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THE CHEMICAL INTERACTION OF ACCELERATED CARBON-14 IONS WITH BENZENE

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Robert Terrence Mullen

(Ph. D. Thesis)

March 14, 1961

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ABSTRACT

Solid benzene at -160° was irradiated with singly charged ^{14}C ions in an isotope separator. Irradiation was performed at three different ion energies: 5000 ev, 90 ev, and 45 ev. The volatile products of irradiation were analyzed by gas-liquid chromatography in conjunction with internal-flow proportional counting. The yields of three products of the irradiations -- ^{14}C-labeled benzene, toluene, and cycloheptatriene--were found to decrease with decreasing ion energy. At a given ion energy the yields of those compounds were found to increase with decreasing energy density (ev per target molecule). The first effect is related to the probability that the ^{14}C species will encounter a suitable reactive species in the ion track. The second effect is a property of the irradiated volume as a whole and is attributed to the destruction of labile intermediates by radicals or other highly reactive fragments. It was found that the toluene-^{14}C produced in this work had the same ring methyl distribution of activities as that formed from ^{14}C nuclear recoil labeling in benzene-2-methylpyrazine solution. No firm conclusions are reached in regard to the mechanism of formation of these products, by some speculative considerations are proposed. In addition to benzene, toluene, and cycloheptatriene, the following ^{14}C-labeled compounds were identified as products of the irradiations: allene, propyne, 1, 2-butadiene, 1, 3-butadiene, 1 and (or) isobutene and 1-butyne. Trace amounts of n-butane, and indirect evidence for propane, were observed.

I. INTRODUCTION

A. General Introduction

1. Scope and Purpose of the Field

The carbon-14-ion irradiations of benzene described here have much in common with the field of "hot atom" chemistry, which is concerned with the chemical effects of nuclear transformations. In fact, according to a generous interpretation of the purview of hot-atom chemistry, made by Willard, the nonnuclear origin of our ^{14}C ions is not held against us, and we may claim to be completely within that area.[1] Many investigations have been made of the hot-atom chemistry of ^{11}C and ^{14}C ions or atoms, produced by nuclear processes, in organic chemical media. These investigations have in common with the work presented here the ultimate goal of determining both the chemical fate of the energetic radiocarbon species and the interactions of the energetic particle with its surroundings that lead to that fate.

The problem of elucidating the chemical effects of the interaction of energetic ^{14}C species with organic chemical compounds has been a subject of active interest for the past fourteen years. When such interactions occur, there are typically formed many organic products incorporating the ^{14}C atom. The novelty and complexity of the chemistry involved have certainly provided much of the interest in this field.

There is, however, a practical aspect to the problem, arising primarily from the fact that some of the ^{14}C has almost always been found in the starting compound itself. That is, a net effect is the replacement of the ^{12}C atom in a molecule of the parent compound by a ^{14}C atom. If suitable methods of radiochemical purification are available, the formation of these so-called "re-entry products"[2] allows this technique to be used for the synthesis of ^{14}C-labeled organic compounds which are difficult or impractical to make by ordinary synthetic methods. Other products, less predictable but more prevalent than the re-entry products, may also be of use.

2. Techniques

a. Accelerated ions

A mass spectrometer was first used as a source of energetic $^{14}C^+$ ions by Croatto and Giacomello in 1954.[3] These workers used the isotope separator* of the Gustav Werner Institute for Nuclear Chemistry at Uppsala, Sweden, and irradiated several solid organic compounds with $^{14}C^+$ ions, as well as paraffin with $^{14}CO^+$ and $^{14}CO_2^+$ ions. Carbon-14 ion irradiation of benzoic acid, stearic acid, cholesterol, and Vitamin B resulted in an incorporation of some of the ^{14}C in the target compound in each case. Following the first isotope separator experiments, other workers from the same group, using the Uppsala machine, have since irradiated benzoic acid[4] and cholesterol[5] with $^{14}C^+$, $^{14}CO^+$, and $^{14}CO_2^+$ ions each; this was reported in 1956. Yields of 2.8% and 1.2% of labeled benzoic acid and cholesterol, respectively, resulted from the carbon-14 ion irradiation.†

The only other use of an isotope separator prior to the work presented here was made by members of the Bio-Organic Chemistry and the Nuclear Chemistry groups of the Lawrence Radiation Laboratory in 1956. Lemmon, Reynolds, Mazzetti, and Calvin irradiated solid benzene at -160°C with a relatively weak beam of

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*It should be mentioned here that an electromagnetic isotope separator is essentially a mass spectrometer designed for the production and subsequent use of separated isotopes, ordinarily after they are collected. A case can be made for calling machines used for the irradiation of substances with separated isotopes "ion accelerators," but this would perhaps lead to the confusion of these devices with the high-energy accelerators used for nuclear research; therefore, the term isotope separator is used throughout this discussion.

†The results of both experiments are given in English in Reference 6.

2-kev $^{14}C^+$ ions.[7,8] A small amount of the ^{14}C was found in benzene and toluene, in agreement with results of ^{14}C recoil experiments (described later) in benzene. In addition to benzene, beta-carotene and morphine were also irradiated with $^{14}C^+$ ions. Activity again was found in the target compounds.[9] These irradiations were done in an analytical mass spectrometer, suitably altered for the ^{14}C work. Their success led to the construction of a bona fide isotope separator and to the benzene irradiations in this dissertation. Irradiations with accelerated but unanalyzed ions have been carried out by gas-discharge techniques. Wolfgang, Pratt, and Roland[10] formed $^3H^+$, $^3H_2^+$ ions in a gas discharge tube and accelerated them onto organic compounds spread in a thin layer on the cathode of the tube. In the same way, Guillaume labeled several organic compounds with the ions provided by discharge in $^{14}CO_2$.[11]

b. Recoiling ions, or atoms

Most of the work in this area has been done by using the nuclear reaction $^{14}N(n,p)^{14}C$ as the source of the energetic ^{14}C species. In this method, the compound to be studied, which must either contain nitrogen or have homogeneously mixed with it a source of nitrogen, is subjected to a thermal neutron flux, and ^{14}C is formed in situ. Conservation of energy and momentum requires the newly formed ^{14}C to have about 45,000 ev kinetic energy, and there is general agreement that this results in the destruction of the chemical bonds which the ^{14}C atom inherited from the ^{14}N atom in the molecule affected.[12] The ^{14}C species thus produced is spoken of as "recoiling," and the method is therefore termed the nuclear-recoil method.

Recoiling ^{11}C ions have also been used. Wolf and Suryanarayana irradiated benzene with fast neutrons, forming ^{11}C in situ by the reaction $^{12}C(n,2n)^{11}C$.[13] In this case the recoil chemistry can be studied in the absence of nitrogenous material. The half life of ^{11}C is only 20.5 minutes ($T_{1/2}$ ^{14}C is 5570 years), and

this is both an advantage and a disadvantage--a good deal more radioactivity is introduced for a given rate of production of ^{11}C than for ^{14}C, but one must move fast to see it. In particular, time-consuming degradation procedures would seem to be precluded.

c. Fast carbon-11 ions

Wolfgang *et al.* have irradiated various hydrocarbons with ^{11}C produced by a neutron-stripping reaction that occurs when a beam of 120-Mev $^{12}C^{+}$ ions passes through a thin platinum foil.[14] This method has in common with isotope-separator experiments the production of the energetic species before it impinges on the organic target material, in contrast to the *in situ* production of recoil techniques.

d. Radiation-induced reactions

Turton has utilized radiation-induced reactions between organic molecules and simple ^{14}C-containing gases (CO_2 and C_2H_2), the source of radiation being ^{85}Kr, a beta emitter.[15] The beta radiation from the ^{85}Kr ionizes, excites, or fragments the ^{14}C-containing gas, and these reactive ^{14}C species then interact with the organic substrate. In this way, benzene-$^{14}CO_2$, pyridine-$^{14}CO_2$, and pyridine-$^{14}C_2H_2$ have been investigated. It should be noted that this technique (and gas-discharge techniques) may not yield results comparable to the nuclear recoil and isotope separator methods because the reactive species may not be (and probably are not) the same. That is, when $^{14}CO_2$ is the source of ^{14}C in the radiation-induced method, reactions due to C, CO, and CO_2 ions, radicals, etc. all may be occurring simultaneously.

3. Essential Equivalence of Techniques

It is apparent from the foregoing discussion that the techniques used in this area differ in several respects--the energy of the carbon isotope used, the energy of the carbon species, and, perhaps, the initial charge state of the carbon species. To be sure, each technique has its pros and cons (as will be discussed later), but the essential

equivalence of these techniques is undisputed. In particular, the effect of the factors mentioned above can be shown to be either unimportant or actually advantageous.

The goal of the experiments performed by these several methods is, in general, the determination of the chemical fate of the energetic radiocarbon atom and the chemical interactions responsible for that fate. ^{11}C and ^{14}C have been the carbon isotopes used, because they are radioactive and hence provide the only means of detecting the presence of the microscopic amounts of products. The slight differences in chemical behavior that occur among different isotopes of an element are quite insignificant in this context, and ^{11}C and ^{14}C are considered equivalent in chemical behavior. The fact that there are large differences in the energetics of the various techniques (^{11}C recoil is 1 Mev; 45-ev $^{14}C^{+}$ ions have been used in this work) does not preclude comparison; rather it allows the effect of particle energy to be explored. Differences in the initial charge state of the radiocarbon species can also be shown to be unimportant.

Single charged $^{14}C^{+}$ ions are used in the isotope separator method. The charge state of recoiling ^{14}C from the n, p reaction is apparently unknown, and the ^{11}C recoil method described probably yields a highly charged $^{11}C^{+}$. As is true for particle energy, charge differences could not preclude comparison, because positive ions passing through matter being a process of charge neutralization and charge exchange when the velocity of the energetic positive ion is of the order of, or less than, the orbital velocity of the electrons concerned.[16] Thus even at the highest energy used in this field, charge neutralization and exchange occur at once, and by the time a ^{14}C or ^{11}C species is slowed down to an energy at which it is stopped by a crystal lattice or solvent cage (throught to be about 25 ev for an ionic crystal),[17] it has probably become a neutral atom, or at least has the same chance of being a neutral atom as the ^{11}C or ^{14}C produced with the different initial energy or charge.

B. Specific Introduction to Benzene Irradiation

1. Previous Investigations

For the purpose of this introductory discussion, the specific area of which this work is considered a part is limited to studies of the interaction of energetic radiocarbon species with organic chemical compounds, either pure or in solution, in any phase. This arbitrarily excludes investigation of energetic radiocarbon species in inorganic compounds, even though some of the products are organic. It further excludes studies of recoiling tritons, as well as recoiling halogens, in organic compounds. Results of these other hot-atom experiments are cited when appropriate in the discussion of the results of this work.

The experiments performed employing the less frequently used isotope-separator, gas-discharge, and radiation-induced-reaction techniques have already been mentioned. No attempt will be made here to list all the investigations made with recoiling ^{14}C or ^{11}C atoms--comprehensive discussions are available elsewhere.[12, 18, 19] Several of the investigations using recoil techniques will be mentioned here either because they directly involve benzene or are of special pertinency to this work.

a. Benzene studies

The first investigation of benzene was reported in 1954 by Ziffereo, who studied the ^{14}C recoil chemistry of the clathrate compound of ammoniacal nickel cyanide and benzene, finding 4% of the ^{14}C produced in benzene-^{14}C.[20] Wolf, Redvanly, and Anderson studied the same system, and reported 1.44% of the ^{14}C in benzene.[21]

Schrodt and Libby examined the ^{14}C recoil chemistry of several aromatic systems, one of which was an 8 mole % solution of aniline in benzene. They found 2.5% of the activity in benzene, 1.7% in toluene, 3.2% in diphenylmethane, and 2.1% in triphenylmethane.[22] Sequential extraction with acetic acid and HCl solutions indicated the presence of amine products. More than 75% of the radioactivity

in nonbasic compounds was found to be nonvolatile upon distillation of the acid-extracted benzene solution to dryness.

In 1956 Wolf, Gordon, and Anderson reported on the thermal-neutron irradiation of a mixture of benzene and 2-methylpyrazine;[2] 1.92% of the activity was found in benzene and 1.05% in toluene, the only products sought. Of particular interest is the finding that not all the toluene activity was in the methyl group--12% was found in the ring of the toluene-^{14}C form. More recently Wolf has reported the results of further experiments on the same system, extrapolating the yields to 0 mole% 2-methylpyrazine. The resulting yields of benzene and toluene were 2.6 and 2.25% respectively.[23]

In 1959 Suryanarayana and Wolf used recoiling ^{11}C ions of about 1 Mev recoil energy to study the effect of change of phase and presence of free-radical scavengers on the yields of labeled benzene and toluene from benzene.[13] Liquid benzene alone gave 4.6 and 2.3% yields of benzene and toluene respectively. Neither the presence of free-radical scavenger [1, 3, 5-trinitrobenzene, diphenylpicryl-hydrazyl (DPPH), and hydroquinone were each tried] nor the change of irradiation phase from liquid to solid affected the yield of toluene, indicating that toluene was not formed through a thermal process. The yield of benzene-^{11}C was decreased from 4.63 to 2.90% upon addition of DPPH to liquid benzene; furthermore, radiation of pure solid benzene at 0°, -78°, and -195° gave only 2.46%, 2.63%, and 3.10% yields of benzene-^{11}C respectively, all considerably less than the 4.63% yield for pure liquid benzene. These results indicate that at least some of the benzene ^{11}C is produced by thermal reactions involving free radicals.

b. Other aromatics

Wolf, Anderson, and others at Brookhaven National Laboratory have focused their attention on two general kinds of products that are typically formed. One of these, called by them the re-entry product, has already been mentioned. The other consists of labeled molecules

containing one carbon atom more than the starting compound, exclusive of carbon analogs of nitrogen-containing parent compounds (which are considered to be re-entry products). This second type of product is called a synthesis product by the Brookhaven group.[2] They have focused their interest on re-entry and synthesis, not only in benzene experiments, but in many others as well. Some of this other work is also of direct interest to us.

Wolf irradiated aniline with thermal neutrons and found 2.8% of the ^{14}C activity in aniline, 0.35% in benzene, and 0.07% in toluene; 86% of the activity of the toluene was in the methyl group, 14% in the ring.[24] Schrodt and Libby have also investigated ^{14}C recoil in aniline, reporting 0.1% yield of benzene and 0.7% of toluene; 23.4% of the total activity was found in 13 different compounds, an unusually complete determination for this type of experiment.[22]

Yang and Wolf examined the ^{14}C recoil chemistry of solid solutions of azobenzene and stilbene varying in composition from 2.33 to 100 mole% azobenzene.[25] They reported finding activity in azobenzene, stilbene, and benzalaniline. Toluene, reported as representing the benzal portion of benzalaniline, was found to have 14% of its activity in the ring, 86% in the methyl group 26% of the activity in the stilbene-^{14}C was found in the two exocyclic carbons, 74% in the two phenyl groups.

c. Theoretical explanations

The first point to be noted in regard to theory is that non exists that is sufficiently comprehensive and consistent with all the observed facts to be of use in the rationalization of the data just cited, to say nothing of the prediction of results in uninvestigated systems.[12] Indeed, if the present trend toward emphasis of chemical considerations is correct, it is not likely that there will be any comprehensive theory, for each chemical system and recoiling species is then a unique problem.

Early theories attempting to explain the results of recoil chemistry emphasized physical considerations of energy loss.[26, 27] Libby suggested that elastic "billiard ball" collisions between atoms of like mass were important (but not exclusively so) in determining product distribution.[26] This theory was applied to recoiling radiohalogen atoms in solid or liquid organic halide compounds, and sought to rationalize the observed formation of labeled parent compound by envisaging a high-energy collision between a recoiling radiohalogen atom and an organically bound halogen atom of like mass, resulting in complete or nearly complete energy transfer to the struck atom, which leaves the scene of impact by breaking through the solvent or crystal cage. The stopped radiohalogen is trapped by the solvent or crystal cage and can then combine with the organic fragment resulting from the original fission. This theory has been questioned on several counts in articles by Willard,[28] Yankwich,[17] Wolf,[13] and Harbottle and Suttin.[29]

Willard has emphasized the importance of the chemical nature of the debris formed as a result of the fragmentation caused by the recoiling atom. Without going into detail of his ideas, it is safe to say that this general point of view is the prevailing one at present--at least insofar as it emphasizes chemical rather than physical phenomena.

That chemical factors are important in determining the chemical fate of the energetic radiocarbon species in the experiments mentioned earlier seems clear from the results cited. The hot-atom chemistry of radiocarbon atoms in organic compounds may or may not lead to product distributions that would be expected from a random attack, and usually do not yield product distribution indicative of specific or selective reaction. Thus, the ratio of the yield of acridine-^{14}C to anthracene-^{14}C, produced by ^{14}C recoil in acridine, is found to be about 17 to 1, fairly near the 13-to-1 ratio expected for purely random ring atom replacement.[30] On the other hand, Brunello and Muxart, studying ^{14}C recoil in quinoline, found the ratio of

quinoline-^{14}C to napthalene-^{14}C to be 36 to 1, far higher than the "statistical" ratio of 9 to 1.[31] Carbon-14 recoil in acetamide, and subsequent hydrolysis of the reaction mixture, gave ^{14}C-labeled acetic acid, propionic acid, and acetone; each of these products was labeled to a greater or lesser extent in every carbon position.[2]

2. The Work Presented Herein

a. The advantages of the isotope separator

Although the investigations carried out by the several techniques discussed earlier are considered fundamentally equivalent so far as the chemical behavior of the radiocarbon species is concerned, they are certainly not equivalent with respect to the treatment received by the other component of the reaction system--the organic target material--nor with respect to the ability to control some important experimental variables.

Nuclear recoil methods suffer from the fact that the systems studied inevitably receive radiation damage from unwanted radiations during the course of exposure to the desired radiation. Irradiation with thermal neutrons from reactors is accompanied by fast-neutron and gamma-ray fluxes. This extraneous radiation may destroy some of the products formed. What is far worse, however, is the possibility that ions, radicals, and fragments formed as a result of these irradiations may affect the chemical fate of the recoiling radiocarbon. In a few ^{14}C recoil experiments, the gamma flux has been varied while the thermal-neutron flux was held constant in order to determine effect of the gamma flux on the product distribution.[22, 31] The gamma flux was found to have relatively little effect in those cases, but as Wolf has pointed out,[12] it may be that saturation levels were being observed in all cases.

The $^{14}N(n,p)^{14}C$ reaction has the additional drawback of requiring the presence of nitrogen in the target system. Although it has been shown in at least two cases that the presence of a given nitrogen source in solution with a nonnitrogenous compound had no effect, beyond

dilution, on the yield of certain products,[23, 25] recent evidence by Wolf has demonstrated that this is not necessarily true for all nitrogen sources and all products.[23] The yield of toluene-^{14}C from solutions of benzene and 2-methylpyrazine was shown to be directly proportional to the mole fraction of benzene, but when 3, 3'- diaminodipropylamine was the nitrogen source with benzene, the plot of toluene yield versus mole fraction benzene showed sharp curvature. The yield of benzene-^{14}C, on the other hand, was still directly proportional to the mole fraction of benzene.

A third drawback to ^{14}C recoil is that it allows no variation of the initial energy of the radiocarbon species formed. Recoil energy is rigidly fixed for a given reaction by energy and momentum conservation.

The disadvantages of the gas-discharge and radiation-induced-reaction techniques have already been mentioned. They may well be useful for the synthesis of labeled products, but the multiplicity of reacting species would seem to preclude their use for theoretical investigations.

An isotope separator was constructed and used in this work because it avoids the difficulties inherent in the recoil and other techniques. The most important potential advantage of an isotope separator is the ability to vary the energy of the impinging ions. Obviously, no radiation damage is suffered by the targets except the damage due to the desired ions, which is really not damage at all, but it an integral part of the process under investigation. Finally, the isotope separator has the potential of giving information concerning the chemical nature of the energetic ^{14}C species at the time it undergoes a particular reaction. By irradiating with CH^+ or CH_2^+ ions, etc., and observing the relation of product yield to the type of ion, information bearing on that question may be obtained.

It must be admitted, however, that there are limitations inherent in the use of an isotope separator. One is confined to the irradiation of solids because the target compound is in the vacuum

system of the separator and must have a very low vapor pressure to avoid being pumped away. Constant attention is required during an isotope-separator irradiation, which is not the case in most recoil techniques. Because of this, the total radioactivity introduced into the sample through the use of the isotope separator in this work was considerably less than commonly achieved by recoil methods. All things considered, however, there seems much to be gained by the use of an isotope separator.

d. The choice of benzene as the subject of irradiation

Benzene was chosen as the subject of ^{14}C ion irradiation for several reasons The yields of benzene-^{14}C and toluene-^{14}C from the preliminary isotope-separator irradiation of benzene with 2-kev ^{14}C ion was in fair agreement with the results of ^{14}C recoil in benzene, showing that, at the very least, benzene and toluene production was not seriously affected by any of the difficulties associated with the recoil method. This is important because it allows new data obtained with the isotope separator to be considered complementary to recoil data. Although a good deal of very interesting work has been done on benzene by recoil methods, the lack of definitive answers to the questions generated by the recoil experiments makes it highly desirable to be able to pool data from several sources.

- Only four products of ^{14}C recoil in benzene-nitrogen source system had been found, accounting for only a small fraction of the total ^{14}C activity. Little was known of the mechanism of formation of two very interesting products, benzene and toluene, the latter being particularly interesting because it is 12% ring-labeled. Our ability to vary the energy of the ^{14}C ions could perhaps lead to some knowledge of the mechanism of these reactions.
- New knowledge of the reaction of benzene with ^{14}C ions might well be applicable to a certain extent to aromatic compounds in general.
- Benzene has a sufficiently low vapor pressure at -160° that it would not be pumped away during irradiation. In order to avoid

condensation of $^{14}CO_2$ (the source of the ^{14}C ions), the temperature of the target cold finger, onto which the substance to be studied is bled, cannot be much lower than -160°.

e. The limited goal of benzene irradiation

As has been emphasized, the result of hot-atom processes in condensed organic chemical systems is usually complex, both with respect to the multiplicity of products formed and with respect to the number of routes by which a given product can be made in the energy-rich situation prevailing. Therefore, although the general or ultimate goal of hot-atom chemistry is a complete understanding of the chemical fate of the hot atom and the paths to that fate, in practice it is both natural and desirable to focus one's attention in a given experiment on products that are most amenable to analysis and that are particularly interesting or useful. This has been a common practice in this field.

In work reported here, our interest was confined solely to the volatile products, that is, those which could be collected at -195° by vacuum distillation from the target area at room temperature. Furthermore, we were more concerned with some volatile products than others. For reasons mentioned earlier, labeled benzene and toluene were expected to be found and were of special interest to us, being particularly interesting in themselves, and fruitful products to consider, since information about them was available from recoil experiments. Although cycloheptatriene had not been found from recoil experiments in benzene, and was never sought so far as we know, it seemed a likely and equally interesting product and was actively sought by us.

The limited goal of this work, then, was twofold: First, to study as a function of ion energy the yields of ^{14}C-labeled benzene, toluene, and cycloheptatriene, if indeed they were found. Second, to at least qualitatively identify any other volatile products that might result from the irradiation.

II. EXPERIMENTAL PROCEDURE

A. Isotope Separator

1. Description

a. General description

The isotope separator used in this work was especially constructed for that purpose. It has been briefly described in a Lawrence Radiation Laboratory Report,[32] but since reports of that type are not always readily available, it will also be described here, and in greater detail.

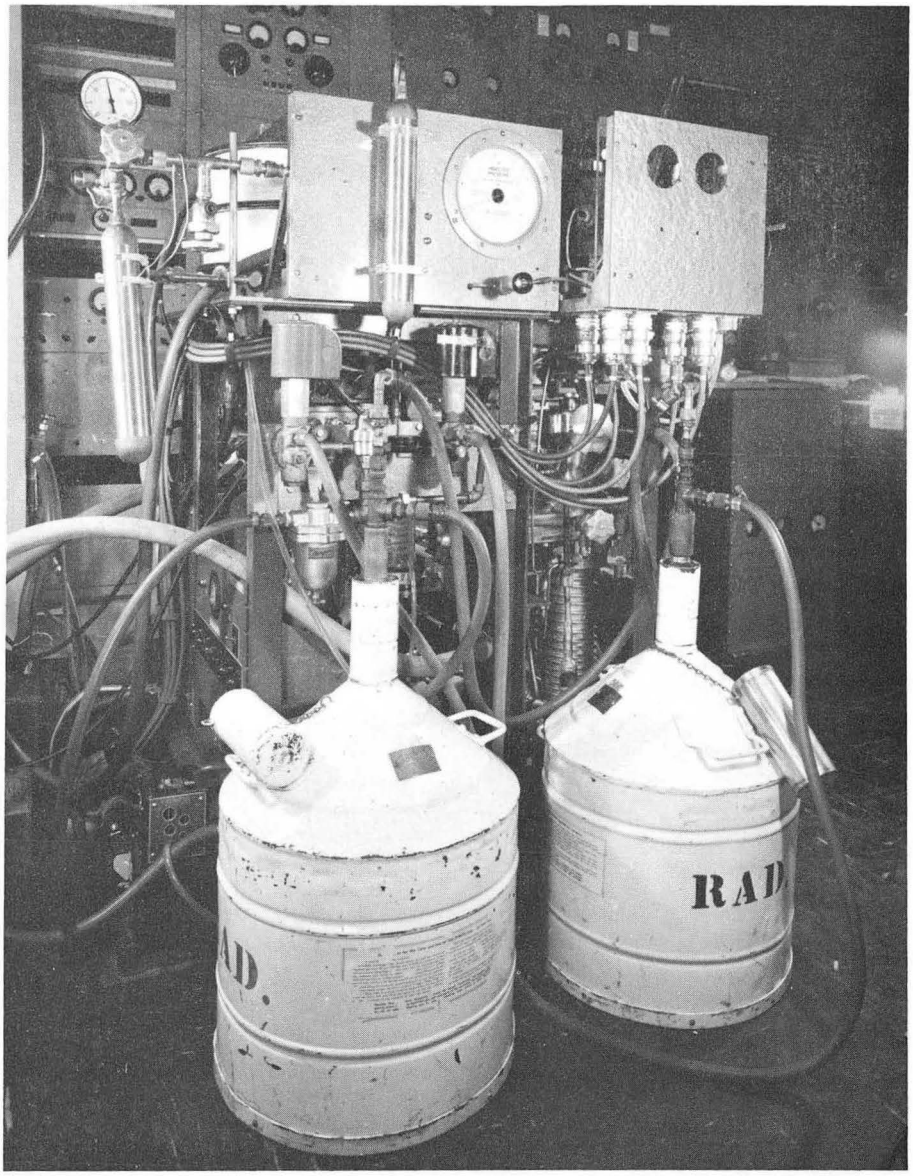
The design and construction of the isotope separator were primarily the responsibility of Mr. Frederick L. Reynolds of the Nuclear Chemistry Group of the Lawrence Radiation Laboratory. At the time the author began work on this problem, the construction of the isotope separator was essentially complete, although rather extensive modification and "debugging" were done during the next two years. See Figs. 1, 2, and 3.

The isotope separator is a single-direction focusing spectrometer with a 90-deg sector magnet of 15 cm nominal radius of curvature. It is designed for the irradiation of solid samples with ions produced by gas discharge. Its operation, in brief, is as follows.

The source gas is bled into the ionization source and ions are produced, extracted, and focused on a slit. The ions then enter the magnetic field, where they are separated, and the desired ions are allowed to pass through an exit slit and impinge upon the target material. The several sections of the machine will be discussed individually.

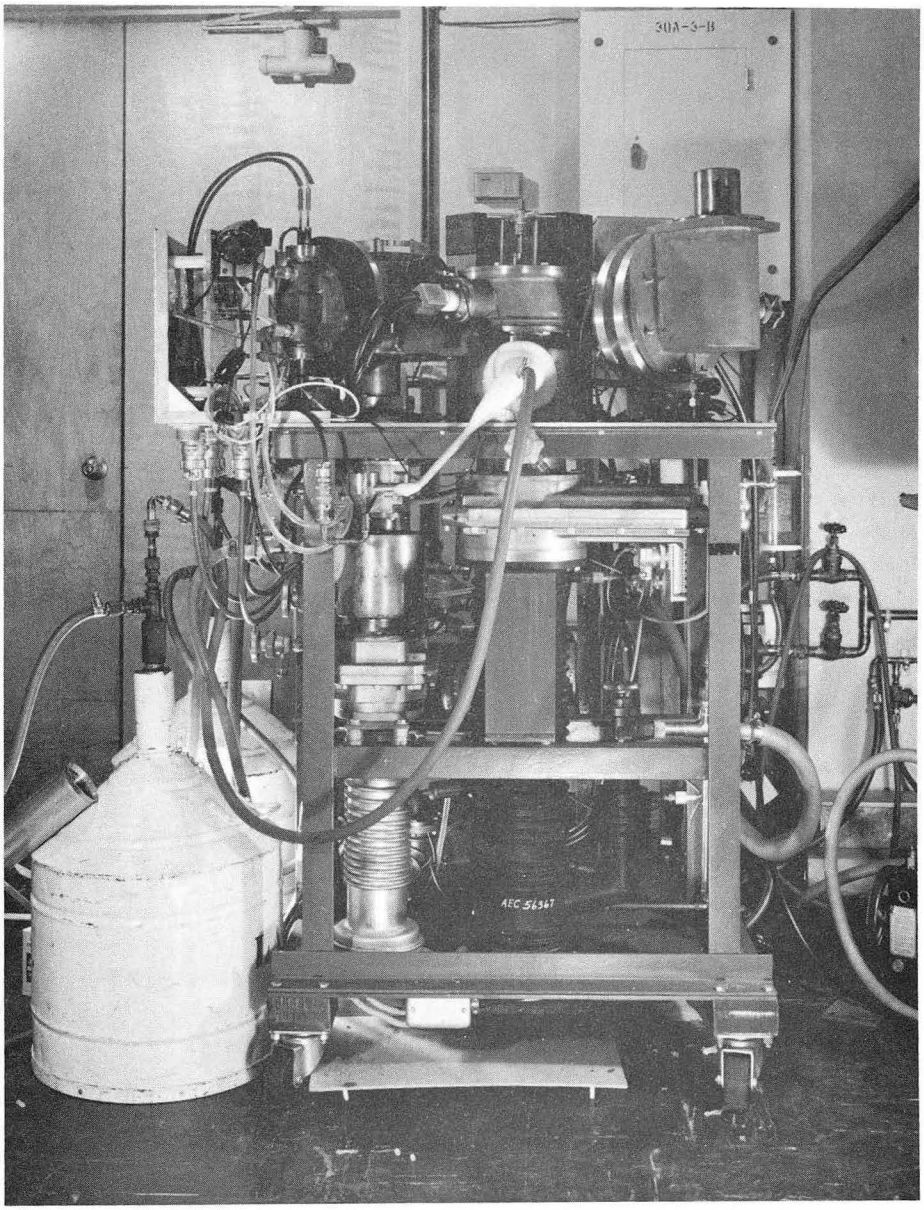
b. Gas supply system

The gas supply system is shown in Fig. 4. Its function is to allow gas to be bled from a low-pressure supply into the ion source at a constant rate. The pressure of the source gas in the central reservoir is held nearly constant by means of a solenoid valve actuated by a relay and a pressure-sensing device. When the pressure



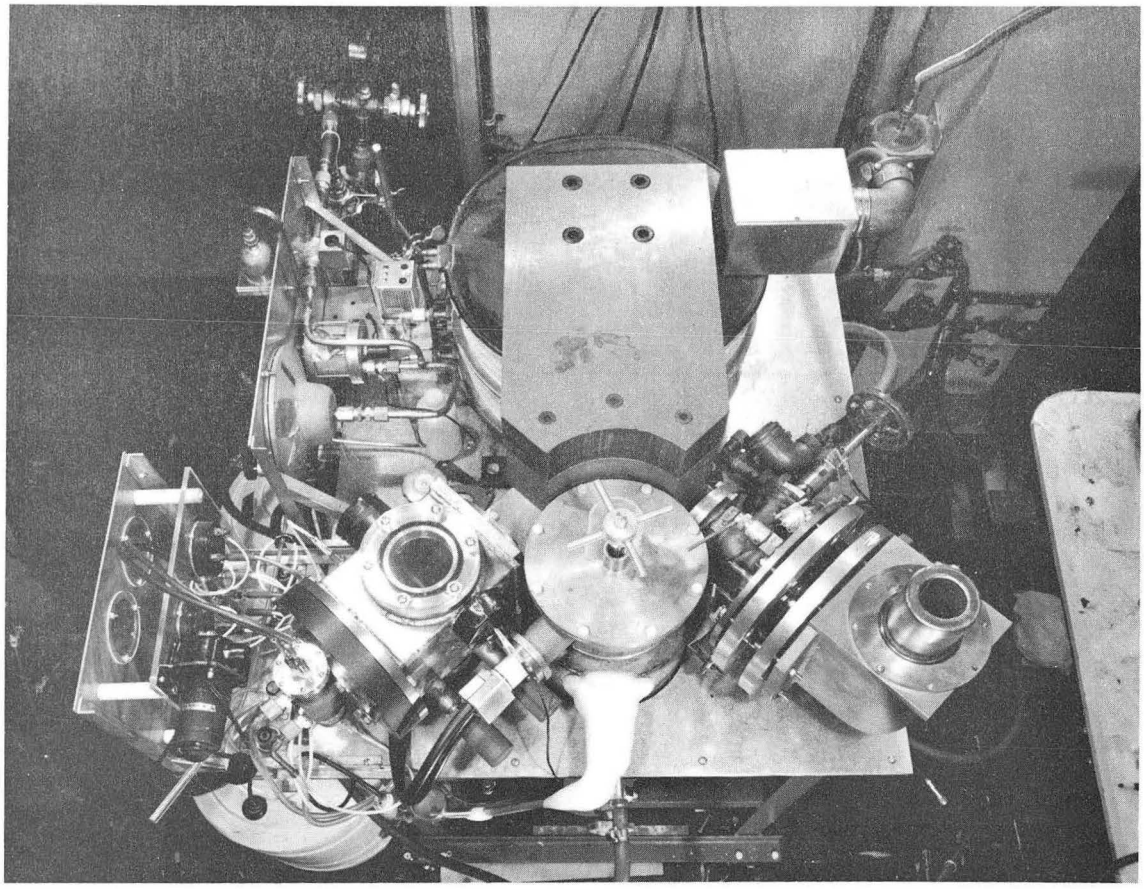
ZN-2750

Fig. 1. Front view of isotope separator.



ZN-2751

Fig. 2. Side view of isotope separator.



ZN-2752

Fig. 3. Top view of isotope separator.

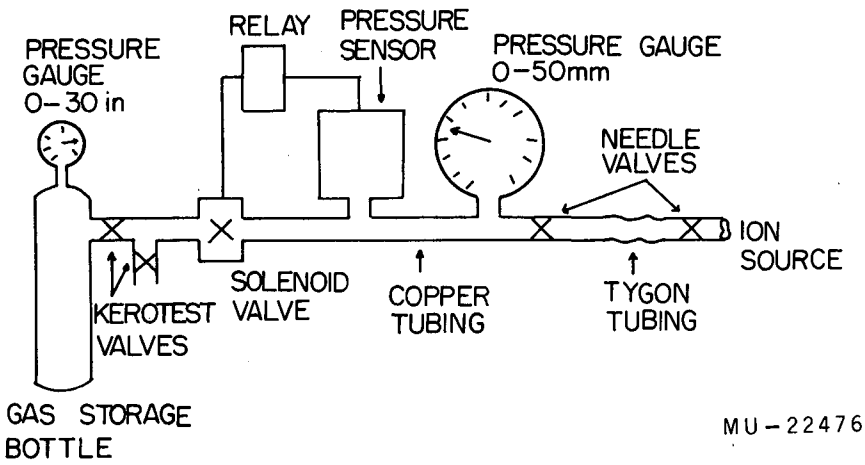


Fig. 4. Source gas supply system.

drops below about 12 mm, the solenoid is opened and gas is admitted from the high-pressure primary reservoir into the low-pressure section until the pressure there rises to about 13.5 mm. In this way a single position of the final needle valve yields a nearly constant feed rate, which is necessary for smooth operation of the separator. The gas storage bottle, accounting for most of the volume of the high-pressure primary reservoir, is a steel cylinder fitted with a mechanical pressure gauge and a Kerotest valve. Gastight connection of the storage bottle to the rest of the supply system is made by means of a neoprene gasket compressed by a metal nut and nipple. This type of connection is used extensively throughout the separator.

c. Ion source

The ion source, along with the electrode system, is shown in Fig. 5. It is a low-voltage capillary arc type, chosen because it provides a fairly intense beam of ions with relatively little energy spread. This type of ion source was first used in a separator by Yates,[33] who followed the design by Tuve, Dahl, and Hafstad.[34] Arc sources in general are in common use in isotope separators because of the properties mentioned above.

The ion source is constructed of stainless steel. The upper and lower sections of the arc chamber are 2.5 cm in diameter, and taper in to give a central capillary 5 mm in diameter and 1.5 cm long. Ions are extracted through a 0.6-mm hole in the capillary wall. The rhenium filament and the tantalum anode both terminate near the beginning of the capillary section. Gas is admitted through a needle valve located near the base of the anode. The anode and cathode are both attached to stainless steel discs through glass insulators, and can be easily removed from the ion source proper.

Figure 6 shows the electrical circuits involved in the operation of the arc discharge. To start the arc, gas is admitted near the anode section by cracking the needle valve slightly, a potential difference of 500 v is applied between the filament and the anode, and

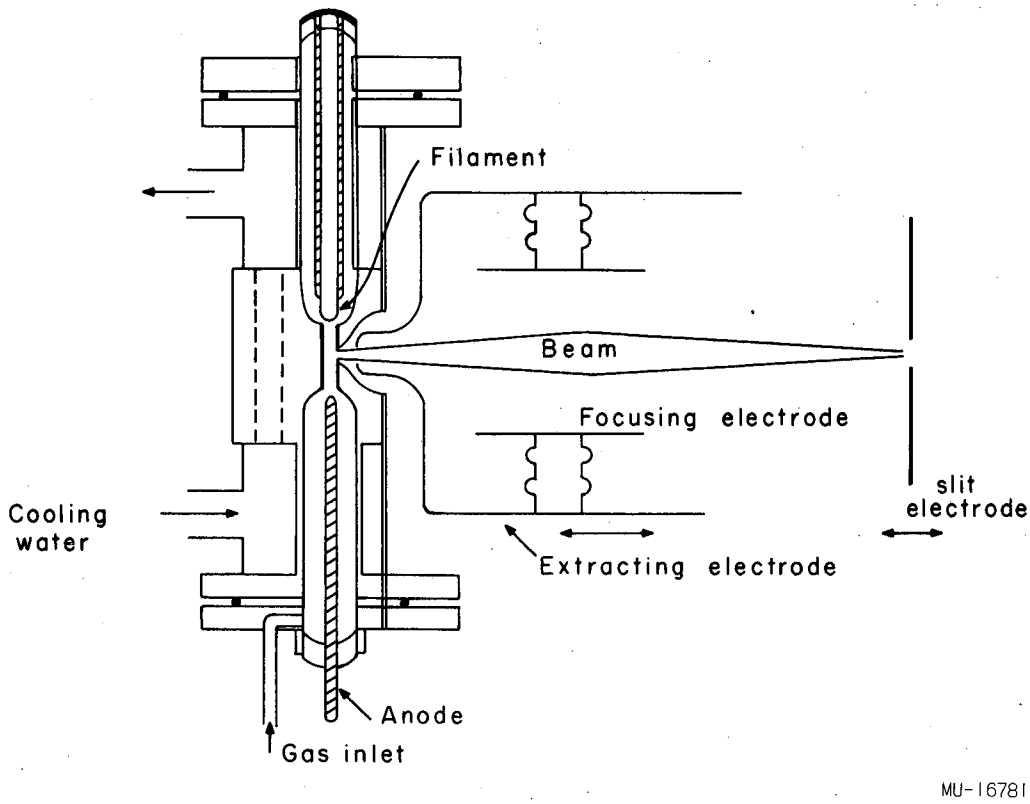


Fig. 5. Cross section of ion source and electrode system.

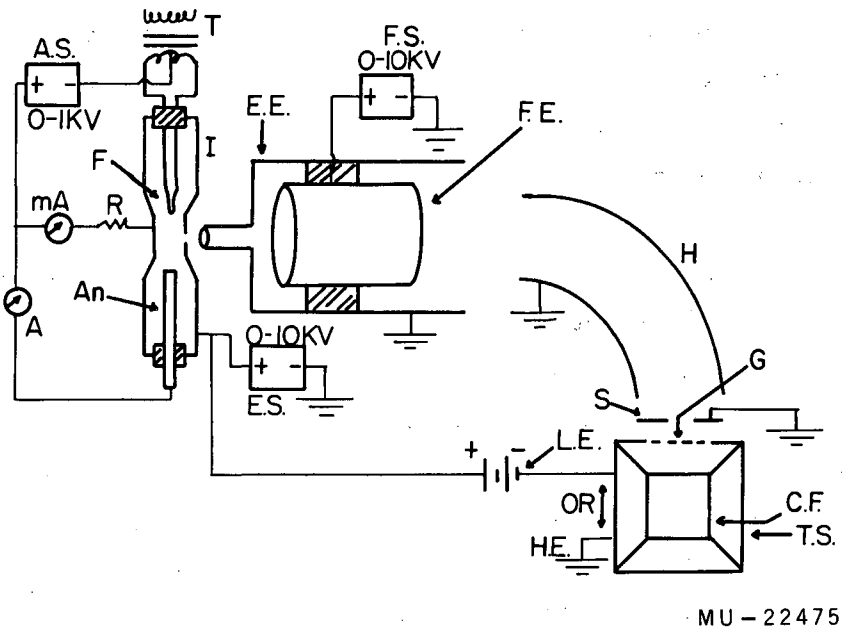


Fig. 6. Schematic of electric circuit of isotope separator.
H = Analyzer tube in magnetic field
S = Wide exit slit (9.5 mm)
b = Copper grid
T. S. = Target section
C. F. = Target cold finger
L. E. = Connection for low-energy irradiation
H. E. = Connection for high-energy irradiation
▭ = Insulators
A. S. = Arc voltage power supply
E. S. = Extraction voltage power supply
F. S. = Focusing voltage power supply
T = Transformer
F = Filament
An = Anode
R = 40-K ohm resistor
mA = milliammeter
A = Ammeter
I = Ion source
E. E. = Extraction electrode
F. E. = Focusing electrode

the alternating current through the filament is increased until the arc first strikes, then the filament current is increased while the arc current is simultaneously decreased, until a final voltage of 40 to 80 v, giving an arc current of about 1 amp, is realized. The arc first strikes between the filament and the wall of the ion source, but as the ion density increases, the conductivity of the plasma between the filament and anode becomes greater than the conductivity of the filament-wall circuit, which is limited by a 40-k-ohm resistor, and the main arc is then formed between the filament and anode. As shown in Fig. 6, the whole ion source and associated electronics is at high voltage (+ 5000 v) during operation and the voltage difference between the filament and the anode is superimposed upon the positive extraction voltage.

The ion source is cooled by the passage of distilled water through the steel block from which the source is machined. This water is circulated by a "sine-wave" pump and is cooled by passage through a small heat exchanger. The filament assembly is further cooled by a blower, the air stream of which is directed against the glass insulators of the filament assembly.

This ion source was the second one tried. The first was similar in most details, but it did not allow rapid and easy changing of the filaments. Since even rhenium filaments burn out in 2 to 5 hours when CO_2 is the source gas, ease of filament replacement was soon seen to be necessary. The problem of filament lifetime is discussed later.

d. Electrode system

The extraction and focusing electrodes are shown in Fig. 5. The extraction electrode is a hollow aluminum cylinder of 8 cm diameter, tapering at the end nearest the ion source to a 5-mm opening through which ions are admitted. The extraction electrode is grounded and some of the positive ions formed in the ion source, which is at + 5000 v, are pushed from the source to and into the extraction electrode.

Mounted inside the extraction electrode on insulated stand-offs is the focusing electrode, a 4-cm-wide cylinder of aluminum. It is operated at a positive potential only slightly less than the extraction voltage. This electrode has no effect on the energy of the ions, serving only to collimate the ion beam to a width of about 3 mm. The whole electrode assembly can be moved relative to the ion source along the source-electrode axis by means of a rack-and-pinion mount connected to an external handle through a vacuumtight O-ring seal. Thus the optimum electrode position can be empirically determined.

Not shown in Fig. 5, but added later to the electrode assembly, are two pairs of split-plate electrodes at right angles to each other. These plates were added to give additional control of the ion beam position independently in the horizontal and vertical direction. One plate of each pair is always grounded, so it is attached directly to the grounded extraction electrode; the other plate of each pair is attached to the extraction electrode through insulated stand-offs and can be maintained at ± 0 to 600 v. The need for these split-plate electrodes was found to depend strongly on the position of the whole electrode section with respect to the ion source. If the electrode assembly was as close as possible to the source, the ion beam tended to kick to one side and the split plates were essential, but when the electrodes were positioned a few cm back, the beam was centered and the split plates then did little good. The beam intensity tended to maximize in the latter position, so it was used and the split plates proved to be of little utility.

Following the electrode assembly is a metal plate with a vertical slit, 2.4 mm wide. This entrance-slit plate is bound in a bakelite frame and can be independently moved by a rack-and-pinion mount. The ion beam intensity was found to be insensitive to its position.

As was the case for the ion source, the electrode system described here is a modification of the first one tried. It differs from the first chiefly in the mobility of the electrodies and entrance slit.

e. The electromagnet

The electromagnet is a 90-deg C-shaped sector of 15 cm radius of curvature. It is water-cooled, requiring about 190 ma current to give the approx 2500-gauss field needed to bend 5000 ev $^{14}C^{+}$ ions in an arc of 15 cm radius.*

f. Target section

The target end of the isotope separator is shown in Fig. 7. The target holder is a cold finger, cubical at the bottom where it intercepts the ion beam and cylindrical at the top. Solid samples can be painted on its surface and volatile samples are frozen on, being bled in through a sample-inlet valve located immediately in front of the holder below the path of the beam. The target holder can be removed through a hole at the top of the terminal section. It is secured by screws and makes a vacuumtight connection through an O-ring seal. It can be turned in place, even under vacuum, to present a fresh target face to the beam. This feature was not used in the work reported here.

Positioned across the mouth of the target section is a fine copper grid, through which the ion beam must pass before it reaches the target holder. Its purpose is to provide an equipotential plane for the deceleration of ions in low-energy radiations. The whole target section is mounted on a pyrex cylinder, which electrically isolates it from the rest of the separator, allowing a decelerating potential to be applied to the target for low-energy runs.

The exit-slit assembly is mounted on a brass cylinder positioned between the end of the trajectory tube (that is, the portion of the separator lying in the magnetic field) and the pyrex pipe. It consists of a 2.4-mm-wide exit slit followed by a pair of split plates and a 9.5-mm-wide slit. A saw-tooth voltage can be applied across

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*See Appendix I for a brief discussion of the equations of motion of ions in a magnetic field.

