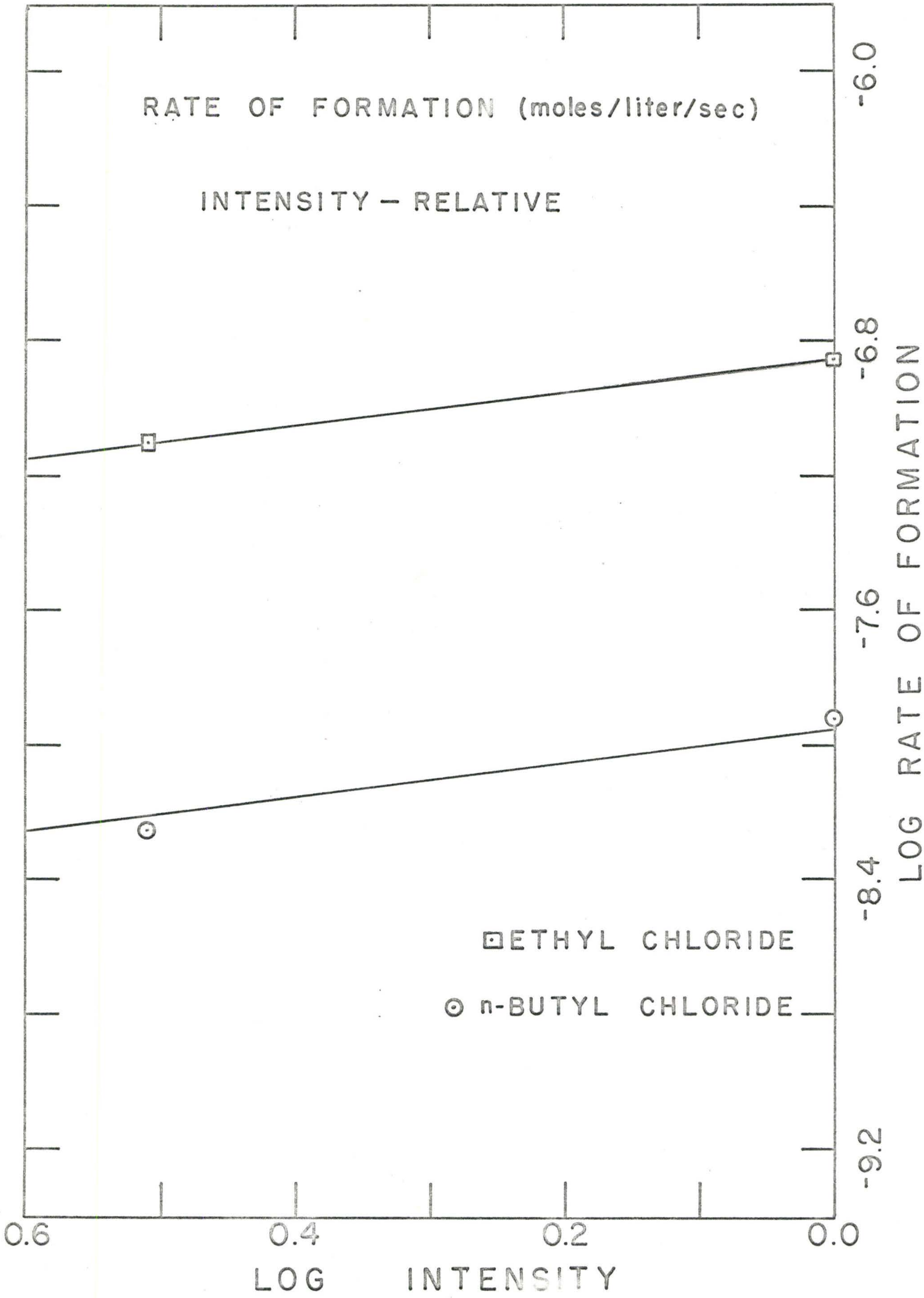
* C_2H_4 760 mm. pressure
HCl 10 mm. pressure
Intensities of radiation 8.3 x 10^5 rads/hr and 2.6 x 10^5 rads/hr.

Log-log plots of this data are shown in Fig. 23. The two lines have been drawn with slopes of 1/2 as predicted by the mechanism discussed in Chapter 3. The data thus indicate a root intensity dependence for the rates of formation of the two products.

F. Material Balance of HCl

The amount of HCl consumed in a given irradiation was determined by subtracting the weight of HCl recovered after the irradiation from that known, from pressure measurements, to be present before the irradiation. This value was compared with the amount of HCl used,

Figure 23. Rates of Formation of C_2H_5Cl and 1-C_4H_9Cl at Two Radiation Intensities



calculated from the peak areas of the observed products. The results are given in Table XX. The initial HCl and C_2H_4 pressures were 2 mm. and 760 mm. respectively.

TABLE XX

Material Balance of HCl

HCl consumed (weight difference) (mg.)	HCl consumed (peak areas) (mg.)
0.31 ± 0.03	0.25
0.55 ± 0.03	0.60
0.85 ± 0.03	0.79

The experimental error for the weight difference measurements is based on the precision of the balance. No appropriate errors can be assigned to the chromatographic peak areas but in the judgement of the experimenter, the data indicate that the HCl consumed is accounted for by the four products, ethyl chloride, 1,-chlorobutane, 2-chlorobutane and 1,2-dichloroethane.

G. HCl - NO Irradiations

To determine whether the NOCl, formed by the reaction of NO with chlorine atoms, was itself undergoing a radiation induced reaction, irradiations were carried out at three total doses. The results are shown in Table XXI.

TABLE XXI

Rate of formation of NOCl for various total doses

Irradiation time (hr.)	Weight AgCl found (mg.)	Weight NOCl (from AgCl) (mg.)	Rate of formation NOCl (moles/1/sec x 10^9)
5.0	6.1	2.4	4.0
10.0	12.9	5.0	4.2
15.0	17.8	6.9	3.8

It may be seen that the average rate of formation of NOCl is 4.0 x 10^{-9} moles/l/sec at 30° C. The concentration of reactants was 4.1 x 10^{-2} moles/l HCl and 1.6 x 10^{-3} moles/l NO. The rate of formation of chlorine atoms can thus be taken to be 4.0 x 10^{-9} gram-atoms/l/sec. The rate of decomposition of HCl molecules will be 2.0 x 10^{-9} moles/l/sec if the mode of formation of chlorine atoms is as discussed in Chapter 3. The rate constant for this decomposition will have a value of 4.9 x 10^{-8} sec.$^{-1}$.

H. Chain Length of Reaction

The sum of the rates of formation of the chlorinated products (Table XVI) was divided by the rate of production of chlorine atoms (section G.) to give the chain length. The chain length was found to be a function of HCl concentration, decreasing from 5.3 x 10^3 at 0.2 mm. HCl to 3.2 x 10^3 at 30 mm. HCl. This calculation assumes that only the energy deposited in the HCl leads to reaction products. This assumption will be justified in Chapter 3.

I. Effect of Addition of Excess C_2H_5Cl on production of 2-C_4H_9Cl

It was postulated that the formation of 2-C_4H_9Cl might be due to a secondary reaction of the C_2H_5Cl. An irradiation was carried out in which about 10 times the amount of C_2H_5Cl formed in an average irradiation was added initially. The initial pressures of HCl and C_2H_4 were 2 mm. at 760 mm. respectively. The rate of formation of 2-C_4H_9Cl was observed. Table XXII gives the results.

TABLE XXII

Rate of formation of 2-C_4H_9Cl in the presence of a relatively high concentration of C_2H_5Cl.

Initial C_2H_5Cl (moles)	Final C_2H_5Cl (moles)	Rate of formation of 2-C_4H_9Cl (moles/l/rad x 10^{12})
0	3.6×10^{-6}	1.2
3.6×10^{-5}	4.0×10^{-5}	1.4

It may be seen that the rate of formation of 2-C_4H_9Cl has not been significantly altered by the presence of excess C_2H_5Cl.

J. Adsorption of HCl on Glass

The results of the experiment designed to check the extent of adsorption of HCl on 25 g. of glass wool are summarized in Table XXIII.

TABLE XXIII

Count rate observed for various HCl pressures at 25°C.

