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The effect of oxygen on the recoil reactions of carbon-11 in hydrocarbons

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THE EFFECT OF OXYGEN ON THE RECOIL REACTIONS
OF CARBON-11 IN HYDROCARBONS

by

Dale Byron De Vries

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

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INTRODUCTION

Hot-Atom Chemistry

The term hot-atom chemistry is used to designate that portion of the field of radiation chemistry which is concerned with the chemical reactions in which atoms with abnormally high energies participate. A hot atom is an atom which possesses electronic excitation or kinetic energy much in excess of ordinary thermal equilibrium values, and thus may undergo chemical reactions which are forbidden at the usual thermal energies. Since an atom with higher energy can react chemically with a molecule in a much different fashion than when the atom and molecule are in thermal equilibrium, and are limited to processes that have small activation energies, the variation of chemical products from reactions at different energies greater than thermal energies is of considerable interest.

Hot atoms may be produced in several different ways, the most common methods being the use of ultraviolet radiation, ionizing radiation, and nuclear transformations (1). Monochromatic ultraviolet radiation is the best method of producing hot atoms, since given the necessary spectroscopic data, the energy of the hot atom is known precisely. However, the energy range of hot atoms is quite limited

with this method. Ionizing radiation is considerably less selective, and usually produces a variety of excited states. But in this case also, the energy range of the hot atom is limited.

Nuclear transformations have been used most extensively for the production of hot atoms. The recoil energies of hot atoms resulting from nuclear transformations vary from about 100 ev to 2×10^6 ev. Thus, the hot atoms produced by this method have much higher energies than those produced by ultraviolet radiation, since 2000 \AA is equivalent to about 6 ev. They are also much more energetic than those produced with ionizing radiation, since most ionization potentials are on the order of 10 ev. This has resulted in the use of the term "hot-atom chemistry" synonymously with "chemical effects of nuclear transformations."

General Principles

Historical development

One of the first indications that the recoil of an atom due to the conservation of momentum following a nuclear process might be of importance was noted in 1904 by Brooks (2). It was observed that the decay products

of radioactive radon displayed a greater volatility than was expected. Some years later, the chemical consequences of this phenomenon were studied by Lind and Bardwell (3) when they measured the rate of reaction of hydrogen and oxygen both in the presence and in the absence of recoil atoms.

In 1934, Fermi and his co-workers (4) found that the species resulting from the neutron irradiation of a large number of elements were isotopic with the irradiated element and could not be separated from the target material by ordinary chemical methods. In that same year, Szilard and Chalmers (5) centered attention on the recoil atom itself. They proposed that if momentum was conserved during the bombardment of an atom by a neutron as it was during radioactive decay, a separation of the recoil atom from the parent compound was possible. Neutron bombardment of ethyl iodide, followed by the addition of iodine plus a reducing agent, and subsequent precipitation with silver ion, showed that a substantial fraction of the radioactive iodine produced could be separated from the ethyl iodide. It was concluded that the iodine had indeed left the parent molecule due to its recoil energy, and that this same effect would be observed in other systems provided the following criteria are met:

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

- 2) Isotopic exchange between the parent species and the radioactive species does not occur.

It was soon observed that neutrons with only thermal energy would cause rupture of the carbon-iodine bond (6). This rupture was then ascribed to the recoil energy given the iodine atom during the gamma ray emission in the $I^{127}(n, \gamma)I^{128}$ process.

Soon after these basic experiments, a study of the recoil atoms resulting from the (n, γ) process in alkyl halides showed that these atoms could cause chemical synthesis (7). Lu and Sugden (8) found that the addition of aniline to the organic halide reduced the amount of activity found in organic combination compared to that found from the pure compound. The dilution effect of organic compounds containing atoms with masses much different from those of the halogens was studied by Libby (9). Suess (10) and Libby (11) indicated that in almost all cases the recoil process caused the chemical bonds holding the atom to be broken. As a result of this work, it was seen that any activity found in the parent molecule resulted from a recombination process. Up to this time, only the (n, γ) reaction had been used for activation purposes. However, in 1940, ethyl bromide was activated using gamma radiation (12). Qualitatively, the results were the same as those obtained for the neutron bombardment of ethyl bromide, and

it was concluded that the recoil method of separation need not be limited to the (n,γ) reaction.

Using the results of the studies of the neutron activation of organic halides as a basis, Libby (13) proposed the elastic collision model of recoil reactions in 1947. Subsequently, this theory was modified and extended (14, 15). With the accumulation of more data on the organic halide systems, it was found that there was considerable divergence between the results predicted by this theory and the results found experimentally. On the basis of this evidence, Willard (16) proposed the random fragmentation theory of recoil reaction mechanisms. The details of these theories, as well as their limitations, will be discussed in a later section.

Following the publication in 1953 of the random fragmentation theory, studies of systems other than organic halides were more widely undertaken. Schrodt and Libby (17) found that in labeling n-pentane with C^{14} from the $N^{14}(n,p)C^{14}$ reaction only 25% of the activity was found in the n-pentane and the remainder was found in higher molecular weight products. During the succeeding years recoil methods were used with a great deal of success in labeling organic compounds with carbon-14 or tritium (18, 19). Since the theories which had been proposed for recoil reaction mechanisms were not applicable to tritium in many

respects, a somewhat specific model for tritium recoil reactions was postulated (20, 21).

The study of the recoil reactions of halogens in organic media also continued during this time (22, 23, 24, 25). Most of this work was done on gas and liquid phase reactions, and some of the data for gas phase reactions of recoil iodine and bromine has been interpreted using the Estrup-Wolfgang tritium theory (26). In addition to this, a study of recoil processes in the solid state has led Harbottle and Sutin (27) to propose a theory of recoil reaction mechanisms which is mainly applicable to the solid state.

Operational criteria

The theories put forth to explain the nature and distribution of products resulting from recoil processes have, in general, divided the reactions taking place into two groups: high-energy or "hot" reactions and low-energy or "thermal" reactions. Some experimental methods or operational criteria are needed to distinguish between these two types of reactions. The two criteria most generally used have been the effect of a change of phase and the effect of added radical scavenger. It has been assumed that high-energy reactions are relatively insensitive to phase changes

and that organic retention¹ would be higher in the solid than the liquid phase (13, 14). The addition of radical scavengers presumably should affect only the yield² of the products formed by thermal processes. These processes have been looked upon as being controlled by the thermal diffusion of a recoil atom that has been degraded in energy (24, 28). As will be seen in the following section, the application of these criteria to some systems has resulted in difficulty in correlating theory with experimental observation.

Theories proposed

The first model to be proposed for recoil reaction mechanisms was Libby's elastic collision theory (13). This

¹The term "retention" has generally been used to denote that portion of the activity produced that is not extractable from the original sample by a given method. For example, by using the proper solvent, active inorganic halide may be extracted from an alkyl halide sample. The activity not extracted by the solvent is assumed to be organically bound and is called the organic retention. It should be noted that the term "parent retention" does not imply that the bonds to the activated atom have not broken during recoil, but rather, that the recoil atom has recombined to form another molecule of the same type.

²As used here, the term "yield" does not have the same significance as when speaking of the yield of a chemical reaction. The percentage of the activity found in a specific chemical species is defined to be the yield, and thus might be more properly termed the "radiochemical yield."

theory assumes that the recoil atoms interact with other atoms in the system as if they were in free space. Thus, the collision of a recoil atom with an atom of similar mass results in almost complete energy transfer, leaving the atom and the radical produced by the collision "caged" by the solvent surrounding them. These two species would then react leading to the formation of activated parent molecules. If the recoil atom were to collide with an atom of widely different mass (for example, hydrogen in the case of recoiling halogen), the collision results in a small energy loss and the recoil atom escapes before it can react with the radical produced. Therefore, according to this theory, organic retention is due to collision with atoms of roughly the same mass, and active species other than the parent molecule would be produced by inelastic collisions after the recoil atom has undergone several collisions with atoms of different mass. Accordingly, the dilution of the parent compound should reduce the number of collisions leading to organic retention. An effect of this kind was observed on dilution (8, 9).

Friedman and Libby (14) found that organic retention of bromine was greater in the solid phase than in the liquid for the propyl bromides. They proposed that bromine substitution occurs in the high-energy region by elastic collisions which lead to parent retention, and that in an

"epithermal" region (when the recoil atom has an energy of about 10 ev.) hydrogen substitution occurs leading to organic but not parent retention. It is this "epithermal" process which is enhanced in the solid phase since the "reaction cage" is stronger than in the liquid phase. This theory was further extended by Miller, Gryder, and Dodson (15) when they derived explicit expressions for the organic retention as a function of the nature and extent of dilution. They assumed that every recoil atom forms an excited complex with the diluent and that this complex decomposes to give the observed products.

The validity of the assumption that momentum transfer events experienced by a recoil atom in a condensed phase are identical to those experienced in the gas phase has been questioned by Willard (16). It has also been shown by the use of radical scavengers that organic retention may result from both thermal and non-thermal processes (28, 29, 30). This evidence is in direct opposition to the predictions of the elastic collision theory. In general, it has been found that total organic retention increases in the solid phase in agreement with the theory (29, 30, 31, 32). However, it has also been shown that parent retention may in some cases be less in the solid phase than in the liquid (32), and that there may be no phase effect on organic retention for some organic halides (33). Thus, while the

elastic collision theory stimulated much experimental work in an attempt to correlate theory with observation, its usefulness as a mechanistic hypothesis lies primarily in explaining some gas phase reactions.

In an attempt to explain all these results, Willard formulated the random fragmentation theory (16). This theory assumes that the recoil atom interacts with solvent molecules as a whole rather than with individual atoms. The recoil atom imparts some of its kinetic energy to the specific solvent molecule involved in the interaction, but in this process it also imparts some energy to the surrounding molecules in a condensed phase. This results in random bond rupture and radical production in the vicinity of the collision. This process repeats itself along the track of the recoiling atom until it has nearly reached thermal energies. At this point, the atom finds itself in a "nest" of radicals produced near the end of its path. If it immediately reacts to form a stable compound, the reaction is considered a hot process. However, if it does not react in this "nest," it will diffuse in the system and undergo thermal reactions. This does not completely rule out reactions due to purely elastic collisions, but it does minimize the importance of these processes and makes the nature of the molecular debris at the end of the path the most important product determining feature of the system.

While this theory avoids any prediction concerning phase effects, and is supported by the wide variety of radioactive products usually observed, the distribution of these products is not as expected from purely random fragmentation of bonds and production of radicals (14, 30, 32, 33, 34, 35).

Recent trends

As early as 1950, Miller and Dodson (36) took into account the chemical environment of the hot atom when the experimental results which they obtained for recoil chlorine in hydrocarbons did not agree with the predictions of their proposed extension of Libby's theory. This trend away from a purely physical model can be seen in much of the more recent work (19, 25). With respect to the chemical environment, it is useful to define hot reactions as those which take place while the recoil fragment has a high kinetic energy and is not in thermal equilibrium with the system. Thermal reactions are defined as those which take place while the recoil atom is in thermal equilibrium with its surroundings.

It would seem reasonable that a thermal radical reaction would be affected by scavenger in the system and, since radical reactions are often diffusion dependent, a

change of phase might also affect product yields from such a reaction. Whether or not a particular hot reaction is affected by radical scavenger or change of phase cannot be stated with certainty. Evidence has been presented that some reactions may proceed by ionic or ion-molecule mechanisms (23, 25), in which case the evaluation of phase and scavenger data is difficult.

In general, if the yield of a specific product is sensitive to both a change in phase and to added radical scavenger, that product is probably formed by a thermal reaction. Hot reactions are most likely insensitive to added scavenger, but they may not be insensitive to phase changes. However, if the yield of a product is insensitive to both a phase change and to added scavenger, the product probably results from a hot reaction.

Carbon-11 Recoil Studies

The first investigations of recoil reactions involving carbon-11 were carried out with inorganic systems. Rowland and Libby (37) studied the $C^{12}(\gamma, n)C^{11}$ reaction in liquid and solid carbon dioxide. They found that the carbon-11 activity was equally distributed between carbon monoxide and carbon dioxide for the solid phase, but in the liquid phase about 98% of the activity was found to be carbon

monoxide. The results were similar in a comparison between solid sodium bicarbonate and a solution of sodium bicarbonate. These results did not agree with those obtained by McCallum and his co-workers (38, 39). They irradiated anhydrous sodium carbonate, calcium carbonate, and sodium bicarbonate with gamma radiation and found very little radioactive carbon monoxide. Most of the carbon-11 activity was found in carbon dioxide, oxalic acid, and glyoxylic acid. Small amounts of activity were also found in formic acid and glycollic acid. It was suggested that since Rowland and Libby had used boiling sulfuric acid to liberate the gases, the large yields of carbon monoxide and carbon dioxide could have been the result of decomposition of the organic acids formed.

In 1958, Suryanarayana and Wolf (40) reported on the results of the $C^{12}(n,2n)C^{11}$ reaction in benzene. After bombarding pure liquid benzene, it was found that 4.5% of the total carbon-11 produced was stabilized in the re-entry product, benzene, and 2.2% in the synthesis product, toluene. The benzene yield was reduced, but the toluene yield was unaffected by a change to the solid phase or by the addition of 1,1-diphenyl-2-picrylhydrazyl as a scavenger. It was felt that this indicated that benzene was formed by both hot and thermal processes, and that toluene was formed by a hot process only. The formation of toluene was

envisioned as the reaction of a carbon-11 fragment with benzene to form a seven member ring intermediate which rearranges to toluene.

