

1965

# Recoil chemistry of carbon-11 in liquid hydrocarbons

Donald Eldon Clark  
*Iowa State University*

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Physical Chemistry Commons](#)

## Recommended Citation

Clark, Donald Eldon, "Recoil chemistry of carbon-11 in liquid hydrocarbons " (1965). *Retrospective Theses and Dissertations*. 4079.  
<https://lib.dr.iastate.edu/rtd/4079>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

This dissertation has been  
microfilmed exactly as received

66-2954

CLARK, Donald Eldon, 1936-  
RECOIL CHEMISTRY OF CARBON-11 IN  
LIQUID HYDROCARBONS.

Iowa State University of Science and Technology  
Ph.D., 1965  
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

RECOIL CHEMISTRY OF CARBON-11 IN LIQUID HYDROCARBONS

by

Donald Eldon Clark

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:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University  
Of Science and Technology  
Ames, Iowa

1965

## TABLE OF CONTENTS

	Page
INTRODUCTION	1
Recoil Chemistry	1
Carbon Recoil Studies	8
Purpose of This Investigation	27
EXPERIMENTAL PROCEDURES	29
Materials	29
Sample Preparation and Irradiation	30
Radiochemical Assay	32
Radiochemical Yield Determinations	39
DOSIMETRY	45
Preliminary Remarks	45
Fricke Dosimetry	49
Glass Dosimetry	55
Summary	57
RESULTS AND DISCUSSION	58
Dose and Scavenger Studies	58
Product Yields from Selected Compounds	66
Benzene-methylcyclopentane Mixtures	79
CONCLUSIONS	85
BIBLIOGRAPHY	86
ACKNOWLEDGMENTS	93

## INTRODUCTION

## Recoil Chemistry

Atoms which have much more kinetic energy than they would have if they were in thermal equilibrium with their surroundings are commonly called hot atoms. This term is also used to designate atoms that are in excited electronic states.

Because the possible reactions available to such atoms are generally quite different from those ordinarily observed, there has been considerable interest in the chemistry of hot atoms.

A number of techniques have been employed for the production of hot atoms, usually involving the use of ultraviolet radiation, ionizing radiation, accelerators, or nuclear transformations. Hot atoms may also result from radioactive decay, especially from the electronic conversion phenomena associated with some types of decay. In the cases where the daughter nuclei are also radioactive, the study of their behavior is possible. The energies of hot atoms produced by ultraviolet radiation or by ionizing radiation are limited to a few ev, while the use of a heavy ion accelerator allows control of translational energies over a wide range of values.

Recoil chemistry is the study of hot atoms that are produced via nuclear transformations and these will be referred

to as recoil atoms throughout this discussion. Nuclear processes are highly energetic with energies typically in the Mev range. Because they must carry off their share of the available energies in order to conserve momenta, the recoil atoms almost always have sufficient kinetic energy to escape from the original molecules. Typical recoil energies range from  $10^2$  to well over  $10^6$  ev, while bond energies are only a few ev. The recoil atoms lose their excess energies through interactions with their environment and eventually become incorporated into chemically stable species. If the recoil nuclei also happen to be radioactive, a radiochemical assay can be performed to determine their ultimate chemical fate. Through proper variation of the experimental parameters, it may be possible to obtain valuable information about the reaction mechanisms and even the energetics involved.

The first reported investigation in the field of recoil chemistry was by Szilard and Chalmers (1) in 1934. In recognition of their contribution, the production of radioactive hot atoms by means of a nuclear reaction has been subsequently referred to in the literature as the Szilard-Chalmers process. They observed that some of the radioactive iodine produced by the  $^{127}\text{I}(n,\gamma)^{128}\text{I}$  reaction in ethyl iodide could be separated

from the parent compound, indicating that chemical bonds had been broken when the iodine-128 was formed. In the following year, Amaldi et al. (2) obtained similar results with thermalized neutrons and it was concluded that the iodine-128 recoiled upon emission of the gamma ray, thus breaking the carbon-iodine bond.

During the forties, a number of Szilard-Chalmers experiments were reported for various organic halides; the emphasis was mostly on determining the proportion of activity retained in the organic phase following a liquid extraction procedure, a quantity referred to as the organic retention. In 1940, the  $(\gamma, n)$  reaction was shown to give the same results as the  $(n, \gamma)$  reaction in ethyl bromide (3). A number of other nuclear reactions have since been used for recoil studies, including the  $(n, \alpha)$ ,  $(n, p)$ ,  $(n, 2n)$  and  $(p, pn)$ .

Libby (4) summarized the pertinent information which was known by 1947, listing the following facts as being of particular importance:

- 1) Organic retention was generally high, about 50%, and the activity was mostly in the form of the target molecule.
- 2) Dilution of the organic halide with hydrocarbons

or ethanol before the irradiations reduced the organic retention nearly to zero. A very small dilution of bromobenzene by aniline caused a considerable reduction in the organic retention.

- 3) Organic retention values of only a few percent resulted when samples were irradiated in the vapor phase.

In this paper, Libby also put forth the first proposal attempting to explain these experimental results, his so-called "billiard ball collision" hypothesis. He reasoned that only collisions with other halogen atoms could result in nearly complete transfer of momentum and energy from the recoil atom in a single elastic collision. When such an event occurs, the de-energized recoil atom and the radical formed by displacement of a halogen atom will be located closely together. Indeed, one might think of them as being trapped in a "cage" formed by the surrounding molecules and that the recoil atom is able to escape this "cage" only if it has sufficient energy. If neither of the species can escape the "cage", they will dissipate their excess energies to the local environment and react with one another to form a stable molecule.



According to Libby, the organic retention should be given by the following equation:

$$\text{Organic retention} = \epsilon/\nu \quad (\text{Eq. 1})$$

where  $\nu$  is the energy of the C-X bond and  $\epsilon$  is the minimum energy required for the recoil atom to escape from the "cage". A number of organic halides had been studied and the "cage" energies appeared to vary from 30-75% of the C-X bond energies. The other active species were thought to result from inelastic collision processes occurring after the recoil atom had lost a sufficient amount of its initial energy through elastic collisions with atoms of different masses. Since dilution would increase this probability and because there is no "cage" effect operative in the vapor phase, this argument did account for the experimental results, at least in a qualitative manner.

When it was realized that much of the organic retention was often due to forms other than the parent structure, Fox and Libby (5) broadened the original hypothesis to include "epithermal reactions". The epithermal energy region was envisioned to extend from near thermal values, about 0.025 ev, to perhaps several times the energies involved in chemical bonding. A recoil atom with energy in the epithermal range would collide inelastically with an entire molecule, forming

organic radicals, and radical recombination in the "cage" could give a variety of labeled organic products differing from the target compound.

An extension of Libby's hypothesis was given by Miller et al. (6) in 1950. They derived mathematical expressions for the relative yields of particular products formed in high energy reactions as functions of the nature and extent of dilution. Their basic assumptions were that the processes could be described by billiard ball mechanics and that the recoil atom would be restricted to a reaction "cage" after losing most of its energy. It was soon shown, however, that their predictions did not agree with the experimental results of some liquid phase studies (7).

In 1960, Estrup and Wolfgang (8) extended these ideas to gaseous systems where there is no reaction "cage". Excellent agreement between theory and experiment has been obtained for the energetic reactions of tritium with methane (9) and with other compounds (10). However, the assumption that the important recoil processes in condensed phases can be described by billiard ball mechanics appears to be incorrect.

Willard (11) questioned the basic assertion that elastic collisions play a dominant role in the liquid state. He pro-

posed an alternative model in his so-called "random fragmentation" hypothesis. Instead of undergoing elastic collisions with individual atoms, he assumed that the recoil atom would experience predominantly inelastic encounters with entire molecules. This would result in a random disintegration of the molecules, thereby producing a variety of molecular wreckage in the path of the recoil atom. Near the end of its path, after the recoil atom had lost most of its initial energy, it would be located in a "nest" of radicals. If it combined directly with one of these radicals to form a stable molecule, this would be considered a hot process. Another possible mode of reaction would involve the thermal diffusion of the recoil atom away from this cluster of free radicals, so that it could react with a molecule by a thermal process.

Willard suggested that certain operational criteria could be used to distinguish between the products formed by hot and thermal reactions. Changes in phase, temperature variations, or the presence of radical scavenging agents, in low but effective concentrations, were assumed to greatly affect the yields of products resulting from thermal reactions. On the other hand, the effect of varying these parameters on the yields of products arising from hot processes should be rela-

tively small.

Since Willard's approach quite naturally emphasized the diverse nature of the molecular debris formed in the path of the recoil atom, the variety of products which was often observed could be entirely rationalized from his hypothesis. However, the relative yields of these products were inconsistent with this model in many cases (12-15).

Perhaps the main criticism which can be made about these early theoretical approaches is that they attempted to explain everything in terms of oversimplified physical models without regard to chemical considerations. That they have provided a remarkable stimulation for experimentalists is exemplified by the fact that well over a thousand scientific papers on various aspects of recoil chemistry have appeared.

Walton (16) recently pointed out the inability of any of the existing theories to explain the experimental results obtained for compounds in the condensed phase. He suggested that future theoretical treatments should consider the relative importance of excited electronic states to the chemistry of recoil atoms.

In recent years, the trend has been a retreat from using the purely physical picture. Instead, the emphasis has been

on the chemical environment in which the recoil atom is found.

A number of reviews and fairly comprehensive articles have been published (10,11,14,17-25) which, when taken in their entirety, present a very complete view of the field.

### Carbon Recoil Studies

In the case of carbon, there are two isotopes, with mass numbers 11 and 14, that can be used for recoil studies.

Carbon-14 decays with a half-life of 5720 years, emitting a soft (0.155 Mev) beta ray (26); it is produced with thermal neutrons by the  $^{14}\text{N}(n,p)^{14}\text{C}$  reaction, the cross section being 1.75 barns (26). The Q value for this reaction is -0.626 Mev.

Since this energy must be shared between it and the emitted proton in such a way that the momentum is conserved, the carbon-14 recoils with about 0.042 Mev of kinetic energy. Bond energies are on the order of only a few ev, so it appears certain that the recoil atom must break loose from the original molecule and move into its surroundings like a projectile.

One inherent disadvantage to carbon-14 studies is that long bombardment periods are necessary with the available neutron fluxes in order to obtain detectable amounts of the material. This is due to the long half-life of the nuclide, as well as to the small cross section for its formation. The

time-integrated flux of neutrons and gamma radiation, to which a sample must be exposed in order to get sensible amounts of activity, may actually cause modification of the tagged products. If bombardments are carried out in regions of a reactor with low gamma ray flux - such as the "thermal columns" - the radiation damage should be reduced.

Carbon-11, which decays by positron emission with a half-life of 20.4 minutes (26), has been produced by the following nuclear reactions (19):  $^{12}\text{C}(n,2n)^{11}\text{C}$ ,  $^{12}\text{C}(\gamma,n)^{11}\text{C}$ ,  $^{12}\text{C}(p,pn)^{11}\text{C}$ ,  $^{14}\text{N}(p,\alpha)^{11}\text{C}$ , and  $^{16}\text{O}(p,pn\alpha)^{11}\text{C}$ . Another method of producing carbon-11 involves the use of a neutron-stripping reaction, brought about by accelerating a beam of carbon ions to 120 Mev in a heavy ion accelerator and allowing it to pass through a platinum foil (27,28). In all of these reactions, the carbon-11 atoms will have initial energies of at least several Kev.

Most of the current work in carbon recoil chemistry is done with carbon-11. If one has access to an appropriate accelerator, reasonable yields of activity are easily achieved with short irradiation times, because of the short half-life.

The experimental degrees of freedom are generally greater than for experiments taking place in a reactor and all that is

required is a rapid method of assay. It was first shown by Evans and Willard (29) that tracer quantities of material could be rapidly and effectively separated and radioassayed by means of gas chromatography. This method has been vitally important to carbon-11 recoil studies.

The first carbon recoil experiments were with carbon-14 in inorganic compounds. It was reported as early as 1948 that when ammonium nitrate solutions were bombarded with neutrons, the carbon-14 was distributed 56% as carbon monoxide and 44% as carbon dioxide (30). Rowland and Libby (31), the first to use the  $^{12}\text{C}(\gamma, n)^{11}\text{C}$  reaction for recoil studies, observed that 95-100% of the activity appeared as CO when liquid carbon dioxide or sodium bicarbonate solutions were irradiated. The activity was about equally divided between the forms CO and CO<sub>2</sub> when the irradiations were of solid carbon dioxide or crystalline sodium bicarbonate. It was postulated that  $^{11}\text{CO}_2$  was formed by hot radical processes occurring in the paths of the recoil atoms, while the  $^{11}\text{CO}$  resulted from the thermal reactions of recoil carbon atoms with carbon dioxide or water.

McCallum and his co-workers (32,33), also using the photo-nuclear reaction to produce carbon-11, irradiated anhydrous sodium bicarbonate, sodium carbonate, and calcium carbonate.

However, they used a much less drastic acid treatment to liberate the gases and reported very different results. They reported that the activity from all three irradiated compounds was distributed as 22%  $\text{CO}_2$ , 3%  $\text{HCOOH}$ , 39%  $(\text{COOH})_2$ , 25%  $\text{HOOCCHO}$  and 10%  $\text{HOOCCH}_2\text{OH}$ . They also reported a post-irradiation annealing effect. When the crystals were heated, they observed a decrease in the acid-soluble products and a corresponding increase in labeled  $\text{CO}_2$ , until all of the activity was in this form above  $500^\circ\text{C}$ . This seemed to indicate that the observed products resulted from the reactions of some unreacted species, trapped in the crystalline lattices, with the solvent. They speculated that the annealing process served to promote reactions of these species with displaced oxygen atoms. It appeared that the recoil atoms had an oxidation number of four at the time of the final collisions in those crystals, since all of the carbon-11 was in that oxidation state after the annealing.

Later experiments in which sodium formate crystals were irradiated (34) showed that the activity was distributed as 5%  $\text{CO}$ , 4%  $\text{CO}_2$ , 15%  $\text{HCOOH}$ , 6%  $(\text{COOH})_2$ , 11%  $\text{HOOCCHO}$ , 31%  $\text{HOOCCH}_2\text{OH}$ , 15%  $(\text{CHO})_2$  and 14%  $\text{HOCH}_2\text{CHO}$ . In this instance, thermal annealing resulted in an increase in the active forms of  $\text{CO}_2$ ,



HCOOH and  $(\text{COOH})_2$ , as well as the appearance of a new form,  $(\text{CH}_2\text{OH})_2$ . Not all of the recoil atoms appeared to have the same oxidation number at the time of the final collisions in sodium formate crystals. It was argued that perhaps some were in the form of CO with oxidation number two at that time, since that was the most common oxidation state after the annealing process.

Yankwich and co-workers (35-38), studying the ammonium halides with the  $^{14}\text{N}(n,p)^{14}\text{C}$  reaction, have also presented evidence that reactive fragments could be trapped in crystalline lattices.

Wolf and his co-workers (19,39,40), using both  $^{11}\text{C}$  and  $^{14}\text{C}$ , have studied the recoil chemistry of carbon in gaseous ammonia and in gaseous, liquid and solid methylamine. Methane- $^{14}\text{C}$  accounted for over 90% of the activity when ammonia was bombarded with neutrons (39). However, in experiments where  $^{11}\text{C}$  was produced in ammonia, they reported nearly equal amounts of  $^{11}\text{CH}_4$  and  $^{11}\text{CH}_3\text{NH}_2$  under conditions of minimal radiation damage, while a 10,000-fold increase in dosage resulted in nearly 100%  $^{11}\text{CH}_4$  (40). These experiments indicated that modification of the primary products had occurred to a considerable degree during the neutron bombardments.

MacKay et al. (28) reported  $^{11}\text{CH}_4$  as the major product from ammonia under conditions of severe radiation damage, but  $^{11}\text{CH}_3\text{NH}_2$  was not observed under the most mild dose conditions obtainable. They were apparently troubled with impurities on the walls of their sample containers, however, since equal amounts of  $^{11}\text{CH}_4$  and  $^{11}\text{CO}$  were reported to be the products of recoil carbon-11 plus hydrogen. It has been reported that  $^{11}\text{CO}$  was the major product for a number of inorganic compounds, including oxygen, nitrogen (cf. hydrogen), and some of the oxides of carbon, sulfur and nitrogen (39,41).