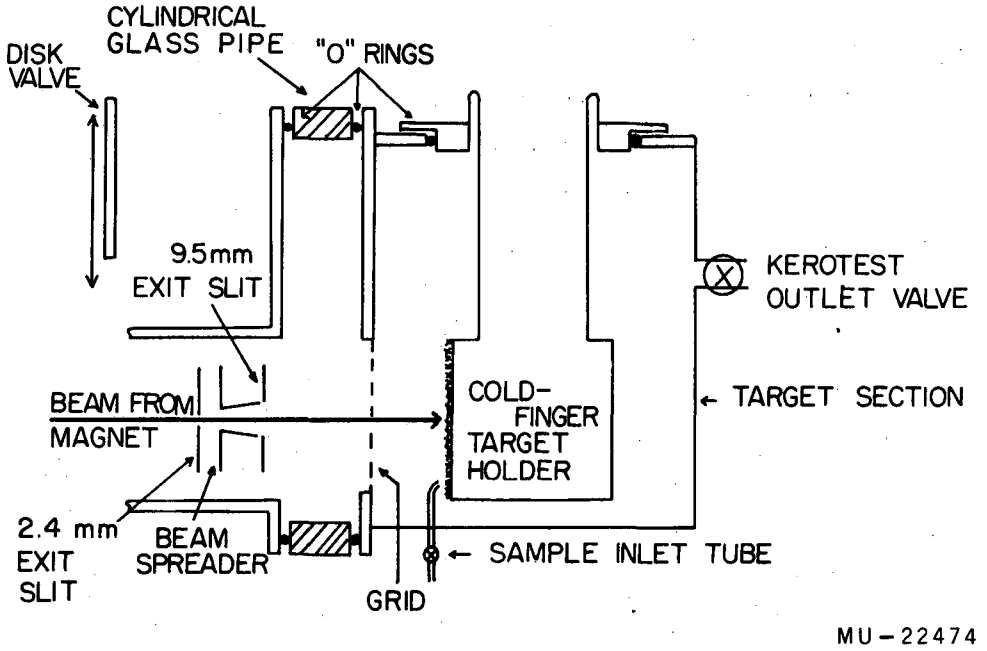


Fig. 7. Cross section of the target end of the isotope separator.

the split plates, causing the beam to oscillate a few millimeters in the horizontal direction, thereby covering a larger area of sample.

Not shown in Fig. 7 (see Fig. 9) is a rectangular metal plate, located immediately behind the 9.5-mm exit slit. This plate can be pivoted down across the slit opening to intercept the beam for measurement of the beam intensity. The several components of the assembly are electrically isolated from one another; the two slits are grounded, as is one of the two split plates of the beam spreader, and the plate for current measurement is, of course, connected to a meter.

For irradiation with high-energy ions (see Fig. 6), the target section is grounded and the ions then strike the target with the full energy given by the potential drop between the ion source at positive high voltage and the grounded target. For low-energy runs the target section is connected through a battery of appropriate potential to the ion source, the target being connected to the negative pole. The target then is at high positive voltage and the net potential drop between source and target--hence the final energy of the ions after acceleration and deceleration--is simply that supplied by the battery.

The target section is fitted with a Kerotest valve for roughing out and for collection of volatile products, and the whole rear end of the separator can be isolated from the rest of the machine by a disc valve located between the end of the trajectory tank and the exit-slit assembly.

g. Pumping System

Figure 8 shows a schematic diagram of the pumping system of the isotope separator. There are actually two independent systems--one near the ion source, the other at the center of the trajectory tank. Each consists of a liquid nitrogen trap, valved at top and bottom, followed by an oil diffusion pump and a mechanical forepump. The base pressure of the separator is about 4×10^{-6} mm. The pressure of various parts of the machine is measured by two ionization gauges and two vacuum thermocouple gauges. One of the ion gauges is near

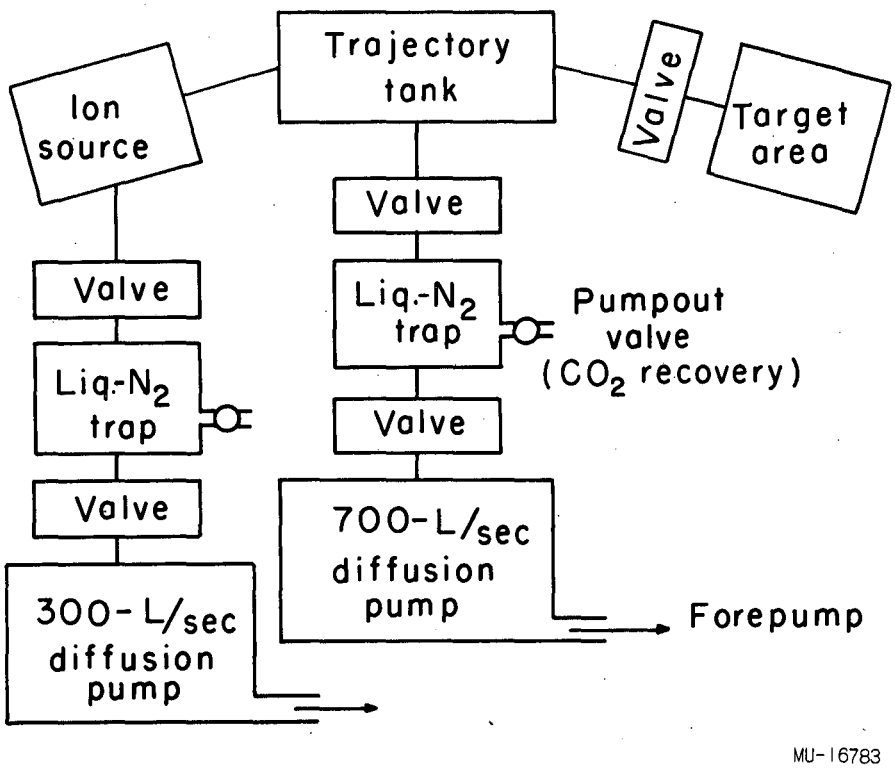


Fig. 8. Schematic representation of the pumping system of the isotope separator.

near the trajectory tank, the other between the source liquid nitrogen trap and the source diffusion pump. The thermocouple gauges are located between the mechanical pump and the diffusion pump of each pumping system.

The liquid nitrogen traps are filled automatically at preset intervals. These traps are needed to protect the diffusion pumps and to trap diffusion pump oil, but they were also intended to trap $^{14}CO_2$ when that gas was used as the source of $^{14}C^+$ ions.

2. Some Problems, Modifications, and Techniques Associated with the Use of the Isotope Separator

a. Beam-intensity measurement

Determination of the beam intensity during an irradiation is necessarily done intermittently. The location of the interceptor has already been described. Figure 9 shows the method of current measurement finally settled on. The interceptor plate is positioned about 2 mm behind the final exit slit. Its position is controlled by a lever extending out the vacuum system through an O ring. For intensity measurement the plate is rotated until it covers the exit slit. The ion current is fed through a resistor to ground, and the potential drop across the resistor is measured by a 10-mv recording potentiometer. The beam current is obtained through Ohm's law. For 1-μa full-scale deflection, a 10-K resistor is used; for 10 μa, a 1-K resistor is substituted; 1% resistors are used.

This simple method proved highly satisfactory. Early a vibrating-reed electrometer was used for the current measurement, and it, too, was quite satisfactory when it worked, but for some reason it could not always be counted on to work. Actually, the vibrating-reed electrometer is designed for the measurement of currents much smaller than the 1- to 10-μa beams produced by the isotope separator; perhaps this bears on the lack of reliability.

A small portable microammeter was used for a few experiment. This device is less accurate than the others, but its main drawback is that it does not allow the use of a recorder.

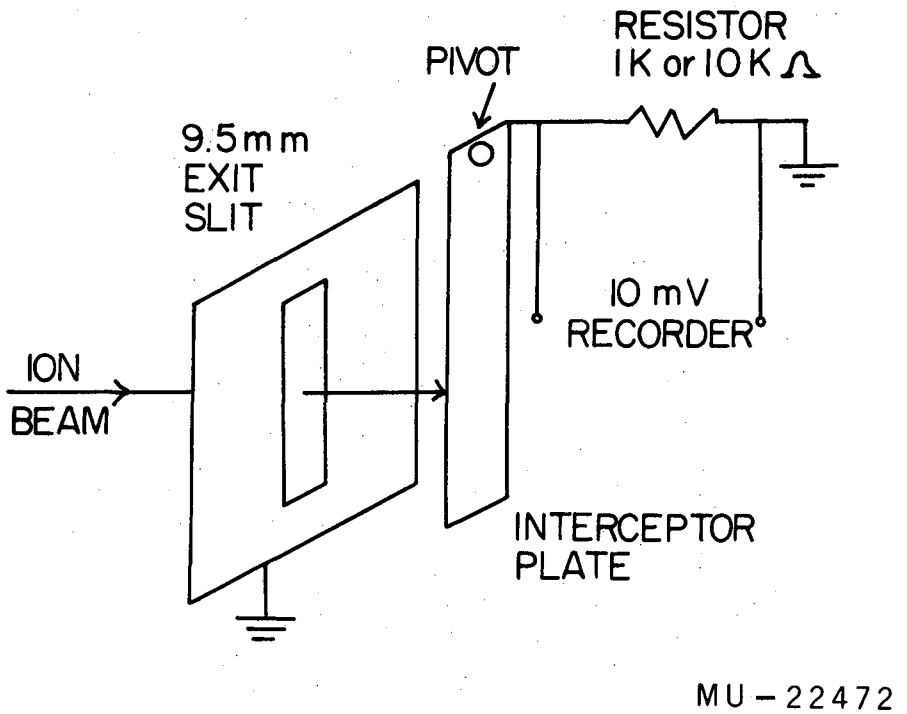


Fig. 9. Schematic representation of the device for intermittent measurement of the ion beam current.

Knowledge of the intensity of the ^{14}C ion beam is, of course, needed for the calculation of the yield of the products formed. The product of the average beam current and the time of irradiation gives the number of coulombs of ions introduced into the sample, and the total amount of radioactivity introduced is calculated from this.

The phenomenon of secondary-electron emission, however, makes it virtually certain that the current measured is greater than the true positive ion current.[35] If the positive ion beam impinging on the nichrome collector plate causes the ejection of secondary electrons from the plate, the total current measured is then the sum of the current due to the impinging positive ion and the current due to the ejected electrons.

The magnitude of secondary-electron emission is uncertain, but there is reason to believe that it is not very large. The evidence for this is an almost threefold increase in current observed upon application of high positive voltage to the target section (as is done in low-energy irradiation) while an ion beam is hitting the collector plate under steady conditions. Changing the potential of the target section from that of ground to about +5000 v certainly cannot cause a real increase in the positive ion current at the collector plate; this effect is probably due to secondary-electron emission. In fact, Dawton and Smith state "In receivers having an additional electrode used either for increasing ion acceleration. . . or for retardation. . . , the secondary emission effects generally completely masked the real ion current. . . "[36]

In all cases, the final exit slit is grounded and the collector plate, 2 mm behind the exit slit, is at +3 to 30 mv. When the target section, located several centimeters behind the collector plate (see Figs. 6 and 9) is grounded, the collector plate is surrounded by surfaces at ground potential while it itself is at a small positive potential, hence perhaps acting to a certain extent as its own secondary-electron suppressor. When the target section is at high positive voltage, however,

the secondary electrons are strongly attracted to it and the total current increases almost threefold, that is, almost two secondary electrons are emitted per 5000 v positive ions arising at the collector plate. It should be emphasized that the positive ions strike the plate with 5000 ev energy regardless of the target potential--deceleration occurs only after the ions leave the immediate vicinity of the grounded exit slit. The secondary-electron emission observed when the target is at high positive voltage is in fair agreement with the secondary-electron emission from the conversion dinode of an electron multiplier for 5000 ev alkali metal ions (2.1 to 3.4 secondaries per positive ion).[37]

The ratio, at constant beam intensity, of the current measured with 90 v difference between source and target to that measured with the target grounded was found to be 2.80 ± .03. This ratio was independent of the beam intensity over the range measured. When 45 v difference was maintained between source and target, the ratio was 2.58 ± .11. When irradiations were done at 90 v or 45 v, the observed average currents were then divided by the appropriate correction factors, so that all yields are calculated on a common basis (5000v)--that is, the relative differences observed as a function of energy are valid when such correction is made, even though the absolute yields may be in error. For the reasons given above, the 5000 ev currents are probably not very far off.

b. Modification of the slit system

The isotope separator was designed to give a 1-μa beam of ^{14}C ions from high-specific-acitivity $^{14}CO_2$. Since the greatest enrichment ordinarily available is about 50 to 60%, a ^{12}C beam from $^{12}CO_2$ should be about 2 μa to reach that goal. After a great deal of difficulty, a 1-μa beam of ^{12}C from ordinary CO_2 was achieved, and several irradiations were carried with the $^{14}C^+$ intensities in the range 0.1 to 0.2 μa. These intensities were obtained with the 2.4-mm entrance slit (shown in Fig. 5) and the exit slit

assembly (shown in Fig. 7) in place. The resolution achieved under these conditions is illustrated by the mass spectrum of carbon dioxide, 20% enriched in ^{14}C, shown in Fig. 10. Ions of adjacent mass number in the region of mass 12 to 20 are completely resolved. The 17, 18, and 19 peaks are undoubtedly $^{16}OH^+$, $H_2{}^{16}O^+$, and $H_3{}^{16}O^+$, and are always seen in the CO_2 mass spectrum. The source of the water peaks is unknown, but they can hardly be due to water present in the CO_2--the method of generation of the carbon dioxide from $Ba^{14}CO_3$ certainly removes all but the last traces of water. This water may result from reaction of oxygen produced by ionization of CO_2 with hydrocarbons from the diffusion pump oil, but this too is hard to accept, as the liquid nitrogen traps between the diffusion pumps and the machine should be very effective in trapping pump oil.

The resolution illustrated in Fig. 10 is actually better than is necessary for the pursuit of this problem. The ions adjacent to the mass 14 peak are present in quite small amounts, and since mass 13 is due to $^{13}C^+$ and mass 15 is probably due to $^{12}CH_3{}^+$, the chemical nature of the adjacent ions is such as to make their presence in small amounts in the mass 14 beam relatively harmless. Since we were not satisfied with the ^{14}C intensities obtained under these conditions, it seemed worth while to see if a sizable increase in ion transmission could be obtained at a relatively small cost in resolution, which we felt we could safely tolerate.

To that end, the slit system was rather drastically modified. The entrance-slit plate was removed completely, and the narrow exit slit and the beam spreader were removed from the rear section, leaving only the wide (9.5-mm) exit slit in the machine. The modified system is shown in Fig. 6. The effect of this modification was quite gratifying and is illustrated in Fig. 11, showing a mass spectrum of CO_2 enriched 40% in ^{14}C and diluted to 1:3 with argon. A five- to sixfold increase in the $^{14}C^+$ ion intensity was realized with only a

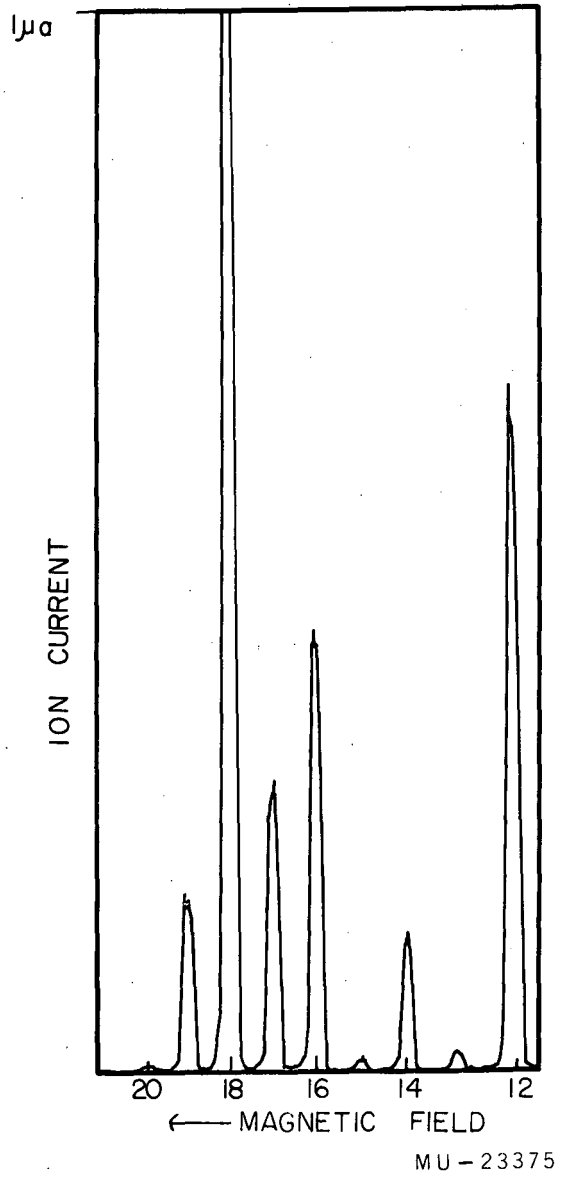


Fig. 10. Mass spectrum of CO_2 - 20% C^{14} in the region M/e = 12-20. Narrow (2.4 mm) entrance and exit slits in place.

surprisingly small decrease in resolution, as can be seen in Fig. 11. Ions of adjacent mass number are no longer completely separable, but it is clear that only a small fraction of what little mass 13 and mass 15 there is, is contaminating the mass 14 peak. During irradiation, one of course adjusts the magnetic field to maximize the $^{14}C^{+}$ ion intensity; that is, one "sits" on the peak maximum as indicated by the arrow in Fig. 11. This arrangement was used in the last six irradiations.

c. Filament lifetime

The most serious problem encountered in the development of the isotope separator was rapid filament burnout when carbon dioxide was used as the source of $^{14}C^{+}$ ions. Tungsten was the first filament material tried; it proved absolutely worthless: CO_2 had to be highly diluted with argon in order to strike an arc, and even then it was difficult to start and unstable once it was struck, and filament burnout occurred in a matter of minutes.

Tantalum wire (20 and 30 mils) was tried next, and although far superior to tungsten, it was still unsatisfactory. Again, an arc could not be struck in pure CO_2; it was necessary to dilute the CO_2 with argon by as much as 3:1. Even then, tantalum had the same defects as tungsten, but to a lesser degree. The arc was somewhat unstable, and tantalum filaments rarely lasted longer than 1 hour at moderate operating conditions. If the arc was struck in pure argon, though, filament lifetimes of as much as 10 hours were achieved, indicating that chemical attack and not positive-ion bombardment was the main cause of filament burnout.

Methane was then tried as the source gas to see if the absence of oxygen would improve the arc stability and increase filament lifetime. It, too, had to be diluted with argon, but only slightly--a 3:1 mixture of methane and argon was satisfactory, whereas a 1:3 mixture of CO_2 and argon was needed. Methane-C^{14} furnished about as many $^{14}C^{+}$ ions as did $^{14}CO_2$ of the same specific activity.

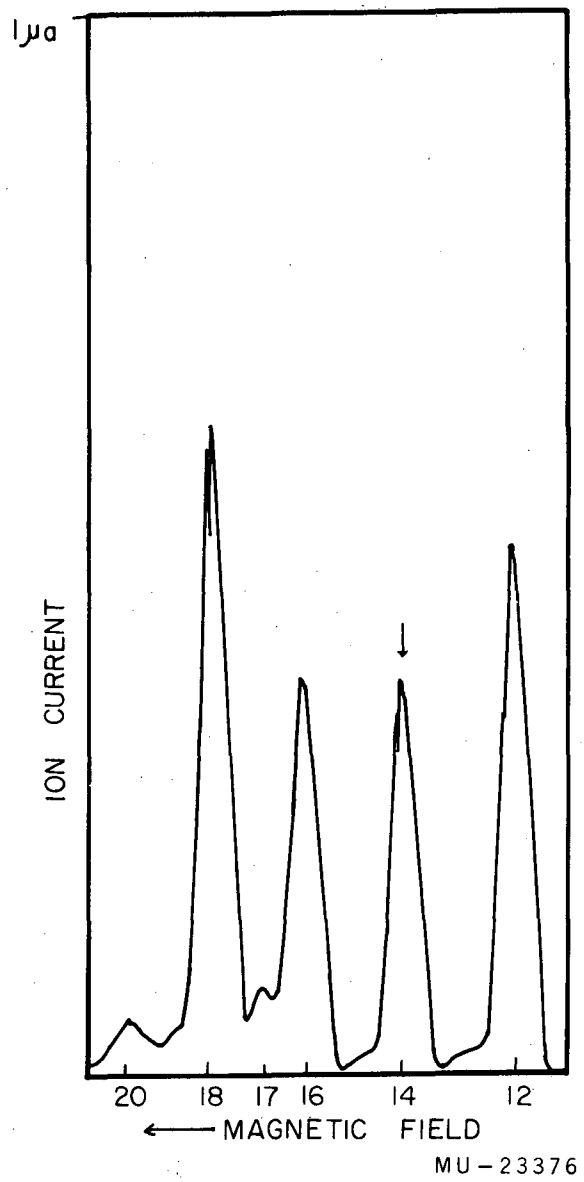


Fig. 11. Mass spectrum of argon-CO_2, 3:1. CO_2 is 40% ^{14}C. Only the wide (9.5 mm) exit slit is in place.

Filament lifetime in methane-argon was longer--an average of 1.5 to 2 hours was obtained. This was still uncomfortably short, but it was felt that it could be tolerated. As mentioned earlier, the ion source was modified to allow rapid changing of the filaments, and we were about ready to accept these limitations.

One last attempt was made, however, to find a more suitable filament metal. Rhenium foil, about 5 mils thick and 1/16 inch wide, was tried, and was found decidedly superior to tantalum. With a rhenium filament, an arc could be easily struck in pure CO_2 and the arc was quite stable. Filament lifetime increased to about 2.5 to 3 hours and lifetimes as long as 5 to 6 hours were occasionally obtained.

This was a welcome result, not only because of the more desirable ion-source performance but also because the use of methane is inconvenient and it poses several limitations on the use of the separator. Methane-C^{14} must be made by reduction of $^{14}CO_2$, which is a nuisance, and it is harder to handle and recover because it is noncondensable in liquid nitrogen. Dilution with argon reduces the ^{14}C beam proportionately. Furthermore, the slit modification described earlier could not have been made if methane were used, because methane furnishes as many ions of mass 15 (12 CH_3^+, 14 CH^+) and mass 13 (12 CH^+) as it does of mass 14, which, in itself, is a mixture (14 C^+, 12 CH_2^+). As will be discussed later, methane has its place as a source of ions such as $^{14}CH^+$ or $^{14}CH_2^+$, but it is clearly inferior to CO_2 as a source of $^{14}C^+$ ions.

Only when rhenium was used for the filament was it possible to push the arc current to the point (about 1.5 amp) where the desired $^{14}C^+$ ion intensity was approached with the narrow slits in place.

d. CO_2 recovery

The filament failure was the most serious problem encountered in the development of the separator, but it was not the most vexing. That honor goes to the recovery of un-ionized $^{14}CO_2$, because it should have been so easy and was, in fact, so troublesome.

The first tests of ^{14}C recovery clearly indicated that at least 80% of the CO_2 was converted to CO in the ion source, hence the liquid nitrogen traps of the separator were useless for ^{14}C recovery. A recovery train consisting of a copper oxide furnace followed by two efficient bubblers containing 1 N sodium hydroxide was attached to the exhaust of the mechanical forepumps of the separator. Helium was bled into the system at the pump exhaust at a slow rate (a few cc per minute). Recovery was poor, ranging from a few percent to about 20% at best. Tests for leaks were negative. More, larger, and hotter copper oxide furnaces were tried, to no avail. Solid debris formed in the ion source accounted for only a few percent of the activity introduced. One-half liter of air was bled into the separator with the arc off and collected at the end of the recovery system over water in a graduate cylinder; 490 ± 10 cc of air was collected and no more, in agreement with previous tests for leaks.

To test the copper oxide and absorption bubblers separately from the machine, sodium formate was dehydrated quantitatively by sulfuric acid to provide a known amount of CO, which was found to be quantitatively recovered as CO_2. Finally, the technique of leak-hunting with a soap solution showed the presence of large leaks around the exhaust fittings of the mechanical pumps. Why the earlier tests for leaks were negative is still a mystery; the fact remains that the author undoubtedly holds the records for "lost" carbon-14.

When the leaks were fixed, recovery in subsequent irradiations rose to 70 to 80%. Even though a liquid nitrogen trap preceded the copper oxide furnace, the active carbon dioxide from the oxidation of ^{14}CO was diluted four- to sixfold by inactive CO_2, rendering the recovered $^{14}CO_2$ useless for further irradiations. (CO_2 enriched 20 to 40% in ^{14}C was used in the irradiations.) The source of this dilution is unknown--the only possibility that we have been able to imagine is that it results from methane produced by thermal cracking

of diffusion pump oil or, less likely, mechanical pump oil. The recovery system was usually left in place for days following an irradiation, as the time required for capture is not known; perhaps that could be shortened to hours, giving a large decrease in the dilution of the radioactivity.

e. Control of benzene input rate

Benzene (or any volatile material) is bled from a glass tube through a needle valve into the target section of the separator, emerging from a narrow copper tube located near the target cold finger as shown in Fig. 7. At first the benzene input rate was controlled by leaving the benzene in the tube at room temperature and just barely cracking the needle valve until a slight pressure rise was indicated on the ionization gauge near the middle of the trajectory tank. This proved to be a very poor technique. The deflection of the ion gauge in response to the pressure rise was so small for the desired input rate (less than approx 100 μl/hr) that it was quite hard to detect. Hence the input rate was irreproducible, and, far worse, one could never be quite sure that benzene was being admitted at all. The pressure rise was small because most, if not virtually all, of the benzene was condensing as desired on the target cold finger, which was cooled to -160°. Control could have been improved by setting the valve opening before the cold finger was cooled, but the method seemed poor in principle and another was tried and found to be satisfactory.

The needle valve was completely opened and the input rate controlled through the vapor pressure of the benzene in the input tube by thermostating it at low temperature. The rate of diffusion through an orifice is proportional to the pressure difference across the orifice, everything else being constant.[38] The input rate with the benzene at 0° and the needle valve wide open was found by putting 1.00 ml benzene into the tube and letting it flow into the target section, which

was pumped by a mechanical pump. The pressure near the outlet valve of the target section was followed as a function of time by a vacuum thermocouple gauge. As long as benzene remained in the input tube, the pressure was constant, and the duration of the pressure plateau was taken as the input time for 1 ml benzene at 0°. It was found to be 3750 μl/hr. The benzene temperature needed to give the desired input rate can then be calculated. One irradiation was carried out with the benzene at -78°, giving a calculated input rate of about 3 μl/hr. As will be discussed later, this seemed to be too low, and in the following seven irradiations the benzene was held at -45° by a slurry of chlorobenzene at its melting point, giving a calculated input of about 85 μl/hr. The actual input rate at -45° was actually about 55 μl/hr.

f. Product collection

The last technique connected with the use of the isotope separator that merits comment is the method of collection of the volatile products after irradiation. In all cases, the rear end of the separator under high vacuum, was isolated from the pumping system of the machine by closing the disc valve shown in Fig. 7, and the products were collected by vacuum distillation through the outlet valve of the target section to a receiver cooled in liquid nitrogen. What was varied was the nature of the receiver and the manner in which the distillation was carried out.

At first, a rather small glass receiver was used, about 25 cc in volume, the entrance to which was connected to the outlet valve of the target section and the exit to a mechanical pump through appropriate adapters. The two joints communicated through a narrow tube running the length of the vessel. This receiver was designed to allow centrifugation of the approx 200 μl of condensate down into the conical chamber for removal via a 50- or 100-μl Hamilton syringe for analysis. It was used for the collection of products from several

irradiations, but was dropped because of many defects. It was not sufficiently efficient for the quantitative collection, in a flow system, of the low-boiling labeled compounds (C_3, C_4, etc.) which proved to be present; its design did not allow the vacuum tightness of the collection system to be determined, and it did not allow the exclusion of air from the collected material--discoloration of the originally colorless sample occurred, in one irradiation, upon exposure to air and warming to room temperature.

A larger spiral glass trap fitted with several stopcocks was next used for collection in a static vacuum distillation. The trap was connected to the target, evacuated by a mechanical pump, and then closed off from the pump. The outlet valve on the target section was then opened and the distillation was allowed to continue until the pressure, as measured by a vacuum thermocouple gauge located between the target and the trap, fell to its initial level (1 to 10 microns). This worked nicely once, but the second time it was tried, either a plugged stopcock or a plugged glass frit caused the loss of much of the condensate; hence a more trouble-free technique was sought.

Figure 12 shows the apparatus finally chosen for collection. Here, too, a static vacuum distillation is carried out--the receiver is first evacuated and the Kerotest valve to the mechanical pump is then closed and the outlet valve to the target section opened. The isopentane slurry is removed from the cold finger and hot water poured into it; the benzene and volatile products are thereby given minimum time to adsorb on other surfaces in the target section. After the pressure returns to its original value, a mixture of carriers is admitted under vacuum into the target section and distilled into the receiver. Addition of carrier amounts of known or suspected products at this point is done to aid the collection of these products, which are all present in microscopic amounts (except benzene-^{14}C). Carriers are added only after the products have been brought to room temperature and collected, in order to exclude any chance of reaction

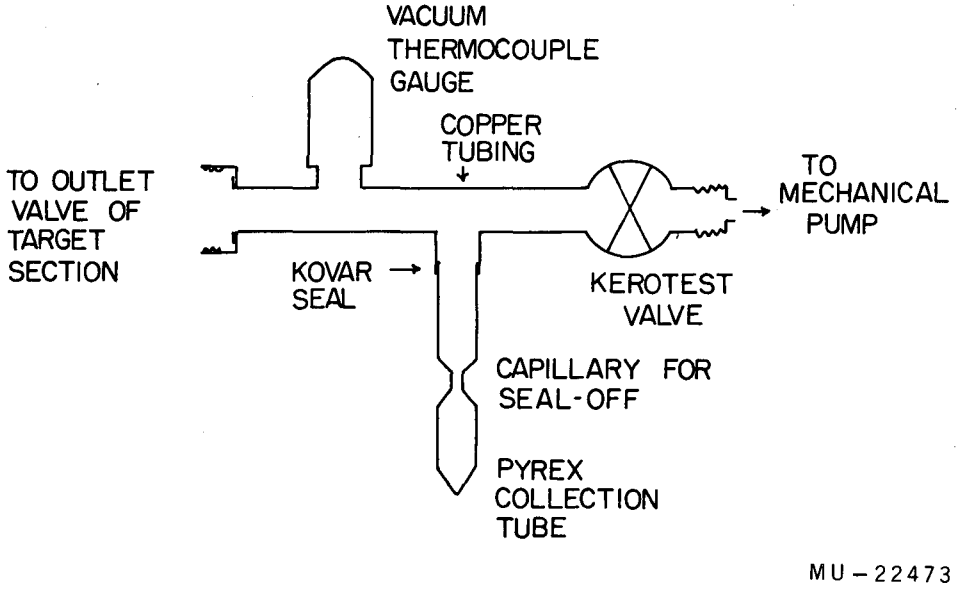


Fig. 12. Schematic representation of product-collection apparatus.

with trapped radicals or other highly reactive species with the carrier material. After collection, the receiver is sealed off under vacuum and stored in liquid nitrogen. A new receiver is then blown onto the receiver assembly for subsequent re-use.

3. The Irradiation of Benzene

a. Materials used

Carbon-14 dioxide was generated from barium carbonate-^{14}C obtained from Oak Ridge. Generation was done by dripping concentrated cp sulphuric acid on the barium carbonate *in vacuo*. The $^{14}CO_2$ was freed of traces of water and SO_2 by passage through a large coil cooled to -78° by a dry ice isopropanol slurry and then condensed at -196° in an evacuated steel glass storage bottle previously described. Base pressure of the vacuum system was 10 to 30 microns; 2 to 3 millimoles of CO_2 was usually generated at a time.

The benzene used in all irradiations was Baker and Adamson reagent grade, purified by gas liquid chromatography (GLC) by passing about 200-μl portions through a 5-foot-long one 1/2-inch-wide column of Apiezon-L on crushed firebrick (a Ucon column of the same dimensions was used for the purification of the benzene in earlier irradiations). The carrier gas was helium, dried by passage through a Drierite column.

Carrier toluene was was Baker and Adamson reagent grade, used without further purification. Cycloheptatriene carrier had been synthesized previously by the Bio-Organic Group through a reaction of diazomethane with benzene, and was purified at that time by gas chromatography and stored in evacuated sealed glass tubes. When discoloration occurred on exposure to air, the cycloheptatriene was rechromatographed--no volatile compounds other than cycloheptatriene were found. Low-boiling petroleum either was Baker and Adamson reagent grade and was used without further purification. Carrier n-pentane was Phillips Petroleum technical grade, and was purified by gas chromatography. Carrier ethyl benzene and ortho-, meta-, and paraxylene were Eastman Kodak products of unknown grade and

were used without further purification. A mixture of these four compounds was analyzed by gas chromatography and no other compounds were detected.

b. Details of a typical "good" irradiation--B11

(1) Source gas 3.03 millimoles of $^{14}CO_2$ was generated for use in B11 and subsequent irradiations. The specific activity of the CO_2 was 12.4 mC per millimole, giving a ^{14}C content of 19.5%.

(2) Preparation and maintenance of the target cold-finger coolant.

Isopentane, held at its melting point (-160.5°) was used as the target coolant. It was chosen because at -160° benzene condenses and remains on the cold finger, and CO_2 does not. The pressure of carbon dioxide in the target section cannot be more than about 10^{-5} mm. The vapor pressure of CO_2 is 6.10^{-3} mm at -160°.[39] The vapor pressure of benzene at -160° is apparently not known, but a vapor pressure of about 10^{-10} mm at -160° is given by use of the vapor pressure equation for the temperature range -30° to -58°.[40] Even if this is low by an order of magnitude or so, the vapor pressure of benzene at -160° is still well below the base pressure of the separator (approx 4×10^{-6} mm).

The isopentane and the target cold finger were separately precooled to near -160° by liquid nitrogen, and the cold isopentane was then poured into the well. It was brought to its melting point by immersing a glass thimble filled with liquid nitrogen into the target cold finger. A sheath of solid isopentane builds up on the glass thimble and the unsolidified liquid soon equilibrates at -160°. The temperature of the liquid was measured throughout the irradiation by an iron-constantan thermocouple referred to ice water. The glass thimble was filled with liquid nitrogen from time to time to balance the heat loss. Once during this irradiation the isopentane liquid was inadvertently allowed to warm up to -154°C--an unusual occurrence.

(3) Benzene input

240 μl of benzene was placed in the sample delivery tube, which was then attached to the target section (see Fig. 7) by a nipple sealed with a teflon gasket. The benzene was cooled to -196° and the air was evacuated from the tube. The benzene was thermostated at -45° by placing a Dewar containing a slurry of chlorobenzene at its melting point (-45°) under the input tube. Benzene was then bled onto the target surface for 25 minutes before the irradiation began. Since the area of the target face is 58 cm^2, and benzene was admitted at a rate of about 55 μl per hour, one can calculate that a layer of benzene 37,000 A thick was laid down on the target face before irradiation, if one assumes the benzene is uniformly distributed over the target face.

A benzene layer is put on the target surface before irradiation to insure that all the ^{14}C ions striking the target remain in the benzene. The range of 5-kev ^{14}C ions in benzene or in anything else is unknown, but the most liberal estimate puts it at a few hundred angstroms or less, so that the thickness of the layer put down before irradiation is well on the safe side.

Benzene was admitted continuously throughout the irradiation. An input rate of 55 μl per hour is equivalent to 1.04×10^{17} molecules per second. Hence the ratio of the input rate of benzene molecules to that of ^{14}C ions is about 1.7×10^{4} for a 1-μa ^{14}C beam.

(4) Irradiation

The arc was struck by the procedure described earlier and the irradiation was begun. The irradiation went smoothly (unfortunately an atypical occurrence) and lasted for 2.45 hours, after which time the filament burned out. The operating conditions were stable and are presented in Table I. The current was measured from time to time during the irradiation by using the arrangement depicted in Fig. 9--these data are presented in Table II.

The total ^{14}C activity (A_T^o) introduced into the sample is calculated as follows:

Table I. Operating conditions--B11

Ion energy	+5000 v
Arc current	1.05 amp.
Arc voltage	80 v
Extraction voltage	+5000 v
Focusing voltage	+5300 v[a]
Horizontal split-plate voltage	0 v
Vertical split-plate voltage	0 v
Average $^{14}C^{+}$ current	0.69 μa
Running pressure	1.1×10^{-5} mm Hg
$^{14}CO_2$ input rate	0.29 mMole/hr
Benzene input rate	60 μl/hr
Target temperature	-160°C
Time of irradiation	2.45 hr

[a]Usually the focusing voltage is less than the extraction voltage for maximum beam intensity.

Table II. $^{14}C^{+}$ current measurement--B11

Time	$^{14}C^{+}$ current (μa)	ΔTime (min)	Average current (μa)	Charge (μa-min)
11:09	0.630			
		14	0.650	9.10
11:23	0.670			
		11	0.668	7.35
11:34	0.665			
		17	0.672	11.42
11:51	0.680			
		36	0.672	24.20
12:27	0.665			
		25	0.666	16.65
12:52	0.668			
	(Magnetic field adjusted)			
12:53	0.680			
		25	0.701	17.52
1:18	0.722			
		14	0.757	10.58
1:32	0.792			
		5	0.792	3.96
1:37	Filament failed			

Totals: Time = 147 min = 2.45 hr Q_T = 100.8 μa-min = 1.68 μa.hr

Average $^{14}C^{+}$ Current = 0.69 μa

Total ^{14}C Activity, $A_T^0 = 8.94 \times 10^6$ dpm

Introduced = 4.03 μC

(i) The number of $^{14}C^{+}$ ions delivered is given by

$$N_T = Q_T N_0 / F,$$

where N_T = number of ions,

Q_T = total charge delivered, in coulombs,

N_0 = Avogadro's number = 6.02×10^{23} singly charged ions per equivalent,

F = Faraday's constant = 9.65×10^{4} coulombs per equivalent.

A convenient unit of charge for this work is the microampere-hour (μa-hr) = 3.6×10^{-3} coulomb. The number of ions per μa-hr is calculated from the above expression as 2.25×10^{16} ions/μa-hr

(ii) The calculated activity is, then,

$$A_T^0 = \frac{-dN_T}{dt} = \lambda N_T ,$$

where λ = the decay constant of $C^{14} = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5570\lambda} = 2.37 \times 10^{10} \text{min}^{-1}$;

hence $A_T^0 = 2.37 \times 10^{10} \text{ min}^{-1} \times 2.25 \times 10^{16} \text{ ions} \times Q_T \ \mu\text{a-hr}$,

$$A_T^0 = 5.32 \times 10^{6} \ \frac{\text{disintegrations per minute (dpm)}}{\mu\text{a-hr}} \times Q \ \mu\text{a-hr},$$

or, since 1 μC = 2.22×10^{6} dpm/min,

$$A_T^0 = \frac{2.40 \mu C}{\mu a\text{-hr}} \times Q_T \ \mu\text{a-hr}.$$

No correction is made for the presence of $^{15}N^{+}$ and $^{12}C^{16}O^{++}$ in the m/e = 14 peak. The contribution of these ions is known from observation of the mass spectra of pure $^{12}CO_2$ to be insignificant, i.e., less than 1% of the $^{14}C^{+}$ intensity.

(5) Product collection

At the end of the irradiation, the rear end of the separator was isolated from the rest of the machine by closing the disc valve illustreated in Fig. 7. The collection device shown in Fig. 12 was attached to the outlet valve of the target section, evacuated by a mechanical pump to about 10 microns, closed to the pump, and opened to the target section.

Table III. Irradiation data

Code No. of irradiation	Net[a] ion energy (ev)	Source[c] gas	Arc current (amp)	Arc voltage (volts)	Average[d] $^{14}C^{+}$ current (μa)	Time (hr)	Total charge (μa-hr)	Total[e] activity (μC)	Slit[f] system	Method[g] of beam measurement	Method of[h] benzene input–rate and constancy
B4	5000	Argon-CO_2 2:1 28.6% ^{14}C	1.15	80	0.054	0.84	0.045	0.108	narrow	Vibrating reed electrometer-recorder	Crack input, needle valve steady at ≈ 60 μl/hr
B5	5150	CO_2 19.5% ^{14}C	1.15	80	0.222	3.39	0.753	1.81	narrow	Vibrating reed electrometer-recorder	Crack input, needle valve, perhaps no input 40-60% of run, rate unknown and variable
B6	5000	CO_2 19.5% ^{14}C	0.7 - 0.9	80-90	0.10	1.51	0.151	0.362	narrow	Microammeter	Valve wide open, benzene in input tube held at -78°C, rate steady at ≈ 3μl/hr
B7	5050	CO_2 16.7% ^{14}C	1.2 - 1.4	100	0.162	1.70	0.276	0.661	narrow	Microammeter	Valve wide open, benzene in input tube held at -45°C, rate steady at 55 μl/hr
B8	5050	Argon-CO_2 1.53:1 41.9% ^{14}C	1.0 - 1.15	60 - 65	0.336	6.04	2.03	4.86	wide	Direct use of recorder as potentiometer (see Fig. 9)	Valve wide open, benzene in input tube held at -45°C, rate steady at 55 μl/hr (no input for about 1 hr)
B9	90[b] + 5000	Argon-CO_2 1.53:1 41.9% ^{14}C	1.2 - 1.4	55 - 70	0.33 - 0.46[b]	2.06	0.68-0.95[b]	1.63-2.28[b]	wide	Direct use of recorder as potentiometer (see Fig. 9)	Valve wide open, benzene, in input tube held at -45°C, rate steady at 55 μl/hr (no input for about 1 hr)
B10	90	Argon-CO_2 1.53:1 41.9% ^{14}C	1.6 - 1.8	55	0.434	1.43	0.620	1.49	wide	Direct use of recorder as potentiometer (see Fig. 9)	Valve wide open, benzene, in input tube held at -45°C, rate steady at 55 μl/hr (no input for about 1 hr)
B11	5000	CO_2 19.9% ^{14}C	1.0 - 1.05	80	0.686	2.45	1.68	4.04	wide	Direct use of recorder as potentiometer (see Fig. 9)	Valve wide open, benzene, in input tube held at -45°C, rate steady at 55 μl/hr (no input for about 1 hr)
B12	90	CO_2 19.9% ^{14}C	1.0 - 1.1	55 - 60	0.835	2.65	2.21	5.30	wide	Direct use of recorder as potentiometer (see Fig. 9)	Valve wide open, benzene, in input tube held at -45°C, rate steady at 55 μl/hr (no input for about 1 hr)
B13	45	CO_2 19.9% ^{14}C	0.9 - 1.0	60 - 80	0.702	2.57	1.81	4.35	wide	Direct use of recorder as potentiometer (see Fig. 9)	Valve wide open, benzene, in input tube held at -45°C, rate steady at 55 μl/hr (no input for about 1 hr)

Table III. (cont.)

Temperature of the benzene target	Volume of[j] benzene admitted before irradiation (μl)	Volume of[j] benzene admitted during irradiation (μl)	Volume of carrier mixture added after irradiation (μl)	Total volume of benzene and carriers (μl)	Method of product collection and storage[k]	Code No.
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted	≈400	~50	600	≈1050	Flow distillation into small glass receiver and storage vessel--stored at -10°	B4
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted	≈ 50	?	---	? 200 μl collected	Flow distillation into small glass receiver and storage vessel--stored at -10°	B5
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted	≈120 (estimated from vapor pressure)	4 (estimated from vapor pressure)	250	≈ 374	Flow distillation into small glass receiver and storage vessel--stored at -10°. The product mixture was left in the target section at -78° overnight before collection	B6
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted	51.4	108	120	280	Static distillation into spiral glass trap. Product later distilled into ground-glass-stoppered tube and stored at -10°	B7
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted	≈37	295	260	592	Static distillation into spiral glass trap. Product later distilled into ground-glass-stoppered tube and stored at -10° (Trap plugged, lost some sample)	B8
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted[i]	16.5	166	120	302	Static distillation into seal-off tube (Fig. 12). Stored in evacuated ampule at -196°	B9
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted[i]	75.1	79	20	174	Static distillation into seal-off tube (Fig. 12). Stored in evacuated ampule at -196°	B10
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted	22.9	137	70	228	Static distillation into seal-off tube (Fig. 12). Stored in evacuated ampule at -196°	B11
Held at m. p. of isopentane, -160.5°; temp. rose to -154°C briefly[i]	29.4	173	75	277	Static distillation into seal-off tube (Fig. 12). Stored in evacuated ampule at -196°	B12
Held at m. p. of isopentane, -160.5°; temp. never above -159° unless otherwise noted[i]	39.4	146	30	215	Static distillation into seal-off tube (Fig. 12). Stored in evacuated ampule at -196°	B13

NOTES FOR TABLE III

(a) The method of decelerating the separated $^{14}C^{+}$ ions in the low-energy irradiations is described in Part 1-f of this division (see also Fig. 6). The EMF of the 90-v and the 45-v batteries used to supply the potential difference between the ion source and the target in the low-energy runs was checked with a voltmeter before and after each low-energy run.

(b) See the discussion of B9 which follows this table.

(c) In all cases the % ^{14}C given is the % of CO_2 molecules labeled with ^{14}C. Where argon is mixed with the carbon dioxide, the ratio given is the ratio of the volume of argon to that of CO_2.

(d) The observed ion currents in the 90- and 45-v irradiations were divided by 2.80 and 2.58, respectively, to give the "true" current listed in this column. That is, all currents are normalized to high-energy (5000 v) conditions. See part 2-a of this division for a discussion of this problem. The correction factors were obtained by repeated measurement of an ion beam intensity alternately with the target grounded and with the target at +4910 v or +4955 v (i.e., with a 90- or 45-v battery between source and target). The average current for an irradiation is the weighted average of a series of intermittent measurements made in the manner indicated in Table II.

(e) Calculated as described in part 3-b of this division.

(f) "Narrow" signifies that the 2.4-mm entrance and exit slits and the beam spreader were used. "Wide" signifies that a 9.5-mm-wide exit slit only was used. See part 2-b of this division.

(g) The vibrating-reed electrometer used was an Applied Physics Corp. Model 30-1. The microammeter used was Radio Corporation of America Model WV-84A Ultra-Sensitive DC Microammeter. The recording potentiometer was a Leeds and Northrup Model Speedomax-G, 10 mv full scale deflection. See part 2-a of this division.

(h) See part 2-e of this division.

(i) In the low-energy irradiations, with the target at high positive potential, the isopentane temperature was not measured during irradiation. Experience has shown that as long as a fair-size sheath of solid isopentane is present around the glass thimble containing liquid nitrogen, the liquid in the target well is in equilibrium with the solid and is actually at the melting point of isopentane, -160.5°.

(j) In B4 through B6 the amount of benzene admitted is estimated from observation of the calibrated input tube except where otherwise noted. From B7 through B13, the amount admitted is calculated from the measured input rate and the time of admission. The input rate in these runs, with the benzene thermostatted at $-45^{\circ}C$, was determined by admitting benzene for 3 hr. The input rate by weight loss was 54.9 $\mu l/hr$ and by volume loss was 54.8 $\mu l/hr$. All volumes are for room temperature; change of density with room temperature is ignored.

The fractional change in vapor pressure per degree C, $\frac{d \ln P}{dT}$, is calculated from the vapor pressure equation for benzene to be approx 11% at $-45^{\circ}C$ (Ref. 40). Since the temperature of the chlorobenzene bath never varied from 45° by more than $\pm 0.5^{\circ}$, the input rate is known to be steady within 5% or less throughout B7 through B13.