Lang and Voigt (41) studied the product yields of low molecular weight hydrocarbons resulting from the $C^{12}(\gamma,n)C^{11}$ reaction in cyclohexane and n-hexane. Measurable yields of methane, ethane, ethylene, acetylene, propane, propylene, and four-carbon compounds were found. The major product observed was acetylene, which was found to contain 14% of the total carbon-11 activity in both cases. The change of phase from liquid to solid for cyclohexane produced a decrease in all the product yields except the propylene yield which remained constant. The reaction mechanism proposed was based on Willard's random fragmentation model. The carbon-11 produced has an initial energy of 0.1 to 1 Mev and a charge of +1 or +2. These recoil atoms become neutralized as they dissipate their energy by collision processes or ionization and excitation processes. Eventually, carbon-hydrogen radicals such as $C^{11}H$, $C^{11}H_2$, and $C^{11}H_3$ can be formed, the most abundant species being $C^{11}H$. These species then react with the random distribution of radicals found in the system to produce the observed products. Since scavenger experiments were not performed and phase data alone are not sufficient to distinguish between hot and thermal processes, no conclusion as to the relative

importance of each of these processes for these systems could be drawn.

Wolfgang and his co-workers (42, 43, 44) have studied the products formed by the reaction of carbon-11 produced by a heavy-ion accelerator with several low molecular weight hydrocarbons in the gaseous phase. Acetylene was the major product observed, with most of the remaining activity found in various other gaseous unsaturated compounds. It had been shown previously (45) that oxygen was a good scavenger for radicals and for atomic carbon, so many of the experiments were carried out with about 2% oxygen present. The product distribution obtained was explained by a mechanism in which atomic carbon-11 reacts with the parent molecule by insertion into a carbon-hydrogen bond. The intermediate thus formed may then decompose to form the observed products. The qualitative agreement between the experimental results obtained and the distribution of unsaturated products predicted by this model is quite good for such parent molecules as cyclopropane, propane, ethane, and methane. It was proposed that four-carbon products were not produced by this insertion mechanism, but rather by the reaction of methylene radicals formed as a result of hydrogen pick-up by the atomic carbon. Yields of saturated products could also be explained by this means, since they cannot be explained by insertion mechanisms. In

experiments with unsaturated hydrocarbons, it was found that addition product yields were significantly higher than the corresponding yields with saturated hydrocarbons. This was explained by a mechanism in which the atomic carbon reacts with the double bond to form a cyclic intermediate which can rearrange and lose its excitation energy without decomposing. No evidence was found for any reaction of atomic carbon with single carbon-carbon bonds.

It has been found that radiation induced modifications of primary products can be important in the radiation chemistry of hydrocarbons, and for this reason experiments have been done at low conversion (46, 47). These effects were not absent in Wolfgang's work with atomic carbon, but were measured and found to be small (43). A study was made by Cacace and Wolf (48) of the effect of radiation on the reactions of recoil carbon-11 in ammonia. It was found that the carbon-11 yields of methane and methylamine were affected by the radiation dose received by the sample. Most of the work with carbon-14 recoil atoms has been done using a nuclear reactor which causes the sample to receive a high radiation dose. Consequently, a comparison between carbon-14 data obtained using reactors and carbon-11 data obtained with low-level radiation effects is sometimes difficult. Rack and Voigt (49) have reported the effects of radiation dose on the recoil reactions of carbon-11 in the cyclohexane

system. They found that the gaseous products formed in the irradiation of pure cyclohexane with gamma rays and electrons showed an increase in yield with increasing radiation dose. With the addition of iodine to the samples as a scavenger, the product yields were found to remain constant with increasing radiation dose. If the data obtained for pure cyclohexane are extrapolated to zero dose, the product yields correspond to those found with scavenger present, indicating that the radiation induced reactions leading to product formation are probably thermal radical reactions.

The dependence of recoil carbon-11 product yields on the phase of the system has been the subject of several investigations. Lang and Voigt (41) noted that the yields of most of the gaseous products formed in cyclohexane were reduced by a change from liquid to solid phase. Even the yield of the major product, acetylene, showed this phase effect. MacKay and Wolfgang (50) have indicated that the yields of the major products from the reaction of carbon-11 with ethylene, ethylene oxide, and isobutane are not affected by a change of phase. Their data indicate that the yields obtained from ethylene are not significantly different in the gas, liquid, or solid phase. This same insensitivity to phase was found in ethylene oxide when comparing yields in the gas and solid phase, and in isobutane when comparing the gas and liquid phase. This evidence

leads to the conclusion that the carbon-11 atoms react mainly by insertion into a carbon-hydrogen bond or by addition to a carbon-carbon double bond, and that random fragmentation mechanisms are of minor importance. However, Stöcklin and Wolf (51) found that the product yields are influenced by phase changes for the $C^{12}(n,2n)C^{11}$ reaction in gaseous and liquid ethane, and in gaseous, liquid, and solid propane. In particular, they observed that the acetylene yield was smaller in condensed phases than in the gas phase. The conclusion was drawn that while insertion reactions, which possibly involve methylene radicals instead of atomic carbon, are probably valid models for the formation of low molecular weight products, the application of the operational criteria to these systems is very difficult.

The relationship between the structure of the parent hydrocarbon molecule and the gaseous recoil carbon-11 products formed when that hydrocarbon is subjected to gamma radiation has been studied by Rack, Lang, and Voigt (52). The only labeled gaseous products formed in the reaction of carbon-11 with benzene were methane and acetylene. Reaction of carbon-11 with cyclohexane, n-hexane, 2-methylpentane, and 2,2-dimethylbutane led to a wider variety of labeled products, with acetylene being the most abundant. The product distribution found was consistent with the bond

insertion model. An increase in the yield of ethane and ethylene was noted with a change from cyclic to non-cyclic hydrocarbons. A further increase was observed with increased branching of the carbon chain in the non-cyclic hydrocarbons. The assumption was made that the principal factor determining the total ethane and ethylene yield was the nature of the group attacked by the carbon-11. This total yield was then expressed in the following way:

$$\text{Relative ethane + ethylene yield} = aX + bY + cZ. \quad (\text{Eq. 1})$$

In this expression, X, Y, and Z are the fraction of carbon atoms in the parent molecule in the form CH_3 , CH_2 , and CH , respectively, and thus they are the probabilities for attack at these sites by the recoil carbon-11. The terms a, b, and c are the relative yields of ethane + ethylene for each of the groups individually. These terms were evaluated from benzene, cyclohexane, and ethane data since each of these compounds contains only one type of group. Using the values obtained in this manner, the ethane + ethylene yields for several hydrocarbons were calculated and were found to be in good agreement with the observed total ethane + ethylene yields. These results led to the conclusion that the carbon-11 insertion reaction in saturated hydrocarbons is to a high degree a statistical process.

Purpose of This Investigation

Relatively few studies have been made of recoil carbon-11 reactions in condensed phases; and in particular, little work has been done with liquid hydrocarbon systems. Iodine scavenger experiments have been performed in these systems, but the effect of oxygen has been studied mainly in gaseous systems. The purpose of this investigation is to study the effect of dissolved oxygen on the recoil reactions of carbon-11 in liquid hydrocarbon media.

The use of the $C^{12}(\gamma, n)C^{11}$ reaction for this purpose was made feasible by the availability of the Iowa State University synchrotron. The cross section for this reaction has been found to be 8.3 mb at the 22.5 Mev maximum of the cross section peak (53). The half-life of carbon-11 has been measured as 20.35 ± 0.08 minutes (54). The difficulties presented by the relatively small reaction cross section and the short half-life of the carbon-11 can be overcome by employing a rapid means of product analysis such as gas chromatography. This makes it possible to find the radiochemical yield of a specific product, and thus it is possible to study the effect of oxygen on the reactions leading to the product yields observed.

EXPERIMENTAL

Materials

The hydrocarbons used in this investigation were Research Grade reagents obtained from Phillips Petroleum Company. The manufacturer's stated lot purity for each was:

Benzene	99.93 mol percent
n-Pentane	99.98 mol percent
n-Hexane	99.97 mol percent
Cyclohexane	99.94 mol percent.

Research Grade oxygen obtained from The Matheson Company was used in the scavenger experiments. The lot analysis supplied by the manufacturer showed the following impurity concentrations:

Nitrogen	192.5 ppm
Argon	192 ppm
Carbon dioxide	9 ppm.

These reagents were used without further purification. The tantalum foil irradiated as a dose monitor was obtained from Ethicon Suture Laboratories.

The silica gel (14-20 mesh) used in the chromatographic column was obtained from Fisher Scientific Company. Before packing the column, the silica gel was washed with hot

15.6 N nitric acid, then washed with distilled water, and finally dried at 150°C for twelve hours. After packing, the column was continuously flushed with a stream of helium at 50°C. Commercial Grade methane, ethane, ethylene, acetylene, propane, carbon monoxide, and carbon dioxide from The Matheson Company were used to determine column retention times for these compounds.

Sample Preparation

A sample ampoule of Pyrex glass was filled with approximately 0.3 ml of the hydrocarbon to be irradiated and attached to the vacuum system. The sample was then degassed using the freeze-pump-thaw method. In this method the sample is frozen using a liquid nitrogen bath and the space above the solid is evacuated. After the evacuation, the stopcock to the vacuum system manifold is closed and the sample is allowed to melt. This cycle was repeated three times for each sample.

If a pure hydrocarbon sample was desired, the liquid was again frozen after the degassing and the small-bore neck of the ampoule was quickly sealed. If a sample containing oxygen scavenger was desired, oxygen was admitted to the manifold after the degassing and was allowed to equilibrate with the hydrocarbon at room temperature for

approximately twenty-four hours. The sample was then quickly sealed at room temperature.

Determination of Oxygen Solubility

The samples containing oxygen scavenger were prepared using a procedure very similar to that used by Hornig (55) in her work on the radiolysis of alkyl iodides. The vacuum system used in this method of preparation is shown in Figure 1. The shaded portion of the system is the volume in which the oxygen and hydrocarbon vapor were contained during the equilibration period.

The amount of oxygen contained in the samples prepared in this manner was determined using gas chromatography. The chromatographic column used was the same silica gel column that was used in the product analysis and will be described in that section. In this analysis technique, the thermal conductivity peak area given by a known amount of oxygen is compared to the peak area given by the oxygen contained in a sample after it has been passed through the column. The number of moles of oxygen giving the reference peak can be calculated from the ideal gas law since the volume, pressure, and temperature of the oxygen can be measured.

The number of moles of oxygen present in the sample,

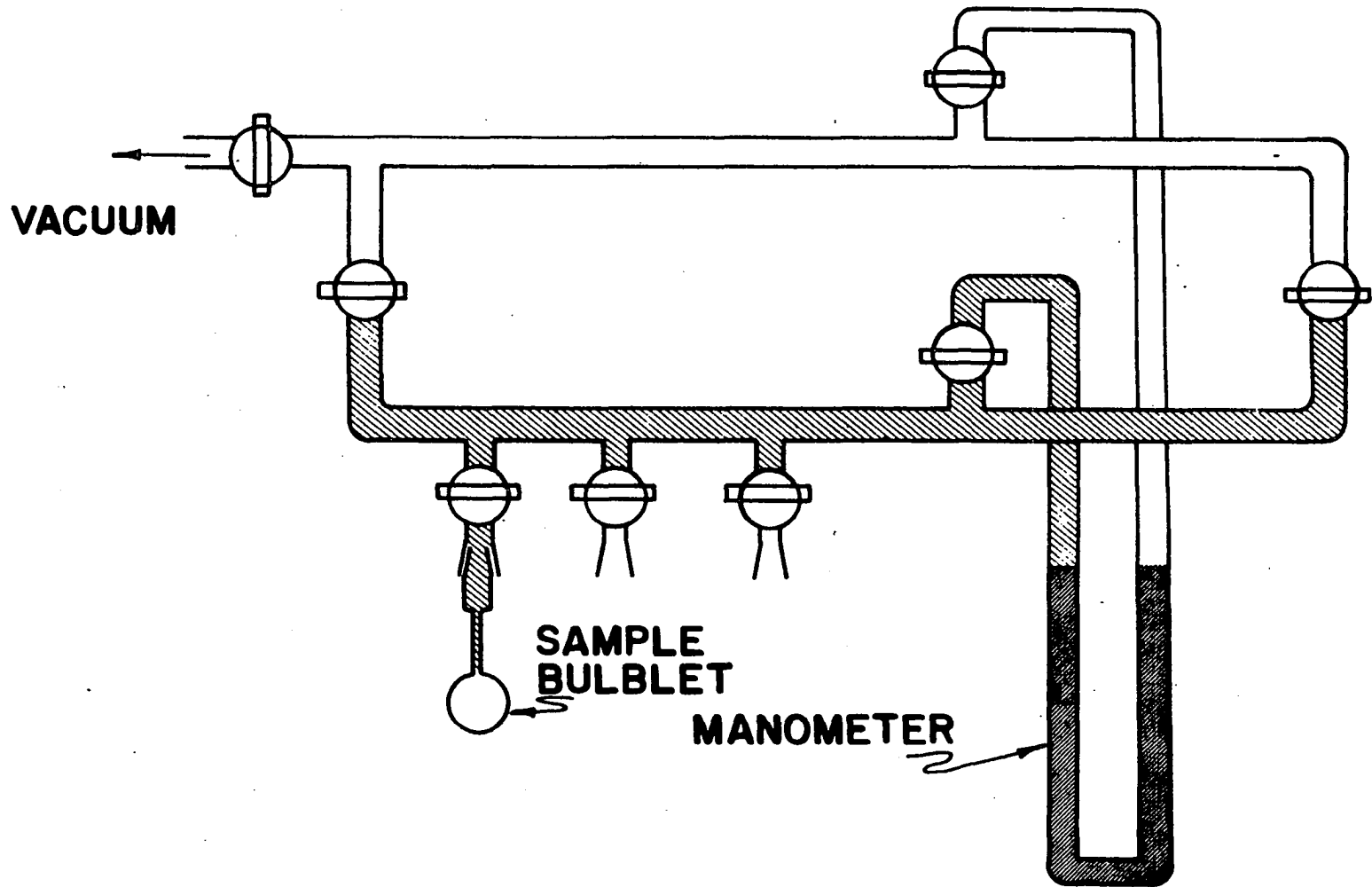


Figure 1. Vacuum system

n_{O_2} , is given by:

$$n_{O_2} = \frac{(\text{Peak area of the oxygen in sample})(\text{Moles of oxygen in reference})}{\text{Peak area of reference}} . \quad (\text{Eq. 2})$$

The number of moles of hydrocarbon in the sample, n_H , is then given by the following:

$$n_H = \frac{(\text{Weight of sample after sealing}) - 32(n_{O_2})}{\text{Molecular weight of hydrocarbon}} . (\text{Eq. 3})$$

The mole fraction of oxygen present in the sample is then:

$$x_{O_2} = \frac{n_{O_2}}{n_H + n_{O_2}} . \quad (\text{Eq. 4})$$

Two oxygen containing samples of cyclohexane and two of n-hexane were taken at random from those prepared and were analyzed by this method. The results of these experiments are given in Table 1. The average mole fraction of oxygen found was 0.0073 for cyclohexane and 0.0032 for n-hexane.