The earliest paper concerning the behavior of recoil carbon atoms in a hydrocarbon medium was published in 1954 by Schrodtt and Libby (42). They found the  $^{14}\text{C}$ -products in n-pentane to be 12% gaseous, 25% as n-pentane itself, and the remainder higher boiling. A later paper (43) described an attempt to characterize the "synthesis" products, those which contained one more carbon atom than the parent molecule, and a wholly different product spectrum was presented (e.g., 2% gaseous activity). Accurate radiochemical assay was very difficult to achieve in their work, since fractional distillation was used to effect the product separations. It is possible that their results for benzene (44) are more reliable,

because the reported products differed more in their boiling points. Only 25% of the activity was volatilized when the solutions were boiled at 359°C. The  $^{14}\text{C}$ -yields were determined to be 2.5% benzene, 1.7% toluene, 3.2% diphenylmethane and 2.1% triphenylmethane.

Suryanarayana and Wolf (45), in the first published experiments to use gas chromatographic separations of carbon recoil products, studied benzene with the  $^{12}\text{C}(n,2n)^{11}\text{C}$  reaction and obtained yields of 4.5% "re-entry", benzene- $^{11}\text{C}$ , and 2.2% "synthesis", toluene- $^{11}\text{C}$ . The benzene/toluene ratio of about two-to-one was later verified by Voigt *et al.* (46), although the yields were found to be somewhat higher. From phase studies and the effects of known radical scavengers, Suryanarayana and Wolf concluded that the toluene- $^{11}\text{C}$  and some of the benzene- $^{11}\text{C}$  were formed by hot processes. They postulated that methylene- $^{11}\text{C}$  would be formed as the recoiling fragment cooled; reaction of this with a benzene molecule would give an excited seven-carbon intermediate which could stabilize directly to toluene- $^{11}\text{C}$ .

Support for the existence of the  $^{11}\text{CH}_2$  radical developed when it was shown that the saturated six-carbon products in liquid n-pentane, as well as the "synthesis" products in

liquid toluene, were distributed as though the hydrogen atoms in the parent compounds were randomly replaced by one labeled methyl group per molecule (47). Doering et al. (48) had shown earlier that photolytically-produced methylene caused such a statistical replacement in liquid n-pentane. This process is now widely referred to as an insertion reaction of methylene into a carbon-hydrogen bond and is recognized as a characteristic reaction of carbenes (49).

Stöcklin and Wolf (50) found the ratio of n-butane- $^{11}\text{C}$ /i-butane- $^{11}\text{C}$  to be about three-to-one when carbon-11 was produced in liquid and in solid propane substrates, thus lending further support for  $^{11}\text{CH}_2$ -insertion. Recent work in this laboratory has also confirmed the statistical distributions of the saturated  $\text{C}_{n+1}$  products obtained from carbon-11 plus liquid  $\text{C}_n$  hydrocarbons.<sup>1</sup>

In the vapor phase, insertion by methylene has been shown to be more selective (51,52); in fact, Frey (52) has shown that the probabilities for methylene-insertion into secondary and tertiary carbon-hydrogen bonds are, respectively, 20% and 50% greater than for insertion into primary carbon-hydrogen

---

<sup>1</sup>Mesich, F. G., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Private communication. 1965.

bonds. The relative radiochemical yields of saturated  $C_{n+1}$  products produced by recoil carbon atoms in various gaseous  $C_n$  alkanes indicated that they probably resulted from insertion by methylene- $^{11}C$  (28,50).

Lang and Voigt (53) determined the yields of volatile  $^{11}C$ -products formed in n-hexane and cyclohexane. In the liquids, nearly one-sixth of the activity was in the form of acetylene, and an equivalent amount of activity was represented by the other gaseous products of methane, ethane, ethylene, propane, propylene and four-carbon compounds. Willard's "random fragmentation" model was employed to rationalize the products as resulting from reactions between the radicals produced in the systems and such  $^{11}C$ -hydrogen fragments as  $^{11}CH$ ,  $^{11}CH_2$  and  $^{11}CH_3$ . Their data also indicated a decrease in the yields of volatile products in going from liquid to solid cyclohexane.

At about the same time, MacKay and Wolfgang (54) published results for carbon-11 interacting with gaseous methane, ethane, propane and cyclopropane. Again, a dominant product was acetylene- $^{11}C$ , accounting for nearly two-thirds of the total volatile activity formed in cyclopropane and for one-third in the other systems. The reaction scheme which they

proposed involved the insertion into a carbon-hydrogen bond of a bare carbon-11 atom, or possibly a  $^{11}\text{CH}$  radical, thus forming an energetically excited carbene intermediate. They reasoned that sufficient energy would be available to rupture two beta-carbon-carbon bonds if necessary, as in cyclopropane, to form acetylene- $^{11}\text{C}$ . The products containing fewer carbons than the parent compound could be formed by more complicated modes of decomposition of the carbene, whereas the unsaturated  $\text{C}_{n+1}$  products would result from de-activation of the excited intermediate.

Wolfgang and his co-workers studied the gas phase reactions of carbon-11 in propylene (28) and in ethylene (55). They concluded that insertion of the carbon-11 into the double bond, as well as into carbon-hydrogen bonds, was occurring. For example, about twice as much allene- and propylene- $^{11}\text{C}$  formed from ethylene as did propane- and propylene- $^{11}\text{C}$  from ethane. Methylene-insertion into olefinic bonds had been reported in photolytic studies (48). The rate of addition to the double bond in ethylene has been shown to be more than twenty times the rate of insertion into the carbon-hydrogen bonds (56). In a later paper (57), Wolfgang reported degradative studies which indicated that the allene- $^{11}\text{C}$  was mostly

center-labeled, in support of the hypothesis that carbon atoms could insert into C=C bonds. The end-labeled allene-<sup>11</sup>C presumably resulted from C-H insertion. Four important papers on ethylene have recently been published by Wolfgang's group (58-61) and a more detailed discussion of these will be given shortly.

In order to assess the applicability of the "random fragmentation" model to carbon recoil studies, MacKay and Wolfgang (62) performed phase studies with several compounds. They observed very little change in product yields under the different conditions and concluded that the insertion mechanism could account for the products formed in condensed systems, but that Willard's model could not. Their data were only preliminary, however, and they later showed that the product yields actually did depend upon the phase (59), in agreement with earlier observations by Lang and Voigt (53). Stöcklin et al. (63) have shown that the carbon recoil products in methane are also phase-dependent. The conclusions of MacKay and Wolfgang, although prompted by erroneous results, do appear to be correct and the observed recoil products in condensed systems can be rationalized by insertion mechanisms, but not by the "random fragmentation" model.

The phase effect can be discussed qualitatively by considering molecules in the condensed state to exist in "cages", or to simply be coupled to the local surroundings. The excited intermediate that is formed by a bond insertion process with a  $C_n$  molecule can be de-excited by transferring its excess energy to the nearby molecules, thus forming a  $C_{n+1}$  product. This process is much less probable in the vapor phase because the lifetime of the intermediate is short compared to the time required for collisional de-activation under ordinary pressures. It has been experimentally observed that the  $C_{n+1}$  products increase in going from the vapor to the liquid state, whereas the decomposition products (fewer than  $n$  carbon atoms) decrease in yield (19,50,53,63). This effect is much less pronounced in going from the liquid to the solid state (50,53,63), so it appears that de-excitation is nearly as efficient in liquids as in solids.

Stöcklin and Wolf (50) reported that the radiochemical yields of four-carbon products from both liquid and solid propane were ~25%. About one-half of those products were olefinic. They reported yields of ~13% for the four-carbon products obtained from gaseous propane, of which only about one-fifth were olefinic. Similar comparisons were given for



the three-carbon products from ethane.

The yields of two-carbon products from gaseous and solid methane were reported to be ~54% and ~66%, respectively (63). The relative insensitivity of the yield of those products to changes in phase was thought to be a reflection of the few degrees of freedom available to methane molecules for de-exciting the activated complexes.

Results obtained in this laboratory (see footnote on page 15) indicated that in liquid n-pentane ~38% of the total activity was in the form of six-carbon products, about 0.4 of which were unsaturated.

Rack and Voigt (64) studied the effects of radiation dose and iodine scavenger on recoil carbon-11 reactions in liquid cyclohexane. They determined that the acetylene-<sup>11</sup>C yield was constant over the investigated dose range and not affected by the radical scavenger. When iodine was present, the yields of the other volatile products were reduced and independent of dose. The four-carbon products disappeared under those conditions. However, in the absence of scavenger, the yields of products other than acetylene were seen to increase with increasing dose. It was suggested that the results were consistent with bond insertion mechanisms and that the portion of

the yields produced in the presence of iodine could be considered as the true hot atom yields.

Rack, Lang and Voigt (65) attempted to correlate the relative yields of two-carbon products obtained in various C<sub>6</sub> substrates with structural differences. They assumed that the total ethane and ethylene yield relative to the acetylene yield would depend primarily on the amount of hydrogen available at the site of the insertion, irrespective of other differences in the molecules. This was expressed as:

$$(\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)/\text{C}_2\text{H}_2 = aX + bY + cZ. \quad (\text{Eq. 2})$$

In this expression, X, Y and Z are the fractions of carbon atoms in the form of -CH<sub>3</sub>, -CH<sub>2</sub> and -CH groups, respectively, in the molecules. The constants a, b and c are the ratios for each of the three groups individually. A value of 0.66 for a was chosen from the oxygen-scavenged reactions of carbon-11 in gaseous ethane (54); 0.13 was chosen for b from results of liquid cyclohexane with iodine present (64); and c was chosen to be zero from results on liquid benzene. The agreement between the calculated and observed values for several hydrocarbons was good. It was concluded that the carbon-11 insertion reactions in saturated hydrocarbons must be random, at least to a large extent.

Wolf (19) has argued that the major part of ethylene- $^{11}\text{C}$  yield from alkanes arises from insertion into primary carbon-hydrogen bonds by the  $^{11}\text{CH}$  fragment, at least when sufficient scavenging action is occurring to eliminate the thermal reactions. Assuming that the total number of  $^{11}\text{CH}$ -insertion events in all hydrocarbons is a constant and that the insertions are completely random, then the ethylene- $^{11}\text{C}$  yield from ethane should represent the maximum attainable. The ratio of the yield of ethylene in any alkane to that obtained from ethane should be given by the number of primary hydrogens in the alkane molecule, divided by the total number of hydrogens. This can be expressed in the following way:

$$(\text{C}_2\text{H}_4)_{\text{alkane}} / (\text{C}_2\text{H}_4)_{\text{ethane}} = n(\text{P}) / n(\text{T}) . \quad (\text{Eq. 3})$$

In the above expression,  $n(\text{P})$  represents the number of primary hydrogens in the alkane and  $n(\text{T})$  represents the total number of hydrogens. The ethylene- $^{11}\text{C}$  yield was 14.8% in gaseous ethane with 4.5% oxygen present as a scavenger. Wolf obtained remarkable agreement between calculated values for this ratio and the experimental results for several alkanes irradiated in the vapor phase with oxygen present.

Stöcklin and Wolf (66) reported that the hot atom yield of acetylene in various gaseous hydrocarbons also showed a

marked structure dependence; for a series of irradiated compounds, the curve of acetylene- $^{11}\text{C}$  yield versus the ratio of primary carbons to total carbons in the molecule was a straight line.

Ache and Wolf (67) used a double tracer technique (see following paragraph) to determine the acetylene- $^{11}\text{C-d}^0$ ,  $^{-d^1}$ , and  $^{-d^2}$  yields from specifically deuterated propanes. Their results indicated that the fraction of the total acetylene- $^{11}\text{C}$  yield due to  $^{11}\text{C}$ -insertion into primary C-H bonds appeared to be 26% greater than that due to insertion into secondary C-H bonds.

Wolfgang and his co-workers first used a double tracer technique in order to study carbon recoil reactions (58,61). This approach was made feasible by the discovery of a gas chromatographic method for separation of deuterated light olefins (68). About equal amounts of labeled  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_3\text{D}$ ,  $\text{C}_2\text{HD}_3$ , and  $\text{C}_2\text{D}_4$ , but much less  $\text{C}_2\text{H}_2\text{D}_2$ , resulted when carbon-11 was allowed to react with an equimolar mixture of oxygen-scavenged  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{D}_6$  (58). These results were consistent with their proposed mechanism which involved  $^{11}\text{C}$ -insertions into C-H and C-D bonds followed by rupture of the C-C bonds to give the labeled  $\text{C}_2\text{H}_3$  and  $\text{C}_2\text{D}_3$  radicals. These radicals could

abstract hydrogen or deuterium to form the final products. The results could also be rationalized by the mechanism of  $^{11}\text{CH-}$  and  $^{11}\text{CD-}$  insertions where electronic rearrangement of the  $\text{C}_2$  fragments would give the final products directly.

For the reactions of carbon-11 with equimolar  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  (58), oxygen-scavenged, the relative yields of allene- $^{11}\text{C}$  products were  $\text{C}_3\text{H}_4$ , 7,  $\text{C}_3\text{D}_4$ ,  $7 \pm 1$ ,  $\text{C}_3\text{H}_3\text{D}$ ,  $1.0 \pm 0.3$ ,  $\text{C}_3\text{HD}_3$ ,  $1.0 \pm 0.3$ , and  $\text{C}_3\text{H}_2\text{D}_2$ ,  $<0.2$ . The low degree of isotopic mixing seemed to indicate that labeled allene resulted primarily from reactions of  $^{11}\text{C}$  with single molecules.

From similar studies on the formation of acetylene in different mixtures (61), it was concluded that both of the hydrogens in that final product were originally from the same carbon atom.

Rather extensive recoil experiments with ethylene have been reported by Wolfgang and his group, specifically on the production of allene and methylacetylene (59) and of acetylene and  $\text{C}_5$  products (60). Application of the resonance rule to this system indicates that the carbon atoms are probably neutral when they reach the energy range where chemical reactions can occur. This is because neutral carbon atoms, once formed, cannot re-ionize at or below  $10^3$  ev. Similarly, the treatment predicts that only relatively low-lying electronic

states of the carbon atoms should be expected to survive to the chemical energy region. The ground state,  $^3P$ , and the first excited states,  $^1D$  and  $^1S$ , should be particularly important when the carbon atoms undergo chemical reaction. These predictions also apply to carbon atoms in other hydrocarbons.

Wolfgang suggests that the reactions of triplet (ground state) carbons with ethylene lead to the formation of acetylene and the  $C_5$  products, but that methylacetylene and allene are formed by reactions of singlet carbon atoms. This hypothesis is supported by their data, but although the argument is quite plausible, it is by no means unequivocal. It is especially compelling to suppose that the  $C_3$  products are formed by addition of singlet carbons to ethylene, since there is no spin restriction on the immediate rearrangement of the singlet adduct to give these products.

The effects of changes in phase on the recoil products from ethylene have been reported by Wolfgang and his co-workers (27,59,60). They also reported the results of experiments in which neon was present in gaseous ethylene targets. The neon was assumed to have the effect of removing most of the energy from the recoiling species by collisional de-

excitation. Their experimental results indicated that acetylene and the C<sub>5</sub> products might have a common precursor, but that a different precursor was responsible for the C<sub>3</sub> products. The addition of oxygen as a scavenger eliminated the C<sub>5</sub> products, but had little effect on the yield of allene. Since the C<sub>5</sub> products were not observed in the presence of oxygen, their precursors must have been able to react much more efficiently with oxygen than with ethylene. It seemed reasonable to suppose that C<sub>3</sub> radicals were the precursors of the C<sub>5</sub> products.

Wolfgang has observed that even in highly moderated systems, in which the reactions probably occur at near thermal energies, the products are at least qualitatively similar to those obtained when no moderator is present. This implies that carbon atoms are intrinsically reactive and that the reactions of thermalized carbons are much like those of the hot atoms. The quantitative differences which are observed indicate that the thermal atoms are more selective, e.g., the ratio of center- to end-labeled C<sub>3</sub> products increase when moderator is added. In the experiments with neon-moderated ethylene, there was no observable temperature dependence, so there can be little difference in the activation energies

between the various modes of reaction. This must mean that these activation energies are close to zero. Exothermic reactions are responsible for the fragmentation products which are not eliminated when the carbon atoms are thermalized.