(k) See discussion in part 2-f of this division.

The pressure fell to "0" microns on the vacuum thermocouple gauge. The collection tube was cooled in liquid nitrogen and the cold isopentane was siphoned out of the target cold finger and an air stream blown in--the pressure rose to 200 microns in a few minutes. Boiling water was poured into the target well, and the outside of the target section was gently heated with a propane hand torch. About 40 minutes after the distillation started, the pressure had fallen to 1 micron.

Seventy μl of a mixture of carriers consisting of benzene (27.2% by volume), toluene (27.2%), n-pentane (27.7%), and cyclo-heptatriene (18.0%) was put in an input tube attached to the target section. The contents were frozen in liquid nitrogen and the air was removed from the tube by the pumping system of the isotope separator. The rear end was then again isolated and the carriers were allowed to distill into the collection tube. The distillation of the toluene and cycloheptatriene through the input needle valve is slow, but if the system is vacuumtight and the operator patient, the pressure eventually returns to its starting point. In this irradiation, the pressure fell from 200 microns to 15 microns in the first 27 minutes of carrier collection. Another hour and 12 minutes was required for the pressure to fall to 3 to 4 microns--the initial value. After the products and carriers were collected, the collection tube was sealed off with a hand torch while the contents were cooled with liquid nitrogen and under vacuum. The sealed ampule was stored under liquid nitrogen until analysis.

c. Tables of data and explanatory remarks for the benzene irradiations

The data concerning all the benzene irradiations are presented in Table III. The first three irradiations done with the isotope separator (B1 through B3) were very short runs with very weak ^{14}C beams, done mainly to see if the technique worked at all. No information was derived from them and they will not be discussed further.

(1) Carriers added

In B4, toluene was added to the whole sample after collection. In B5, a mixture of benzene, toluene, and the three xylenes plus ethyl benzene (C_8's) was added, after collection, to each aliquot of sample just before GLC analysis. In B6 through B13, the carrier mixture was added to the condensed benzene by distillation through the target section into the receiver containing the benzene, and the other products of irradiation, in the manner described in part 2-f and part 3-b of this division. In all cases, benzene, toluene and cycloheptatriene were present in the carrier mixture. In addition, the carrier mixture used in B6 through B8 also contained the C_8's. That used in B7 through B10 also contained low-boiling (30 to 60°) petroleum ether. That used in B11 through B13 also contained n-pentane. In all cases approximately equal volumes of each carrier component were used, except for cycloheptatriene, which was used more sparingly because it was in short supply.

(2) Difficulties with irradiations

Poor techniques, operational errors, and the perversity of the isotope separator plagued several of the early irradiations and invalidated one of them. Those irradiations in which difficulties occurred will be discussed briefly.

B4: Pool collection technique in this run (and in B5 and B6) allowed air to come in contact with the collected products. This probably has no effect on the benzene and toluene-^{14}C formed, but may affect the cycloheptatriene yield.

B5: This irradiation is completely invalidated on two counts. First, the benzene irradiated was not pure; it had accidentally been chromatographed with methane, instead of helium, as the carrier gas. The methane was technical grade and was later found to contain large amounts of other, condensable hydrocarbons. Secondly, the input rate of benzene was erratic and little or none went in at all for a large part of the run.

B8: No benzene was admitted for about 1 hour of this irradiation. Difficulties in the collection of the products resulted in the loss of at least half of the products, and although this irradiation is not considered to be invalid, the corrections required for the calculation of yields are very large.

B9: This was the first 90-volt irradiation and suffers from two difficulties. The $^{14}C^{+}$ ion intensity fell from 0.40 μa at the start of the irradiation to 0.03 μa 43 minutes later, when the intensity was next measured. This drop was due to blockage of the ion-extraction hole by debris sloughed off from the wall of the ion source. The time at which blockage occurred during that interval is unknown, so that there is uncertainty in the total amount of ^{14}C delivered to the benzene target. Secondly, the irradiation was accidentally carried out with 5000-v ions for 23 minutes of the run.

In spite of these difficulties, B9 is still of some slight value to us because the relative amounts of irradiation at 90 v and 5000 v are known (within the limits imposed by the first-mentioned difficulty), and the yields from this irradiation can be compared with those calculated from yields obtained in pure 5000-v and pure 90-v runs.

B. Product Analysis

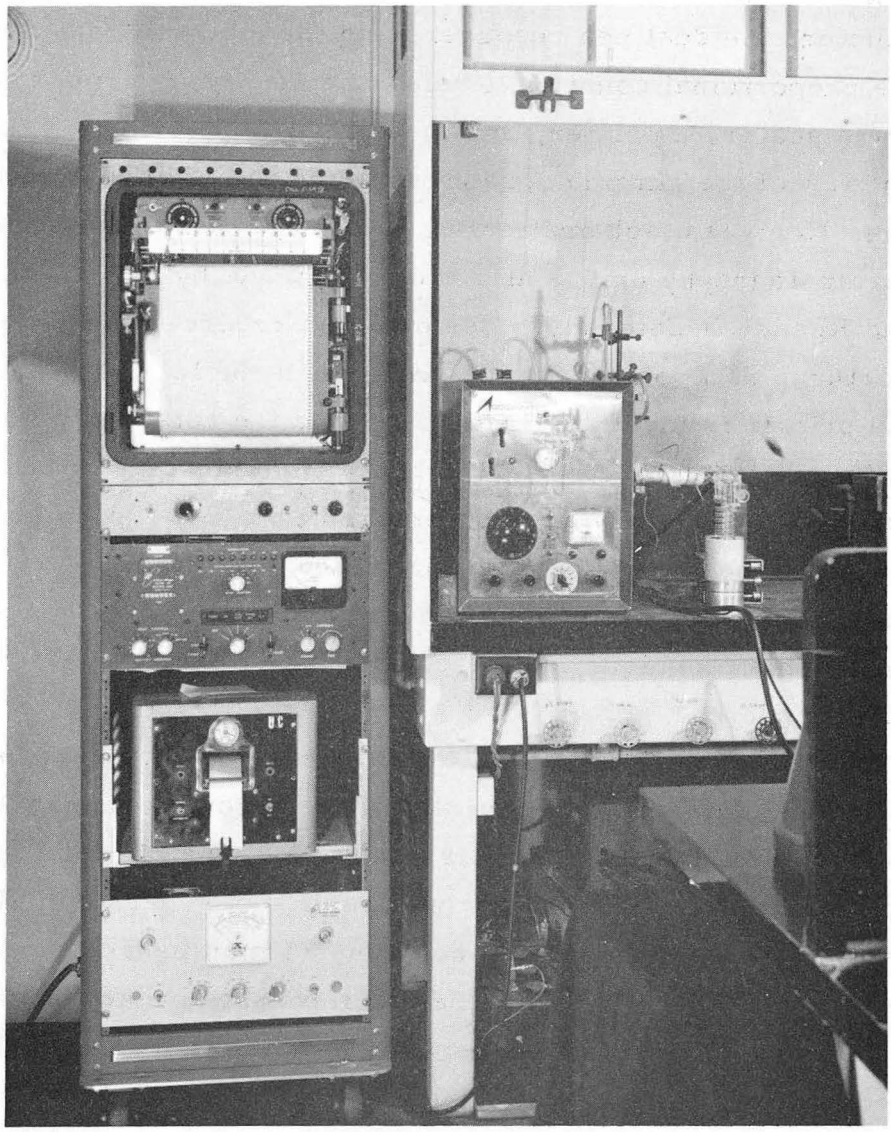
1. Gas Chromatography--Proportional Counting

a. General discussion of apparatus

The method used for the identification and quantitative determination of the products of irradiation was gas-liquid chromatography in conjunction with internal-flow proportional counting (GLC-PC). An internal-flow proportional counter was connected to the outlet of the gas chromatography unit and ^{14}C-labeled products were then detected by virtue of their radioactivity. Except in the case of benzene-^{14}C, all the products were present in microscopic amounts, so that unless carriers were added the only indication of their presence was the signal from the proportional counter.

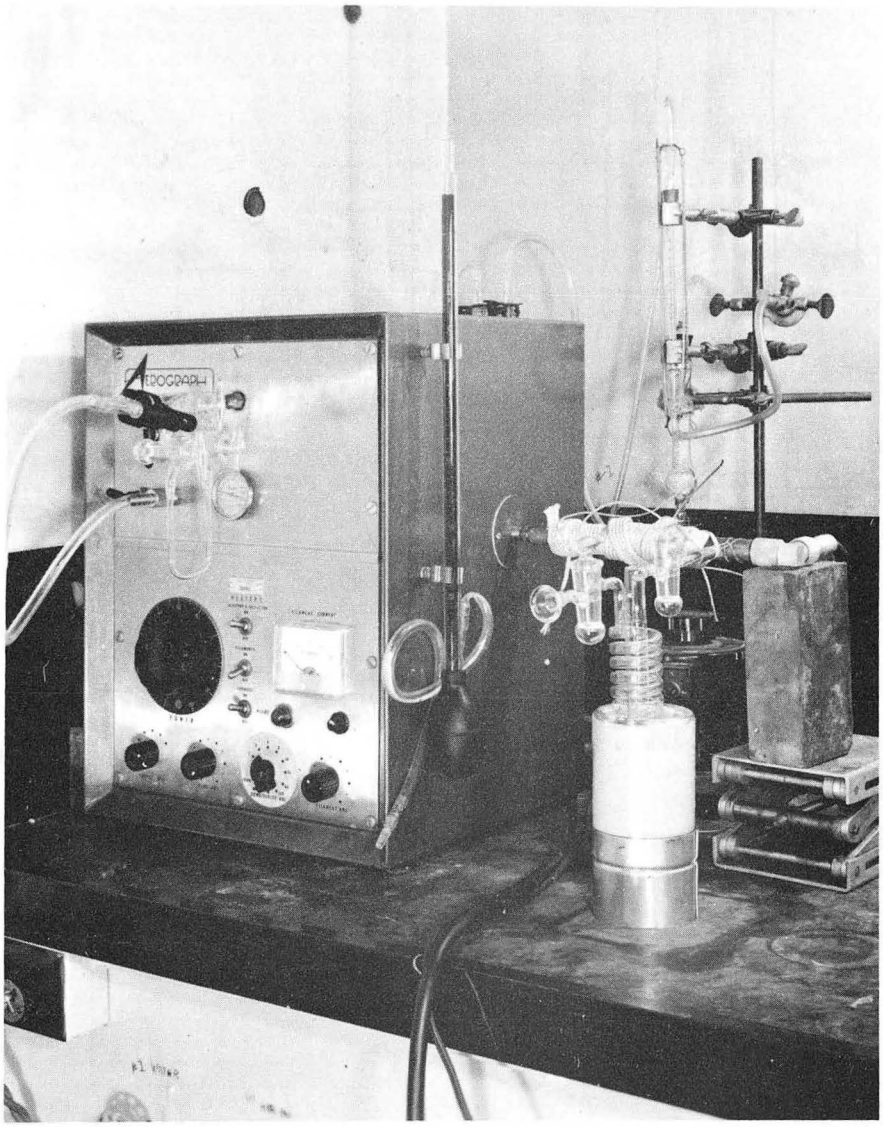
The apparatus used is illustrated in Figs. 13 through 16. Figure 13 gives a view of the chromatography unit, the proportional counter, the dual pen recorder, and the electronics associated with the proportional counting. Below the recorder, from top to bottom, are a scaler, a printer, and a rate meter. Figure 14 shows a close-up view of the chromatography unit and the proprotional counter, and Fig. 15 gives a schematic diagram of the complete setup. The chromatography unit is an Aerograph made by the Wilkens Instrument and Research Company. The dual pen recorder is a Leeds and Northrup Speedomax-G; the scaler is a Nuclear-Chicago Model 182; the printer is made by Tracerlab; and the ratemeter is a Nuclear-Chicago Model 1620B. The proportional counter shown in Fig. 16 was designed by Mr. Irville Whittemore of the Bio-Organic Chemistry Group of the Lawrence Radiation Laboratory, and is a modification of the counter described by Wolfgang and Rowland,[41] who were the first to use this technique for the counting of tritium- and ^{14}C-labeled compounds.

The operation of the apparatus is, in brief, as follows: The sample is injected into the inlet of the chromatography unit and is swept by the methane carrier gas through the chromatography column, in which the components of the sample are separated. The effluent gas carrying the separated components then passes through a thermal conductivity cell, which detects components present in macroscopic amount by virtue of the difference between their thermal conductivity and that of the methane carrier gas. The signal thereby generated is fed to one section (one half) of the dual-pen recorder. The effluent gas then passes through the proportional counter, in which radioactive components give rise to a signal which is fed to a scaler. (The scaler is also the high-voltage supply for the counter.) The scaler passes the counting signal through a ratemeter, which feeds the other half of the dual-pen recorder. The scaler also feeds the signal to a printing register, which prints out, every minute, the number of counts that occurred during that time interval.



ZN-2753

Fig. 13. View of gas-chromatography-internal-flow proportional counter apparatus. In electronics rack are, from top to bottom, a dual pen recorder, a scaler, a printer, and a ratemeter.



ZN-2754

Fig. 14. View of the gas chromatography unit, showing U-shaped sample input tube, proportional counter, and effluent trap in place.

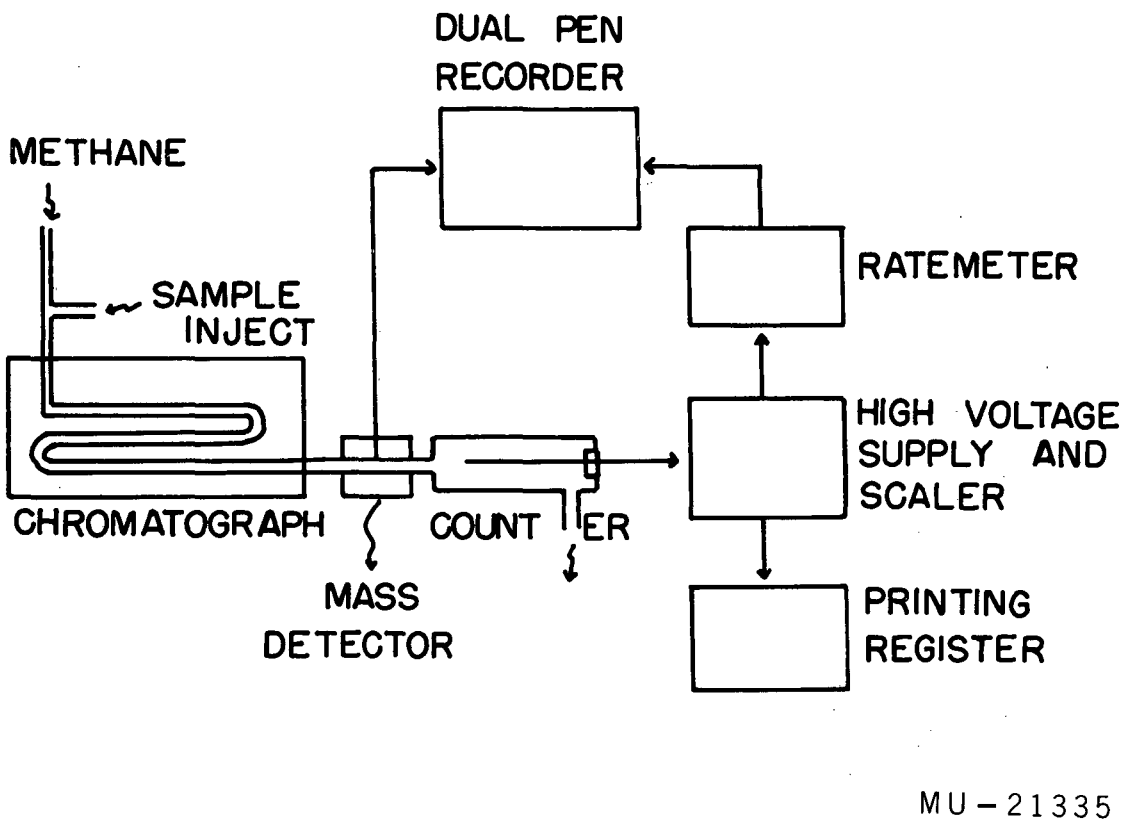
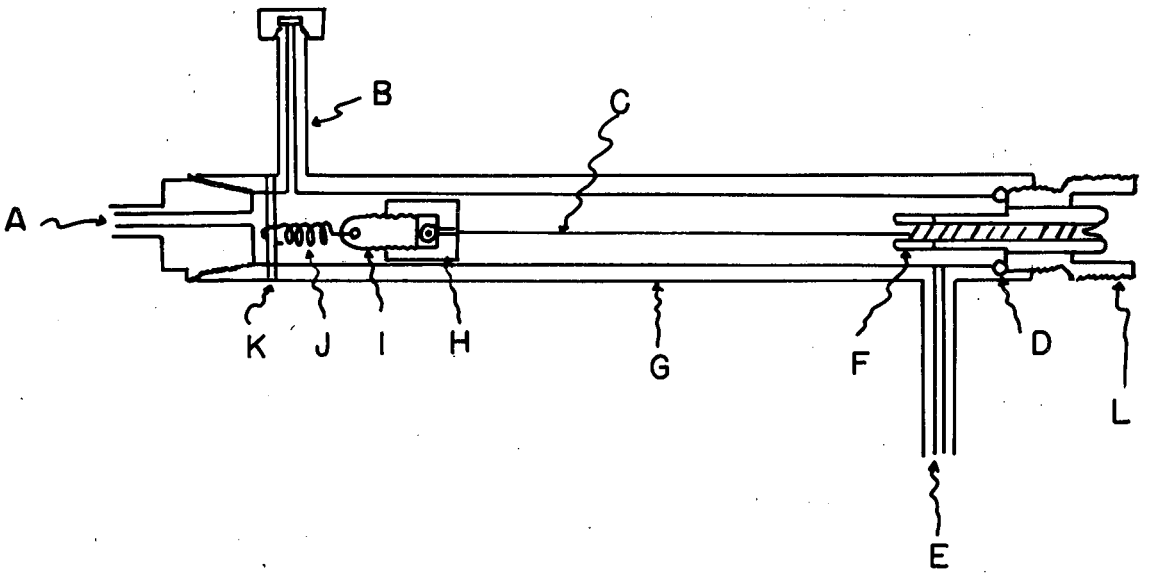


Fig. 15. Schematic of gas-chromatography–proportional-counting apparatus.



MU-21334-A

Fig. 16. Cross section of the proportional counter.
A = Connection to chromatography unit(Ŧ 7/15 inner taper)
B = Inlet for auxiliary counting gas (not used in this work)
C = 2-mil stainless steel wire soldered to receptacle at one end and to washer at other
D = Teflon gasket
E = Gas outlet (Ŧ 7/15 inner taper)
F = Teflon sleeve
G = Brass counter tube
H = Grooved teflon
I = Nylon
J = Weak spring
K = Pin
L = UG-496/U receptacle (modified)

In the following discussion, the recorder trace generated by the passage of macroscopic amounts of effluent through the thermal conductivity cell is called the "mass" trace, and the recorder trace generated in response to the passage of radioactive effluent through the proportional counter is called the "activity" trace. It should be emphasized that in the traces that will be displayed later a mass peak will not be seen corresponding to a given activity peak unless carrier amounts of that compound have been added.

Methane was used as the carrier gas in this work because it is suitable for both proportional counting and gas chromatography with thermal-conductivity cells as mass detector. The thermal conductivity of methane is considerably higher than that of helium, the most commonly used carrier gas in GLC. Therefore the sensitivity of the thermal-conductivity detector is smaller when methane is used than when helium is used. This, however, is no disadvantage in the work described here. The radioactive products of an irradiation are present in such small amounts that no detector depending upon a bulk property for detection indicates the presence of these products. When carrier amounts of certain products were added, enough was taken to make their mass detection quite easy.

The use of the scaler, ratemeter, and printing register merit further comment. The indication made by the ratemeter and displayed by the recorder is the instantaneous count rate occurring at a given time due to the presence of material in the proportional counter. What is needed for the calculation of the total amount of radioactivity in a given product is the total number of counts arising from the passage of that product through the counter. This could be obtained from the area under the ratemeter trace as displayed on the recorder. It is far easier, and more accurate, however, to simply read off the total number of counts occurring from the printing register, which is fed by the scaler. In particular, the printer is of advantage when the detection of very small amounts of radioactivity is desired.

Because the printer is actuated only at intervals (in this work, every minute), the counts obtained from it average out, over a short period, the ratemeter response, and it is much easier to decide whether or not a small activity indication is indeed due to a radioactive component or is merely background noise.

b. Method of determination of the yields of benzene, toluene, and cycloheptatriene

The chromatographic separation of benzene, toluene, and cycloheptatriene for the determination of their yields was done on a 5-foot-long 1/4-inch-wide column containing Apiezon-L (Ap-L) on crushed firebrick. The column was operated at 68 to 70° and the flow rate of the methane carrier gas was about 28 cc/ min. Since benzene, toluene, and cycloheptatriene were always present in macroscopic amounts, care had to be taken to avoid condensation of those compounds in the proportional counter, and the counter was heated to about 80° by insulated heating tape wrapped around it as shown in Fig. 14.

The yield of a given compound, x, is the ratio of the total radioactivity in x, in counts per minute, to the total amount of activity introduced into the benzene during irradiation, i.e., percent yield $x = A_x/A_T^0$, where A_x = radioactivity in compound x, and A_T^0 = total radioactivity introduced into the sample during irradiation. The yield must be based on the calculated activity introduced and not on the actual activity in the collected sample, because only the volatile products (with the exception of methane) were collected and the distribution of activity between volatile and nonvolatile products is very likely to be a function of the conditions of irradiation.

A_x is calculated from the equation

$$A_x = \frac{N_x}{\langle t \rangle} \times \frac{1}{e} \times \frac{V_T}{V_A} = N_x \times \frac{f}{V_c} \times \frac{1}{e} \times \frac{V_T}{V_A} ,$$

where N_x = the number of counts above background arising from the passage of x through the counter; $\langle t \rangle$ is the average residence time

of a molecule of x in the counter; e is the efficiency of the counter; V_T = the total volume of benzene plus carriers from an irradiation; V_A = the volume of the aliquot taken for analysis; V_c = the sensitive volume of the proportional counter; f = the flow rate of the carrier gas through the proportional counter.

The method of determining these parameters is as follows: N_x is obtained from the printer tape, which gives the counts occurring during every minute. Subtraction of background was troublesome throughout this work because of contamination of the counter by other lower-boiling labeled products, which were absorbed on the counter walls. Hence the "local" background prevailing during the time of passage of x through the counter had to be subtracted. This could be determined less accurately than could a pre- or postirradiation background, and imposed severe limitations on the precision of the yield determination. This problem is discussed in more detail later. The $\langle t \rangle$ is the average residence time in the counter, and it is equal to V_c/f, where V_c is in cc's and f is the flow rate in cc/min; f was determined in the earlier analyses by a rotameter which had been calibrated by measuring the volume of effluent gas collected, as a function of time, over water in a graduate cylinder. The rotameter proved to be too insensitive, and flow-rate was measured in the later runs with a soap-film meter. This device is very simple and extremely reproducible (approx 0.3%). The flow rate was measured before (and occasionally after) an analysis by measuring the time a soap film took to sweep out a known volume. The time could be measured to about 0.003 min, using the timer on the scaler. The soap-film meter is shown attached to the right side of the GLC in Fig. 14.

V_c is known from the diameter of the counter and the length of the inner electrode, which is well defined by the stops shown in Fig. 16.

The efficiency e of the counter was determined every day before a sample was analyzed by injecting a known volume of standard toluene-^{14}C (114 dpm/μl). The standard toluene contains 23 dpm/μl

total activity, but only 93±1% of this is actually due to toluene--evidence for this is presented later. The standard toluene was injected with a 50 μl Hamilton syringe, and the volume introduced is known to about 1%. The efficiency is given by

$$e = N_s/\langle t \rangle A_s = N_s f/V_c A_s ,$$

where N_s = the total count above background due to the toluene-^{14}C as obtained from the tape, and A_s = the total toluene activity in counts per minute in the volume of toluene-^{14}C injected. From this expression it can be seen that f and V_c need not be accurately known, so long as they are constant, since their appearance in the expression giving e (efficiency) cancels out their appearance in the equation giving A_x.

The efficiency of the counter was found to depend rather strongly on the counter temperature, decreasing with increasing temperature. It also varied when the counter was taken apart for cleaning and re-assembled. Efficiency, however, was quite constant for a given set of operating conditions. Product analyses were always carried out under conditions identical to those prevailing during efficiency determination.

Before the efficiency was determined, the plateau region of the counter was established by means of an external ^{60}Co source. The plateau region of a proportional counter is that voltage range over which the efficiency of the counter is essentially independent of the voltage. In this work, with the counter heated to 80°, the plateau region ranged from about 2600 v to about 3500 v. The counting voltage was set at 2800 v. In the last few analyses, when the counter was operated at a somewhat lower temperature, the plateau region shifted to higher voltages and lengthened. The counter was then set at 3000 v.

V_t, the total volume of sample from an irradiation, is obtained from the knowledge of the input rate of benzene into the separator and the time of input, and the volume of carrier added. The input rate has been accurately determined as described earlier, and is constant to at

least ± 5%. That all the benzene admitted actually condenses on the target cold finger and is not pumped away during irradiation has been verified by weighing the condensate from irradiation B7. The condensate from that irradiation had been caught in a spiral trap. It was then vacuum-distilled into a tared ground-glass-stoppered receiver. The weight of condensate was 239.5 mg. The weight expected, if all the benzene condensed and remained on the target cold finger--calculated from the input rate and input time of benzene, the volume and composition of the carrier added, and the various densities--was 239.9 mg. Such agreement is, of course, fortuitous, but nevertheless reassuring.

V_a, the volume of aliquot taken, is measured in the 50-μl Hamilton syringe used for injection of the aliquot into the GLC unit.

(a) Handling of sample

In the last five irradiations (B9 through B13) the product was stored in sealed evacuated ampules at -196°. For analysis of an aliquot, the ampule and contents were allowed to come to room temperature, the top of the ampule was knocked off, and an aliquot was withdrawn. The ampule containing the remaining sample was then immediately put into a glass vessel, attached to a vacuum line, and frozen at -196°. The air was removed from the vessel and the sample was vacuum-distilled (base pressure ≈ 30 μ) into another seal-off tube. The sample was gently heated with an infrared lamp during distillation. After the sample had completely condensed in the new seal-off tube (as indicated by the return of the pressure to its initial level), the tube was sealed in vacuo and stored in liquid nitrogen.

(b) Counter contamination and background determination

The problem of counter contamination has already been mentioned. It arises primarily from C_5 or C_6 compounds or both, and is probably due to reaction of alkynes with the copper in the brass counting tube. At first, the inside of the counter was coated with Aquadag, a paste containing colloidal graphite in aqueous suspension. This was necessary to reduce the high-temperature noise that occurred when the column was

heated. It was thought that contamination might be due to absorption of labeled compounds on the graphite, therefore in order to avoid contact of the effluent preceding benzene with either graphite or the bare wall of the counter, the inside of the counter was gold plated. This worked fairly well in one analysis, reducing the high-temperature noise and holding contamination down to a tolerable level, but the gold plating sloughed off when the counter was first cleaned, and time did not allow replating. Contamination and high-temperature noise then reappeared, but a slight decrease in the column temperature reduced the noise to a tolerable level, and the tube was used in its partially-plated condition in the following analyses.

The contamination affected the determination of benzene activity far more severely than that of toluene or cycloheptatriene activity, both of which were essentially free from large uncertainty in background. This can be seen in the traces and the tape plots shown later. Often the benzene activity appeared superimposed on a sharply sloping background, and determination of activity was difficult.

The compounds responsible for contamination were found to be unsaturated, as were all but one of the "prebenzene" products, and bromination of them should increase their retention time by such a large amount that they would be removed from the benzene area. Unfortunately, when the whole sample was brominated before analysis, HBr, arising from reaction of bromine with toluene also added to the lower-molecular-weight unsaturates and increased their retention time so that they then interfered with benzene. The only solution found was to trap the benzene separately, treat it with bromine, and then reanalyze it. This works well, and was done in the analysis of the products of the later irradiations.

A stainless steel counter was designed but was not ready for this work--it may very well be that the problem of contamination will be solved by proper choice of proportional-counter material.

c. Method of prebenzene identification

The most advantageous feature of proportional counting in conjunction with gas chromatograph is that it does not allow one to beg the question. If conditions of chromatography are suitable, radioactive compounds present in the sample will be seen, whether one thinks they should be or not.

When the first analysis of the products of an irradiation was made on our GLC-PC apparatus, the presence of considerable amounts of radioactivity in compounds emerging from the column before benzene (hence "prebenzene") was obvious. Under the conditions used for the analysis of benzene, toluene, and cycloheptatriene, little or no information about the identity of these compounds could be obtained, aside from the fact that they were all probably lower-boiling than benzene and consisted of C_4 (or lower) to C_6 hydrocarbons. An attempt was made during the analysis of benzene, etc., from B7 to learn something of the nature of these prebenzene compounds by brominating a portion of the sample before analysis. However, as described in the preceding discussion, hydrobromination accompanied bromination, and the results could not be interpreted unambiguously. A portion of the B7 sample was also treated with sodium hydroxide solution to see if any of the prebenzene activity was due to $^{14}CO_2$ or to any other acidic compounds, but this, too, yielded no information. Analysis of B7 samples made at different times showed that the prebenzene activity spectrum changed with time, and this prompted a change in the method of product collection and storage to avoid prolonged exposure of the products to air.

Chromatography at room temperature on two widely differing GLC columns allowed the identification of several of the prebenzene compounds from irradiations B11, B12, and B13. One of the columns was the AP-L column already described; the other was a 1/4-inch-wide 10-foot-long column containing dimethylsulfolane (DMS) on acid-washed crushed firebrick. The AP-L column is almost completely insensitive to functional group differences among hydrocarbons, separating them according to their vapor pressure, whereas the DMS

column is highly selective, retention times on it depending strongly on the nature of the functional type of a hydrocarbon.

The characteristics of these columns at operating conditions suitable for the analysis of the prebenzene compounds were determined by measuring the retention times of a variety of hydrocarbons in the range C_2 through C_7. The operating conditions chosen as standard for this work were a column temperature of 22° and a methane carrier gas flow rate of 25.8 cc per minute. The methane carrier gas was cp grade and was partially purified by passage through a coil cooled in an isopropanol slurry. Most of the gaseous hydrocarbons were obtained from the Matheson company in lecture-size bottles, and were cp grade. A cyclinder of allene was kindly loaned to us by Professor H. S. Johnston, who obtained it from the Columbia Organic Chemicals Company; 2-butyne was kindly donated to us by the California Research Corporation, and was an American Petroleum Institute standard sample; 1, 2-butadiene was purchased from the American Petroleum Institute. The rest of the hydrocarbons were obtained from a variety of sources and were for the most part of high degree of purity, which, incidentally, is unnecessary for the present purpose.

The reduced standard retention times thus obtained for both columns are listed in Table IV. The reduced retention time of a compound is the time of emergence of the mass-trace maximum of that compound after injection, minus the time of emergence of the air-peak maximum after injection. This subtraction is done to account for the transit time of a unretarded component (which air is assumed to be), hence the reduced time is a true measure of a compound's retention. Since our GLC unit was not thermostatted, column temperature varied with room temperature. To compensate for the several-percent variation in retention time resulting from a deviation of a few degrees from the standard temperature, the reduced retention time of n-pentane measured at standard conditions was taken as a reference point and all reduced retention times not actually measured at standard conditions were

Table IV. The retention times of some hydrocarbons on AP-L and DMS

Compound	AP-L No.	AP-L t^0_r(min)	DMS No.	DMS t^0_r(min)
Alkanes				
Ethane	1[a]	0.20	2	0.22±0.02
Propane	1[a]	0.75	3	0.62±0.02
Cyclopropane	1	1.48	1	2.32
m-Butane	1[a]	2.88	10[a]	1.79±0.02
Isobutane	2[a]	1.72±0	3[a]	1.14±0.02
m-Pentane	1[a]	9.48	5[a]	4.77±0.01
Isopentane	1[a]	6.72	4[a]	3.60±0.06
Neopentane	1[a]	2.90	1[a]	1.78
n-Hexane	0		2[a]	10.98±0.02
Isohexane	1	20.9	3[a]	9.28±0.07
2,4-Dimethyl pentane	1	40.2	1	15.4
Alkenes				
Ethylene	1[a]	0.12	2	0.25±0
Propylene	1[a]	0.72	1[a]	1.02
1-Butene	1[a]	2.45	3[a]	2.89±0.01
Isobutene	1[a]	2.52	5	3.09±0.03
Cis 2-butene	1[a]	3.65	7[a]	4.40±0.04
Trans 2-butene	1[a]	3.30	4[a]	3.75±0.03
2-Methyl 2-butene	1	11.8	2	11.38±0.03
4-Methyl 2-pentene	1	19.4	1	14.6
1-Heptene	1	78.5	1	49.0
Dienes				
Allene	2	1.10±0	4	3.40±0.01
1,2-Butadiene	1	4.55	3	9.62±0.01
1,3-Butadiene	1[a]	2.70	1[a]	6.52
Alkynes				
Acetylene	1	0.12	1	2.32
Propyne	1	0.90	2	7.18±0.04
1-Butyne	1	2.58	1	15.3
2-Butyne	3	7.05±0.04	2	27.0±0.2
Others				
Carbon dioxide	1	0.05	2	0.60±0.02

[a]Measured at standard conditions.

corrected by the ratio

α = (standard reduced retention time of n-pentane)/(actual reduced retention time of n-pentane at prevailing operating conditions).

In the following discussion, t_r indicates a measured reduced retention time and t_r^0 indicates a standard reduced retention time. That is, $t_r^0 = \alpha t_r$. When retention time is written in full, it is to be understood to mean reduced retention time.

Those compounds whose retention times were determined by measurement at standard conditions are indicated by an asterisk in the column giving the number of measurements made. Where t_r^0 is the average of several measurements the standard deviation of the set is given following the retention time. The determination of retention time under a given set of operating conditions is reproducible to better than 1%. In fact the standard deviations of many of the retention times are no greater than the limit of readability of the recorder chart paper, the smallest division of which is 2.5 mm wide, corresponding to 0.25 minute. This can be read to about 1/10 of a division, or 0.025 minute, and since the reduced retention times are the difference of two measured times, the limit of readability is about 0.050 minute.

We have relatively little information bearing on the error associated with correction from nonstandard to standard conditions. Since the heats of vaporization of these hydrocarbons are not, in general, equal to that of n-pentane, correction by the factor α is only approximate; but it should be a fairly good approximation so long as α differs from unity by only a few percent, as it did when the data in Table IV were obtained. Table V shows t_r^0 for those compounds whose times were measured both at a standard and at nonstandard conditions. Agreement is seen to be fairly satisfactory.

Table V. Comparison of retention times measured at standard and nonstandard conditions

Compound - DMS	t_r^0 measured at standard conditions	t_r^0 measured at nonstandard conditions	α	Relative difference %
n-Butane	1.79	1.79	1.027	0
Isobutane	1.14	1.19	1.027	4.4
Isopentane	3.60	3.72	1.027	3.3
		3.65	0.978	1.4
Compound - AP-L				
Trans 2-Butene	3.30	3.32	1.038	0.6

Figure 17 illustrates the selectivity of the dimethylsulfolane column. Such a linear relation between the log of the retention time and the number of carbon atoms for a homologous series was first noted by James and Martin.[42] This type of plot is widely used, but is not the best measure of column selectivity because of the variation of vapor pressure with functional type for molecules of a given number of carbon atoms. Figure 18 illustrates the well-known relationship between the boiling points and the numbers of carbon atoms for homologous series of hydrocarbons. It can be seen that the downward curvature of the lines in Fig. 17 is due at least in part to the curvature of the plots of boiling point versus carbon number, and also that some of the apparent selectivity is due simply to variation of boiling point with functional type.

Figure 19 shows the log retention times of functional types on dimethylsulfolane as a function of the boiling points of the compounds. This type of plot is less commonly seen but is actually more informative than a plot of log retention time versus carbon number. From Fig. 19 it may be seen that the chief determinant of selectivity is the

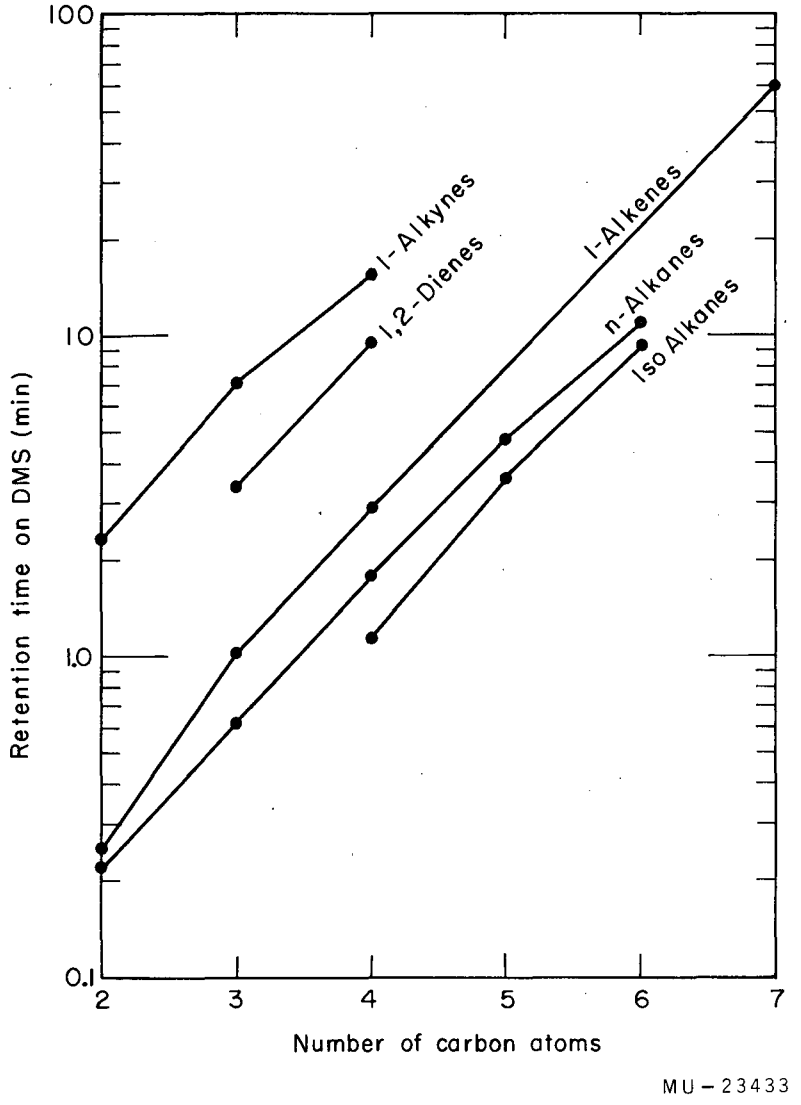


Fig. 17. Plot of log retention time on DMS vs carbon number for some homologous series of hydrocarbons.

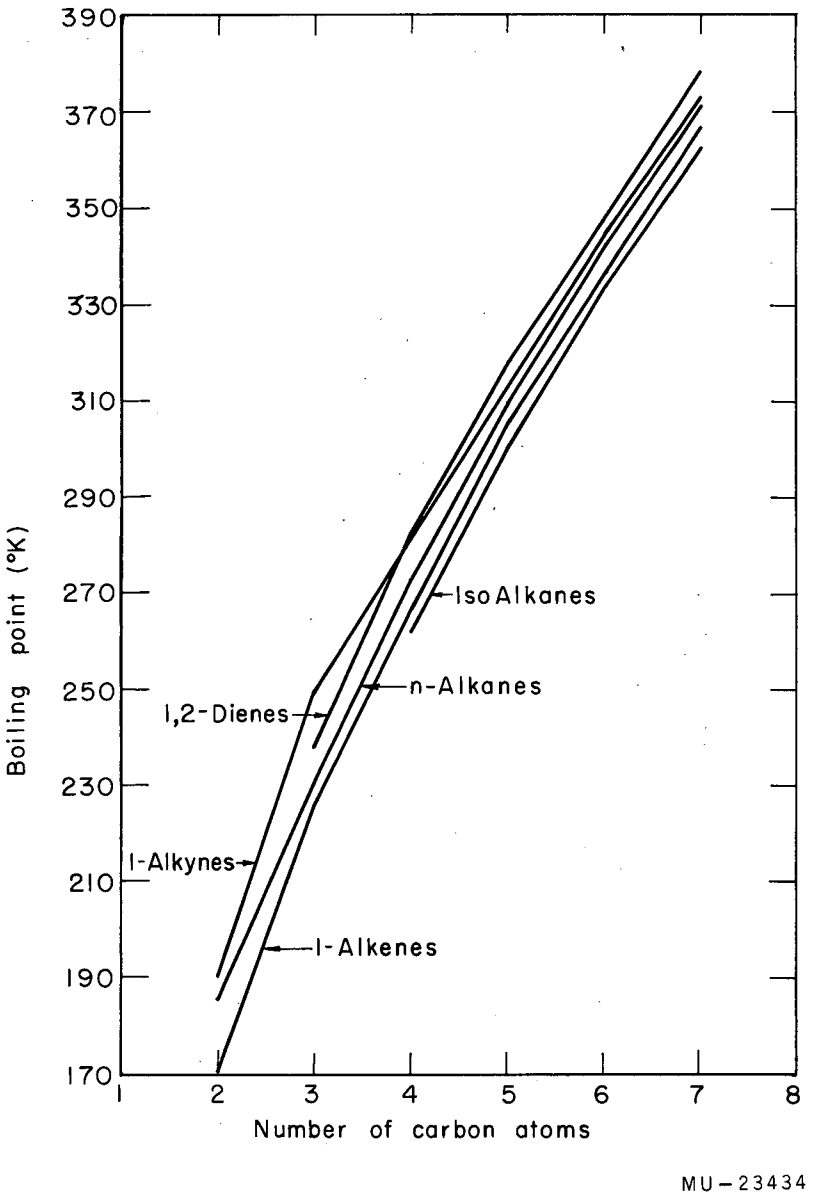


Fig. 18. Plot of boiling point vs carbon number for some homologous series of hydrocarbons.

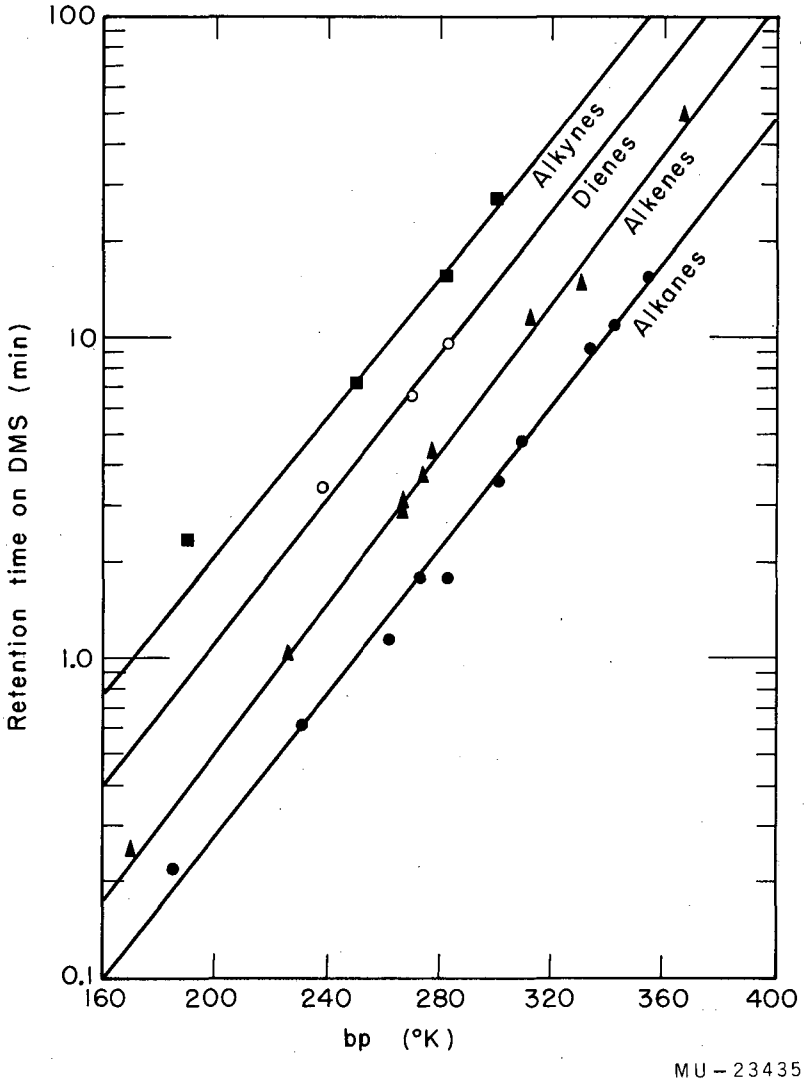


Fig. 19. Plot of log retention time on DMS vs boiling point for some hydrocarbon groups differing in kind and number of multiple bonds. The alkane line is drawn through the n-alkane points.

number and nature of multiple bonds in a hydrocarbon. Small differences between subgroups still persist, but the alkane line, actually drawn through the normal alkane points, is seen to lie quite close to the branched alkane points. Similarly, 1, 2- and 1, 3-dienes seem to be essentially equivalent, as are 1- and 2-alkynes.

Figure 20 illustrates the nonselective nature of the Apiezon-L column. Here we have plotted the log of the retention times of all the hydrocarbons measured on Apiezon-L versus their boiling points. With the exception of cyclopropane and the 1-alkynes, the points are seen to lie very near to the line drawn. Indeed, the boiling point of a hydrocarbon can be approximately established by measurement of its retention time on Apiezon-L.

Figure 21, a plot of retention on DMS versus retention time on APL for the hydrocarbons in the C_2 to C_6 range, further illustrates the great difference in the characteristics of the two carbons. This type of cross plot was also introduced by James, Martin, and Smith.[43]

It is evident that a good deal can be learned about the nature of an unknown hydrocarbon by measuring its retention time on both columns. Knowledge of t_r^0 on AP-L alone gives a fair indication of the boiling point. Knowledge of t_r^0 on both AP-L and DMS is clearly sufficient to establish gross functional group character. In the C_2-to-C_4 range, where the population density of hydrocarbons is not great, knowledge of t_r^0 on both columns is of itself sufficient to establish identity in most cases.

