1960

Recoil reactions of carbon-11 in organic compounds

Charles Eberhardt Lang
Iowa State University

Recommended Citation

Lang, Charles Eberhardt, "Recoil reactions of carbon-11 in organic compounds " (1960). *Retrospective Theses and Dissertations*. 2620.
https://lib.dr.iastate.edu/rtd/2620

RECOIL REACTIONS OF CARBON-11 IN ORGANIC COMPOUNDS

by

Charles Eberhardt Lang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

TABLE OF CONTENTS

I. INTRODUCTION

A. Historical

The study of the chemical effects of nuclear reactions has its origin in some investigations which were conducted in the early part of the twentieth century.

It had been observed by Brooks (1) in 1904 that the decay products of radioactive radon displayed a pseudo-volatility. Likewise, Russ and Makower (2) reported in 1909 that the decay products of certain radioactive species could be conveniently separated from their parent materials by collecting the daughter products on charged plates. In both of these cases the effect was attributed to the momentum of the daughter material which resulted from the necessary conservation of momentum of the emitted particle. In 1934 Fermi *et al.* (3) observed in the bombardment of elements of atomic number greater than thirty with neutrons that the species resulting from the nuclear transformation could not be separated from the parent by the usual chemical techniques. The products were found to be isotopic with the element undergoing the transformation. Szilard and Chalmers (4) suggested that a separation could be achieved if there were a momentum effect operative in the case of nuclear transformations similar to that which had been observed in the case of radioactive decay. That is, if there were a momentum transfer from the impinging neutron to the struck nucleus, then the nucleus would be dislodged from its chemical environment. Consequently, the transformed nucleus would be present under a different chemical form, and it would be amenable to simple separation from its parent material.

Szilard and Chalmers tested their hypothesis in the study of the transmutation of iodine in ethyl iodide by neutron activation. It was found that a large portion of the total activity produced could be separated from the bulk of the ethyl iodide by addition of iodine and a reducing agent, followed by precipitation with silver ion. They concluded that a momentum effect was operative in this case and that the same situation could be realized in other systems provided that the following principles hold:

(1) The product of the nuclear reaction is radioactive.

(2) The radioactive species produced in the new chemical form will not undergo isotopic exchange.

The usefulness of this momentum effect was immediately recognized, and several papers were published in which reports of successful separations of nuclear reaction products were given (5, 6). In tribute to the significance of the contribution of Szilard and Chalmers the field of chemical effects resulting from nuclear transformations has been termed "Szilard-Chalmers Chemistry".

Many studies of the fundamental features of the Szilard-Chalmers effect were made between 1935 and 1947. Glückauf and Fay (7) investigated the (n, γ) transformation in several organic halides in the liquid phase. After extraction of the material with an aqueous solution of carrier halogen and reducing agent, various organic carriers were added to the liquid, and the material was fractionally distilled. For example, with methyl iodide 46% of the total activity appeared in the methyl iodide fraction, and 11% was collected in the methylene iodide fraction. Similar results were obtained for the other substances studied. It had been tacitly assumed prior to this experiment that the activity which was not extractable remained behind in the same chemical constitution as the parent. This work illustrated that the recoil atoms could cause chemical synthesis. Libby (8) and Suess (9) clearly demonstrated that almost all of the atoms severed their chemical bonds in the recoil process. For example, Libby found that about 5% of the Br^{80m} produced by neutron irradiation of ethyl bromide gas was retained in organic combination whereas in the liquid phase the retention was about 75%. This indicated that reformation of the parent material also occurred by a synthesis process, and, furthermore, this synthesis process was greatly reduced in the gaseous state. Lu and Sügden (10) observed that addition of aniline to organic halides caused the organic retention resulting from the (n, γ) reaction to be reduced. Glückauf and Fay (7) and

Libby (11) studied the effect of diluting the alkyl halides with organic materials containing atoms of much different mass from that of the halide. Dilution of carbon tetrabromide with ethanol or carbon disulfide reduced the organic yield. The reduction of the retention was found to be a function of the extent of dilution. Carbon disulfide was relatively more effective than ethanol in lowering the retention.

On the basis of these observations Libby (12) postulated the "Billiard-Ball Collision Theory". The theory was an attempt to explain the features of the Szilard-Chalmers chemistry observed principally in the (n, γ) reaction in organic halides. Essentially, the theory envisions elastic collisions of recoil atoms with atoms of the medium. In some of the collisions between recoil atoms and atoms of similar mass a recoil atom could transfer a large fraction of its energy and would be left behind along with the radical produced in the collision. These two species would be "caged" by the surrounding solvent and could combine to form the active mother material. Collision of a recoil atom with an atom of much different mass would result in a very small energy loss and would insure removal of the recoil atom from the vicinity of the radical produced in the collision. Consequently, only collisions of atoms of approximately equal mass lead to organic retention. Libby stated that if as a result of successive collisions of low energy transfer, the energy of the recoil atom approached bond energy, then inelastic collisions would prevail and material different from the mother substance would result. This type of process was called an epithermal process. The amount of retention was defined by:

$$R = \frac{\epsilon}{\nu} \tag{1}$$

where,

ϵ = "cage" energy.

ν = carbon-halogen bond energy.

According to these postulates, then, the reduction in retention upon vaporization followed naturally from the expected reduction in the "cage" energy. Dilution would enhance non-retentive collisions and hence result in reduction of the organic retention. Addition of aniline would permit interaction of the newly formed active organic species and the aniline molecules according to the following scheme.

$$RX^{*} + \text{Aniline} = R^{+}, \text{Aniline} + X^{*-} \tag{2}$$

where,

X^{*} = radioactive halogen.

This reaction is one of a general class of Menschutkin reactions and is known to occur at elevated temperatures. The activation energy in the Szilard-Chalmers case was provided by the newly formed active mother material.

Friedman and Libby (13) observed in the study of the

Szilard-Chalmers effect in the propyl bromides that the organic retention was greater in the solid phase than in the liquid phase. This so called phase effect was explained in terms of the "Billiard-Ball" theory according to the following reasoning. The organic activity can be considered as consisting of active material chemically identical with the parent, produced by means of a "hot" process, and active material chemically different from the parent material, produced by an epithermal process. Since the "hot" process necessarily occurs in the high energy region, the nature of the environment is of little consequence. Therefore, the retention resulting from the "hot" process is identical in all condensed phases. On the other hand, substances resulting from an epithermal process are initiated by a recoil atom of rather low energy. In this instance, the reaction of the recoil species and the radical produced by it is very likely sensitive to the nature of the phase. Therefore, it is expected that the retention due to epithermal processes is enhanced in the solid phase since the "cage" is stronger.

Libby's theory was extended by Miller _et al_. (14) to include the quantitative consideration of the dilution effect. Assuming elastic billiard-ball collisions and also a steady state between the production of the recoil atoms and the reaction of recoil atoms, they determined explicit expressions for the organic retention as a function of extent of dilution and nature of diluent. It was found by Miller and Dodson (15) shortly after this theory was published that the results obtained in the investigation of diluted alkyl halide systems were not in most cases in agreement with the values predicted by the theory. The only case in which there was good agreement was for the relatively simple system CCl_4 - $SiCl_4$. In general, the Miller extension has been found to be of very limited value in either correlation or explanation of observations made in the field of Szilard-Chalmers chemistry.

The validity of the elastic billiard-ball collision assumption inherent in the theories of Libby and Miller et al. has been questioned by Willard (16). Willard reasoned that the notion of perfectly elastic encounters, similar to those which would occur between species in free space, must be far from the actual process occurring in a condensed medium. Consequently, as an alternate to the Libby theory Willard proposed the "randon-fragmentation" hypothesis. This theory includes the following concepts.

1. Immediately after the recoil atom leaves its parent molecule, it encounters solvent molecules. Rather than transfer its energy by an elastic collision with a single atom in the molecule, it interacts with the molecule as a whole and also with the neighboring molecules, which in a condensed material are interwoven one with another. The energy transfer is, then, essentially achieved in an inelastic process. In some few cases, however, there may indeed be a

perfectly elastic collision process similar to that envisioned by Libby, but by and large the collisions will be inelastic. The result of this process will be a general disruption of the chemical bonds in the molecule struck and also to a lesser extent in the surrounding molecules. Many different types of radicals will be produced. The nature and the relative amounts of these radicals will depend upon the chemical nature of the medium, the energetics involved in the reaction paths, the density of the medium, and the orientation of the molecules. After the first encounter the recoil atom will move off, and after traversing a few molecular diameters, it will encounter another solvent molecule. The fragmentation process will be repeated in this encounter. After several such collisions the recoil atom will reach the end of its path.

2. At the end of its path and before it has been thermalized, the recoiling atom will find itself adjacent to a "pocket" or "nest" of radicals which it has produced in slowing down. It can then react with one of these radicals to form a stable compound. If the recoiling atom escapes reaction at the end of its path, it will diffuse as a thermal atom and may undergo thermal reactions.

Although Willard places a great deal of emphasis upon reactions of the recoiling atom with radicals, he does not discount the possibility that it could react with molecules. Such reactions could occur at the immediate end of the path of the recoiling atom, at which point it is called a "hot" radical reaction, or after the recoiling atom has been thermalized.

B. General Principles

1. Introduction

It is convenient at this point to summarize some of the more general observations which have been made in the field of Szilard-Chalmers chemistry. More extensive discussions of the chemical effects of nuclear transformations can be had by means of reference to the reviews of Willard (16) and Harbottle and Sutin (17).

2. Phase effect

In many systems which have been studied it has been found that the organic retention is greater in the solid phase than it is in the liquid phase. This is, of course, in agreement with the predictions of the Libby theory. In the cases of ethyl iodide, i-butyl iodide, and sec-butyl iodide there is no phase effect (18). It is not possible to rationalize the absence of the phase effect in these systems in terms of Libby's theory; however, there is no such difficulty with Willard's theory because by the very nature of the theory no *a priori* prediction about the effect of the phase can be made.

3. Scavenger effect

Goldhaber and Willard (19) found that the addition of bromine to ethyl bromide caused the organic retention to be reduced and that this reduction was a function of the bromine concentration up to a limiting value of about 0.005 mole fraction of bromine. At bromine concentrations greater than this value the retention was constant. The addition of α, β -dibromoethylene to ethyl bromide also had an effect, except that in this case the retention was enhanced. Both of these materials have the ability to react with any thermal bromine atoms in the system by exchange or addition. A decrease in the organic retention in the bromine-ethyl bromide system implies that the bromine has scavenged the thermal bromine atoms, which in the absence of bromine would have been incorporated into organic material. Likewise, an increase in the organic retention in the α, β -dibromoethylene-ethyl bromide system implies that the α, β -dibromoethylene has scavenged the thermal bromine atoms, which in the absence of this reagent would have been incorporated into inorganic material. That part of the inorganic or organic yield which is insensitive to the scavenger is attributed to non-thermal processes.

Therefore, for the case of ethyl bromide the inorganic and organic products result from both thermal and non-thermal, hot, processes. This is in direct opposition to the predictions of the Libby theory since this theory attributes the production of organic material entirely to hot or epithermal processes and inorganic material entirely to thermal processes. On the other hand, the scavenger effect agrees with the Willard theory which considers product formation as the result of many possible reactions involving both thermal and non-thermal processes.

Several other systems have been investigated and have also shown the scavenger effect.

The importance of the scavenger effect experiments is that they give information regarding the syntheses paths of the observed products.

4. Fundamental processes

The nature of the fundamental processes involved in the Szilard-Chalmers effect is as yet imperfectly understood. A consideration of fundamental processes must include the following points:

(1) The nature of the recoil atom at birth, including its energy and charge characteristics.
(2) The nature of the slowing down mechanism.
(3) The nature of the recoil atom at the end of its path.
(4) The nature of available reaction paths leading to stable products.

Certain features of the above points have been considered for some systems; however, it is not possible at this time to draw any certain conclusions concerning the relationships between the fundamental processes and the nature or quantity of products observed in particular systems.

The recoiling atom is undoubtedly charged as a result of the (n,γ) activation process. For example, Hibdon and Muehlhause (20) observed that in all of the cases of the (n,γ) reactions which they investigated, conversion electrons were emitted. Furthermore, Yosim and Davies (21) found that for the (n,γ) reaction in gold or indium foils charged recoil species could be collected on charged plates held near the foils. This indicated that internal conversion of the gammas were occurring, and this conversion occurred after the emission of the gamma for if emission had been simultaneous with conversion, the charge would have been neutralized in the metal foil.

These results made it necessary to consider charge neutralization and ion-molecule reactions in the study of fundamental processes.

One very interesting piece of information which has been obtained regarding the reaction paths available is the observation that hot radical reactions occur in some of the Szilard-Chalmers systems. A hot radical reaction is defined as a reaction of the recoiling atom, either neutral or charged with a molecule of the solvent.

Hornig _et_ _al_. (22) has observed that iodine activated by the (n,γ) process in methane gas will be incorporated into the methane to the extent of 45%. Since in the gaseous system there is no solvent "cage", the reaction can not be due to a combination of a recoil atom with a radical. Also, the reaction is not attributable to a reaction of a thermal radical with a molecule since iodine radicals produced photochemically did not react with the methane. Consequently, the reaction must be due to a "hot" radical process. Willard has suggested that the reaction is between an ion and a molecule, but it is not possible to exclude with certainty the atom-molecule type reaction.

5. Activation methods

The principle means of activation which has been employed in the study of the Szilard-Chalmers effect is the (n, γ) process. The reasons for the prevalence of this type of activation are the availability of thermal neutrons; the favorable cross sections for this process; and the relatively low background gamma flux associated with thermal neutron sources, with the resultant small effect of radiation damage. To a lesser extent activation by means of isomeric transition, beta decay, and (n, p), (p, n), (n, α), $(n, 2n)$, and (γ, n) reactions have been employed. At the present time studies of the Szilard-Chalmers effect produced by these reactions are receiving more attention.

A number of (γ, n) activations have been made in order that the results of this process could be compared to the (n, γ) process. For example, the study of the (γ, n) activation of copper-63 in copper salicylaldehyde-o-phenylenediimine by Holmes and McCallum (23) yielded results which were similar to those obtained in the (n, γ) activation of the same material (24). Likewise, the results obtained by Collins (25) in the (γ, n) activation of solid cobaltic hexammines were very similar to those obtained by the (n, γ) process (26). Schuler (27) has studied the (γ, n) activation of liquid methyl and ethyl iodides and has found that the organic yields for the $I^{127}(\gamma, n)I^{126}$ reaction agrees with those reported for the $I^{127}(n, \gamma)I^{128}$ reaction (28). McCauley et al. (29) have also reported that the retentions resulting from both $I^{127}(n, 2n)I^{126}$ and $I^{127}(n,\gamma)I^{128}$ reactions in solid alkyl iodides are very similar.