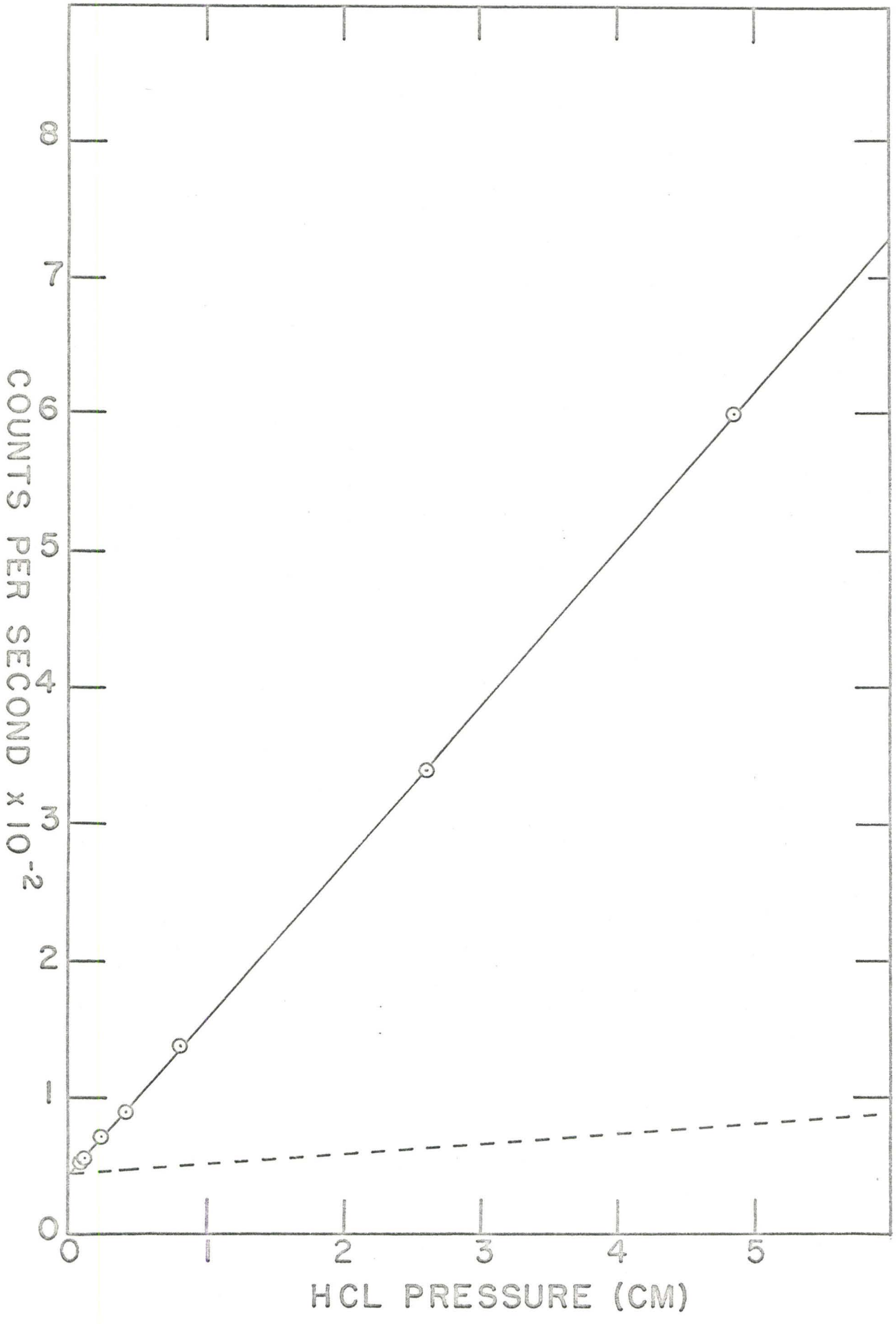
Time of observation (min.)	HCl pressure (cm.)	Counts/sec. (less background)	Counts per second (corrected) *
2	4.85	523	600
5	2.58	295	338
10	0.83	113	138
13	0.44	69	89
16	0.23	52	70
19	0.12	38	54
23	0.06	34	52

* Corrections were made assuming a 38 minute half-life for Cl^{38}. Corrections were also made for the dead-time losses of the Geiger tube.

A plot of the results appears in Fig. 24. Since the line does not go through the origin when extrapolated to zero pressure, this indicates that HCl is adsorbed on the surface of the glass.

The measured activity represents the sum of the activities of the HCl in the gas phase and that adsorbed on the glass. If no adsorption had occurred, the plot in Fig. 24 would have been a straight line with a slope of 100 counts/sec/cm. passing through the origin, which is represented by the function $y=100x$. The experimental data may be represented by the function $y=42 + 115x$. A subtraction of the former function from the latter gives the adsorption isotherm of HCl on pyrex glass at 25°C which is represented by $y=42 + 15x$. The broken line in Fig. 24 represents this isotherm.

Figure 24. Activity Associated with Glass Wool-filled Vessel at Various Pressures of Cl^{38} Labelled HCl



Evidently a monolayer of HCl becomes adsorbed on the surface at very low HCl concentrations. As the pressure is increased, the amount of adsorbed HCl also increases as evidenced by the positive slope of the isotherm. Since no pressure readings could be obtained below 1 mm., the actual shape of the isotherm in this region was not established, however, the sharp rise is completed at pressures below 1 mm.

K. Dosimetry

Fricke dosimetry gave a value of 8.1×10^5 rads/hr. for the rate of deposition of energy in water, when irradiations were carried out in the regular irradiation position. The additional dose received during the advance and withdrawal of the source was found to be 2.1×10^3 rads. The rate of deposition of energy in the C_2H_4 - HCl mixtures was calculated assuming that only C_2H_4 was present. This was done by multiplying the Fricke dosimetry results by the stopping power ratio $\rho^{C_2H_4}_{H_2O}$. The values for the two stopping powers were assumed to be proportional to the number of electrons per gram of material. This assumption is valid for low atomic weight substances if the major mode of interaction of the radiation is by means of Compton scattering. This is the case for the radiation from Co^{60}. A value for the stopping power ratio of 1.03 was calculated in this manner. Strictly speaking, this method of calculating the energy absorption in a gas from Fricke dosimetry is only valid if the stopping power of the wall material is the same as that of the gas. The error introduced is not large in this case.

L. Experiment Designed to Detect 1-Chlorohexane.

A mixture of 0.5 mm. HCl in 760 mm. C_2H_4 was irradiated for 8 minutes, the total dose being 1.2×10^5 rads. The relative amounts of ethyl chloride and 1-chlorobutane formed were 41 and 59 units respectively. No 1-chlorohexane was detected. An upper limit of 1 unit can be placed on the amount of 1-chlorohexane.

M. Measurement of Ion Currents in Irradiated HCl and Air.

The ion currents obtained when various voltages were applied across the HCl - filled silvered irradiation vessel are listed in Table XXIV.

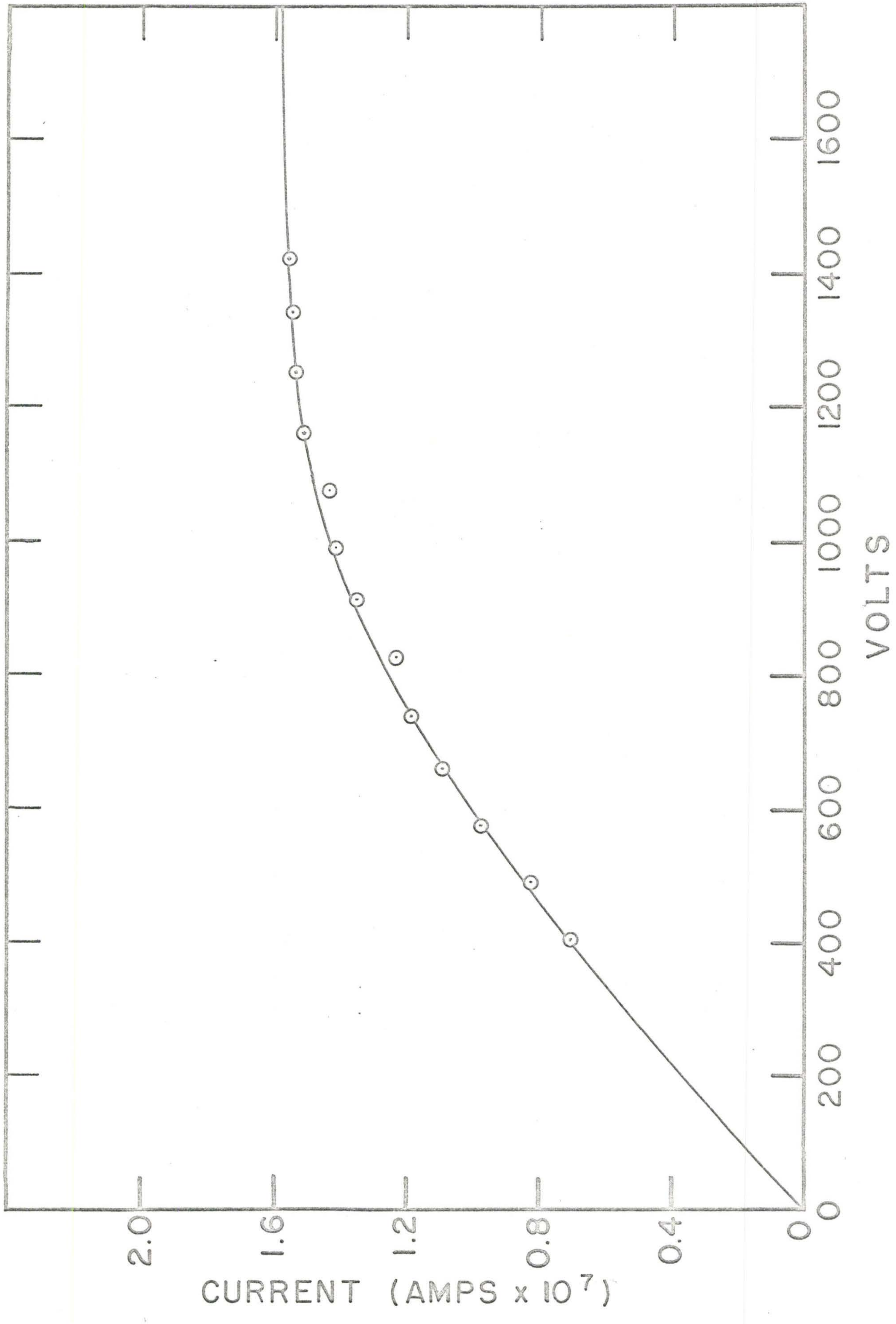
TABLE XXIV

Ion currents in irradiated HCl at 4.0×10^3 rads/hr.

Volts	Current (amps x 10^7)	Volts	Current (amps x 10^7)
410	0.70	1000	1.40
500	0.82	1090	1.42
580	0.97	1170	1.50
690	1.09	1250	1.52
750	1.18	1340	1.53
830	1.22	1420	1.54
910	1.34		

A plot of these results, given in Fig. 25, yields a value of 1.55×10^{-7} amps for the saturation current in HCl. The temperature and pressure of the HCl in the cell was 22°C. and 49 cm. Hg. respectively.

Figure 25. Saturation Ion Current in HCl



Similar measurements made with air in the ionization chamber yielded the results given in Table XXV.

TABLE XXV

Ion currents in irradiated air at 4.0×10^3 rads/hr.