For the analysis of the prebenzene compounds, the sample was injected via syringe onto Apiezon-L both at the high-temperature condition used for the analysis of benzene et al. and at room temperature, and the prebenzene area was collected either in parts or in whole. The prebenzene group or fractions thereof was repeatedly rechromatographed on both columns until correspondence of the activity peaks emerging from one column with those from the other column was established. Effluent was recovered after chromatography by con-

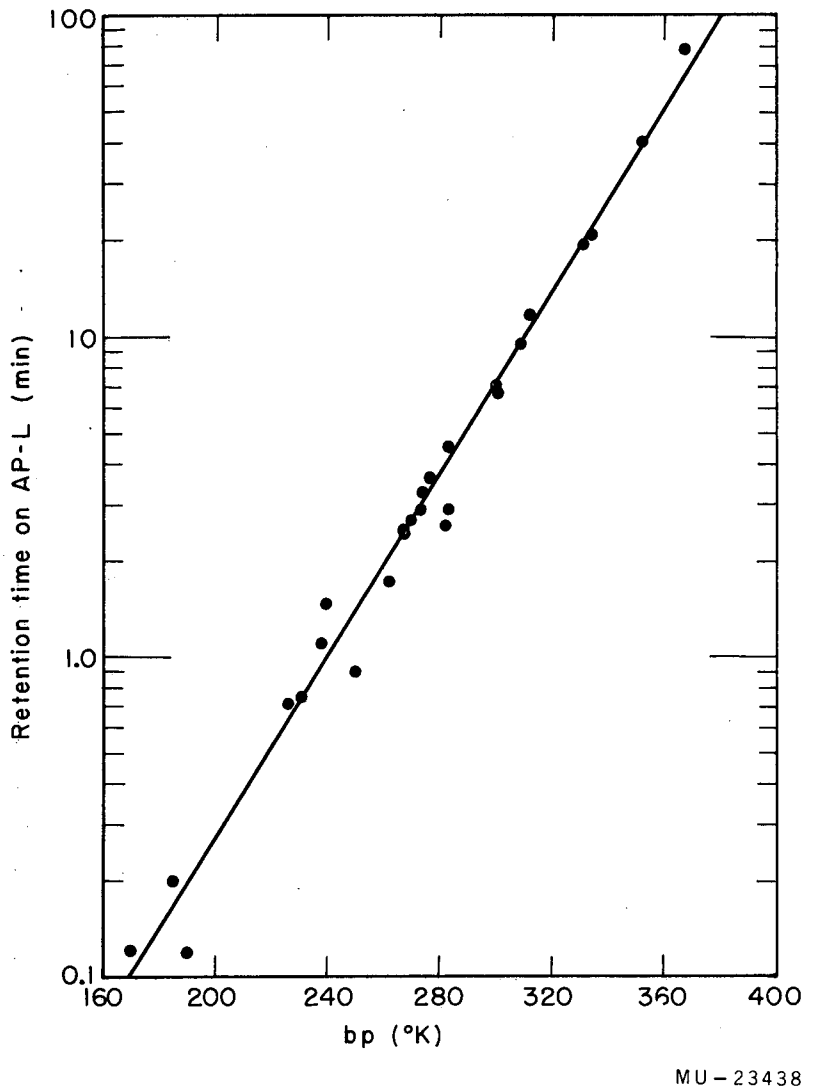


Fig. 20. A plot of log retention time on AP-L vs boiling point for all the hydrocarbons tested. The alkynes and cyclopropene deviate from the rest of the hydrocarbons.

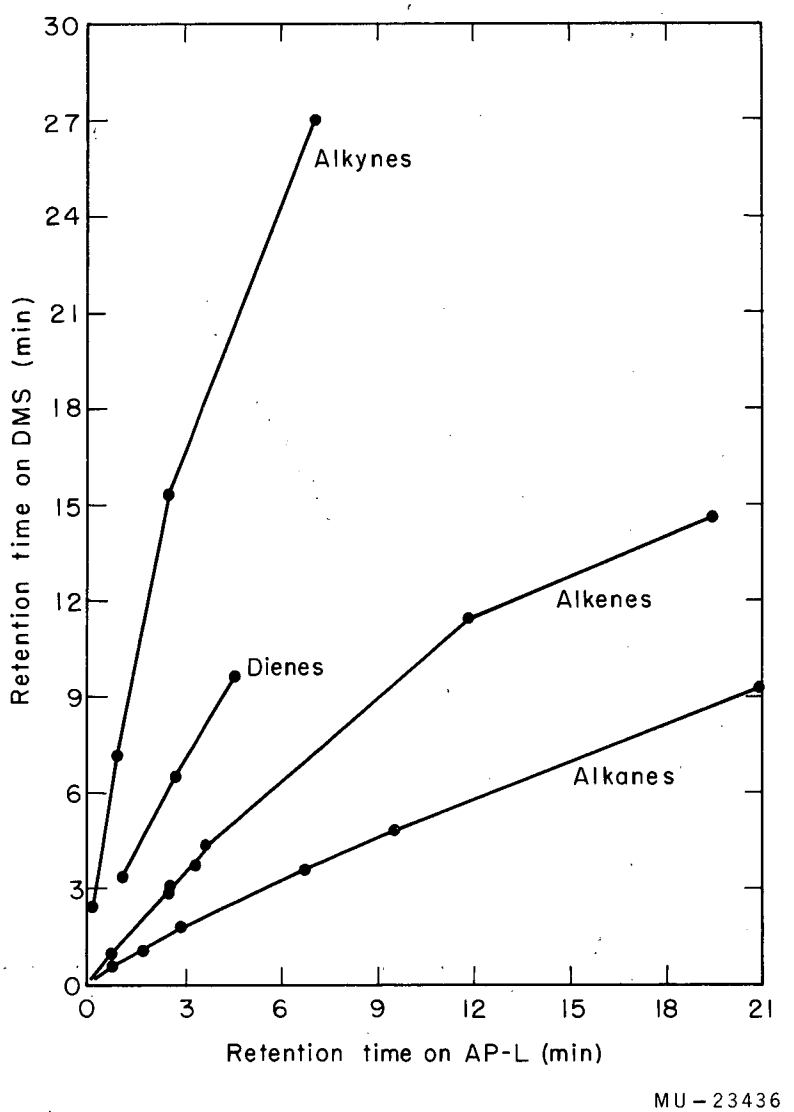


Fig. 21. A plot of retention time on DMS vs retention time on AP-L for some hydrocarbon groups differing in kind and number of multiple bonds.

densation in a spiral glass trap (shown in Fig. 14) cooled in a freezing mixture of isopentane, i.e., at -160°. After recovery, the trap was attached to a vacuum line, cooled in liquid nitrogen, and pumped until the methane was removed. The condensate was then allowed to distill into an evacuated U-shaped trap suitable for reinjection. This trap can be seen in place in Fig. 14. Our GLC unit was modified to allow injection of gaseous samples from the U trap by introducing a bypass line into the incoming carrier-gas stream and by replacing the compression nut used for injection through a silicone gasket by a gas-tight brass adapter which terminated in a T 7/15 joint. Air was removed by flushing the tubing and the transverse section of the U trap with methane, and injection was achieved by closing the transverse stopcock and opening the stopcocks on the U limb. This method of injection proved to be very satisfactory. At first reinjection from the large-volume spiral glass trap used for condensation was attempted but that proved futile--the volume was so large and the flow so turbulent that resolution was very seriously impaired. After some reflection it occurred to the author that any trap well suited to the condensation of microscopic amounts of low-boiling compounds in a fast-moving gas stream was bound to be poor for reinjection, and the U trap with a volume of about 1 cc was designed, tested, and found satisfactory.

Recovery of effluent was not quantitative, and was, of course, increasingly difficult with decreasing molecular weight of the effluent material. Recovery was, moreover, somewhat irreproducible. Because individual components were isolated only after several cycles of chromatography, condensation, distillation, and reinjection, we are not able to state the absolute yields of any of the prebenzene compounds that were qualitatively identified.

Isopentane at -160° was used as trap coolant because the methane carrier gas would condense at a lower temperature. Indeed, the condensability of methane is by far its most disadvantageous property for use in GLC-PC. Another drawback to the use of methane

as a carrier and counting gas is that it is not possible to obtain methane of a suitable degree of purity, in bulk, at reasonable cost. The methane used in this work was of cp grade and was further purified by passage through a coil cooled in a dry ice—isopropanol slurry, but becase of the large amounts of methane passing through the condensate trap, quantities of alkanes (ethane through isopentane), large from the standpoint of gas chromatography, were condensed in the trap. The presence of these alkanes was not entirely undesirable, because they undoubtedly aided the collection of the low-boiling products present in microscopic amounts, and also because they served as convenient reference points when pentane was not present in a fraction. However, the presence of propane, in quantities large enough to overload the column and considerably reduce the retention time of propane, interfered with the unequivocal establishment of propane-C^{14} as a product of irradiation.

When the retention times of an isolated prebenzene component on both columns was determined, a more or less definite identification could be made from knowledge of the characteristics of the two columns. Whenever possible, identity was confirmed by adding carrier amounts of the suspected compound and rechromatographing it on both columns, the shape and position of the activity trace with respect to the mass trace giving a sensitive test of coincidence.

The proportional counter is positioned in series following the mass detector, and its sensitive volume is very large compared with that of the mass detector. Hence the position in time and the shape of an activity trace differ from those of a corresponding mass trace. A detailed derivation of the expected shape and position of an activity trace from a given mass trace is presented in Appendix 2. A few of the results of that derivation will be cited here as criteria for the establishment of coincidence between a mass and an activity trace.

(i) For a mass trace of any shape and degree of symmetry, the activity trace begins $t_d = V_{d/f}$ minutes after the mass trace begins, where V_d is the volume between the mass detector and the beginning of the sensitive volume of the counter.

(ii) For a mass trace of any shape and degree of symmetry, the corresponding activity trace is $V_{c/f}$ minutes wider at its base than the mass trace is at its base, where V_c is the counter volume and f is the carrier-gas flow rate as previously defined.

(iii) For a symmetrical mass trace, the maximum of the activity trace appears $t_d+V_{c/2f}$ minutes after the maximum of the mass trace. The same displacement occurs for the middle of the plateau region of an activity trace from a mass trace of any shape when the volume of gas carrying the sample, V_s, is less than the volume of the counter V_c. When V_s is greater than V_c and the mass trace is asymmetric, the displacement of the activity and mass maxima lies between $t_d+V_{c/2f}$ and $t_d+V_{c/f}$ for a sharply rising mass trace, and between t_d and $t_d+V_{c/2f}$ for a sharply falling mass trace. In the conditions used for the identification of the prebenzene group, V_c = 16 cc, f = 25.8 cc per minute, and t_d = 0.25 minute.
A dual-pen recorder was used for all the prebenzene analyses, and the pen sketching the activity trace was positioned one division (equivalent to 0.25 minute) behind the pen giving the mass trace, thereby compensating for t_d, the dead time. The rise of an activity trace should therefore coincide exactly with the rise of a corresponding mass trace on the chart paper. In most cases the mass trace was seen to be symmetrical or assumed to be so, and V_s was usually greater than V_c, hence an activity maximum should be displaced $V_{c/2f}$ = 0.310 minute from the mass-trace maximum on the chart paper. An activity trace should be 0.620 minute broader than a corresponding mass trace, regardless of the width in time of the mass trace.

The standard reduced retention time of a radioactive component, seem only by virtue of its activity trace, was calculated from

$$t_r^0 = \alpha(t_A - t_{air} - V_{c/2f}) ,$$

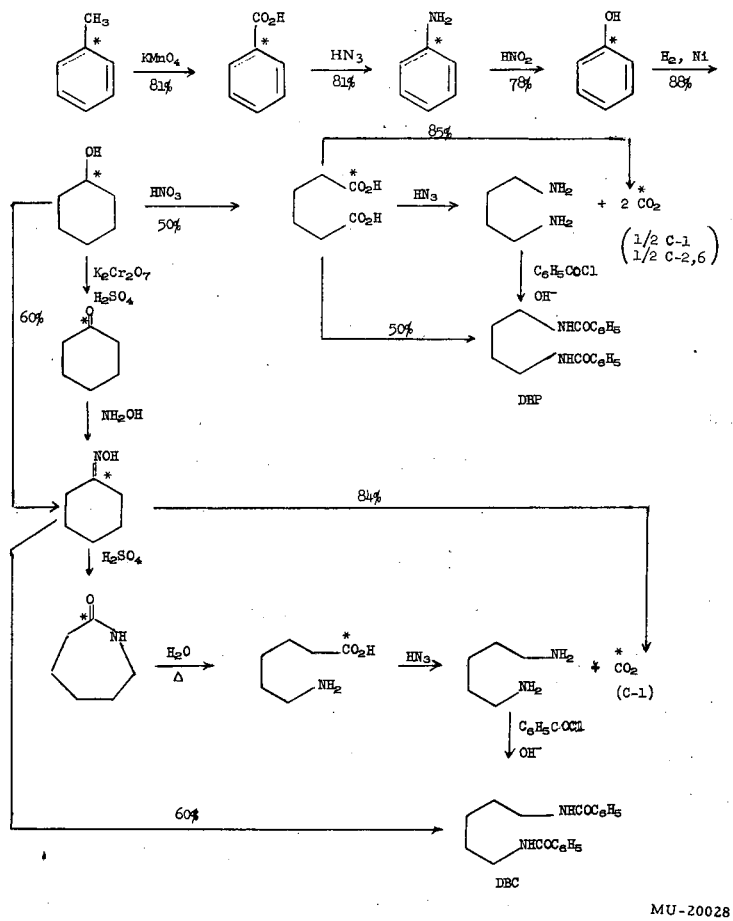


Fig. 22. Toluene degradation scheme.

where t_A is the time of appearance of the activity maximum following injection and t_{air} is the time of appearance of the air-peak mass maximum following injection; t_{air} on DMS was 1.55 to 1.62 minutes, and t_{air} on AP-L was between 0.70 and 0.75 minute. Hence $t_r^0 = \alpha(t_A - 1.90)$ for DMS, and $t_r^0 = \alpha(t_A - 1.04)$ for AP-L.

2. Degradation of Toluene-^{14}C

The toluene-^{14}C from irradiation B7 was degraded to give the distribution of activity between the ring and the methyl group. This was done primarily to determine whether the toluene-^{14}C formed by $^{14}C^+$ irradiation of benzene was made in the same way as the toluene-^{14}C resulting from ^{14}C recoil in benzene and other compounds, the latter having been degraded by Wolf et al.[2] as described in the introduction.

At the onset of the present work, it was intended to carry out a complete ring degradation of toluene-^{14}C resulting from $^{14}C^+$ irradiation of benzene. For a variety of reasons, this was not done, but the results of the practice partial degradations that were made are presented here, not only to allow the author to indicate how a considerable amount of his time was spent, but also because these results bear on the reliability of the one ring-methyl degradation that was performed, in addition to providing the evidence for other statements that have been or will be made.

Figure 22 shows the series of reactions used to give the isotopic content of carbon atoms 1 and 2-6 in the ring of toluene. DBP indicates dibenzoylputrescine and DBC indicates dibenzoylcadaverine. The yields shown are the yields obtained in the sequence which had the best over-all yield. This method was checked with both commerical toluene-1-^{14}C and cyclohexanone-1-^{14}C. Parts of this scheme have been used[44, 45, 46] and checked[45, 46] by other workers in analogous degradation studies of related compounds.

Tables VI and VII give the results of the practice degradation on toluene-1-^{14}C and cyclohexanol-1-^{14}C, respectively. All the compounds except carbon dioxide were counted in a liquid scintillation counter using toluene-1-^{14}C as an internal standard. Both a Packard Tri-Carb Liquid Scintillation Spectrometer, Model 314X, and a counter built by the Lawrence Radiation Laboratory were used; the latter has been described elsewhere.[47] Carbon dioxide was counted in a 250-cc Tolbert-Cary ionization chamber by the rate-of-charge method,[48] using an Applied Physics Corporation vibrating-reed electrometer and a Leeds and Northrup Speedomax-G 6-channel recorder potentiometer. The amount of CO_2 in the chamber was determined by measurement of the CO_2 pressure in an accurately known volume. Correlation between the liquid scintillation counting and ionization chamber counting was determined in two ways. First, the standard benzoic acid used for the initial calibration of the ionization chambers was counted in the liquid scintillation counter, with toluene-^{14}C used an an internal standard. Secondly, ^{14}C-labeled benzoic acid was counted both in a liquid scintillation and, after combusion to CO_2, in the ionization chamber. The results of the two methods were in complete agreement, showing that the liquid scintillation counter gave results that were high relative to the ionization chamber by a factor of 1.102. Therefore, specific activities determined in the ionization chamber from the ion chamber calibration constants were multiplied by 1.10 in order to obtain carbon dioxide specific activities in terms of the scintillation counting standard. The validity of this correlation between the two methods of counting is illustrated by the results listed in Tables VI and VII.

It was mentioned earlier that the standard toluene used for the determination of the efficiency of the internal-flow proportional counter was known to contain about 7% radiochemical impurity. The evidence for this is the data presented in Table VI. It can be seen in Table VI that essentially all the radiochemical impurity is removed upon oxidation of toluene to benzoic acid. It can also be seen from Table VI that the

Table VI. Results of the degradation of toluene-1-C^{14}

Compound	Samples counted	Specific activity (cpm/mM)	Molar specific activity (compared with adipic acid as 100%) (in %)
Toluene	(standard taken as 148 cpm/mM)	15,730	107.7
Benzoic acid	2	14,480	99.1
Aniline	1	14,470	99.0
Phenol	1	14,110	96.6
Cyclohexanol	1	14,080	96.4
Cyclohexanone oxime	3	14,400	98.6
Adipic acid	3	14,610	100
Carbon dioxide-1-carbon	2	14,850	101.6
Carbon dioxide-1- and 2-6 carbons	2	7,180	49.1
DBC	2	244	1.67
DBP	2	189	1.29

Table VII. Results of the degradation of cyclohexanol-1-^{14}C

Compound	Samples counted	Specific activity (cpm/mM)	Molar specific activity (compared with adipic acid as 100%) (in %)
Series 1[a]			
Cyclohexanol	7	113,500	99.8
Cyclohexanone oxime	1	107,800	94.8
Adipic acid	1	113,700	100
Carbon dioxide-1-carbon	2	113,700	100.0
Carbon dioxide-1- and 2-6 carbons	2	55,400	48.7
DBC	not counted[b]		
DBP	2	42.7	0.04
Series 2			
Cyclohexanol	2	112,400	100
Cyclohexanone oxime	3	114,100	101.5
Carbon dioxide-1-carbon	3	113,200	100.8
DBC	2	42.7	0.04

[a]Commercial cyclohexanone-1-^{14}C was hydrogenated and used in these two series.

[b]The dibenzoylcadaverine was contaminated by an active, difficultly separable impurity, believed to be a dipeptide. It occurs only when the Schmidt reaction of ϵ-aminocaproic acid is run in the presence of SO_3.

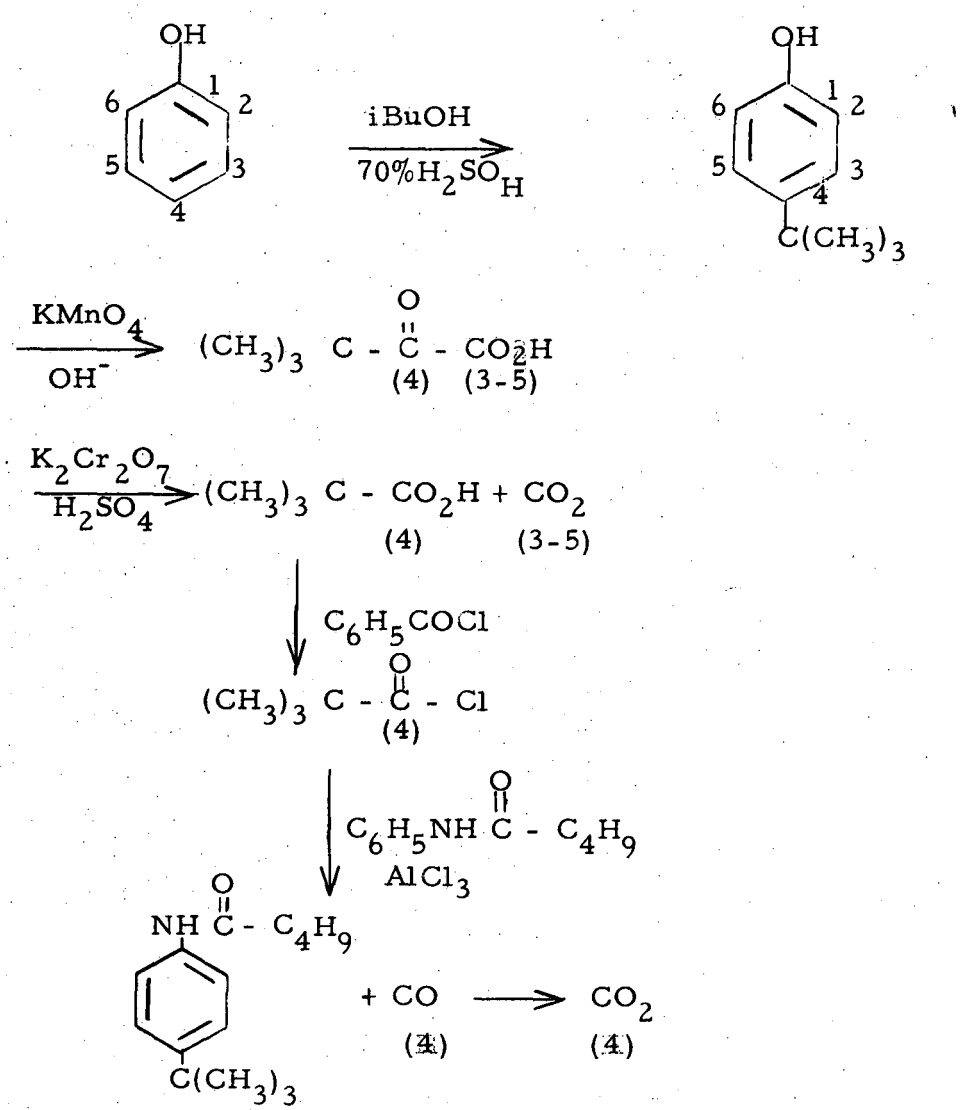


Fig. 23. Portion of tyrosine degradation scheme of Reio and Ehrensvard (Ref. 49).

toluene-1-^{14}C actually contains 98% of its activity in the 1-position. We had intended to use a series of reactions reported by Reio and Ehrensvard to obtain the isotopic content of the 3-5 and the 4-carbons.[49] These reactions are illustrated in Fig. 23. On checking this procedure with phenol-1-^{14}C prepared from toluene-1-^{14}C, we found repeatedly that activity appeared in the carbon dioxide that was supposedly from the 3-5 carbon of the parent phenol. The molar specific activity of the CO_2 was 19.9%, 17.7%, and 19.7% that of the phenol. Obviously, one or more of the above reactions was not going as written, or else some side reaction was also occurring, rendering the method useless for degradative purposes as it stood. It should be pointed out that according to the method of Reio and Ehrensvard, which was followed by us, the trimethylpyruvic acid was not isolated as such. Perhaps if this were done the difficulties observed would be avoided. However, we did not try this.

Alternative methods for obtaining the activity in the 3-5 and 4-carbons were considered, but were not followed to completion. One of those involved the reaction of barium hypobromite with picric acid, which should give bromopicrin the carbon atom of which is from the ring carbon bearing the nitro groups. This reaction has been used by Reio and Ehrensvard in the work mentioned previously. The so-called bromopicrin split could also be applied to o- and p-nitrophenol and perhaps to p-nitrosophenol. Another method, conceived by the author, involved the nitration of toluene, GLC separation of the nitrotoluene isomers, and oxidation of the separated p-nitrotoluene to p-nitrobenzoic acid, followed by decarboxylation and reduction, giving aniline with the amino group attached to the 4-carbon of the parent toluene. The degradation scheme shown in Fig. 22 could then be used to degrade the aniline, giving the isotopic content of the 4- and the 3-5 carbons.

Attempts along this line were stopped when two factors became obvious: (a) a great deal of time would be required for the development

and checking of any of the degradative possibilities outlined above, and (b) it did not seem likely that enough activity could be obtained in toluene in a reasonable time from ion irradiation to make degradation worth while. We had greatly underestimated the difficulty of running the isotope separator for prolonged periods of time. In order to carry out a ring degradation of toluene, it would have been necessary to concentrate exclusively on that goal, ignoring the unique potentialities of the isotope separator. The discontinuation of efforts involving the ring degradation of toluene proved to be a wise step. Shortly after that decision was made, Steinberg and Sixma published an ingenious degradation scheme for toluene, based on the Skraup quinoline synthesis as applied to o- and p-aminobenzoic acid.[50] These workers degraded toluene-^{14}C from ^{14}C recoil in benzene for Wolf;[51] the results of that degradation will be included in the discussion of this work.

a. Ring-methyl degradation of toluene-^{14}C

The sample from irradiation B7 was analyzed for benzene, etc., in six portions. The condensates from these six runs were rechromatographed on AP-L and the toluene-^{14}C was trapped by allowing the effluent gas carrying it to pass through a bubbler containing 500 μl of cold toluene. Fifteen μl was taken for scintillation counting and the remainder was treated with 25 μl of bromine in order to remove any unsaturated radioactive impurities that had not been removed by chromatography. The toluene-^{14}C was then rechromatographed in three portions on a 1/2-inch-wide 5-ft-long column containing Ucon (polyethylene oxide) on crushed firebrick. The front and rear portions of the toluene peak from one of these passes was trapped separately to allow a test for radiochemical purity, a part of the condensate from both the front and the rear sections being taken for scintillation counting.

The toluene was oxidized to benzoic acid by an aqueous solution of potassium permanganate, by a modification of the method of Ullman and Uzbachian.[52] In this procedure 1.36 g of potassium permanganate was dissolved in 22.4 ml of water in a three-necked 100-ml round-

bottom flask fitted with a thermometer, an efficient reflux condenser, and a magnetic stirring bar. The remaining 350 μl of toluene was added to the solution, which was then heated in an oil bath to 90°. The stirred mixture was held between 90 and 95° for 19.5 hr, at which time an additional 422 mg of potassium permanganate was added to the solution, since the odor of toluene was still noticeable. The mixture was then heated at about 100° for an additional 2-1/2 hr. The solution was allowed to cool and the manganese dioxide was removed by suction filtration, first through a coarse, then through a fine, sintered glass funnel. The MnO_2 was washed with two 10-ml portions of water which were added to the filtrate. The filtrate was boiled down to 7.3 ml, cooled to 0°, and added slowly from a 10-ml graduate cylinder to 3.5 ml of chilled, stirred, concentrated HCl. Stirring was contained at 0° for about 10 min. Then the benzoic acid was filtered, washed with a total of 10 ml of chilled water, put in an evacuated desiccator over P_2O_5. After 19 hr in the desiccator the melting point of the benzoic acid was taken and found to be 123.0 - 123.5° uncorr. (lit. $=122^{\circ}$);[53] 182.7 mg = 1.50 mmole of benzoic acid was obtained. The yield was 53.5%. 20.33 mg was taken for scintillation counting.

The remaining benzoic acid was decarboxylated by a Schmidt reaction in concentrated H_2SO_4, according to a method devised by us following the guide lines given in Organic Reactions.[54] The remaining 162 mg of benzoic acid was dissolved in 1.0 ml of cp concentrated H_2SO_4 in a three-necked 30-ml round-bottom flask, fitted with a gas inlet tube through which a thermocouple was also passed into the solution, a gas outlet system, and a tube bent at right angles for the periodic addition of sodium azide. One hundred and two mg of recrystallized sodium azide was put in the addition tube and a flow of helium was started through the reaction vessel and gas-absorption train. The helium gas first passed through a bubbler containing 1 N NaOH, then through a bubbler containing concentrated cp H_2SO_4. Effluent gas passed first through a bubbler(flanked by Drierite tubes)

containing 3% hydrogen peroxide solution, then through a spiral glass trap immersed in liquid nitrogen which, in turn, was followed by a bubbler containing 1 N NaOH solution. The Drierite tubes flanking the hydrogen peroxide bubbler served to protect the reaction system and the carbon dioxide trap from moisture. A by-pass line also led via a three-way stopcock from the peroxide bubbler to a bubbler containing a concentrated solution of barium hydroxide, which was used to detect the beginning and end of the CO_2 evolution.

The sodium azide was added in portions over a period of 45 min. The reaction mixture was stirred by a magnetic stirring bar and was held between 63 and 80° during reaction. Following the azide addition, the reaction mixture was heated for an additional 1-1/4 hr at a temperature ranging from 78 to 116°, after which no barium carbonate precipitate was detectable in the barium hydroxide bubbler.*

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*In our experience with the Schmidt reaction on benzoic acid, adipic acid, and ε-aminocaproic acid, best yields were found to occur when the reaction was carried out at temperatures considerably higher than the 40 to 45° normally considered optimum for the Schmidt reaction on carboxylic acids. The lower temperature is doubtless optimal when reaction is effected by addition of a solution of hydrazoic acid in chloroform to the substrate dissolved in sulfuric acid. It has been suggested in the chapter on the Schmidt reaction in Organic Reactions (Ref. 54) that decrease in yield at higher temperatures in the "normal" method may be due to loss of hydrazoic acid from the reaction system. This could explain the difference between the optimum temperature for the normal method and that which we have used. Whatever the explanation, our yields increased by 25% when the reaction was carried out at 70 to 80°, followed by a heating period at 100° and 110° after reaction.

The carbon dioxide from the carboxyl group of the benzoic acid was caught in the spiral trap cooled in liquid nitrogen. This trap was then attached to a vacuum line, the helium removed, and the CO_2 distilled through two U sections, cooled to -130°, into a known volume where the CO_2 pressure was measured. The CO_2 was then transferred to an ionization chamber and cold carbon dioxide was admitted until the pressure in the chamber was 1 atm. The activity in the CO_2 was determined by the method previously described.

To the cooled mixture of aniline and sulfuric acid, 4 ml of water, followed by 3 g of KOH dissolved in 5 ml of water, was slowly added with cooling. Potassium sulfate came out of solution, and four 2-ml portions of benzene were used to rinse the salt and extract the aniline from the aqueous phase. The benzene extract was dried over magnesium sulfate overnight. The magnesium sulfate was then removed by suction filtration and the benzene solution was evaporated down, first on a steam bath and then by distillation, until a final volume of about 800 μl was reached. The aniline was obtained by GLC on the 1/2-inch Ucon column previously described. The aniline was chromatographed in three portions, and all the condensate from each portion was taken for scintillation counting. The over-all yield of aniline was extremely poor. This was due to the method of recovery and not the reaction itself, as the yield of CO_2 was 85.0%, that usually obtained by us from the Schmidt reaction. All the scintillation counting for this degradation was done on the Packard Tri-Carb counter previously mentioned. Each sample was counted for six or seven 10-minute periods, after which 100 μl of toluene standard was added and the samples were then recounted for eight or nine 10-minute periods.

The counting of aniline was quite troublesome because it was found that the Ucon column used for the purification of the aniline was slightly contaminated, and an additional correction had to be made for this contamination by passing a benzene solution containing cold aniline through the column in the same manner as the ^{14}C-aniline had been

passed through, then counting and subtracting its activity from the activity in the aniline-^{14}C-sample. Since we were working with only a few cpm/μl, or a total activity of 50 to 150 counts above background, this type of correction is extremely undesirable. This is reflected in the poor agreement of the three aniline samples with one another and with the value obtained for the carbon dioxide by ionization chamber counting.

III RESULTS

A. Benzene-Toluene-Cycloheptatriene Yields

1. Mass and Activity Traces

Most of the mass and activity traces from the analyses for benzene, toluene, and cycloheptatriene will be shown. Only those traces containing no additional information are omitted. Since the determination of the activity in a compound is actually obtained from the printing register, several of the "tape plots" are also shown. Here we are plotting against time the number of counts occurring in successive 1-minute intervals, i.e., lines are drawn between the midpoints of histograms each 1 minute wide. Each trace and tape plot is identified by a symbol indicating the irradiation, followed by a number identifying the analysis, e.g., B7-3 is the third analysis of the sample from irradiation B7.

In the analysis of samples from irradiations B6 through B10, separate recorders, synchronized in time, were used for the mass and activity traces. Hence the rise of an activity trace should be seen to be delayed about 1/4 minute from the start of the corresponding mass trace. The activity and mass maxima should be displaced about 1/2 minute. In the analysis of samples from irradiations B11 through B13 the dual-pen recorder previously described was used, and the rises of the activity and mass traces should appear coincident. The maxima should be displaced about 1/4 minute.

In the illustrations to follow, the mass and activity traces are easily distinguished by the noisy nature of the activity trace. Where activity and mass peaks appear coincident and are labeled, the label applies to both the activity and mass peaks. When the label is meant to apply only to a mass or an activity peak, the label is followed by an M or A, respectively, in parentheses. Mass scale changes are not shown, as they have no bearing in this work. Activity scale changes are indicated, at the position made, on the illustrations. The initial

activity scale is indicated as the ordinate maximum.

Irradiation B4

Figure 24 shows a tape plot of the activity in the product of irradiation B4. This analysis was kindly made for us by Dr. Gunther Steinberg of the Shell Chemical Company--at the time it was made we did not yet have our proportional counting facilities. Either because the crude collection technique caused loss of the prebenzene compounds, or because Dr. Steinberg used a stainless steel proportional counter, there is no contamination apparent, and the background determined prior to sample analysis is used in calculating the activity in each component. In Fig. 24 we have subtracted the average background plus 1.5 times the standard deviation from the counts per minute, so that only 7% of the background contributions are expected to appear above the base line. The large peak labeled C_7 appears at the same time as ethyl benzene and m- and p-xylene. The peak appearing between toluene and C_7 may conceivably be due to cycloheptatriene, but this is unlikely, because cycloheptatriene should immediately follow toluene--if it is separated from toluene at all--since cycloheptatriene carrier was not added to this sample and it is possible that the peak labeled toluene may actually include any cycloheptatriene present.

Irradiation B5

This irradiation is invalid for the reasons given on p. 57.

Irradiation B6

In Figs. 25 and 26 the tape plots are superimposed on the mass and activity traces for B6 to illustrate the value of the tape plots in indicating the presence of small amounts of radioactivity--we are dealing here with less than 100 counts from any of the components of interest. The trace from B6-1 is not shown; it is similar to B6-2, but less presentable. In B6-2, shown in Fig. 25, it is evident that any radioactivity in benzene is obscured by the presence of other labeled compounds of similar retention time. The effluent benzene

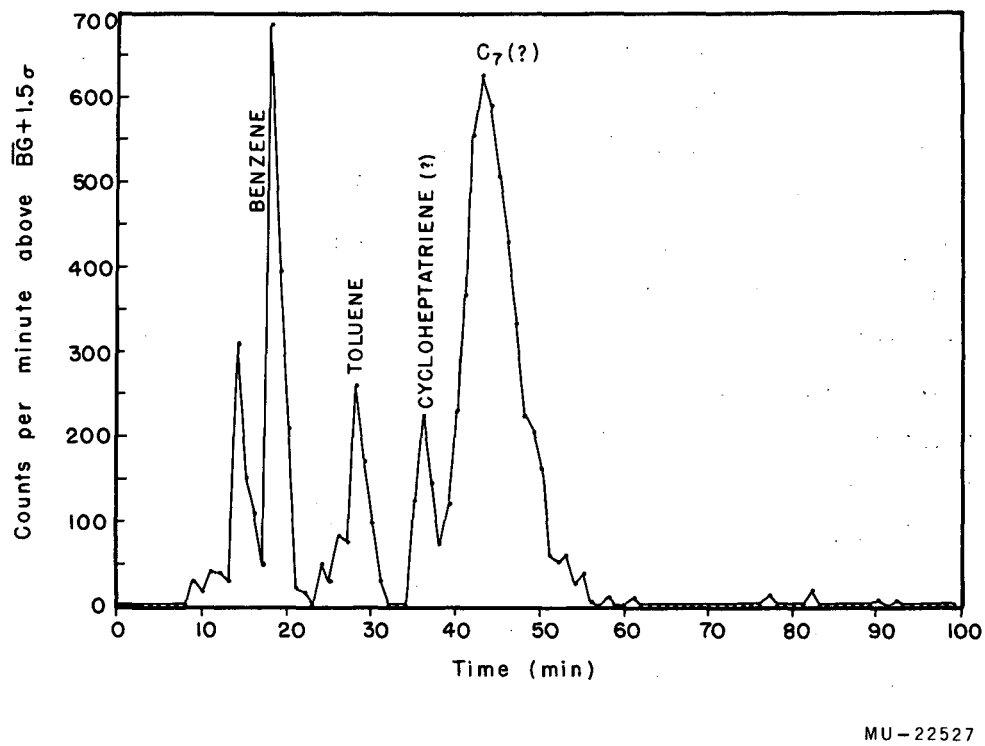


Fig. 24. B4. Plot of counts per 1-minute interval (tape plot) vs time. A silicone column was used for the GLC analysis.

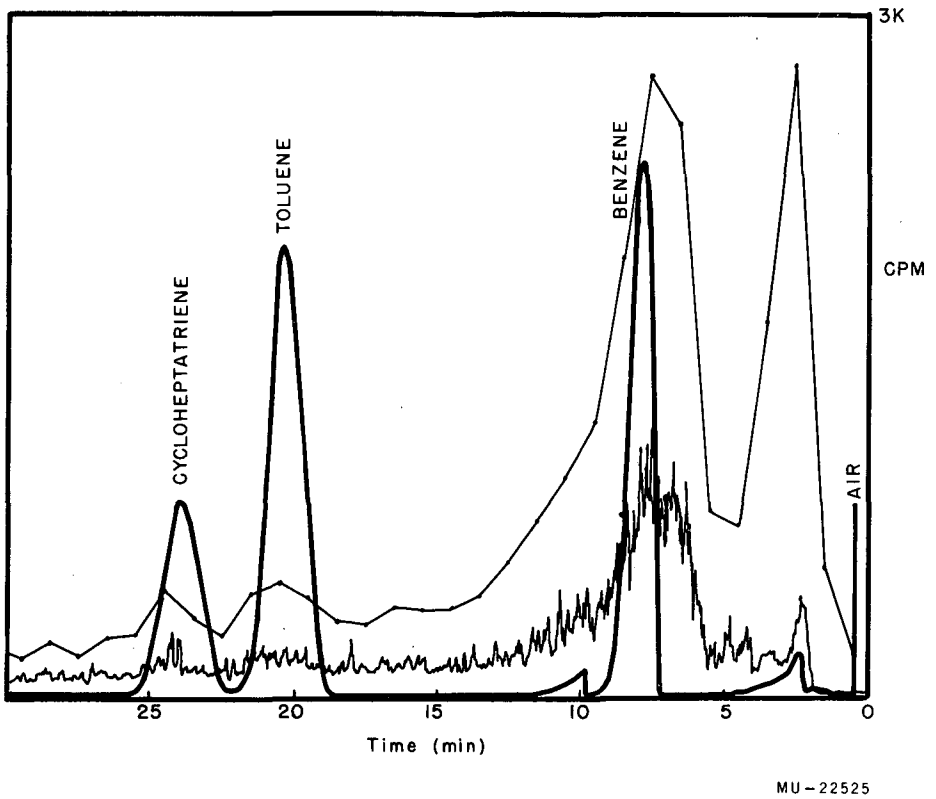


Fig. 25. Trace B6-2. The tape plot is superimposed on the mass trace (heavy, smooth line) and activity trace (light, jagged line).

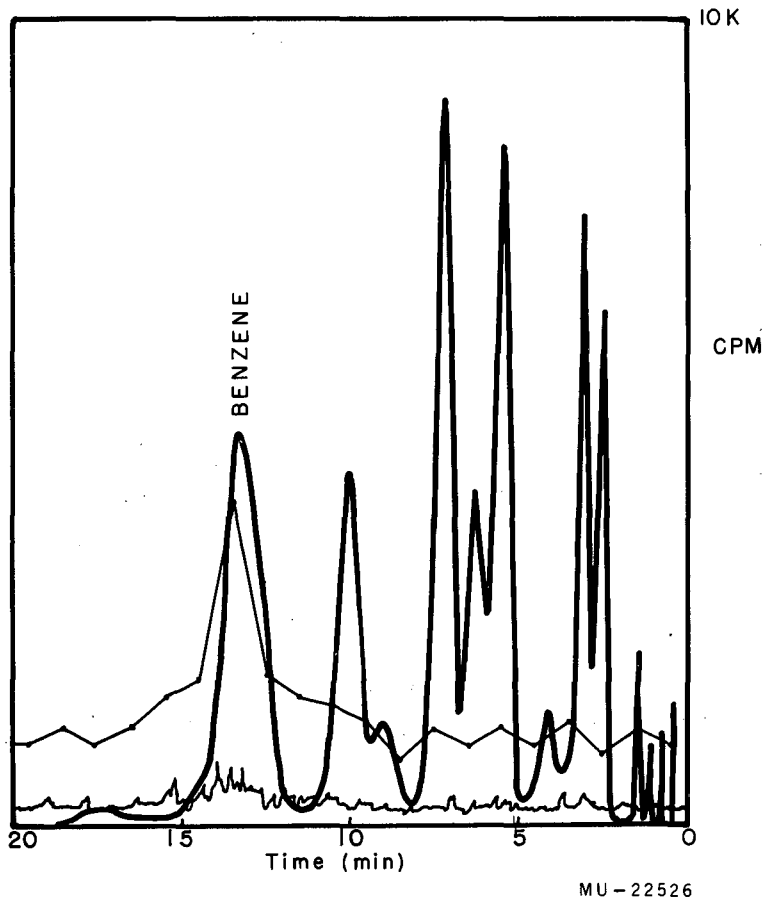


Fig. 26. B6-3. Tape plot is superimposed on the mass and activity traces.

from B6-2 was condensed in a receiver cooled in dry ice, thereby avoiding the co-condensation of the carrier-free radioactive compounds interfering with the benzene analysis. B6-3 shows the reanalysis of the benzene, the tape plot clearly indicating the presence of benzene-^{14}C. The mass peaks preceding benzene in B6-3 are due to impurities present in the methane carrier gas which were condensed along with the benzene from B6-2. In this case, technical grade methane was used without purification, and the mass trace from B6-3 was our first indication of the relatively large amounts of impurity in the methane. From then on cp grade methane was used as the carrier gas. The benzene mass peak in B6-3 is attenuated 16-fold relative to the other mass peaks, so that the amount of impurities present is not as great as it seems.

Irradiation B7

In B7 we have, for the first time, reasonable amounts of benzene, toluene, and cycloheptatriene, all ^{14}C-labeled. Observations are shown in Figs. 27 through 32. B7-1, B7-3, and B7-5 are analyses made 4, 8, and 10 days, respectively, after irradiation. Note the change in the prebenzene activity spectrum with time. By the time the analysis for B7-5 was made, active material not heretofore present overlapped the benzene activity peak. B7-2 is an analysis of a portion of the sample which had been treated with a small amount of 0.1 N sodium hydroxide. This analysis was made the same day as B7-3. Comparison of B7-2 and B7-3 shows a reduction in the prebenzene activity and a slight shifting of peak maxima in B7-2, but the loss in activity may well be due to handling rather than to the hydroxide *per se*. In B7-2 mass peaks due to ethyl benzene and the xylenes can be seen. There was no detectable activity in these C_7 compounds. Since a large C_7 peak was found in the analysis of material from B4, C_7 activity was sought in subsequent irradiation; when it was not found in B7, where relatively large amounts of benzene, toluene, and cycloheptatriene were present, it was thought that the C_7 peak in irradiation B4 must have been due to an artifact, and C_7 carriers were no longer added in the

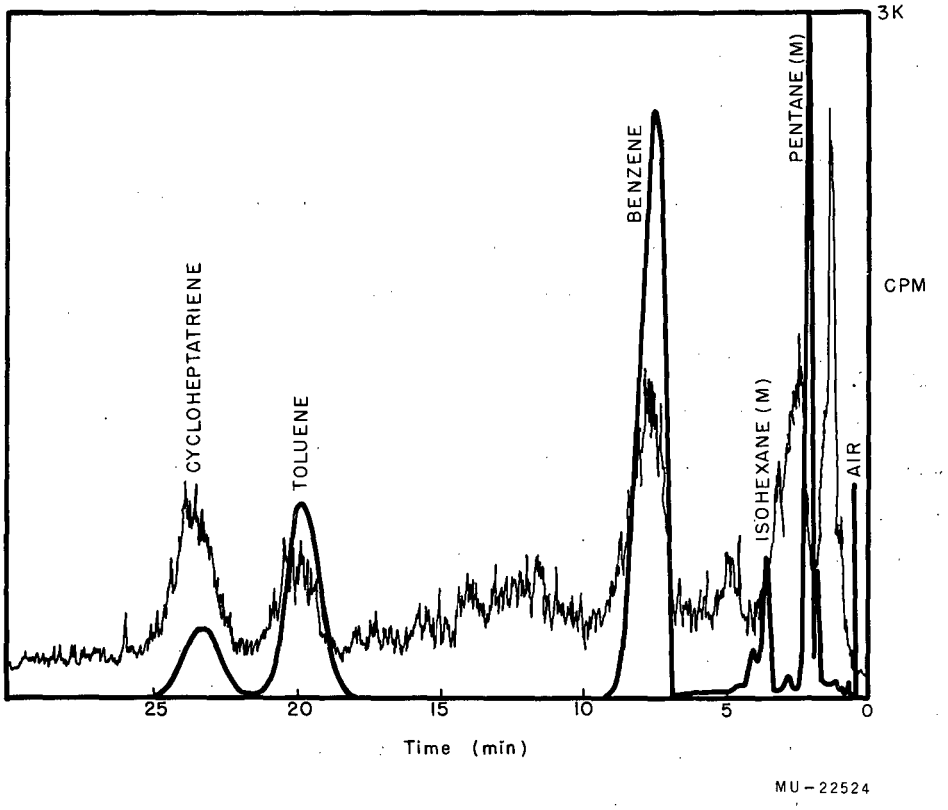


Fig. 27. B7-1, four days after collection.

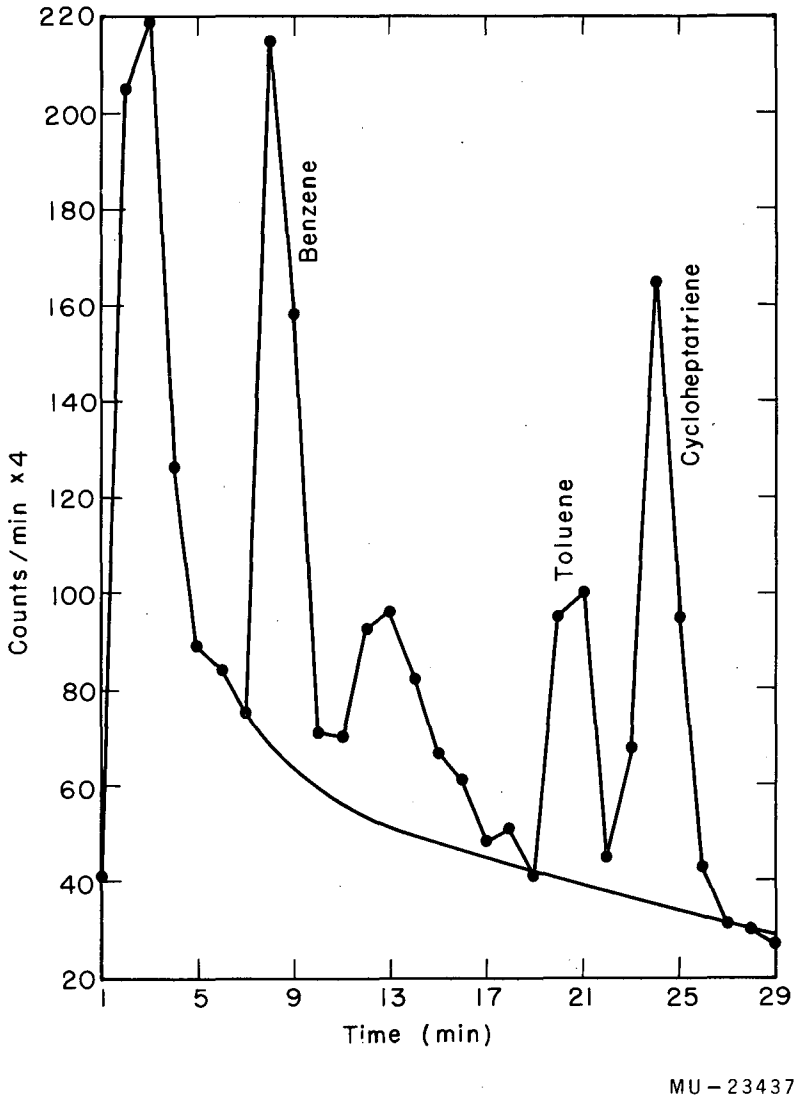


Fig. 28. Tape plot of B7-1. Note the curving background level drawn in.