These results indicate that the ultimate fate of the recoil atom probably does not depend greatly on the initial recoil energy.

6. Product analysis

In the majority of the investigations concerning organic halides the products produced by the nuclear transformations have been isolated by means of fractional distillation. In 1956 Evans and Willard (30) showed that the organic products in these systems could be very conveniently analyzed by means of gas phase chromatography. They studied the (n,γ) activation of bromine in n-propyl bromide and found that the chromatographic method provided a rapid separation together with a much more extensive knowledge of the reaction products than had been provided using fractional distillation. Since the appearance of Willard's paper several Szilard-Chalmers studies have been made in which the analyses were effected by means of gas phase chromatography (31, 32). Gas phase chromatography has been recognized as an extremely useful tool in the field of Szilard-Chalmers chemistry.

7. Carbon-11 recoils studies

Relatively few studies have been made into the nature of the Szilard-Chalmers effect produced by the (γ, n) reaction on carbon-12. Rowland and Libby (33) have investigated the

$C^{12}(\gamma, n)C^{11}$ reaction in solid and liquid carbon dioxide, in solid sodium bicarbonate, and in aqueous solutions of sodium bicarbonate and sodium carbonate. For both solid carbon dioxide and solid sodium bicarbonate the yields of active carbon dioxide and carbon monoxide were about equal; however, in the cases of liquid carbon dioxide and the aqueous solutions of sodium bicarbonate and sodium carbonate the yield of active carbon monoxide was about twenty times that of the carbon dioxide.

Sharman and McCallum (34) and Edwards and McCallum (35) have investigated the chemical effects resulting from the $C^{12}(\gamma, n)C^{11}$ reaction in sodium carbonate, calcium carbonate, and sodium bicarbonate. Upon disolution of these materials after irradiation, active carbonate, carbon monoxide, formic acid, oxalic acid, glyoxylic acid, and glycolic acid were produced. The relative amounts of these products were about the same for all of the materials studied. These authors also observed that if the sodium carbonate crystals were at a series of increasing temperatures before dissolving, the percentage of the carbon-11 present as glyoxylic acid, glycolic acid, and oxalic acid decreased, each at a different temperature, and the corresponding activity appeared instead as carbonate.

A very interesting paper was published by Suryanarayana and Wolf (36) in which the effect of carbon-11 recoils in a benzene substrate was made. The carbon-11 was produced by means of the $C^{12}(n, 2n)C^{11}$ reaction. Benzene and toluene activities were separated by means of gas phase chromotography. About 4.5 and 2.2% of the total activity produced were accounted for in benzene and toluene respectively. Addition of radical scavengers decreased the benzene activity but did not affect the toluene activity. A similar effect was observed with a change in phase from liquid to solid.

II. PURPOSE

It has been shown in the previous section that a considerable amount of work has been done in the field of Szilard-Chalmers chemistry; however, the clear understanding of these systems is as yet not realized. It was previously indicated that the majority of the investigations made into the nature of the Szilard-Chalmers process have been, by and large, restricted to alkyl halides and in particular to the (n, γ) activation of these halides.

It is desirable to obtain more extensive information on the Szilard-Chalmers effect produced by various means of activation in other systems. Since the most common denominator of organic compounds is carbon, it seems inherently reasonable that the Szilard-Chalmers effect on carbon would be of particular interest. Furthermore, since much simpler systems could be employed than those of the alkyl halides, the study of the effect on carbon would very likely give information which would be more easily relatable to the fundamental processes. For these reasons a study into the chemical effects arising from the nuclear transformation of carbon in organic systems was made. The availability of the Iowa State University synchrotron made feasible the study of the (γ, n) activation.

There are two difficulties inherent in the investigation of the Szilard-Chalmers chemistry produced by the $C^{12}(\gamma, n)$

C^{11} reaction. These are the relatively small cross section for the reaction and the short half-life of the carbon-11. The cross section has been determined by Montalbetti <u>et al.</u> (37) to be 13 mb at the 22 Mev maximum of the cross section peak. The half-life is listed as 20.4 min (38). Both of these difficulties can be circumvented, however, by restricting the study to condensed phases and by employing a rapid means of analysis. The rapid means of analysis can be easily provided by a gas phase chromatograph.

In the investigation a gas phase chromatograph was used to analyze the products produced by the interaction of carbon-11 with benzene, cyclohexane, and n-hexane. The purpose of the investigation is to give an account of the kinds of gaseous Szilard-Chalmers products and their relative amounts produced at room temperature and to determine the phase effect and the temperature dependence of these products in order to obtain an insight into the fundamental processes occurring in these systems. A qualitative description of the liquid products produced in the Szilard-Chalmers effect in benzene, cyclohexane, and n-hexane will provide additional information concerning the nature of the fundamental processes and will permit a comparison of the results of the benzene system with the results obtained by Suryanarayana and Wolf in their study of the (n, 2n) activation of carbon in benzene.

III. EXPERIMENTAL

A. Materials

1. Chemicals

The benzene and cyclohexane used in the experiments were Eastman Kodak Co. Spectro Grade. The n-hexane was Research Grade material obtained from the Phillips Petroleum Co. The manufacturer's stated purity for the lot from which the hexane had been taken was 99.96 mole per cent. No further purification was made except that the reagents were dried over sodium wire.

The hydrocarbon gases used in the investigation were obtained from The Matheson Co. and were stated by the manufacturer to be CP grade. These gases included methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, isobutane, butene-1, butene-2, isobutene, and butadiene.

2. Chromatographic columns

A ten foot silica gel column was prepared by packing Fisher silica gel (14-20 mesh) into a pyrex glass spiral of six mm inside diameter. This column was heated to about 150°C and flushed for several hours with helium gas in order to effect the removal of any adsorbed material. It was always flushed for at least two hours before being used in a particular analysis.

In the columns which are described next Johns-Mansville celite 22 was used, and it was prepared according to the following procedure. A firebrick of the material was pulverized, and the powder was sieved in order to obtain the desired mesh. The material was then treated with a 1:1 mixture of hydrochloric acid and water. It was then washed several times with distilled water and dried. The dry celite was finally fired in a muffle furnace at 1000°C for several hours.

A column of dioctylphthalate on celite was prepared by adding 43 grams of the organic material dissolved in acetone to 100 grams of 48-65 mesh celite. The mixture was stirred, and the acetone solvent was removed by carefully heating the mixture on a steam bath followed by vacuum desiccation. The column mixture was then firmly packed into a pyrex glass spiral of six mm inside diameter and 12 feet total length.

A mixed column of six feet of diisodecylphthalate and 16 feet of dimethylsulfolane on celite was prepared in a manner similar to that of the dioctylphthalate column. In this case, however, the column packing was made according to the ratio of 40 grams of organic liquid to 100 grams of 28-35 mesh celite.

A 12 foot n-decane column was prepared using 48-65 mesh celite and n-decane in the ratio of 67 grams of n-decane to 100 grams of celite. In this case it was not possible to apply the organic material to the supporting celite via an organic solvent because of the high volatility of the n-decane. That is, in removing the solvent the n-decane was also invariably removed. Consequently, the n-decane was added directly to the celite, and then the mixture was stirred very thoroughly and finally allowed to equilibrate in a sealed container.

A 12 foot ethylacetoacetate column consisting of 67 grams of organic liquid to 100 grams of 48-65 mesh celite was prepared in exactly the same manner as the n-decane column.

3. Sample preparation

The following procedure was employed in the preparation of samples for bombardment.

A sample tube of eight pyrex tubing with a fragile break tip at one end and a standard taper at the other was filled with two ml of the liquid. The sample tube was then placed on a vacuum line, cooled with a liquid nitrogen bath, and evacuated until the material froze and for a few minutes thereafter. This removed the major portion of the air over the liquid. The vacuum was then closed, and the material was allowed to melt. The freezing-pumping cycle was repeated twice in order to insure removal of the last traces of the air. After the final evacuation the sample was sealed off, and the ampules obtained were about eight cm in length and contained about one gram of liquid. In all cases the samples were prepared under a vacuum of less than five microns. Fisher Nonaq stopcock grease was used as the lubricant on the vacuum line.

B. Bombardments

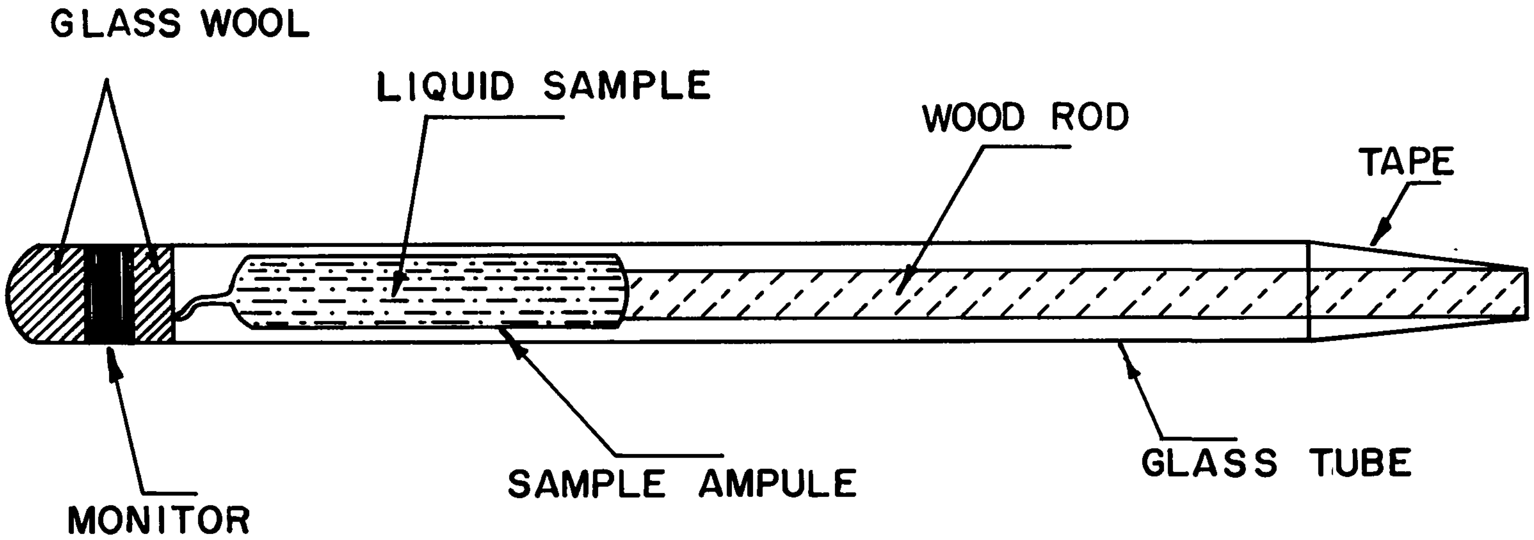
The Iowa State University synchrotron was used as a source of gammas to produce the photonuclear reaction $C^{12}(\gamma, n)C^{11}$ in the materials studied. Bombardments were made at the maximum energy of the synchrotron, 47 Mev, for a constant time period of one hour. The very low cross section of the reaction coupled with the short half-life of the carbon-11 made near saturation bombardments necessary.

The total activity was estimated to be about 0.3 mc/ml. This value serves only as an indication of the activity obtained in a typical run since the true activity would necessarily depend on the magnitude of the gamma flux, which in turn would be a function of the operating condition of the synchrotron during the run.

The only emitter observed in these experiments was carbon-11.

The room temperature bombardments were carried out in an apparatus which is shown in Figure 1. The sealed end of this 12 mm pyrex glass tube was stuffed with about one cm of glass wool which was followed by a five mm thick plug of Synthane plastic used as a monitor for the beam. Another small portion of glass wool was placed behind the plug, and this was followed by the sample. The contents of the apparatus were

Figure 1. Room temperature irradiation apparatus


GLASS WOOL
LIQUID SAMPLE
WOOD ROD
TAPE
MONITOR
SAMPLE AMPULE
GLASS TUBE

held firmly in place with a wood rod which was taped to the outside of the glass tube. The positions of the plug and ampule, relative to one another, were the same in all bombardments.

For bombardments which were made at low temperatures, 0 and -78°C, a somewhat different apparatus was used, shown in Figure 2, which consisted of an inner pyrex tube surrounded by a double walled glass jacket. The space between the walls was filled with a thermal insulating material, and the jacket itself contained the coolant. The inner portion of the apparatus was filled as described previously, except that prior to the introduction of the sample ampule the sample was frozen and equilibrated with the coolant material.

Both irradiation apparatuses were mounted in the sample holder of the synchrotron so that the gamma beam passed along the axis and parallel to the sides of the tube and then through the monitor and sample.