Volts	Current (amps x 10^7)	Volts	Current (amps x 10^7)
90	0.41	830	1.51
170	0.68	910	1.53
250	0.92	1000	1.54
330	1.10	1040	1.56
410	1.24	1170	1.57
500	1.34	1250	1.58
580	1.40	1340	1.59
690	1.45	1420	1.59
750	1.48		

The saturation current, determined from the plot of the data in Fig. 26, is 1.60×10^{-7} amps at 75 cm. and 25° C.

N. Contribution of Excited-Molecule Decomposition to the Initiation Reaction, Determined by Ionization Chamber Experiments

A plot of current vs. volts for an HCl - C_2H_4 mixture in the presence of a mc. source of Co^{60} is given in Fig. 27. From this graph it can be seen that the proportional region for this particular mixture commences at about 4000 volts. The irradiation with the high intensity source was carried out with the applied voltage slightly

Figure 26. Saturation Ion Current in Air

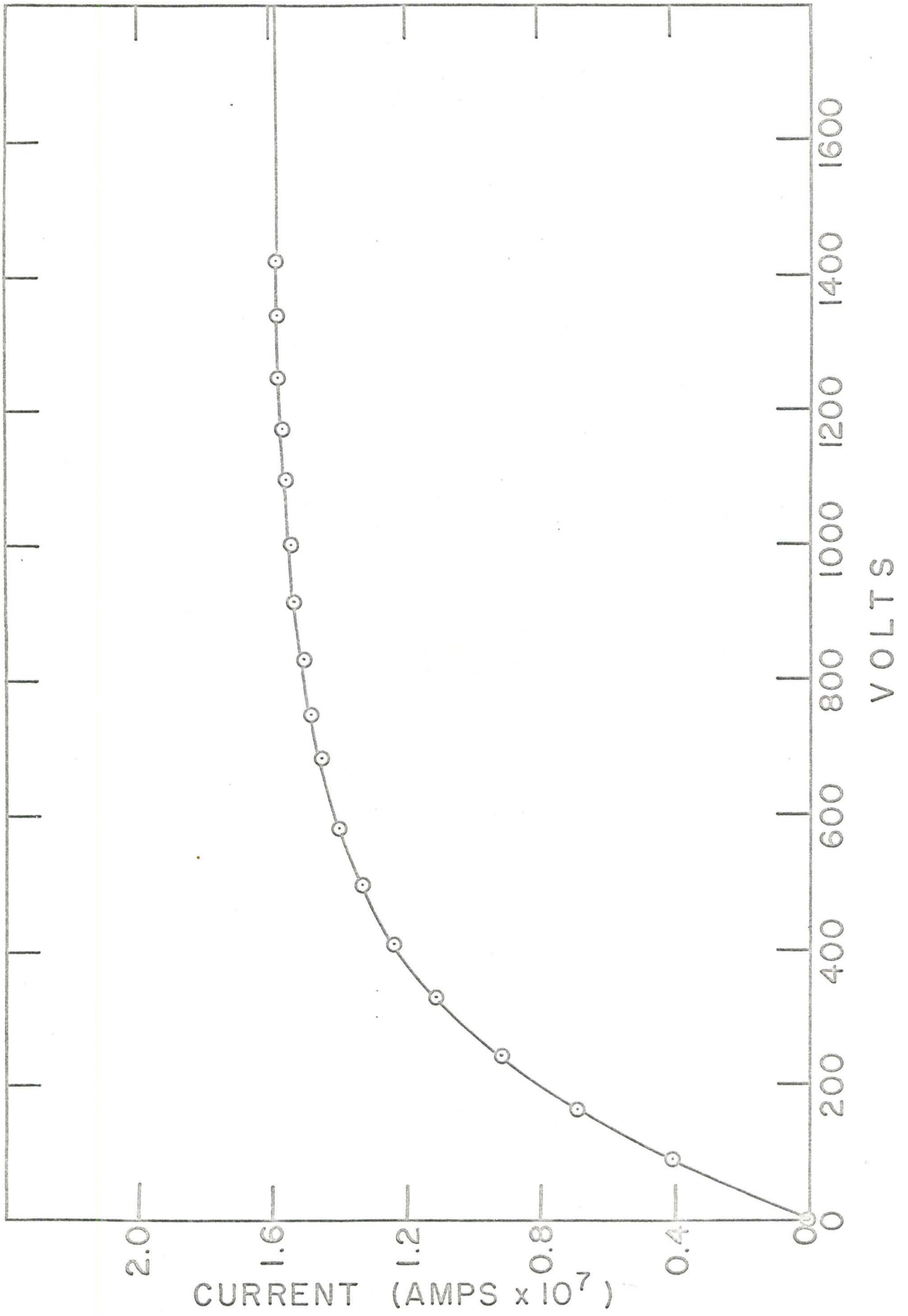
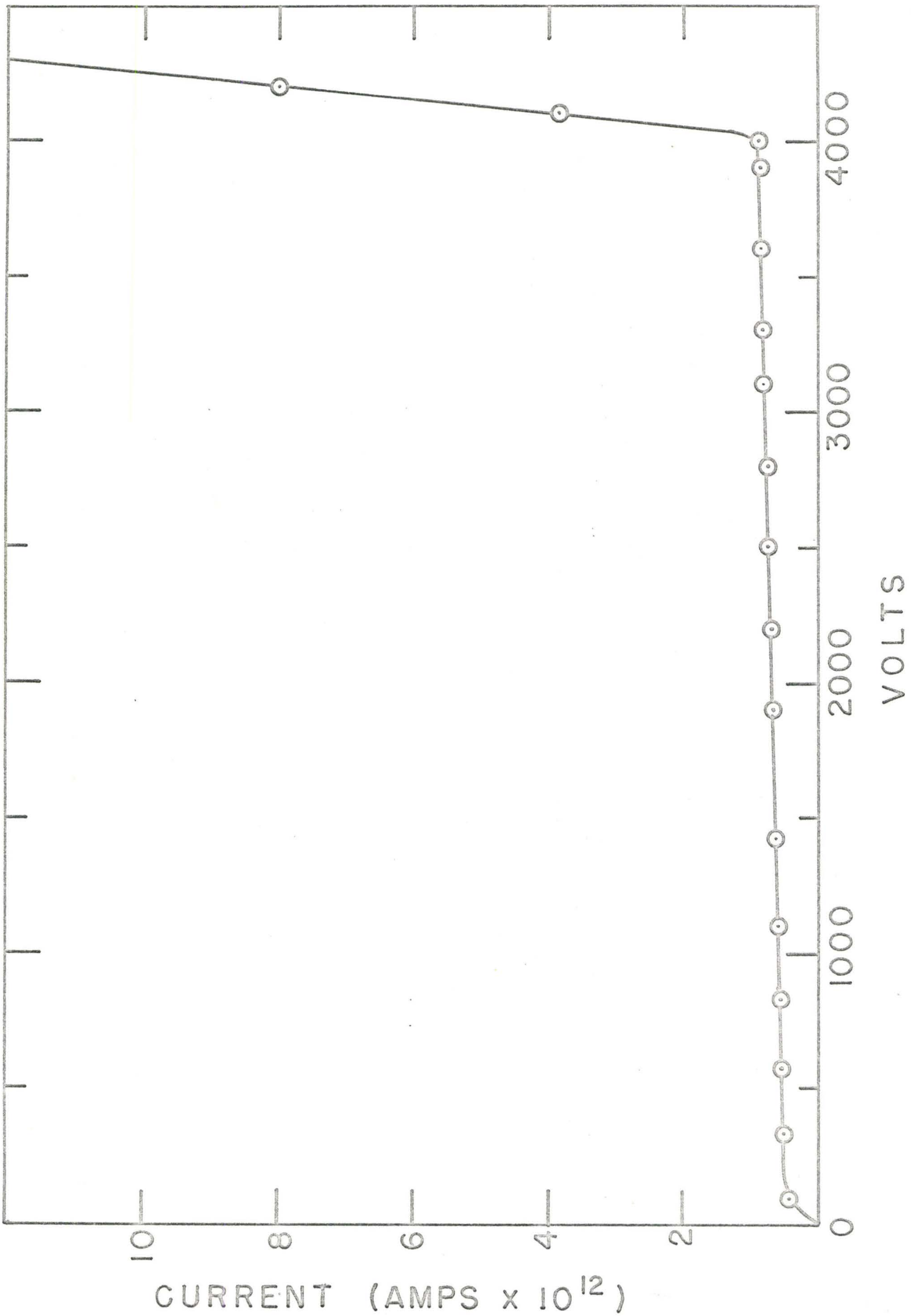


Figure 27. Determination of Proportional Region for a C_2H_4-HCl Mixture



below this value. The mixture was 6.4 mole percent HCl in C_2H_4, having a total pressure of 19.5 cm. Hg. at 0°C. The chromatographic peak areas of ethyl chloride were determined for irradiations with and without the high voltage, the results being:

C_2H_5Cl	peak area (no voltage)	5250 units
C_2H_5Cl	peak area (3800 v.)	6680 units

The enhanced yield with the applied electric field has been considered to be due to an increase in the number of excited molecules in the system, since at 3800 volts there is no increase in the number of ions over those present without an applied potential.

CHAPTER 3

DISCUSSION AND CONCLUSIONS

A. Summary of Experimental Kinetic Data

The variation of the four parameters, HCl concentration, ethylene concentration, surface to volume ratio and radiation intensity has yielded results which have led to a reaction mechanism which gives kinetic expressions in agreement with the experimental data. The rates of formation of ethyl chloride and 1-chlorobutane have been shown in Chapter 2 to be consistent with the following expressions:

$$\frac{d(C_2H_5Cl)}{dt} = \frac{K_1\ (HCl)\ (C_2H_4)^{1/2}\quad I^{1/2}}{S^{1/2}}$$

$$\frac{d(1\text{-}C_4H_9Cl)}{dt} = \frac{K_2\ (HCl)^{\circ}\ (C_2H_4)^{3/2}\quad I^{1/2}}{S^{1/2}}$$

where K_1 and K_2 are constants. These relations hold in the HCl concentration range studied except below about 1 mole percent HCl in C_2H_4. The fact that the rate of formation of ethyl chloride with respect to HCl concentration appears to be linear at concentrations below 1 mole percent will be discussed when the complete rate expression is compared with the data.