#### Purpose of This Investigation

Most of the carbon recoil studies done previously have concerned themselves with reactions in the vapor phase. Although these studies have been plagued with experimental difficulties, such as surface contaminations and reactions occurring on the walls of the sample vessels, a fairly clearcut view of the behavior of carbon recoil atoms in gaseous hydrocarbons has begun to appear. Such a position has only been reached after the accumulation of sufficiently reliable information for different systems, however. These data do not yet exist for liquid hydrocarbons.

The purpose of this investigation has been to study the product spectra that result from reactions of carbon-11 with various hydrocarbons in the liquid phase. The spectra of recoil products resulting from these compounds are quite complicated, since even polymeric forms are produced. Obtaining an accurate assay of all of the products in a single run is nearly impossible from an experimental point of view, because



the experiment must be completed within a few half-lives. This investigation was therefore restricted to the study of the fragmentation or gaseous products which resulted when carbon-11 was allowed to react with various C<sub>5</sub>-C<sub>7</sub> compounds.

The availability of an electron synchrotron at Iowa State University has made this study feasible. The  $^{12}\text{C}(\gamma, n)^{11}\text{C}$  reaction occurred in the samples when they were exposed to the bremsstrahlung beam of the synchrotron. Under the conditions of the irradiations, up to about  $10^9$  carbon-11 atoms could be produced in a moderate period of time. Carbon-11 was the only activity which was observed in the samples.

## EXPERIMENTAL PROCEDURES

## Materials

The hydrocarbons used in this study were Research Grade, obtained from Philips Petroleum Company. The impurities (in most cases the manufacturer's stated purities were in excess of 99.95 mole percent) failed to register on the most sensitive thermal conductivity scale of the gas chromatograph. These reagents were therefore considered to be sufficiently pure for this study and were used directly as obtained from the manufacturer. In those instances where the reagent bottles were stored for prolonged periods, sodium wire was added to reduce the moisture content. The tantalum foil, used as a beam monitor in some of the experiments, was obtained from Ethicon Suture Laboratories.

The product separations were accomplished by gas-solid chromatography, using silica gel (14-20 mesh) as the solid material. The silica gel, obtained from Fisher Scientific Company, was washed with concentrated nitric acid and rinsed completely with distilled water. It was then oven-dried at 125°C. for one day, after which it was suitable for packing into the columns. Flushing with helium gas prior to the experiments was also a standard procedure used throughout the

study.

The columns were calibrated with Commercial Grade gases obtained in lecture bottles from The Matheson Company. Although the addition of carrier compounds did not affect the results, the usual practice was to add some carrier at the beginning of each experiment. Acetylene was shown to react with the unwashed silica gel and so it was commonly added as a carrier, in order to assure that tracer amounts of the compound were not being lost.

#### Sample Preparation and Irradiation

The samples, 0.15 to 0.30 gm, were sealed in Pyrex ampoules with a vacuum degassing technique. The ampoules or bulblets were connected to the stopcocks of a vacuum line and the solutions were frozen with liquid nitrogen. The stopcock to the vacuum system was then opened and the space above the frozen sample was evacuated. After complete evacuation, the stopcock was closed and the sample allowed to melt. Once again the sample was frozen and the procedure was repeated. Then the sample was refrozen, the stopcock to the vacuum line was opened, and the small-diameter portion of the bulblet sealed about an inch above the solid.

Exposure of the samples to the bremsstrahlung beam of the

electron synchrotron produced the carbon-11 in situ by the  $^{12}\text{C}(\gamma, n)^{11}\text{C}$  reaction. The bulblets were taped to a specially constructed Synthane sample holder that could be positioned within a probe arrangement extending into the acceleration chamber of the synchrotron. By proper adjustment of the probe, the samples could be favorably positioned with respect to the beam. The irradiation periods varied from about five minutes to an hour. Electron energies of both 47 and 70 Mev were used in the runs; the results at the two energies were identical.

The  $^{12}\text{C}(\gamma, n)^{11}\text{C}$  reaction used in this study is endoergic to the extent of 18.7 Mev. The excess  $\gamma$ -ray energy in each case must be shared between the emitted neutron and the carbon-11 atom. Since the cross section for the reaction is largest for  $\gamma$ -rays with energies of 20-25 Mev, typical recoil energies will be on the order of 0.5 Mev (46).

Although the recoil atoms are initially formed at very high energies, it is assumed that they will not undergo reactions until most of their energies are dissipated. For this reason, the results should apply to carbon atoms in general that are excited to energies on the order of 10-30 ev and allowed to react with these systems.

DeVries and Voigt (69) and Lang (70) have calculated that

the initial charges on the carbon-11 atoms are +1 or +2. It has also been demonstrated that neutral species are involved by the time that energies are reached where reactions can occur (59,69). The maximum range that might be expected for the recoil atoms in these liquid hydrocarbons is about  $10^{-3}$  cm (69); this distance will be traversed in about  $10^{-9}$  second (69). Since the time between beam bursts is much longer,  $>10^{-2}$  second, all of the carbon-11 atoms formed in one burst will have reacted before the next one occurs.

#### Radiochemical Assay

A gas chromatograph, designed and built by R. Clark and W. Stensland of the Ames Laboratory, was used to perform the product separations. DeVries and Voigt (69) have given a complete description of the basic design which was used. The chromatograph was operated isothermally from room temperature to about  $60^{\circ}\text{C}.$ , depending upon the particular column in use. It was equipped with a thermal conductivity detector, the output of which was traced by one pen of a two-pen Bristol Dynamaster recorder. The recoil products were not detected by the thermal conductivity unit since they were present only in trace amounts.

Methane, ethane, ethylene and acetylene were the

pertinent recoil products in this study. It was found that these could be efficiently separated by silica gel, using helium as the carrier gas. This was used as the column material in all of the experiments. Under the usual operating conditions, retention times for the gases were generally less than an hour, but the liquids were essentially trapped on the columns. After several runs had been made with a given column, we would observe a discoloration of the silica gel and a corresponding decrease in the column's efficiency. It was therefore necessary to change the columns frequently, although the useful lifetimes were extended by replacing the first portion of the silica gel after each run. Periodic surveillance of the condition of the silica gel was facilitated by the use of glass columns.

The irradiated sample was placed in a sample breaker and the glass bulblet was shattered at the appropriate moment. The helium carrier gas, along with the hydrocarbon carrier, would then sweep the sample onto the column and the product separation would proceed. The helium flow carried the eluted products out of the chromatograph and directly through a glass counting cell located in a well-type NaI(Tl) scintillation crystal. The crystal was 2 inches high and 1.5 inches in

diameter, with a 1.5 inch deep, 0.75 inch diameter well. The assembled photomultiplier and crystal were shielded by about 3 inches of lead. The gas flowed next through a gas flow-rate meter and finally into a laboratory hood for exhaust. This experimental setup has been presented in detail by DeVries and Voigt (69).

Some experiments with  $2\pi$ - and  $4\pi$ -proportional counters, to detect the positrons, established the superiority of the scintillation method for this particular study. Scintillation counting of the penetrating annihilation gamma rays was used to determine the activities of the different products. The electronic circuitry which was employed allowed the second pen of the recorder to function as a rate meter (69); the activity could be simultaneously measured with a Nuclear-Chicago Decade Scaler, Model 186.

In the early phase of this study, the prevailing background was around 250 counts/min, which was low enough compared to the usual amounts of activity that favorable counting statistics generally prevailed. However, if the activity was less, the relative magnitude of the background became more important. To reduce the background, a single-channel analyzer was installed to function as a discriminator. It was

used in the integral mode to eliminate signals corresponding to gamma ray energies below about 0.4 Mev; this reduced the background to around 100 counts/min, thus increasing the precision of the experiments.

The chart, showing activity versus time, recorded graphically the results of each experiment: a series of radioactivity peaks. Either the peak areas or the counts recorded during the same time interval could be used, since the counts/area ratio was constant throughout the study. They were corrected for decay from the time when the beam was turned off. Wolfgang and Rowland (71) have given the following equation to relate the activity to the observed counts in a flow counter:

$$A = RF/V \quad (\text{Eq. 4})$$

where A is the activity, R is the observed counts, F is the flow rate of the gas, and V is the volume of the counting chamber. The above expression was used in this study; the corrected counts were multiplied by the flow rate, so that AV was actually calculated. The effective counting volume was determined to be 2.47 ml and similar flow rates were used in all of the experiments. The quantity AV was then taken to represent the activity due to a given product at the end of



the irradiation.

The number of radioactive atoms present at the end of the irradiation,  $N$ , is given by the following expression:

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

where  $\sigma$  is the cross section,  $\phi$  is the flux,  $N_0$  is the original number of parent atoms,  $\lambda$  is the decay constant, and  $t$  is the time of irradiation. The total number of the radioactive atoms produced during the irradiation,  $N_T$ , is given by the following equation:

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

Using Equation 5, plus the fact that the activity at the end of the irradiation,  $A_0$ , is equal to  $\lambda N$ , the following expression is obtained for the total number of radioactive atoms produced:

$$N_T = A_0 t / (1 - e^{-\lambda t}). \quad (\text{Eq. 7})$$

In the case of the recoil products,  $AV$  was assumed to be directly proportional to  $A_0$  and was standardized to a one gram sample. The quantity  $\bar{N}$  was calculated according to the expression

$$\bar{N} = AVt/w(1 - e^{-\lambda t}) \quad (\text{Eq. 8})$$

where  $w$  represents the sample weight in grams.

In order to compare the results of different runs, one

needs to have a measure of the total amount of activation which has occurred in each. The irradiation times are not a very helpful basis of comparison because of differences in beam intensity, placement, etc., from one run to another. At the beginning of this study, a strip of tantalum foil was wrapped around each sample to monitor the beam. A complete description of this method has already been given (69). The monitor activity, as determined with a Geiger-Mueller counter, was shown to be due almost entirely to the beta decay of the 8.1 hour tantalum-180m. The activity of the tantalum foil at the end of the irradiation,  $A_{Ta}$ , was then used to calculate an  $\bar{N}$ -value for tantalum by the following equation:

$$\bar{N}_{Ta} = A_{Ta}t / (1 - e^{-\lambda_{Ta}t})g \quad (\text{Eq. 9})$$

where  $g$  is the weight of the foil. This was taken to be a measure of the integrated radiation fluxes to which the samples were exposed. The dose determined by Equation 9 was then used as a basis of comparing the results for different runs. However, the use of such an external monitor involves certain inherent difficulties. For example, it was difficult to reproduce the relative positioning of the monitor and the sample from one run to another. Also, the final yields of carbon-11 were more sensitive to the variations in flux

occurring during the irradiations than were the final yields of the longer-lived tantalum-180m. These difficulties were circumvented, however when it was shown that the  $\bar{N}$ -values for acetylene- $^{11}\text{C}$  were better dose indicators than were the  $\bar{N}_{\text{Ta}}$ -values for a given hydrocarbon. But the obvious difficulty which did remain concerned the  $t/(1-e^{-\lambda t})$  term in Equation 7. By using this term to calculate the monitor yields for the different runs, the beam fluctuations during the irradiations are neglected. The fact that these were not negligible was reflected in the data, but it was not possible to measure the fluctuations.

In an attempt to find a better monitor, some experiments were done to determine the activities produced in the glass bulblets themselves. The major short-lived activities were carbon-11, probably produced by the  $^{16}\text{O}(\gamma, n\alpha)^{11}\text{C}$  reaction, and oxygen-15, a 2.0 minute positron emitter. Some experiments were performed in which the activity of the shattered glass fragments of a bulblet was compared to that of the sample which it had contained. Over 96% of the total activity was due to the sample itself. Therefore it was decided that the sample plus bulblet could serve as its own monitor.

A housing was constructed to contain the sample over a

2.5 x 2.5 cm NaI(Tl) crystal in order to maintain a constant geometry for counting. All of the samples were counted at twelve minutes after the irradiations, since by this time the oxygen-15 activity was negligible compared to the carbon-11. With this monitor the  $t/(1-e^{-\lambda t})$  factor, as well as the sample weight, cancelled out when the monitor yields were compared to the product yields. The relative yield of a particular product was then calculated by the following:

$$Y = AV/A^0(^{11}\text{C}) \quad (\text{Eq. 10})$$

where Y is the relative radiochemical yield and  $A^0(^{11}\text{C})$  is the activity of the carbon-11 monitor, corrected for decay to the end of the irradiation.

The carbon-11 monitor proved to be quite effective in eliminating most of the experimental scatter. As will be described later, the absolute acetylene- $^{11}\text{C}$  yield in methylcyclopentane was determined to be 17.8%; all of the other product yields for all of the other systems could then be calculated by the use of Equation 10.

#### Radiochemical Yield Determinations

At the time when this study was undertaken, the only information available on the absolute radioyields of the gaseous products from liquid hydrocarbons was from the work of

C. Lang (70) of this group. Lang determined the acetylene yields to be 15% and 14%, respectively, from the liquids n-hexane and cyclohexane. The experimental procedure which was used involved the irradiation of Carbon Pearls, in the same manner as used for the hydrocarbon samples. Portions of the carbon were ignited in an oxygen atmosphere and the oxides were counted by the gas-flow technique. In all of the runs, a Synthane plug was positioned near the samples and served as a beam monitor.

In Lang's work, all of the irradiations were external to the acceleration chamber of the synchrotron and all were of one hour's duration, so that the dose conditions were different than those in this study. In order that this study would be self-consistent, it was decided that the radioyields should be redetermined. The carbon-11 yield in a solid carbon sample might not be truly equivalent to the yield which would be obtained in a liquid hydrocarbon sample, even though these yields were corrected for the differences in carbon density. In principle, a preferable method would involve the determination of the total carbon-11 yield in samples identical to those used for the other runs.

Preliminary experiments, in which the samples were passed

directly through the counting cell by the helium flow gas, proved to be quite futile. A different approach which was successful was made with the experimental arrangement shown diagrammatically in Figure 1.

The sample was placed in the sample breaker and the air was driven out of the system. The bulblet was broken; the sample was vaporized and swept through a bed of  $\text{CuO}$  at  $750^{\circ}\text{C}.$ , oxidizing the hydrocarbon completely to carbon dioxide and water. The gases passed through a sulfuric acid scrubber which removed all of the water. The carbon dioxide was then frozen in the liquid nitrogen trap in order to collect all of it without also collecting an excessive quantity of the helium flow gas.

When all of the carbon dioxide was trapped, stopcock I was turned to exhaust, stopcock II was turned from exhaust to open for the gas collection vessel, and the liquid nitrogen dewar was removed. The gas collection vessel was initially filled with a strongly acid solution of sodium sulfate; a leveling bulb was used to maintain a negative pressure as the carbon dioxide vaporized and expanded into this vessel. After complete vaporization, stopcock I was turned so that the helium flow purged the trapping vessel of carbon dioxide and

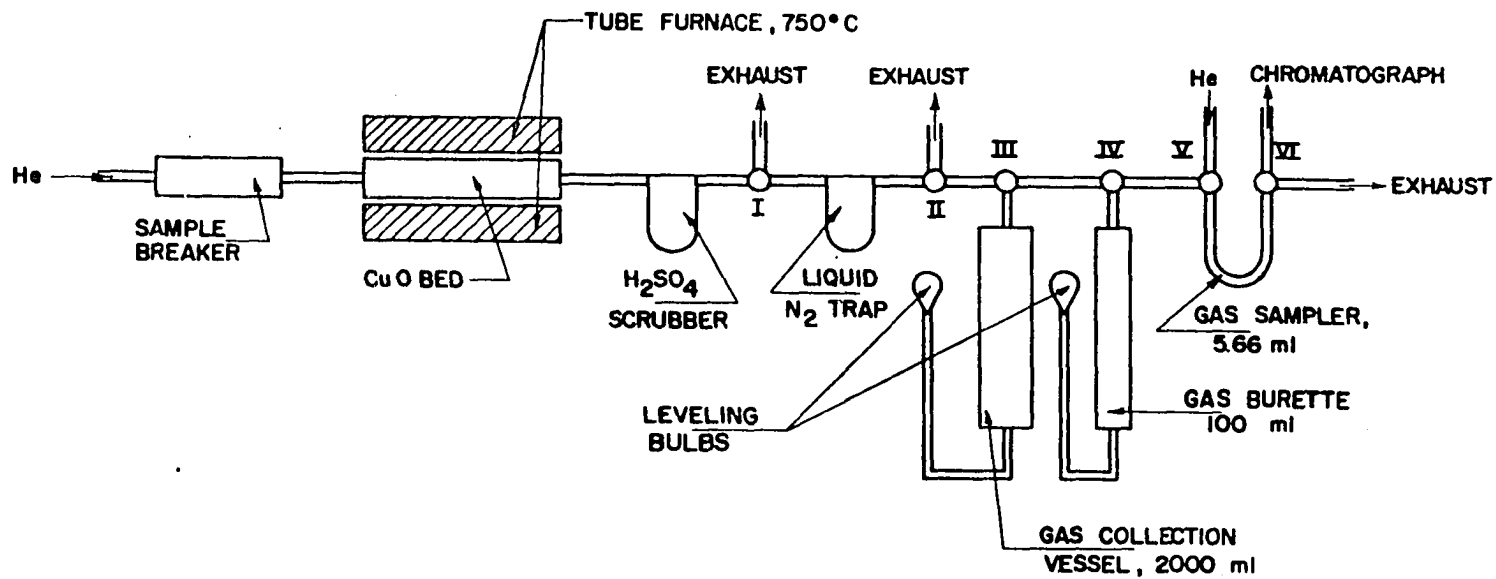


Figure 1. Apparati used for the total combustion experiments

all of the gas was isolated in the collection vessel.