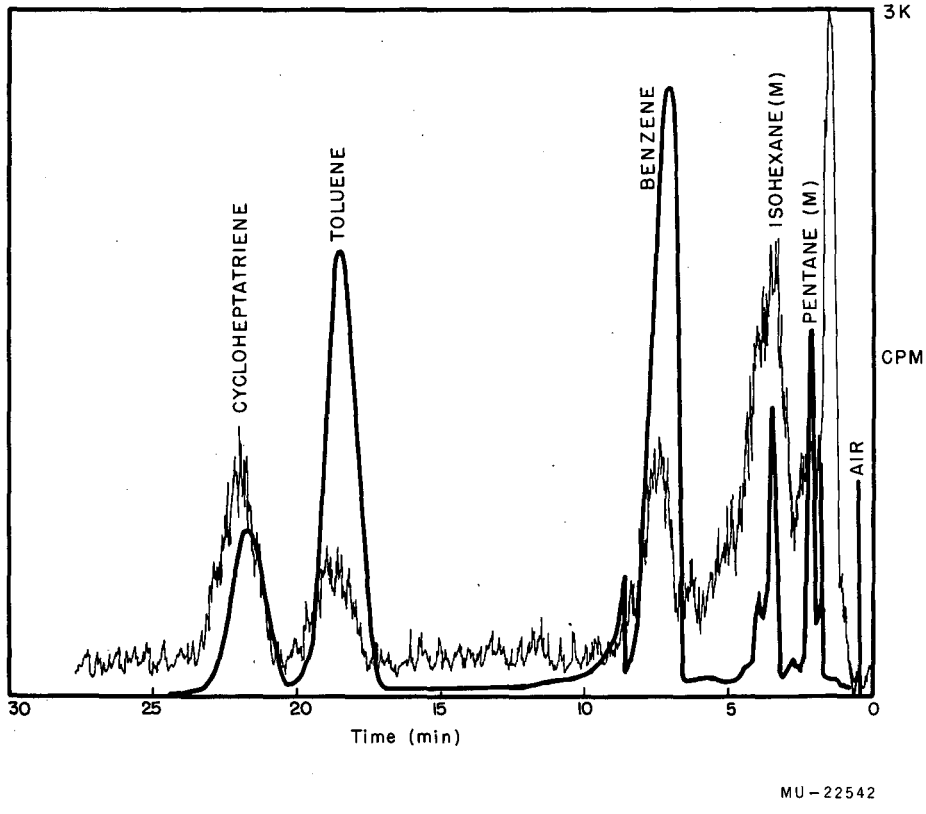


Fig. 29. B7-3, eight days after collection.

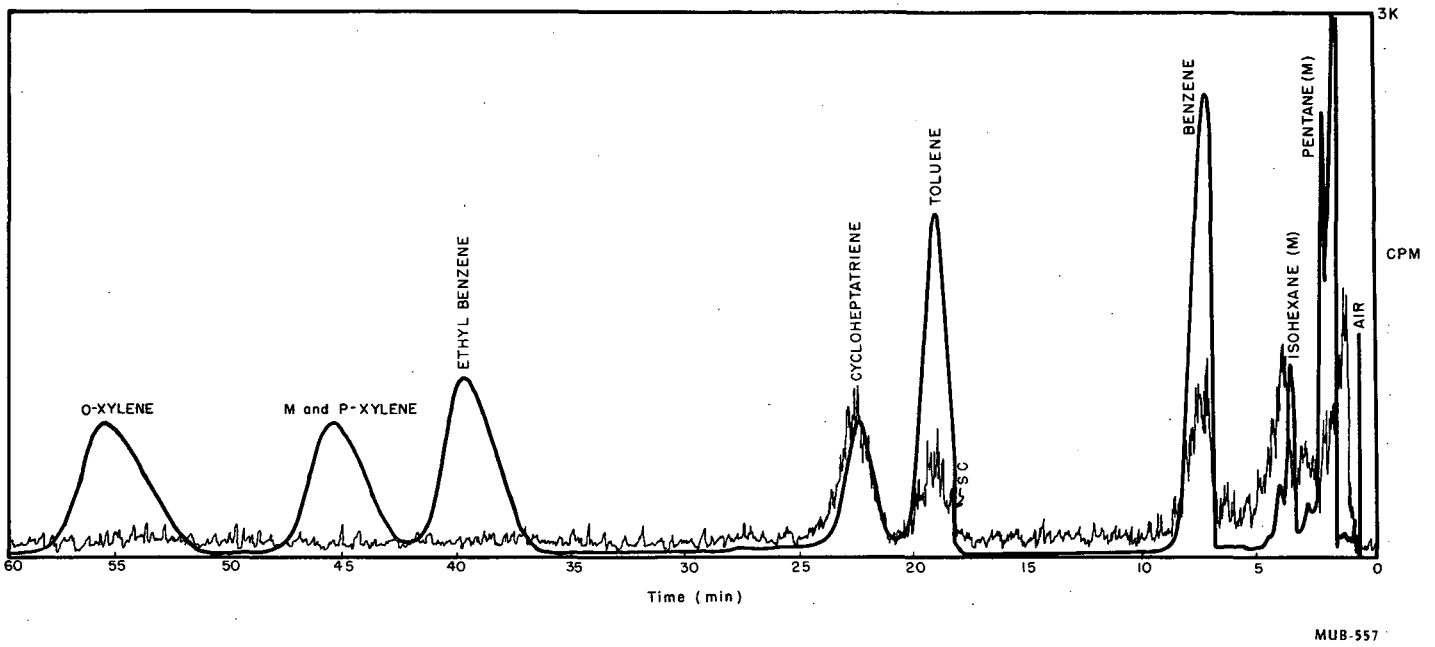


Fig. 30. B7-2, eight days after collection, treated with 0.1 N NaOH before analysis.

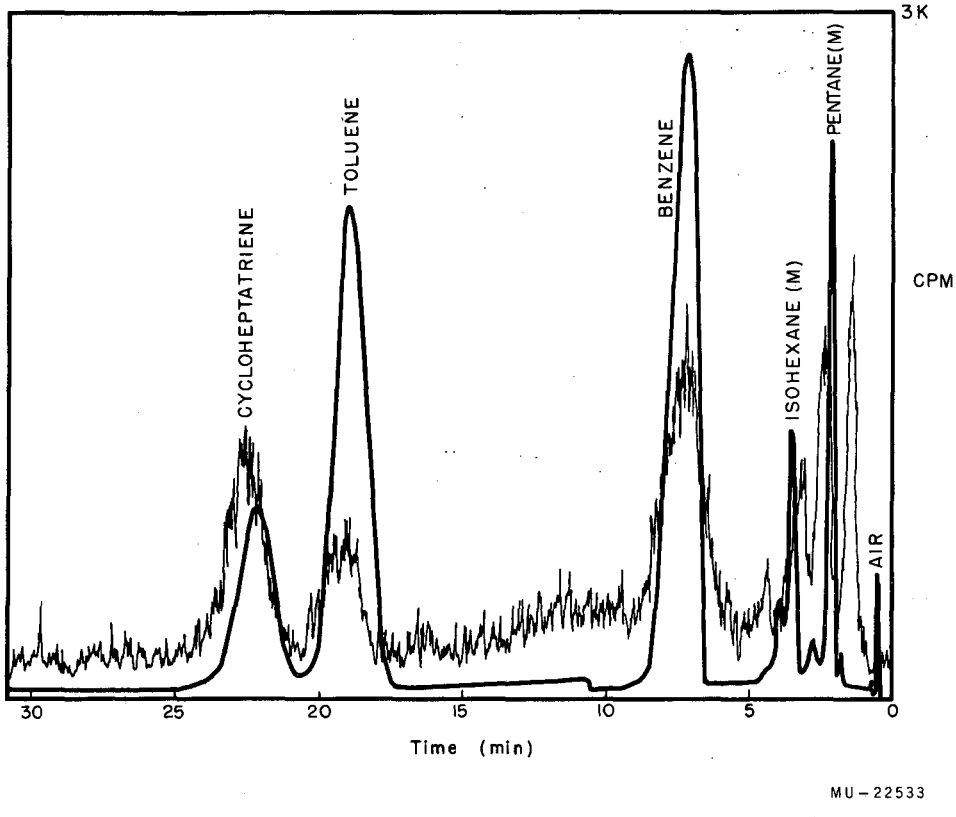


Fig. 31. B7-5, ten days after collection.

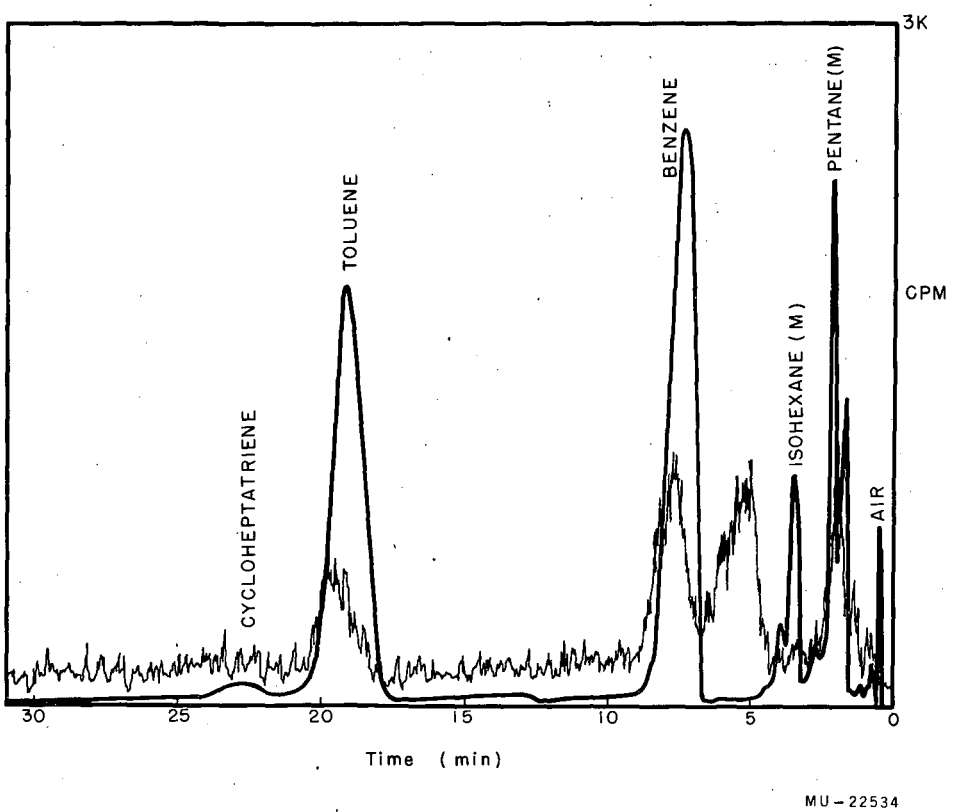


Fig. 32. B7-4, ten days after collection, treated with bromine before analysis.

irradiations following B7. As we shall see later, C_7 activity mysteriously reappeared in the product of irradiation B11.

B7-4 shows the analysis of a portion of the sample that had been treated with 1 μl of bromine. This treatment and analysis were made the same day as was B7-5. Comparison of B7-4 and B7-5 shows that bromination has a marked effect on the prebenzene spectrum, old activity peaks disappearing and new ones arising. The active material overlapping benzene in B7-5 is seen to have been removed by bromination in B7-4. Almost all of the cycloheptatriene was removed by bromination, confirming that identification if additional confirmation is needed. The benzene and toluene activity peaks remain, as they should, strengthening their identification. The small residue of cycloheptatriene seen in the mass trace is matched by a small residue of activity, not easily detectable from the activity trace but clearly evident from the tape plot. Since most or all of the prebenzene compounds were expected to be unsaturated, there was hope that bromination would completely clear away the interfering activity in those compounds, and the appearance of new activity peaks preceding benzene was somewhat puzzling for a while. It was eventually concluded that they must be due to hydrobromination, the HBr resulting from bromination of a small amount of the toluene. This conclusion is confirmed by the fact that bromination produced about the same effect in the prebenzene material from irradiation B10 as did hydrobromination.

Figure 28 shows the tape plot of the activity in B7-1. It is shown primarily to illustrate the difficulties we had with counter contamination, which resulted in variation of background during an analysis. A tape plot taken alone can be very misleading, and must be used in conjunction with the mass and activity traces for determination of the proper background slope. Even then, choice of background in the benzene area is somewhat arbitrary, to say the least. In B7-1, observation of the mass and activity traces of benzene showed that no benzene activity should appear during the seventh minute but should appear during the eighth, ninth, and tenth minutes. Furthermore, observation of the

activity traces from this and the other analyses showed that desorption of contamination activity occurs exponentially, as would be expected. Hence, a smoothly curving background level was indicated. For that reason, and also because it is certain that benzene activity is appearing during the tenth minute, we would not want to draw a line between the seventh and tenth minutes and take that for the effective benzene background, as might appear reasonable from a casual observation of the tape plot alone. For toluene and cycloheptatriene the choice of the local background level is much easier than for benzene, but still cannot be done casually. Careful consideration of the mass and activity traces, showing the time intervals during which activity due to toluene or cycloheptatriene must be occurring, is needed for proper choice of background. Although it appears from the tape plot that activity resolution of toluene and cycloheptatriene is not complete, such is not actually the case, and the activity appearing during the twenty-second minute can be seen from the traces to be due entirely to toluene in this case.

The background determinations, or rather estimates, in all the analyses of the radiation products were (a) made only after careful observation of the mass and activity traces, (b) made in a consistent manner for all the analyses, and (c) not changed, once made, regardless of the disturbing (although not surprising) lack of reproducibility in some cases.

Irradiation B8

This is shown in Fig. 33. Note the scale change to 3K preceding the benzene peak in B8-1.

Irradiation B9

B9-1, not shown, had a very sharply falling background level during the passage of benzene, and the benzene, toluene, and cycloheptatriene effluent from B9-1 was condensed in dry ice for rechromatography. B9-2 (Fig. 34) shows the reanalysis of those compounds. Collection of effluent is not quantitative (80 to 85%), and varies slightly

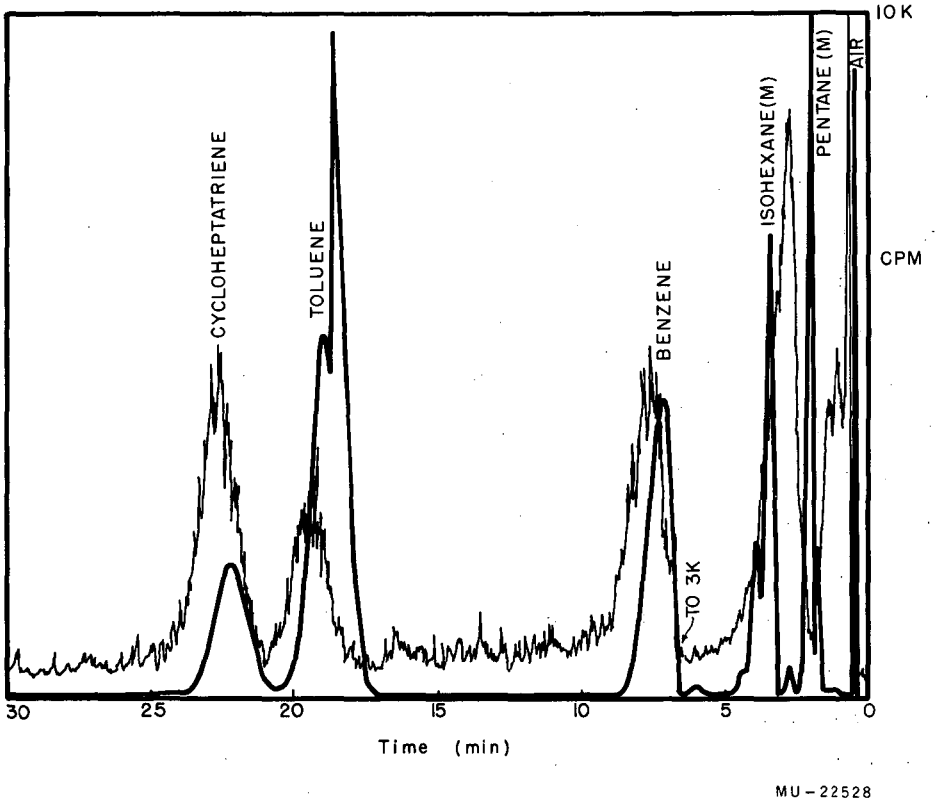

10 K
CPM
CYCLOHEPTATRIENE
TOLUENE
BENZENE
TO 3K
ISOHEXANE(M)
PENTANE (M)
AIR
30
25
20
15
10
5
0
Time (min)
MU-22528

Fig. 33. B8-1.

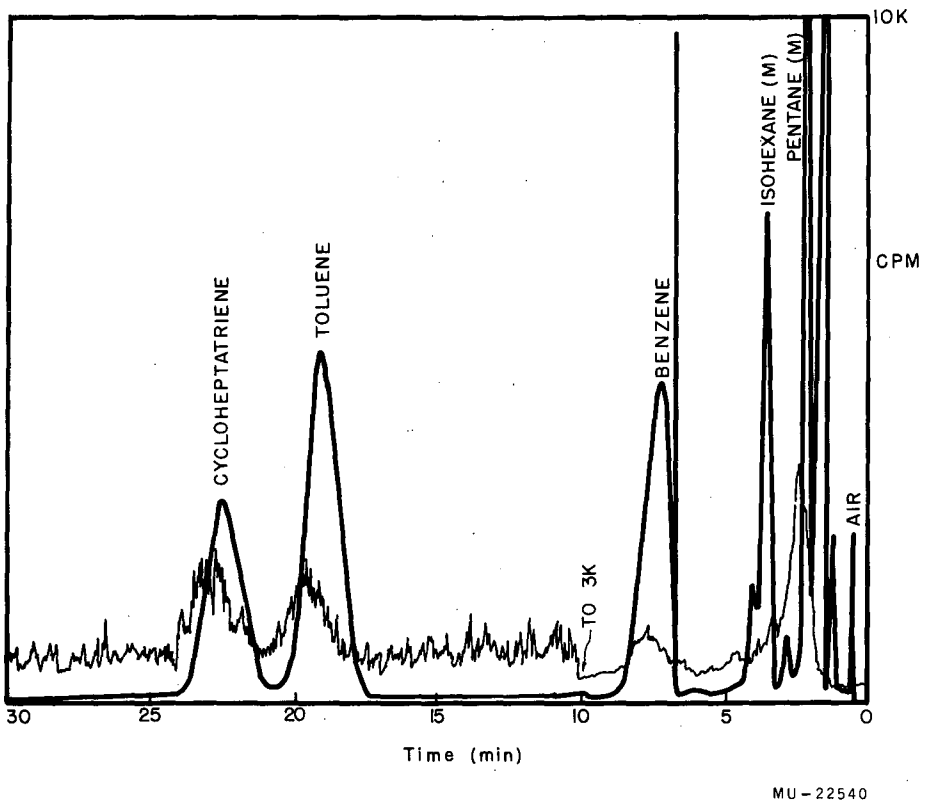

10K
CPM
CYCLOHEPTATRIENE
TOLUENE
BENZENE
ISOHEXANE (M)
PENTANE (M)
AIR
TO 3K
30
25
20
15
10
5
0
Time (min)
MU-22540

Fig. 34. B9-2.

from compound to compound. Hence the areas under the mass peaks are used for the calculation of activity in condensed and rechromatographed samples. Activities calculated from B9-1 are in excellent agreement with those from B9-2, which is surprising and doubtless fortuitous in the case of benzene, since the background level was falling very rapidly in B9-1.

Irradiation B10

B10 was the first all-low-energy irradiation, and since the yields of benzene, etc., were reduced, the problem of contamination is relatively more serious. Figure 35, showing B10-1, illustrates the sharply falling contamination level in the area of benzene; note the scale change immediately preceding the emergence of benzene. Figure 36 shows the tape plot from B10-1, on which benzene activity appears as a shoulder, or plateau, on the sharply falling background slope. This tape plot is shown as an illustration of contamination at its worst, or, more exactly, as an illustration of the greatest amount of contamination encountered that still allowed an estimate of the component activities. The effluent from B10-1 was condensed and rechromatographed, but with only slight improvement in the resolution of the benzene peak. A portion of the B10 sample was treated with bromine, the analysis of which is shown in Fig. 37. Although treatment with bromine did not remove all the prebenzene contaminants, it helped a great deal, the background falling much less rapidly near benzene in B10-3 than in B10-1 and B10-2. The yields from all the irradiations are tabulated later, but it is worth mentioning that the relative standard deviation for four B10 benzene determinations, made under widely differing degrees of background contamination, is about 9%. This figure is not cited as a desirable degree of reproducibility, but it is, perhaps, a good deal better than might be expected from observation of the B10-1 tape plot shown in Fig. 36.

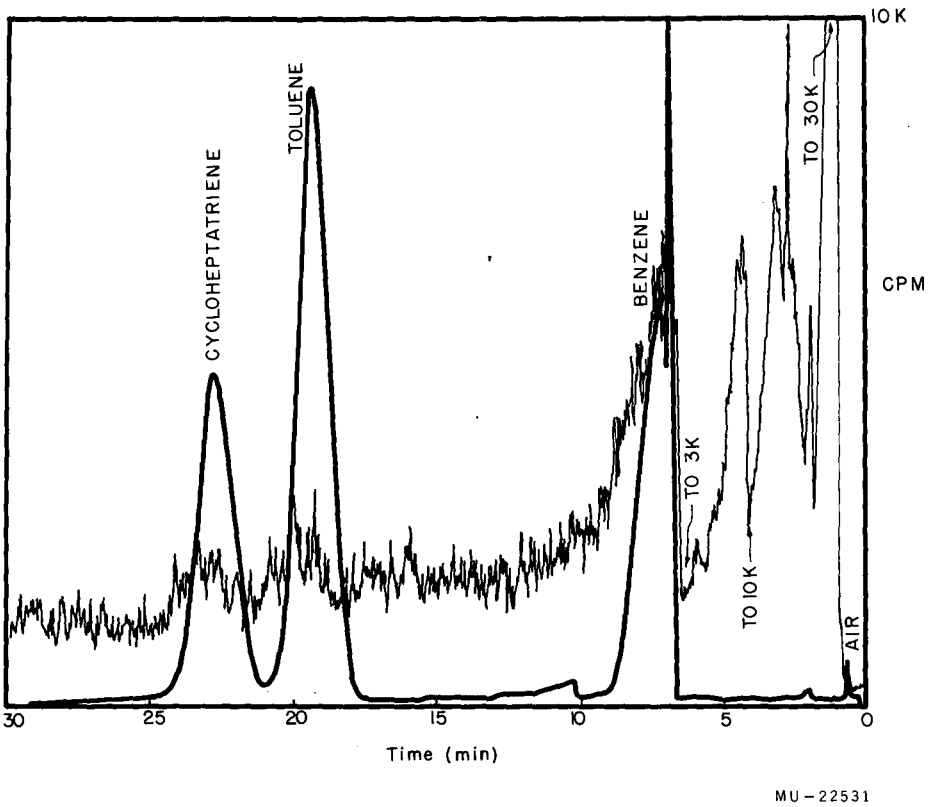


Fig. 35. B10-1. Note the several changes on the activity scale.

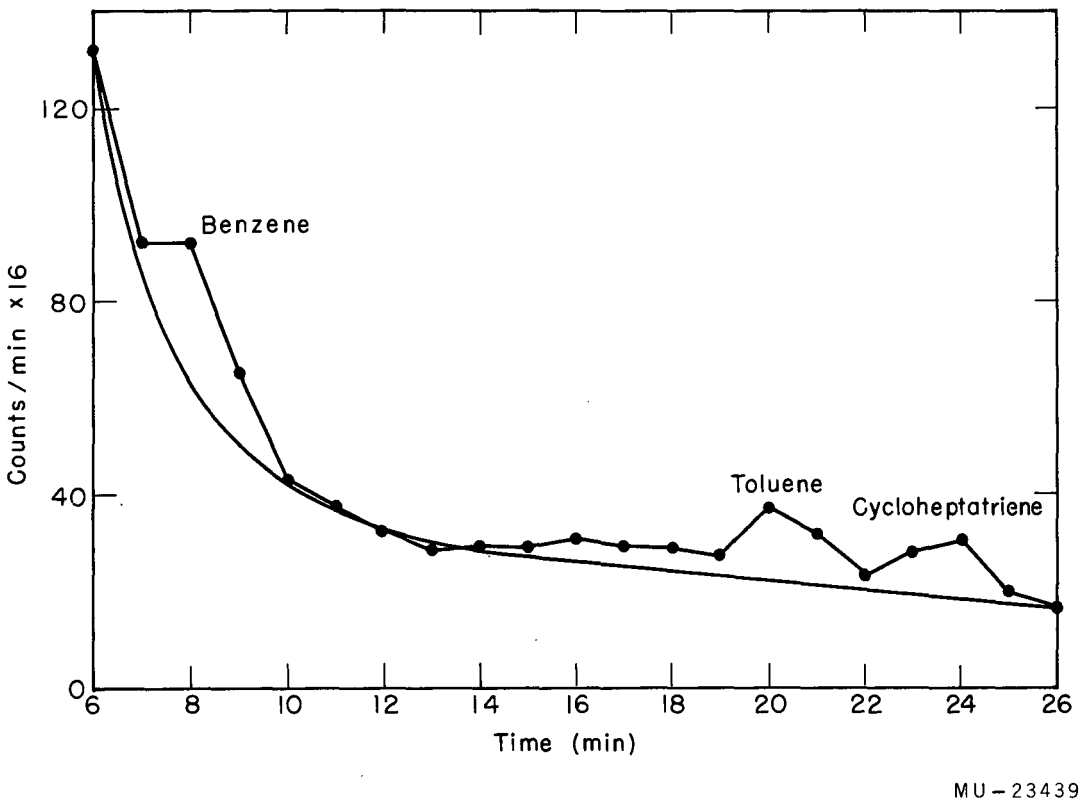


Fig. 36. Tape plot of B10-1. Note the rapidly falling background level in the benzene region.

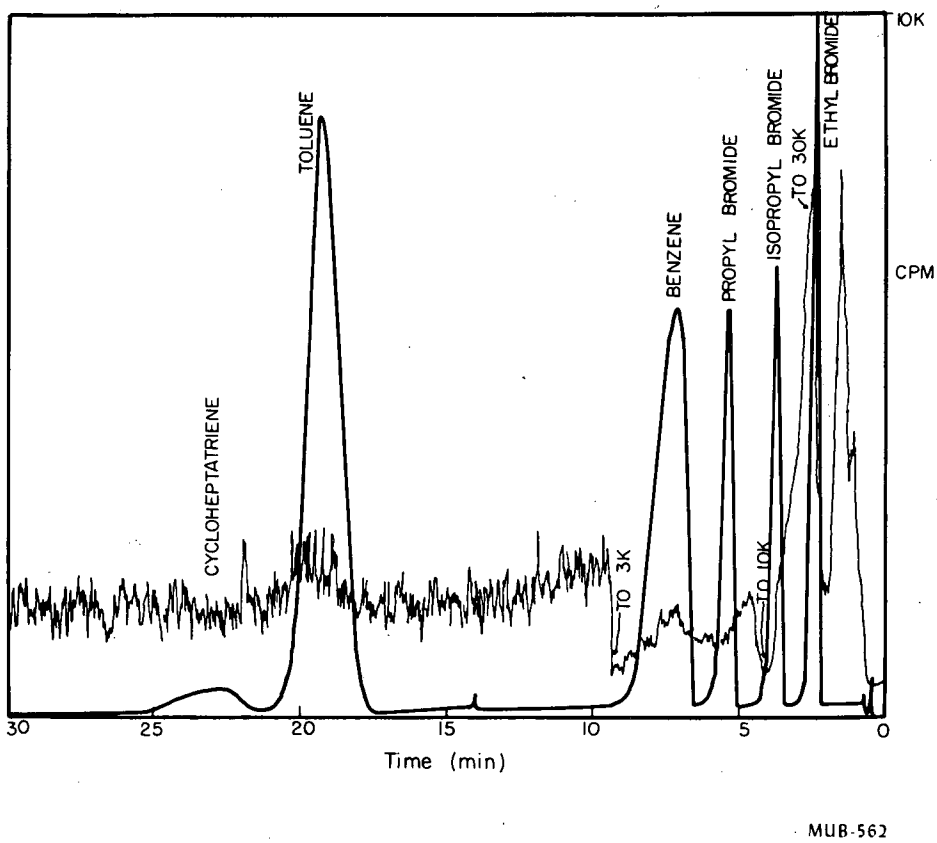


Fig. 37. B10-2. Sample treated with bromine before analysis.

An attempt was made to correlate some of the new activity peaks appearing after bromination with ethyl, propyl, and isopropyl bromide, as shown (in Table IX) for B10-3. Although it appears as though ethyl bromide does coincide with an activity peak, close inspection indicates that it cannot, in fact, be coincident.

Irradiation B11

Analysis of the first portion of sample from B11 was interrupted by a power failure, which occurred shortly after benzene had emerged from the column and ended in the middle of the emergence of toluene. The values obtained for the activity in benzene and cycloheptatriene are useful, but the trace is not shown. This unfortunate lapse on the part of the power company brings home the insufficiently appreciated point that gas chromatography, in addition to its obvious power and utility, is virtually unique in present-day chemistry in being independent of electricity in its fundamental operation. Counting may cease, the recorder may come to a halt, the furnace may cool off, but chromatography survives.

Another portion of sample was analyzed and the trace of that analysis is shown in Fig. 38. Figure 39 shows the tape plot from the same analysis. Note the scale change to 3 K shortly before the emergence of benzene in B11-2. The counter was gold-plated on the inside in this analysis, resulting in considerable decrease in the degree of contamination. Unfortunately, as mentioned earlier, the gold plating sloughed off upon cleaning, and the counter was not replated. The prebenzene area from B11-1 and B11-2 was trapped separately for further analysis, and the benzene, toluene, and cycloheptatriene from B11-1 and B11-2 were trapped separately and pooled for a later analysis, shown in Fig. 40. Note the scale change to 10 K shortly after the benzene peak appeared and went off scale. The peak immediately preceding benzene is on the 3 K scale and is not as serious a contaminant as it appears at first glance. In this figure, activity peaks in the C_7 region are clearly seen for the first time since irradiation

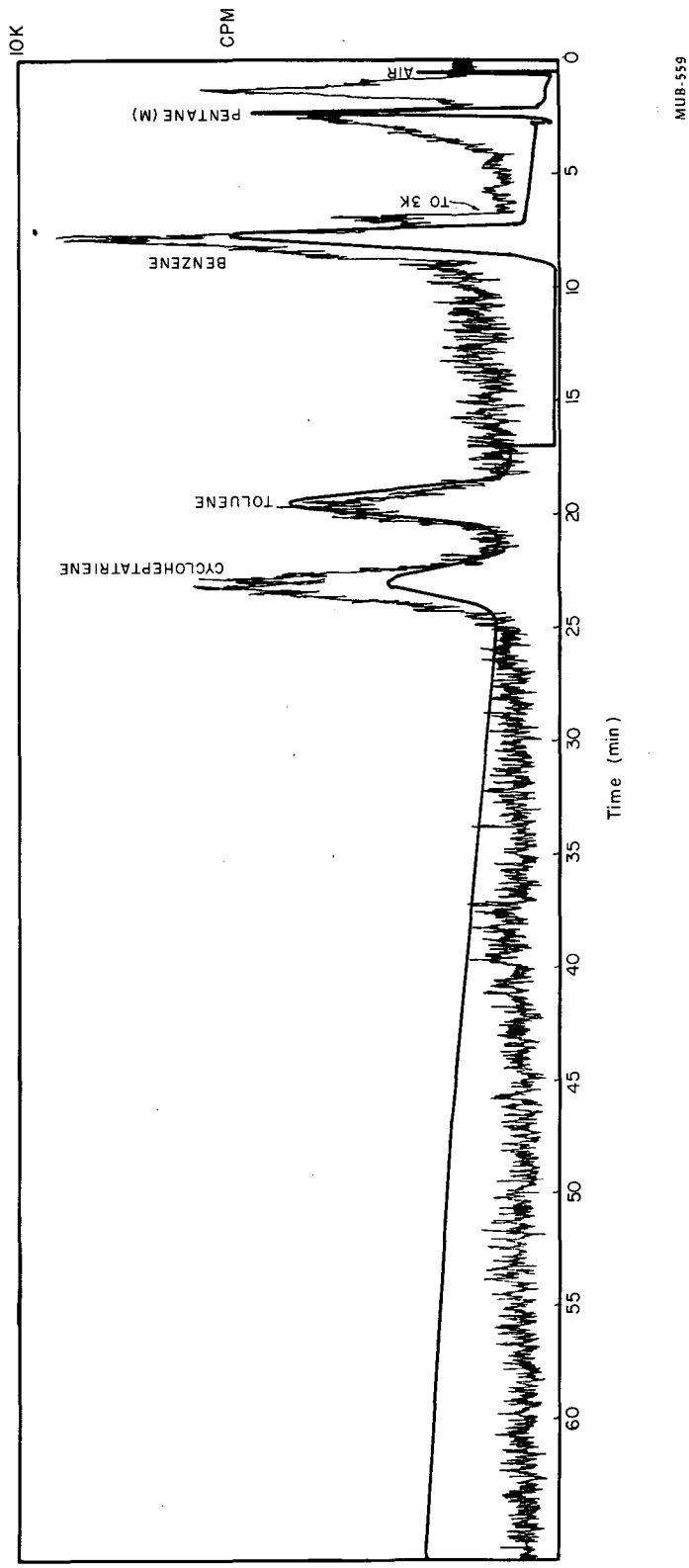

10K
CPM
AIR
PENTANE (M)
TO 3K
BENZENE
TOLUENE
CYCLOHEPTATRIENE
0
5
10
15
20
25
30
35
40
45
50
55
60
Time (min)
MUB-559

Fig. 38. B11-2.

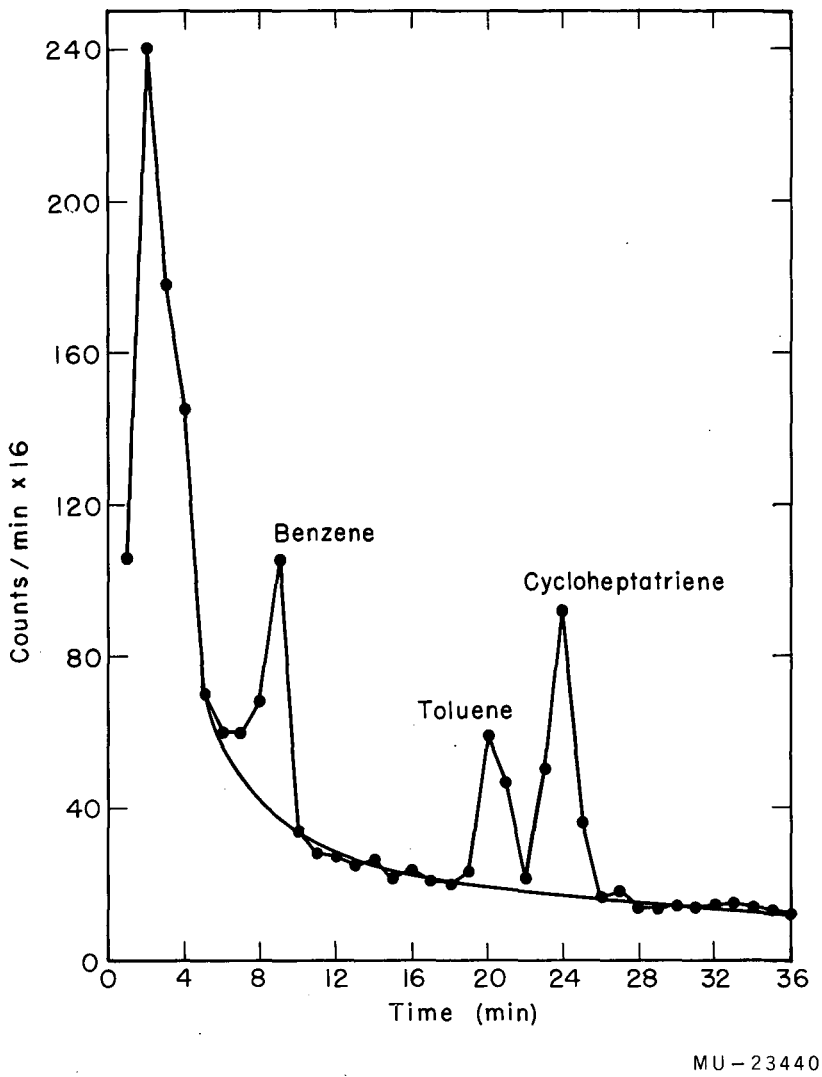


Fig. 39. Tape plot of B11-2.

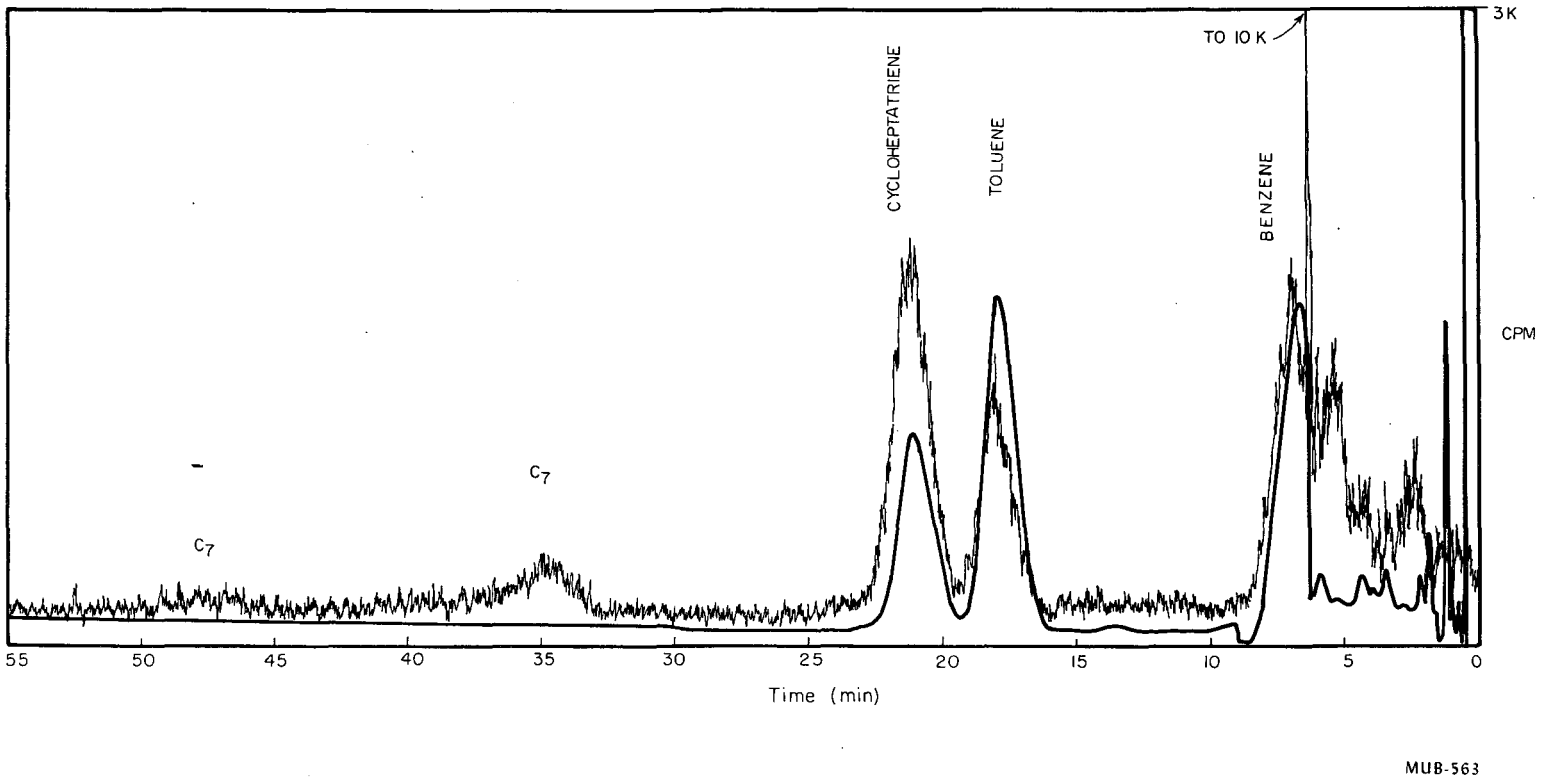


Fig. 40. B11-15: re-analysis of the condensate from B11-1 and B11-2. Note that the scale was changed after the benzene activity trace went off scale.

B4. The peak at about 35 minutes is approximately where ethyl benzene would be expected to emerge, and the barely discernible peak at 48 minutes is in the proper position for o-xylene. These C_7 peaks can also be seen in the trace B11-2, but they were not noticed at the time that analysis was made, so no C_7 carrier was added for the later analysis shown in Fig. 40.

Irradiation B12

In Fig. 41, showing analysis B12-1, the worst case of contamination is illustrated. Benzene is not detectable at all, and benzene and toluene and cycloheptatriene are barely noticeable. It should be noted that the contamination level is on the 10 K scale in the benzene-through-cycloheptatriene area--that is, the degree of contamination is approximately 6000 cpm. The counter was dismantled and cleaned, and a new strategy was used for analysis B12-2, shown in Fig. 42. Here the counter was not attached to the exit of the GLC unit until immediately before benzene emerged, thereby avoiding contact with most of the contaminating prebenzene compounds. The benzene activity peak is still obscured, but toluene and cycloheptatriene are analyzable in this case. Benzene was analyzed by rechromatographing the benzene condensate trapped separately from B12-1 and B12-2. This reanalysis is shown in Fig. 43, where it can be seen that the benzene activity is still obscured by other active compounds coinciding with benzene. The benzene from this analysis was condensed and treated with a small amount of bromine and again reanalyzed, as shown in Fig. 44. Here it can be seen that most of the impurities have been removed, only a small activity peak immediately preceding benzene remaining in the immediate area of benzene. In this case, there is virtually no counter contamination from the small amounts of prebenzene compounds remaining, and the extent of overlap of the small peak preceding benzene can be readily calculated.

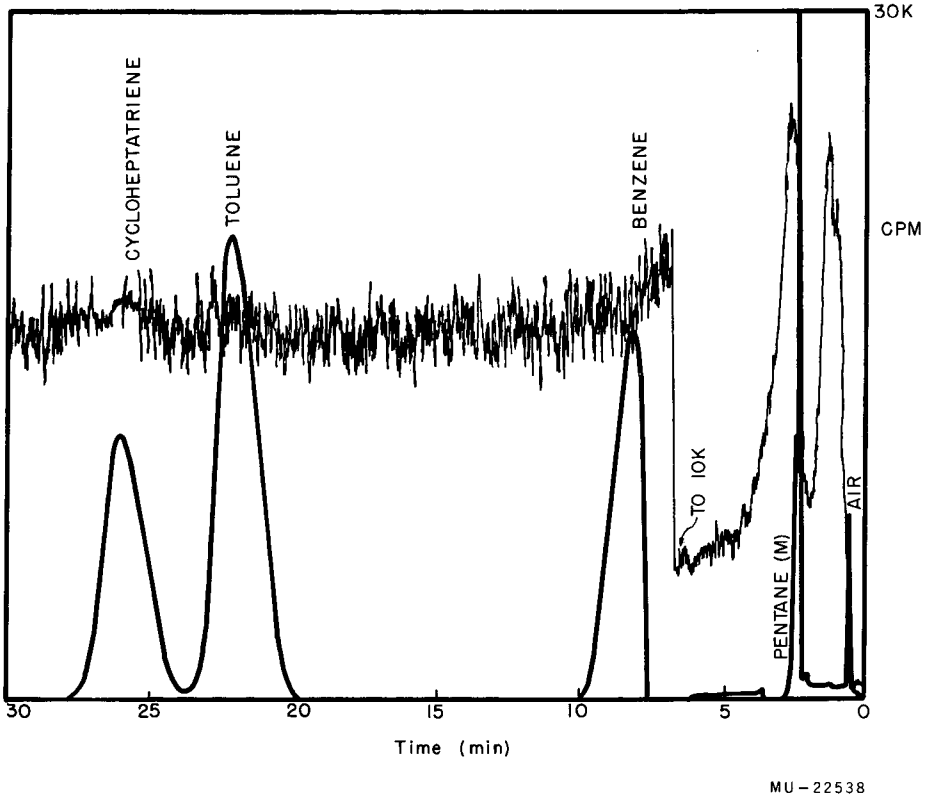


Fig. 41. B12-1. Note the extreme contamination--approx 6000 cpm.

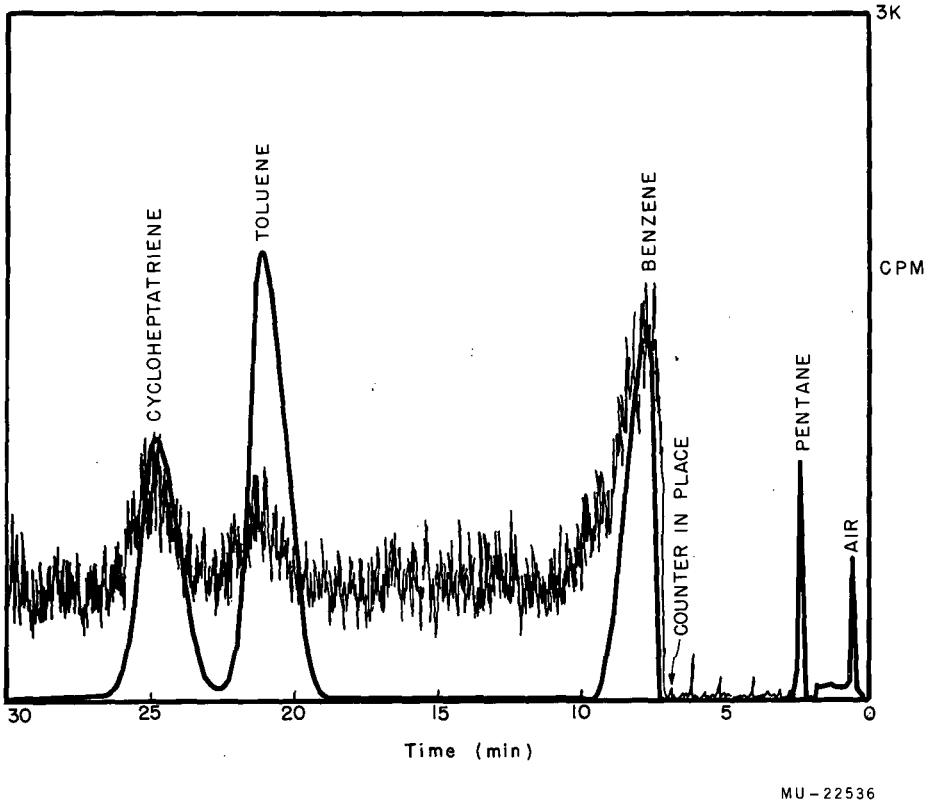


Fig. 42. B12-2. The counter was not attached to the GLC outlet until benzene began to emerge.