The dependence of the other two products, 2-chlorobutane and 1,2-dichloroethane, on the four parameters is not known as completely.

The rates of formation of both were observed to become independent of HCl concentration above about 1 mole percent. The rate of formation of 1,2-dichloroethane was found to be dependent on the square root of the surface area.

B. Reaction Mechanism

The reaction mechanism which gives kinetic expressions in agreement with the observed experimental data is given in the eleven reactions below:

Initiation

$$\mathrm{HCl} \xrightarrow{k_1 I} \mathrm{H^\bullet} + \mathrm{Cl^\bullet} \tag{1}$$

$$\mathrm{H^\bullet} + \mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{Cl^\bullet} \tag{2}$$

$$\mathrm{H^\bullet} + \mathrm{C_2H_4} \longrightarrow \mathrm{^\bullet C_2H_5} \tag{3}$$

$$\mathrm{^\bullet C_2H_5} + \mathrm{HCl} \longrightarrow \mathrm{C_2H_6} + \mathrm{Cl^\bullet} \tag{4}$$

Propagation

$$\mathrm{Cl^\bullet} + \mathrm{C_2H_4} \xrightarrow{k_2} \mathrm{^\bullet C_2H_4Cl} \tag{5}$$

$$\mathrm{^\bullet C_2H_4Cl} + \mathrm{HCl} \xrightarrow{k_3} \mathrm{C_2H_5Cl} + \mathrm{Cl^\bullet} \tag{6}$$

$$\mathrm{^\bullet C_2H_4Cl} + \mathrm{C_2H_4} \xrightarrow{k_4} \mathrm{^\bullet C_4H_8Cl} \tag{7}$$

$$\mathrm{^\bullet C_4H_8Cl} + \mathrm{HCl} \xrightarrow{k_5} \mathrm{C_4H_9Cl} + \mathrm{Cl^\bullet} \tag{8}$$

$$\mathrm{^\bullet C_2H_4Cl} + \mathrm{HCl_{ads}} \xrightarrow{Sk_6} \mathrm{Cl\ C_2H_4Cl} + \mathrm{H^\bullet} \tag{9}$$

Termination

$$\mathrm{Cl^\bullet} + \mathrm{^\bullet C_2H_4Cl} \xrightarrow{Sk_7} \mathrm{ClC_2H_4Cl} \tag{10}$$

$$Cl^{\cdot} + {}^{\cdot}C_4H_8Cl \xrightarrow{Sk_8} ClC_4H_8Cl \qquad (11)$$

In reactions (9), (10) and (11), S is related to the surface area. The C_4H_9Cl formed in reaction (8) represents both 1-chlorobutane and 2-chlorobutane.

C. Kinetic Expressions

The kinetic expressions derived from the reaction mechanism, (see Appendix I) using the steady state approximation, are as follows:

$$\frac{d\,(C_2H_5Cl)}{dt} = \left[\frac{2k_1Ik_2k_3^2\,k_5\,(HCl)^4\,(C_2H_4)}{\left(S\,k_7k_5\,(HCl) + Sk_8k_4\,(C_2H_4)\right)\left(k_3\,(HCl) + k_4\,(C_2H_4)\right)}\right]^{1/2}$$

$$\frac{d\,(C_4H_9Cl)}{dt} = \left[\frac{2k_1Ik_2k_4^2\,k_5\,(C_2H_4)^3\,(HCl)^2}{\left(Sk_7k_5\,(HCl) + Sk_8k_4\,(C_2H_4)\right)\left(k_3\,(HCl) + k_4\,(C_2H_4)\right)}\right]^{1/2}$$

$$\frac{d\,(C_2H_4Cl_2)}{dt} = \left[\frac{2k_1Ik_2k_6^2\,k_5\,(HCl)^2\,(C_2H_4)\,A^2\,S^2}{\left(Sk_7k_5\,(HCl) + Sk_8\,k_4\,(C_2H_4)\right)\left(k_3\,(HCl) + k_4\,(C_2H_4)\right)}\right]^{1/2}$$

The denominators in all three expressions are identical. The A in the third expression is a surface constant, and I refers to radiation intensity. Separate expressions were not required for 1-chlorobutane and 2-chlorobutane as will become apparent in the discussion below. The second expression above actually represents the sum of the rates of formation of the two chlorobutanes. Since 1-chlorobutane predominates this expression is a close approximation to the correct one for 1-chlorobutane. At sufficiently high HCl concentrations, the above three expressions can be simplified to:

$$\frac{d\,(C_2H_5Cl)}{dt} = \left[\frac{2k_1Ik_2k_3\,(C_2H_4)}{Sk_7}\right]^{1/2} \cdot (HCl)$$

$$\frac{d\,(C_4H_9Cl)}{dt} = \left[\frac{2k_1Ik_2k_4^2}{Sk_7k_3}\right]^{1/2} \cdot (C_2H_4)^{3/2}$$

$$\frac{d\,(C_2H_4Cl_2)}{dt} = \left[\frac{2k_1Ik_2k_6^2\,(C_2H_4)\,A^2\,S}{k_7k_3}\right]^{1/2}$$

These expressions show that the mechanism is consistent with the experimental data for HCl concentrations above 1 mole percent. The complete expressions will be compared with the experimental data in the next section.

D. Comparison of the Rates of Formation of Ethyl Chloride and 1-Chlorobutane, at Various HCl Concentrations, with the Theoretical Rates Derived from the Complete Rate Expressions

The complete rate expressions for ethyl chloride and 1-chlorobutane were compared with the experimental data shown in Table XVI. The relative values of the constants which were used to calculate the theoretical rates are given in Table XXVI. The value of k_1I was taken from section G. Chapter 2 and that of k_2 was the value required by the experimental data. The other constants are relative to k_4 which was taken as unity.

TABLE XXVI

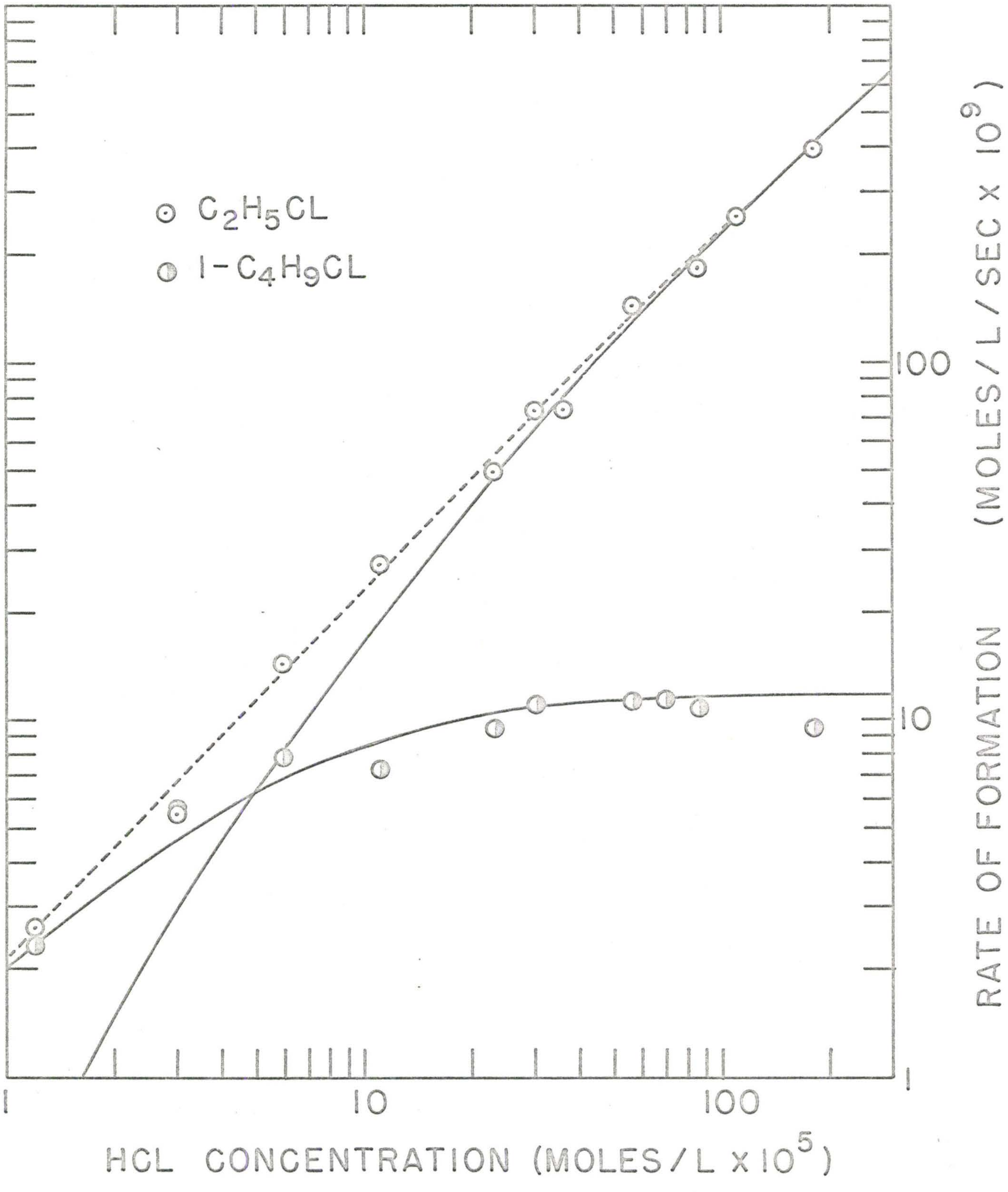
Values of rate constants used to calculate the theoretical rates of formation of ethyl chloride and 1-chlorobutane

k_1I	(liter/mole/sec.)				
(sec. $^{-1}$)	k_2	k_3	k_4	Sk_7	Sk_8
4.9×10^{-8}	1.1×10^5	1.1×10^4	1.0	1.0×10^3	1.0×10^3

As explained in Appendix IV the value of k_1I, determined by the HCl - NO experiments is probably the same for the HCl - C_2H_4 system.