Table 1. Solubility of oxygen in hydrocarbons

Sample number	Hydrocarbon	n_{O_2} ($\times 10^5$)	n_H ($\times 10^5$)	X_{O_2}
160	Cyclohexane	2.03	308.45	0.0065
161	Cyclohexane	2.80	343.45	0.0081
170	n-Hexane	0.78	281.16	0.0028
185	n-Hexane	1.22	339.65	0.0036

Sample Irradiation

The $C^{12}(\gamma, n)C^{11}$ reaction was produced by using the bremsstrahlung from the Iowa State University electron synchrotron. Irradiations were made for various time periods ranging from five to sixty minutes at a maximum electron energy of 47 Mev. Samples were positioned inside the acceleration chamber of the synchrotron by means of the probe arrangement shown in Figure 2. The glass ampoule was held inside the probe with the sample holder shown in Figure 3. The procedure for irradiating materials in this manner has been discussed in detail by Hammer and Bureau (56, 57, 58).

The dose rate to which samples irradiated in this

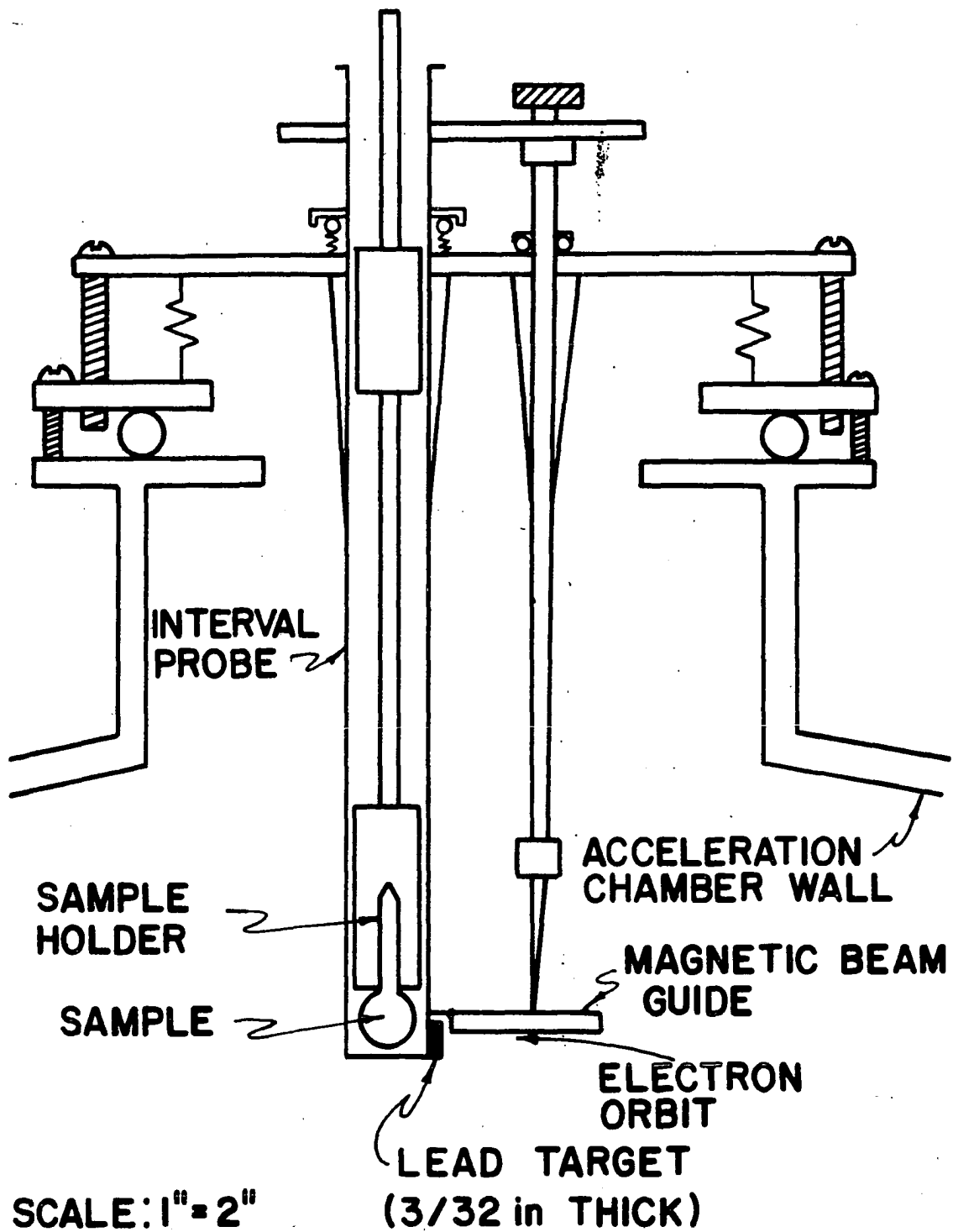


Figure 2. Internal synchrotron probe

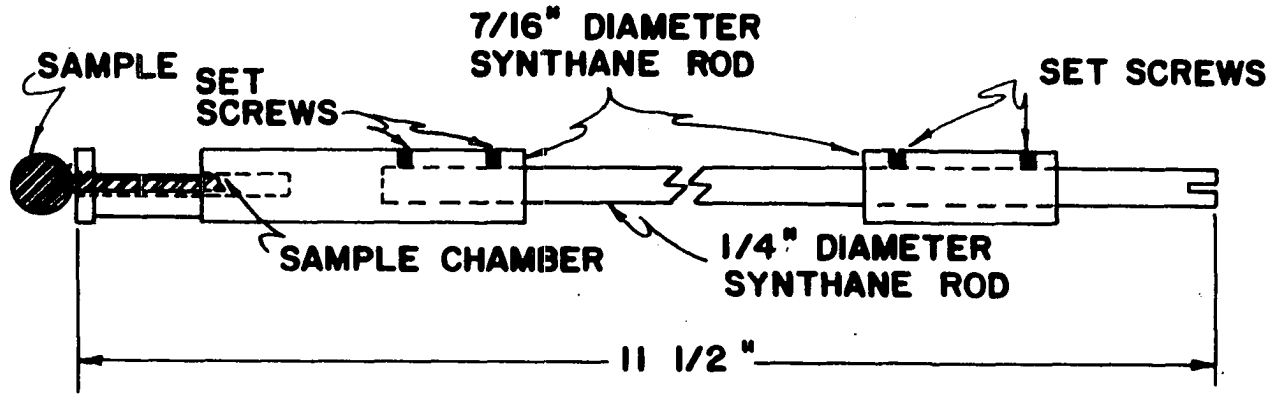


Figure 3. Sample holder

manner were subjected has been estimated by two techniques (52). Measurement of the time of disappearance of iodine from a hydrocarbon sample gave a dose rate of about 10^{19} ev/g min. Measurement of the dose rate with a Fricke dosimeter gave a value of 3×10^{19} ev/g min. A third method of measurement using the color change in cobalt glass during the irradiation has given a dose rate of 3.5×10^{19} ev/g min.¹

In order to monitor the intensity of radiation received by the sample during a given irradiation, a strip of tantalum foil 0.0005 inch thick was wrapped around the sample. The foil was positioned so that the x-ray beam passed through it before passing through the sample.

Product Analysis

Since the first use of gas chromatography in 1956 by Evans and Willard (59) to identify the products resulting from a recoil process, this method has become one of the major analytical tools used by workers in the field of hot-atom chemistry. The product analyses in this

¹Clark, D. E., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Dose rate determination using cobalt glass dosimetry. Private communication. 1963.

investigation were accomplished using this technique as outlined below. The chromatograph used was built by W. Stensland and D. Clark of the Ames Laboratory.

Many different column materials are available for use in gas chromatography, but choosing the particular material which is most suitable for the type of analysis being done involves several factors. Since carbon-11 has such a short half-life, a column material which allowed product elution times of less than one hour but still gave good separations was desired. It was found that silica gel could provide clean separations between the low molecular weight hydrocarbons which were produced in the recoil reactions. It was found in work with oxygen-containing samples of n-pentane that for high oxygen pressures over the sample, considerable amounts of labeled carbon monoxide and carbon dioxide were formed. Silica gel was also found to be useful in determining whether or not these oxides were formed during the irradiation of samples containing much less oxygen than the pentane samples, since these oxides were separated completely from the low molecular weight hydrocarbons.

The helium carrier gas flow is diagramed in Figure 4. After the helium has passed through a rotameter, it enters a preheat loop in the oven. The chromatograph was kept at a constant temperature of 50°C during all the analyses.

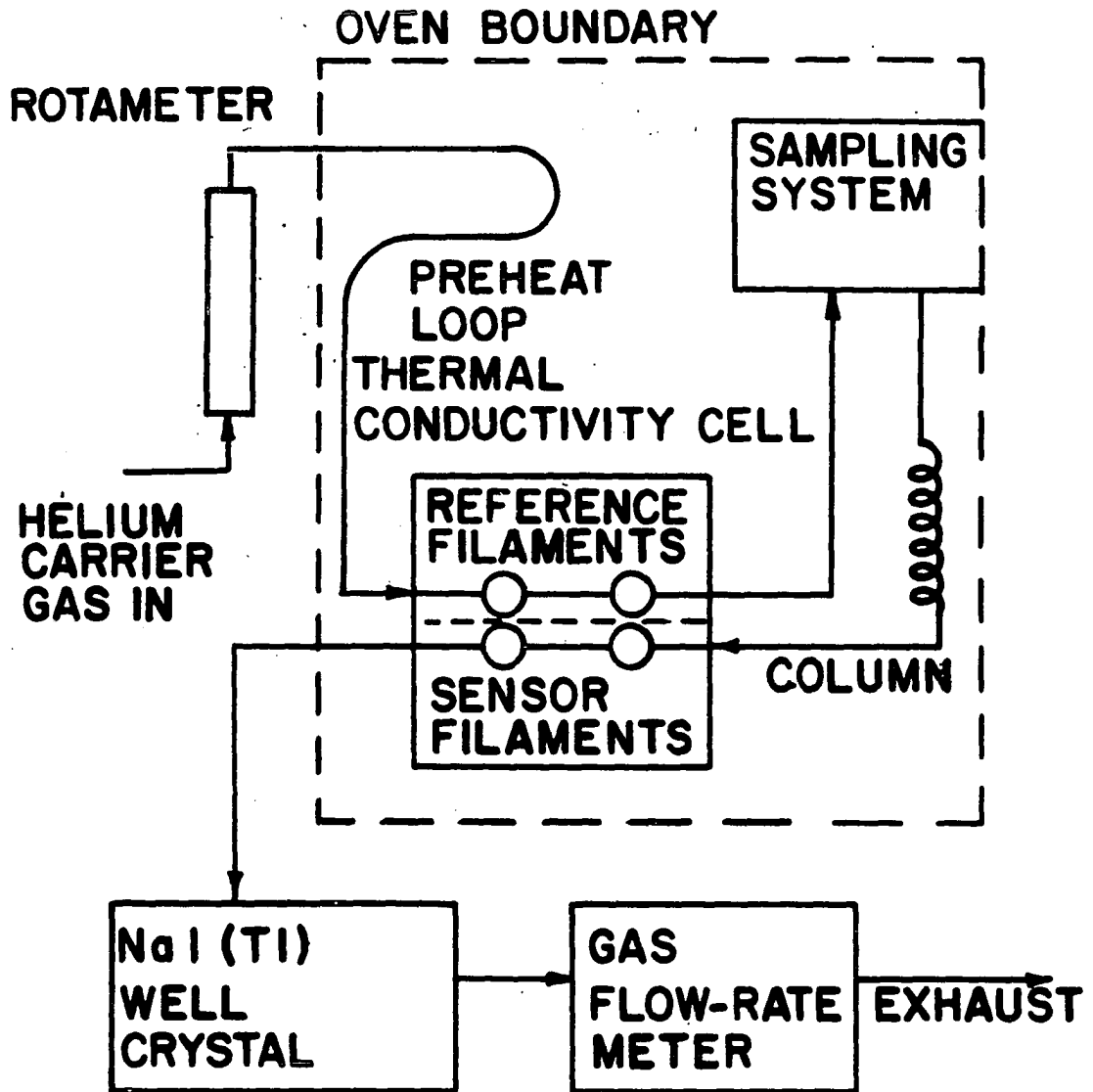


Figure 4. Helium carrier gas flow diagram

The carrier gas then enters the reference filament chambers of a Gow-Mac thermalconductivity cell, Model 9285. The gas then moves to a sampling system containing a bulb crusher which allows the entire sample to be introduced into the gas stream. As the sample is swept through the column, a twelve foot glass helix filled with 14-20 mesh silica gel, the products are separated since their rates of adsorption on silica gel differ.