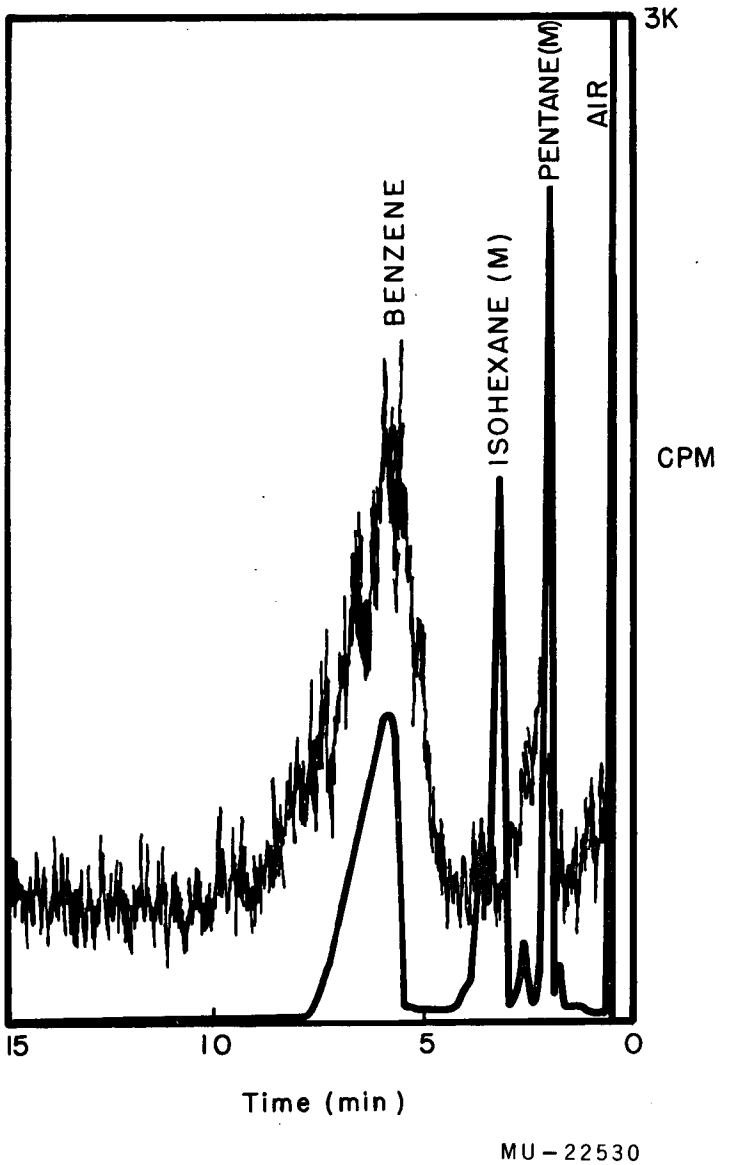
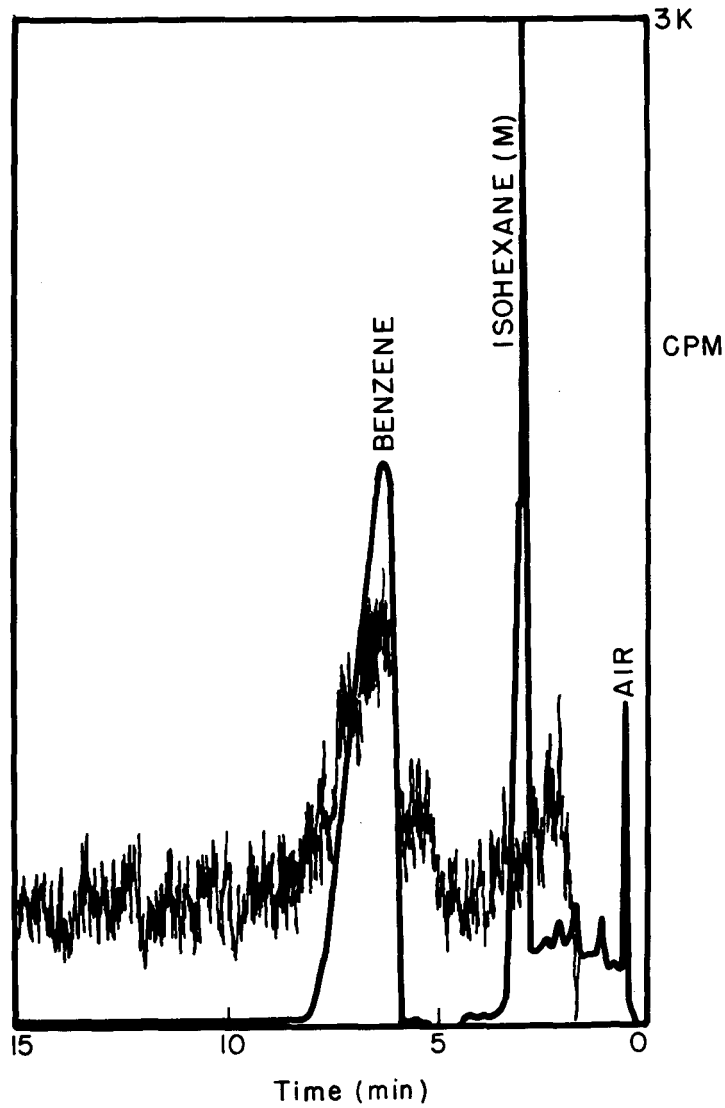


Fig. 43. B12-15. Reanalysis of the benzene condensate from B12-2.



MU-22529

Fig. 44. B12-16. Reanalysis of the benzene condensate from B12-15, treated with bromine before analysis.

Irradiation B13

Here, again, counter contamination caused great difficulty in the analysis, and in Fig. 45, showing analysis B13-1, there is no benzene activity detectable even on the tape plot. Another portion of the sample from B13 was chromatographed without counting and the benzene, toluene, and cycloheptatriene were condensed and then analyzed, as shown in Fig. 46. This technique succeeded in eliminating contamination, allowing the small amounts of activity from this 45-volt irradiation to be estimated.

2. Tables of Data and Explanatory Remarks for Benzene, Toluene, and Cycloheptatriene Yield

The yields of benzene, toluene, and cycloheptatriene are calculated as described in II, B-1-b from the data presented in Tables VIII and IX. Consideration of the yields for B9, the mixed-energy irradiation, must await discussion of the yield trends observed for the other irradiations.

The only parameter involved in the yield calculation that requires further comment is V_t, the total volume of sample. In irradiations B7, B10, B11, and B12, determination of V_t gave no difficulty and was calculated as described previously. Determination of V_t for the other irradiations was not without complication, especially in irradiation B8, where most of the sample was lost, and these will be discussed here.

In irradiation B4 approximately 450 μl of benzene was estimated to have been admitted into the isotope separator, but the GLC mass trace areas for toluene and benzene indicated that only 328 μl of benzene was present--600 μl of toluene had been added to the collected benzene by pipette and hence was accurately known. Therefore, a total volume of 930 μl, rather than the 1050 μl estimated, was used for the yield calculations in B4. In B6 the amount of benzene admitted was roughly estimated from the vapor pressure of benzene at 0° for the pre-irradiation input and at -78° for the input during irradiation.

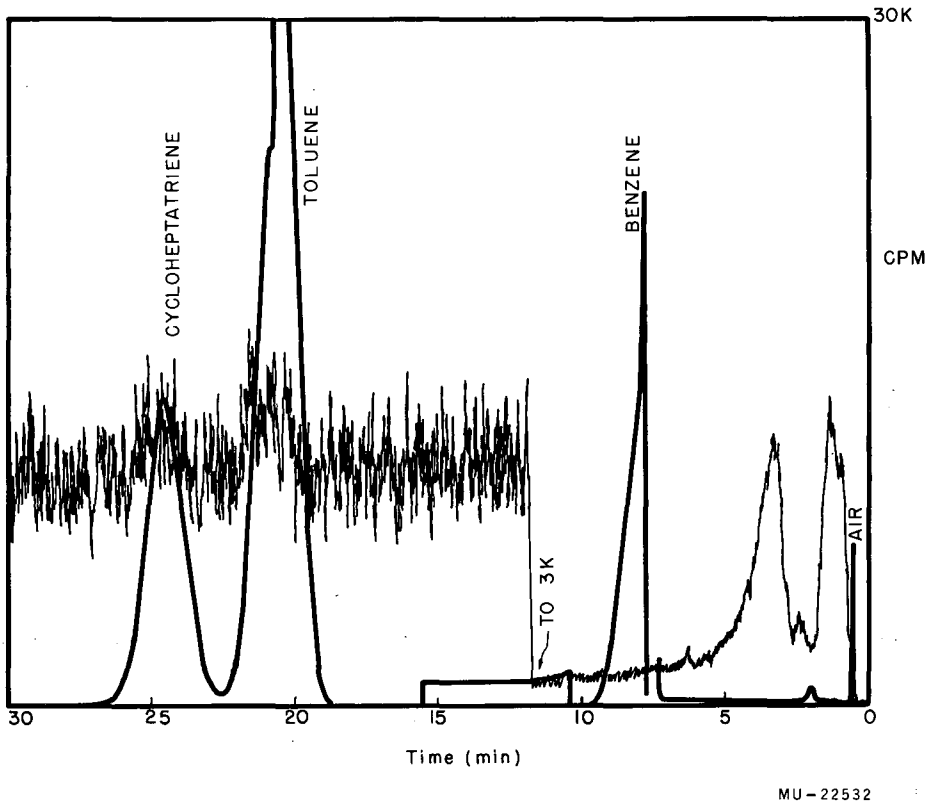


Fig. 45. B13-1. Contamination is more than 1000 cpm.

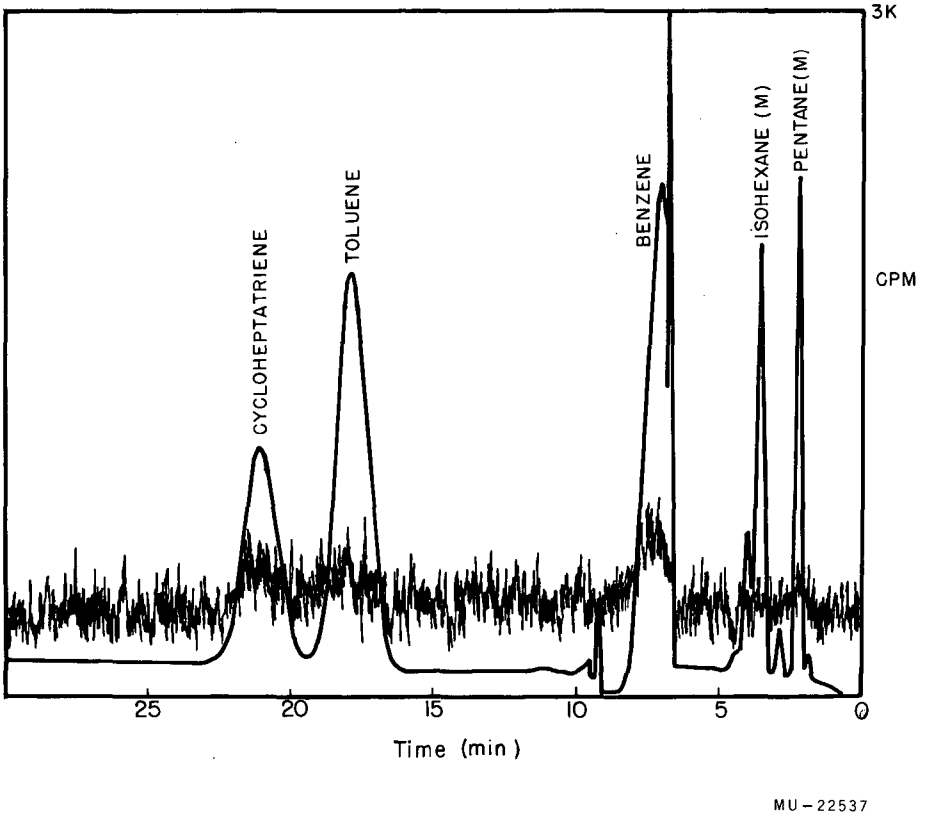


Fig. 46. B13-19. Analysis of the condensate from prior GLC passage. Note the elimination of the prebenzene compounds.

Table VIII. Benzene, toluene, and cycloheptatriene yield data for the high-energy irradiations

5000-ev irradiations	N^-			V_a (μl)	e (%)	V_c (cc)	f (cc/min)	V_t (μl)	A^-			A_T^o (dpm ×10^6)	Yield		
	Benzene (counts)	Toluene (counts)	Cyclohepta-triene (counts)						Benzene (dpm×10^3)	Toluene (dpm×10^3)	Cyclo-heptatriene (dpm×10^3)		Benzene (%)	Toluene (%)	Cyclo-heptatriene (%)
B4	1495	762	-	440	75	150	250	930[a]	7.01	3.58	-	0.240	2.92	1.49	
B6-1	-	68.8	55.2	13.8	50.9	16	26.9	270[a]	-	4.37	3.52	0.805	-	0.54	0.48
B6-2	-	121	78	29.0	50.9	16	26.9	270[a]	-	3.66	2.36		-	0.42	0.29
B6-3	190	-	-	29.0	50.9	16	26.9	270[a]	5.75	-	-		0.72	-	-
B7-1	1004	488	924	30.2	52.1	16	26.9	280	30.1	14.6	27.7	1.47	2.05	0.99	1.88
B7-2	668	528	1020	29.0	48.5	16	26.9	280	22.3	17.6	34.1	1.47	1.52	1.20	2.32
B7-3	656	516	1000	30.2	48.5	16	26.9	280	21.0	16.6	32.1	1.47	1.43	1.13	2.18
B7-4	1060	532	144	28.0	50.0	16	27.7	280	37.6	18.4	4.98	1.47	2.56	1.25	-
B7-5	-	592	1140	31.2	50.0	16	27.7	280	-	18.4	35.4	1.47	-	1.25	2.41
B11-1	2580	-	3360	15.0	60.9	16	28.2	228	114		148	8.99	1.27	-	1.65
B11-2	1520	1216	2100	9.9	60.9	16	28.3	228	102	81.5	135	8.99	1.14	0.83	1.57
B11-15	5860	4760	9030	30.0	91.5	15	28.2	228	91.4	74.1	141	8.99	1.02	0.91	1.50
B8-1	1180	880	1882	30.6	53.8	15.1	28.0	$\left(\begin{matrix}592\\ \times 1.92\end{matrix}\right)^a$	151	113	242	10.8	1.40	1.07	2.25

[a] V_t estimated as described in III-2.

Table IX. Benzene, toluene, and cycloheptatriene yield data for the low-energy irradiations

Low-energy irradiations	N^- Benzene (counts)	N^- Toluene (counts)	N^- Cyclo-heptatriene (counts)	V_a (μl)	e (%)	V_c (cc)	F (cc/min)	V_t (μl)	A^- Benzene (dpm×10^3)	A^- Toluene (dpm×10^3)	A^- Cyclo-heptatriene (dpm×10^3)	A_T^o (dpm ×10^6)	Yield Benzene (%)	Yield Toluene (%)	Yield Cyclo-heptatriene (%)
90 ev															
B10-1	720	491	438	31.6	56.4	15.5	27.5	174	12.5	8.52	7.59	3.31	0.39	0.26	0.23
B10-2	608	320	280	28.7	56.4	15.5	27.5	174	11.6	6.81	5.83	3.31	0.35	0.21	0.18
B10-3	593	477	-	32.2	56.4	15.5	27.5	174	10.6	8.12	-	3.31	0.32	0.24	-
B10-4	421	248	249	22.5	56.4	15.5	27.5	174	10.2	6.05	6.07	3.31	0.31	0.18	0.18
B12-2	-	509	832	30.5	85.8	16	29.1	277	-	9.80	16.0	11.8	-	0.083	0.14
B12-16	1104	-	-	28.0	91.5	15	28.0	277	18.0	-	-		0.15	-	-
45 ev															
B13-1	-	408	288	25.5	78.3	16	28.0	215[a]	-	7.67	5.41	9.65	-	0.079	0.056
B13-19	323	224	236	14.0	91.5	15	28.0	215	10.1	7.01	7.39	9.65	0.105	0.073	0.076
Mixed-energy irradiation															
B9-1	856	512	664	30.1	53.8	15.1	26.0	302	27.5	16.5	21.3	3.62	-	-	-
B9-2	708	440	536	23.8	53.8	15.1	25.5	302	28.2	17.5	21.4	5.07 5.07	-	-	-

[a] V_t estimated as described in III-2.

Difficulty was experienced in the collection of the carriers, but not of the benzene, following B6, and the GLC mass areas indicated that only about 140 μl of carrier was present in the collected sample if the estimated volume of benzene, 124 μl, was correct. This was assumed to be the case and the total volume used in the B6 yield calculations was taken as 270 μl rather than the 374 μl indicated in Table III as the total volume admitted to the separator. In B8, as mentioned previously, a large fraction of the sample was lost because of difficulties in the collection apparatus. Quantitative collection of the products of irradiation is of course highly desirable, and was in fact achieved--or very nearly so--in many of the irradiations, but it is not necessary for the calculation of the yields. All that is required for yield calculation is the knowledge of the fraction of total sample represented by the aliquot being analyzed, provided the composition of the aliquot is the same as the composition of the whole sample. In B8 the volume of benzene and carrier collected was only slightly more than half of the volume known to have been admitted, but the mode of sample loss was such that fractionation of the material would not be expected. Therefore, recourse to gas chromatography mass areas was again had in an attempt to salvage this irradiation in spite of the serious volume loss. The ratio of the toluene area to that of benzene was almost twice what it should have been if the loss of benzene and carrier were proportionately equivalent. This was not the case, and so the total volume used for the B8 calculation is the total volume of benzene and carrier known to have been admitted × 1.92, the latter being the factor correcting for the greater proportional loss of the benzene than of the carrier. Although this volume correction is very large, it is apparently valid in principle, as the yields obtained from B8 are in excellent agreement with those from the other 5000-v irradiations. Nevertheless, the B8 data must not be taken very seriously.

In B13, the sole 45-v irradiation, the volume of product collected was estimated to be only 138 μl, far less than the 215 μl known to have been admitted. As described earlier, the condensate from B7 had been weighed, and the volume calculated from the weight was in perfect agreement with the volume calculated to have been admitted during B7. With the exception of B8 the volume of condensate actually caught was approximately determined by marking the miniscus level in the sealed ampule and after the ampule had been emptied, filling it with water to the mark and weighing it. If this is done very carefully, volumes good to about 5% can be obtained, although errors of as much as 10 or 15% are very easy to make. This was done to serve as a rough check on the total volume calculated to have been admitted and assumed to have been quantitatively collected.

In all cases except B13 the calculated and crudely observed volumes agreed within 10%. In two cases, they agreed within 1%. Hence, we are quite sure that in B13 either benzene was lost or the input rate was sharply reduced, perhaps by partial occlusion of the input tube valve by a piece of dust. The latter could hardly have been the case, though, because the accurate measurement of the input rate was made after the irradiation B13 was carried out. Earlier, before B7, when the -45° thermostatting was first done, a cruder determination by volume only gave 60 μl per hour, with an uncertainty of about 10%, as the input rate. Therefore, we are quite sure that the input rate was indeed constant throughout irradiations B7 through B13.

The benzene, then, must have been lost, and we must know how it was lost in order to determine whether fractionation was likely to have occurred. If the target cold finger had been allowed to warm up to the point where benzene and products of irradiation were being sublimed away during irradiation, then fractionation would be very likely to occur, but if the loss occurred during collection, when the benzene and all of the other products of interest are in the gaseous state because of the large volume of the target section, then mechanical loss of sample would not be expected to lead to fractionation provided

selective adsorption were not occurring. Since the temperature of the isopentane bath was not actually measured during irradiation because of the high voltage on the target section, we cannot be sure that target warming did not occur, but a sizable sheath of solid isopentane existed around the liquid nitrogen cold finger throughout the entire irradiation, and in the past there has never been any difficulty in maintaining the cold finger temperature to within a half a degree or so as long as a fair amount of solid was built up around the liquid nitrogen thimble. So it is not believed that loss occurred in this manner.

It is believed that loss of sample probably occurred because of incomplete closure of the Kerotest valve on the sample-collection apparatus (Fig. 12) leading to the mechanical pump. Difficulty in completely closing this valve had been noted before. Indeed, a monkey wrench had to be used in some cases. Since the valve leads to an operating mechanical pump, no pressure rise is noted on the vacuum thermocouple gauge, but the sample would simply be lost in part through leakage. Since this, the most likely cause of sample loss, should not lead to fractionation, the calculated input volume of 215 μl was used for the calculation of yields from B13.

In addition to the above-mentioned corrections concerning the sample volumes, correction was also made, for all irradiations, in V_a, the aliquot volume whenever an aliquot was analyzed after chemical treatment or condensation following a prior pass, using the ratios of the mass trace areas to determine sample fractionation, if any. Correction for fractionation could be made quite accurately and was always quite small, usually a few percent or less. In fact, it was quite surprising to note that no detectable fractionation occurred in many cases following, for example, agitation of an aliquot portion with a small amount of bromine, even though a volume loss of 20% or so was usually noted. This loss must have been mechanical rather than due to evaporation.

3. The Relationship of Yield to Some Experimental Parameters

Table X shows the average percent yields of benzene, toluene, and cycloheptatriene together with the two experimental parameters whose variation was found to correlate with the yields. The β in Table X is the ratio of ^{14}C ions to benzene molecules in the portion of the solid benzene actually irradiated by the ion beam. That is, it is the ion density. The value of β is calculated from the equation $\beta = \bar{I}/rF$, where $\bar{I}$ is the average ^{14}C ion current taken as ions/sec, r is the benzene input rate in molecules/sec, and F is the fraction of the target face actually covered by the ion beam. The values for the three parameters needed in the calculation of β are listed in Table XI.

Clear, distinct trends are evident from the data presented in Table X. First, at a given ion energy, the yields of all three compounds, with but one exception, decrease with increasing β, that is, with increasing ion density; or, more fundamentally, the yields decrease with increasing ϵ, the energy density. Secondly, there is a strong dependence of yield on the ion energy, E *per se*, since the yields of all three compounds fall with decreasing ion energy in spite of the concomitant decrease in ϵ, the dependence of yield on E obviously overpowering the inverse relation between yield and ϵ.

It was not our intention in this work to investigate the effect of ϵ on yield at a given E. In fact, no observable effect was expected, and the variables controlling ϵ were allowed to wander over a wide range, as can be seen in Table XI. The discovery of the inverse correlation of yield with ϵ at constant E came, then, as a surprise, and a pleasant one at that, for it removed to a large extent the onus of irreproducibility from the yield data for the 5000-ev and 90-ev irradiations. It is ironical that the effect that we have stumbled on is much better characterized than the effect that was explicitly sought; several irradiations have been carried out at a given E and varying ϵ, but not the converse.

Table X. The effect of ion energy and energy density on the yield of benzene, toluene, and cycloheptatriene

Irradiation	Average percent yield[a]			E (ev/ion)	β[b] (Ions/molecule $\times 10^{-5}$)	$\beta E = \epsilon$ (ev/molecule)
	Benzene	Toluene	Cycloheptatriene			
B4	2.92	1.49	-	5000	6.17	0.309
B7	1.89±0.45	1.16±0.10	2.20±0.20	5050	20.1	1.02
B8	1.40	1.07	2.25	5050	23.7	1.20
B11	1.14±0.10	0.87±0.04	1.57±0.06	5000	40.1	2.00
B6	0.72	0.48±0.06	0.38±0.11	5000	229	11.4
B10	0.34±0.03	0.22±0.03	0.20±0.03	90	25.4	0.0229
B12	0.15	0.083	0.14	90	48.8	0.0439
B13	0.10	0.076±0.003	0.060±0.01	45	41.0	0.0184

[a] Where yields have been determined in multiplet, the standard deviation for the set is given following the average value of the yield.

[b] See the text and Table XI for the calculation of β.

Table XI. The variation of the parameters determining the ion density

Irradiation	$r^{(a)}$ (Benzene molecules/sec)	$\bar{I}^{(b)}$ ($^{14}C^{+}$ Ions/sec)	$F^{(c)}$ Fraction of target face covered by ion beam	$\beta = \bar{I}/rF^{(d)}$ (Ions/mole$\times 10^{-5}$)
B4	$\approx 1.13\times 10^{17}$	3.37×10^{11}	0.0483	6.17
B6	$\approx 5.65\times 10^{15}$	6.24×10^{11}	0.0483	229
B7	1.04×10^{17}	1.01×10^{12}	0.0483	20.1
B8	8.63×10^{16}	2.10×10^{12}	0.103	23.7
B10	1.04×10^{17}	2.71×10^{12}	0.103	25.4
B11	1.04×10^{17}	4.28×10^{12}	0.103	40.1
B12	1.04×10^{17}	5.21×10^{12}	0.103	48.8
B13	1.04×10^{17}	4.38×10^{12}	0.103	41.0

[a]The values for r for B4 and B6 are quite rough, whereas those for B7 through B13 are accurately known. In B8, where no benzene was admitted for about 1/6 of the time of irradiation, the average value of 5/6 of 1.04×10^{17} was used.

[b]Calculated from the average ion current (in μa) by the conversion factor, 1 μa = 6.24×10^{12} ions/sec.

[c]F was varied by change in the slit system and elimination of the beam spreader near the exit slit. The area covered by the beam in the two cases was determined from the area of the polymer observed following the 5000-v irradiations (see p. 153). As no polymer was observed following the 90- and 45-v irradiations, the area covered by the beam in those cases is not directly determinable. It was been assumed here that the area covered is the same at low energy as at 5000 v.

Table XI. The variation of the parameters determining the ion density (cont.)

[d]Use of this equation implies that the benzene is spread evenly over the whole target face; since the benzene input tube is located near the base of the target; this probably is not the case, but it is reasonable to assume β is proportional $\bar{I}/rF$ regardless. This would be true, for example, if the benzene were laid down in a triangular wedge pattern, being thickest near the base, thinnest at the top.

On attempting to find the functional relationship of Y and ϵ, and of Y and E, we are forced to conclude that we cannot do so with any reasonable degree of security, particularly in the latter case--the data are not good enough and, above all, there are not enough points. If, however, we cannot state the functional relationship of Y (yield) and ϵ, we can be a good deal more specific about the relation than to merely qualitatively state that it exists.

It was found for the 5000-ev irradiations that a log-log plot of the yields of the three compounds as a function of β gave what can be loosely construed as a straight line, indicating a power relation. That is, $Y_i = a_i \cdot (\beta)^{-n_i}$, where n_i is less than 1 for all three compounds, being 0.38 for benzene, 0.36 for toluene, and 0.74 for cycloheptatriene. These plots are shown in Figs. 47 through 49. Although it is believed that the yield is fundamentally related to ϵ rather than to β, ϵ is, of course, directly proportional to β at a given ion energy, and the 5000 ev is plotted as a function of β rather than of ϵ as a matter of convenience.

The power equation was the only one found, out of the many tried, that even approximately represented all the points for all the three compounds, part of the reason for its relative success no doubt being the insensitive nature of log-log plots. Aware of this insensitivity, and cognizant of the uncertainty of the yield data for B4, B6, and B8, we do not regard the power equation as representing the true functional

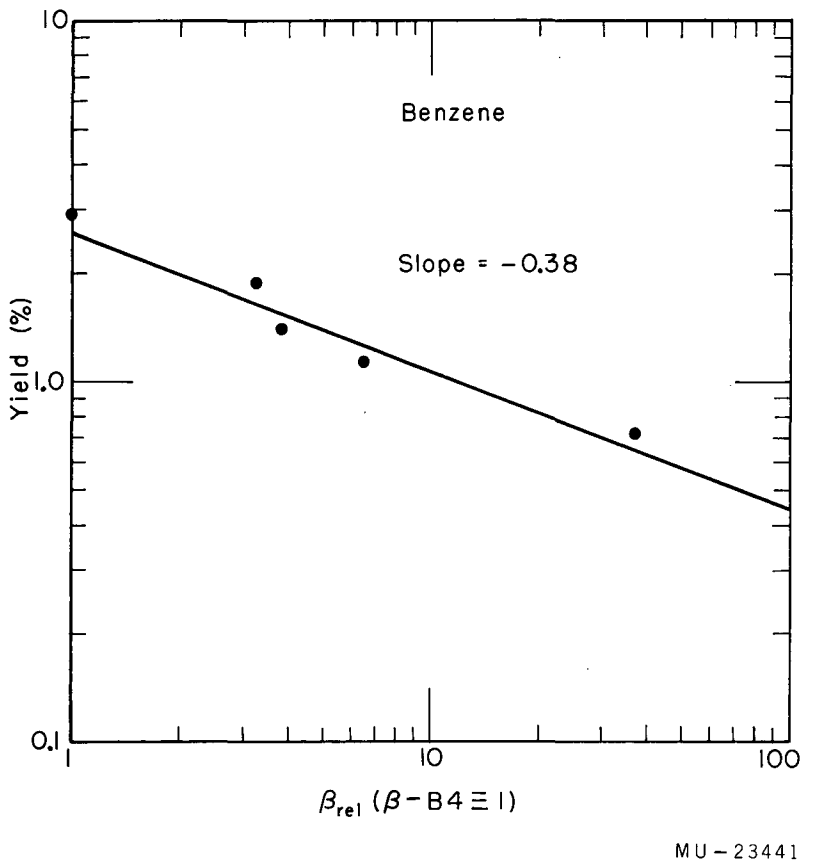


Fig. 47. Log-log plot of the benzene yields vs ion density for the 5000-ev irradiation.

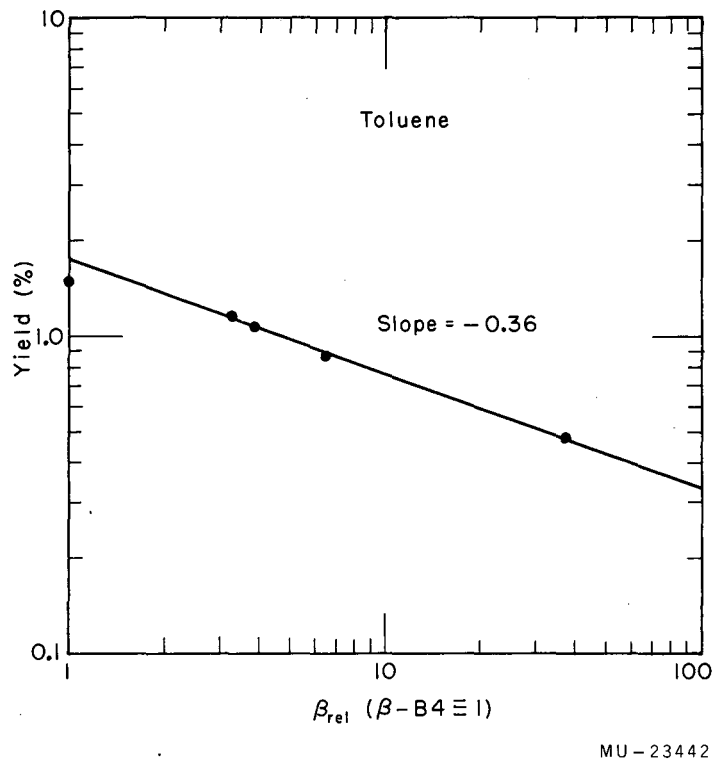


Fig. 48. A log-log plot of the toluene yields vs ion density for the 5000-ev irradiations.

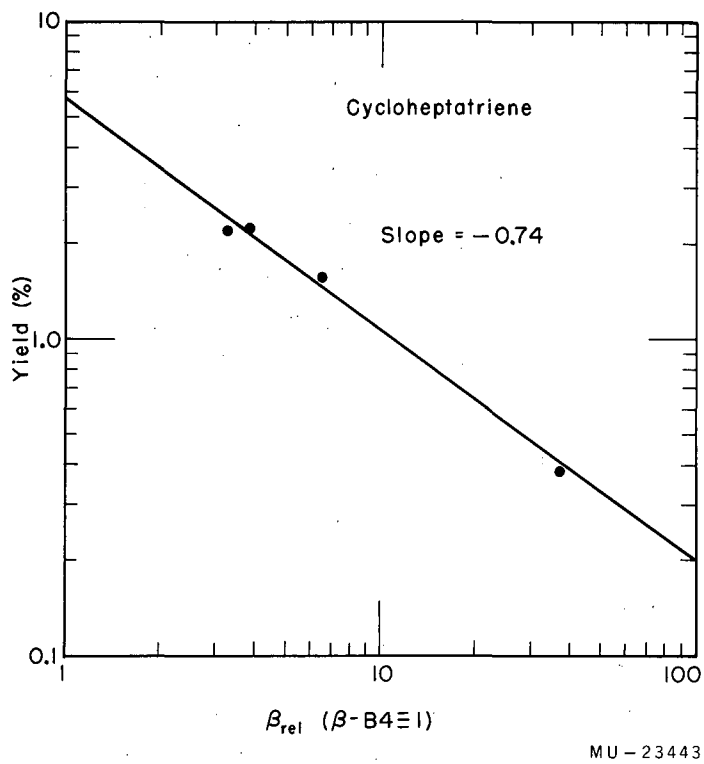


Fig. 49. A log-log plot of the cycloheptatriene yields vs ion density for the 5000-ev irradiations.

dependence of yield on ϵ, but rather as approximately describing the numerical variation of Y with ϵ over the range measured. The true relation may be quite complex, for although we may hope we should certainly not expect such a complicated phenomenon to give a simple answer.

The question then arises as to the constancy of the approximate dependence of Y and ϵ over a large range of ϵ. Examination of the data in Table X for B10 and B12, the two 90-ev irradiations, shows that a much stronger dependence is needed to bring the benzene and toluene yields for these two irradiations into coincidence, but that the cycloheptatriene yields are still adequately represented by the exponent of the power equation obtained from the 5000-ev experiments. Since there are only two 90-ev irradiations, and since the relative uncertainty in the yields is rather large, this question cannot be answered; for the purpose of attempting to unravel the effect of ϵ and E, it is assumed that the dependence of Y on ϵ is constant over the whole range of ϵ involved. If this is assumed, the yields may then be multiplied by ϵ, raised to the appropriate power for each compound. The yields thus corrected (and therefore in good agreement for each ion energy) may be averaged for each compound at each ion energy and the averaged, corrected yield for each compound plotted in some fashion against ion energy. This was done for a number of trial functions, and no clear relation of yield to ion energy was found, although a power function (log-log plot) was not too far off.

Plotting the data in this way, one is dealing with only three points, and although no manipulation of the data can obscure the fact that we have done experiments at but three energies, it is possible, if one is looking for a power relation, to plot the data in a more informative (although somewhat contrived) manner one whose chief virtue is that it permits a display of the data from each irradiation, thereby allowing individual data obviously out of accord with the rest to be noticed.

For if it is assumed that the effects of E and ϵ on the yield are separable, and if power functions are assumed for both effects, then for a given compound a log-log plot of Y versus E^x/β must yield a straight line for some value of x. The slope of that line must be n, whatever the value of x turns out to be, for n is the exponent already determined for the power function giving the relation of Y to ϵ at a given E. When the proper value of x is chosen, the resulting straight line is represented by the equation

$$Y = k\,(E^x/\beta)^n = k\,E^{xm}/\beta^n\,.$$

If β, the ion density, were the fundamental parameter as such, then the dependence of Y on E would go as the xm power of E. But since it is much more reasonable to assume that it is $\beta E = \epsilon$, the energy density, which is the fundamentally significant parameter, we rewrite the above equation to give

$$Y = E^{xn + n}/\,(\beta E)^n = E^{x(n + 1)}\,/\,\epsilon^n\,,$$

where the intrinsic dependence of Y on E goes as the x(n + 1) power. Success in finding a proper x would not only vindicate the choice of power functions for E and ϵ and give the exponents for those functions, but also would confirm our assumption of the separability of the effect due to E and the effect due to ϵ, since we know that the effect due to ϵ at constant E goes as ϵ^{-n}.

Figure 50 shows such a plot for benzene with x = 1.25. Only the point for B10, the first 90-ev irradiation, lies farther from the line drawn than is expected from estimated experimental error. The benzene yield from B10 would have to be reduced by one-third, going from 0.34% to 0.22%, to fall on the line. The points for the 5000-ev irradiations will lie on a given line equally well for any choice of x; the three low-energy points, however, will swing above or below the line as x is increased or decreased. A plot of the same kind with x = 1.00 puts the B10 point--that is, the one that is third from the bottom in Fig. 50--very close to the line for the 5000-ev irradiations,

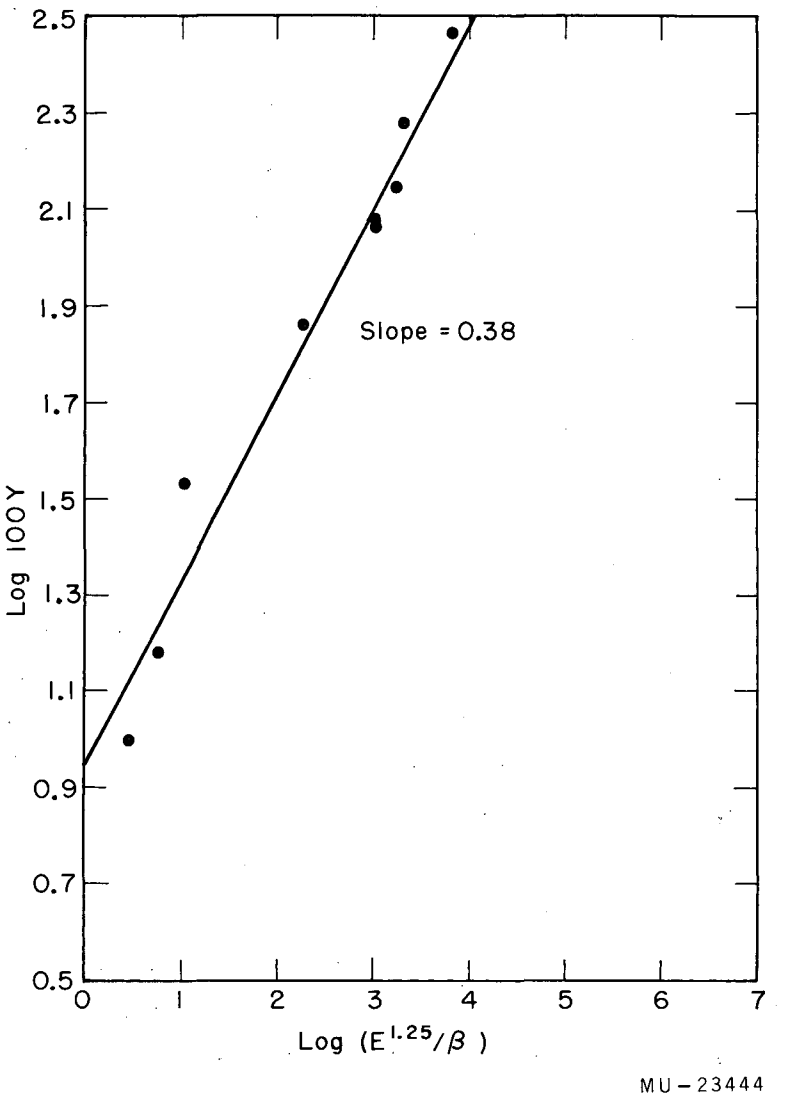


Fig. 50. A log-log plot of the benzene yields x 100 vs $E^{1.25}/\beta$.

but causes the B13 and B12 points to fall far below that line. A plot with $x = 1.50$ puts the B12 and B13 points very close to the line but pushes the B10 point far above it. The plot shown here with $x = 1.25$ is about the best that can be made giving equal weight to all irradiations. If it is correct, the benzene yield varies as $E^{0.86}$. If, on the other hand, we had reason to believe something was seriously wrong with the benzene yield for B10, we would prefer the plot with $x = 1.50$, having all of the points, save that for B10, lying very near to the line. This would give an E dependence going as the 0.95 power of E. Since we have no reason to discount the B10 experiment, the benzene plot shown is preferred.

The situation with toluene is much the same as that for benzene. No choice of x yields a straight line near which all the points lie. Plots were made with $x = 1.0$, 1.25, 1.50, and 2.0. As was the case for benzene, $x = 1.0$ and $x = 1.5$ give good agreement for one or two points, completely discounting another; $x = 1.25$ gives approximately equal weight to all the low-energy irradiations. That plot is shown in Fig. 51. If the three low-energy points were reasonably close to the line drawn in Fig. 51--which they are not--the exponent of E would be 0.79. By way of comparison, $x = 1$ corresponds to an exponent of 0.70, and $x = 1.5$ corresponds to an exponent of 0.88.

A similar plot for cycloheptatriene was found to give best results when x was chosen as 0.79, corresponding to a dependence on the 1.32 power of E (Fig. 52). As these exponents are significantly different from those found for benzene or toluene over a wide range of choice of x for both compounds, it was of interest to see if choice of an x value giving an exponent nearer to the benzene and toluene cases would still produce a reasonable linearity of the cycloheptatriene points so a plot was made with $x = 0.37$, corresponding to an E exponent of about 1.00, as shown in Fig. 53. It can be seen that such a reduction in x makes a quite large difference no semblance of linearity remaining between the 5000-ev and low-energy points. The

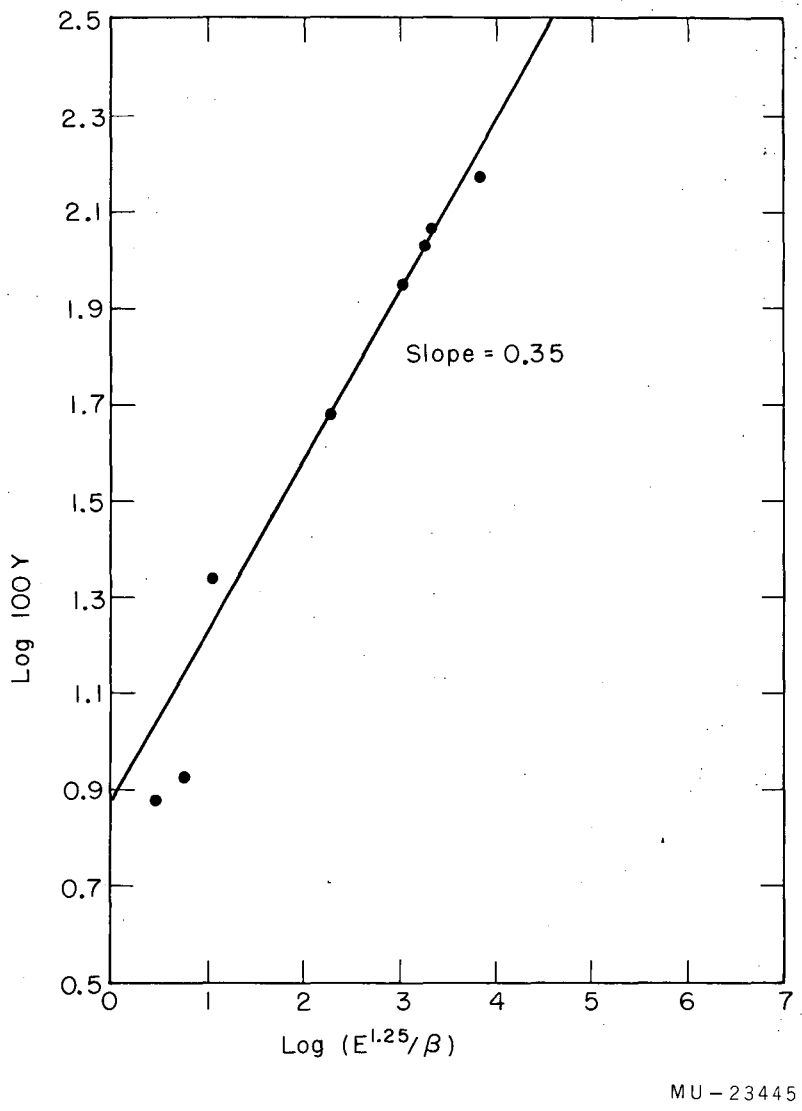


Fig. 51. A log-log plot of the toluene yields x 100 vs $B^{1.25}/\beta$.

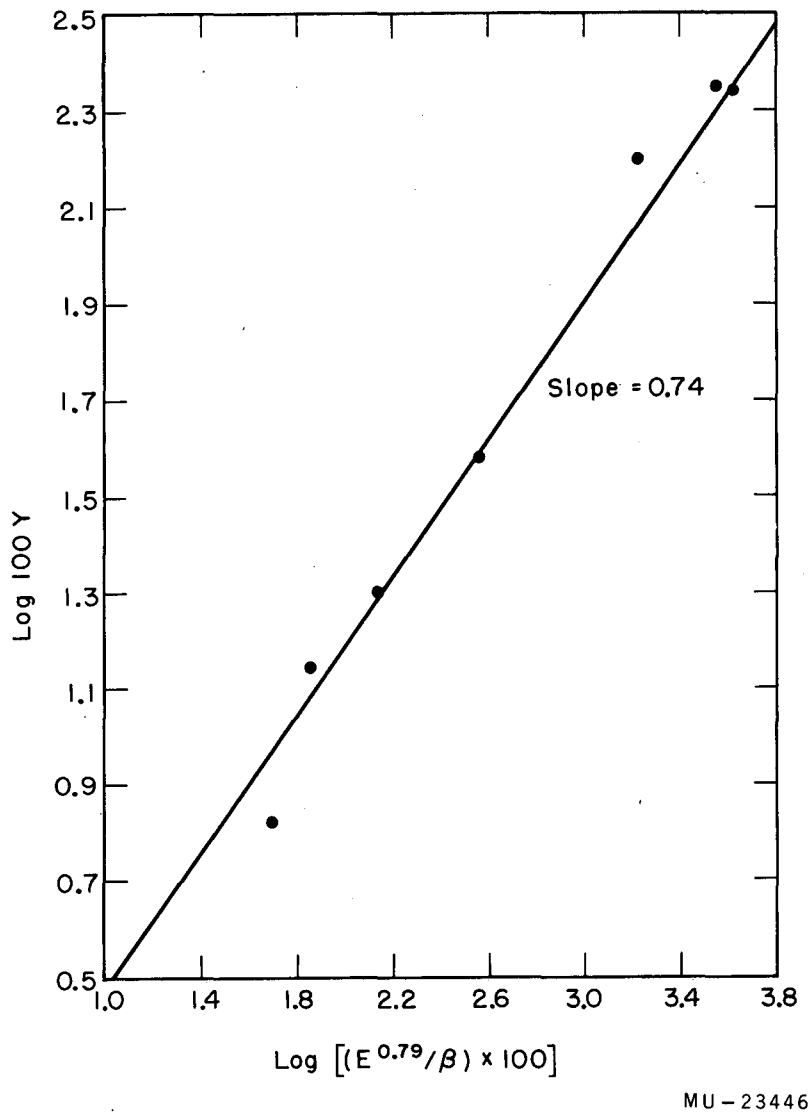


Fig. 52. A log-log plot of the relative cycloheptatriene yields (yield for B13 ≡ 1) vs $E^{0.79}/\beta$.