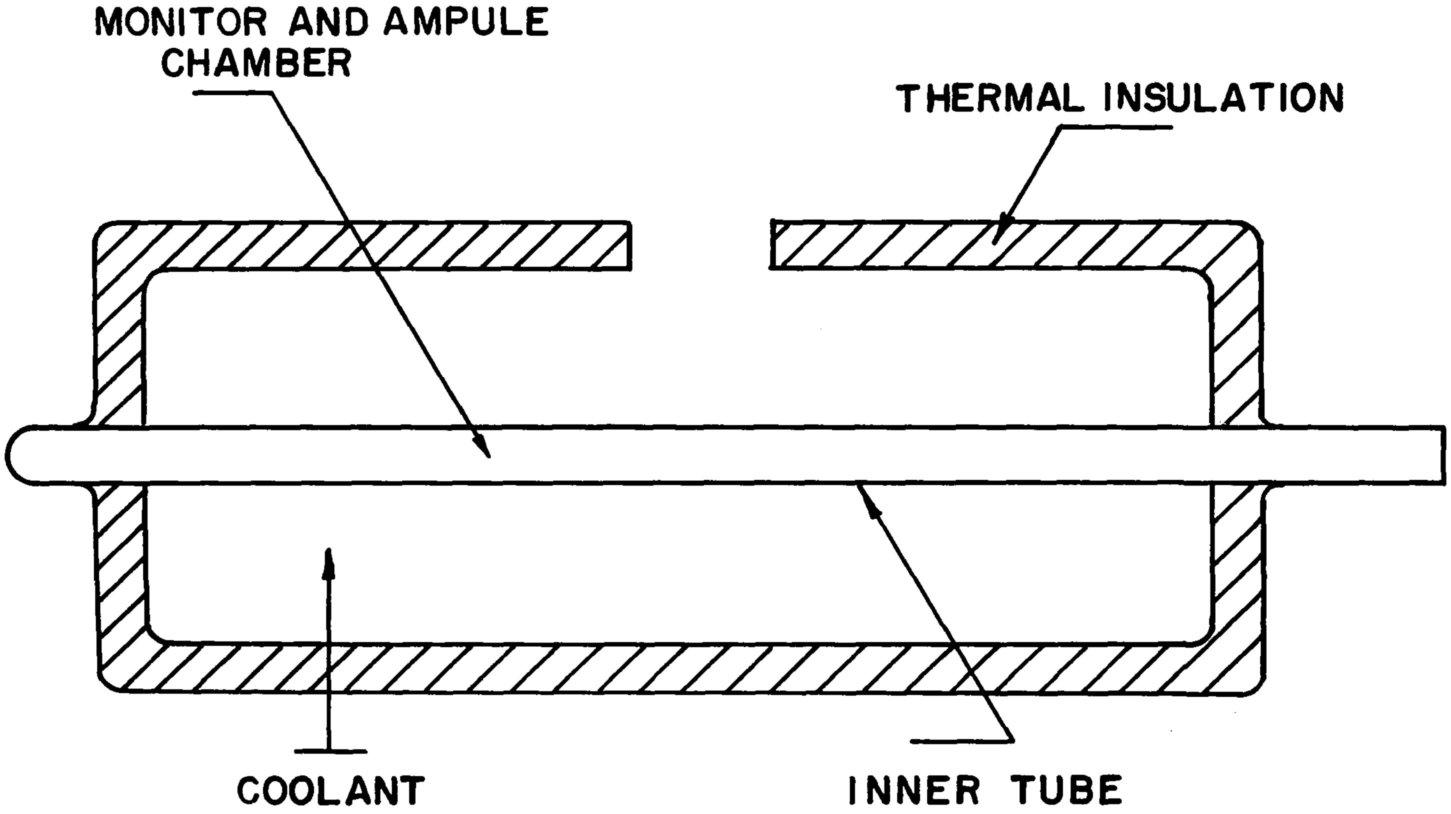
C. Product Analysis

1. Introduction

The Szilard-Chalmers products were analyzed and counted according to a procedure suggested by Evans and Willard (30). The general features of this procedure are given below.

A portion of the irradiated sample is introduced onto

Figure 2. Low temperature irradiation apparatus


MONITOR AND AMPULE CHAMBER
THERMAL INSULATION
COOLANT
INNER TUBE

the column of a gas phase chromatograph. After the column has effected a separation, the products are passed through an appropriate counting cell. A recording of the activity as a function of time provides a record of the various products. The identification of the products is made by comparing the elution times of the products to the elution times of known materials.

In the present investigation the products of interest were the gaseous hydrocarbons from methane through the butanes. As produced by the irradiation, these materials were dissolved in the irradiated liquids. They were removed from solution by "flushing" the liquid with helium. The gaseous products were passed through the chromatographic column, separated and counted. The small amount of liquid picked up by the helium carrier was removed from the gas stream by adsorption on the chromatographic column. The schematic diagram of the analysis system is shown in Figure 3.

2. Sampling apparatus and procedure

The flushing apparatus is shown in Figure 4. The sintered glass plate fitted into the pyrex tube supported the liquid sample ampules in such a way that helium entering into the apparatus via the side arm could sweep up through the liquid.

The following procedure was used to introduce the gaseous products into the analysis system (confer Figure 3).

The flushing apparatus containing the sample ampule was

Figure 3. Analysis system

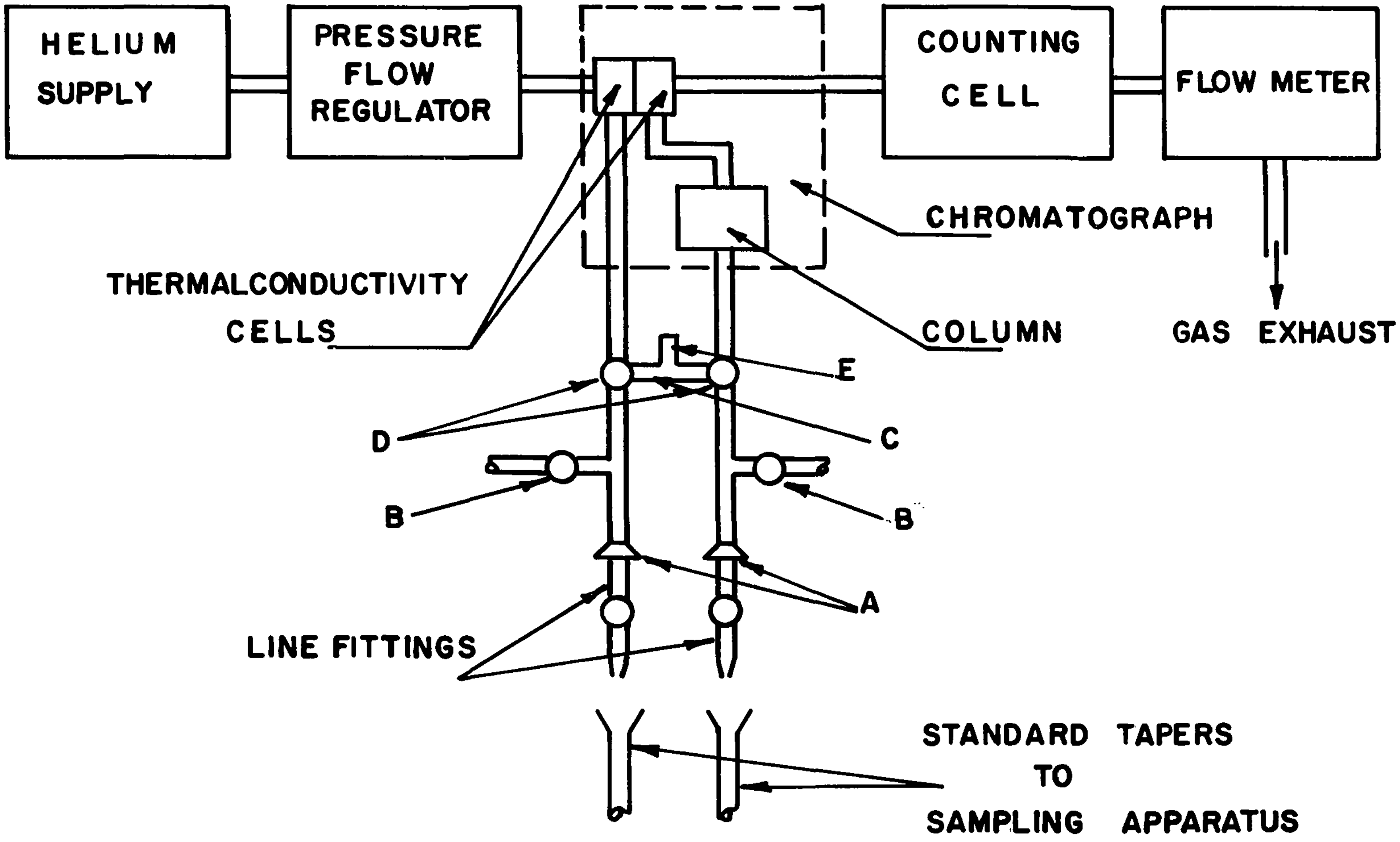
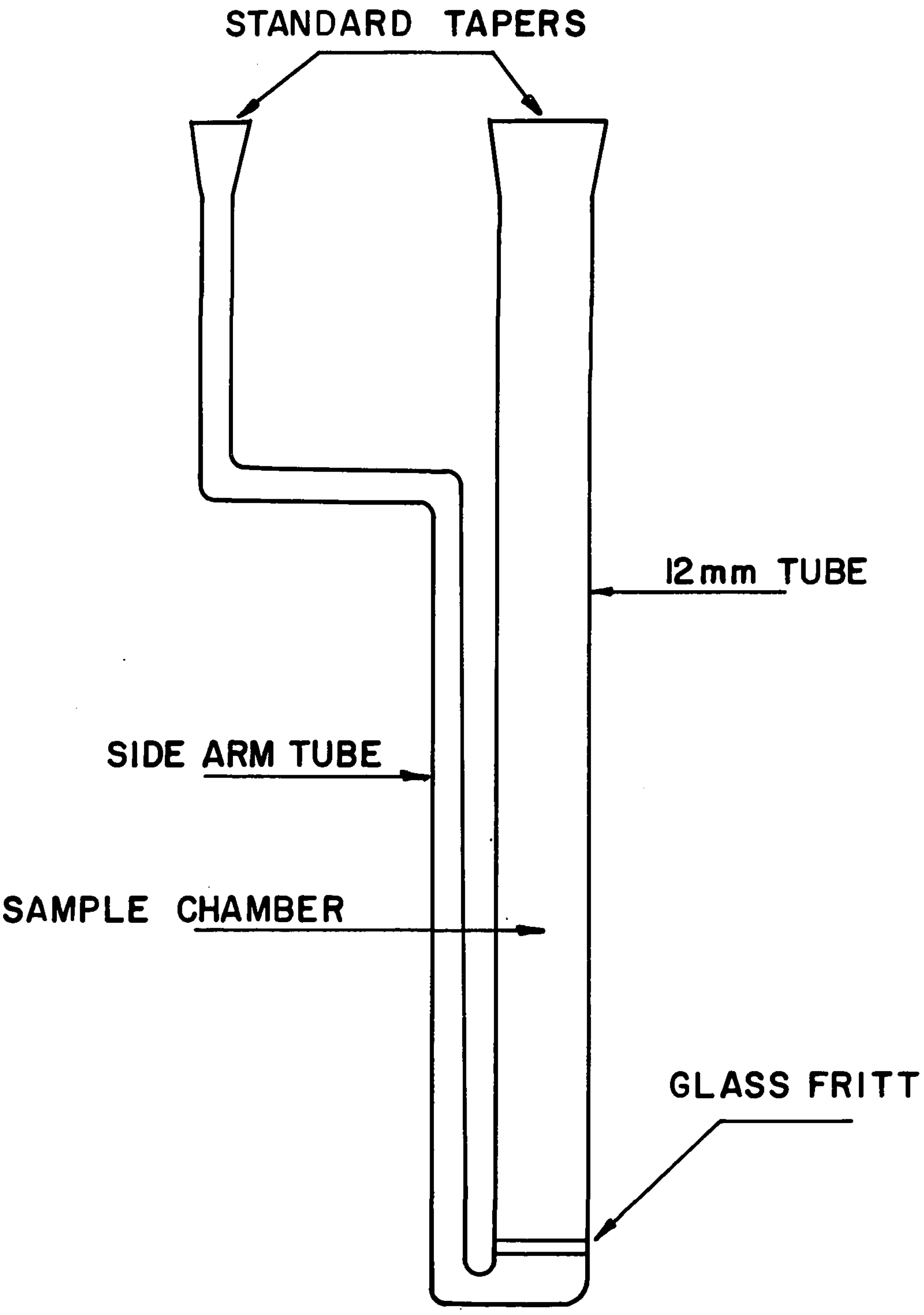

HELIUM SUPPLY
PRESSURE FLOW REGULATOR
COUNTING CELL
FLOW METER
CHROMATOGRAPH
THERMALCONDUCTIVITY CELLS
COLUMN
GAS EXHAUST
E
D
C
B
B
A
LINE FITTINGS
STANDARD TAPERS TO SAMPLING APPARATUS

Figure 4. Sampling apparatus


STANDARD TAPERS
12mm TUBE
SIDE ARM TUBE
SAMPLE CHAMBER
GLASS FRITT

attached to the vacuum line at A and evacuated through B. The sampling apparatus was then removed from the vacuum line, and the fragile break tip was shattered. The apparatus was replaced on the line, and the fittings between the apparatus and the helium line, C, were evacuated. The apparatus was finally closed to the vacuum, and by adjustment of the stopcocks, D, helium was diverted into the apparatus, flushing the liquid and carrying the products onto the chromatographic column.

In those cases in which liquid products were analyzed, the liquid sample was introduced onto the column by injection of a hypodermic syringe into inlet E.

3. Chromatograph

The chromatograph was a Consolidated Engineering Corporation instrument, Model X 26-201. The instrument was provided with a thermostated oven, temperature control, attenuator, thermal conductivity detectors, and the usual appurtenances of gas phase chromatographs.

Helium was used as the carrier gas and as obtained from the U. S. Bureau of Mines had a purity in excess of 99.99%. The carrier gas pressure was operated between one and 18 psig, depending on the particular column used. The silica gel column provided a low resistance to gas flow, and, consequently, a low pressure gave a good flow. On the other hand, the dimethylsulfolane-diisodecylphthalate column provided a high resistance and required the use of pressures near 18 psig to achieve a good flow rate.

The flow rate of the carrier was regulated with a differential-pressure type flow controller which was part of the chromatograph.

The flow rate of the gas was measured using an apparatus which was suggested by Keulemans (39) and is described in Figure 5. A measure of the time which was needed for a soap bubble, formed by manipulation of the flexible tube, to pass the fiducial marks together with the volume of the apparatus provided the flow rate in ml/min.

4. Counting apparatus and equipment

The Szilard-Chalmers products were counted as flowing gases in an apparatus which is shown in Figure 6. After the chromatographic separation the products together with the helium carrier flowed down the inner tube and passed through the counting chamber which was exposed to the sensitive volume of a sodium iodide (thallium activated) crystal.