Due to the much lower thermal conductivity of the products compared to helium, the resistance of the sensor filaments in the thermal conductivity cell is changed compared to the reference filaments when a given product is eluted from the column and passes through the sensor filament chambers. After passing through the chambers, the product is next passed through a scintillation crystal by means of the apparatus shown in Figure 5. Finally, the gas flows through a flow rate meter with the exhaust entering a hood.

A schematic diagram of the detection system is given in Figure 6. The four filaments in the thermal conductivity cell are incorporated into a Wheatstone bridge, and the signal resulting from the unbalancing of the bridge due to a product passing through the sensor chambers is traced by one pen of a Bristol Dynamaster two-pen recorder. Identification of the products was made by measuring elution

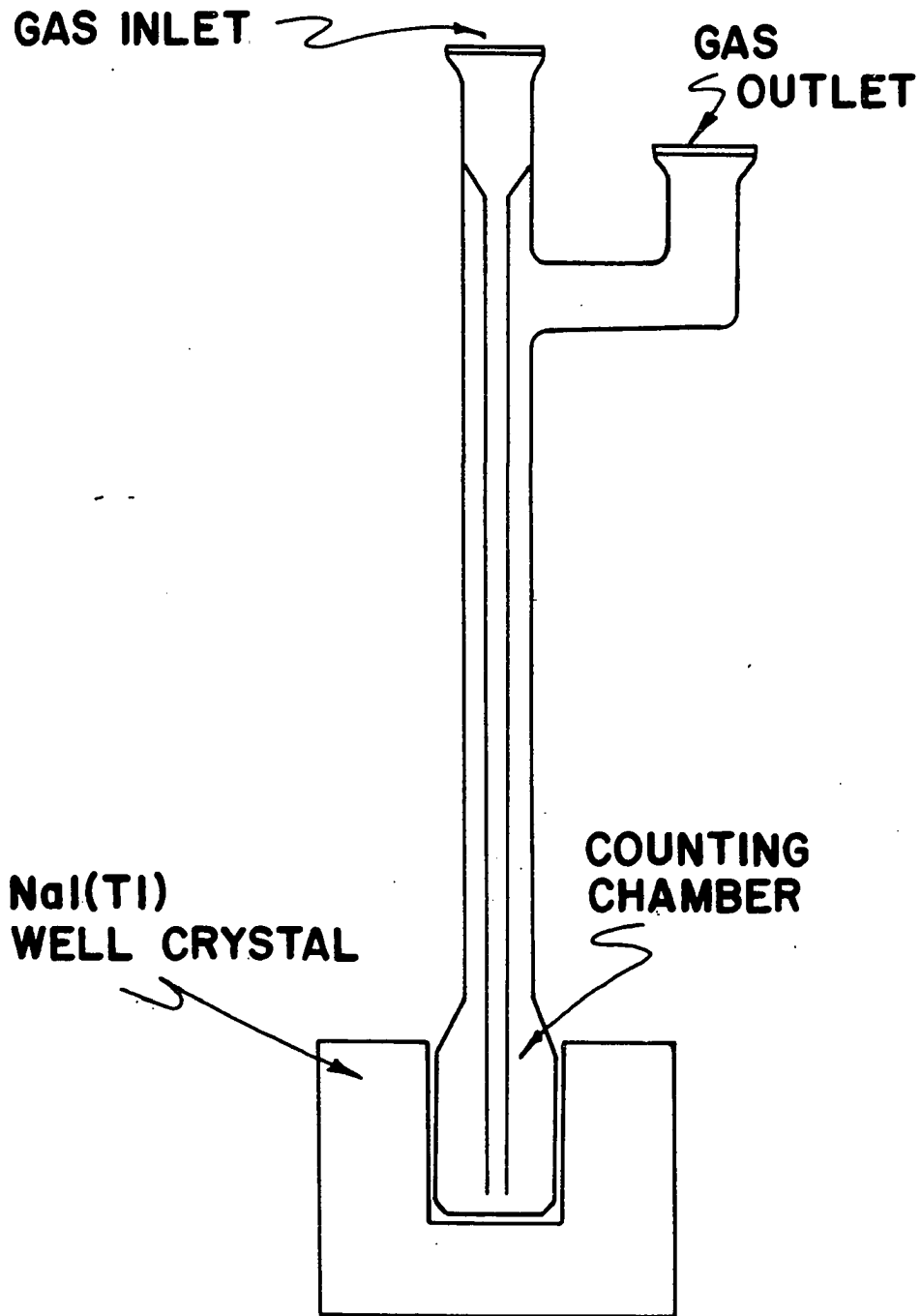


Figure 5. Counting apparatus

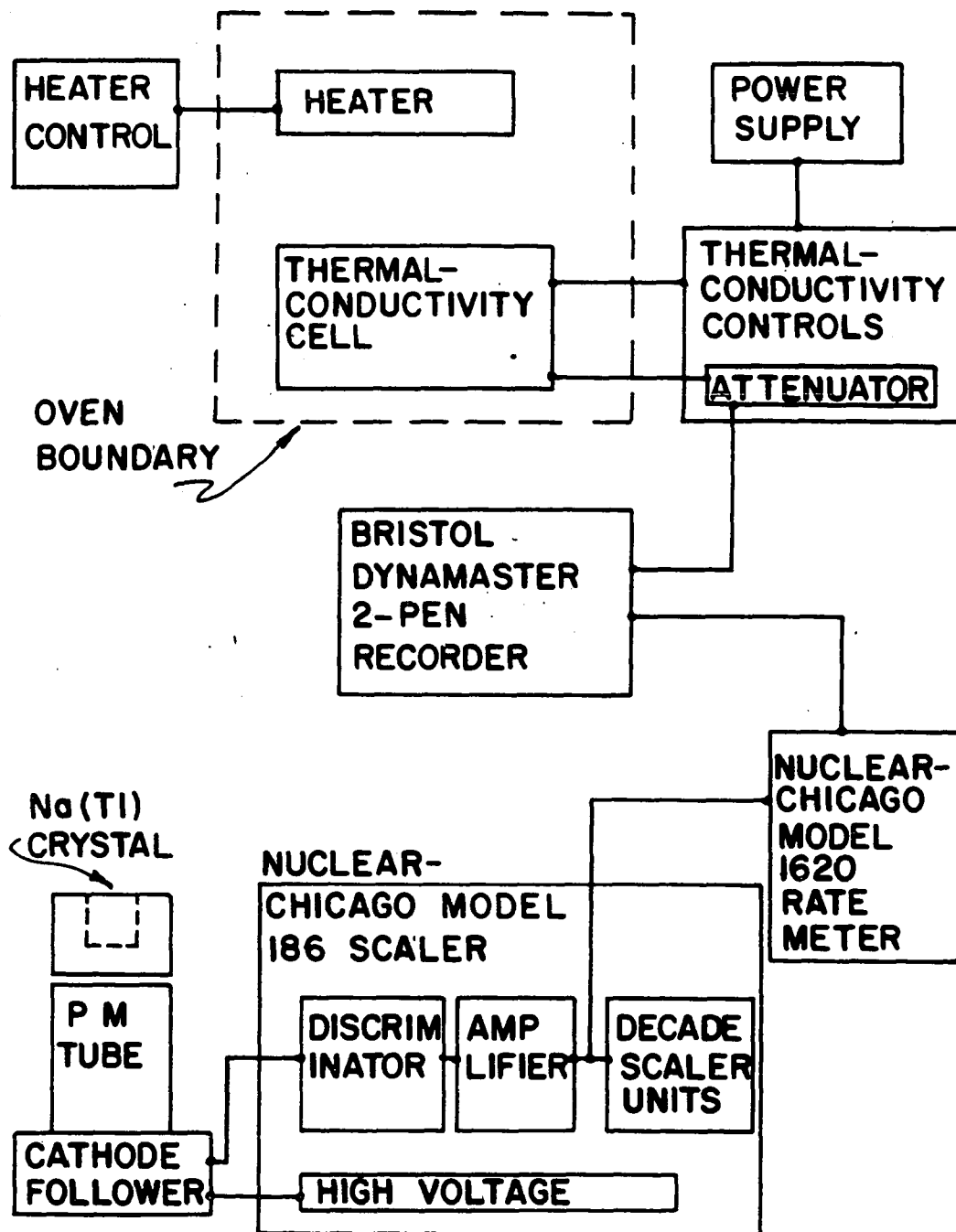


Figure 6. Schematic diagram of the detection system

times of known hydrocarbons using the thermal conductivity cell for detection.

A Harshaw Chemical Company NaI(Tl) scintillation crystal, Type 7F8, was used to detect the products containing carbon-11. The crystal was 1.5 inches in diameter by 2 inches thick and contained a well which was 0.75 inch in diameter and 1.5 inches deep. The crystal was mounted on an RCA 6342-A photomultiplier tube which together with a cathode follower were contained in a Berkeley Vial Counter, Model 2250. In addition to shielding this detector with a Berkeley Lead Shield, Model 2254, a housing of two inch thick lead bricks was built around the apparatus to ensure a low background. The voltage supply for the photomultiplier tube and linear amplification of the signal from the cathode follower were provided by a Nuclear-Chicago Decade Scaler, Model 186, as shown in Figure 6. The scaler was adapted so that it was possible to record the activity with the second pen of the Bristol recorder simultaneously with the measurement of the activity using the decade scaler units. The signal traced by the recorder was first passed through a Nuclear-Chicago Rate Meter, Model 1620. Two half-life determinations showed that the only radioactive isotope present during the analyses was carbon-11.

The activity of the tantalum foil monitor was measured using a Tracerlab TGC-2 mica end-window Geiger-Mueller tube

housed in a Technical Associates Lead Shield, Model AL 14A, and connected to a Nuclear-Chicago Decade Scaler, Model 186. The gamma-ray spectrum of the foil was determined using a Radiation Counter Laboratories 256 Channel Pulse Height Analyzer, Model 20611. The spectrum obtained indicated that both Ta^{180m} and Hf^{180m} were produced in the foil. Hf^{180m} decays to stable Hf^{180} by gamma-ray emission, while Ta^{180m} decays $\sim 83\%$ by electron capture to Hf^{180} and $\sim 17\%$ by β emission to stable W^{180} . Since the monitor was counted with a Gieger-Mueller tube which has a gamma-ray counting efficiency of only a few percent, the activity observed in the monitor was almost entirely due to the β -decay of the 8.1 hour Ta^{180m} .

EXPERIMENTAL RESULTS

Calculation of Product Yields

During the synchrotron irradiation of a sample, the number of radioactive atoms present is dependent on the rate at which they are produced and the rate at which they decay. In this situation, the number of radioactive atoms present at any time during the irradiation is given by the well-known equation:

$$N = \frac{\sigma\phi N_0}{\lambda} [1 - e^{-\lambda t}], \quad (\text{Eq. 5})$$

where

N = number of radioactive atoms present at time t

σ = cross section for reaction

ϕ = flux

N_0 = number of parent atoms present at $t=0$

λ = decay constant of the nuclide produced

t = time.

The total number of radioactive atoms produced during the irradiation is:

$$N_T = \sigma\phi N_0 t, \quad (\text{Eq. 6})$$

where

N_T = total radioactive atoms produced

t = total irradiation time.

Solving Equation 6 for the quantity $(\sigma\phi N_0)$ and substituting this into Equation 5 yields the following result:

$$N_T = \lambda N_0 \left[\frac{t}{1 - e^{-\lambda t}} \right] \quad (\text{Eq. 7})$$

Since activity, A , is defined by the equation,

$$A = - \frac{dN}{dt} = \lambda N, \quad (\text{Eq. 8})$$

Equation 7 then becomes:

$$N_T = A_0 \left[\frac{t}{1 - e^{-\lambda t}} \right], \quad (\text{Eq. 9})$$

where A_0 is the activity at the end of the irradiation period. It is therefore possible to use the value of N_T as a measure of the total dose received by the sample during the irradiation. In order to calculate the activity A_0 in Equation 9, a measurement of the activity must be made after the irradiation has been completed. Thus,

$$A_0 = A e^{\lambda T}, \quad (\text{Eq. 10})$$

where A is the activity measured at a time T after completing the irradiation.

Since the products in which the carbon-11 became stabilized were flowing through the counting chamber during the analysis, only a relative activity dependent on the geometry of the system could be measured. Each product containing carbon-11 produced a Gaussian shaped peak on the recorder strip chart as it passed through the chamber. An equation relating the activity to the total counts observed for a flow-proportional counter has been given by Wolfgang and Rowland (60). The expression given is the following:

$$A = \frac{Rf}{v} , \quad (\text{Eq. 11})$$

where

R = total counts observed

A = activity

v = volume of the counting chamber

f = flow rate of gas.

Since the peak recorded on the strip chart was a plot of activity versus time, the area of the peak was a measure of the total counts observed. Therefore, R was found by measuring the peak area with a planimeter. In those cases where the peak did not remain on the recorder scale, the

peak was counted with the scaler, and the area calculated using the ratio of counts to area units determined from another peak observed during the same analysis.

Two difficulties arise from the use of Equation 11. The first is that for the counting arrangement used, the counting volume could not be determined precisely because it extended beyond the crystal well. However, if there is little fluctuation of the flow rate of the gas from one analysis to another, this volume may be regarded as constant. The second difficulty is that an error is introduced in the determination of the total counts due to the decay of a product while it is passing through the chamber. This error is small if the emergence time, the time between the beginning and end of an activity peak, is less than the half-life of the isotope being measured. Since the longest emergence time of the peaks observed was twelve minutes, the error involved was small.