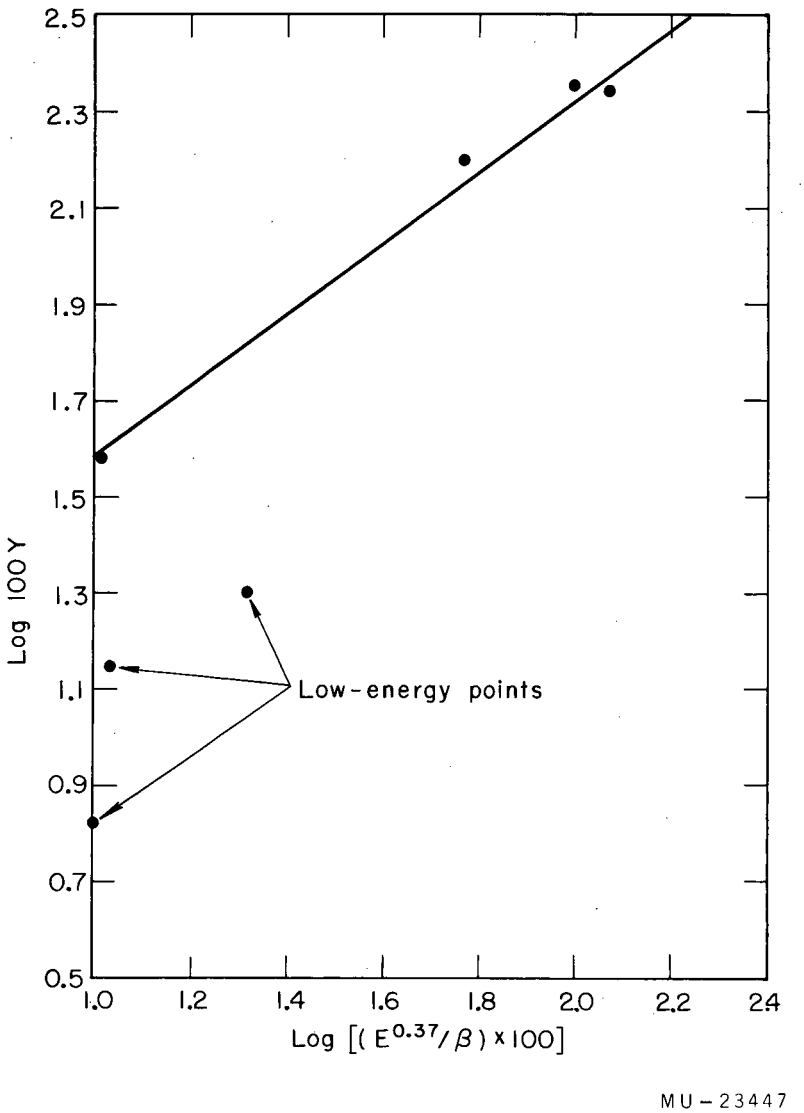


Fig. 53. A log-log plot of the relative cycloheptatriene yields (yield for B13 ≡ 1) vs $E^{0.37}/\beta$.

large difference in the exponent found for cycloheptatriene compared with that for benzene and toluene seems to be significant in spite of the large element of artificiality in treating the data in this way.

From the foregoing it may be seen that the yields of benzene, toluene, and cycloheptatriene can be approximately represented in the E range 45 to 5000 volts and ϵ range 0.0184 to 11.4 ev per molecule by the following equations:

$$Y(B) = 1.10\times10^{-3}\,(E^{0.86}/\epsilon^{0.38}), \qquad (1)$$

$$Y(T) = 1.37\times10^{-3}\,(E^{0.79}/\epsilon^{0.36}), \qquad (2)$$

$$Y(C) = 3.08\times10^{-5}\,(E^{1.32}/\epsilon^{0.74}), \qquad (3)$$

where E is in electron volts and ϵ is in ev/molecule. Writing the equations in this form assumes the complete separation of the effect due to E from that due to ϵ. This has not been proved, but is strongly suggested by the partial success of the plots made from the above equations. We wish to be quite clear that the true functional nature of the dependence of yield on ϵ and E are not considered to be necessarily represented by these equations. This is particularly true for E. It should be noted that the above equations do not possess the proper boundary properties, yield certainly not going to infinity as E goes to infinity or ϵ to zero. This, however, is a rather trivial point, as minor modifications in the above equations, quite unwarranted by the adequacy with which they describe the data, could provide suitable boundary properties.

A rough check on the worth of the above equations is given by the mixed-energy irradiation, B9 (see page 109). For the 5000-ev part, ϵ is 1.75 ev/molecule. Substitution of that value in the yield equations gives yields of benzene, toluene, and cycloheptatriene of 1.34%, 0.94%, and 1.51% respectively. The number of μamp-hr of irradiation at 5000 ev is known accurately, and multiplication of the total activity introduced at high energy by these yields gives the total calculated activity in the three compounds due to the 5000-volt portion. Substraction of those activities from the total observed activities in the three

compounds gives the activity due to the 90-volt portion of the irradiation.

As ϵ at low energy is about 0.0222 ev per molecule, expected benzene, toluene, and cycloheptatriene yields, at 90 volts, of 0.22%, 0.19%, 0.20% are obtained. The total activity introduced at 90 volts is not known, but the low-energy yields can be calculated for the limiting values. The benzene, toluene, and cycloheptatriene yields are 0.37%, 0.14%, and 0.08% respectively at one extreme, and 0.47%, 0.23%, and 0.12% respectively at the other extreme. The value thus obtained for benzene is too high and that for cycloheptatriene too low regardless of the actual activity introduced at 90 volts. This calculation is very sensitive to errors in both the experimental determination of total activity in each compound and in the calculation of the high-energy contribution. In view of this, the check provided by the B9 irradiation should be regarded as moderately satisfactory.

B. Results of the Ring-Methyl Degradation of Toluene-^{14}C from Irradiation B7

The method of ring-methyl degradation and the counting techniques used are described in II-B-2. All the samples, with the exception of the CO_2 from the methyl group of toluene, were counted by liquid scintillation counting, and the results of those determinations are given in Table XII. The total activity, d, in the sample counted is given by

$$d = \frac{(C_1 - B)}{e} = (C_1 - B) \times S / (C_2 - C_1) ,$$

where C_1 is the counts per minute observed for the sample including background; B is the background count rate; e is the efficiency of the scintillator system; S is the known amount of activity added as internal standard after determination of C_1; and C_2 is the count rate after addition of internal standard to the sample. In the case reported here the Ucon-GLC column was found to be contaminated, and correction for the extraneous activity introduced into the sample from

the Ucon column was necessary. Here d^0 indicates the total activity in a given sample after correction for the contamination by the Ucon column. As can be seen in Table XII, the correction is quite small for toluene but is very large for aniline. The difference is due to the higher column temperature and faster gas flow rate used in the chromatography of the aniline samples.

Table XII shows that the specific activity of the toluene following chromatography on APL, but before treatment with bromine and chromatography on Ucon, is significantly higher than the specific activity of the toluene following further purification. This is probably due to contamination of the APL column.

Table XIII gives the average specific activities of the purified toluene, the CO_2 representing the methyl group of toluene, and the aniline representing the toluene ring. The three aniline samples, with a relative standard deviation of more than 30%, do not agree well with one another, and their average does not agree well with the values for the parent toluene and the methyl group CO_2. The probable error in the aniline determination is so great, however, that the check (or lack thereof) afforded by the aniline is meaningless in the present case, and our knowledge of the ring-methyl distribution of activity must be based solely on the one ionization-chamber determination of the activity in the CO_2 from the methyl group. This situation is neither surprising nor disappointing to this writer, whose experience with liquid scintillation counting of very small amounts of activity has been essentially all bad and whose experience with ionization-chamber determination of modest amounts of activity has been quite good.

Although it is somewhat of an understatement to say that the results of this degradation must be considered to be tentative, the author is personally satisfied that the ring-methyl distribution of activity in the toluene from this 5000-ev irradiation is the same as that of toluene from ^{14}C recoil in benzene and aniline, where the methyl activities range from 86% to 88% of the whole.[24]

Table XII. The results of the liquid scintillation counting in the ring-methyl degradation of toluene-C^{14} from irradiation B7

Sample[a]	C_1 - B[b] (cpm)	e[c] (%)	d (dpm)	d^0 (dpm)	Amount	Specific activity (dpm/mmole)
Toluene-AP-L	113.6±3.7	70.5	161±5	-	15μl	1140±38
Toluene-UCON, front of peak	102.4±3.4	70.2	146±5	144±5	15μl	1020±34
Toluene-UCON, rear of peak	106.9±1.7	70.1	152±2	150±5	15μl	1060±17
Benzoic Acid	114.4±4.3	64.6	177±7	-	20.3 mg	1070±41
Aniline-1	35.3±2.5	62.0	56.9±4.0	36.3±5.0	11.5μl	288±40
Aniline-2	60.8±2.2	53.0	115±4	40.0±5.3	21.2μl	172±23
Aniline-3	50.5±2.5	61.5	82.1±4.0	40.0±6.6	10.9μl	334±56
Toluene blank-2	11.5±2.3	68.0	16.9±3.3		141 μl	
Toluene blank-3	6.5±1.9	70.2	9.3±2.7		120 μl	
Aniline blank-1	13.1±1.9	63.5	20.6±3.0		9 μl	
Aniline blank-2	44.4±2.1	59.1	75.0±3.5		33 μl	
Aniline blank-3	27.1±3.4	64.3	42.1±5.3		13 μl	

[a]Tolune-APL indicates the aliquot taken from the toluene after chromatography on APL before bromination and subsequent chromatography on Ucon. The toluene and aniline blanks were chromatographed on Ucon in the same manner as their respective ^{14}C counterparts.

Table XII. The results of the liquid scintillation counting in the ring-methyl degradation of toluene-C^{14} from irradiation B7

[b]Each sample was counted for six or seven 10-minute periods, both before and after addition of internal standard. The standard deviation given after each value in Table XII is the observed standard deviation for the counting only. The background was found to be 15.4±1.2 cpm.

[c]The efficiency of each sample was determined by addition of 100μl of toluene-^{14}C standard with a specific activity of 123 dpm/μl.

Table XIII. The results of the ring-methyl degradation of toluene-C^{14} from irradiation B7

Compound	Average specific activity (dpm/mmole)	specific activity of toluene (%)	Sum of specific activity of methyl and ring (%)
Toluene[a]	1050±26[b]		
CO_2 from the methyl group of toluene	915±15[c]	87.0±2.6	
Aniline—average	264±84[b]	25.1±8.0	112.1±8.4
Aniline—"best" sample	172±29[d]	16.4±2.7	103.4±3.8

[a]The average value for toluene is calculated from the values for the front and rear portions of the Ucon effluent and from the value of the benzoic acid.

[b]The standard deviation is that observed for the components of the average. For toluene, the observed total standard deviation of 26 cpm is only slightly greater than the counting standard deviation of 19 cpm. Hence, a relative standard deviation of 1.7% is found for noncounting errors, mainly in the determination of the amount of sample. For

Table XIII. The results of the ring-methyl degradation of toluene-C^{14} from irradiation B7 (cont.)

aniline, the observed standard deviation of 84 cpm is much larger than the observed counting standard deviation of 24 cpm. This is partly due to errors in the measurement of the small volumes taken via Hamilton syringe, but is primarily a reflection of the crudity of the correction for contamination.

[c]The total activity in the ionization chamber (sample plus background) was found by the rate-of-charge method of be 1154±13 dpm, on the basis of seven determinations of rate of charge. The background for the same chamber filled with 1 atm of $^{12}CO_2$ was found the next day to be 120.3±3.7 dpm, on the basis of nineteen determinations of rate of charge. The activity due to the sample was, therefore, 1034±14 dpm. The amount of $^{14}CO_2$ taken for analysis was found to be 1.13±0.01 mmoles, a relative standard deviation of 1% being assumed for the error of this measurement. The standard deviation of 15 dpm includes the uncertainty due to measurement of the amount taken.

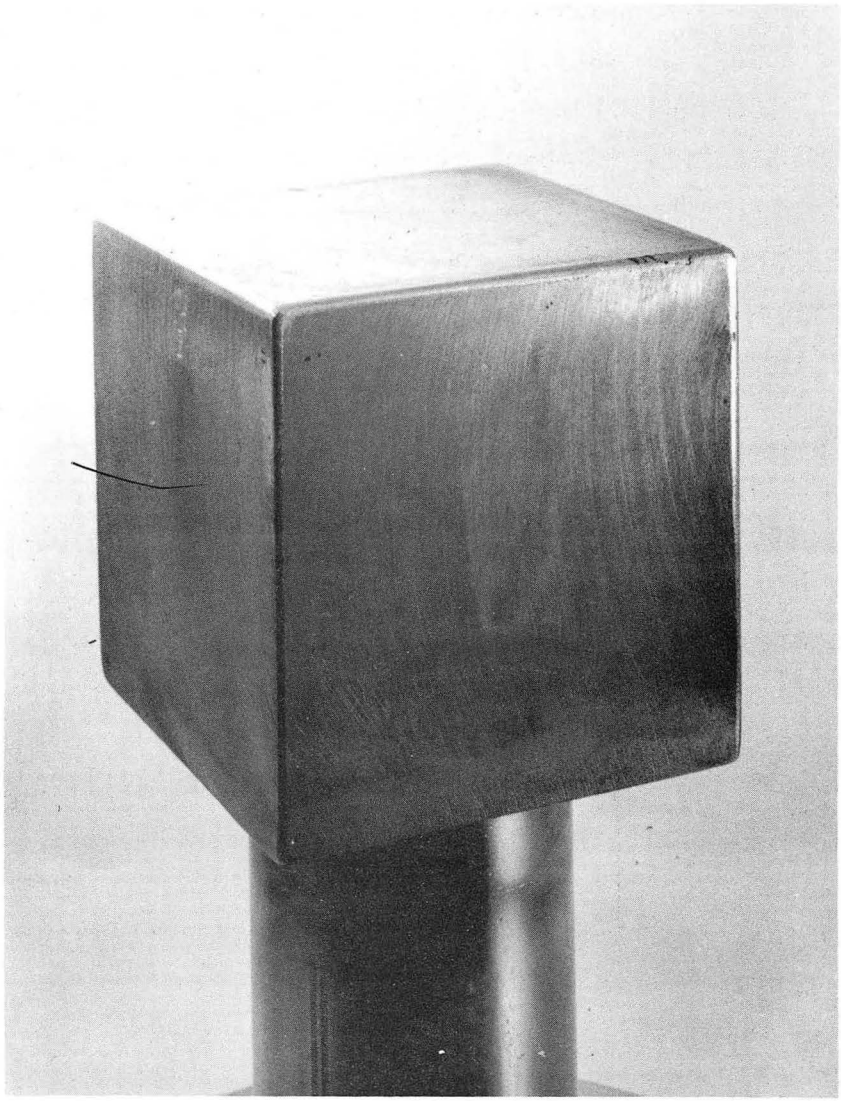
[d]The standard deviation due to counting alone is 23 cpm, and a relative standard deviation of 10% is assumed for the error due to volume measurement and contamination correction to give the total standard deviation of 29 cpm.

C. Polymer Formation

Following irradiation B7, the target cold finger was removed from the target section to allow the exit-slit plate to be changed, and a yellow solid, approximately rectangular in shape, was found on the face of the cold finger. The area covered by the polymer delineates the area of the ion beam striking the target. In this case the polymer covered an area of about 2.8 cm^2, being 3.5 cm high and 0.8 cm wide. Since the width of the polymer area was about three times that of the exit slit used in B7 and prior irradiations, the beam apparently diverged laterally between the exit slit and the target, as it should because of the beam spreader.

The solid was wiped off the target face with a piece of cotton moistened with carbon disulfide, and the cotton was then extracted with carbon disulfide in a Soxhlet extractor. A ratemeter laboratory monitor indicated activity in the solid, as would be expected, but no activity was extracted from the cotton bearing the solid into the carbon disulfide after prolonged extraction. We had hoped to determine the amount of activity in the polymer by extraction in the carbon disulfide followed by liquid scintillation counting, and also wished to obtain an infrared spectrum of the solid in order to compare it with published spectra of the polymeric solid resulting from electron irradiation of benzene.[55] No other solvent was tried.

Following irradiation B8, like its predecessors a 5000-v irradiation, the cold finger was removed and polymer was again noted. A picture of the solid on the cold finger is shown in Fig. 54. We then attempted to obtain an infrared spectrum, using a KBr-pressed disc, but apparently did not have enough material to allow this to be done. The flaky solid which was scraped off the cold finger face was not weighed but was estimated to have been about 0.1 mg at most. Polymer was again observed on the cold finger after irradiation B11, another 5000-v run, and no polymer was found after the 90- and 45-v irradiations. When the exit-slit width was increased to 9.5 mm for B8 and subsequent



ZN-2755

Fig. 54. A view of the yellow solid left on the target cold finger after collection of the volatile products of irradiation B-8. The solid is approximately centered on the face of the cold finger.

irradiations, the area covered by the polymer increased to about 6 cm^2, that is, quadrupling the exit slit width and removing the beam spreader resulted in a twofold increase in the width of the beam at the target surface.

Although very little was learned about the nature of the polymer, it was quite useful to us in its delineation of the area covered by the beam. An attempt was made to determine the area covered by the low-energy beams photographically, using Ilford Q2 plates. We did not expect to get an image from the 90-v ions, but thought it was worth trying. As expected, we were unsuccessful. The level of fogging was so severe that even if the 90-v ions produced an image it would have been obscured. An image of a 5000-v ion beam was obtained, however, and corresponded to the shape and dimensions of the polymer although it appeared less homogeneous than the polymer

D. Results of the Qualitative Analysis of the Prebenzene Compounds

The techniques used for the identification of the prebenzene compounds and the criteria established for the coincidence of activity and mass peaks have been described in detail in II-B-1-c. We shall here present most of the traces made during the prebenzene analysis, together with necessary commentary on them. For the most part the traces themselves tell the story of this analysis better than can be done verbally, which is why so many are presented; but the reduced time scale necessary for presentation so reduces the readibility that the sensitive criteria for coincidence cannot be appreciated from the traces as presented here. As stated earlier, the readability of the chart paper in this work is about 0.05 min, while the readability of the traces presented here is on the order of 1/4 to 1/2 min. If, for example, a sharply rising activity trace began 0.10 min later than a mass trace, we would consider that coincidence had not been established, but so fine a distinction cannot be seen on the traces illustrated here.

Those compounds whose identity was eventually established are labeled as such on the earlier traces, even though their identity at the time the earlier traces were made was unknown. Again, when a name is meant to apply only to an activity peak, it is followed by (A); when it is meant to apply only to a mass peak, it is followed by (M). Where a mass peak and an activity peak appear coincident and no symbol follows the name, the peak is to be understood to apply to both the mass and the activity peaks. The initial activity scale is indicated as the ordinate maximum; when change of scale is made it is so indicated on the trace at the time made. When individual compounds, or groups of compounds, were collected separately after chromotography, such fractionation is indicated by arrows bracketing the fraction collected on the upper border of the trace. The cut is referred to by the arabic numeral designating the fraction at the upper border. The traces will be referred to by code number rather than by figure number, e.g., B11-4 indicates analysis number 4 of the material from irradiation B11. When a trace which is referred to is not shown here, it will be so stated.

1. Activity Traces

Irradiation B11

The prebenzene condensate from B11-1 and B11-2 was reinjected onto DMS to give B11-3 (Fig. 55), and the condensate from B11-3 was then rerun on AP-L, giving B11-4 (Fig. 56). At the time B11-4 was made, it was thought that many of the compounds seen in B11-3 must have been lost, but reinjection of B11-4 condensate on DMS, giving B11-6, indicated that such was not the case, for the B11-6 contains all the peaks shown on B11-3. Material is lost, to be sure, but no product is lost completely. Comparison of the C_3 and C_4 activity areas in B11-4 with the areas of the C_3 and C_4 components indicated in B11-3 shows that the C_4's are condensed more efficiently than are the C_3's.

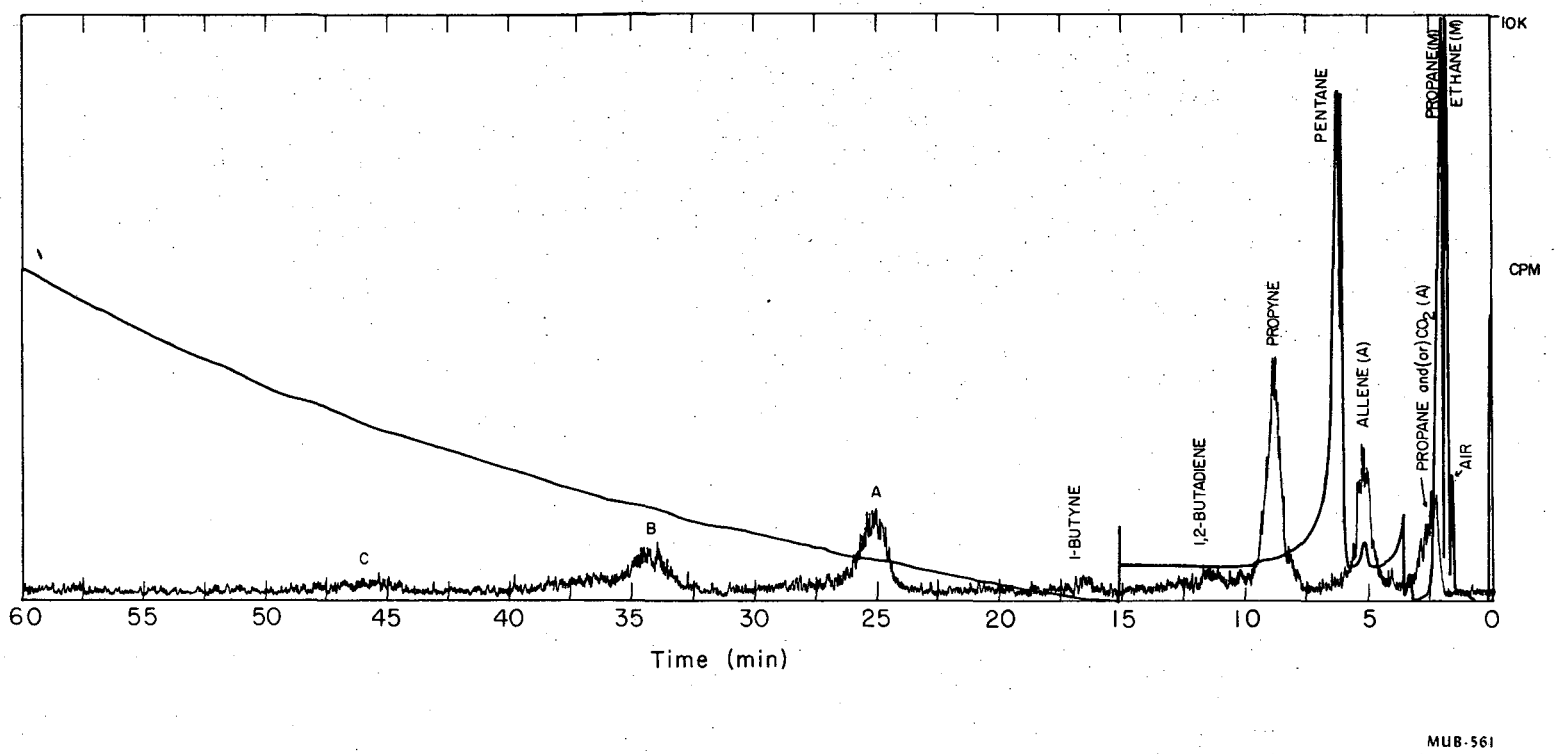


Fig. 55.B11-3: DMS analysis of the prebenzene condensate from B11-1 and B11-2.

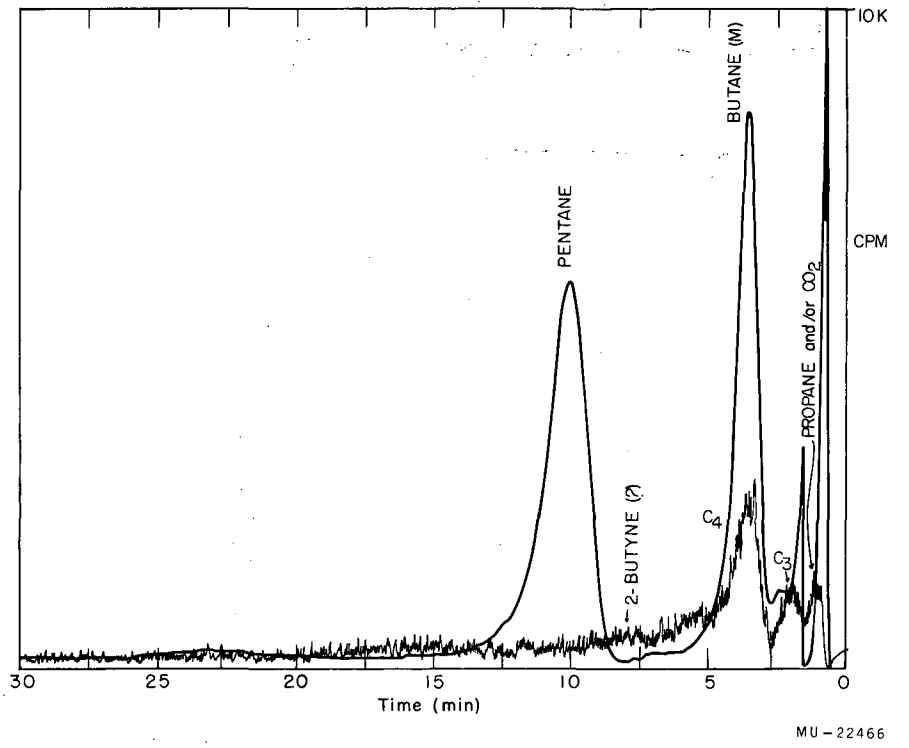


Fig. 56. B11-4: AP-L analysis of condensate from B11-3.

The effect on the activity spectrum of repeated condensation and handling is shown by B11-5, a trace made of fresh sample from B11 on AP-L (Fig. 57). Comparison of it with B11-4 shows two striking differences. First, the area designated D in B11-5 is barely visible in B11-4; secondly, a very large carbon dioxide activity peak is seen in B11-5, whereas in B11-4 we are not sure of the identity of the peak that is labeled "propane and/or CO_2." In any case, it is much smaller than the CO_2 peak in B11-5. The activity in the D area was never identified; probably the area is complex and most of the components have very long retention times on DMS. Furthermore, some or most of the components of the D area are much more labile than C_3 and C_4 components, the D area appearing and disappearing somewhat capricously during the prebenzene analysis. From its position on B11-5 alone, the activity peak labeled CO_2 could not be identified. C_2 hydrocarbons would also appear at the same place. However, reinjection of the condensate from B11-5 on DMS, giving B11-7 (not shown), definitely excludes assignment of that activity to any C_2 hydrocarbons. In fact, no C_2 activity was found in the prebenzene analysis at all.

Upon treatment with bromine, all but one of the activity peaks in the condensate from B11-7 were removed, only CO_2 and(or) propane remaining; that trace is not shown. Bromination of whole sample was repeated on another portion of B11 material with the same results.

Irradiation B13

The analysis of the prebenzene compounds from B13 was next done; here establishment of correspondence of activity peaks on one column to those on the other was begun. B13-2 (Fig. 58) shows the DMS prebenzene spectrum of the condensate from B13-1. The effluent from B13-2 was trapped in fractions as indicated. B13-3 (Fig. 59) shows the first cut from B13-2 rerun on AP-L. There are two points worth noting about B13-3. One is that, in this case as in most of the others, distinction between propane and CO_2 on AP-L cannot

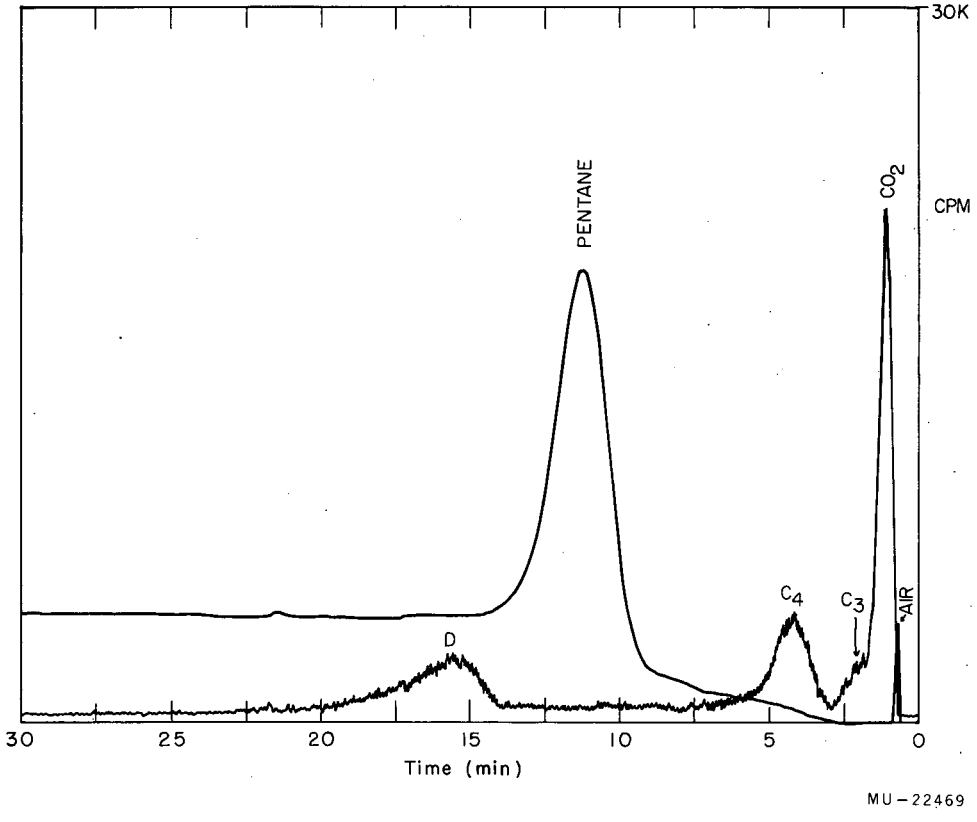


Fig. 57. B11-5: AP-L analysis of whole sample.

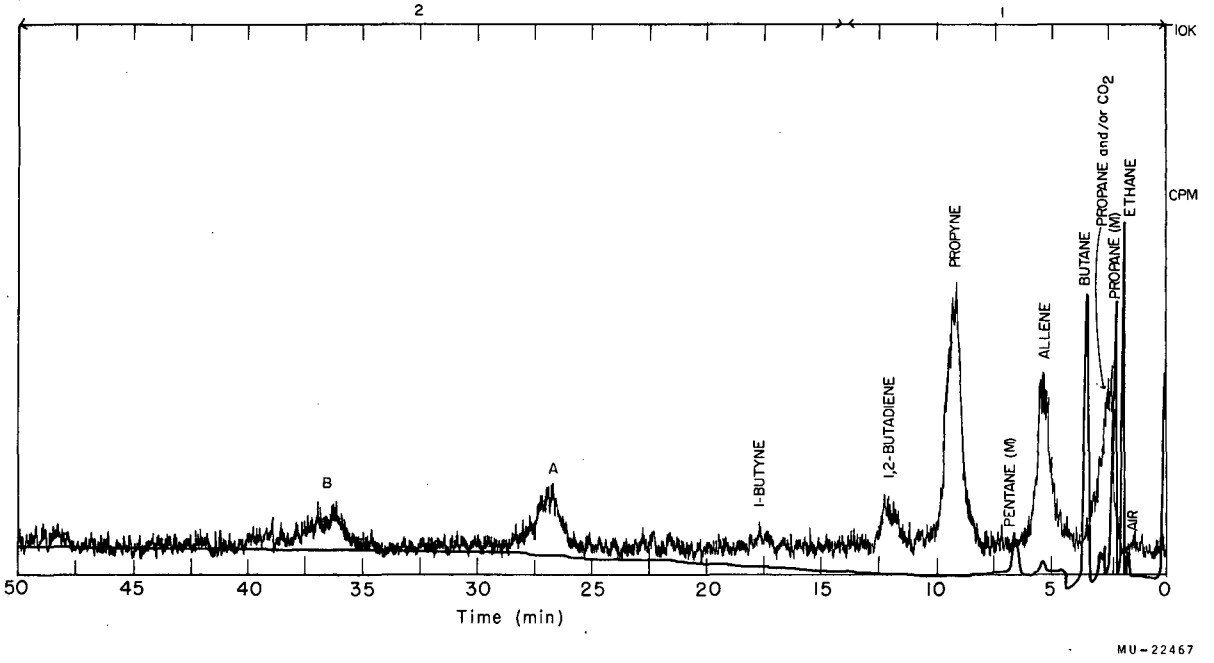


Fig. 58. B13-2: DMS analysis of the prebenzene condensate from B13-1. Note fractional collection of B13-2 condensate (upper border).

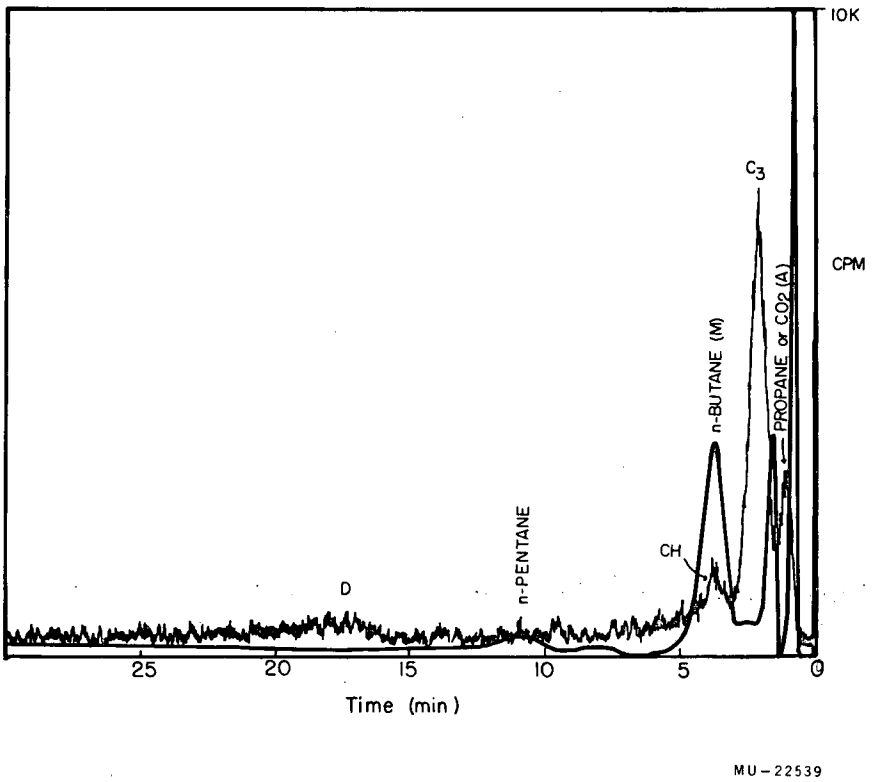


Fig. 59. B13-3: AP-L analysis of the first cut from B13-2.

be made, although the two should be separable, as difficulty arises from the condensation of large amounts of propane from the methane carrier gas with resultant shortening of propane retention time so that it overlaps CO_2. Secondly, the activity peak labeled C_4 cannot be due to 1, 2-butadiene, which was indeed present in that fraction, but must be due to C_4 compounds such as 1, 3-butadiene or 1-butene or isobutylene present in relatively small amounts in the activity areas predominantly due to allene and propyne. Finally, a small activity area is seen in the D region, probably due to de novo synthesis of the material responsible for that peak.

The second fraction of B13-2 was rerun on AP-L, giving B13-4 (Fig. 60). Here we see no activity in the C_2 or C_3 region, activity in the C_4 area due to A and B and, again, activity in the D area. The condensate from B13-4 was cut into fractions. The first cut from B13-4 was rerun on DMS, as shown in B13-6 (Fig. 61), regenerating peaks A and B. By this time the small amount of activity due to 1-butyne was undetectable. The second, or D, cut of B13-4 was also rerun on DMS but no detectable activity peak was found; this trace is not shown.

The condensed effluent from B13-3 was rechromatographed on DMS (B13-5, Fig. 62), the propane and (or) CO_2 peak was let go, and the allene and propyne peaks were collected separately. By this time the identity of the propyne peak was strongly suspected, but it was thought that the activity peak soon to be identified as allene was a C_4, probably 1- or isobutylene. When the propyne cut was rechromatographed on AP-L (B13-8, Fig. 63), the first evidence establishing its identity was obtained, its retention time being definitely that of propyne and not that of 1, 3-butadiene--a less likely possibility but one which was not considered out of the question at that time. Rechromatography of the allene peak on AP-L shown in B13-9 (Fig. 63) established it, of course, as a C_3, much to our surprise; in retrospect there is no reason for surprise--we simply were expecting it to be a C_4.

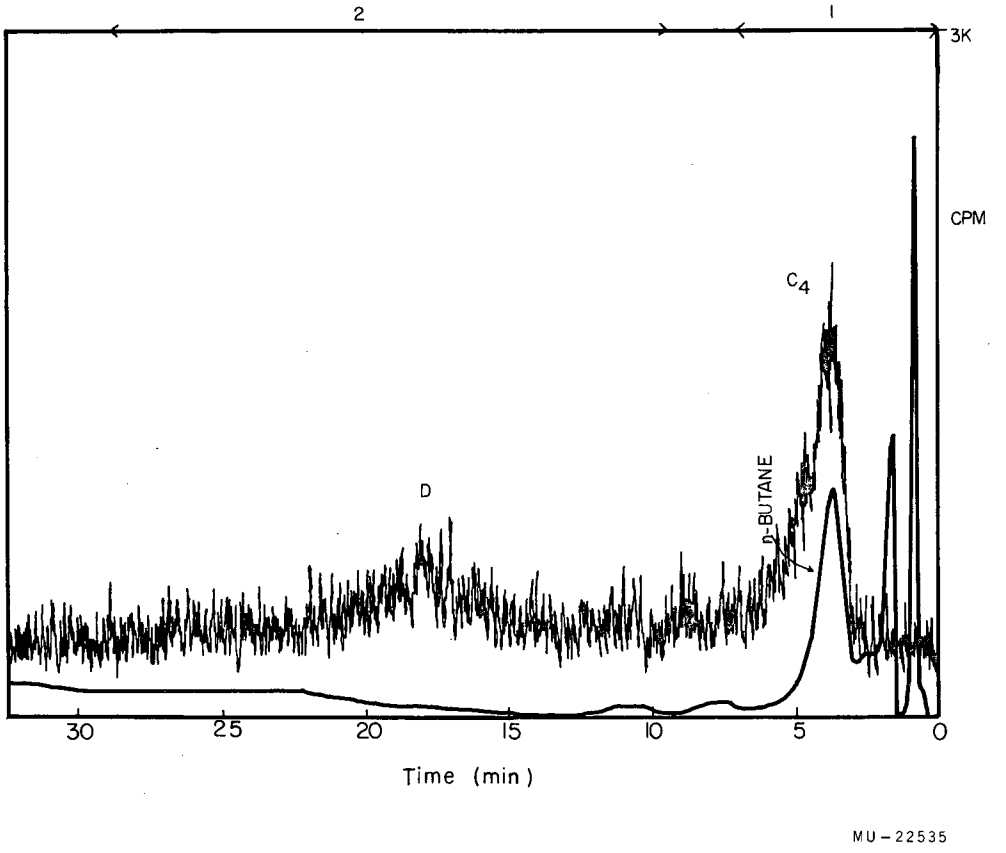


Fig. 60. B13-4: AP-L analysis of the second cut from B13-2. Note fractional collection.

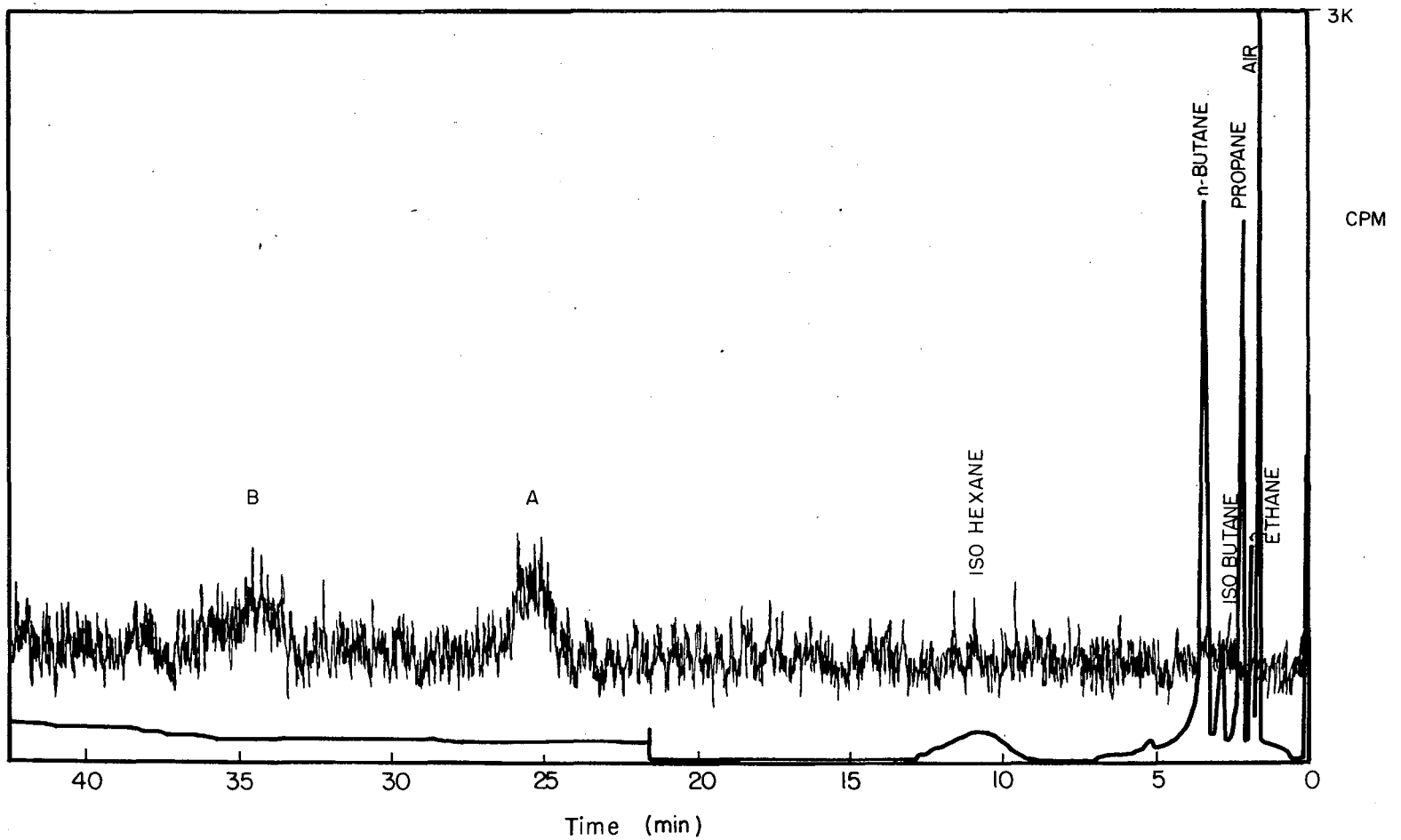


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Fig. 61. B13-6: DMS analysis of the first cut from B13-4.

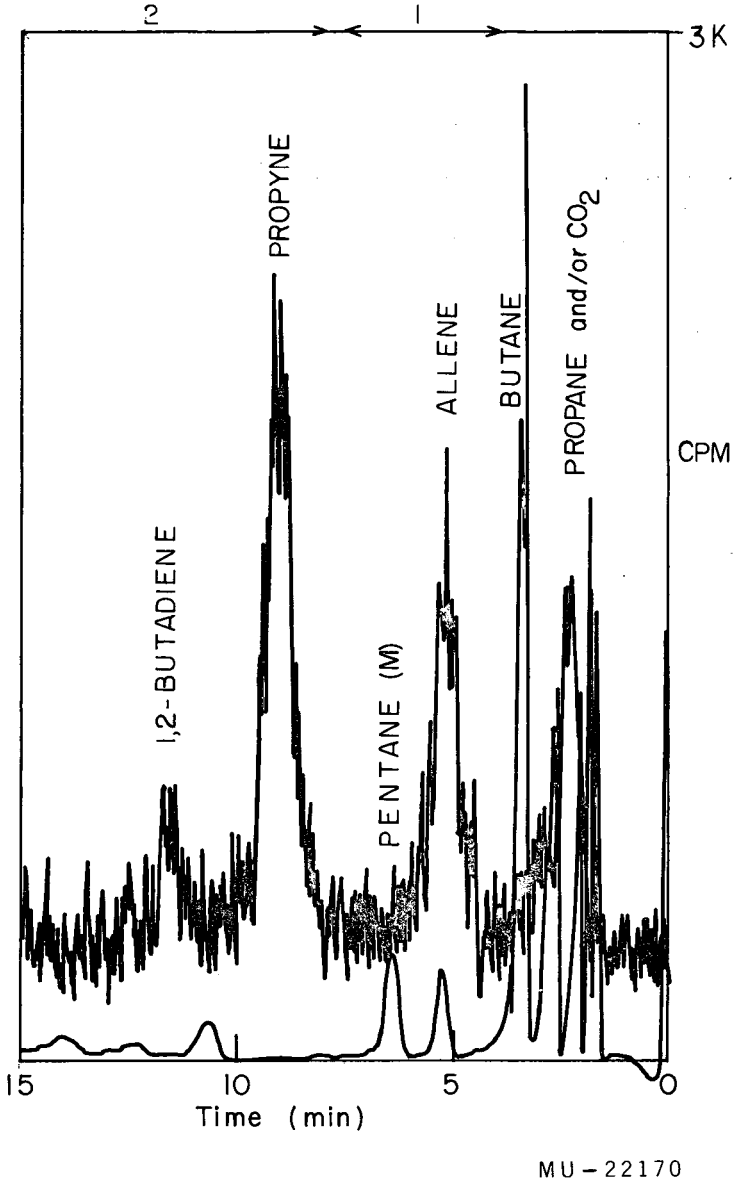


Fig. 62. B13-5: DMS analysis of condensate from B13-3. Note fractional collection.

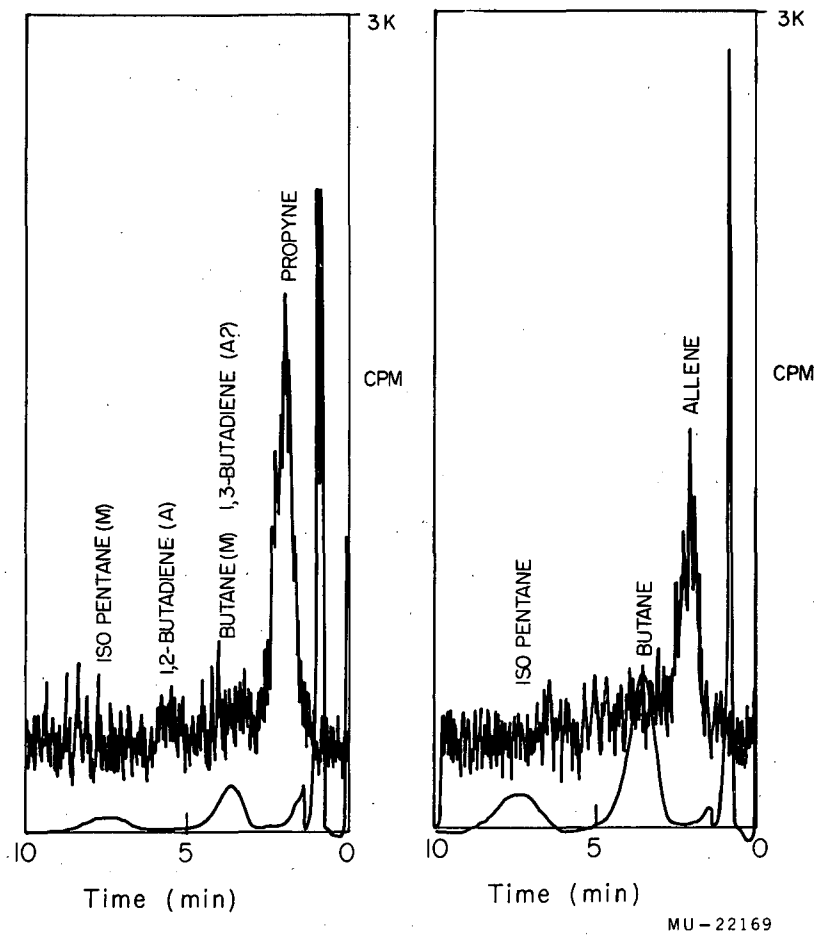


Fig. 63. B13-8 and B13-9: AP-L analysis of first (allene) and second (propyne) fractions from B13-5.