The crystal, 1.5 inches in diameter by one inch thick with a 3/4 inch hole through its center, was mounted on an RCA 5819 photomultiplier tube which together with a cathode follower were contained in a Berkeley Vial Counter, Model 2250. The voltage supply for the photomultiplier tube was provided by a Model 2001 Berkeley Decimal Scaler. A Nuclear-Chicago Scaling Unit, Model 162, provided a combination linear amplifier and discriminator. The discriminator was necessary in order to eliminate extraneous background so that

Figure 5. Gas flow rate meter

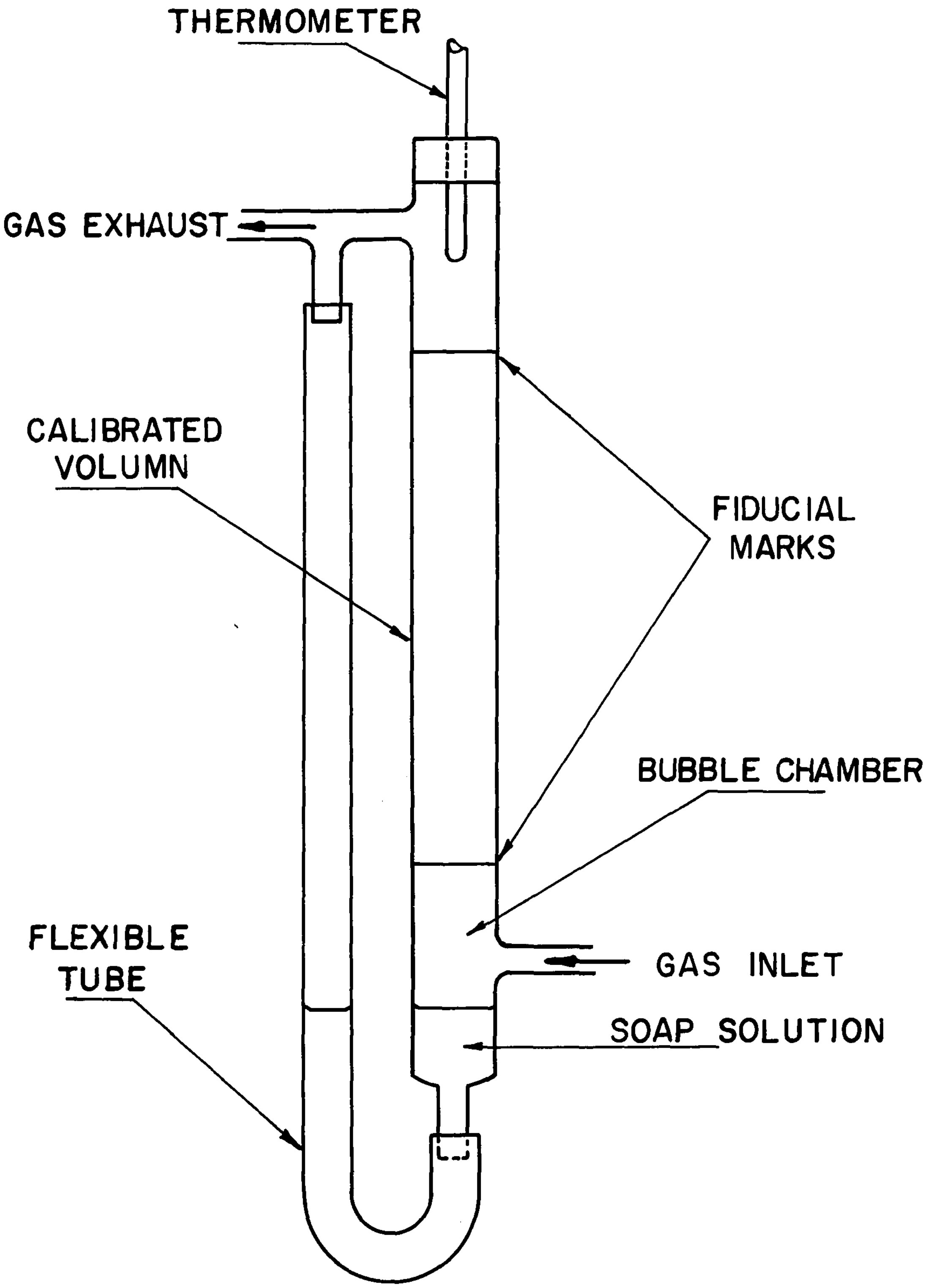
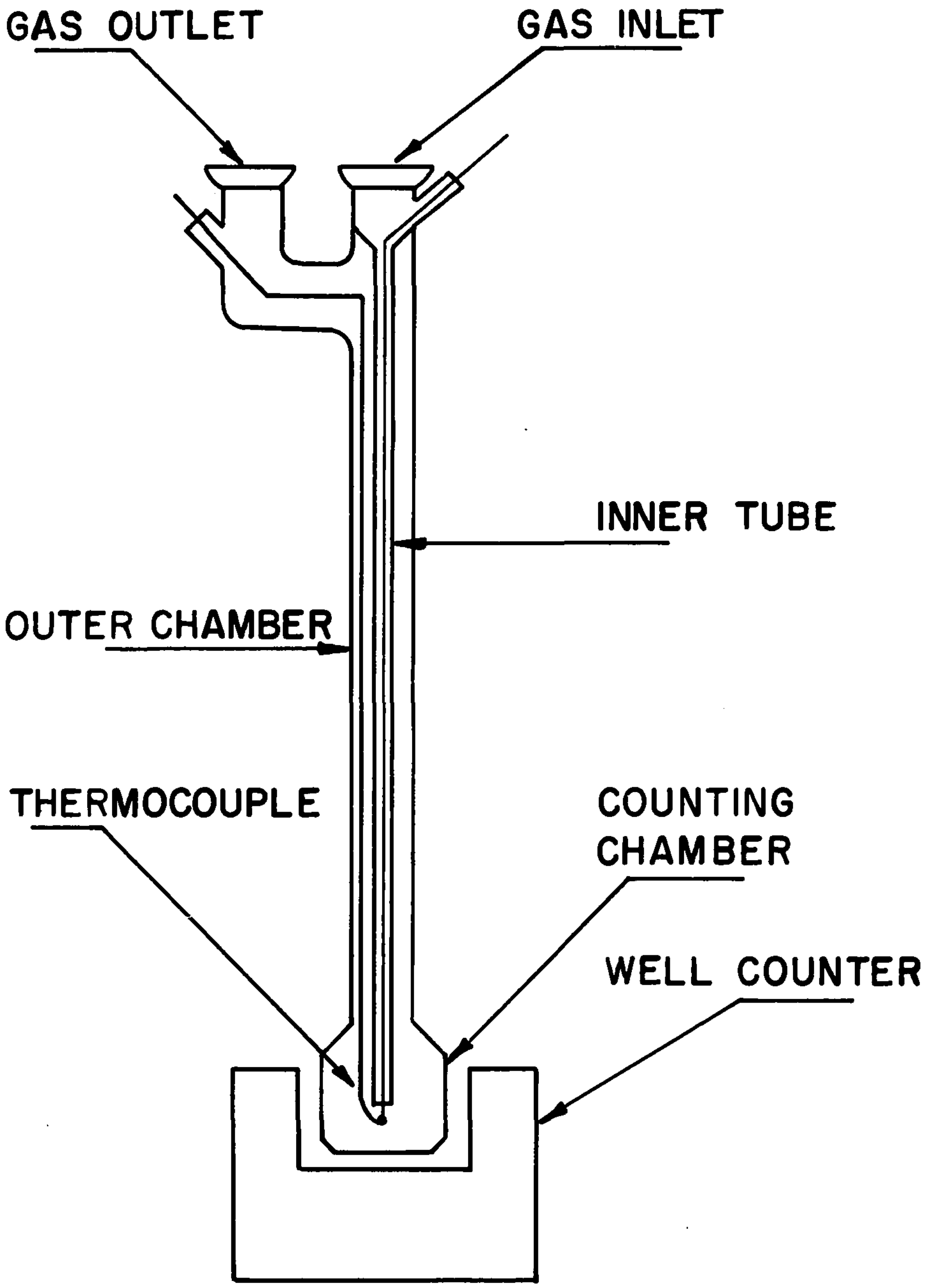

THERMOMETER
GAS EXHAUST
CALIBRATED VOLUMN
FIDUCIAL MARKS
BUBBLE CHAMBER
GAS INLET
SOAP SOLUTION
FLEXIBLE TUBE

Figure 6. Counting apparatus

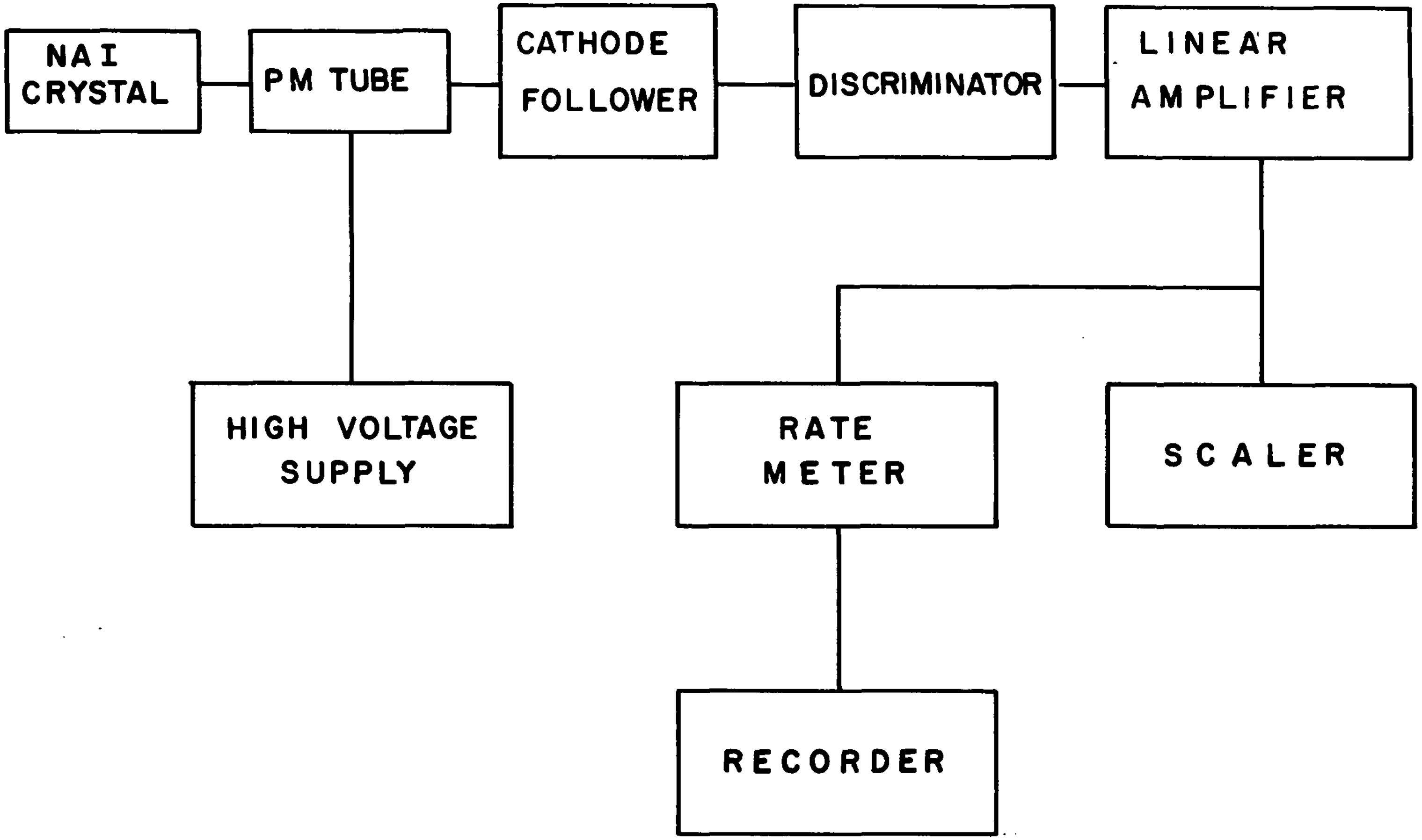

GAS OUTLET
GAS INLET
INNER TUBE
OUTER CHAMBER
THERMOCOUPLE
COUNTING CHAMBER
WELL COUNTER

the low counting levels in some of the samples could be detected. The rate meter was a Nuclear-Chicago, Model 1620, instrument. A Brown Recording Potentiometer was used to provide the activity record. The schematic diagram of the counting circuitry is shown in Figure 7.

The counting system was always standardized before use by counting a standard cesium-137 sample in a fixed geometry.

The activity of the Synthane monitor was determined by counting the carbon-11 annihilation photopeak using a Nuclear-Chicago Gamma Ray Spectrometer, Model 1820.

Figure 7. Schematic diagram of the counting circuitry


NAI CRYSTAL
PM TUBE
CATHODE FOLLOWER
DISCRIMINATOR
LINEAR AMPLIFIER
HIGH VOLTAGE SUPPLY
RATE METER
SCALER
RECORDER

IV. EXPERIMENTAL RESULTS

A. Introduction

The analysis system measured the activity of the gaseous components as they passed through the counting cell. The activity versus time plot was a Gaussian shaped curve which is a consequence of the chromatographic analysis (40). The activity was, of course, not an absolute activity but rather a relative value, contingent upon the geometry of the counting arrangement and the characteristics of the crystal and counting circuitry.

It was necessary to convert the activity-time record into the specific activity of the component so that quantitative comparisons between components could be made. In principle the total counts observed in a "flowing" system can be related to the activity of the component by means of the following expression (41).

$$A = \frac{Nf}{v} \tag{3}$$

where,

A = activity of component.
N = total counts of component.
f = flow rate of material.
v = volume of counting cell.

The total count is, of course, the area under the activity-time curve. In practice, however, there were some difficulties involved in applying this expression to the data obtained. For example, it was not possible to determine the counting volume precisely because part of this volume extended outside of the crystal well; however, since the volume was a constant, it was possible to circumvent this difficulty by coupling the volume with the activity to produce a modified expression for the activity

$$A' = Av = Nf \tag{4}$$

Another difficulty was the complication introduced into the determination of the total counts due to the decay of the products during the analysis. However, if the time of emergence is short with respect to the half-life of the carbon-11, the error introduced into the total counts is small. The emergence time is defined as the time between the onset of the activity peak and the termination of the peak. In all cases the emergence time was less than about seven minutes so that the area under the peak represented the true activity, and A' was calculable using equation 4.

The following method was employed in the evaluation of the activities of the products. The area under the activity-time curve, measured with a planimeter, was multiplied by the gas flow rate to obtain the activity, A'. This activity was corrected to the end of the irradiation by application of the exponential decay law using a $t_{\frac{1}{2}}$ value of 20.4 min. The decay corrected activity was standardized to a constant synchrotron flux and to a standard one gram sample. All areas were expressed in terms of the 10 K scale. The resultant value for the activity is termed the empirical activity, A^*, one unit of which is equal to

$$28 \frac{\text{counts}}{\text{min}} \times \text{ml}.$$

It is not necessary for the purpose of comparing the results of the irradiations of the various liquids or the various products of the same liquid to have a knowledge of either the absolute activity or of the per cent of the total activity which each product represents. The percentage of activity can be obtained, however, from the ratio of the empirical activity of the product to the empirical activity of the irradiated material as a whole.