Substituting A_0 from Equation 10 into Equation 9 and dividing by the weight of the sample irradiated, w , yields the result:

$$\bar{N} = \frac{N_T}{w} = \frac{Ae^{\lambda T}}{w} \left[\frac{t}{1 - e^{-\lambda t}} \right], \quad (\text{Eq. 12})$$

where \bar{N} can now be used to measure the dose received by the sample during one irradiation relative to another. Since

the tantalum foil was counted in a fixed geometry with a Geiger-Mueller tube, its activity could be used in Equation 12 directly. However, since the carbon-11 activity became stabilized in many different products which were analyzed using a flowing gas system, Equation 12 must be modified by substituting the expression for A found in Equation 11.

This gives the following result:

$$\bar{N} = \frac{Rfe^{\lambda T}}{vw} \left[\frac{t}{1 - e^{-\lambda t}} \right], \quad (\text{Eq. 13})$$

where \bar{N} is subject to the restrictions noted previously. The quantity \bar{N} may then be interpreted as the radiochemical yield of a given product containing carbon-11.

Determination of Radiation Dose Monitor

Using Equations 12 and 13, there are two possible ways of measuring the dose received by the sample during the irradiation. The first involves the use of an external monitor such as tantalum which is in no way involved in the recoil processes that occur. If, however, it is found that the yield of one of the products resulting from recoil processes in the system as calculated with Equation 13 is directly proportional to \bar{N} for the external monitor calculated with Equation 12, then the yield of that product may

be used as a dose monitor.

The rate of production of a given radioactive nuclide during an irradiation is dependent on three quantities: the cross section σ , the number of parent atoms N_0 , and the synchrotron flux ϕ . The cross section is a function of energy and remains constant. The number of parent atoms situated in the path of the beam was dependent on the positioning of the sample inside the target probe of the synchrotron. Since the activity produced in a sample decreases rapidly as a function of the distance from the end of the probe (58), it is important that the tantalum foil be positioned at the same place in the probe relative to the sample bulb for each irradiation. It was difficult to reproduce the same relative positioning from one sample to the next, so there was some error involved in the use of tantalum as a monitor. The synchrotron flux was largely dependent on the operating condition of the machine itself, and for this reason the amount of activity produced for a given irradiation time varied from irradiation to another. To a lesser extent the flux varied during a single irradiation.

If possible, it would be desirable to use one of the products as an internal monitor to avoid the errors resulting from the problems discussed above. The yield of the major two-carbon product, acetylene, was found to be

proportional to the amount of Ta^{180m} produced in the foil within the error introduced by those things discussed above. The values of \bar{N} for both the tantalum foil and the acetylene produced during the irradiation of pure benzene, cyclohexane, and n-hexane are given in Table 2. The results for samples of cyclohexane and n-hexane containing oxygen are given in Table 3. In order to serve as a monitor, the acetylene yield, in addition to exhibiting a direct proportionality to the tantalum yield, should not be affected by a change in experimental conditions such as the addition of oxygen to the system. A plot of \bar{N}_{Ta} versus $\bar{N}_{C_2H_2}$ for pure benzene is given in Figure 7. In Figures 8 and 9, plots of these quantities for both pure and oxygen containing samples of cyclohexane and n-hexane, respectively, are given. All of these plots show a direct proportionality between the acetylene and the tantalum yields which is unaffected by the addition of oxygen.

Therefore, it was considered to be demonstrated that the acetylene yield could be used as a dose monitor for those systems studied. The quantity which was plotted versus the dose for the products resulting from recoil was the yield of a specific product per unit monitor response. For example, the methane data for a given hydrocarbon was plotted as $\bar{N}_{CH_4}/\bar{N}_{C_2H_2}$ versus $\bar{N}_{C_2H_2}$. This sort of data treatment was sensitive to any changes which might occur

Table 2. Yields of Ta^{180m} and acetylene from pure hydrocarbons

Irrad- iation time (min- utes)	Benzene			Cyclohexane			n-Hexane		
	Sam- ple num- ber	\bar{N}_{Ta} (x 10 ⁻⁸)	$\bar{N}_{C_2H_2}$ (x 10 ⁻⁶)	Sam- ple num- ber	\bar{N}_{Ta} (x 10 ⁻⁸)	$\bar{N}_{C_2H_2}$ (x 10 ⁻⁶)	Sam- ple num- ber	\bar{N}_{Ta} (x 10 ⁻⁸)	$\bar{N}_{C_2H_2}$ (x 10 ⁻⁶)
5	119	0.95	2.66	125	0.78	4.31	134	0.94	6.68
	101	1.14	2.76	121	1.01	6.24	129	0.88	7.97
	120	1.58	5.48	124 ^a	1.21	5.93			
				123	1.27	8.77			
10	111	1.90	7.92	122	2.35	15.65	155	0.54	3.00
				105	2.69	20.12	128	1.96	12.53
							138	2.55	18.94
15							130	3.28	23.37
							133	2.93	26.76
20	103	5.05	20.66	148	2.91	11.75	132	3.65	23.80
				112	3.51	19.55			
30	104	6.88	22.35	126	6.91	32.44	139	3.54	18.89
				106	7.03	38.54	131	3.80	33.23
							136	6.33	50.67
40				108	8.54	46.98			
45							135	8.28	67.14
50	110	8.66	31.92						
60	102	11.03	40.83	107	10.10	58.63	127	9.36	64.84

^aIrradiation time was 6 minutes.

Table 3. Yields of $\text{Ta}^{180\text{m}}$ and acetylene from oxygen containing hydrocarbon samples

Irrad- iation time (min- utes)	Cyclohexane $X_{\text{O}_2} \approx 0.0073$			n-Hexane $X_{\text{O}_2} \approx 0.0032$		
	Sam- ple num- ber	\bar{N}_{Ta} ($\times 10^{-8}$)	$\bar{N}_{\text{C}_2\text{H}_2}$ ($\times 10^{-6}$)	Sam- ple num- ber	\bar{N}_{Ta} ($\times 10^{-8}$)	$\bar{N}_{\text{C}_2\text{H}_2}$ ($\times 10^{-6}$)
5	181	0.66	1.30	174	0.30	1.53
	163	0.65	2.81	169	0.33	1.75
				167	0.11	2.21
				166	0.81	4.77
10	157	0.33	1.64			
	178	1.28	5.85			
15				165	1.52	8.80
				173	2.06	13.81
20	177 ^a	1.67	8.34			
	184	2.23	12.41			
30	156	1.57	4.83	172	2.25	16.08
	182	2.58	8.05			
60	158	1.63	9.00			

^aIrradiation time was 17.67 minutes.

in product yield trends, but at the same time avoided some of the errors discussed in using Equation 13. The error associated with any one ratio is estimated to be about 10%.