The theoretical curves, shown by solid lines, along with the experimental points, are illustrated in Fig. 28. It will be noted that since all the constants appear in both expressions, the normalization of the theoretical curves to the experimental data was a natural consequence rather than forced. The agreement can be seen to be good for 1-chlorobutane at all HCl concentrations and for ethyl chloride at high HCl concentrations. The two rate expressions predict that the HCl concentration at which the rate of formation of 1-chlorobutane becomes independent of HCl concentration should be the same at which the rate of formation of ethyl chloride becomes linearly dependent on HCl concentration. This is not experimentally observed and therefore the mechanism, as given above, can not be entirely correct. A possible explanation is that a minor mode of formation of ethyl chloride, which is relatively more important at low HCl concentrations, has been overlooked. The formation of ethyl chloride by the reaction of a chloroethyl radical with adsorbed HCl

Figure 28. Comparison of Theoretical Expression with Experimental Data of C_2H_5Cl and $1\text{-}C_4H_9Cl$



would be such a reaction:

$$^{\bullet}C_2H_4Cl + HCl_{ads} \xrightarrow{Sk_6'} C_2H_5Cl + Cl^{\bullet}$$

This reaction is similar to that which has been suggested for the formation of 1,2-dichloroethane, the rate expression for the two reactions being identical in form. The addition of such a function to the ethyl chloride curve yields the dotted line in Fig. 28, assuming a value for Sk_6' about 70 times that of Sk_6. The corrected curve agrees with the data quite closely.

If this reaction is indeed occuring to an extent which would correct the curve in Fig. 28, this means that the extraction of a hydrogen atom from an HCl molecule adsorbed on the surface is favoured over the extraction of a chlorine atom to give 1,2-dichloroethane by about 70 to 1. This does not necessarily mean, however, that the probability of a chloroethyl radical extracting a hydrogen atom is only 70 times greater than that of extracting a chlorine atom from HCl since the adsorbed HCl is probably highly oriented as a result of hydrogen bonding to the glass. This would mean that extraction of the chlorine would be sterically favoured over that of the hydrogen atom, making the above probability, perhaps, orders of magnitude larger than 70 to 1.

The hypothesis that ethyl chloride is forming by a reaction with adsorbed HCl, suggests that its rate of formation should fall off less rapidly with increased surface than predicted by the mechanism which does not include this mode of formation. The data in Fig. 22

does not appear to substantiate this argument, however, it is noted that the decrease in the rate of formation of 1-chlorobutane with increasing surface area is greater than that for ethyl chloride. It is suggested that a possible explanation for this lies in the fact that the reaction, being a chain process, is exceedingly sensitive to chain breaking impurities. If the act of adding glass wool to increase the surface area, were accompanied by the addition of small amounts of such impurities, this would lead to a fall-off of the rate of formation of 1-chlorobutane greater than that predicted by the mechanism, while that of ethyl chloride could fall-off in the expected manner.

This hypothesis could be checked by carrying out surface variation experiments at very low HCl concentrations. The effect of increased surface would be more marked under these experimental conditions.

E. The Formation of 2-chlorobutane

The formation of 2-chlorobutane is not as easily explained as that of ethyl chloride and 1-chlorobutane. Since the rate of formation of 2-chlorobutane was found to parallel that of 1-chlorobutane in all experiments in which it was observed, it has been concluded that the mode of formation of the two compounds is kinetically similar. To account for this, it is postulated that the $\cdot CH_2CH_2Cl$ radical is in chemical equilibrium with the $CH_3\dot{C}HCl$ radical. These two radicals lead to 1-chlorobutane and 2-chlorobutane respectively through reaction sequence 7 and 8 (page 109). It has been experimentally shown (Chapter 2, Section I.) that the $CH_3\dot{C}HCl$ radical does not arise from C_2H_5Cl by means of a radiation induced secondary reaction and it is unlikely that the rearrangement:

$$\cdot CH_2CH_2CH_2CH_2Cl \longrightarrow \cdot CH_2CH_2CH(Cl)CH_3 ,$$

could take place to any great extent since the rearrangement site is remote from the free radical centre.

A complete mechanism which includes the formation of $CH_3\dot{C}HCl$ is given below:

Initiation

$$HCl \xrightarrow{k_1 I} H^{\cdot} + Cl^{\cdot} \qquad (1)$$

$$H + HCl \longrightarrow H_2 + Cl^{\cdot} \qquad (2)$$

$$H^{\cdot} + C_2H_4 \longrightarrow {}^{\cdot}C_2H_5 \qquad (3)$$

$$^{\cdot}C_2H_5 + HCl \longrightarrow C_2H_6 + Cl^{\cdot} \qquad (4)$$

Propagation

$$^{\cdot}Cl + C_2H_4 \xrightarrow{k_2} {}^{\cdot}CH_2CH_2Cl \qquad (5)$$

$$^{\cdot}CH_2CH_2Cl \rightleftharpoons CH_3\dot{C}HCl \qquad (5a)$$

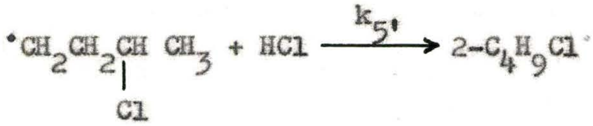
$$^{\cdot}CH_2CH_2Cl + HCl \xrightarrow{k_3} C_2H_5Cl + Cl^{\cdot} \qquad (6)$$

$$CH_3\dot{C}HCl + HCl \xrightarrow{k_{3'}} C_2H_5Cl + Cl^{\cdot} \qquad (6a)$$

$$^{\cdot}CH_2CH_2Cl + C_2H_4 \xrightarrow{k_4} {}^{\cdot}C_4H_8Cl \qquad (7)$$

$$CH_3\dot{C}HCl + C_2H_4 \xrightarrow{k_{4'}} {}^{\cdot}CH_2CH_2CH(Cl)CH_3 \qquad (7a)$$

$$\cdot C_4H_8Cl + HCl \xrightarrow{k_5} 1\text{-}C_4H_8Cl + Cl \qquad (8)$$



$$\cdot CH_2CH_2\underset{Cl}{CH}\,CH_3 + HCl \xrightarrow{k_{5'}} 2\text{-}C_4H_9Cl \qquad (8a)$$

$$\cdot CH_2CH_2Cl + HCl_{ads} \xrightarrow{Sk_6} ClCH_2CH_2Cl + H\cdot \qquad (9)$$

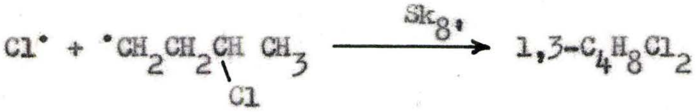
$$CH_3\dot{C}HCl + HCl_{ads} \xrightarrow{Sk_{6'}} CH_3CHCl_2 + H\cdot \qquad (9a)$$

Termination

$$Cl\cdot + \cdot CH_2CH_2Cl \xrightarrow{Sk_7} ClCH_2CH_2Cl \qquad (10)$$

$$Cl\cdot + CH_3\dot{C}HCl \xrightarrow{Sk_{7'}} CH_3CHCl_2 \qquad (10a)$$

$$Cl\cdot + \cdot CH_2CH_2CH_2CH_2Cl \xrightarrow{Sk_8} 1,4\text{-}C_4H_8Cl_2 \qquad (11)$$



$$Cl\cdot + \cdot CH_2CH_2\underset{Cl}{CH}\,CH_3 \xrightarrow{Sk_{8'}} 1,3\text{-}C_4H_8Cl_2 \qquad (11a)$$

Since the amount of 1-chlorobutane formed is much greater than that of 2-chlorobutane, being about 20 to 1, the expression derived for 1-chlorobutane in part C. is a good approximation to the correct one. The rate expression for the production of 2-chlorobutane would have an identical form to that of 1-chlorobutane only if the equilibrium expressed in reaction 5a is very rapid in relation to the rates of consumption of the $CH_3\dot{C}HCl$ radical. No experimental difference in the kinetics of the 1-chlorobutane and 2-chlorobutane has been found and thus it is assumed that the equilibrium is indeed rapid. Since the proportions of 1-chlorobutane and 2-chlorobutane have been found to be about 20 to 1 at room temperature, a difference in the stability of the two radicals of about 2 Kcal per mole would be expected if their reactivities were similar. The estimated difference (Appendix II) is about 4 Kcal/mole. This value, which was obtained from the difference of two larger numbers, is reasonably close to that required to account for the observed proportions.

The hypothesis that these two species are in equilibrium could be checked by carrying out radiolysis of HCl - C_2H_4 mixtures at various temperatures. The relative proportions of the two chlorobutanes would be expected to be temperature dependent.