Through the use of stopcocks III and IV and the two leveling bulbs, portions of the gas were transferred to the gas burette which also contained the salt solution. The volume of each portion at room pressure was determined from the scale of the burette. Each portion was then expelled through stopcock IV and an aliquot from each was trapped in the gas sampling device.

The volume of the gas sampler had been determined to be 5.66 ml by gravimetric means, using an ascarite-magnesium perchlorate U-tube to trap a large number of samples of carbon dioxide from a lecture bottle. Each aliquot was equilibrated with the room pressure and then passed through the chromatograph and the flow counter.

A 6 inch silica gel column was used to give the carbon dioxide peaks the characteristic Gaussian shape. For each aliquot thermal conductivity and radioactivity peaks were recorded on the chart. A total of about a dozen aliquots were obtained for each sample. Each aliquot included about as much helium as carbon dioxide, but since the area of the thermal conductivity peak was proportional to the amount of carbon dioxide present (see Reference 72 for a complete discussion),



it was possible to calculate the helium/carbon dioxide ratio. Samples of inactive carbon dioxide were taken before and after each run to determine the peak area for a standard volume of the gas under the conditions of the experiment.

The first experiments were done with nonirradiated samples. When the material balances indicated that a sample could be completely oxidized to carbon dioxide in this way, and that the gas could be fully recovered, it was felt that this approach was experimentally sound. Samples of cyclohexane were irradiated and were run according to the above procedure. Tantalum foil was used here as the beam monitor. Three runs gave an average value of 33.70 for the ratio  $\bar{N}(\text{total } ^{11}\text{C})/\bar{N}_{\text{Ta}}$  with a probable uncertainty in the value of 10-15%.

As will be discussed in a later section, after these experiments a series of runs was made in which the recoil products in methylcyclopentane were assayed, also using the tantalum monitor, establishing the radiochemical yields in that system. Subsequently, the yields of products from other systems were determined by comparison to methylcyclopentane through the carbon-11 monitor.

## DOSIMETRY

## Preliminary Remarks

Hammer and Bureau (73-75) have discussed the operation of the synchrotron as used for these irradiations. Electrons were accelerated to energies of 47 or 70 Mev and allowed to impinge upon a 0.32 cm thick lead plug, thereby producing the bremsstrahlung beams. The dosimetry studies reported here were done at the lower synchrotron energy, although the following remarks will be applicable to both.

Richtmyer et al. (76) have given the following formula, which may be considered to apply for the radiative losses in energy of the relativistic electrons under the conditions at the synchrotron:

$$-\frac{dE}{dx} = \frac{n Z^2 r_e^2 E}{137} 4 \left[ \ln\left(\frac{183}{Z^{1/3}}\right) + \frac{2}{9} \right]. \quad (\text{Eq. 11})$$

In the above formula,  $r_e = 2.8 \times 10^{-13}$  cm,  $Z = 82$  for lead,  $E = 47$  Mev and  $n$  represents the number of lead nuclei per  $\text{cm}^3$ . This formula gives 88 Mev/cm for  $-dE/dx$ , so the electrons should undergo an average radiative loss of about 28 Mev while passing through the lead plug.

Richtmyer et al. (76) also give about 17 Mev/cm for the average loss in energy of 47 Mev electrons due to the ioniza-

tion and excitation of lead atoms, corresponding to an energy loss of about 5.4 Mev in the lead plug.

It is clear that the samples were exposed to large fluxes of electrons and x-rays of varying energies as well as the bremsstrahlung. It is therefore important to consider the possibility that radiation-induced modifications may have occurred in samples during the irradiations. In order to evaluate the relative magnitude of radiation damage effects, a determination of the amounts of energy absorbed by the samples was necessary.

One characteristic of the synchrotron is that the electron beam is discontinuous. Pulses of electrons are produced with durations of about  $4 \times 10^{-8}$  sec, compared to the time intervals between pulses of about  $1.7 \times 10^{-2}$  sec. There are from  $10^8$  to  $10^{11}$  electrons per burst with the most probable value being on the order of  $10^9$  according to Bureau<sup>2</sup>. If this value ( $10^9$  electrons per burst) is used, with an operating rate of 59 bursts/sec and 47 Mev as the beam energy, the rate of energy delivery by the beam is  $1.7 \times 10^{20}$  ev/min.

A 47 Mev electron will produce about 8.1 ion pairs per

---

<sup>2</sup>Bureau, A. J., Department of Physics, Iowa State University of Science and Technology, Ames, Iowa. Private communication. 1964.

millimeter of air. This would be equivalent to about 6200 ion pairs per millimeter in a solution with the density of water, assuming that the ratio of electron densities is about the same as the ratio of the densities. If the average pathlength through the sample is taken as 5 mm and if 35 ev are required to produce each ion pair, a 47 Mev electron would be expected to deposit  $1.1 \times 10^6$  ev in the sample or 2.2% of its original energy. With the above value for the energy delivery rate of the beam, this would amount to an average dose rate of about  $2 \times 10^{19}$  ev/gm min for a 0.2 gm sample. This could also be expressed as  $3.2 \times 10^5$  rad/min, a rad being defined as that dose incurred when 100 ergs of energy are absorbed by a gram of material.

Rack et al. (65) were able to make an estimate of the dose rate at the synchrotron by observing the disappearance of color in a solution of  $I_2$  and 2,2-dimethylbutane. The iodine appeared to be depleted in about 15 minutes in a sample which originally contained  $1.3 \times 10^{-3}$  mole fraction of  $I_2$ . With the assumption that 25 ev would be absorbed for each iodine molecule to react, a dose rate of  $\sim 10^{19}$  ev/gm min was calculated.

Some clarification is needed concerning the term dose rate as used above. In the first place, the total absorbed

dose was estimated and then treated as though it applied to the entire sample. The beam available at the synchrotron is small in cross-sectional area compared to the sample and therefore, although some scattering occurs, the immediate radiation damage effects in the system will tend to be localized in a zone defined by the beam placement, etc. In this region, which is also the region in which most of the carbon-11 is produced, the dose will be larger than the over-all result indicates. If, for example, the sample absorbed  $10^{20}$  ev and this zone actually constituted 0.1 gm of a 0.2 gm sample, the dose to the zone (i.e., the region of interest) would be  $10^{21}$  ev/gm.

Once the total dose was determined, the dose rate was found by dividing the result by the time of irradiation. This was actually only done to facilitate the calculation of dose to samples for different irradiation times and is not truly a measure of the rate at which energy is deposited to the samples. For instance, suppose that a sample absorbs  $10^{19}$  ev/gm in one minute. The actual exposure time to the beam would be  $59 \times 4 \times 10^{-8}$  min =  $2.36 \times 10^{-6}$  min which means that the true dose rate during bursts was  $2.1 \times 10^{25}$  ev/gm min. The distinction between the integrated dose rate and the true

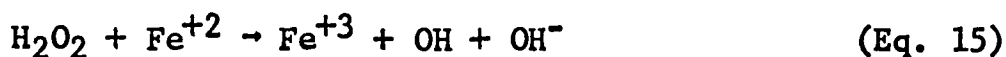
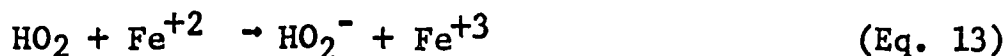
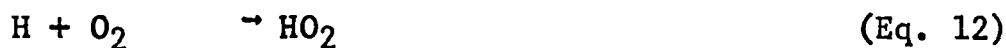
instantaneous dose rate should be kept in mind.

A contribution to radiation damage in the system will also be made by the emitted neutrons and the recoiling carbon-11 nuclei, but as Lang and Voigt (53) have indicated this additional dose is less than 1% of the total. The decay of carbon-11 during an irradiation will only provide a negligible dose.

### Fricke Dosimetry

The use of an acid solution of ferrous sulfate as an x-ray dosimeter was first proposed by Fricke (77) in 1929, and the system has subsequently been referred to in the literature as the Fricke dosimeter. A chemical dosimeter offers the advantage that it can be irradiated in the same vessel used to contain samples. Since the Fricke dosimeter has been studied extensively and its response to radiation is well documented, it was used for the first phase of the dosimetry.

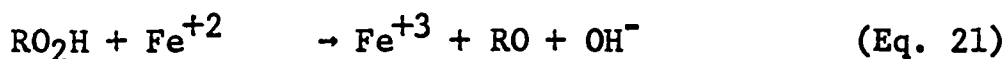
Hart (78) has indicated that the free radicals OH and H are the most important intermediates produced by radiation-induced reactions in water and that  $H_2$  and  $H_2O_2$  are the principal radiolysis products. When the aerated Fricke solution is subjected to radiation the following reactions are assumed to occur:



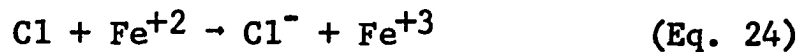
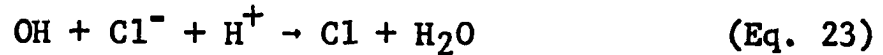
The G value is used in radiation chemistry to denote the number of molecules undergoing change for each 100 ev absorbed. It appears from the above reactions that three  $\text{Fe}^{+3}$  result for each H, one for each OH, and two for each  $\text{H}_2\text{O}_2$ . Another way of expressing this is the following equation:

$$G(\text{Fe}^{+3}) = 2 G(\text{H}_2\text{O}_2) + 3 G(\text{H}) + G(\text{OH}) . \quad (\text{Eq. 17})$$

This indicates that any factor that influences the yields of these radical and molecular species will accordingly affect the yield of  $\text{Fe}^{+3}$ . One result of this is that the presence of small amounts of organic impurities are able to increase the  $\text{Fe}^{+3}$  yield (79) according to the following reactions:



The net result of this is that three  $\text{Fe}^{+3}$  are formed for each OH radical instead of only one. There is a way to counteract this effect, fortunately, since the addition of chloride ion to the Fricke solution allows the following reactions to take place:



A practical upper limit of about 40,000 rad exists for the Fricke dosimeter when oxygen is present only to the extent that it is part of the dissolved air, but oxygenation could extend this limit to about 200,000 rad. However, oxygen is quite effective down to very low concentrations and the dosimeter is reliable until that point is reached. Once the oxygen is depleted, other reactions with the solute predominate and the G value is changed.

Associated with the track formed by the passage of a particle such as an electron through matter are spurs resulting from the motion of the secondary electrons. These spurs contain radicals and other molecular debris, as do the primary tracks. Rotblatt and Sutton (80) have pointed out that these spurs tend to become interconnected at very high dose rates and that radical-radical reactions can occur at



the expense of radical-solute reactions. An important consequence of this is that the yield of  $\text{Fe}^{+3}$  decreases under these conditions.

Schuler and Allen (81) have made perhaps the most precise determination of  $\text{Fe}^{+3}$  yield by measuring the energy input from a Van de Graaf generator. Their value of  $G(\text{Fe}^{+3}) = 15.45 \pm 0.11$  is applicable to cobalt-60 radiation and to energetic electrons. Anderson (82) obtained a value of  $G(\text{Fe}^{+3}) = 15.2 \pm 0.4$  at an instantaneous dose rate of  $2.8 \times 10^{23}$  ev/gm min. He noted a decrease in the G value at higher dose rates and at  $10^{25}$  ev/gm min a value of  $\sim 10$  was obtained.

Weiss (83) originally reported that the  $\text{Fe}^{+3}$  yield increased in cylindrical cells as the internal diameter fell below 8 mm. A 6% increase in that yield was found in 4 mm I.D. cells by Weiss et al. (84), compared to earlier reports of a 3% increase. The increased yield was due to the fact that more secondary electrons were produced per unit volume in the glass walls of the container than in the solution.

Spectrophotometric determination of the amount of  $\text{Fe}^{+3}$  formed appears to be the most convenient and accurate method of analysis. A temperature coefficient of +0.7% per degree Centigrade has been reported for the molar extinction coeffi-

cient of  $\text{Fe}^{+3}$ , making temperature control or correction important (85). A molar extinction coefficient of 2193 liter/mole was obtained at  $21.2^{\circ}\text{C}$  on the Beckman Model DU Spectrophotometer which was used for these experiments.

The solution was made up according to specifications given by Weiss et al. (84) with the following composition: 0.4134 gm  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Baker; A.C.S. Specification, fine crystal type); 0.0758 gm  $\text{NaCl}$  (Baker; A.C.S. Specification); 22 ml  $\text{H}_2\text{SO}_4$  (Allied Chemical; C.P., 95.5-96.5% acid); and sufficient triply distilled water to make a total volume of one liter.

A series of runs was made at the cobalt-60 source of the Veterinary Medicine Research Institute, Iowa State University. Glass vials (21 mm O.D.) used to contain the Fricke solution were filled to a depth of 30-45 mm and exposed to the source. A complete description has been given of the installation as well as some dose determinations which were made in it (86). The doses received at a calibrated position in the source were calculated. Eight runs gave a value of  $13,300 \pm 100$  rad/min which was in agreement with previous calibrations at the source.

A set of samples of Fricke solution sealed in the Pyrex

glass bulblets was exposed to the cobalt-60 source. Considerable care had to be taken in sealing these samples since blanks indicated that some oxidation might occur in the sealing process. Beckman microcells were needed for the analyses of these samples. The entire procedure probably contained considerable error, but results were finally obtained which were reproducible to about 10%. This was considered to be sufficiently precise that the procedure could be used for determinations at the synchrotron.

Four samples were irradiated at the synchrotron (Table 1) and the results indicate a linear relation between  $\bar{N}_{Ta}$  and the concentration of  $Fe^{+3}$  within a standard deviation of  $\sim 20\%$ . The instantaneous dose rate to the samples appears to be on the order of  $10^{25}$  ev/gm min and so the appropriate G value to be used in these calculations is probably between 10 and 15. Calculated values for the integrated dose in rads divided by  $\bar{N}_{Ta}$  for G values of 10 and 15 are respectively  $0.0173 \pm 0.0035$  and  $0.0115 \pm 0.0023$ , implying the Dose/ $\bar{N}_{Ta}$  is probably between 0.01 and 0.02, with the upper value probably more accurate. It is doubtful that any better precision is possible for this type of experiment and the uncertainty in the final answer is largely a reflection of the uncertainty in

the G value.

Table 1. Results of Fricke dosimetry at the synchrotron

Sample No.	Time of irradiation (sec)	$\bar{N}_{Ta} \times 10^{-6}$	$Fe^{+3} \times 10^4$ (mole/liter)
S-11	5	2.40	5.4
S-2	5	2.95	5.9
S-12	10	4.80	6.0
S-3	10	3.65	6.7

Since the dose received by a sample is largely a function of the electron density, the dose measured in this way will be somewhat different from that which would have been received by a hydrocarbon. The Fricke solution contains  $0.553 N_0$  electrons per gram where  $N_0$  is Avogadro's number whereas cyclohexane, for example, contains  $0.570 N_0$  electrons per gram. Thus, in the case of cyclohexane, the correction would be  $0.570/0.553$  for a net increase in the actual dose received. However, it is apparent that this correction is within experimental error and can be neglected.