B. Runs at 30°C

1. Benzene

Twelve bombardments were made upon benzene at the usual operating temperature of the synchrotron. Six of these runs were analyzed using the n-decane column. The activity curves indicated the presence of methane and some two carbon activity. The n-decane column provides a good separation between one, two, three, and four carbon materials but can not separate materials within the groups. Analysis of two of the runs with the silica gel column confirmed the presence of methane and established the absence of ethane and ethylene activity. The silica gel column yields a convenient separation of methane, ethane, and ethylene. All other hydrocarbons have prohibitively long retention times on this column. The use of the dimethylsulfolane-diisodecylphthalate column (DMS-DIDP) in the analysis of four of the runs confirmed the presence of methane and established that the two carbon activity was acetylene. No propane, propylene, isobutane, ethane-ethylene, or four carbon activity was observed. The DMS-DIDP column can separate methane, ethane-ethylene, propylene, propane, isobutane, acetylene, and n-butane but does not separate ethane and ethylene from one another. Propyne together with the other four carbon materials have retention times greater than that of n-butane and were not analyzed for. It was found in the studies with the DMS-DIDP column that the isobutane peak preceded the acetylene. This is contrary to the elution sequence reported by Fredericks and Brooks (42) who stated that acetylene preceded isobutane.

Identification of the activity peaks in these and the other runs were made by the simultaneous analysis of carrier hydrocarbons which were introduced together with the gaseous activity.

A typical activity plot, Figure 8, shows the results obtained from a bombardment of benzene at 30°C and analyzed by means of the DMS-DIDP column. The sample inlet point is on the right of the chart and the activity is shown as a function of time, with the interval between the vertical chart markings equal to 7.2 min. This chart speed was also used in the other graphs discussed later. The smooth curve is a plot of the thermal conductivity of the carrier material as a function of time. The thermal conductivity peaks proceeding from right to left across the chart, excluding the first sharp peak which was caused by a scale change, are methane, ethane-ethylene, propane, propylene, isobutane, acetylene, n-butane, and butene-1. The chart indicates the presence of only methane and acetylene activity. It is also seen that the activity peak precedes the corresponding thermal conductivity peak. This is due to the combination of the gas flow rates which were used and the relative positions of the pens on the recorder.

The quantitative evaluation of these runs yielded A^* values which are given in Table 1.

Figure 8. Activity plot of Szilard-Chalmers products from benzene at 30°C analyzed with a DMS-DIDP column

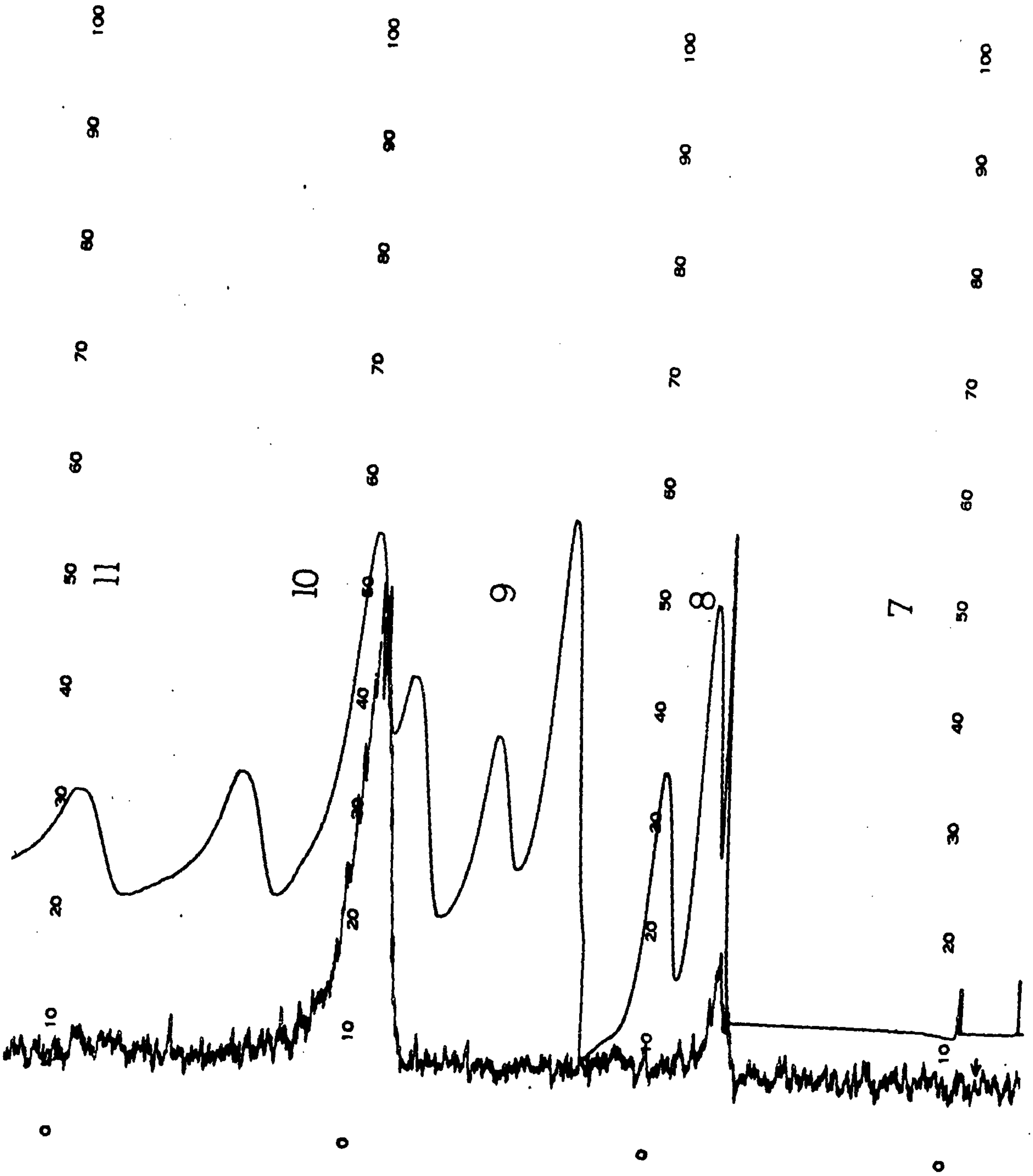

11
10
9
8
7
0
10
20
30
40
50
60
70
80
90
100

Table 1. Gaseous Szilard-Chalmers products from benzene at 30°C

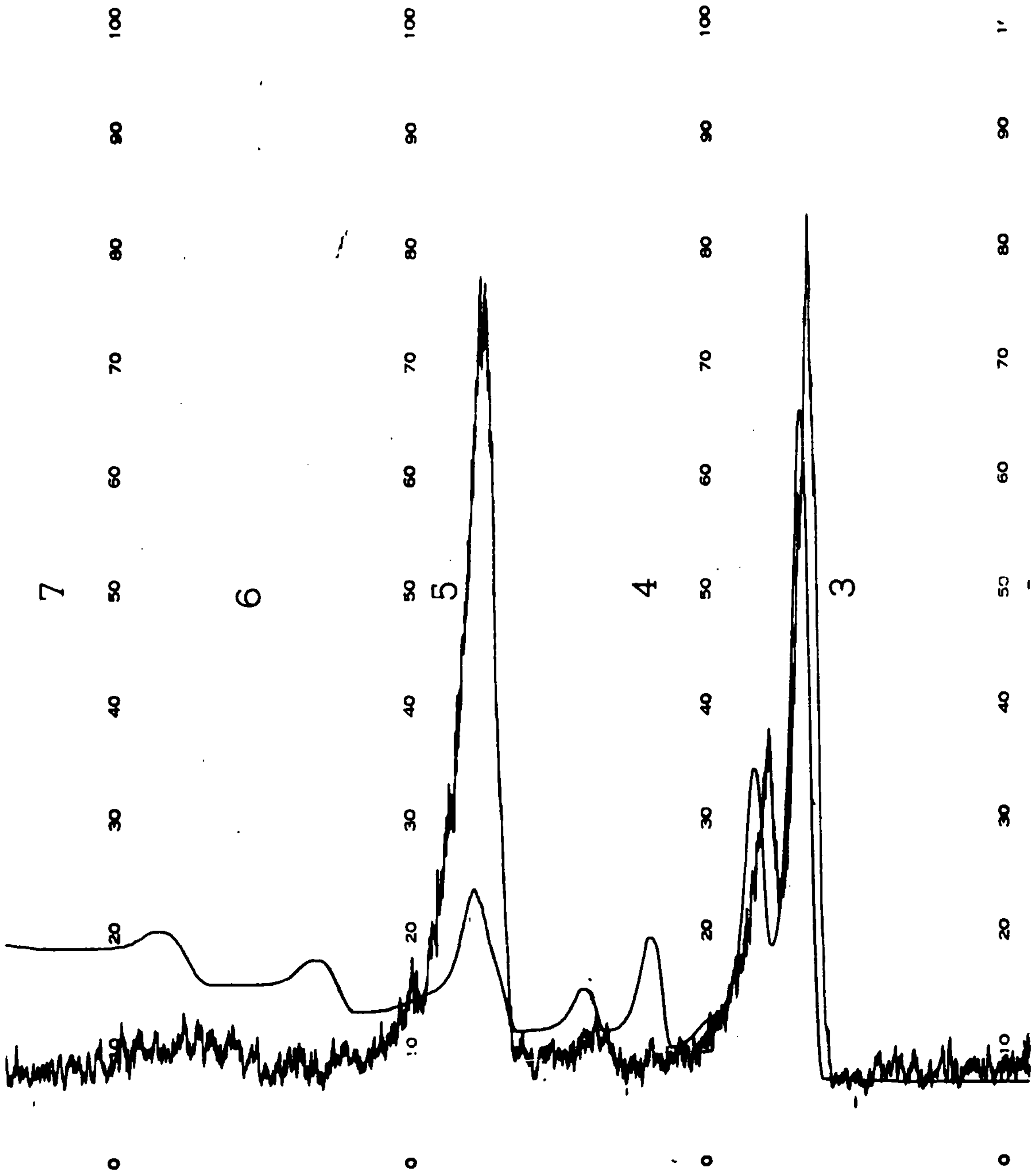
Run number	Column	$A^* \times 10^{-4}$	
		CH_4	C_2H_2
24	n-decane	0.21	1.6
25	n-decane	0.21	2.0
26	n-decane	0.12	1.9
35	silica gel	0.18	-
36	silica gel	0.21	-
58	DMS-DIDP	0.10	1.5
59	DMS-DIDP	0.14	1.6
60	DMS-DIDP	0.12	1.6
61	DMS-DIDP	0.15	1.6

2. Cyclohexane

The analysis with the n-decane column of the products resulting from the bombardment of cyclohexane indicated in the two runs studied that methane together with two and three carbon activity was produced. Three additional runs in which the ethylacetoacetate column (EAA) was employed confirmed the presence of methane and demonstrated the presence of an acetylene-isobutane activity peak. Ethane-ethylene and propylene-propyne activity peaks were also identified. No four carbon or propane activities were observed. Since the EAA column could not resolve the acetylene-isobutane, the ethane-ethylene, and the propylene-propyne peaks, it was necessary to analyze runs using other columns. Six runs with the silica gel column confirmed the production of methane and ethylene, and four of these runs indicated the production of ethane as well. The absence of ethane in the two runs is perhaps not surprising since in any case the amount produced was marginal, and for a run in which the amount of activity induced in the cyclohexane was small, there might easily be produced a non-observable amount of ethane activity. The identification of ethane activity in the four runs indicates that ethane is, indeed, produced in this system. The analysis of six runs with the DMS-DIDP column showed that the acetylene-isobutane peak was composed of only acetylene activity. Methane, ethane-ethylene, propylene, and four carbon activity peaks were also identified but no propane was observed. The four carbon activity which was observed in these runs and also in some runs which are described later may be any combination of the various four carbon hydrocarbons other than isobutane; however, no attempt was made to resolve this material in any run. Propyne was not analyzed for in this system.

Figure 9 shows a typical run made on the DMS-DIDP column. The sample injection point is on the right of the chart, and the plot of activity versus time indicated the presence of methane, ethane-ethylene, propylene, acetylene, and four carbon activity. The smooth curve is the thermal

Figure 9. Activity plot of Szilard-Chalmers products from cyclohexane at 30°C analyzed with a DMS-DIDP column


7
6
5
4
3
0
10
20
30
40
50
60
70
80
90
100

conductivity of the hydrocarbon carriers and the peaks are from the right methane, ethane-ethylene, propane, propylene, isobutane-acetylene, butane, and butene-1. In this particular run the isobutane and acetylene peaks were not clearly resolved; however, in other experiments a good resolution of these materials was achieved. The absence of propane activity is readily seen.

Figure 10 describes a typical activity plot obtained using a silica gel column. Three activity peaks, methane, ethane, and ethylene are observable here together with their corresponding thermal conductivity peaks. The injection point is on the right, and the peaks are read from this point across the chart. The first thermal conductivity peak can be neglected since it was caused by a scale change in the thermal conductivity sensitivity. The methane peak was recorded on the 30 K activity scale and the ethane and ethylene peaks were recorded on the 10 K activity scale.

The A^* values which were obtained from these runs are given in Table 2. The absence of entries in this table and others does not necessarily mean that the respective components were not observed. Frequently quantitative calculations were not made because the resolution of the peaks was not sufficiently distinct.