F. The Formation of 1,2-Dichloroethane

It was at first suspected that the observed 1,2-dichloroethane was formed by the termination reaction 10:

$$Cl^{\bullet} + {}^{\bullet}C_2H_4Cl \xrightarrow{Sk_7} ClC_2H_4Cl.$$

This mode of formation would have required the rate to be linearly dependent on HCl concentration which it was not. Experimentally, its rate of formation becomes independent of HCl concentration and its rate of formation is greater than the rate of initiation. This implies that it has a further mode of production, involving a chain process. Its production was also found to depend on the square root of the available surface area. This is consistent with reaction 9:

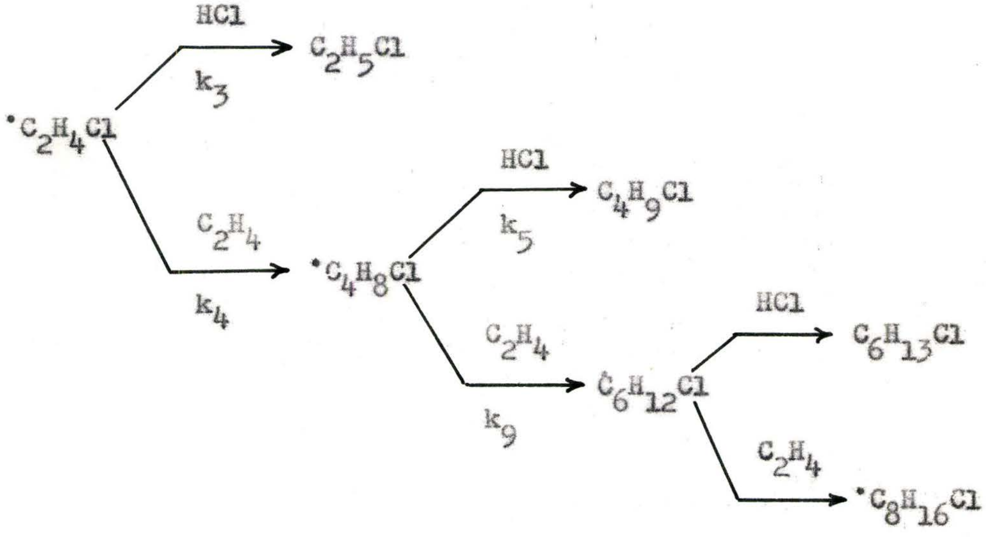
$$ {}^{\bullet}C_2H_4Cl + HCl_{ads} \xrightarrow{Sk_6} 1,2\text{-}C_2H_4Cl_2 + H^{\bullet} \qquad (9) ,$$

providing it is assumed that the concentration of adsorbed HCl is independent of HCl pressure. The results of the experiment with radioactive HCl described in Chapter 2, Section J., show that HCl is adsorbed on glass surfaces even at very low HCl pressures. It may be seen from the isotherm represented by the broken line in Fig. 24 that the amount of adsorbed HCl is virtually constant in the range of pressures (up to 3 cm.) in which the reaction kinetics were studied.

The required HCl and surface dependences are given by reaction 9 which is thus considered to be the main mode of formation of 1,2-dichloroethane. Varying small proportions, depending on the particular reaction conditions, are also formed by termination reaction 10.

G. Further Addition Reactions Leading to Higher Molecular Weight Chlorinated Hydrocarbons.

Since it has been shown that the addition of a chloroethyl radical to ethylene to give a chlorobutyl radical is a fairly common reaction, it might be expected that the addition of a chlorobutyl radical to ethylene to give a chlorohexyl radical would occur to very nearly the same extent. The end product of this reaction would be 1-chlorohexane as shown in the following sequence:



This reaction sequence reveals that the proportion of 1-chlorohexane will be greatest in reactions where the concentration of HCl is low. An attempt to find 1-chlorohexane in the reaction products was unsuccessful, as shown by the results given in Chapter 2, Section L. Here the molar proportion of C_2H_4 to HCl was 1540 to 1. For these conditions it was found that the amount of ethyl chloride, 1-chlorobutane and 1-chlorohexane were in the proportions of $41:59:<1$. Thus, the selected conditions have yielded no measureable 1-chlorohexane, even though the 1-chlorobutane was favoured over the ethyl chloride. This implies that the rate constant ratio k_5/k_9 is more than 100 times greater than k_3/k_4, and suggests that the proximity of a chlorine atom to the free radical centre enhances the rate of addition as opposed to extraction.

H. Examination of Other Possible Mechanisms

In an effort to determine whether other mechanisms would give rate expressions in agreement with the observed results, the various possible initiation and termination sequences were individually investigated. (See Appendix III) The determination of the rate expressions for the formation of ethyl chloride and 1-chlorobutane showed that only the mechanism given in section B., with possible modifications of Sections D. and E., gave expressions in agreement with the experimental data.

The important observation arising from the above investigation is the fact that the ethylene is apparently not taking part in the initiation. In other words, energy deposited in the ethylene does not lead to any of the observed reaction products. Although unquestionably the ethylene is undergoing a series of complex reactions under the influence of the radiation, these not being chain reactions will have relatively small G values. The yields of the resulting products will thus be insignificant compared to the yields of those being formed by means of the chain process.

I. The Initiation Process

Since it has been kinetically shown that the ethylene does not contribute significantly to the formation of chlorine atoms, it is assumed that all the initiation comes about by the direct interaction of the gamma rays and fast electrons with the HCl. There are two main ways in which this interaction takes place; ionization and excitation.

When interaction of the radiation takes place to give ions, by far the most common event will be that in which an HCl^+ ion is formed, along with a secondary electron. Several reactions involving HCl^+ have been proposed (35) to account for the production of chlorine atoms in irradiated HCl. These reactions can all be excluded in the case of the HCl - C_2H_4 experiments described in the present work as the HCl^+ ion is probably neutralized by a charge transfer reaction with ethylene. The ionization potential of ethylene is 2 eV below that of HCl, favouring this charge transfer process.

The reaction: $HCl + e^- \longrightarrow H + Cl^-$, has been given (35) as a possible reaction occuring in irradiated liquid HCl. This reaction has been shown to be an insignificant contributor to the initiation process in the gaseous HCl - C_2H_4 system. The application of a high voltage across the irradiation vessel did not result in a measureable decrease in product yield. The magnitude of the field was high enough to cause the major fraction of the electrons and positive ions to be collected while not high enough to cause secondary dissociative excitation.

From these observations it has been concluded that in the presence of ethylene, the decomposition of HCl occurs mainly through the dissociation of electronically excited HCl molecules. When ionizing radiation and fast charged particles dissipate energy by excitation, it is mainly by causing excitation to the lowest electronically excited state (cf 1). Spectroscopic data (36) shows that the lowest excited state of HCl dissociates, the maximum intensity of the continuum occuring at 8.1 eV above the ground state. It has been shown, (Appendix V), that it is energetically possible to explain the observed rate of initiation as arising solely from the decomposition of excited molecules.

Experimental evidence has been given in Chapter 2, Section N. to support the view that excited molecules are contributors to the initiation process. These results, however, do not prove that excited molecules are the sole contributors although the discussion above would indicate that this is indeed the case.

The initiation reactions thought to occur in the system are:

$$HCl \rightsquigarrow HCl^* \longrightarrow H^\bullet + Cl^\bullet \qquad (1)$$

$$H^\bullet + HCl \longrightarrow H_2 + Cl^\bullet \qquad (2)$$

$$H^{\bullet} + C_2H_4 \longrightarrow {}^{\bullet}C_2H_5 \qquad (3)$$

$${}^{\bullet}C_2H_5 + HCl \longrightarrow C_2H_6 + Cl \qquad (4)$$

Reactions (2) and (3) both have activation energies of about 4 Kcal/mole (37,38) and since the ethylene concentration was in excess in all the experiments, reaction (3) probably predominates. The important thing to note is that regardless of the reaction which the hydrogen atom undergoes, the end result of the dissociation in (1) is the production of two chlorine atoms. Since neither H_2 nor C_2H_6 are produced by a chain mechanism, the quantities formed would be too small to be quantitatively determined by the techniques used in this work. In any case, the production of hydrogen from ethylene by the hydrogen split-out mechanism would make interpretation of such data difficult.

J. The Termination Process

The termination reactions which give kinetic expressions in agreement with the experimental data, predict the formation of 1,2-dichloroethane and 1,4-dichlorobutane. No 1,4-dichlorobutane was chromatographically detected and it appears that the 1,2-dichloroethane which was observed came almost entirely by the chain reaction involving the adsorbed HCl.

The termination reaction:

$$Cl^{\bullet} + Cl^{\bullet} + S \longrightarrow Cl_2 + S\ ,$$

might have been expected to occur but no trace of chlorine could be found in the reaction products. Also, it has been shown in Appendix III that the kinetics do not agree with the experimental data when the mechanism having this reaction as the major termination process is considered. It must therefore be concluded that this mode of termination is not important.

K. Suggestions for Further Work

The reaction mechanism discussed in the preceding sections has satisfactorily explained the formation of the four products observed for the reaction conditions employed. Certain aspects of the mechanism, however, have been presented as postulates, which lead to predictions which can be subjected to further experimentation.

(1) Concentration studies

The mechanism predicts that at sufficiently high HCl concentrations, only ethyl chloride will be observed as a product. Further work is necessary to check the hypothesis that ethyl chloride is partly being formed by means of a surface reaction.

(2) Temperature studies

Reaction rates at various temperatures should give the activation energy of the initiation reaction as well as that of the addition of a chlorine atom to ethylene. Differences in the activation energies for the other reactions could also be obtained. In particular, however, temperature variation could be used to check the mechanism postulated to explain the formation of 2-chlorobutane. If the proposed mechanism is correct, the relative proportions of 1-chlorobutane and 2-chlorobutane should become more nearly equal at high temperatures.

(3) Applied voltage studies

The measurement of product yields at various voltages could shed more light on the actual mode of interaction of the gamma rays and fast electrons with the reactants.