#### Glass Dosimetry

Glassy substances appear darkened when exposed to high levels of radiation. The degree of darkening, which can be measured spectrophotometrically, has been shown to be a quantitative function of dose for some glasses (87). A form of

cobalt glass has been described which is useful for measuring doses as large as  $10^7$  rad and which is reliable for dose rates of over  $10^8$  rad/min (88,89). Some of this glass was obtained from Bausch & Lomb Optical Company, Rochester, New York, in the form of rectangular pieces measuring 15 x 6 x 1.5 mm. Several samples of the cobalt glass were exposed to the cobalt-60 source and the subsequent changes in optical density were measured with a Beckman Model DU Spectrophotometer at  $460 \text{ m}\mu$ . The changes in optical density were plotted versus the doses determined by the Fricke dosimeter and the resulting curve was in agreement with published results (90).

Two samples of the cobalt glass, each wrapped with a strip of tantalum, were irradiated at the synchrotron and the doses which they received were found from the calibration plot mentioned above (Table 2). The resulting value of  $\text{Dose}/\bar{N}_{\text{Ta}} = 0.015 \pm 0.002$  agrees with the Fricke dosimeter results. Since this value is also likely to be a lower limit due to the very high dose rate at the synchrotron (91) the two methods of dosimetry appear to be complementary.

Table 2. Results of glass dosimetry at the synchrotron

Sample no.	Time of irradiation (min)	Dose (rad) x 10 <sup>-6</sup>	$\bar{N}_{Ta} \times 10^{-6}$	Dose/ $\bar{N}_{Ta}$
I	5	2.3	182	0.0126
II	4	3.1	181	0.0171

### Summary

The Fricke dosimeter gave a value of 0.01-0.02 for Dose/ $\bar{N}_{Ta}$  at the synchrotron and the glass dosimeter gave a value of 0.013-0.017. Since it is desirable to have an estimate of the degree of radiation damage which occurred in an irradiated sample, the value 0.02 should give an upper limit which can be suitably applied. One of the longest (50 min) sample irradiations with a beam of typical intensity resulted in  $N_{Ta} \sim 50 \times 10^7$ , which implies that the sample received a dose of  $10^7$  rad or  $1.25 \times 10^{20}$  ev per sample containing  $1.4 \times 10^{21}$  molecules. Thus the integrated dose was  $\sim 0.1$  ev per molecule and the integrated dose rate was  $1.2 \times 10^{19}$  ev/gm min - about the same as the values found earlier by estimating the dose rate. Similarly, an upper limit for the integrated dose can be calculated for any sample irradiated at the synchrotron with the tantalum monitor. Since most irradiations are for 5-20 minutes, the typical integrated dose values will be in the range of 0.01-0.05 ev per molecule.

## RESULTS AND DISCUSSION

## Dose and Scavenger Studies

The results which were obtained for a series of irradiated methylcyclopentane samples are presented in Table 3. The  $\bar{N}(\text{C}_2\text{H}_2)/\bar{N}_{\text{T}_a}$  ratios were calculated according to Equations 8 and 9; their values were nearly constant for both scavenged and unscavenged samples, as shown graphically in Figure 2. Thus the acetylene yield may be used as an internal dose monitor for this system as other workers have done for different hydrocarbon systems (64,65,69). After the appropriate corrections for differences in carbon density between the two parent compounds, these ratios along with the ratio for  $\bar{N}(\text{total } ^{11}\text{C})/\bar{N}_{\text{T}_a}$  from the cyclohexane yield experiments, 33.70, were used to calculate the absolute acetylene yields for each of the nine runs with unscavenged samples. A least squares' analysis of the resulting values gave the following expression for the percentage yield of acetylene from methylcyclopentane:

$$Y(\text{C}_2\text{H}_2) = (17.8 \pm 0.8) - (0.114 \pm 0.061) \times 10^{-9} \times \bar{N}(\text{C}_2\text{H}_2) . \quad (\text{Eq. 25})$$

The "zero dose" value of 17.8 was taken to be the acetylene yield for this system; all of the other yields were calculated by comparison with this through the carbon-11 monitor using

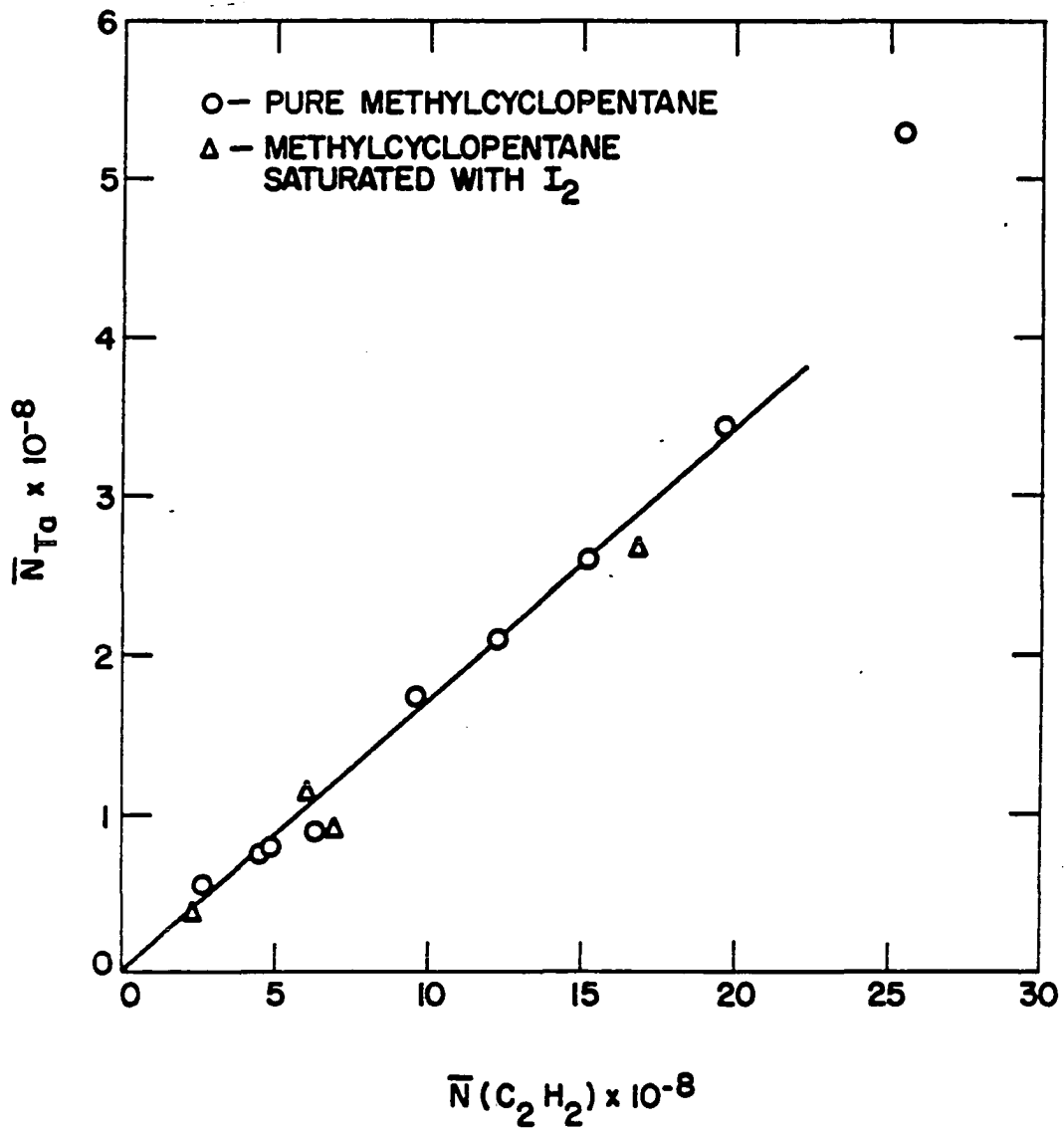


Figure 2. Plot of dose measured by  $^{180m}\text{Ta}$  yield versus that measured by acetylene yield for methylcyclopentane



Equation 10.

Table 3. Volatile product and monitor yields from methylcyclopentane samples

Sample number	$\bar{N}(\text{C}_2\text{H}_2) \times 10^{-8}$	$\frac{\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6}{\sum \text{C}_2}$	$\text{CH}_4/\text{C}_2\text{H}_2$	% $\text{C}_2\text{H}_2$	$\bar{N}(\text{C}_2\text{H}_2)/\bar{N}_{\text{Ta}}$
80	25.05	0.293	0.540	13.6	4.74
86	19.57	0.285	0.493	16.4	5.70
79	15.01	0.266	0.456	16.6	5.77
78	14.71	0.304	0.472		
83	12.23	0.255	0.445	16.7	5.81
75	9.64	0.266	0.447	16.1	5.62
81 <sup>a</sup>	8.96	0.274	0.486		
74	6.34	0.266	0.418	20.3	7.07
77	4.85	0.285	0.381	18.0	6.26
76	4.58	0.261	0.413	17.3	6.04
85 <sup>a</sup>	4.28	0.276	0.406		
84	2.70	0.268	0.376	14.0	4.88
82 <sup>a</sup>	2.30	0.267	0.382		
178 <sup>b</sup>	16.85	0.216	0.207	18.2	6.34
176 <sup>b,a</sup>	9.28	0.145	0.194		
179 <sup>b</sup>	6.79	0.227	0.183	21.6	7.54
174 <sup>b</sup>	6.14	0.183	0.199	15.8	5.51
175 <sup>b,a</sup>	3.67	0.148	0.186		
177 <sup>b</sup>	2.43	0.150	0.181	17.9	6.24

<sup>a</sup>Electron beam at 70 Mev; others were at 47 Mev.<sup>b</sup>Sample saturated with iodine.

The effects of radiation dose and iodine scavenger on the ratio  $\text{CH}_4/\text{C}_2\text{H}_2$  are shown in Figure 3. This ratio was independent of dose for the iodine-containing samples. For pure samples of methylcyclopentane, however, the ratio was dose-dependent with values invariably larger than those for

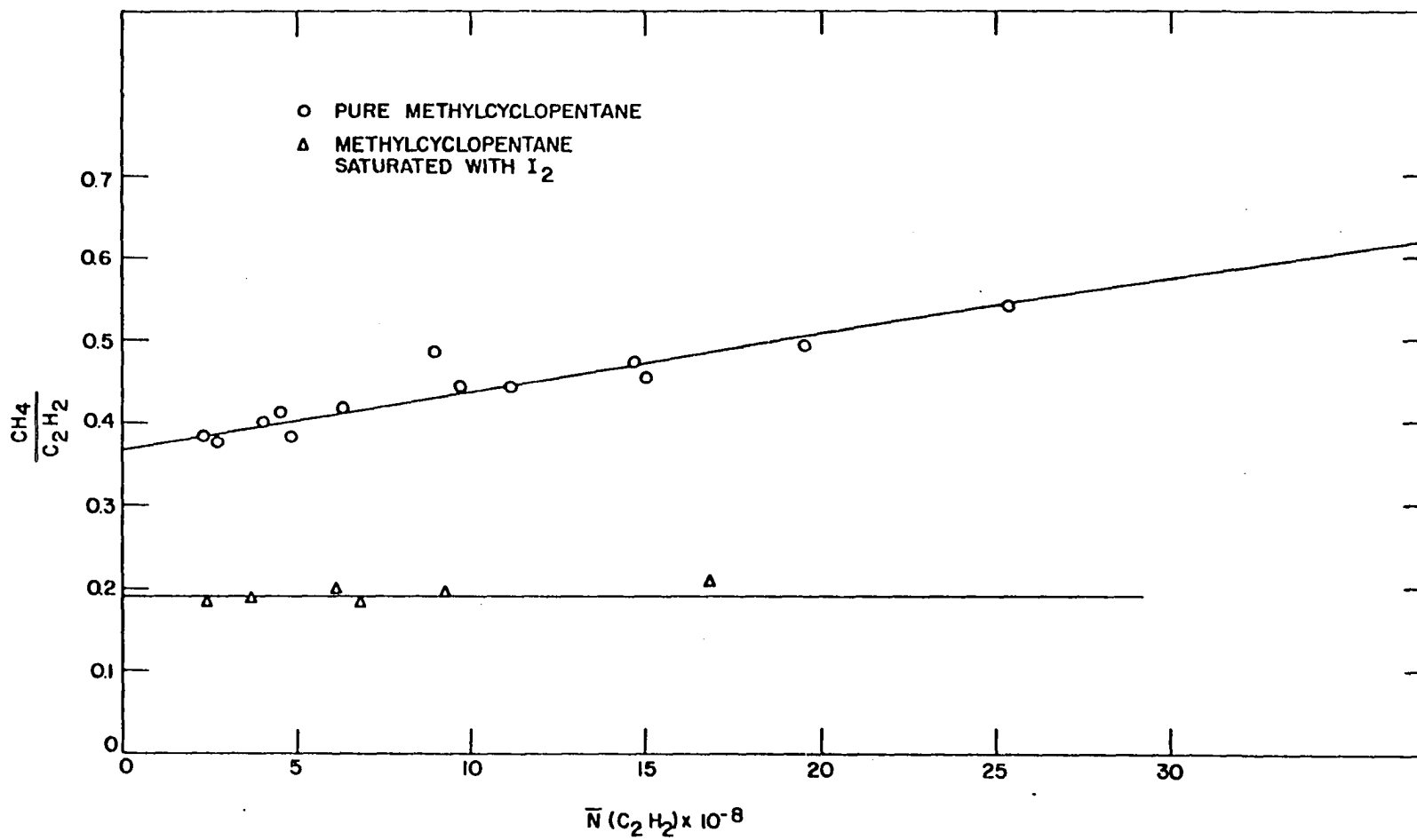


Figure 3. Plot of methane/acetylene ratio versus dose for methylcyclopentane

the scavenged system. The lower methane yield from the scavenged system implies that it probably has a radical precursor that can react with the iodine. Comparison with results recently published by Schuler (92) shows that the decrease in methane yield is balanced by the  $^{11}\text{CH}_3\text{I}$  yield. It seems reasonable to suppose that methane results from the formation of  $^{11}\text{CH}_3$  radicals, which abstract hydrogen atoms from the substrate rather than undergo insertion-type reactions. Hydrogen abstraction must occur before the radicals have diffused appreciable distances since only about half of them are scavenged by the iodine.

Radiation dose has a rather marked effect on the methane yield from unscavenged methylcyclopentane samples (Figure 3). The curve is similar to the ones obtained by DeVries and Voigt (69) for samples of n-hexane and cyclohexane.

From the dosimetry results it does not seem likely that the organic substrates should have been appreciably altered even at the higher doses. Radiolysis of the labeled compounds to give secondary products likewise should not have occurred to any great degree. The G values for the production of specific radiolysis products from liquid hydrocarbons are generally on the order of 0.1. For the longest irradiation

tions (doses  $\sim 0.1$  ev per molecule), these would have been present in mole fraction concentrations of only  $\sim 10^{-4}$ . On the other hand, the G value for hydrogen formation is around 5 for the pure samples, but only about 2 for the iodine-containing samples (93). It may be that the buildup of hydrogen promoted the formation of methane. Hydrogen could have reacted with some of the  $^{11}\text{C}$ ,  $^{11}\text{CH}$  and  $^{11}\text{CH}_2$  radicals, as well as with  $^{11}\text{CH}_3$  radicals, which might have otherwise reacted to form other products.

This effect would not be observed with target compounds such as benzene which are able to dissipate the absorbed energy without undergoing much decomposition. The G value for hydrogen formation in benzene is only about 0.04 (93). In agreement with this, DeVries and Voigt (69) found no change in the methane yield from benzene over a wide dose range.

The effect of radiation dose on the two-carbon product yields from pure methylcyclopentane was much less pronounced (Figure 4). The small increase with dose in the yield of ethane plus ethylene was nearly balanced by the apparent decrease in acetylene yield (Equation 25). This probably is attributable to the reduction of some of the acetylene by radiolytically produced hydrogen.