3. Hexane

Two runs in which the EAA column was used indicated the

Figure 10. Activity plot of Szilard-Chalmers products from cyclohexane at 30°C analyzed with a silica gel column

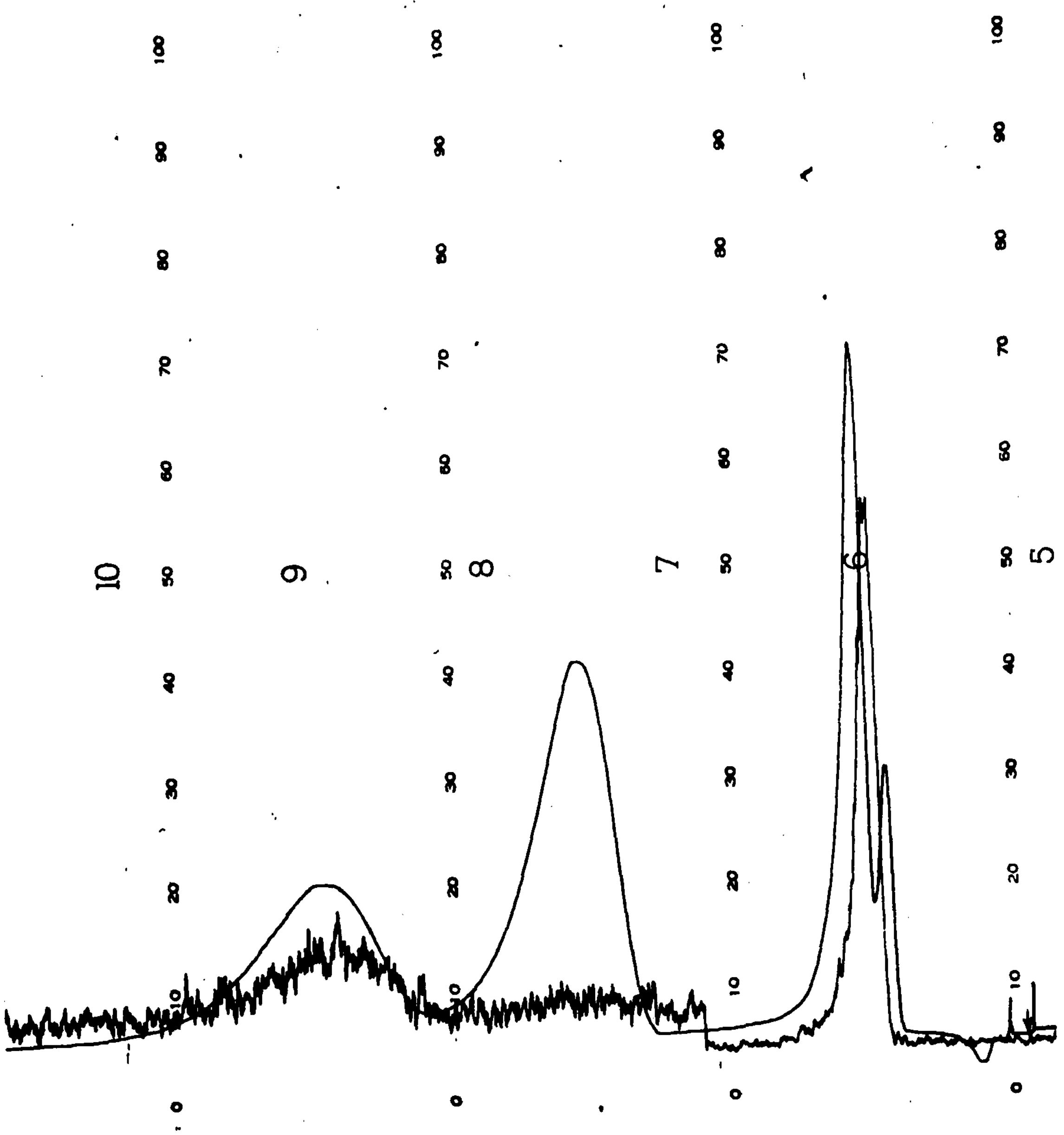

10
9
8
7
6
5
0
10
20
30
40
50
60
70
80
90
100

Table 2. Gaseous Szilard-Chalmers products from cyclohexane at 30°C

		$A^* \times 10^{-4}$					
Run number	Column	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_4's
32	EAA	-	-	-	3.6	0.13	-
33	EAA	-	-	-	4.1	0.21	-
44	silica gel	1.6	0.15	0.66	-	-	-
45	silica gel	2.1	0.19	0.80	-	-	-
69	DMS-DIDP	1.5	1.2[a]		3.8	0.34	0.54
70	DMS-DIDP	1.3	1.2[a]		3.5	0.29	0.52
71	DMS-DIDP	1.8	1.2[a]		4.6	0.23	0.57
72	DMS-DIDP	1.6	1.1[a]		3.9	0.28	0.45
75	silica gel	2.4	-	0.64	-	-	-
76	silica gel	2.3	-	0.77	-	-	-
77	silica gel	2.3	0.19	0.89	-	-	-
78	silica gel	1.8	0.20	0.80	-	-	-

[a] Combined ethane and ethylene peaks.

presence of methane, ethane-ethylene, propylene-propyne, acetylene-isobutane, and four carbon activity peaks. Analysis of four runs with the silica gel column established that both ethane and ethylene activity was produced along with methane activity. Nine runs made on the DMS-DIDP column indicated that acetylene, propylene, and four carbon activity were formed along with methane and ethane-ethylene activity. Isobutane activity was not observed and propane activity was observed in only two runs. The lack of identification of the propane in the other runs must be attributed either to its low activity or to a possible masking of the small propane peak by the relatively large neighboring ethane-ethylene or propylene peaks. No attempt was made to analyze for propyne.

Figure 11 shows the activity plot obtained from the analysis of a hexane sample with the DMS-DIDP column. The sample injection point is on the right and the smooth curve represents the plot of thermal conductivity of the carriers. The other curve is the activity plot. The thermal conductivity peaks are from right to left methane, ethane-ethylene, propane, propylene, isobutane, acetylene, and butane. The formation of methane, ethane-ethylene, propane, propylene, acetylene, and four carbon activity is clearly indicated.

Figure 12 shows the activity plot obtained with the silica gel column. The injection point is on the right and

Figure 11. Activity plot of Szilard-Chalmers products from n-hexane at 30°C analyzed with a DMS-DIDP column

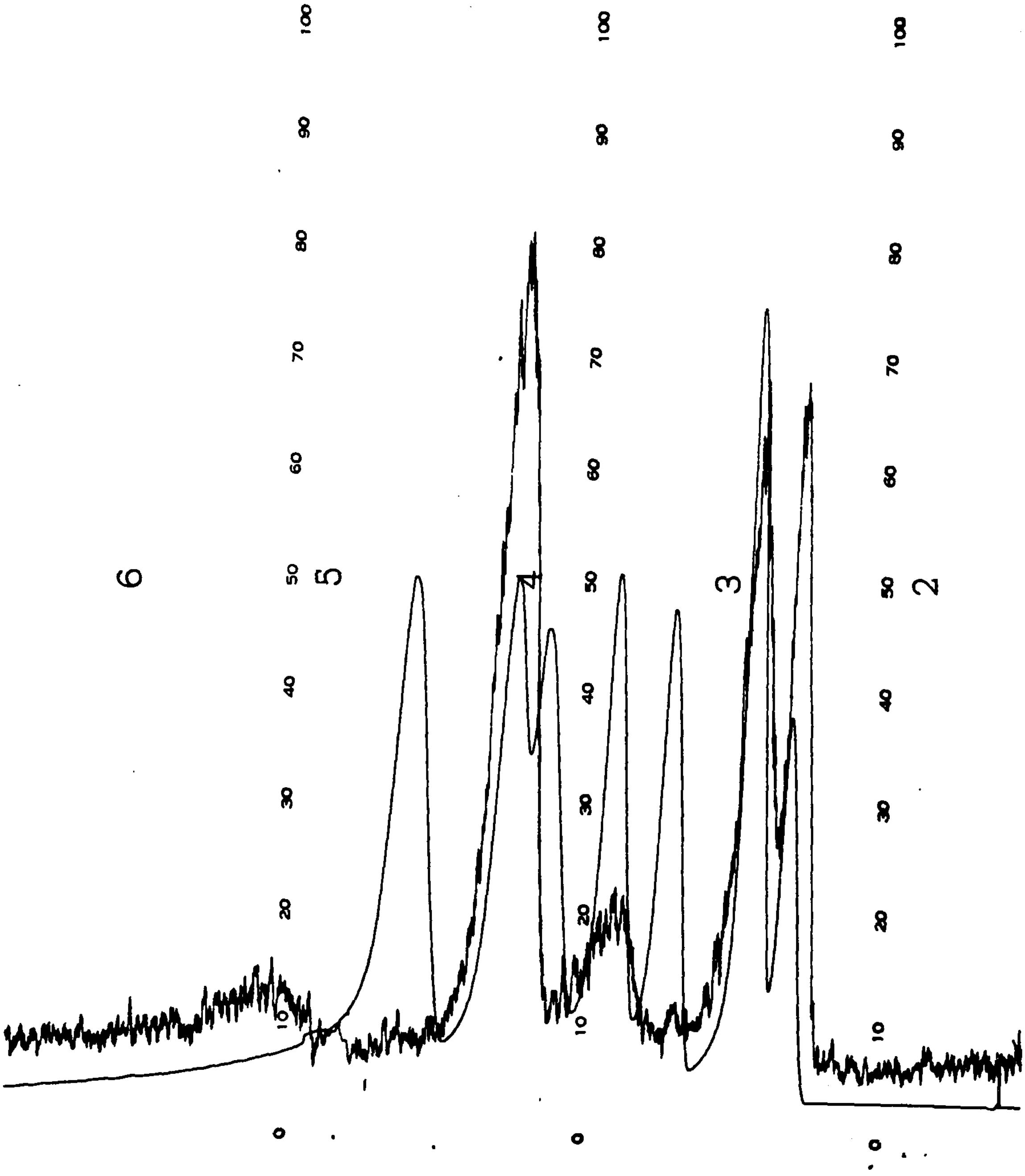
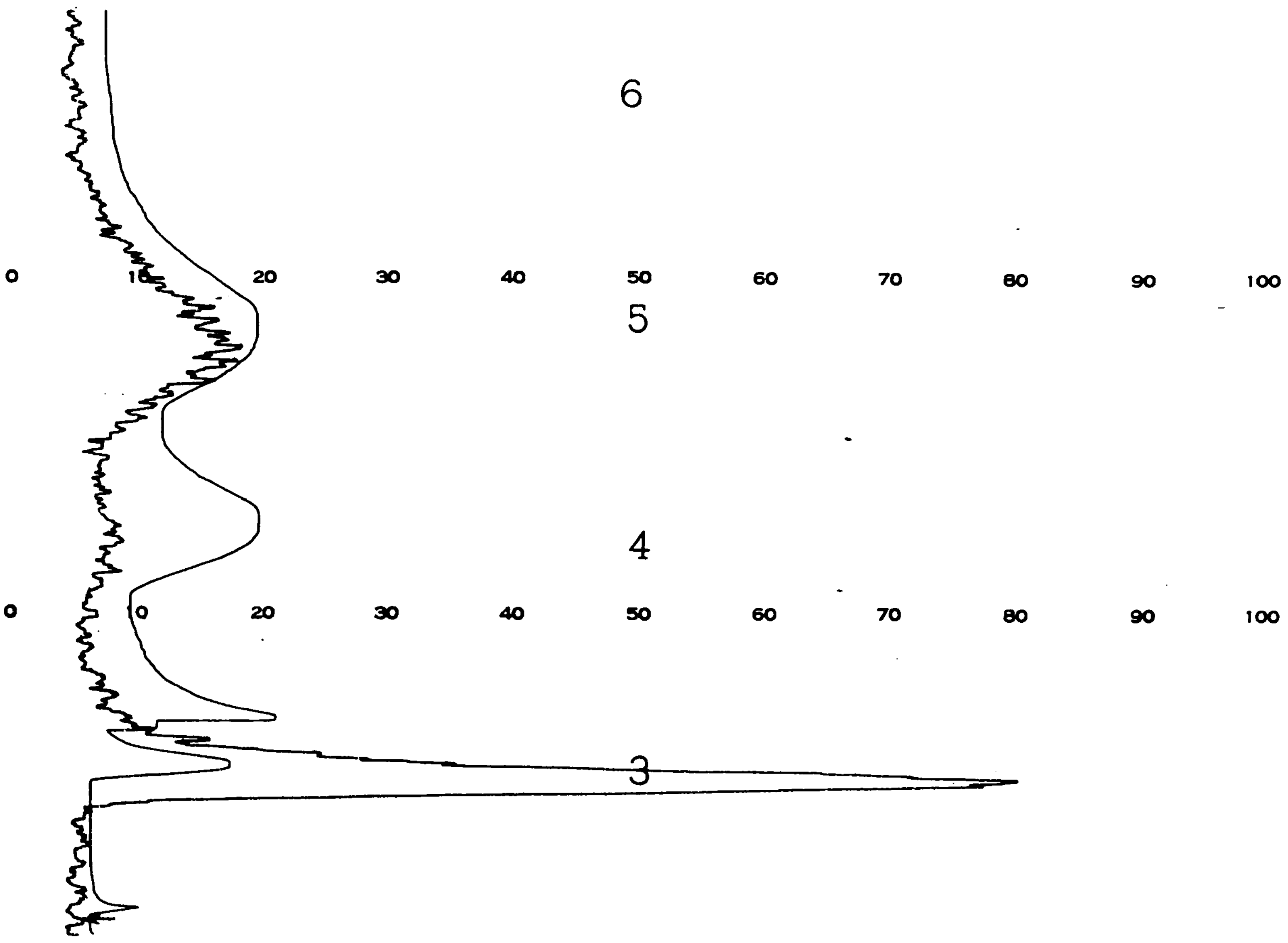

6
5
4
3
2
0
10
20
30
40
50
60
70
80
90
100

Figure 12. Activity plot of Szilard-Chalmers products from n-hexane at 30°C analyzed with a silica gel column


6
0
10
20
30
40
50
60
70
80
90
100
5
4
0
10
20
30
40
50
60
70
80
90
100
3

the smooth curve is the thermal conductivity of the carriers. The first thermal conductivity peak reading from the right is methane. The next peak is a pseudo-peak induced by a sensitivity change. The ethane and ethylene thermal conductivity peaks follow. The presence of methane, ethane, and ethylene activity is indicated.

The A^* values obtained for hexane are listed in Table 3.

C. Runs at 0°C

1. Benzene

Benzene which was bombarded at 0°C was analyzed with the DMS-DIDP column. The four runs indicated that acetylene activity was produced. No methane, ethane, ethylene, propane, propylene, isobutane, or four carbon activity was produced and an analysis for propyne was not made.

The values of A^* which were obtained from the runs are given in Table 4.

2. Cyclohexane

Seven runs were made using the DMS-DIDP column. All of these runs indicated the production of methane, ethane-ethylene, propylene, acetylene, and four carbon activity; however, no propane was observed and no analysis for propyne was made. The silica gel was used in five runs and in each case methane activity was observed. In four of the runs ethylene was observed and in one of these four a small ethane

Table 3. Gaseous Szilard-Chalmers products from n-hexane at 30°C

		A* x 10^{-4}						
Run number	Column	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4's
34	EAA	-	-	-	3.6	-	0.57	-
40	silica gel	1.6	0.21	1.6	-	-	-	-
41	silica gel	1.8	0.26	1.7	-	-	-	-
42	silica gel	1.8	0.24	1.7	-	-	-	-
43	silica gel	1.9	0.37	1.7	-	-	-	-
51	DMS-DIDP	1.0	-	-	4.5	-	1.2	1.4
55	DMS-DIDP	2.0	1.4[a]		2.8	0.10	0.66	0.61
56	DMS-DIDP	1.2	1.6[a]		3.4	0.17	0.73	0.96
65	DMS-DIDP	1.5	2.2[a]		4.2	-	0.89	0.73
66	DMS-DIDP	1.5	2.6[a]		5.0	-	0.91	0.85
67	DMS-DIDP	1.3	2.3[a]		4.3	-	0.94	0.71
68	DMS-DIDP	1.4	2.1[a]		4.1	-	0.86	0.72

[a] Combined ethane and ethylene peaks.