APPENDIX I

DERIVATION OF RATE EXPRESSIONS

Using the steady state approximation, the following expressions can be written down from the mechanism outlined in Part III, Chapter 3, Section B.:

$$\frac{d(Cl^{\bullet})}{dt} = 0 = 2k_1I(HCl)-Sk_7(Cl^{\bullet})(^{\bullet}C_2H_4Cl)-Sk_8(Cl^{\bullet})(^{\bullet}C_4H_8Cl) \qquad (1)$$

$$\begin{aligned}\frac{d(^{\bullet}C_2H_4Cl)}{dt} = 0 = {}& k_2(Cl^{\bullet})(C_2H_4)-k_3(^{\bullet}C_2H_4Cl)(HCl)\\ &-k_4(^{\bullet}C_2H_4Cl)(C_2H_4)-Sk_7(Cl^{\bullet})(^{\bullet}C_2H_4Cl)\\ &-Sk_6(^{\bullet}C_2H_4Cl)(HCl_{ads}) \qquad (2)\end{aligned}$$

$$\begin{aligned}\frac{d(^{\bullet}C_4H_8Cl)}{dt} = 0 = {}& k_4(^{\bullet}C_2H_4Cl)(C_2H_4)-k_5(^{\bullet}C_4H_8Cl)(HCl)\\ &-Sk_8(Cl^{\bullet})(^{\bullet}C_4H_8Cl) \qquad (3)\end{aligned}$$

I = radiation intensity

S = surface area

The above equations, when solved, lead to complicated rate expressions which would be very difficult to deal with. In order to make the expressions more manageable, some simplifications can be made. Equation (1) cannot be simplified. However, it will be observed in expression (2) that the terms $Sk_7\ (Cl^{\bullet})(^{\bullet}C_2H_4Cl)$ and $k_6\ HCl_{ads}\ (^{\bullet}C_2H_4Cl)$ will be small in comparison to the terms $k_3\ (HCl)(^{\bullet}C_2H_4Cl)$ and $k_4\ (C_2H_4)(^{\bullet}C_2H_4Cl)$ if $Sk_7(Cl^{\bullet})$ and $Sk_6\ HCl_{ads}$ are a great deal smaller than $k_3(HCl)$ and $k_4(C_2H_4)$. This should be the case for $Sk_7(Cl^{\cdot})$ since the chlorine atom concentration is undoubtedly a great deal lower than that of HCl or C_2H_4 and the rate constant would not be expected to outweigh this concentration difference. Since the amount of 1,2-$C_2H_4Cl_2$ formed was much less than C_2H_5Cl and C_4H_9Cl in all the experiments, $Sk_6\ HCl_{ads}\ (^{\cdot}C_2H_4Cl)$ can also be neglected. By an argument similar to that used above, the $Sk_8(Cl^{\cdot})(^{\cdot}C_4H_8Cl)$ term can be neglected in the third expression. Using these simplified equations the following expressions are obtained for the steady state concentrations of the three free radicals:

$$(Cl^{\cdot}) = \left[\frac{2k_1Ik_5\ (HCl)^2 \quad k_3(HCl) + k_4\ (C_2H_4)}{k_2\left(Sk_7k_5\ (HCl) + Sk_8k_4\ (C_2H_4)\right)\ \left((C_2H_4)\right)}\right]^{1/2}$$

$$(^{\cdot}C_2H_4Cl) = \left[\frac{2k_1Ik_2k_5\ (HCl)^2\ (C_2H_4)}{\left(Sk_7k_5\ (HCl) + Sk_8k_4\ (C_2H_4)\right)\left(k_3\ (HCl) + k_4\ (C_2H_4)\right)}\right]^{1/2}$$

$$(^{\cdot}C_4H_8Cl) = \left[\frac{2k_1Ik_2k_4{}^2\ (C_2H_4)^3}{k_5\ \left(Sk_7k_5\ (HCl) + Sk_8k_4\ (C_2H_4)\right)\left(k_3\ (HCl) + k_4\ (C_2H_4)\right)}\right]^{1/2}$$

The rates of formation of the various products are given by:

$$\frac{d(C_2H_5Cl)}{dt} = k_3\ (HCl)\ (^{\cdot}C_2H_4Cl)$$

$$\frac{d(C_4H_9Cl)}{dt} = k_5\ (HCl)\ (^{\cdot}C_4H_8Cl)$$

$$\frac{d(ClC_2H_4Cl)}{dt} = Sk_6\ (^{\cdot}C_2H_4Cl)\ HCl_{ads}$$

Since HCl_{ads} has been found to be essentially independent of HCl pressure in the range of pressures used, $HCl_{ads} = AS$ where A is an adsorption constant.

The rate expressions given in Part III, Chapter 3, Section B. follow from these relations.

APPENDIX II

CALCULATION OF HEAT OF FORMATION OF $^{\bullet}CH_2CH_2CL$ AND $CH_3\overset{\bullet}{C}HCL$

To enable this calculation to be carried out, it has been assumed that the heats of formation of the two radicals can be obtained from the heats of formation of 1,2-dichloroethane and 1,1-dichloroethane by subtracting the energy required to break a carbon-chlorine bond. This value is probably not too different for the two compounds as evidenced by the fact that the carbon-chlorine bond lengths in CH_3Cl and CH_2Cl_2 differ by less than one percent.

The heats of formation of 1,2-dichloroethane and 1,1-dichloroethane, in the liquid phase, were calculated from their heats of combustion and found to be -62.1 and -58.4 Kcal/mole respectively. The value for the carbon-chlorine bond energy given by Pauling (39) is 78.5 Kcal/mole. The heats of formation of $^{\bullet}CH_2CH_2Cl$ and $CH_3\overset{\bullet}{C}HCl$ are +16.4 Kcal/mole and +20.1 Kcal/mole respectively. The $^{\bullet}CH_2CH_2Cl$ is therefore the more stable by about 4 Kcal/mole.

APPENDIX III

CONSIDERATION OF VARIOUS POSSIBLE MECHANISMS

The reaction mechanism leading to the formation of ethyl chloride, which includes the initiation and termination reactions which have been deemed possible, is as follows:

Initiation by interaction of radiation with HCl

$$HCl \overset{k_1 I}{\rightsquigarrow} H^\bullet + Cl^\bullet \qquad (1)$$

$$H^\bullet + HCl \xrightarrow{k_2} H_2 + Cl^\bullet \qquad (2)$$

$$H^\bullet + C_2H_4 \xrightarrow{k_3} {}^\bullet C_2H_5 \qquad (3)$$

$${}^\bullet C_2H_5 + HCl \xrightarrow{k_{3a}} C_2H_6 + Cl^\bullet \qquad (4)$$

Initiation by interaction of radiation with ethylene

$$C_2H_4 \overset{k_4 I}{\rightsquigarrow} {}^\bullet C_2H_3 + H^\bullet \qquad (5)$$

$$H^\bullet + HCl \xrightarrow{k_2} H_2 + Cl^\bullet \qquad (6)$$

$$H^\bullet + C_2H_4 \xrightarrow{k_3} {}^\bullet C_2H_5 \qquad (7)$$

$${}^\bullet C_2H_5 + HCl \xrightarrow{k_{3a}} C_2H_6 + Cl^\bullet \qquad (8)$$

$${}^\bullet C_2H_3 + HCl \xrightarrow{k_5} C_2H_4 + Cl^\bullet \qquad (9)$$

Propagation

$$Cl^\bullet + C_2H_4 \xrightarrow{k_6} {}^\bullet C_2H_4Cl \qquad (10)$$

$$\cdot C_2H_4Cl + HCl \xrightarrow{k_7} C_2H_5Cl + Cl\cdot \qquad (11)$$

Termination

$$Cl\cdot + Cl\cdot \xrightarrow{Sk_8} Cl_2 \qquad (12)$$

$$\cdot Cl + \cdot C_2H_4Cl \xrightarrow{Sk_9} ClC_2H_4Cl \qquad (13)$$

$$\cdot Cl + H\cdot \xrightarrow{Sk_{10}} HCl \qquad (14)$$

$$\cdot Cl + \text{wall} \xrightarrow{Sk_{11}} 1/2\ Cl_2 \qquad (15)$$

$$\cdot C_2H_4Cl + \cdot C_2H_4Cl \xrightarrow{Sk_{12}} Cl\ C_4H_8Cl \qquad (16)$$

For the purpose of examining the various possible combinations of reactions, the reaction in which the addition of a chloroethyl radical to ethylene takes place has been excluded to simplify the derivations. The rate expression for ethyl chloride which is obtained will thus be the rate of formation at HCl concentrations where the addition reaction is a negligible contributor. Following the method used by Trotman-Dickenson (38) in his examination of the mechanisms of the photo-chlorination of unsaturated molecules, two general cases will be considered. Case I: only HCl decomposition leads to initiation. Five subcases have been dealt with, each of the termination reactions in turn being considered to be the main mode of termination.

The second general case is that in which the ethylene is considered to be the main contributor to the initiation. The same termination reactions as in Case I have been considered in the five subcases.

In the derivations, the following symbolism has been used:

$x = (Cl^{\bullet})$ $\qquad A = (HCl)$

$y = (^{\bullet}C_2H_4Cl)$ $\qquad B = (C_2H_4)$

$z = (H^{\bullet})$

Case I

(a) Termination reaction (12) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_1IA + k_6Bx - k_7Ay - Sk_8x^2 \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay \qquad (2)$$

(1) + (2) $\quad 2k_1IA - Sk_8\,x^2 = 0 \qquad \therefore\ x = \left[\frac{2k_1IA}{Sk_8}\right]^{1/2}$

$$\therefore\ y = \frac{k_6B}{k_7A}\left[\frac{2k_1IA}{Sk_8}\right]^{1/2}$$

$$\frac{d\,(C_2H_5Cl)}{dt} = k_6B\left[\frac{2k_1IA}{Sk_8}\right]^{1/2}$$

(b) Termination reaction (13) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_1IA - k_6Bx + k_7Ay - Sk_8xy \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay - Sk_8xy \qquad (2)$$

The third term may be neglected as it will be small compared to the second.