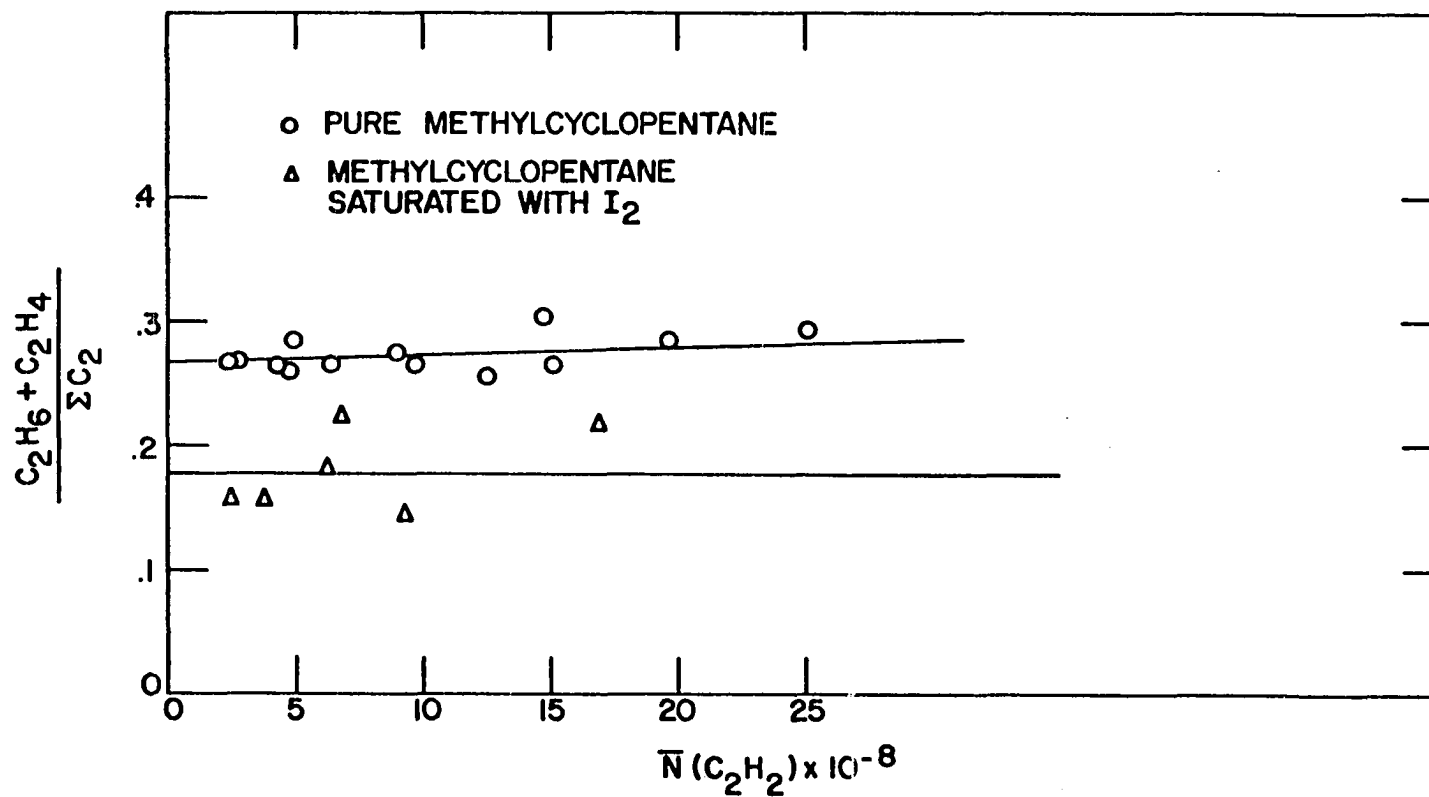


Figure 4. Plot of (ethane plus ethylene)/two-carbon ratio versus dose for methylcyclopentane

Since the acetylene yield was not affected by the iodine, (Table 3) the smaller  $(C_2H_6 + C_2H_4) / \sum C_2$  ratio for the scavenged samples (Figure 4) resulted from a reduction in the yield of ethane and ethylene.

The apparent insensitivity of the acetylene yield to iodine is significant in this particular system where nearly all of the hydrogens are primary or secondary. An insertion reaction in this case would produce a  $C_2$  fragment with at least two hydrogens and possibly more. In order to become an acetylene molecule, such a fragment would have to lose any extra hydrogens and undergo electronic rearrangement. These processes must also be fairly rapid since they must occur before the fragment encounters the scavenger. On the other hand, the precursors of ethane and ethylene apparently diffuse through the media before the stable molecules are formed and consequently can react with the iodine.

The results of a dose study with methylcyclohexane as the target are presented in Table 4. The acetylene yield was determined to be 11.6% by the carbon-11 monitor, compared to an average value of 11.5% for three runs with the tantalum monitor. For purposes of comparing with methylcyclopentane results on a common dose basis,  $\bar{N}^*$  was calculated by multi-

plying  $\bar{N}$  by 17.8/11.6.

Table 4. Yield ratios for the volatile products from samples of methylcyclohexane

Sample number	$\bar{N}^*(C_2H_2) \times 10^{-8}$	$CH_4/C_2H_2$	$C_2H_6/\sum C_2$	$C_2H_4/\sum C_2$
97	24.16	0.805	0.108	0.319
95	22.55	0.686	0.088	0.288
96	6.37	0.554	0.061	0.250
94	5.79	0.494	0.060	0.267
98	4.11	0.527	0.058	0.260
100	2.80	0.495	0.049	0.219
93	2.34	0.474	0.072	0.242
99	2.09	0.477	0.053	0.232

The curve of  $CH_4/C_2H_2$  versus dose (Figure 5) is similar to the one obtained for methylcyclopentane (Figure 3). The curves for  $C_2H_6/\sum C_2$  and  $C_2H_4/\sum C_2$  versus dose were drawn separately (Figure 6) to illustrate their relative contributions to the total two-carbon yield. These results are about as expected if the postulate of radiolytically produced hydrogen acting as a reducing agent is correct.

#### Product Yields from Selected Compounds

As indicated by the dose studies, modification of the primary products can definitely occur during irradiation of the samples. It is possible to approximate the "zero dose" condition, however, provided the irradiation times are short.

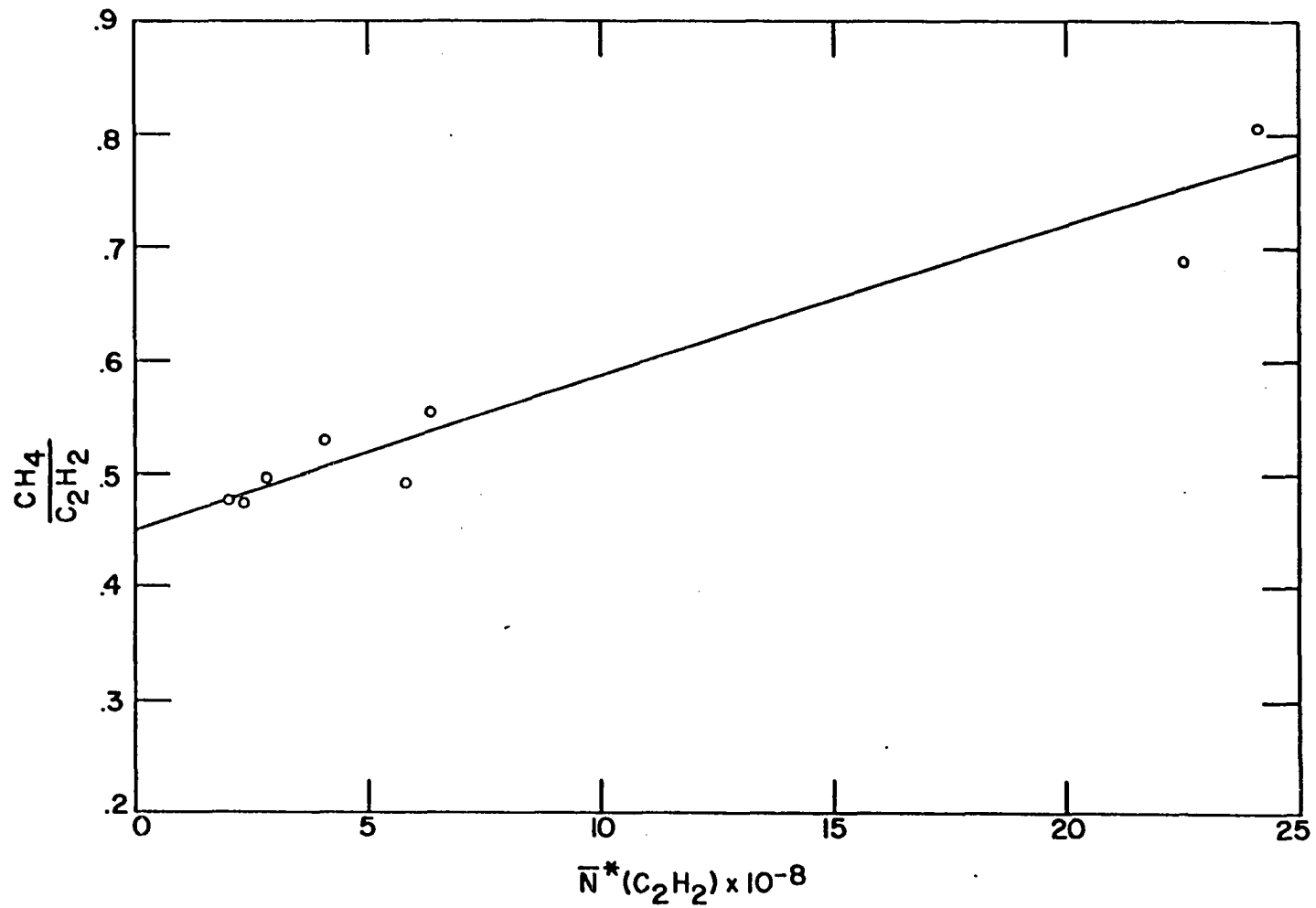


Figure 5. Plot of methane/acetylene ratio versus dose for methylcyclohexane



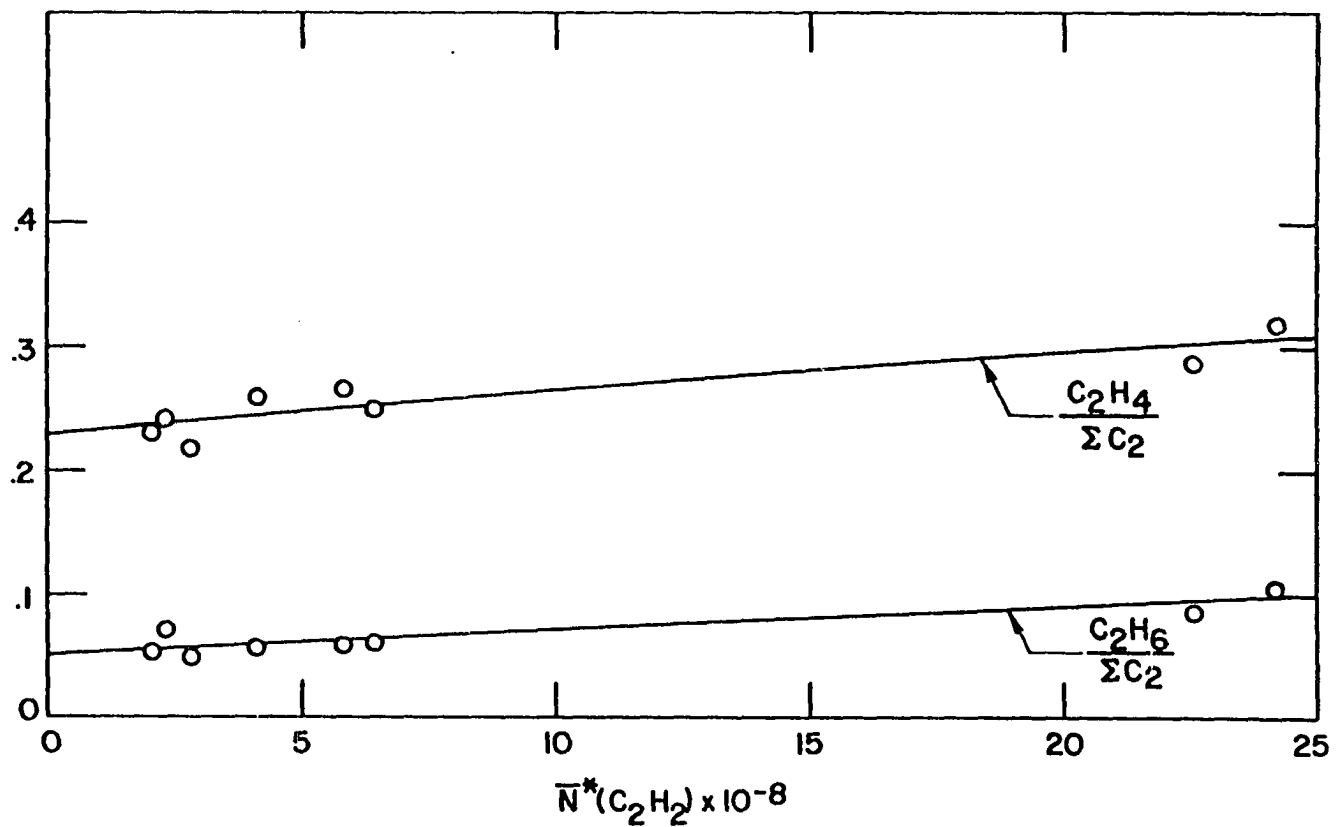


Figure 6. Plots of ethane/two-carbon and ethylene/two-carbon ratios versus dose for methylcyclohexane

This eliminates the need of making many runs in order to extrapolate the curves to zero radiation dose with precision. The results obtained at low dose (irradiation times of about five minutes) will be presented in this and the following section. Although these conditions are assumed to be nearly equivalent to the idealized "zero dose" conditions, it should be remembered that the yields of products other than acetylene may be slightly higher than would be obtained in the latter case.

The yields of methane, ethane, ethylene and acetylene from 14 different parent compounds are given in Table 5. The reported results were generally the averaged values for several runs; the agreement among runs for the same system was usually quite good. The target compounds were chosen to include some which differed in basic structure from straight chain hydrocarbons, such as olefins, cyclics, aromatics and branched chain compounds.

Benzene is unique in this series in that neither ethane nor ethylene was observed as a product. Acetylene production in benzene can be explained as resulting from  $^{11}\text{C}$ -insertion into the double bonds accompanied by migration of hydrogen and the subsequent decomposition of the reaction complexes.

Table 5. Absolute yields of methane and two-carbon products from various liquid hydrocarbons under near "zero dose" conditions

Hydrocarbon target	%C <sub>2</sub> H <sub>2</sub>	%CH <sub>4</sub>	%C <sub>2</sub> H <sub>6</sub>	%C <sub>2</sub> H <sub>4</sub>
2,2-dimethylbutane	30.47	5.21	2.64	17.90
2,3-dimethylbutane	24.51	6.61	1.91	14.92
n-pentane	22.12	8.30	1.46	9.90
3-methylpentane	21.80	7.45	1.90	10.52
2-methylpentane	21.61	7.96	2.00	11.58
n-hexane	19.85	7.92	1.50	7.53
hexene-1	18.70	2.18	0.53	4.97
methylcyclopentane	17.80	6.59	0.80	5.80
hexene-2	14.68	7.63	0.88	5.72
methylcyclohexane	11.60	5.22	0.80	3.71
cyclohexene	13.14	2.71	0.46	1.73
cyclohexane	12.59	6.55	1.14	3.05
benzene	5.60	0.19		
toluene	4.88	0.43	0.08	0.61

It could also arise from insertions of <sup>11</sup>C into C-H bonds.

Both of these mechanisms have been proposed for the acetylene-<sup>11</sup>C produced from ethylene as the target (27,60,61). Rack, Lang and Voigt (65) have reported that the yield of acetylene-<sup>11</sup>C was apparently not affected by the presence of scavenger. This suggests that insertions by <sup>11</sup>CH may also be important. In the cases of <sup>11</sup>CH-insertion into C-H bonds, there would be enough hydrogens at the reaction sites to form C<sub>2</sub>H<sub>2</sub> fragments which could undergo rapid electronic rearrangement to form acetylene without being affected by the iodine.

The activated complexes formed with benzene must have especially favorable modes of stabilization leading to build-up products. Only four products with fewer than eight carbon atoms accounting for only about one-fourth of the total activity (19,46), have been observed: methane, acetylene, benzene and toluene. Most of the activity is probably in the form of products with more than one phenyl group.

Only small amounts of ethane and ethylene were observed to be produced from toluene (Table 5), presumably arising from the methyl groups. Toluene is similar to benzene, as expected, in that most of the activity is in the form of very high boiling compounds. The xylenes and ethylbenzene have been observed as products (19). Styrene might also be expected, but it has not been reported.