Table 4. Gaseous Szilard-Chalmers products from benzene at 0°C

Run number	Column	$A^* \times 10^{-4}$ C_2H_2
104	DMS-DIDP	1.3
105	DMS-DIDP	1.2
117	DMS-DIDP	1.5
118	DMS-DIDP	0.86

peak was observed. It is difficult from the data available to identify ethane as a definite product in the 0°C cyclohexane system.

The A^* values which were obtained from these runs are listed in Table 5.

D. Runs at -78°C

1. Benzene

Four bombardments of benzene at -78°C were made, and the products were analyzed with the DMS-DIDP column. The only product which was observed was acetylene. No methane, ethylene, propane, propylene, isobutane, or four carbon activity was recorded and no analysis for propyne was made.

The A^* values which were obtained from these runs are

Table 5. Gaseous Szilard-Chalmers products from cyclohexane at 0°C

		$A^{*} \times 10^{-4}$					
Run number	Column	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_4's
106	DMS-DIDP	-	-	-	4.4	0.31	1.0
109	silica gel	1.7	-	0.60	-	-	-
110	silica gel	1.7	0.08	0.60	-	-	-
112	silica gel	1.7	-	-	-	-	-
113	silica gel	1.6	-	0.51	-	-	-
114	silica gel	1.3	-	0.46	-	-	-
119	DMS-DIDP	1.0	-	0.74	2.0	0.25	0.45
120	DMS-DIDP	-	-	-	2.9	0.22	0.48
121	DMS-DIDP	-	-	-	2.5	0.35	0.74
122	DMS-DIDP	-	-	-	2.8	0.24	0.52
123	DMS-DIDP	-	-	-	3.2	0.34	0.63

given in Table 6.

Table 6. Gaseous Szilard-Chalmers products from benzene at -78°C

Run number	Column	$A^* \times 10^{-4}$ C_2H_2
97	DMS-DIDP	0.94
98	DMS-DIDP	0.83
99	DMS-DIDP	0.97
103	DMS-DIDP	0.82

2. Cyclohexane

Five runs were made and analyzed with the DMS-DIDP column. In all of these runs methane, ethane-ethylene, propylene, and acetylene activity peaks were observed; however, in no case was propane or isobutane observed. Since a very small four carbon activity peak was observed in only one run, it can not be said with certainty that this observation makes a positive identification of four carbon material as a product in this system. In four runs which employed the silica gel column methane activity was observed and in three of these runs ethylene was also observed. The absence of ethylene in a single run does not mitigate against the positive identification of this material as a product in the cyclohexane system.

The A^* values for these runs are given in Table 7.

E. Liquid Products

1. Introduction

Several irradiations were made on benzene, cyclohexane, and hexane at room temperature in order to determine the qualitative nature of the liquid products. The analysis procedure was similar to that described previously except that a dioctylphthalate column was used, and a 0.1 ml sample was introduced directly into the column. In most cases the liquid sample was degassed in order to insure the removal of dissolved gaseous products. The dioctylphthalate column resolves hexane, cyclohexane, benzene, and toluene in that order as a function of retention time.

2. Benzene

Two runs were made in which a benzene activity peak was observed as well as an additional peak having a longer retention time. The benzene activity peak followed the benzene thermal conductivity peak. This was also the case with the hexane and cyclohexane peaks in the hexane and cyclohexane runs respectively. This order of activity peak to thermal conductivity peak was opposite to that which was observed in the gaseous activity runs. In one of these runs carrier toluene was added before the analysis, and it is possible that the peak of higher retention may be attributed

Table 7. Gaseous Szilard-Chalmers products from cyclohexane at -78°C

				$A^* \times 10^{-4}$		
Run number	Column	CH_4	C_2H_4	C_2H_2	C_3H_6	C_4's
96	DMS-DIDP	-	-	1.4	0.28	0.36
100	DMS-DIDP	-	-	1.5	0.33	-
101	DMS-DIDP	-	-	1.0	0.13	-
102	DMS-DIDP	-	-	0.69	0.21	-
115	silica gel	1.7	0.34	-	-	-
116	silica gel	1.5	0.52	-	-	-
124	silica gel	1.7	0.58	-	-	-
125	silica gel	1.5	-	-	-	-

to toluene.

Three additional runs were made, and the activity peak structure was the same as that observed in the previous runs except that a small activity peak preceded the benzene activity peak. In one of these runs carrier cyclohexane, hexane, and toluene were added prior to the analysis. This small activity peak can not be attributed to either cyclohexane or hexane since the activity peak preceded both of these thermal conductivity peaks. Again there is evidence that the final activity peak may be toluene.

One other run was made in which an attempt was made in order to check the possibility that the small activity peak could be due to gaseous activity products. The analysis procedure was exactly the same as that employed in the gaseous activity runs except that the dioctylphthalate column was used. The run indicated that the gaseous products were, indeed, resolved and also that the retention time was short and could possibly correspond with that of the small activity peak.

3. Cyclohexane

Four runs were made in which the cyclohexane activity peak was observed. In addition two rather large peaks were observed to follow the cyclohexane peak. Also in two of these runs an additional small peak with longer retention time was observed. In one of these runs carrier hexane, benzene, and toluene were added before the analysis. The run indicated that the first part of the double type peak may be benzene. In this case the small final peak was not observable, and, consequently, no comparison of this peak to the thermal conductivity position of toluene could be made; however, in another of these runs carrier toluene was added and the results indicate that the final small peak may be toluene.

4. Hexane

Three runs were made in which the hexane activity peak was observed. In addition a large double type peak was observed to follow the hexane peak.

Two additional runs were made, and the activity peak structure was essentially the same as that observed in the previous runs. In both of these runs the total amount of activity was considerably less than that in the previous runs, and consequently, it was difficult to establish the structure of these peaks with good precision. In one of these runs carriers cyclohexane, toluene, and benzene were added before the analysis. It seems likely that the double type peak is due in part to cyclohexane; however, little can be said about the contribution of benzene and toluene.

V. DISCUSSION

A. Summary

1. Introduction

The results which were obtained in the irradiation of benzene are summarized in Table 8 and of cyclohexane and n-hexane in Table 9. The values listed are averages of the number of determinations which is given in the parentheses before the listings. The errors listed are standard deviations.

Table 8. Average A* values for the products from benzene

	A* x 10^{-4}		
Product	30°C	0°C	-78°C
Methane	(9) 0.16 ± 0.04	-	-
Acetylene	(7) 1.7 ± 0.2	(4) 1.2 ± 0.2	(4) 0.89 ± 0.07

2. Benzene

The only gaseous products which were observed in the benzene system at room temperature were methane and acetylene, with about ten times as much acetylene produced as methane.

With a change in phase from liquid to solid methane was no longer observable, and the acetylene activity was reduced.

Table 9. Average A^* values for the products from cyclohexane and hexane

	$A^* \times 10^{-4}$			
	Cyclohexane			Hexane
Product	30°C	0°C	-78°C	30°C
Methane	(10) 1.9 ± 0.4	(6) 1.5 ± 0.3	(4) 1.6 ± 0.1	(11) 1.5 ± 0.3
Ethane	(4) 0.18 ± 0.02	(1) 0.08	-	(4) 0.27 ± 0.06
	(4) 1.2 ± 0.1	-	-	(6) 2.0 ± 0.4
Ethylene	(6) 0.76 ± 0.09	(5) 0.58 ± 0.11	(3) 0.48 ± 0.10	(4) 1.7 ± 0.1
Acetylene	(6) 3.9 ± 0.4	(6) 3.0 ± 0.7	(4) 1.2 ± 0.3	(8) 4.0 ± 0.6
Propane	-	-	-	(2) 0.14 ± 0.04
Propylene	(6) 0.25 ± 0.07	(6) 0.28 ± 0.05	(4) 0.24 ± 0.08	(8) 0.84 ± 0.18
4-Carbon	(4) 0.52 ± 0.05	(6) 0.64 ± 0.19	(1) 0.36	(7) 0.85 ± 0.25

A further reduction in the amount of acetylene was observed with a decrease in the temperature in the solid phase. According to Libby's theory (13) methane and acetylene should be produced by means of an epithermal process, and, consequently, the amount of these materials should be enhanced in the solid phase. On the other hand, the phase effect results for the benzene system agrees with the Willard theory (16) which states that either an increase or decrease in the amounts of the various products is possible with a change in phase.

The liquid products runs established the formation of benzene and also at least one other material of intermediate molecular weight, which is quite likely toluene. These results agree in a qualitative sense with those reported by Suryanarayana and Wolf (36) who observed the formation of benzene-C^{11} and toluene-C^{11} as a result of the $C^{12}(n, 2n)C^{11}$ reaction in benzene.

3. Cyclohexane

The diversity of gaseous products from the irradiation of liquid cyclohexane is much wider than that for the liquid benzene system. In addition to methane and acetylene activity, ethane, ethylene, propylene, and four carbon compounds were observed. Also the amounts of methane and acetylene were larger for cyclohexane than for benzene. Ten times as much methane and about two times as much acetylene were produced in cyclohexane than in benzene. The next most abundant products were, respectively, ethylene and four carbon material. Ethane and propylene, the least prevalent products, were produced in about equal amounts.

The phase studies showed that methane, acetylene, ethane, and ethylene all decreased in amount with a change from the liquid to solid phase. In the case of ethane no activity at all was observable at -78°C. Methane, ethylene, and acetylene also decreased with a decrease in temperature in the solid state. The amount of propylene produced was apparently constant with respect to both phase and temperature. The four carbon material appeared to increase with a change in phase and then dropped with a decrease in temperature in the solid state. Although this behavior for the four carbon is possible, it seems unlikely in face of the behavior of the other products especially when the standard deviation of the four carbon 0°C value is taken into consideration. In all cases except possibly for that of the propylene, the phase effect which was observed is contrary to the phase effect predicted by the Libby theory, but in agreement with the Willard theory. Just as in the case of the benzene products the gaseous products in the cyclohexane system should in terms of Libby's theory result from epithermal processes and, consequently, should be enhanced in going from the liquid to solid state.

Product diversity was also evident in the liquid products. Active cyclohexane together with at least three other compounds of intermediate molecular weight were observed.

4. Hexane

Of the three materials studied n-hexane provided the largest number of gaseous products together with the greatest abundance of these products in almost every case. Only in the case of methane was the amount produced in n-hexane less than the corresponding amount in cyclohexane. The major product was acetylene followed by ethylene, methane, four carbon, propylene, ethane, and propane. The four carbon and propylene amounts were about the same.

The liquid products runs showed the formation of hexane activity together with at least two other components of intermediate molecular weight.

No phase or temperature studies were made on hexane because the low temperature at which n-hexane freezes, -94°C, could not be held for a significantly long enough time under the bombardment conditions used in these experiments.

B. Interpretation

A question which is common to all Szilard-Chalmers studies is, What determines the nature of the products, and by what mechanisms are the products formed? It can be said with confidence that this question has never been satisfactorily answered in any particular Szilard-Chalmers investigation although many attempts to do so have been made.

The reason why no unequivocal answer has ever been obtained is because of the complexity of the systems together with the paucity of observables available to the investigator. In a typical Szilard-Chalmers system a recoil atom is born with a high energy together with a positive charge. The recoil atom then proceeds to lose this energy in a series of collisions with the molecules of the medium in which ionization and excitation processes occur. Eventually the recoil atom is slowed down to near thermal energy and may participate in a number of processes including charge neutralization reactions, radical reactions, and reactions with molecules. The recoil atom may escape reaction at this point and instead proceed on and become thermalized. As a thermal species it may participate in radical reactions or react with molecules, and in some systems it may even escape reaction altogether. The only observable available to the investigator, with the possible exception of some information regarding charge distribution, is the radioactive products formed. He had no knowledge of the fate of the molecular residue from which the recoil atom originated or of the many non-radioactive products which must be produced as a consequence of the molecular destructions caused by the slowing down of the recoil atom, the charge neutralization processes, and both the hot and cold radical reactions which simultaneously yield radioactive and non-radioactive products. Likewise, he has no direct information concerning the slowing down process itself or of the competition of various reactions which lead to the products. The investigator must instead construct his theory from the deductions which he can make from the distribution and amounts of the products which he can observe together with what additional information he obtained from phase, temperature, and scavenger studies. In spite of the limitations inherent in Szilard-Chalmers studies each investigator has in his own way added something to the answer of the aforesaid question, and no doubt future studies will result in eventual complete realization of the answer to this question. It is consequently, important to consider this question in relation to the study which is reported here. Also an additional question which is raised in regard to this research and which must be considered is, On what basis can the differences in the product distributions between benzene, cyclohexane, and hexane be rationalized?

The energy of recoil can be calculated for an atom resulting from a (γ, n) reaction by means of the following equation in which the momentum imparted to the atom by the impinging gamma ray is neglected (43).

$$E_r = (E + Q)\,\frac{m}{m + M} \qquad (5)$$

where,

E_r = recoil energy.

E = energy of the gamma ray.

Q = energy released in the nuclear reaction.

m = neutron mass.

M = recoil atom mass.

For carbon-11 with Q equal to -18.7 Mev and E at the cross section peak equal to 22 Mev (37), E_r has a value of 0.35 Mev.

If the recoil atom does not sever all of its bonds in the recoil process, a portion of the energy appears as internal energy of the complex. The internal energy can be calculated from the following expression (44).

$$E_i = E_r \frac{M'}{M + M'} \qquad (6)$$

where

E_i = internal energy of the complex.

E_r = recoil energy of the atom.

M' = mass of the substituents on the recoil atom.

M = mass of the recoil atom.

Even in most favorable cases where M' equals one, hydrogen, the internal energy of carbon-11 recoil complex would be about 30,000 ev which is greatly in excess of the 4 ev carbon-hydrogen bond energy. Consequently, rupture of all substituents to the carbon-11 is assured.

The unbonded carbon-11 recoil atom is undoubtedly ionized as a result of its high kinetic energy. The energy of an electron having the same velocity as the recoiling atom is given by

$$E_e = \frac{m}{M} E_r \tag{7}$$

where,

E_e = energy of the electron.

E_r = energy of the recoil atom.

m = mass of the electron.

M = mass of the recoil atom.

If E_e is near the binding energy E_B of an electron there will be a finite probability for electron loss by the moving atom. This probability reaches a maximum for E_e equal to E_B and falls off for E_e less than E_B (45). Taking the first, second, and third ionization potentials of carbon in ev's as 11.3, 24.4, and 47.9 (46) the minimum values of the recoil energy necessary to produce the first, second and third electron loss are respectively 0.23 Mev, 0.49 Mev, and 0.98 Mev. On this basis a charge of +1 seems certain but charges of greater than +2 are quite unlikely.