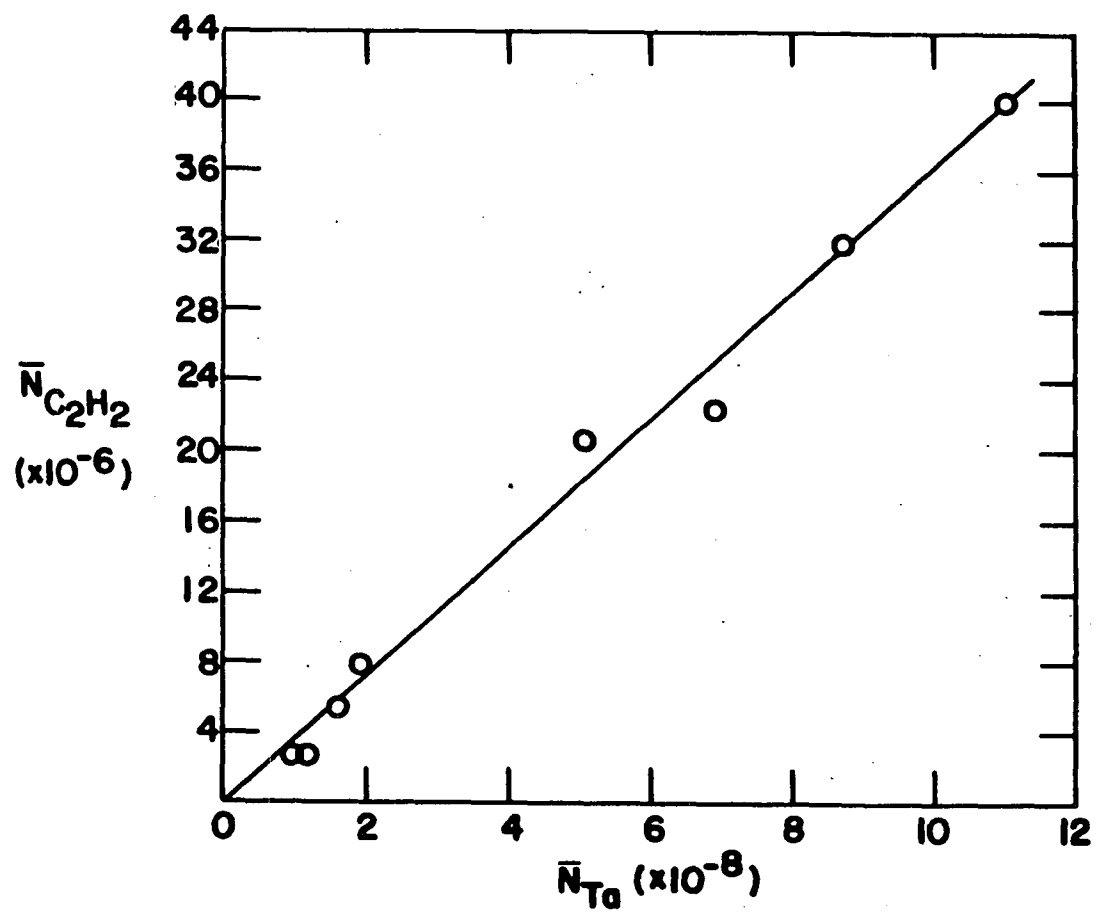


Figure 7. Plot of acetylene yield versus Ta^{180m} yield for benzene

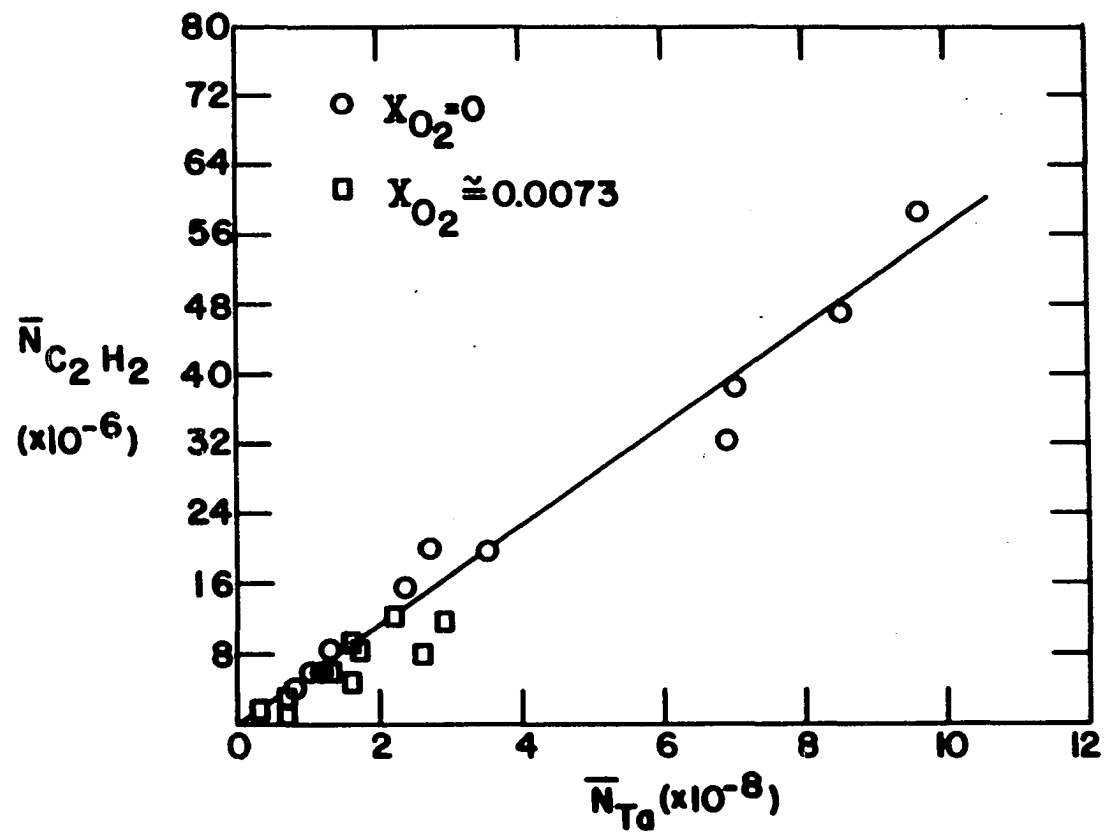


Figure 8. Plot of acetylene yield versus Ta^{180m} yield for cyclohexane

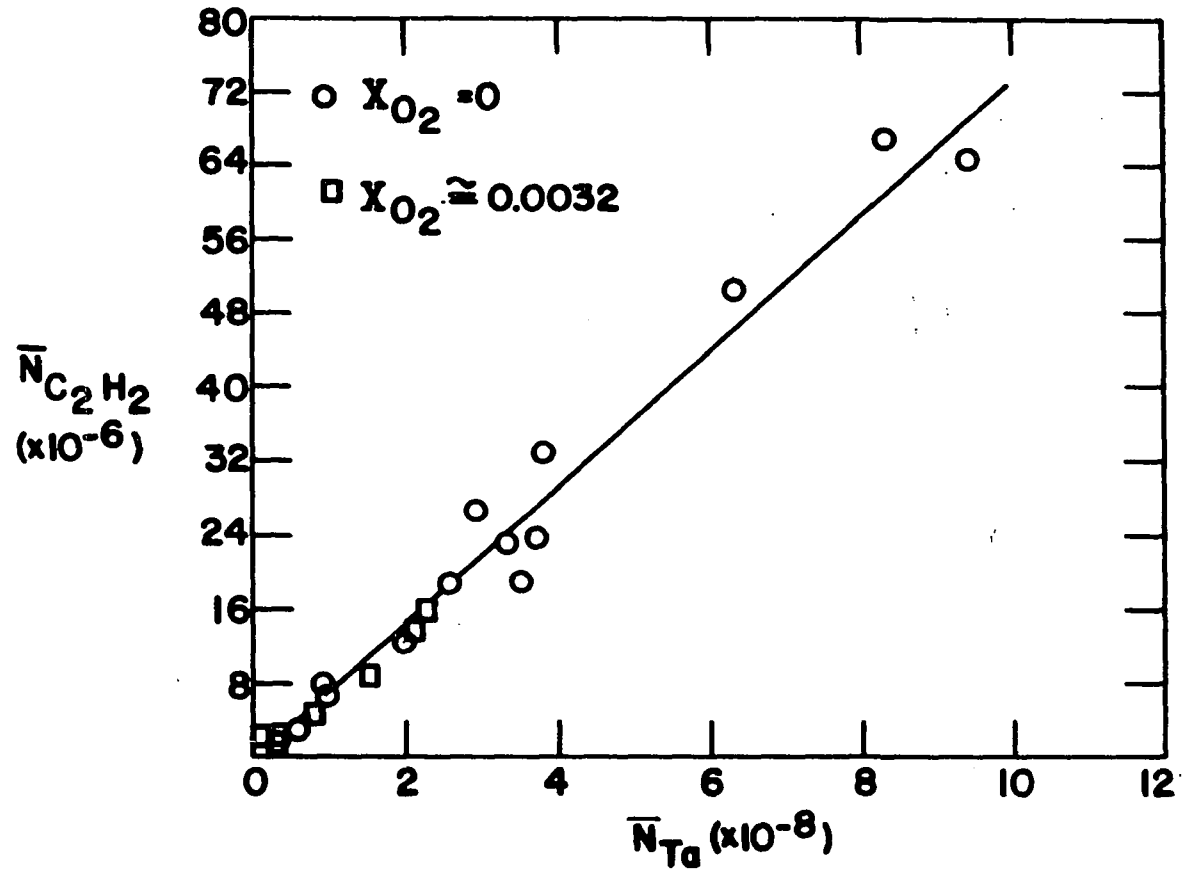


Figure 9. Plot of acetylene yield versus Ta^{180m} yield for n-hexane

Benzene

The only gaseous products containing carbon-11 from benzene found by Lang (61) were methane and acetylene. He irradiated the benzene samples outside the synchrotron acceleration chamber and found the ratio of methane to acetylene to be ~ 0.1 . The results for pure benzene obtained in this study are presented in Table 4. No work was done with oxygen-containing benzene samples. In Figure 10, the ratio of the methane to acetylene yield is plotted versus the radiation dose as measured by the acetylene yield. The ratio remains constant at 0.030 ± 0.008 for a wide dose range. While this value is considerably less than that observed by Lang it agrees very well with other published results (52):

Table 4. Methane-acetylene ratios for benzene

Sample number	Irradiation time (minutes)	$\bar{N}_{C_2H_2}$	\bar{N}_{CH_4}
		($\times 10^{-6}$)	$\bar{N}_{C_2H_2}$
119	5	2.66	0.037
101	5	2.76	0.040
120	5	5.48	0.021
111	10	7.92	0.023
103	20	20.66	0.024
104	30	22.35	0.034
110	50	31.92	0.022
102	60	40.83	0.037

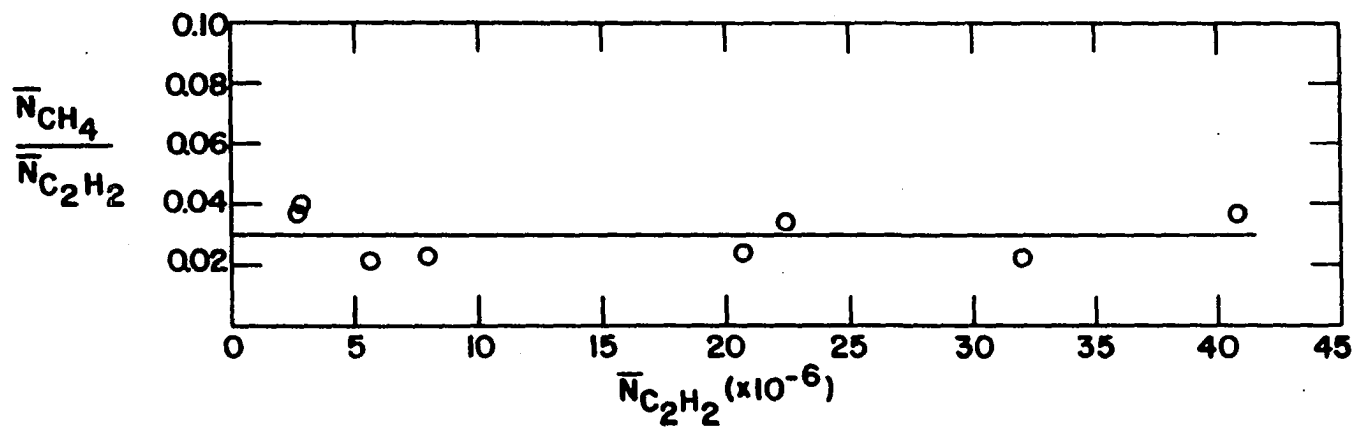


Figure 10. Plot of methane-acetylene yield ratio versus dose for benzene

Cyclohexane

With cyclohexane, the other two-carbon hydrocarbons, ethane and ethylene, are observed in addition to acetylene, and the methane yield increases by a large amount. This diversity of products and the increase in the methane yield in the cyclohexane system compared to benzene are in agreement with previous work (41, 61). The methane-acetylene, ethane-acetylene, and ethylene-acetylene yield ratios are given in Table 5. A plot of the methane-acetylene ratio versus dose is given in Figure 11. Plots of the ethane-acetylene and ethylene-acetylene ratios versus dose are shown in Figure 12. The results for samples containing oxygen scavenger were not significantly different from the results for pure cyclohexane.

The product yield ratios at "zero" dose may be obtained by extrapolating the curves plotted in Figures 11 and 12. The methane-acetylene ratio obtained in this manner is 0.53. The ratios for ethane and ethylene are 0.06 and 0.21, respectively. In a very qualitative way, these ratios are in agreement with those presented by Rack and Voigt (49) for the irradiation of pure cyclohexane. However, the plots of yield ratio versus dose presented here

Table 5. Product ratios for cyclohexane

Sample number	X_{O_2}	Irrad- iation time (min- utes)	$\bar{N}_{C_2H_2}$	$\frac{\bar{N}_{CH_4}}{\bar{N}_{C_2H_2}}$	$\frac{\bar{N}_{C_2H_6}}{\bar{N}_{C_2H_2}}$	$\frac{\bar{N}_{C_2H_4}}{\bar{N}_{C_2H_2}}$
			($\times 10^{-6}$)			
125	0	5	4.31	0.63	0.080	0.21
124		6	5.93	0.56	0.059	0.21
121		5	6.24	0.65	0.071	0.18
123		5	8.77	0.52	0.068	0.20
148		20	11.75	0.51	0.071	0.22
122		10	15.65	0.61	0.084	0.25
112		20	19.55	0.67	0.100	0.25
105		10	20.12	0.63	0.075	0.26
126		30	32.44	0.86	0.130	0.31
106		30	38.54	0.82	0.118	0.30
108		40	46.98	0.85	0.089	0.33
107		60	58.63	0.89	0.091	0.30
157	0.0073	10	1.64	0.63	0.044	0.21
183		5	2.24	0.53	0.068	0.23
163		5	2.81	0.47	0.046	0.20
176		5	4.78	0.57	0.048	0.22
156		30	4.83	-	0.064	0.28
178		10	5.85	0.54	0.050	0.23
182		30	8.05	0.69	0.099	0.25
177		17.67	8.34	0.56	0.058	0.23
184		20	12.41	0.70	0.077	0.25

are quite different from those reported previously. The ratios obtained in this study are in fair agreement with the data given for low dose in the report mentioned above, but the extrapolated ratios given are considerably lower than those found in this study.

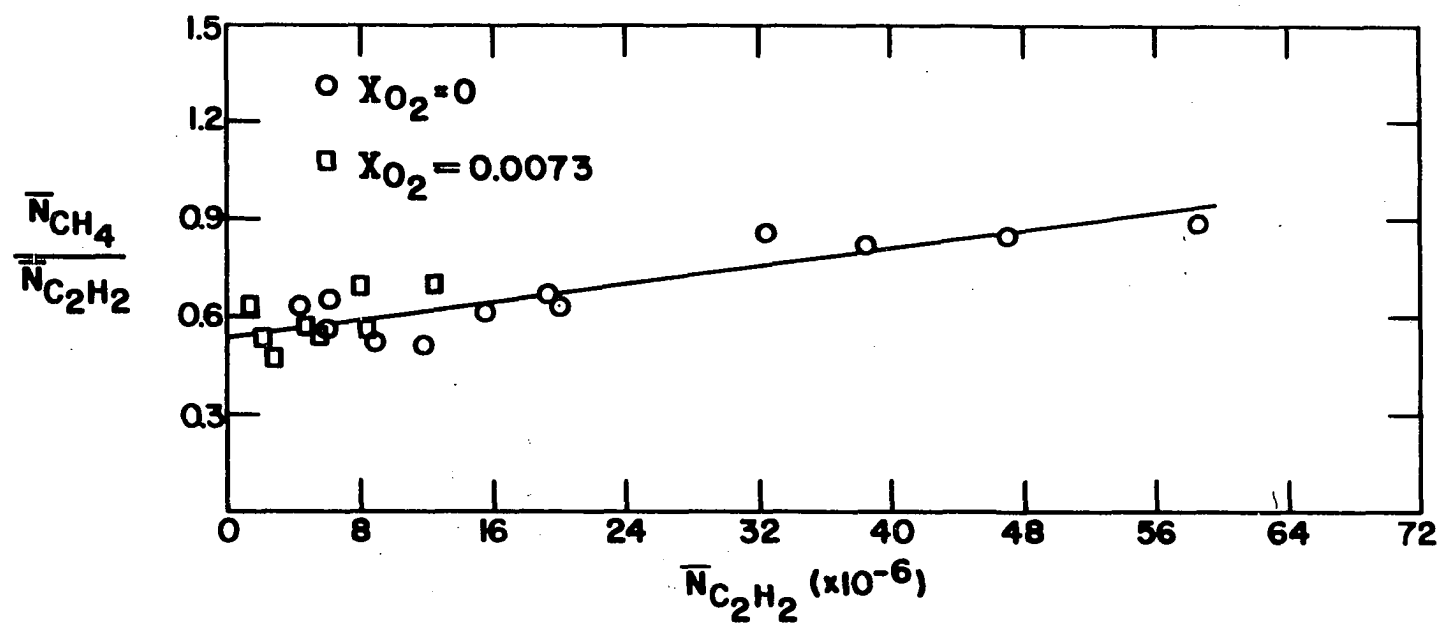


Figure 11. Plot of methane-acetylene yield ratio versus dose for cyclohexane

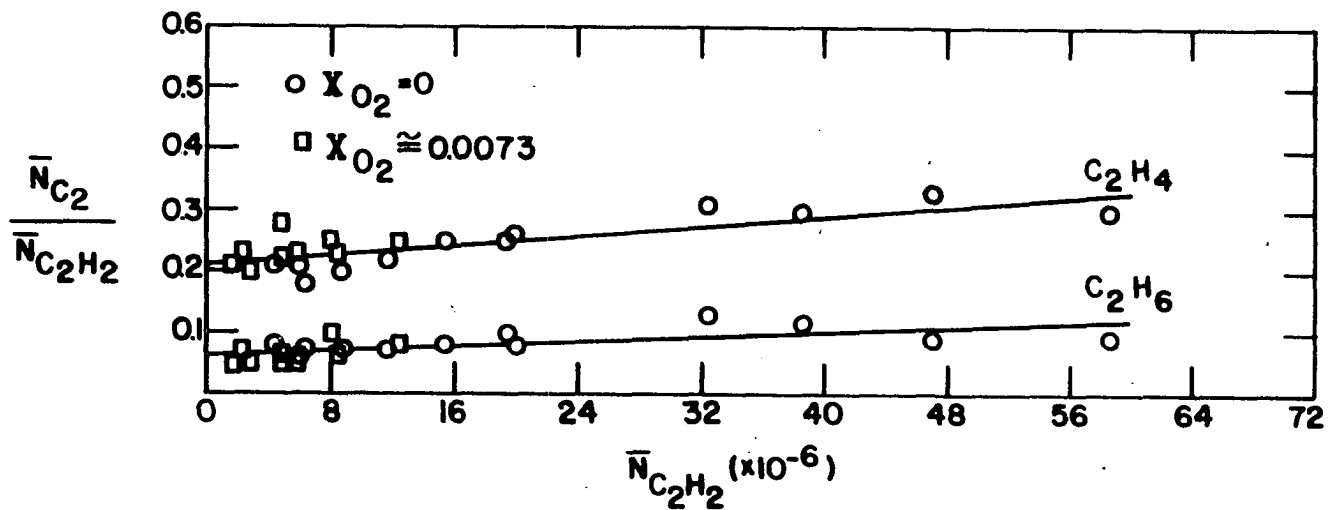


Figure 12. Plot of ethane-acetylene and ethylene-acetylene yield ratios versus dose for cyclohexane

n-Hexane

The irradiation of n-hexane produces the same tagged products as those found for cyclohexane. The product yield ratios, however, change appreciably from those found for cyclohexane. These observations are consistent with those of Lang and Voigt (41) for irradiations outside the synchrotron acceleration chamber. The methane-acetylene, ethane-acetylene, and ethylene-acetylene ratios for n-hexane are given in Table 6. These ratios are shown plotted versus dose in Figures 13 and 14. It should be noted that again there is no significant change in the yield ratios when oxygen scavenger is present.