A comparison of the products from cyclohexane and cyclohexene (Table 5) shows a marked decrease in methane but a relatively smaller decrease in the two-carbon yields when going to the olefinic form. The smaller methane yield is probably a reflection of the additional reactions that are possible with the double bond in cyclohexene. Methane is presumably formed only after a sufficient number of encounters have occurred which were unsuccessful in producing stable

molecules. In this sense then, the methane yield mirrors the reactivity of the target molecules towards the recoil species.

The products observed from recoil carbon reactions with n-hexane, hexene-1 and hexene-2 are also given in Table 5. Comparison of the product spectra from n-hexane and hexene-1 leads to the same conclusions mentioned above. However, the methane yield from hexene-2 was relatively high; it was nearly the same as the yield from n-hexane. In this case there may be a steric hindrance to the approach of the labeled fragment to the double bond, thus complicating the comparison.

An interesting trend is apparent when the yields of C<sub>2</sub> products from the various target compounds (Table 5) are compared. The largest yields were obtained from compounds with branched chain structures. The yields also appear to increase according to the degree of branching. Lang, Rack and Voigt (65) also noted this trend, but their observations were essentially of liquid hydrocarbons containing iodine. Wolf (19) showed that the ethylene-<sup>11</sup>C yields from a number of oxygen-scavenged gaseous hydrocarbons were dependent on the relative amounts of primary hydrogens in the target molecules. Stöcklin and Wolf (66) also reported on the structural dependence of acetylene-<sup>11</sup>C yields in those systems.

The trend which is observed here would be expected if the fragmentation products from these liquids actually do result from insertion reactions. If an insertion event occurs with a primary C-H bond, the activated complex that would be formed can decompose to give a C<sub>2</sub> fragment by rupturing a single C-C bond. On the other hand, if a secondary C-H bond is involved, such a fragment could only be formed by the rupture of two C-C bonds which would necessarily require more excitation energy.

Wolf (19) has argued that the major portions of the acetylene, ethylene and ethane yields arise from insertions into C-H bonds by the respective fragments <sup>11</sup>C, <sup>11</sup>CH and <sup>11</sup>CH<sub>2</sub>. If this is correct, it would seem plausible to suppose that the ethane and ethylene yields would be more sensitive to the extent of branching in the target molecules than would the acetylene yields. This follows from the reasonable assumption that the <sup>11</sup>CH and <sup>11</sup>CH<sub>2</sub> should be less energetic on the average than the <sup>11</sup>C. If these three reacting species are always produced in the same relative amounts for all liquid hydrocarbon targets, the absolute percentage yields of ethane and ethylene should depend primarily on the structure of the parent molecules. This can be expressed mathematically by the

following equation:

$$\%(\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4) = Ax + By + Cz. \quad (\text{Eq. 26})$$

In the above expression,  $x$ ,  $y$  and  $z$  are the respective fractional amounts of primary, secondary and tertiary hydrogens in the target molecule;  $A$ ,  $B$  and  $C$  are absolute yield contributions of each group. The value for  $C$  may be taken as equal to zero, since neither product was observed from benzene samples. From the yields obtained from liquid ethane by Stöcklin and Wolf (50), a value of 16.6% can be used for  $A$ . In Table 5, the results for cyclohexane indicate a value of 4.19% for  $B$ .

The absolute ethane plus ethylene percentage yields for a number of compounds were calculated using these values for the constant terms in Equation 26. The results of those calculations, along with the experimental values, are shown in Table 6. The general agreement appears to be good enough to indicate that the basic postulates are valid. The disagreement between the experimental and calculated values for the alkenes and toluene is perhaps an indication of the additional reaction modes possible with the double bonds. In the cases of 2,3- and 2,2-dimethylbutane, the experimental values were significantly higher than those predicted. This is not unexpected since the C-CH<sub>3</sub> bond strengths are especially low for these two compounds. Thus, the probabilities that the activated

complexes formed with these molecules will become fragmented can be expected to be larger than for the other cases. The agreement between experimental and calculated values for the simple alkanes was excellent.

Table 6. Comparison of experimental and predicted results for the two-carbon yields from various liquid hydrocarbons

Hydrocarbon target	% (C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub> )		(C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub> ) / $\sum$ C <sub>2</sub>	
	Calc'd.	Exp.	Calc'd.	Exp.
2,2-dimethylbutane	14.8	20.5	0.46	0.40
2,3-dimethylbutane	14.2	16.8	0.42	0.41
n-pentane	10.4	11.4	0.37	0.34
3-methylpentane	11.9	12.4	0.39	0.36
2-methylpentane	11.9	13.6	0.39	0.39
n-hexane	9.5	9.0	0.35	0.31
hexene-1	6.6	5.5	0.27	0.23
methylcyclopentane	7.0	6.6	0.29	0.27
hexene-2	9.7	6.6	0.33	0.31
methylcyclohexane	6.5	4.5	0.28	0.28
cyclohexene	3.3	2.2	0.20	0.14
toluene	4.1	.7	0.12	0.12
propane	13.4	12.8 <sup>a</sup>	0.43	0.41 <sup>a</sup>
isobutane	14.9	14.9 <sup>b</sup>	0.44	0.46 <sup>b</sup>
ethylene	4.2	~1.7 <sup>c</sup>	0.25	<0.2 <sup>c</sup>

<sup>a</sup>Reference 50.

<sup>b</sup>Reference 62.

<sup>c</sup>Reference 60.

The formation of ethane or ethylene is apparently four times more probable when a single C-C bond has to be broken than when two of them must be broken. At least this is implied from the chosen values of the constants.



Another interesting trend can be seen from the results in Table 5. As the total yield of C<sub>2</sub> products increased from one system to another, a smaller proportion of it appeared as acetylene. A similar trend was reported by Rack, Lang and Voigt (65) for iodine-scavenged systems. An attempt to express the present trend mathematically, in order to predict the ratio of ethane plus ethylene to the total C<sub>2</sub> yield,  $\sum C_2$ , for different unscavenged systems, was successful. The following equation was used:

$$(C_2H_6 + C_2H_4) / \sum C_2 = Dx + Ey + Fz . \quad (\text{Eq. 27})$$

The terms x, y and z are again the fractional amounts of primary, secondary and tertiary hydrogen atoms, respectively, in the target molecules; D, E and F are the ratios resulting from reactions at the different sites. From the results for benzene (Table 5), F was taken as zero. The value of 0.25 was taken for E from the results for cyclohexane (Table 5). From the results for irradiated liquid ethane reported by Stöcklin and Wolf (50), D was taken as 0.49.

The experimental and calculated values for this ratio are given in Table 6; the agreement was excellent for the results of this study, as well as for those published by other laboratories.

Equation 27 differs from that used by Rack, Lang and Voigt (see Equation 5, page 36) to calculate the  $(C_2H_6 + C_2H_4)/C_2H_2$  ratios for scavenged systems. In their equation, the x, y and z terms denoted the respective fractions of carbon atoms in the molecule which were in the forms of  $CH_3$ ,  $CH_2$  and  $CH$  groups. Since no studies of this type with scavenged liquid systems had been previously reported, it was also necessary for them to choose one of the constants from published results for an oxygen-scavenged gaseous system.

What the present treatment indicates is that once a  $C_2$  fragment has been produced, the amount of hydrogen available at the site of the insertion will be the principal factor in determining the degree of unsaturation in the  $C_2$  molecule formed from it. However, it is assumed that the three reacting species,  $^{11}C$ ,  $^{11}CH$  and  $^{11}CH_2$ , have different probabilities for producing  $C_2$  fragments from insertions into equivalent bonds.

The methane, ethane and ethylene yields from iodine-scavenged systems are presented in Table 7. The yields of those products were lower in the scavenged than in the unscavenged systems (Table 5), due to the action of iodine on their precursors. Since the acetylene yields were not affected by the scavenger and were given for the pure compounds in Table

5, they were not included in Table 7.

Table 7. Absolute product yields for iodine-containing samples and the fractional decrease in yields due to scavenger action

Hydrocarbon target	%CH <sub>4</sub>	%C <sub>2</sub> H <sub>6</sub>	%C <sub>2</sub> H <sub>4</sub>	Fractional decrease in % (C <sub>2</sub> H <sub>6</sub> +C <sub>2</sub> H <sub>4</sub> )
2,2-dimethylbutane <sup>a</sup>	3.66		14.93 <sup>b</sup>	0.27
n-hexane	5.12	0.94	5.46	0.29
2,3-dimethylbutane <sup>a</sup>			11.52 <sup>b</sup>	0.32
2-methylpentane	3.67	0.73	7.89	0.37
methylcyclopentane	3.38	0.60	3.30	0.41
cyclohexane <sup>c</sup>	3.65		1.64 <sup>b</sup>	0.61

<sup>a</sup>Calculated from data in Reference 65.

<sup>b</sup>Ethane and ethylene not resolved.

<sup>c</sup>Calculated from data in Reference 64.

The fractional decreases in the yields of ethane plus ethylene which were observed in going from the pure hydrocarbons to the scavenged systems are also shown in Table 7. The greatest fractional decrease was observed with cyclohexane, where all of the molecular carbons had two hydrogens. In that system, the C<sub>2</sub> fragments which were precursors to ethane and ethylene presumably had to abstract the necessary number of hydrogen atoms to form the stable molecules. Before the abstraction of hydrogen was completed and the fragments became stabilized, they probably diffused through the media.

When iodine was present, the fragments could have encountered and reacted with iodine molecules while diffusing, thus reducing the yields. In systems where the insertions were likely to involve methyl groups, the fractional decreases in yield were smaller. In those cases, there were more hydrogen atoms available at the reaction sites, so that abstraction by diffusive processes was probably less important.

#### Benzene-methylcyclopentane Mixtures

The product spectra from benzene and methylcyclopentane were seen to be quite dissimilar (Table 5). Therefore, it was thought that it might be worthwhile to investigate the effect of irradiating mixtures of the two compounds.

Thirteen samples of six different mixtures were irradiated and assayed in the usual way. The product yields obtained from each sample are given in Table 8, along with the yields from the two pure compounds for comparison.

The methane yield versus the mole fraction of benzene for each mixture sample is shown in Figure 7. The individual values all fall below the curve drawn for the case of strict dependence on the degree of mixing, but not significantly so. The two-carbon product yields appear to be simply related to the relative molar concentrations of benzene and methylcyclopentane (Figure 8).

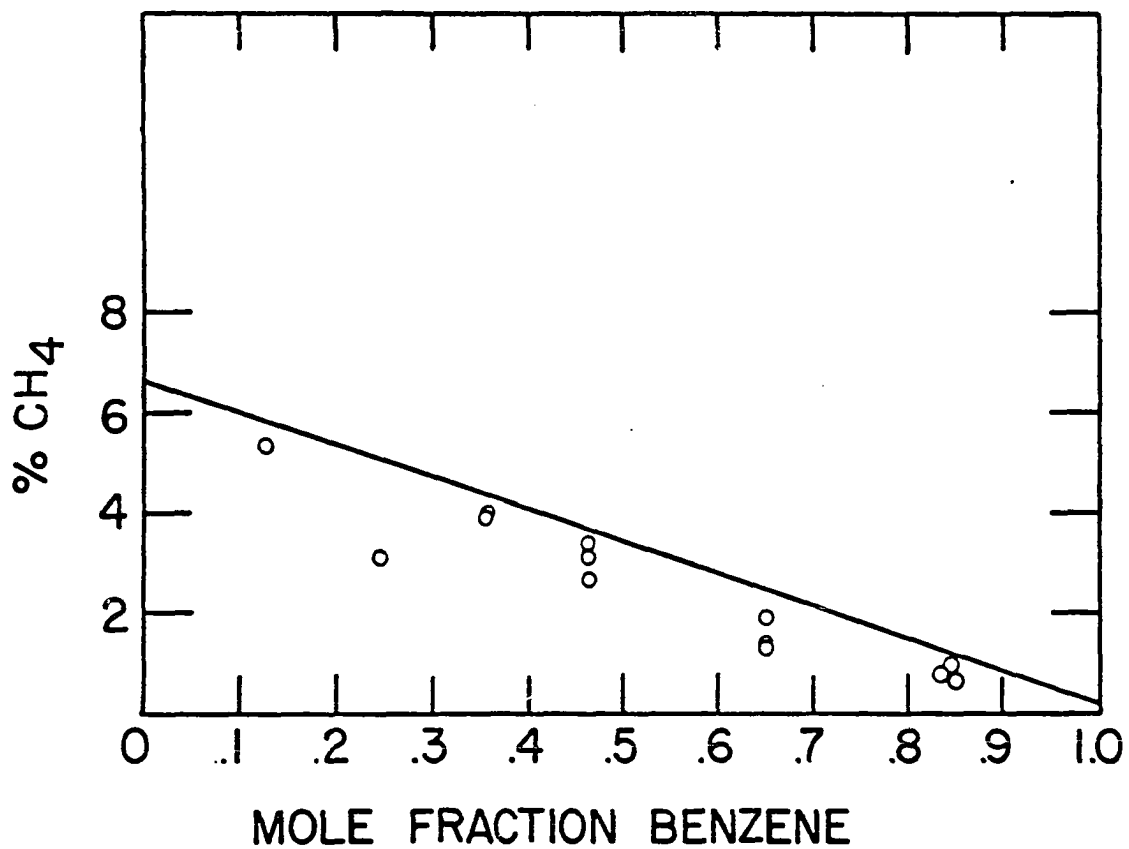


Figure 7. Plot of methane percentage yield versus mole fraction benzene for benzene-methylcyclopentane mixtures

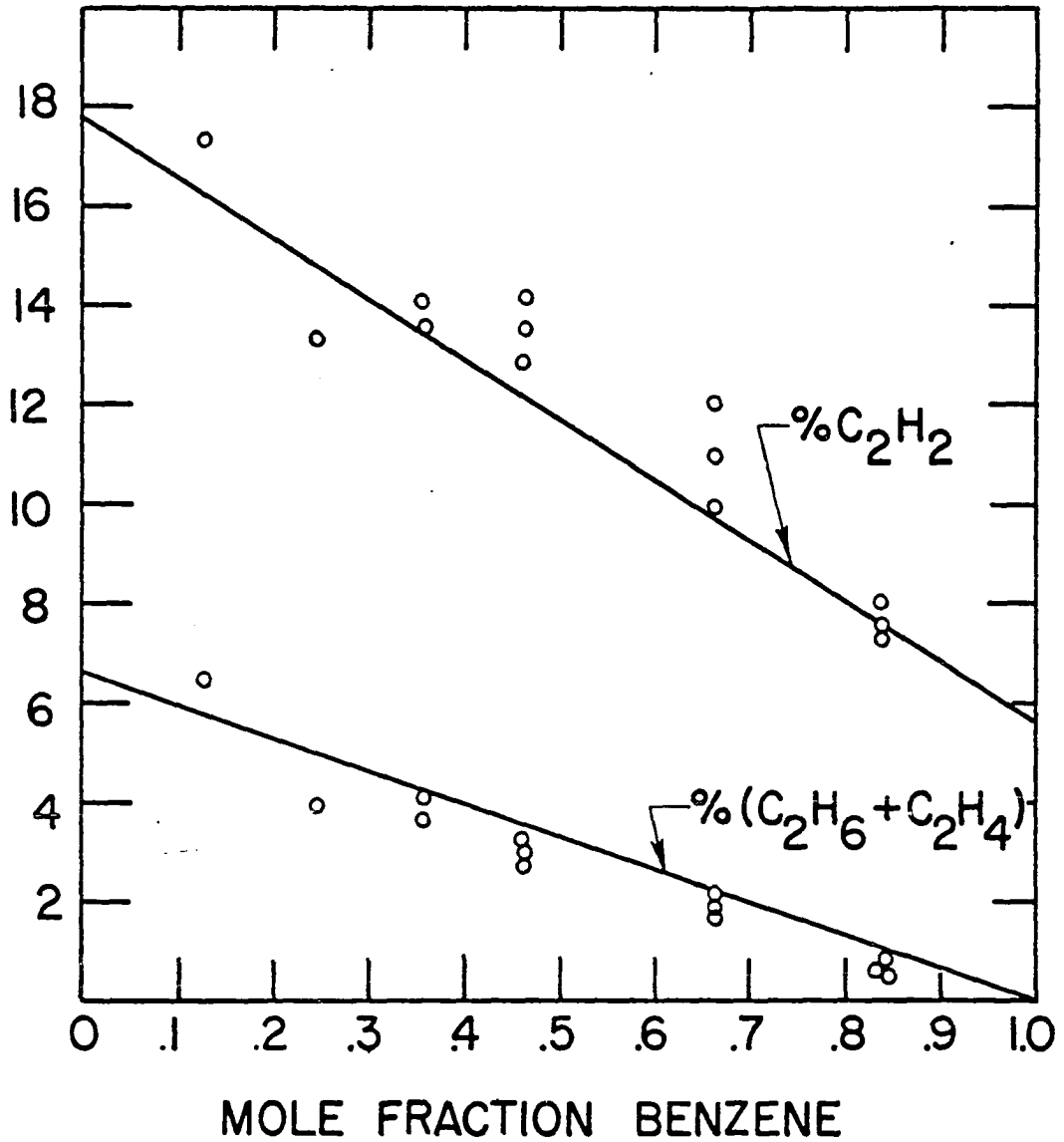


Figure 8. Plots of ethane and ethylene percentage yields versus mole fraction benzene for benzene-methylcyclopentane mixtures



The specific examples of products given above are the ones of particular interest in this study. For parent  $C_n$  compounds, other examples which might be mentioned are the addition  $C_{n+1}$ , the "re-entry"  $C_n$  and the "buildup"  $C_{n+m}(m>1)$  products.