Consequently one can envision in the three systems studied the production of carbon-11 recoil atoms with initial energy of about 0.35 Mev and charge of +1 or possibly +2. These recoil atoms slow down dissipating their energy by a combination of ionization and excitation processes together with radical producing collisions. When the recoil atoms energy drops below about 48 ev formation of carbon-hydrogen complexes is possible since the internal energy would be only about 4 ev. There is no paucity of hydrogen atoms in the benzene, cyclohexane, and hexane; consequently, formation of carbon-11-hydrogen complexes of the form $C^{11}H$, $C^{11}H_2$, and $C^{11}H_3$ is to be expected in the slowing down process. The corresponding singly charged species are also possible; however, only for $C^{11}H_3$ in cyclohexane and hexane and possibly for $C^{11}H$ in cyclohexane are the ionization potentials for the formation of $C^{11}H_3$ and $C^{11}H$ lower than those for the respective parent materials (47).

Assuming, then, that the carbon-11 recoil atoms are incorporated into various hydrogen complexes when they reach the end of their path, it is possible to construct a possible mechanism by which the observed Szilard-Chalmers chemistry of liquid hexane and liquid cyclohexane is rationalized using the Willard "random fragmentation" theory. That is, it is assumed that the products are produced as a result of reactions of $C^{11}H$, $C^{11}H_2$, and $C^{11}H_3$ with free radicals which the carbon-11 produces in the slowing down process. These reactions may occur either in the hot or thermal regions. In the absence of scavenger experiments it is not possible to assess the relative contribution of these hot and thermal reactions; it is assumed that both types of processes occur.

It is difficult to explain the formation of acetylene in terms of any radical mechanism except one which involves $C^{11}H$

radicals. Furthermore, the production of CH_2 radicals in the slowing down of the recoil atoms in both hexane and cyclohexane is possible. Interaction of $C^{11}H$ with CH_2 in a hot process,

$$:\underset{\cdot}{C}^{11}H + :CH_2 \longrightarrow \cdot C^{11}H = CH_2 \longrightarrow C^{11}H \equiv CH + H\cdot \quad (8)$$

is suggested as a possible synthesis path for acetylene. Since CH_2 could also react with $C^{11}H_3$ by means of,

$$:C^{11}H_2 + :CH_2 \longrightarrow C^{11}H_2 = CH_2 \quad (9)$$

$$\begin{tikzcd}
\cdot C^{11}H_3 + :CH_2 \arrow[r] & C^{11}H_3 - \underset{\cdot}{C}H_2 \arrow[r, "H\cdot"] \arrow[dr] & C^{11}H_3 - CH_3 \quad (10) \\
 & & C^{11}H_2 = CH_2 + H\cdot \quad (11)
\end{tikzcd}$$

it seems unlikely on the basis of the small ethane and ethylene yields compared to acetylene in both the hexane and cyclohexane system that the abundance of $C^{11}H_2$ and $C^{11}H_3$ is very large in either system. On this basis the most prevalent carbon-11-hydrogen recoil complex is assumed to be $C^{11}H$. Reactions of the type,

$$\cdot CH_3 + :\underset{\cdot}{C}^{11}H \longrightarrow CH_3 - \underset{\cdot\cdot}{C}^{11}H \longrightarrow CH_2 = C^{11}H_2 \quad (12)$$

$$\begin{tikzcd}
R - \underset{\cdot}{C}H_2 + :\underset{\cdot}{C}^{11}H \arrow[r, dash] & R - CH_2 - \underset{\cdot\cdot}{C}^{11}H \arrow[dl] & \\
R - CH = C^{11}H_2 & & (13)
\end{tikzcd}$$

which are certainly possible with hot $C^{11}H$ radicals and also possible with cold radicals are postulated as the possible mechanism for the production of unsaturated materials. Methyl, ethyl, and propyl radicals are undoubtedly prevalent in the hexane system, as they are in electron radiolysis of hexane (48), and can no doubt be produced from cyclohexane by multiple bond rupture together with subsequent hydrogen abstraction. In both hexane and cyclohexane butyl, pentyl, and hexyl radicals should be possible and would if reaction 13 is correct lead to unsaturated materials of five, six, and seven carbon skeletons. In addition in the cyclohexane system cyclohexyl radicals are no doubt produced and could lead to formation of substituted cyclohexane products. It is quite possible that these higher carbon compounds contribute to the liquid products which were observed in both cyclohexane and hexane. Reactions of the types,

$$\cdot CH_3 + :C^{11}H_2 \longrightarrow CH_3 - \underset{\cdot}{C}{}^{11}H_2 \xrightarrow{H\cdot} CH_3 - C^{11}H_3 \tag{14}$$

$$\longrightarrow CH_2 = C^{11}H_2 + H\cdot \tag{15}$$

$$R - \underset{\cdot}{C}H_2 + :C^{11}H_2 \longrightarrow R - CH_2 - \underset{\cdot}{C}{}^{11}H_2 \xrightarrow{H\cdot}$$

$$R - CH_2 - C^{11}H_3 \tag{16}$$

$$\longrightarrow CH_2 = C^{11}H_2 + R\cdot \tag{17}$$

$$\cdot CH_3 + \cdot C^{11}H_3 \longrightarrow CH_3 - C^{11}H_3 \tag{18}$$

$$R - \underset{\cdot}{C}H_2 + \cdot C^{11}H_3 \longrightarrow R - CH_2 - C^{11}H_3 \tag{19}$$

are postulated to occur to a lesser extent. The reactions which lead to ethylene are known to occur in hot processes (49) whereas those which lead to the saturated materials may proceed in the thermal region. Since $C^{11}H_2$ and $C^{11}H_3$ are assumed to be much less prevalent than $C^{11}H$, the unsaturated compounds of C_3's and higher, reaction 13, are favored over the corresponding saturated materials, reactions 16 and 19. This is in agreement with the relative yields of propane and propylene in both the hexane and cyclohexane cases. Reaction 19 could account for the observed hexane-C^{11} in the hexane system. Ethylene is favored by a number of reaction paths, 9, 11, 12, 15, and 17 and, consequently, the rather large yields of ethylene in both cyclohexane and hexane is expected. Presumably methane is produced from all three carbon-11 complexes, $C^{11}H$, $C^{11}H_2$, and $C^{11}H_3$ by means of hydrogen abstraction in either thermal or "hot" processes. The lower yields of most of the gaseous products in the cyclohexane system relative to the hexane system is probably due to the relatively fewer methyl, ethyl, and propyl, radicals which are produced in the cyclohexane. Production of these species in cyclohexane involves rupture of two bonds together with subsequent hydrogen abstraction whereas a single bond rupture yields these radicals in hexane. The formation of cyclohexane-C^{11} is possible by means of reaction of $C^{11}H_2$ with a pentyl diradical with subsequent cyclization.

Assuming that the gaseous products in the benzene system result from an interaction of carbon-11-hydrogen complexes with radicals, the striking contrast of the liquid benzene results compared to those of either hexane or cyclohexane is perhaps not surprising in view of the well known stability of benzene to radiation damage (50). If acetylene is produced by reaction 8 or possibly by

$$:\underset{\cdot}{C}{}^{11}H + :\underset{\cdot}{C}H \longrightarrow CH\equiv C^{11}H \tag{20}$$

$$:C^{11}H_2 + :\underset{\cdot}{C}H \longrightarrow C^{11}H_2{=}\underset{\cdot}{C}H \qquad C^{11}H\equiv CH + H\cdot \tag{21}$$

it would seem that $C^{11}H$ or $C^{11}H_2$ ought to react with other radicals which are produced in addition to CH or CH_2 to give a diversity of products. The absence of the observation of product diversity for benzene is difficult to rationalize on this basis unless for some reason, perhaps associated with the radiation stability of benzene, the concentration of radicals other than CH or CH_2 is very small.

Methane can be accounted for by successive hydrogen abstractions of the carbon-11-hydrogen complexes in either "hot" or thermal processes. It is somewhat difficult to see how benzene-C^{11} could be formed by a radical mechanism; however, Suryanarayana and Wolf (36) attribute this type of mechanism to be responsible for the formation of benzene-C^{11} in the $C^{12}(n, 2n)C^{11}$ activation in benzene. These authors also attribute the formation of the toluene-C^{11}

which they observed to a reaction of $C^{11}H_2$ with benzene and this mechanism may be responsible for the formation of toluene which was observed in this study.

VI. BIBLIOGRAPHY

1. Brooks, H., Nature, 70, 270 (1904).

2. Russ, S. and Makower, W., Proc. Roy. Soc. (London), A82, 205 (1909).

3. Fermi, E., Amaldi, E., D'Agostino, O., Rasetti, F., and Segrè, E., Proc. Roy. Soc. (London), A146, 483 (1934).

4. Szilard, L. and Chalmers, T. A., Nature, 134, 462 (1934).

5. Amaldi, E., D'Agostino, O., Fermi, E., Pontecorve, B., Rasetti, F., and Segrè, E., Proc. Roy. Soc. (London), A149, 522 (1935).

6. Fay, J. W. J. and Paneth, F. A., J. Chem. Soc., 384 (1936).

7. Glückauf, E. and Fay, J. W. J., J. Chem. Soc., 390 (1936).

8. Libby, W. F., Science, 93, 283 (1941).

9. Suess, H., Z. physik. Chem., B45, 297 (1939).

10. Lu, C. S. and Sugden, S., J. Chem. Soc., 1273 (1939).

11. Libby, W. F., J. Am. Chem. Soc., 62, 1930 (1940).

12. Libby, W. F., J. Am. Chem. Soc., 69, 2523 (1947).

13. Friedman, L. and Libby, W. F., J. Chem. Phys., 17, 647 (1949).

14. Miller, J. M., Gryder, J. W., and Dodson, R. W., J. Chem. Phys., 18, 579 (1950).

15. Miller, J. M. and Dodson, R. W., J. Chem. Phys., 18, 865 (1950).

16. Willard, J. E., Ann. Rev. Nuclear Sci., 3, 193 (1953).

17. Harbottle, G. and Sutin, N., Adv. in Inorg. Chem. and Radiochem., 1, 267 (1959).

18. Levey, G. and Willard, J. E., J. Am. Chem. Soc., 74,

6161 (1952).

19. Goldhaber, S. and Willard, J. E., J. Am. Chem. Soc., 74, 318 (1952).

20. Hibdon, C. T. and Muehlhause, C. O., Phys. Rev., 88, 943 (1952).

21. Yosim, S. and Davies, T. H., J. Phys. Chem., 56, 599 (1952).

22. Hornig, J. F., Levey, G. and Willard, J. E., J. Chem. Phys., 20, 1556 (1952).

23. Holmes, O. G. and McCallum, K. J., J. Am. Chem. Soc., 72, 5319 (1950).

24. Duffield, R. B. and Calvin, M., J. Am. Chem. Soc., 68, 1129 (1946).

25. Collins, K. C., Photonuclear activation of cobalt in solid coordination compounds. Unpublished M. S. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955.

26. Zuber, A., Chemical effects of neutron capture in some cobaltic hexamines. Unpublished Ph. D. Thesis. New York, N. Y., Library, Columbia University. 1954.

27. Schuler, R. H., J. Chem. Phys., 22, 2026 (1954).

28. Levey, G. and Willard, J. E., J. Am. Chem. Soc., 74, 6161 (1952).

29. McCauley, C. E., Hilsdorf, G. J., Geissler, R. R., and Schuler, R. H., J. Am. Chem. Soc., 78, 3246 (1956).

30. Evans, J. B. and Willard, J. E., J. Am. Chem. Soc., 78, 2909 (1956).

31. Evans, J. B., Quinlan, J. E., Sauer, M. C., and Willard, J. E., J. Phys. Chem., 62, 1351 (1958).

32. Gordus, A. A. and Willard, J. E., J. Am. Chem. Soc., 79, 4609 (1957).

33. Rowland, F. S. and Libby, W. F., J. Chem. Phys., 21, 1493 (1953).

34. Sharman, L. J. and McCallum, K. J., J. Am. Chem. Soc.,

77, 2989 (1955).

35. Edwards, W. J. and McCallum, K. J., Can. J. Chem., 34, 189 (1956).

36. Suryanarayana, B. and Wolf, A. P., J. Phys. Chem., 62, 1369 (1958).

37. Montalbetti, R., Katz, L., and Goldemberg, J., Phys. Rev., 91, 659 (1953).

38. Smith, J. H. C. and Cowie, D. B., J. Appl. Phys., 12, 78 (1941).

39. Keulemans, A. I. M., Gas chromatography. 1st ed. New York, N. Y., Reinhold Publishing Corp. 1957.

40. Phillips, C., Gas chromatography. London, England, Butterworths Scientific Publications. 1956.

41. Wolfgang, R. and Rowland, F. S., Anal. Chem., 30, 903 (1958).

42. Fredericks, E. M. and Brooks, F. R., Anal. Chem., 28, 297 (1956).

43. Barnes, J. W., Burgus, W. H., and Miskel, J. A. Chemical phenomena accompanying nuclear reactions. In Wahl, A. C. and Bonner, N. A., eds. Radioactivity applied to chemistry. pp. 244-283. New York, N. Y., John Wiley and Sons, Inc. 1951.

44. Suess, H., Z. physik. Chem., B45, 312 (1940).

45. Seitz, F. and Koehler, J. S. Displacement of atoms during irradiation. In Seitz, F. and Turnbull, D., eds. Solid state physics. Vol 2. pp. 307-442. New York, N. Y., Academic Press, Inc. 1956.

46. Moore, C. E. Atomic energy levels. National Bureau of Standards Circular No. 467. 1949.

47. Field, F. H. and Franklin, J. L. Impact phenomena. New York, N. Y., Academic Press, Inc. 1957.

48. Dewhurst, H. A., J. Phys. Chem., 62, 15 (1958).

49. Royals, E. E. Advanced organic chemistry. Englewood Cliffs, N. J., Prentice-Hall, Inc. 1954.

50. Inokuti, M., Isotopes and Radiation, 1, No. 1 (1958).

VII. ACKNOWLEDGMENTS

The author wishes to acknowledge with sincere gratitude the guidance of Dr. A. F. Voigt during the course of this investigation.

The author also wishes to thank Mr. Richard Clark and Mr. Wayne Stensland for their many valuable suggestions concerning the chromatographic and counting systems and Mr. Joseph Kivel for preparation of some of the columns and for many suggestions made during the course of the investigation.

Special appreciation is extended to Mr. Dale DeVries for his assistance during the many synchrotron irradiations that were conducted.