The "zero" dose product yields may be obtained from Figures 13 and 14. The methane-acetylene ratio is 0.41, the ethane-acetylene ratio is 0.065, and the ethylene-acetylene ratio is 0.42. Thus, with respect to the acetylene yield, more two-carbon products are formed in n-hexane than in cyclohexane. At the same time, less methane is formed in the n-hexane system. These ratios are in substantial agreement with data presented for pure n-hexane (41), but are about twice as large as those reported for samples of n-hexane containing 0.0061 mole fraction of iodine (52).

Table 6. Product ratios for n-hexane

Sample number	X_{O_2}	Irradiation time (minutes)	$\bar{N}_{C_2H_2}$	$\frac{\bar{N}_{CH_4}}{\bar{N}_{C_2H_2}}$	$\frac{\bar{N}_{C_2H_6}}{\bar{N}_{C_2H_2}}$	$\frac{\bar{N}_{C_2H_4}}{\bar{N}_{C_2H_2}}$
			($\times 10^{-6}$)			
155	0	10	3.00	0.43	0.051	0.41
134		5	6.68	0.45	0.058	0.42
129		5	7.97	0.39	0.050	0.35
128		10	12.53	0.44	0.079	0.49
139		30	18.89	0.57	0.079	0.46
138		10	18.94	0.41	0.084	0.44
130		15	23.37	0.51	0.079	0.44
132		20	23.80	0.53	0.081	0.47
133		15	26.76	0.43	0.074	0.41
131		30	33.23	0.43	0.073	0.41
137		15	45.53	0.57	0.116	0.50
136		30	50.67	0.47	0.095	0.42
127		60	64.84	0.54	0.079	0.43
135		45	67.14	0.61	0.102	0.50
174		0.0032	5	1.53	0.34	0.055
169	5		1.75	0.48	0.069	0.42
166	5		4.77	0.37	0.063	0.41
165	15		8.80	0.42	0.065	0.42
173	15		13.81	0.44	0.078	0.43
172	30		16.08	0.50	0.083	0.45

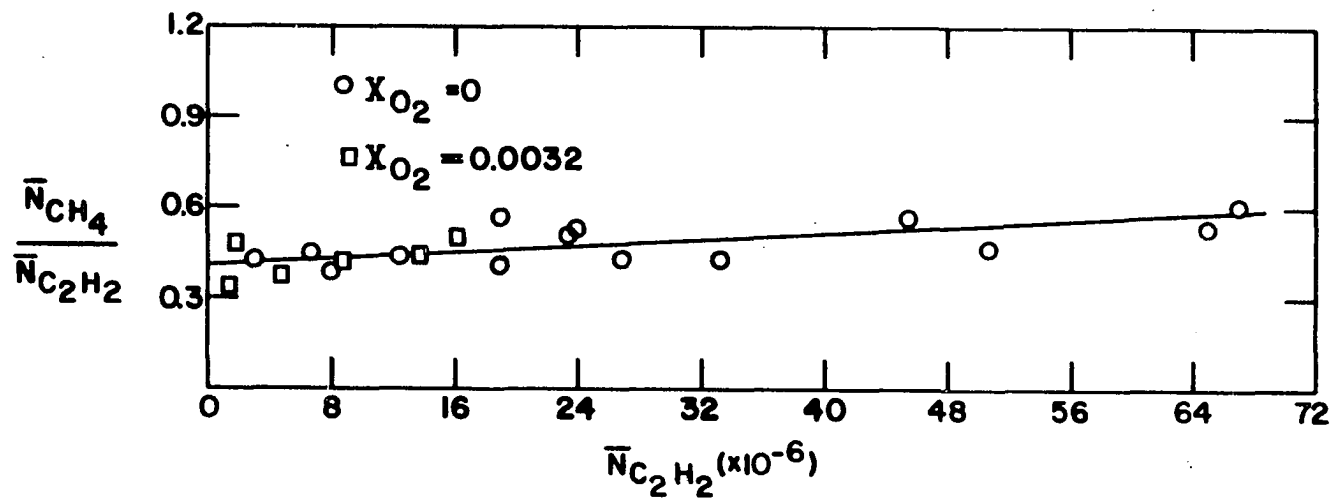


Figure 13. Plot of methane-acetylene yield ratio versus dose for n-hexane

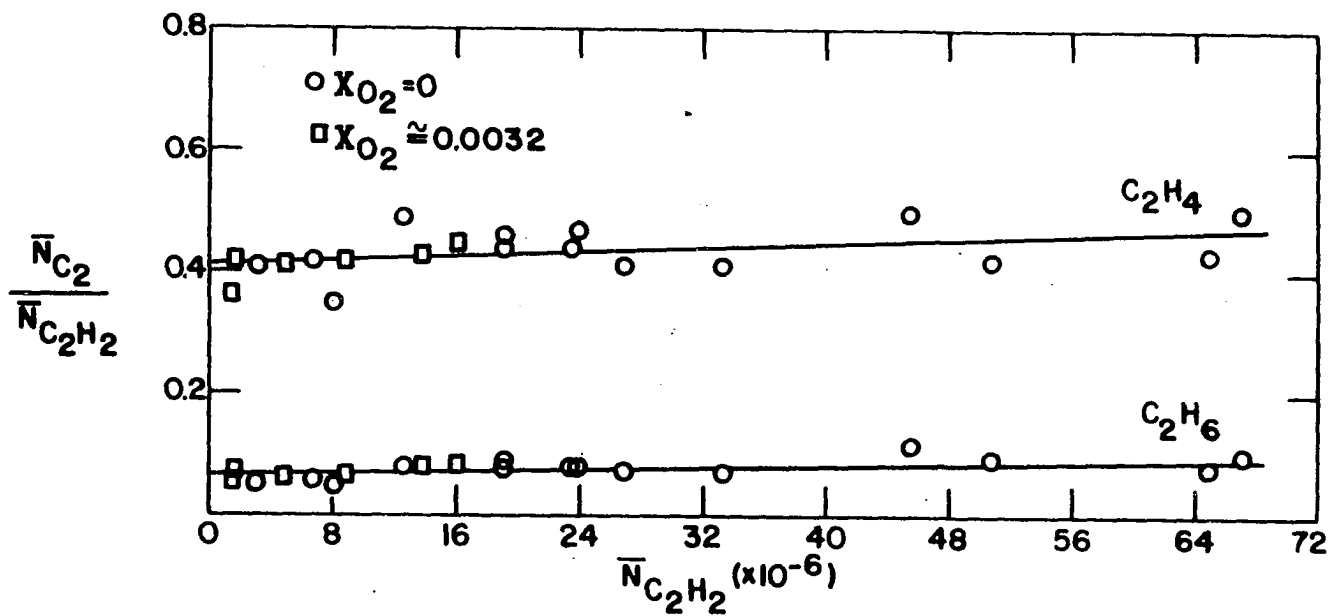


Figure 14. Plot of ethane-acetylene and ethylene-acetylene yield ratios versus dose for n-hexane

DISCUSSION OF RESULTS

In a discussion of the mechanism by which stable chemical products are formed due to the recoil process, the nature of the recoiling species should be considered. The carbon-11 recoil energy can be calculated for the $C^{12}(\gamma,n)C^{11}$ process from a knowledge of Q for the reaction and the energy of the impinging gamma ray. If the momentum given the atom by the gamma ray is neglected, the recoil energy may be calculated using the equation:

$$E_r = (E + Q) \frac{m_1}{m_1 + m_2}, \quad (\text{Eq. 14})$$

where

E_r = recoil energy

E = gamma ray energy

Q = energy of reaction

m_1 = emitted particle mass

m_2 = recoil particle mass.

The value of Q for the $C^{12}(\gamma,n)C^{11}$ reaction is -18.7 Mev. The recoil energy given a carbon-11 atom by the 22.5 Mev gamma ray at the cross section peak maximum is 0.32 Mev. The reaction cross section falls from 8.3 mb at the peak to about 1 mb at a gamma ray energy of 33 Mev (53). The

recoil energy of a carbon-11 atom produced by a 33 Mev gamma ray is 1.2 Mev. Since the number of gamma rays present in the synchrotron beam decreases with increasing gamma ray energy, relatively few carbon-11 atoms having recoil energies above 1 Mev are produced. Since these energies are well in excess of chemical bond energies, it is highly improbable that any of the bonds to the activated carbon will fail to rupture.

The recoil carbon-11 dissipates its energy by a series of interactions with its environment of hydrocarbon molecules. These interactions can be ionization and excitation processes or radical producing collisions. Harvey (62) has indicated that heavy particles with a velocity of about 2×10^8 cm/sec lose energy mainly by collision processes. The mean energy of the carbon-11 produced is near 0.35 Mev, and this energy gives an initial velocity of 2.5×10^8 cm/sec. For a 1.0 Mev carbon-11 atom, the initial velocity of the recoiling atom is 4.2×10^8 cm/sec. The range of recoil particles with velocities of this order of magnitude in a medium of atoms of a given mass and atomic number can be calculated using the following equation given by Bohr (62, 63):

$$R_o = kE \left[\frac{M_2(M_1 + M_2)}{M_1} \right] \left[\frac{(Z_1^{2/3} + Z_2^{2/3})^{1/2}}{Z_1 Z_2} \right], \quad (\text{Eq. 15})$$

where

R_0 = range in $\mu\text{g}/\text{cm}^2$

k = experimental constant which is a function of $\frac{M_1}{M_2}$
and E

E = energy of recoil particle in Mev

M_1 = mass of recoil particle

M_2 = mass of atoms in the stopping medium

Z_1 = atomic number of recoil particle

Z_2 = atomic number of atoms in the stopping medium.

For a 1.0 Mev carbon-11, Equation 15 gives a range of 226 $\mu\text{g}/\text{cm}^2$ in hydrogen and 850 $\mu\text{g}/\text{cm}^2$ in carbon. Since the recoil atom is actually moving through a hydrocarbon medium, the stopping effects of the hydrogen and carbon must be weighted using the following equation given by Friedlander and Kennedy (64):

$$\frac{1}{R_t} = \frac{w_1}{R_1} + \frac{w_2}{R_2}, \quad (\text{Eq. 16})$$

where

R_t = total range in the molecular environment

w_1 = fraction by weight in the molecule of atoms in
which the range is R_1

w_2 = fraction by weight in the molecule of atoms in
which the range is R_2 .

Calculating R_t from Equation 16 and dividing it by the appropriate density gives a range for a 1.0 Mev carbon-11 atom of 8.0×10^{-4} cm in benzene, 7.8×10^{-4} cm in cyclohexane, and 8.9×10^{-4} cm in n-hexane. Since few carbon-11 atoms are produced with recoil energies greater than 1.0 Mev these ranges can be considered maximum ranges.

The energy absorbed by the sample from the synchrotron beam is not a continuous function of time. The reason for this is that a burst of from 10^8 to 10^{11} electrons is injected into the acceleration chamber 59 times per second. The duration of this burst, which is the time during which carbon-11 is produced, is about 4×10^{-8} second and the time between bursts is 1.7×10^{-2} second. The mean velocity of the carbon-11 fragment lies somewhere between an initial velocity of 4.2×10^8 cm/sec and its velocity at thermal energies of about 7×10^4 cm/sec. If it is assumed that the recoil fragment spends more time near thermal energies, the mean velocity can be taken as 10^6 cm/sec. Using this velocity and the range calculated above for a 1.0 Mev carbon-11, the time elapsed between the production and thermalization of the carbon-11 is on the order of 10^{-9} second. This time is much shorter than the time between synchrotron beam bursts, and therefore essentially all of the recoil atoms produced in one burst have dissipated their excess kinetic energy before a new group of recoil

atoms is formed.

The extent to which the carbon-11 is ionized due to its high kinetic energy has been calculated by Lang (61). By considering the recoil energy needed to lose an orbital electron, he finds that the most probable charge on the carbon-11 is +1. He finds that a charge of +2 is possible but that any higher charge is quite unlikely. Harvey (62) has indicated that, very roughly, the charge of a recoil particle, Z^* , is related to its velocity V and atomic number Z by the following equation:

$$Z^* = Z^{1/3} \left[\frac{V}{V_0} \right], \quad (\text{Eq. 17})$$

where

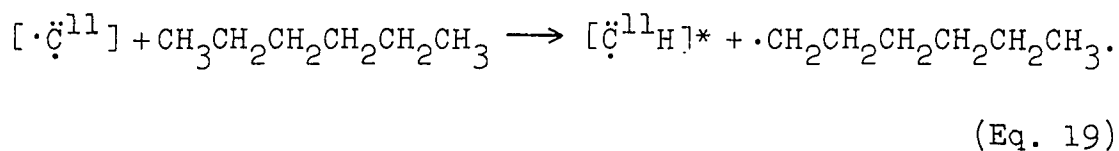
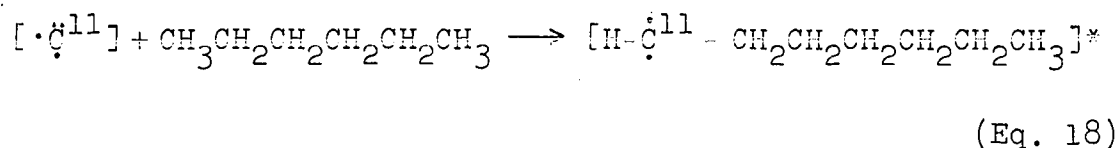
$$V_0 = \frac{e^2}{h} = 2.2 \times 10^8 \text{ cm/sec.}$$

The value of Z^* for a 0.35 Mev carbon-11 atom with a velocity of 2.5×10^8 cm/sec given by Equation 17 is +2.1. This is in agreement with the charge calculated by Lang, and therefore the carbon-11 may be considered to have a charge of +1 or +2 when it is born.