Since the product distributions are so different for benzene and methylcyclopentane, the various reaction pathways are of differing importance to each. From the earlier remarks concerning the products from benzene, it was concluded that the major products probably result directly from reactions of  $^{11}C$  and  $^{11}CH$ . In benzene only relatively small amounts of  $^{11}CH_2$  would be expected to be formed, but in methylcyclopentane it must be produced to a much larger extent. The latter compound, being a  $C_6$  alkane, would be expected to yield relatively large amounts of saturated  $C_7$  products upon reaction with recoil carbon atoms (19, 46). The major products from methylcyclopentane, except for acetylene, are probably formed directly from insertion reactions involving  $^{11}CH$  and  $^{11}CH_2$ .

Perhaps the experimental results would be easier to interpret by considering a specific case. For instance, with an equimolar mixture of benzene and methylcyclopentane, a given recoil carbon atom would have a 50% chance of encountering a given type of molecule. If its energy was suffi-



ciently low, the probability that it would undergo a reaction such as shown in Equation 28 (i.e. to give a labeled product or fragment) would depend solely upon the particular molecule encountered. Likewise the  $^{11}\text{CH}$  and  $^{11}\text{CH}_2$  species produced in such an environment would have equal probabilities of encountering either type of molecule. The probabilities that the various reactions will occur, the cross sections, are of course different for the two compounds. The experimental results for this case would presumably imply that 50% of the inserting species reacted with methylcyclopentane molecules and 50% with benzene.

The conclusion which can be drawn from this is that the reaction cross sections for equivalent species with methylcyclopentane and benzene molecules must be similarly related to the energies. This follows from the reasonable assumption that the reacting species will have energies over a whole range of possible values. Thus it could be concluded that these two molecules have nearly equivalent energy thresholds for their respective reactions with  $^{11}\text{C}$ ,  $^{11}\text{CH}$  and  $^{11}\text{CH}_2$ . This conclusion would be in agreement with the proposal by Wolfgang and his co-workers (27,59,60) that the activation energies for insertion reactions are nearly zero.

## CONCLUSIONS

Through the examination of the product distributions resulting from the reactions of recoil carbon-11 atoms with various liquid hydrocarbons, it is possible to surmise a great deal about the reaction pathways available to such a species. Three primary species,  $^{11}\text{C}$ ,  $^{11}\text{CH}$  and  $^{11}\text{CH}_2$ , all uncharged, appear to be responsible for the products formed in these systems. The reactions which are involved seem to be formally analogous to insertion reactions into C-H and C=C bonds initially forming activated complexes. These can either decompose to form molecular fragments, which are eventually stabilized, or they can become stabilized by transferring their excess energies to the adjoining molecules. The simplest mode of decomposition involves rupturing the beta-carbon-carbon bonds to give  $\text{C}_2$  fragments. The  $\text{C}_2$  products formed in this way were studied extensively in this study. Products formed by more complicated modes of decomposition, such as  $\text{C}_3$ , etc., were not determined since they were present in only relatively small amounts. The findings of this study appear to confirm the above mechanisms.

## BIBLIOGRAPHY

1. Szilard, L. and Chalmers, T. A., *Nature*, 134, 462 (1934).
2. Amaldi, E., D'Agostino, O., Fermi, E., Pontecorvo, B., Rasetti, F., and Segre, E., *Proc. Roy. Soc. (London)*, A149, 522 (1935).
3. Barkas, W. H., Carlson, P. R., Henderson, J. E., and Moore, W. H., *Phys. Rev.*, 58, 577 (1940).
4. Libby, W. F., *J. Am. Chem. Soc.*, 69, 2523 (1947).
5. Fox, M. S. and Libby, W. F., *J. Chem. Phys.*, 20, 487 (1952).
6. Miller, J. M., Gryder, J. W., and Dodson, R. W., *J. Chem. Phys.*, 18, 579 (1950).
7. Miller, J. M. and Dodson, R. W., *J. Chem. Phys.*, 18, 865 (1950).
8. Estrup, P. J. and Wolfgang, R., *J. Am. Chem. Soc.*, 82, 2665 (1960).
9. Estrup, P. J. and Wolfgang, R., *J. Am. Chem. Soc.*, 82, 2661 (1960).
10. Wolfgang, R., U.S. Atomic Energy Commission Report, NYO-1957-50 [New York Operations Office, AEC], (1964).
11. Willard, J. E., *Ann. Rev. Nuclear Sci.*, 3, 193 (1953).
12. McCauley, C. E., Hilsdorf, G. J., Geissler, P. R., and Schuler, R. H., *J. Am. Chem. Soc.*, 78, 3246 (1956).
13. Schuler, R. H. and McCauley, C. E., *J. Am. Chem. Soc.*, 79, 821 (1957).
14. Willard, J. E., in *Chemical effects of nuclear transformations*, Vol. 1, pp. 215-227, Vienna, Austria, International Atomic Energy Agency, 1961.

15. Gordus, A. A. and Willard, J. E., *J. Am. Chem. Soc.*, 79, 4609 (1957).
16. Walton, G. N., *Radiochimica Acta*, 2, 108 (1964).
17. Wolf, A. P., *Ann. Rev. Nuclear Sci.*, 10, 259 (1960).
18. Willard, J. E., *Nucleonics*, 19, No. 10, 61 (1961).
19. Wolf, A. P., *Adv. in Phys. Org. Chem.*, 2, 201 (1964).
20. Campbell, I. G., *Adv. in Inorg. Chem. and Radiochem.*, 5, 135 (1963).
21. Harbottle, G. and Sutin, N., *Adv. in Inorg. Chem. and Radiochem.*, 1, 267 (1959).
22. Harbottle, G., *in* *Radioisotopes in the field of recoil chemistry*, pp. 375-391, Vienna, Austria, International Atomic Energy Agency, 1962.
23. Willard, J. E., *Ann. Rev. Phys. Chem.*, 6, 141 (1955).
24. Siuda, A., *Polish Atomic Energy Commission Information Center Report*, 6, (1963).
25. Willard, J. E., *in* *Chemical effects associated with nuclear reactions and radioactive transformations*, [in press], Vienna, Austria, International Atomic Energy Agency, 1964.
26. Friedlander, G., Kennedy, J. W., and Miller, J. M., *Nuclear and radiochemistry*, New York, N.Y., John Wiley and Sons, Inc., 1964.
27. MacKay, C. and Wolfgang, R., *Science*, 148, 899 (1965).
28. MacKay, C., Pandow, M., Polak, P., and Wolfgang, R., *in* *Chemical effects of nuclear transformations*, Vol. 2, pp. 17-26, Vienna, Austria, International Atomic Energy Agency, 1961.
29. Evans, J. B. and Willard, J. E., *J. Am. Chem. Soc.*, 78, 2908 (1956).

30. Norris, L. and Snell, A., *Nucleonics*, 5, No. 3, 18 (1948).
31. Rowland, F. S. and Libby, W. F., *J. Chem. Phys.*, 21, 1493 (1953).
32. Sharman, L. J. and McCallum, K. J., *J. Am. Chem. Soc.*, 77, 2989 (1955).
33. Edwards, W. J. and McCallum, K. J., *Can. J. Chem.*, 34, 189 (1956).
34. McCallum, K. J. and Edwards, W. J., *in* Chemical effects of nuclear transformations, Vol. 2, pp. 57-62, Vienna, Austria, International Atomic Energy Agency, 1961.
35. Yankwich, P. E. and Vaughan, J. D., *J. Am. Chem. Soc.*, 76, 5851 (1954).
36. Yankwich, P. E. and Cornman, W. R., *J. Am. Chem. Soc.*, 78, 1560 (1956).
37. Yankwich, P. E., *Can. J. Chem.*, 34, 301 (1956).
38. Yankwich, P. E. and Marteney, P. M., *in* Chemical effects associated with nuclear reactions and radioactive transformations, [in press], Vienna, Austria, International Atomic Energy Agency, 1964.
39. Yang, J. Y. and Wolf, A. P., *J. Am. Chem. Soc.*, 82, 4488 (1960).
40. Cacace, F. and Wolf, A. P., *J. Am. Chem. Soc.*, 84, 3202 (1962).
41. Dubrin, J., MacKay, C., Pandow, M., and Wolfgang, R., *J. Inorg. Nucl. Chem.*, 26, 2113 (1964).
42. Schrodt, A. G. and Libby, W. F., *J. Am. Chem. Soc.*, 76, 3100 (1954).
43. MacKay, C. F. and Libby, W. F., *J. Am. Chem. Soc.*, 79, 6366 (1957).

44. Schrodtt, A. G. and Libby, W. F., J. Am. Chem. Soc., 78, 1267 (1956).
45. Suryanarayana, B. and Wolf, A. P., J. Phys. Chem., 62, 1369 (1958).
46. Voigt, A. F., Clark, D. E., and Mesich, F. G., in Chemical effects associated with nuclear reactions and radioactive transformations, [in press], Vienna, Austria, International Atomic Energy Agency, 1964.
47. Wolf, A. P., in Chemical effects of nuclear transformations, Vol. 2, pp. 3-15, Vienna, Austria, International Atomic Energy Agency, 1961.
48. Doering, W. von E., BATTERY, R. G., Laughlin, R. G., and Chandhuri, N., J. Am. Chem. Soc., 78, 3224 (1956).
49. Kirmse, W., Carbene chemistry, New York, N.Y., Academic Press, 1964.
50. Stöcklin, G. and Wolf, A. P., J. Am. Chem. Soc., 85, 229 (1963).
51. Frey, H. M. and Kistiakowsky, G. B., J. Am. Chem. Soc., 79, 6373 (1957).
52. Frey, H. M., J. Am. Chem. Soc., 80, 5005 (1958).
53. Lang, C. E. and Voigt, A. F., J. Phys. Chem., 65, 1542 (1961).
54. MacKay, C. and Wolfgang, R., J. Am. Chem. Soc., 83, 2399 (1961).
55. MacKay, C., Polak, P., Rosenberg, H., and Wolfgang, R., J. Am. Chem. Soc., 84, 308 (1962).
56. Rabinovitch, B. S., Tschuikow-Roux, E., and Schlag, E. W., J. Am. Chem. Soc., 81, 1083 (1959).
57. Marshall, M., MacKay, C., and Wolfgang, R., Tetrahedron Letters, 29, 2033 (1963).

58. Dubrin, J., MacKay, C., and Wolfgang, R., J. Am. Chem. Soc., 86, 959 (1964).
59. Marshall, M., MacKay, C., and Wolfgang, R., J. Am. Chem. Soc., 86, 4741 (1964).
60. Dubrin, J., MacKay, C., and Wolfgang, R., J. Am. Chem. Soc., 86, 4747 (1964).
61. Dubrin, J., MacKay, C., and Wolfgang, R., J. Chem. Phys., 41, 3267 (1964).
62. MacKay, C. and Wolfgang, R., Radiochimica Acta, 1, 42 (1962).
63. Stöcklin, G., Stangl, H., Christman, D. R., Cumming, J. B., and Wolf, A. P., J. Phys. Chem., 67, 1735 (1963).
64. Rack, E. P. and Voigt, A. F., J. Phys. Chem., 67, 198 (1963).
65. Rack, E. P., Lang, C. E., and Voigt, A. F., J. Chem. Phys., 38, 1211 (1963).
66. Stöcklin, G. and Wolf, A. P., in Chemical effects associated with nuclear reactions and radioactive transformations, [in press], Vienna, Austria, International Atomic Energy Agency, 1964.
67. Ache, H. and Wolf, A. P., in Chemical effects associated with nuclear reactions and radioactive transformations, [in press], Vienna, Austria, International Atomic Energy Agency, 1964.
68. Cvetanovic, R. J., Duncan, F. J., and Falconer, W. E., Can. J. Chem., 41, 2095 (1963).
69. DeVries, D. B. and Voigt, A. F., U.S. Atomic Energy Commission Report, IS-866 [Iowa State Univ. of Science and Technology, Ames. Inst. for Atomic Research], 1964.
70. Lang, C. E., Recoil reactions of carbon-11 in organic compounds, unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1960.

71. Wolfgang, R. and Rowland, F. S., *Anal. Chem.*, 30, 903 (1958).
72. Dal Nogare, S. and Juvet, R. S., *Gas-liquid chromatography*, New York, N.Y., Interscience Publishers, 1964.
73. Hammer, C. L. and Bureau, A. J., *Rev. Sci. Instr.*, 26, 594 (1955).
74. Hammer, C. L. and Bureau, A. J., *Rev. Sci. Instr.*, 26, 598 (1955).
75. Bureau, A. J. and Hammer, C. L., *Rev. Sci. Instr.*, 32, 93 (1961).
76. Richtmyer, F. K., Kennard, E. H., and Lauritsen, T., *Introduction to modern physics*, New York, N.Y., McGraw-Hill, 1955.
77. Fricke, H. and Morse, S., *Phil. Mag.*, 7, 129 (1929).
78. Hart, E. J., *J. Chem. Educ.*, 36, 266 (1959).
79. Dewhurst, H. A., *Trans. Faraday Soc.*, 48, 905 (1952).
80. Rotblatt, J. and Sutton, H. C., *Proc. Roy. Soc. (London)*, 255, 490 (1960).
81. Schuler, R. H. and Allen, A. O., *J. Chem. Phys.*, 24, 56 (1956).
82. Anderson, A. R., *J. Phys. Chem.*, 66, 180 (1962).
83. Weiss, J., *Nucleonics*, 10, No. 7, 28 (1952).
84. Weiss, J., Allen, A. O., and Schwartz, H. A., *Proc. Intern. Conf. Peaceful Uses Atomic Energy, United Nations*, New York, 14, 179 (1956).
85. Bastian, R., Weberling, R., and Pallilla, F., *Anal. Chem.*, 25, 284 (1953).



86. Kivel, J., Gamma radiolysis of carbon-14 labeled iso-butane, unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1960.
87. Kreidl, N. J. and Blair, G. E., *Nucleonics*, 17, No. 10, 58 (1958).
88. Kreidl, N. J. and Blair, G. E., *Nucleonics*, 14, No. 3, 82 (1956).
89. Kreidl, N. J. and Blair, G. E., *Nucleonics*, 14, No. 1, 56 (1956).
90. Blair, G. E., *J. Am. Ceramic Soc.*, 43, 426 (1960).
91. Schall, P., *Nucleonics*, 17, No. 10, 68 (1959).
92. Schuler, R. H., *J. Phys. Chem.*, 68, 1618 (1964).
93. Spinks, J. W. T. and Woods, R. J., *An introduction to radiation chemistry*, New York, N.Y., John Wiley and Sons, Inc., 1964.

## ACKNOWLEDGMENTS

The author wishes to thank Dr. Adolf F. Voigt for his guidance throughout the course of this investigation.

Mr. Wayne Stensland and Mr. Richard Clark provided valuable assistance through their suggestions concerning the chromatographic and counting systems. Mr. Clark also assisted in the sample combustion experiments.

Dr. Al Bureau and Mr. John McConnell deserve especial thanks for operating the synchrotron during the many irradiations.

Dr. Joseph Pickens, Jr. made valuable suggestions concerning the dosimetry and assisted with the cobalt-60 irradiations.

The author also wishes to thank Dr. Dale DeVries and Mr. Frank Mesich for the many helpful discussions he had with them.

This study would not have been possible without the encouragement and understanding of the author's beloved wife, Beverly.