(1) + (2) $\quad 2k_1IA - 2Sk_8xy = 0 \qquad \therefore\ x = \frac{k_1IA}{Sk_8y}$

subst. in (2) $\frac{k_1Ik_6AB}{Sk_8y} - k_7Ay = 0$

$\therefore\ k_1Ik_6AB - Sk_8k_7Ay^2 = 0$

$\therefore\ y = \left[\frac{k_1Ik_6B}{Sk_8k_7}\right]^{1/2}$

$\therefore\ \frac{d(C_2H_5Cl)}{dt} = k_7A\left[\frac{k_1Ik_6B}{Sk_8k_7}\right]^{1/2}$

(c) Reaction (14) main contributor to the termination process

$\frac{dx}{dt} = 0 = 2k_1IA - k_6Bx + k_7Ay - Sk_{10}\,xz$ (1)

$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay$ (2)

$\frac{dz}{dt} = 0 = k_1IA - k_2Az - k_3Bz - Sk_{10}xz$ (3)

(1) - (3) + (2)

from (3): $z = -\frac{k_1IA}{k_2A + k_3B}$ (4)

$\therefore\ x = \frac{2(k_2A + k_3B)}{Sk_{10}}$ (5)

subs. (5) in (2) $y = \frac{2k_6B\ (k_2A + k_3B)}{k_7A\ Sk_{10}}$

$\therefore\ \frac{d(C_2H_5Cl)}{dt} = \frac{2k_6B\ (k_2A + k_3B)}{Sk_{10}}$

(d) Reaction (15) main contributor to the termination process

$\frac{dx}{dt} = 0 = 2k_1IA - k_6Bx + k_7Ay - Sk_{11}x$ (1)

$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay$ (2)

(1) - (2): $2k_1IA - Sk_{11}x = 0 \quad \therefore \quad x = \frac{2k_1IA}{Sk_{11}}$

$$y = \frac{k_6B\ 2k_1IA}{k_7ASk_{11}}$$

$$\frac{d(C_2H_5Cl)}{dt} = \frac{2k_1Ik_6A}{Sk_{11}}$$

(e) Reaction (16) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_1IA - k_6Bx + k_7Ay \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay - Sk_{12}y^2 \qquad (2)$$

(1) + (2) $\quad 2k_1IA - Sk_{12}y^2 = 0$

$$\therefore y = \left[\frac{2k_1IA}{Sk_{12}}\right]^{1/2}$$

$$\therefore \frac{d(C_2H_5Cl)}{dt} = k_7A\left[\frac{2k_1IA}{Sk_{12}}\right]^{1/2}$$

Case II

(a) Reaction (12) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_4IB - k_6Bx + k_7Ay - Sk_8x^2 \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay \qquad (2)$$

(1) + (2) $\quad 2k_4IB - Sk_8x^2 = 0$

$$\therefore x = \left[\frac{2k_4IB}{Sk_8}\right]^{1/2}$$

$$\therefore y = \frac{k_6B}{k_7A}\left[\frac{2k_4IB}{Sk_8}\right]^{1/2}$$

$$\therefore \quad \frac{d(C_2H_5Cl)}{dt} = k_6B\left[\frac{2k_4IB}{Sk_8}\right]^{1/2}$$

(b) Reaction (13) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_4IB - k_6Bx + k_7Ay - Sk_9xy \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay - Sk_9xy \qquad (2)$$

The third term may be neglected as it will be small compared to the second.

$$(1) + (2) \qquad 2k_4IB - Sk_9xy = 0$$

$$x = \frac{2k_4IB}{Sk_9y}$$

Substitute in (2), disregarding the third term

$$\therefore \quad \frac{k_6B\ 2k_4IB}{Sk_9y} - k_7Ay = 0$$

$$\therefore \ y = \left[\frac{2k_6k_4IB^2}{k_7A\ Sk_9}\right]^{1/2}$$

$$\therefore \quad \frac{d(C_2H_5Cl)}{dt} = \left[\frac{2k_7k_6k_4IB^2A}{Sk_9}\right]^{1/2}$$

(c) Reaction (14) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_4IB - k_6Bx + k_7By - Sk_{10}xy \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7By \qquad (2)$$

$$\frac{dz}{dt} = 0 = k_4IB - k_2Az - k_3Bz - Sk_{10}xy \qquad (3)$$

$$(1) + (2) - (3) \qquad k_4IB + k_2Az + k_3Bz = 0$$

$$\therefore \quad z = -\frac{k_4IB}{(k_2A+k_3B)}$$

$$\therefore\ x = \frac{2(k_2A + k_3B)}{Sk_{10}}$$

$$\text{and } y = \frac{2k_6B\ (k_2A + k_3B)}{k_7A\ S\ k_{10}}$$

$$\therefore\ \frac{d(C_2H_5Cl)}{dt} = \frac{2k_6B\ (k_2A + k_3B)}{Sk_{10}}$$

(d) Reaction (15) main contributor to the termination process

$$\frac{dx}{dt} = 0 = 2k_4IB - k_6Bx + k_7Ay - Sk_{11}x \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx + k_7Ay$$

(1) + (2) $x = \frac{2k_4IB}{Sk_{10}}$

$$\therefore\ y = \frac{2k_4Ik_6B^2}{Ak_7Sk_{10}}$$

$$\frac{d(C_2H_5Cl)}{dt} = \frac{2k_4Ik_6B^2}{Sk_{10}}$$

(e) Reaction (16) main termination:

$$\frac{dx}{dt} = 0 = 2k_4IB - k_6Bx + k_7Ay \qquad (1)$$

$$\frac{dy}{dt} = 0 = k_6Bx - k_7Ay - Sk_{12}y^2 \qquad (2)$$

(1) + (2) $y = \left[\frac{2k_4IB}{Sk_{11}}\right]^{1/2}$

$$\frac{d(C_2H_5Cl)}{dt} = k_7A\left[\frac{2k_4IB}{Sk_{11}}\right]^{1/2}$$

This is the only mechanism, other than the one which has been accepted as the mechanism of the reaction (I(b)) which gives a rate expression for ethyl chloride in agreement with the experimental results. When the full mechanism was worked out, including the formation of 1-chlorobutane, the rate expression for this product did not agree with the experimental results as it predicted that it depended on the square of the HCl concentration at high HCl concentrations while it was experimentally observed to become independent of HCl concentration.

APPENDIX IV

A VALUE FOR k_1I

An absolute value for the rate constant of the initiation reaction $HCl \xrightarrow{k_1I} H^{\bullet} + Cl^{\bullet}$ has been obtained. This was done by observing the rate of production of NOCl in irradiated NO-HCl mixtures, the value obtained being 4.9×10^{-8} sec^{-1}. The validity of transferring the value of k_1I found in the absence of ethylene, to systems containing ethylene, requires some discussion. The question as to whether or not the presence of the ethylene is leading to additional initiation must be answered. Since the kinetic expressions derived from mechanisms which assume that the ethylene leads to initiation do not agree with the experimental results, this suggests that initiation resulting from ethylene decomposition is unimportant.

Irradiation studies on mixtures of ethylene and deuterated ethylene (24), has shown that essentially all the molecular hydrogen produced in the radiolysis results from molecular hydrogen split-out. This observation in itself does not rule out the possibility that hydrogen atoms are being produced, as any that were produced would undoubtedly be scavenged by the ethylene to produce ethyl radicals. The independence of the rate of initiation on ethylene concentration, however, does give evidence to the fact that the removal of a hydrogen atom from an ethylene molecule is a relatively rare event.

If the ethylene is not contributing to the rate of initiation, the question remains as to whether or not it is preventing some reaction from taking place which is a significant contributor to the rate of formation of chlorine atoms in the HCl - NO system. The ionization potential of NO is about 4 eV below that of HCl. It is thus quite possible that the presence of the NO in the HCl - NO irradiations leads to the elimination of the ion-molecule reactions involving HCl^+. If this is indeed the case, this would indicate that ion-molecule reactions are not contributing to the rate of production of chlorine atoms, even in pure HCl, since Lee et al (40) have found that the G value for hydrogen formation in irradiated HCl is 8.0. This would predict a G value of 16 for the rate of production of chlorine atoms which is the value obtained from the HCl-NO experiments described in this work.

From these considerations, it would appear that all the chlorine atoms arise by the dissociation of molecules which have been excited from the ground state to the lowest excited state by the direct interaction of the radiation.

APPENDIX V

CALCULATION TO SHOW THAT ON ENERGETIC GROUNDS, THE OBSERVED RATE OF FORMATION OF CHLORINE ATOMS CAN BE EXPLAINED AS ARISING SOLELY FROM THE DISSOCIATION OF EXCITED MOLECULES

The calculation requires the knowledge of the rate of formation of chlorine atoms, the rate of formation of ions and the rate of deposition of energy in HCl. The rate of formation of chlorine atoms at the distant irradiation position used for the ion current measurements was found to be 6.7×10^{12} atoms/g/sec. Since it has been postulated that one dissociation of an HCl molecule leads to the production of two chlorine atoms, this gives a value of 3.4×10^{12} dissociations/g/sec. for the rate of dissociation of HCl. The rate of dissipation of energy by this process is thus 2.7×10^{13} eV/g/sec., assuming the average value of 8.1 eV for the excitation energy of HCl.

Ion current measurements gave a value of 1.98×10^{12} ion pairs/g/sec. for the rate of production of ion pairs. Assuming that the majority of the positive ions formed are HCl^+ ions, this leads to a value of 2.5×10^{13} eV/g/sec. for the rate of dissipation of energy by ionization. A recent value of 12.6 eV (41) for the first ionization potential of HCl has been used.

Ion current measurements with air gave a value of 1.7×10^{12} ion pairs/g_{air}/sec. for the rate of production of ion pairs in air.

Taking a value of 32.5 eV for W_{air}, this means that the rate of deposition of energy in the air was 5.5×10^{13} eV/g_{air}/sec. Multiplying this value by the stopping power ratio for HCl and air, obtained from reference 40, ($\rho^{HCl}_{air} = 1.16$), gives the rate of deposition of energy in the HCl as 6.4×10^{13} eV/g_{HCl}/sec. Since the sum of the rates of dissipation of energy by ionization and excitation to the lowest excited state is only 5.2×10^{13} eV/g_{HCl}/sec., this indicates that it is energetically possible for all the chlorine atoms to be originating from excited molecule decomposition.

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