In the process of dissipating its energy the recoiling atom is able to pick up hydrogen from its environment to form carbon-hydrogen ions or neutral radicals. The ionization potentials of the $[\cdot\ddot{C}]$, $[\cdot\ddot{C}H]$, $[:CH_2]$, and $[\cdot CH_3]$

radicals are 11.264 ev (65), $11.13 \pm .22 \text{ ev}$ (66), $11.82 \pm .05 \text{ ev}$ (67), and $9.840 \pm .002 \text{ ev}$ (68), respectively. The ionization potential of benzene has been reported as 9.24 ev (69) and 9.9 ev (70). The ionization potentials of cyclohexane and n-hexane have been reported to be 10.79 ev and 10.46 ev respectively (71). With the exception of the CH_3 species in cyclohexane and n-hexane, it appears likely that the CH_x fragments which are formed are neutral radicals and that the initial charge on the carbon-11 atom is transferred to the hydrocarbon medium.

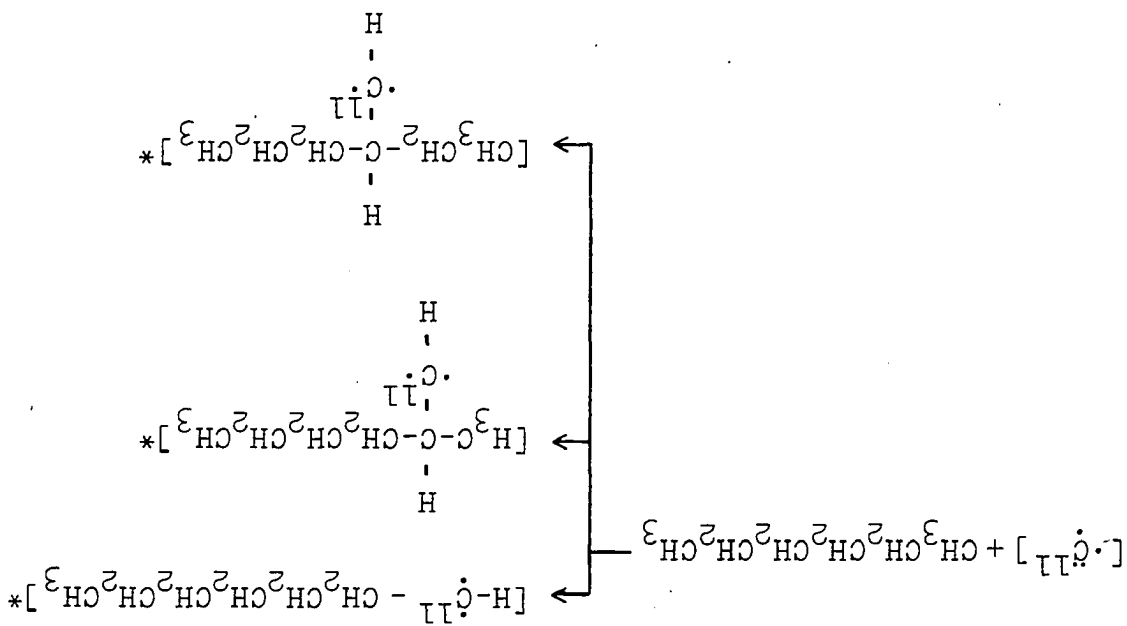
From the above discussion, it seems quite likely that the carbon atom is neutral by the time it undergoes its first reactive collision. The radical concentration due to radiation damage is probably small, though not negligible, compared to the concentration of hydrocarbon. Most of the collisions undergone by the carbon-11 as it dissipates its energy will be with hydrocarbon molecules. These collisions, which take place while the recoiling atom is above thermal energies, will result in either bond formation with the hydrocarbon or hydrogen abstraction to form a CH_x fragment and a radical. As an example, the possible reactions of $[\cdot\overset{11}{\text{C}}]$ with n-hexane are described in Equations 18 and 19.



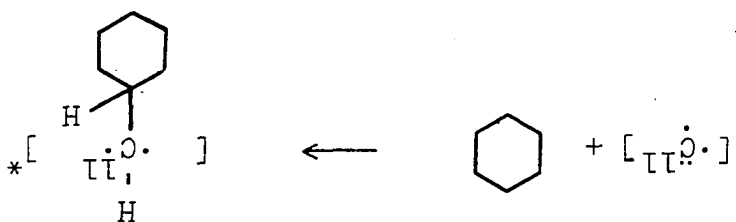
The type of reaction shown in Equation 18 has commonly been called a bond insertion reaction, while the reaction in Equation 19 may be looked upon as a hydrogen abstraction process. The production of CH_x fragments in the system proceeds either by a series of direct abstractions, or by a series of insertion reactions in which the carbon-carbon bond formed by the insertion is broken and the carbon-hydrogen fragment carries off one more hydrogen than it had before insertion. At present it is impossible to say which process actually occurs to form CH_x fragments, but the net result of either process is hydrogen abstraction.

In the systems used in this study, the major product in all cases was acetylene. This has been found to be true for a wide variety of systems (41, 43, 44, 49, 50, 51, 52). The large scale formation of acetylene is a strong argument for carbon atom insertion into a carbon-hydrogen bond. The possible intermediates resulting from $[\cdot\ddot{C}^{11}]$ insertion into a carbon-hydrogen bond in benzene, cyclohexane, and

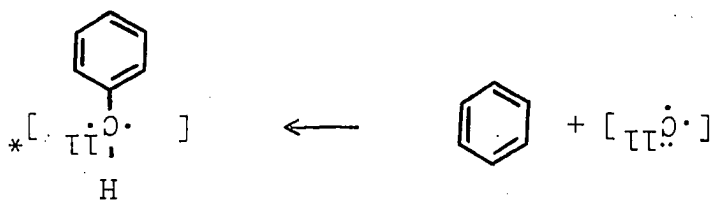
(Eq. 22)



(Eq. 21)



(Eq. 20)



n-hexane are shown in Equations 20, 21, and 22:

Three intermediates are possible in the reaction of $[\cdot\overset{11}{\text{C}}]$ with n-hexane, whereas only one is possible in the reaction with benzene and cyclohexane. It would be expected that the benzene intermediate would be the most resistant to decomposition to form acetylene due to its bond structure. If the recoil carbon-11 attacks a molecule randomly, about one-third of the time the straight-chain intermediate will be formed in n-hexane which means that only one carbon-carbon bond need be broken in this case compared to cyclohexane where two carbon-carbon bonds must be broken in the intermediate to form acetylene. Therefore, it might be expected that the acetylene yield would increase from benzene to cyclohexane to n-hexane. From Figures 7, 8, and 9, it is seen that the yields of acetylene from benzene, cyclohexane, and n-hexane compared to a tantalum monitor are in the ratio 1.00:1.56:2.00, which is the trend expected from the intermediates described.

For the production of ethylene it is postulated that the principal mechanism is like that described above, only the fragment which is inserted is now a $[\cdot\overset{11}{\text{C}}\text{H}]$. The ethane formed is a result of the insertion of a $[\text{:}\overset{11}{\text{C}}\text{H}_2]$ into a carbon-hydrogen bond of the hydrocarbon. Since the energy to decompose the complex formed must come from the recoiling fragment, it would be expected that as more hydrogen becomes attached to the carbon-11, the less likely

it would be that the fragment would bring enough energy into the complex to cause decomposition. Thus, there should be less ethylene than acetylene formed for a given compound since the $[\cdot\overset{11}{\text{C}}\text{H}]$ fragment would be less energetic than the $[\cdot\overset{11}{\text{C}}]$. This is indeed the case for the systems studied as the ethylene-acetylene ratio was found to be less than one. In benzene, no two-carbon products other than acetylene were observed at all. It was also found that much less ethane than ethylene was produced in cyclohexane and n-hexane. This is in agreement with the idea that on the average $[\text{:}\overset{11}{\text{C}}\text{H}_2]$ fragments will be less energetic than $[\cdot\overset{11}{\text{C}}\text{H}]$ fragments. These trends would indicate that the intermediates formed from methylene and methyne radicals are better able to absorb the remaining recoil energy than those formed from free carbon atoms. Another way of stating this is to say that if the recoil carbon-11 undergoes a series of insertion reactions, as it gains more hydrogen it loses energy until it will eventually form an intermediate which can stabilize, form a product by decomposing the intermediate, or form $[\cdot\overset{11}{\text{C}}\text{H}_3]$ which cannot undergo an insertion reaction.

The methane yield is probably due to hydrogen pick-up either by a series of insertion reactions or by simple abstraction. Either means of hydrogen addition to the recoil carbon-11 is a step-wise process, so that the final step

to form methane must be either a hydrogen abstraction by a $[\cdot\text{C}^{11}\text{H}_3]$ fragment or the reaction of such a fragment with an $[\text{H}\cdot]$. It appears from the methane yield in benzene that very little $[\cdot\text{C}^{11}\text{H}_3]$ is formed in this system. This is probably due to the formation of toluene from stabilization of the intermediate formed by the reaction of $[\cdot\ddot{\text{C}}^{11}\text{H}]$ or $[\text{:C}^{11}\text{H}_2]$ with benzene. The methane yield is greater in cyclohexane than in n-hexane, while the reverse is true of the two-carbon product yields. Very likely this is due to the fact that if a CH_x fragment attacks one of the methyl groups in n-hexane only one carbon-carbon bond need be broken in the intermediate to form either a two-carbon product or another CH_x fragment. Thus, eventual formation of $[\cdot\text{C}^{11}\text{H}_3]$ leading to the production of methane is more likely to occur in cyclohexane than in n-hexane.

If the insertion reactions were the only processes leading to product formation, the product yields should not be sensitive to radiation dose. However, it is obvious from the plots of product yield ratios versus dose that the yields of products other than acetylene are dose dependent, some to a greater degree than others. The effect of radiation damage has been studied for several systems (48, 49, 72). A measure of the radiation damage to be expected in a system can be made by calculating the radiation dose per molecule of sample present. Wolfgang has indicated that

the radiation damage in the systems which he has studied using a heavy ion accelerator was due to a dose of about 0.01 ev/molecule (43, 50). A range of values from 1.4×10^{-3} to about 10^{-4} ev/molecule has been given by Wolf in his work with low molecular weight hydrocarbons (51, 72). It has been shown that changing the dose over a range of 10^{-4} to 1.0 ev/molecule does affect the product yields resulting from reactions of recoil carbon-11 (48). Taking the average sample size in this study to be 0.2 gram, and using the dose rate of 3.5×10^{19} ev/g min given previously, the dose per molecule of sample for a sixty minute irradiation is 0.3 ev/molecule. For a five minute irradiation the result is 2.4×10^{-2} ev/molecule. The radiation damage from a synchrotron irradiation results from an electron flux through the sample in addition to the gamma ray flux. Thus, it is reasonable to assume that radiation induced secondary reactions are taking place in the system to some extent. These could be thermal radical reactions or radiation induced decomposition of higher molecular weight products. Extrapolation of the yield ratios to "zero" dose gives values for those ratios which have a minimum contribution due to secondary reactions.

Oxygen has been used as a scavenger for thermal radicals in several studies made by Wolfgang and his co-workers (43, 44, 50). Wolf has pointed out that care must be taken

in the use of oxygen since above about 0.5 volume percent in gaseous systems it not only acts as a radical trap but begins to compete with the hydrocarbon for energetic carbon-11 atoms to form carbon monoxide (51). The decrease in the yields of acetylene and ethylene due to the reaction of oxygen at high concentrations with recoil atoms has been demonstrated by Wolf (72). He also feels that since oxygen is a good alkyl radical trap and hydrogen atom trap, reduction of unsaturated products by hydrogen atoms probably takes place in unscavenged systems. The mole fraction of oxygen in the samples used in this study was small and the oxygen was intended to act as a radical scavenger only. Labeled carbon monoxide would be formed if the oxygen were to compete for energetic carbon-11 atoms. Carbon monoxide is eluted from a silica gel chromatographic column before methane, and since no carbon-11 containing carbon monoxide was observed in any of the analyses it may be assumed that oxygen acts only as a radical scavenger in this study. The yields of the products formed in short irradiations of cyclohexane and n-hexane are not affected by the addition of oxygen to the system. Therefore, these yields may be considered to be the result of insertion reactions with little contribution from thermal radical processes.

SUMMARY

Since the values of product ratios found by extrapolation to "zero" dose and those found with oxygen scavenger present are the same, the product yields giving these ratios can be considered the result of reactions undergone by the carbon-11 before it has reached thermal energies. The contribution to these yields of radiation induced reactions or thermal radical reactions is small. The method of hydrogen pick-up by the recoiling carbon-11 may be considered formally as a series of insertion reactions which take place at an energy between 15 and 50 ev. The energy needed to rupture bonds in the intermediate resulting from the insertion process comes from the recoil fragment. The yield of a specific product in a specific system then depends on the nature of the CH_x fragment attacking the parent hydrocarbon molecule, and the structure of the intermediate formed with respect to its ability to become stabilized or to decompose in a specific manner.

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