Since we were certain it was a C_3 from its retention time on AP-L, and since we knew it was not propane, propene, propyne, or cyclopropane, we were fairly sure it was either allene or cyclopropene, the only two remaining C_3 hydrocarbons. Cyclopropene is so unstable that its persistent presence throughout the analysis seemed unlikely. Hence, allene was the most reasonable candidate. It was obtained and its retention times in AP-L and DMS were determined and found to agree nicely with that of the activity peak, t_r^0 for allene being 1.10 min or AP-L and 3.40 min on DMS, while the allene activity peak had t_r^0 equal to 3.22 min on DMS and 1.02 min on AP-L. t_r^0 for propyne was 0.90 min on AP-L and 7.18 min on DMS; the times for the propyne activity peak were 0.90 min on AP-L and 7.18 min on DMS.

Our faith in the precision of this technique has grown to the point where we would not now consider it at all likely that the propyne activity peak on DMS could be 1, 3-butadiene, and we would not consider very seriously the possibility of the allene peak's being either 1-butene or isobutene, with lower retention times, or cis or trans 2-butene with slightly higher retention times than allene is known to have on DMS.

To confirm the identification of allene and propyne, a fresh sample from B13 was run on AP-L as shown in B13-10 (Fig. 64), the C_3 and C_4 fractions being trapped separately. Carrier amounts of allene and propyne were then added to the C_3 cut, which was rerun on AP-L in B13-11 (Fig. 65). Far too much carrier was added, so although coincidence was established, the esthetic quality of the B13-11 trace is somewhat less than we might desire. The skewness of the peaks and shortening of the retention times is due, of course, to overloading of the column. Here, too, allene and propyne were trapped separately for rechromatography on DMS, shown in B13-13 (Fig. 66) and B13-16 (Fig. 67). Again coincidence is found to be established.

Carrier 1, 3-butadiene was added to the C_4 cut from B13-10, which was then run on DMS as shown in B13-12 (Fig. 68). Again, far

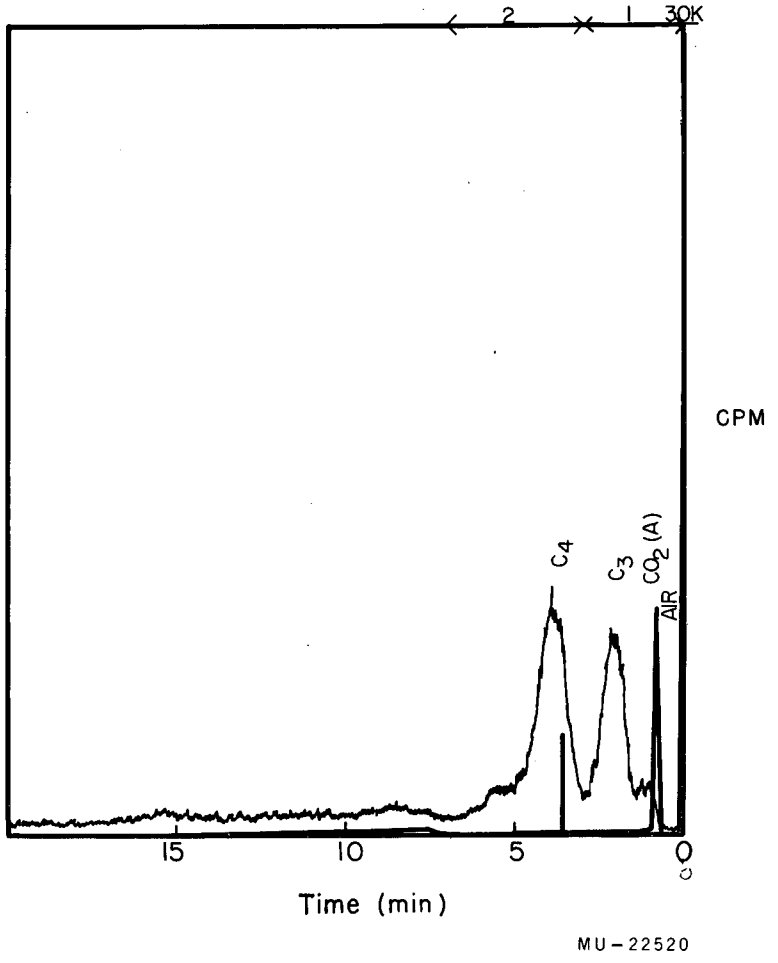


Fig. 64. B13-10: AP-L analysis of whole sample. Note fractional collection.

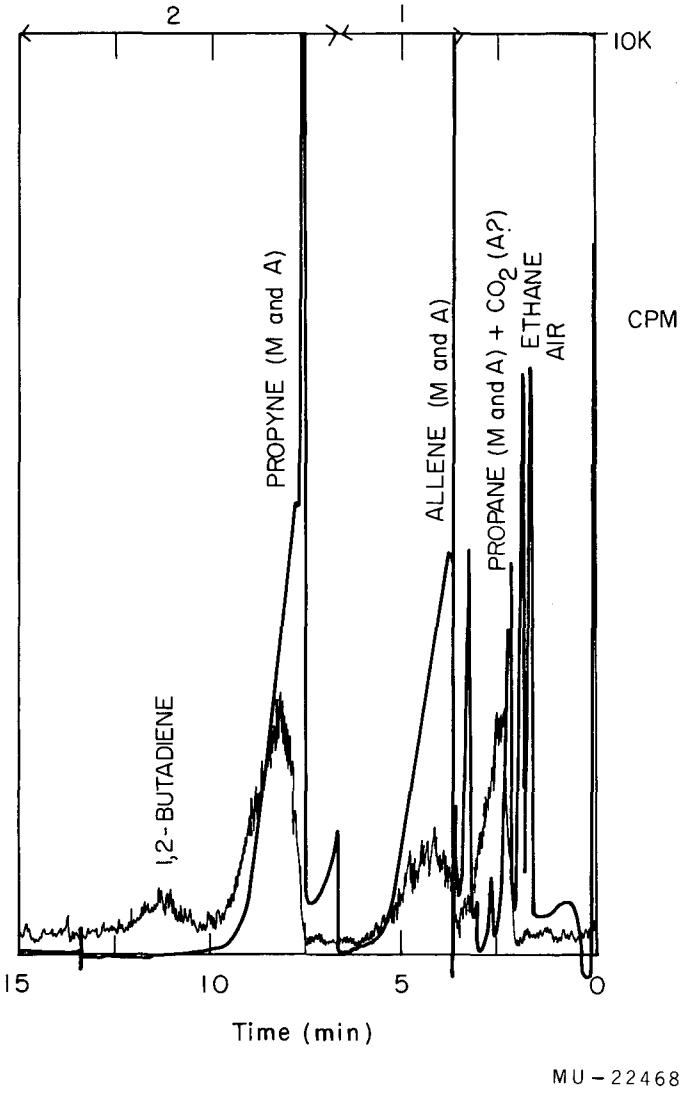


Fig. 65. B13-11: DMS analysis of first (C_3) cut from B13-10. Note fractional collection.

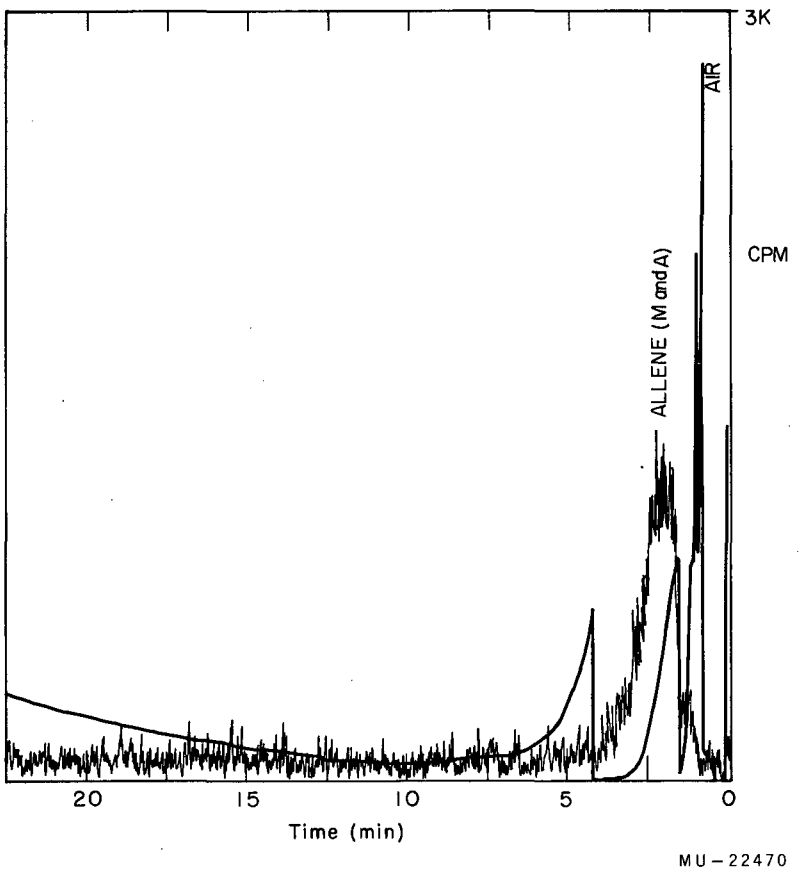


Fig. 66. B13-13: AP-L analysis of first (allene) cut from B13-11.

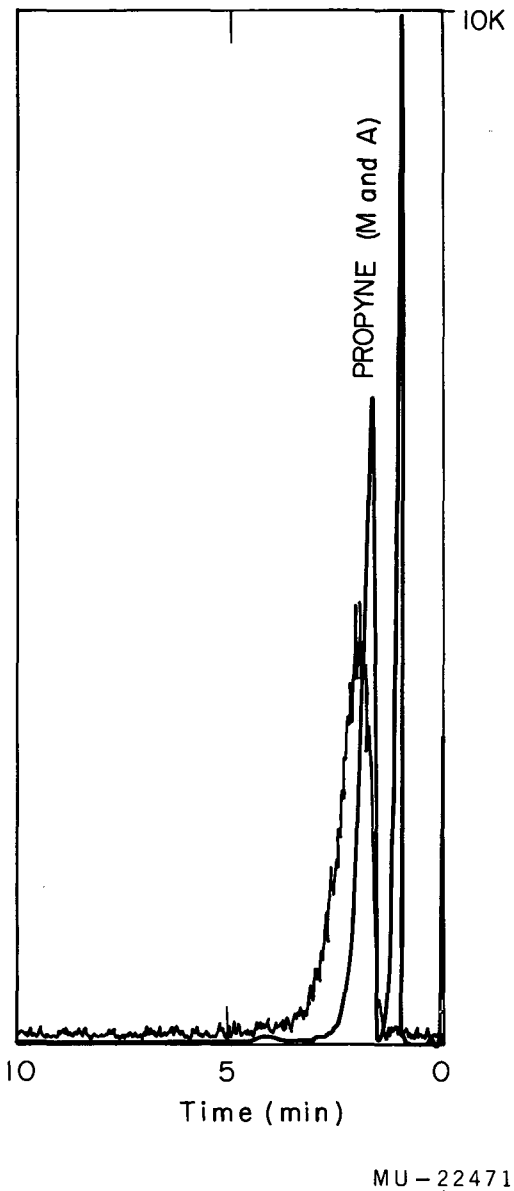


Fig. 67. B13-16: AP-L analysis of second (propyne) cut from B13-11.

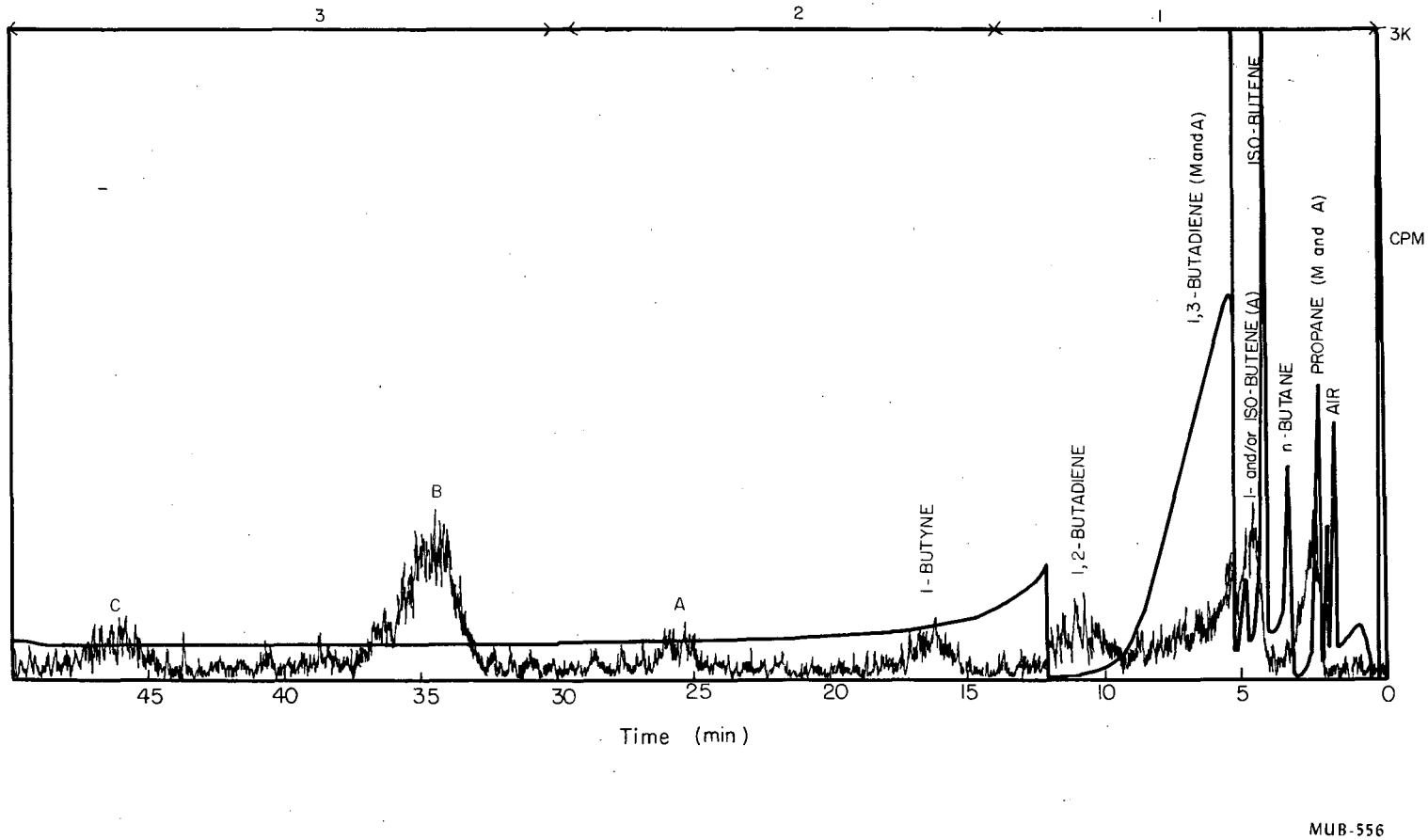


Fig. 68. B13-12: DMS analysis of second (C_4) cut from B13-10. Note fractional collection.

too much carrier was added, causing skewness and shortening of the retention time of the 1, 3-butadiene peak. Although 1, 3-butadiene is indicated in B13-12 as being present and, indeed, is present, we did not conclude so from this trace, this decision being reached only after 1, 3-butadiene was clearly indicated from analysis of B12, as will be shown. The C_4 effluent from B13-12 was trapped in three portions for rechromatography on AP-L. This is shown for cuts 1, 2, and 3 in B13-15, B13-17, and B13-18, respectively (Fig. 69). In B13-15 we see, in addition to small amounts of activity in 1, 2-butadiene, and the normal C_4 range, an activity peak in the C_3 area, coincident with the propane mass peak. This peak was also seen in B13-12. This could be due, of course, to incomplete separation of the C_3 and C_4 cuts in B13-10, but then we would expect to see allene and propyne, which is not the case. This is not the first example of apparent reaction of the ^{14}C-labeled prebenzene compounds to give rise to new products, nor is it the most striking. Examination of B13-11 shows a definite 1, 2-butadiene peak present under circumstances whereby the cocondensation of 1, 2-butadiene with the C_3's from B13-10 is out of the question, 1, 2-butadiene being somewhat higher boiling than most of the other C_4's and its retention time on AP-L therefore being quite far removed from that of the C_3's. This phenomenon is seen again in analysis of the B12- prebenzene compounds. Apparently 1, 2-butadiene is made from the mixture of ^{14}C-allene and -propyne, and ^{12}C-ethane, -propane, -butane, and -isopentane, the latter arising from impurities in the methane. We are, in fact, in no position to assert that any of the prebenzene compounds are primary products of ion irradiation. We are, moreover, hard put to draw the line between primary and secondary products, although there is no difficulty in deciding that at least some of the 1, 2-butadiene found is formed by reactions so far removed from the process of irradiation as to be beyond the scope of our interest in the present work. It should be pointed out that identification of the 1, 2-butadiene peak was not made until after the B12 material had been analyzed.

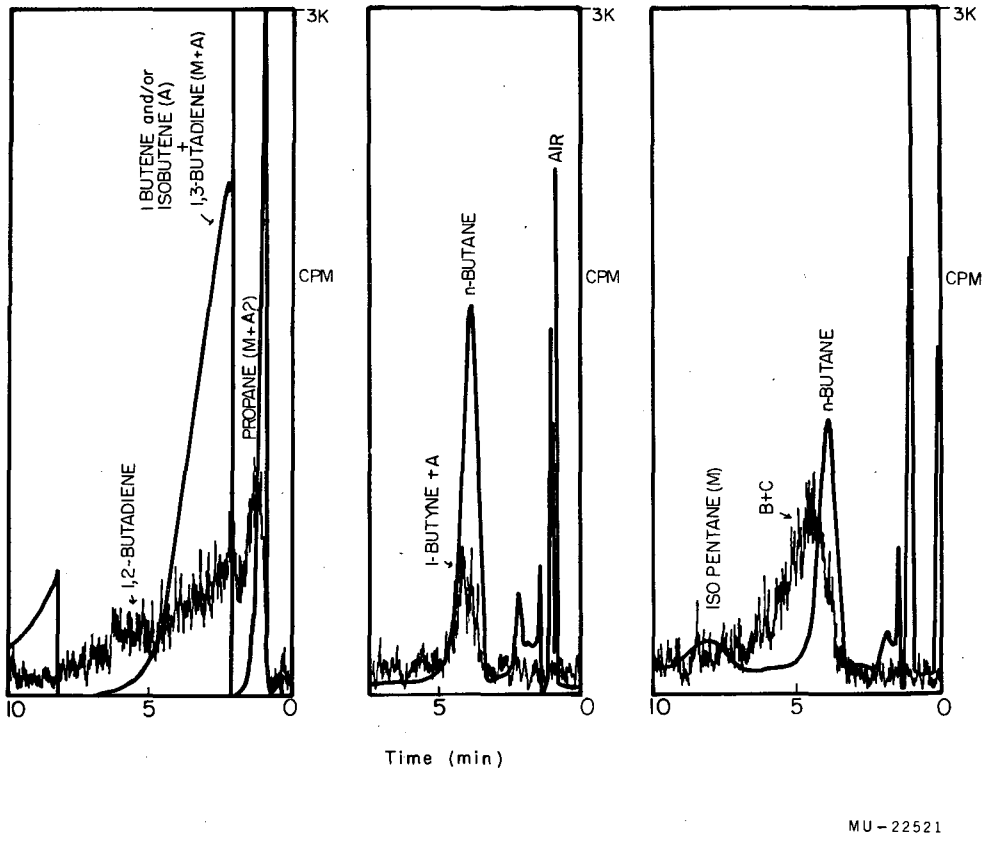


Fig. 69. B13-15, B13-17, and B13-18: AP-L analysis of (from left to right) first, second, and third cuts of C_4 group from B13-12.

Irradiation B12

The analysis of the B12 prebenzene compounds was done in the same manner as that of the B13 material, but yielded much clearer information about the C_4 group. B12-6 (Fig. 70) shows the trace from analysis of all the B12 prebenzene compounds on DMS, cuts being made as indicated. To the C_3 cut, carrier amounts of allene and propyne were added in an attempt to get a more presentable trace showing the mass and activity peaks for those two compounds. As can be seen in B12-7 (Fig. 71), showing the rechromatography of the C_3's on DMS, this goal was not reached. Apparently considerable loss was incurred during condensation or distillation of the compounds. The allene activity peak is on the 30 K, which is why it appears so minuscule. Again, 1,2-butadiene is seen to have been synthesized from the propyne-allene mixture.

Because of the relative peak heights of CO_2 in the B12-6 and what we have labeled propane in B12-7, it is fairly certain that propane was present in B12-7, although it can hardly be seen on the trace as presented here. The four fractions from B12-7 were rerun on DMS; the first three fractions are shown in B12-8, B12-9, and B12-10, respectively (Fig. 72). B12-8 is a rather strange trace, giving the only hint of the existence of propene seen in the prebenzene analysis, as well as containing a mysterious peak in the C_4 region.

1-3-Butadiene and 1-butyne were added to the C_4 fraction from B12-6, which was then rechromatographed on DMS, as shown in B12-12 (Fig. 73), where confirmation of the identity of 1,3-butadiene and 1-butyne is seen to be established. Very little contamination of the C_4 cut by C_3 material occurred, although there may be a small amount of propyne in the tail of the 1,3-butadiene peak. There is, however, no question about the identity of the peak proper. A very small peak due to butane is present, and a somewhat larger one due either to 1-butene or isobutylene, or both, may be seen. A small shoulder, possibly due to cis-2-butene, is also present. Carrier amounts of 1-butene and

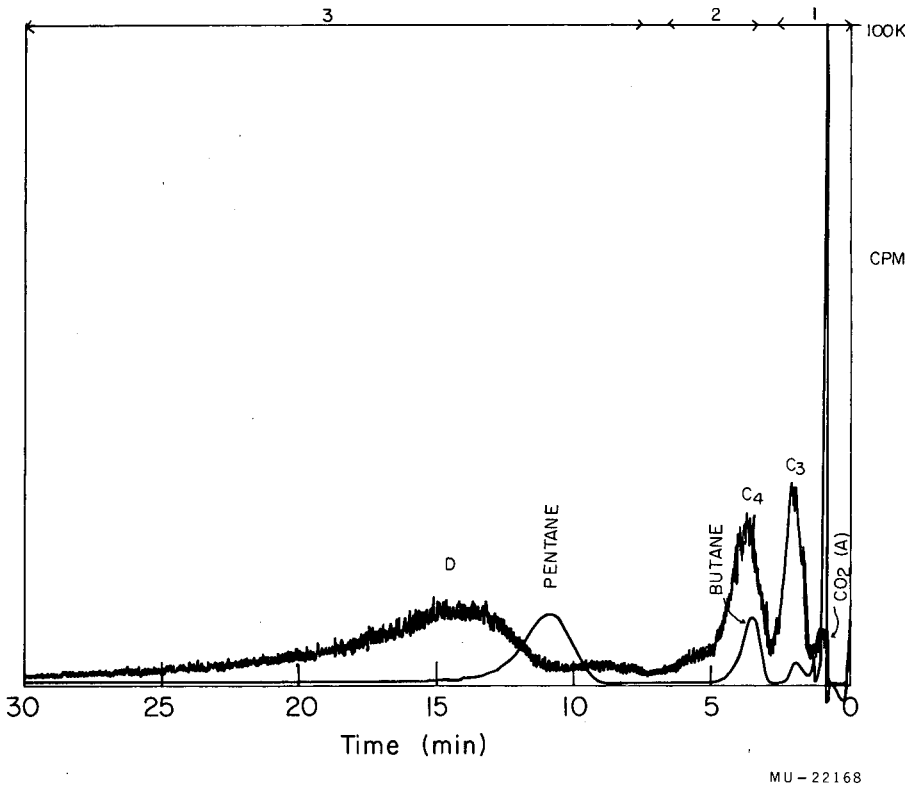


Fig. 70. B13-6: AP-L analysis of all of the prebenzene group from B12, previously separated by GLC without counting. Note fractional collection.

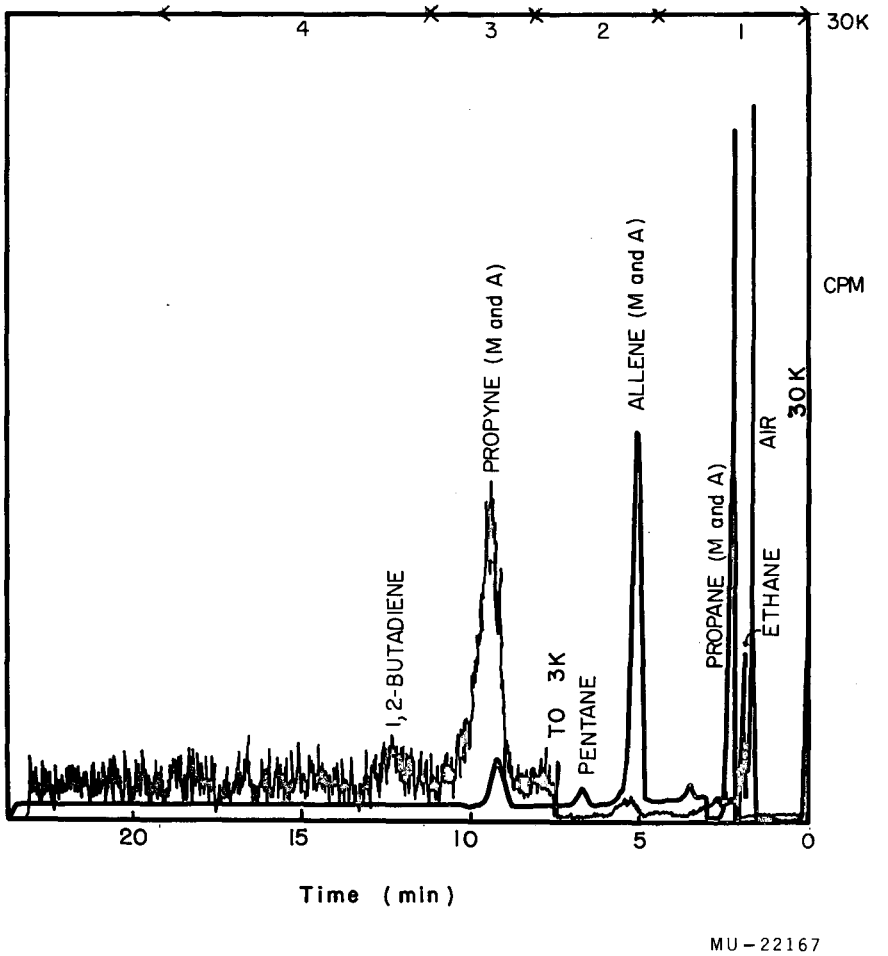


Fig. 71. B12-7: DMS analysis of the first (C_3) cut from B12-6. Note fractional collection.

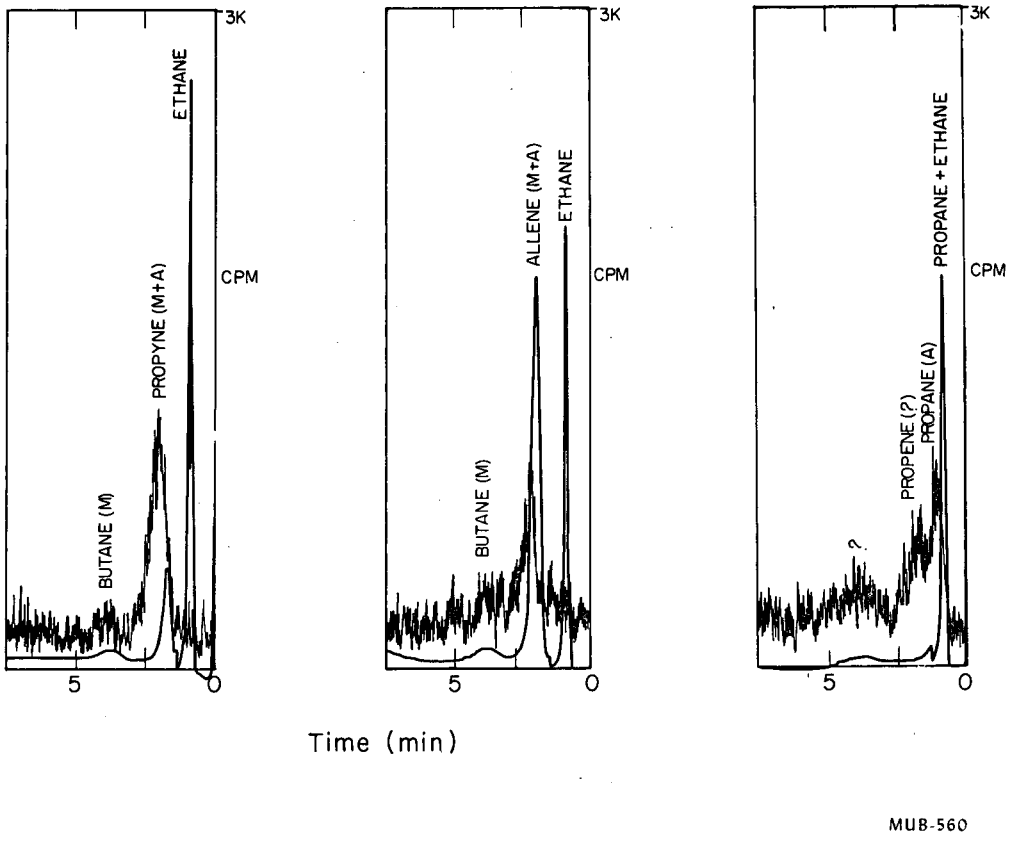


Fig. 72. B12-8, B12-9, and B12-10: AP-L analysis of (from left to right) third, second, and first C_3 cuts from B12-7.

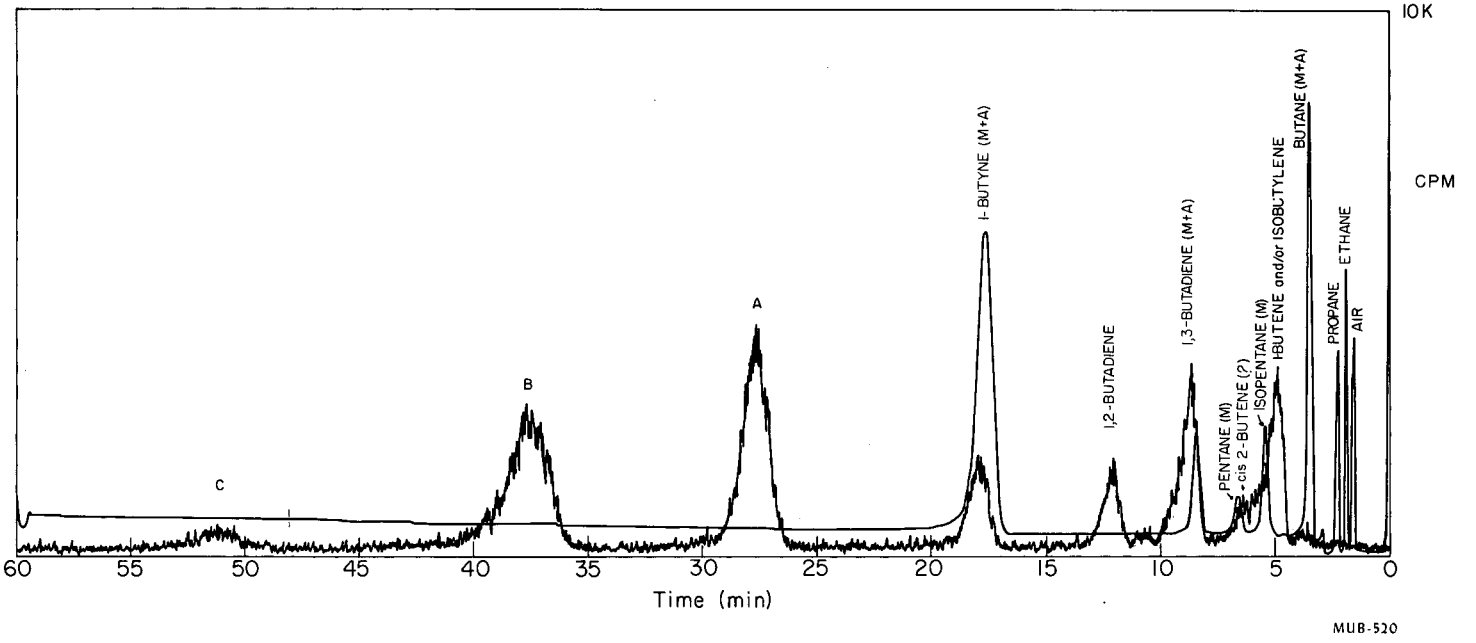


Fig. 73. B12-12: DMS analysis of second (C_4) cut from B12-6.

isobutylene were added to the condensate from B12-12, but an accident unfortunately occurred, causing the loss of the material, so no further confirmation of the C_4 compounds was possible. The C_5-C_6 fraction in the D area was rerun on DMS at a higher flow rate than usual in the hope that material could then be detected in reasonable time, but no activity peaks were seen.

Our failure to identity any of the components of the D area is due, in part, to the labile nature of those compounds, but is primarily due to the fact that their retention times on DMS are apparently so very long that they are never seen at all. Attempts to run the DMS column at temperatures somewhat higher than the room temperature used throughout this analysis proved impossible. At 40° the vapor pressure of dimethylsulfolane is apparently high enough to cause enough of it to be swept out of the column to poison the proportional counter. Of course, a shorter column could have been used, but this was not done. For further work it would seem worth while to attempt to make, or obtain, higher-molecular-weight analogs of dimethylsulfolane, hoping that selectivity would be retained upon substitution of larger alkyl groups for the methyl groups.

At this point we had no 1, 2-butadiene, but its retention times on DMS and AP-L were estimated from the graphs shown in Figs. 19 and 20. When 1, 2-butadiene was obtained, its retention time was found to be 9.62 min on DMS and 4.55 min on AP-L, whereas the activity peak in question had a retention time of 9.78 min on DMS and 4.50 min on AP-L. Even though simultaneous mass and activity peaks were not obtained for this compound, because of the loss of the B12 material, it is felt that this identification is secure.

2. Summary of Prebenzene Identifications

The following compounds, in decreasing order of security, are considered to have been identified in the prebenzene group from irradiations B11 through B13: (a) allene and propyne, on the basis of coincident mass and activity peaks on both columns; (b) 1, 3-butadiene

and 1-butyne, on the basis of coincident mass and activity peaks on DMS and approximate knowledge of the activity peak retention time on AP-L; (c) 1, 2-butadiene, on the basis of its retention time on AP-L and DMS; (d) 1- and (or) isobutene, on the basis of retention time on DMS and approximate knowledge of position on AP-L; (e) n-butane (in very small amount), on the basis of coincident mass and activity peaks on DMS and approximate knowledge of position on AP-L.

The following compound is considered to be indirectly identified as being present; propane, on the basis of coincident mass and activity peaks on DMS and AP-L and activity peak intensity relative to that of carbon dioxide.

The following compound is thought to be responsible for the C_4 activity peak labeled B on the DMS traces: butadiyne, on the basis of some assumptions made by the author concerning the nature of selectivity on the DMS column. This will be discussed shortly.

The following compounds have been looked for, single or occasional evidence for their presence has been seen, but such evidence has been transitory and unconfirmed: propene, cis-2-butene, and 2-butyne. We may conclude that if these compounds are present at all they appear in amounts small relative to other prebenzene compounds.

The following compounds were sought, could have been seen, but were not found: ethane, ethene, acetylene, and cyclopropane.

The following activity peaks were consistently, or often, seen but were not identified: the C_5-C_6 activity peak labeled D on the DMS traces, the C_4 activity peak labeled A on the DMS traces (this will be discussed shortly), and the C_4 or C_5 activity peaks labeled C on the DMS traces.

3. Speculation Regarding the Identity of Activity Peaks A and B

When the C_4 activity spectrum on DMS was first seen, it was thought that the peak labeled A might be due to buteneyne and that labeled B might be due to butadiyne. If the speculations, or assumptions, we are about to make are indeed correct, then the former assignment must be incorrect and the latter correct. These assignments can, of course, be verified experimentally by obtaining the compounds in question and measuring their retention times, and the author intends to do so in the future, but we were unable to obtain these compounds commercially and did not wish to devote time to their synthesis, as their importance in the present work is not vital.

From the slopes drawn for the several functional groups in Fig. 19, the selectivity of the dimethylsulfolane column at a given temperature may be calculated, as has been done by Van der Wiel.[56] We may define the DMS selectivity factor, s, for a given functional group as the ratio of the retention time for a hypothetical member of that group to that of a hypothetical alkane of the same boiling point. This information can be obtained from Fig. 19 by making a vertical cut at a given temperature. A cut at 283°K, the boiling point of butadiyne, gives t_r^0 - alkane = 2.38 min and t_r^0 - alkyne = 17.0 min, i.e., s-alkyne = 7.15. If we may assume that s-diyne = 2 × s-yne, then we would expect butadiyne to have t_r^0 = 2 × 7.15 × 2.38 = 34.0 min on DMS. The retention time of activity peak D on DMS is, in fact, 34.0 min. If, now, a cut is made at 278°K, the boiling point of buteneyne, t_r^0 - alkane = 210 min, t_r^0 - alkene = 4.20 min, and t_r^0 - alkyne = 15.0 min. Hence, s-alkene = 2.00 min and s-alkyne = 7.14 min. If the selectivity factors are additive, buteneyne would be expected to have a retention time on DMS of (2.00 + 7.14) × 2.10 = 19.2 min. Activity peak A, however, has a retention time on DMS of 24.4 min, a significant difference from the calculated time.

If the selectivity factors for individual multiple bonds are indeed additive, we would then conclude that activity peak B is probably due to butadiyne but that activity peak A is probably not

due to buteneyne. We have little evidence bearing on the additivity of selectivity factors, but what there is tends to confirm it. A vertical cut at 280°K gives s - alkene = 2.0 min and s - diene = 4.05 min, that is, hydrocarbons containing two double bonds, whether they be conjugated or cumulative, are selectively retained just about twice as long as hydrocarbons containing one double bond. To be sure, two plus two is the same as two times two, but it is less reasonable to expect the selectivity factors to be multiplicative rather than additive. What is particularly striking in the diene-alkene comparison is that there is little difference between 1, 2- and 1, 3-dienes. One would not have been surprised to find that a conjugated diene was affected quite differently from a cumulative diene, or that a conjugated diene did not at all act like a compound simply bearing two double bonds. But this is not the case. From the three diene points that we have, it appears as though all that is important in the determination of s, at least to the first approximation, is the number and kind of multiple bonds in a hydrocarbon. This view was also substantiated by the alkynes, 2-butyne lying on the same line as the propyne and 1-butyne, where one might have expected the absence of acetylenic hydrogen in 2-butyne to have made a significant difference. Likewise, the 1- and 2-alkenes, to a first approximation, may be considered equivalent in their retention times on DMS, whatever differences there are between them being quite small compared with the differences between other bond types.

The difficulty with the above argument does not lie with the assumption of additivity of the selectivity factors, but, rather, with the question of the peak A - buteneyne correlation, or the lack thereof. If this peak A is not buteneyne, then what is it? We are running short on C_4 hydrocarbons. If peak A is not buteneyne, then buteneyne is probably not present. If so, why is it absent when most of the other unsaturated C_4 hydrocarbons are present, or at least are suggested? We have no answer to the second question, but to speculate on the first we return once more to our graphs and our assumptions.

Since the retention time of peak A on DMS, 24.4 min, is too large for it to be buteneyne, if our assumption of additivity of selectivity factors is correct, and since we are quite sure from its retention time on AP-L that it is a C_4, then peak A must contain an assembly of multiple bonds which will give it a larger selectivity factor than an eneyne. A triene will not do, for its selectivity factor would be three times 2.00 = 6.00, whereas the eneyne already had a selectivity factor of 9.14, so we turn to a diyne with an assumed selectivity factor of 14.3. If peak A is a diyne and if the diyne selectivity factor is 14.3, then an alkane of the same boiling point as A should have a retention time on DMS of 24.4/14.3 = 1.71 min. From Fig. 19 it is seen that an alkane with t_r^0 = 1.71 min on DMS should have a boiling point of about 270°K (-3°C). From trace B13-18 (Fig. 69) we know that peak A has a retention time on AP-L of about 2.88 min. Reference to Fig. 20 indicates that a compound having a retention time of 2.88 min on AP-L should have a boiling point of about 272°K (-1°C). Peak A, therefore, has all the credentials for a diyne of boiling point about -1 to -3°C. Unfortunately, such a C_4 diyne is not known; butadiyne, the only known C_4 diyne, has a boiling point of about +10°C, and we have already decided that butadiyne must be peak B, if our arguments are correct.

The retention time of peak B on AP-L is 3.28 min, corresponding to a boiling point of +3°C, whereas butadiyne has a boiling point of +10°C. This, however, need not disturb our feeling that peak B may be due to butadiyne, because the alkynes measured on AP-L had somewhat shorter retention times for their boiling points than the rest of the hydrocarbons measured. This does mean, however, that the agreement of the boiling points calculated for peak A from AP-L and those calculated for it from DMS is probably fortuitous, since we are assuming for the purpose of this speculation that peak A is also a diyne. The author does not take the arguments and inferences given here very seriously, and can hardly expect the reader to do so, but he is sufficiently intrigued by the question of the identity of peak A to intend to answer these questions experimentally in the future.

4. Semiquantitative Aspects of the Prebenzene Investigation

As discussed earlier, it is not possible to state the yields of any of the prebenzene compounds identified in this investigation, nor is it possible to state accurately the over-all fraction of activity in the prebenzene group as a whole, but rough estimates can be made. As judged from those analyses of whole sample made on AP-L at room temperature, the over-all prebenzene yields for irradiations B11, B12, and B13 are respectively 8%, 8%, and 5%. The difference between B13, the 45-ev irradiation, and B11 and B12, 5000 and 90 ev respectively, may not be significant.

The only information available from the earlier irradiations consists of the high-temperature traces on AP-L. Here the unknown contribution of $^{14}CO_2$ to the prebenzene group, severe contamination, and unexpectedly large activity peaks, going off scale, etc., make activity estimates virtually meaningless. In B10-1, however, the first trace from this 90-volt irradiation (Fig. 36), there is obviously much more prebenzene activity than in the other traces, more than 90% of the total activity seen in the counter being due to the prebenzene group. $^{14}CO_2$, however, could be contributing as much as a third or half of the prebenzene activity. Even so, the remaining activity is larger than that seen in other 5000- and 90-ev irradiations. In B7, a 5000-ev irradiation, the prebenzene activity does not account for more than a few percent of the total activity introduced in the irradiation. If any dependence of prebenzene activity on ion energy or energy density exists, it is not apparent from the crude estimates that we can make. Moreover, there is no reason to believe that it is valid to consider the prebenzene group as a whole.

If we cannot calculate yields for the prebenzene compounds identified in B11 through B13, we might expect the ratios of activity in compounds of comparable boiling point to be meaningful. Collection and handling losses should be equivalent in that case. The ratio of propyne to allyne is approximately constant in all three

irradiations analyzed, being about 2:1. Likewise in the C-4 group, compounds A and B, the predominant members of that group, appear with one exception (B13-12) in fairly consistent ratio, there being slightly more A than B in most cases. It is probably safe to estimate that the yield of any of the compounds identified or peaks isolated does not exceed about 1%.

In B11, the 5000-ev irradiation, and B12, a 90-ev irradiation, the activities in the C5-6 area, the C_4 area, and the C_3 area are approximately in the ratio of 5:3:2. In B13, the 45-ev irradiation, the C4/C3 ratio is still about 3:2, but little or no C_5-C_6 is visible in B13-10, the only trace of fresh B13 sample analyzed on AP-L at room temperature.

The drop in prebenzene activity in B13 compared with B12 is in approximate agreement with the drop in total activity found in the B13 sample relative to that of B12. The total activity from liquid scintillation counting of whole sample for B12 was 14.9% of the total introduced, while that for B13 was 11.1%. In comparison, the total activity in whole sample from B11, a 5000-ev irradiation, was 22.7%. Most, but not all, of the difference between B11 and B12 (a 5000-ev and a 90-ev irradiation, respectively) is accounted for by the drop in the yields of benzene, toluene, and cycloheptatriene. In all cases, the total activity found in the prebenzene group and in benzene, toluene, and cycloheptatriene is less than that found in the whole sample, so no doubt there are C_9 and perhaps higher-molecular-weight products in the sample which are not seen under the conditions of chromatography used for the analysis of benzene, toluene, and cycloheptatriene. Perhaps we have been collecting products as high-boiling as di- or triphenylmethane, the most logical candidates for the remaining activity, since they were found as products of $^{14}C^+$ recoil in benzene-aniline by Schrodt and Libby.[22]

E. Results of a 90-ev $^{14}C^+$ Irradiation of 1-Hexyne

When allene and propyne were identified as products of $^{14}C^+$ irradiation of benzene, it was thought that they might arise from reaction of the ^{14}C species, perhaps in the form of carbene, with acetylene, which is the major organic product of low molecular weight from the radiolysis of benzene.[57] In order to test whether $^{14}C^+$ ions, or their progeny, have any particular affinity for addition to triple bonds, 1-hexyne was irradiated with 90-ev $^{14}C^+$ ions, the object being to look for a large activity peak in the C_7 region. 1-Hexyne, kindly loaned to us by Prof. Prausnitz, was chosen because of its sufficiently low vapor pressure at -160°. Ninety electron volts was chosen as the ion energy in order to minimize fragmentation of the 1-hexyne and maximize the chance of addition to the parent compound. For the same reason, the hexyne in the input tube was held to -45°, giving an input rate of about 350 to 400 μl/hr, about seven times as fast as benzene was put in. After irradiation n-heptane was added as a C_7 carrier in the usual manner.

The results of this irradiation, shown in Fig. 74, are strikingly negative. Almost no activity was detected in the C_7 region. As was the case for benzene at the same ion energy, the majority of the activity detected is concentrated in the area C_2 or C_3 through C_5C_6. Surely if any very fast addition of ^{14}C to triple bonds occurred, it was not to the triple bond of 1-hexyne, unless, of course, addition to the parent compound was accompanied by a large increase in internal energy which could not be lost by collision or radiation before secondary dissociation occurred.

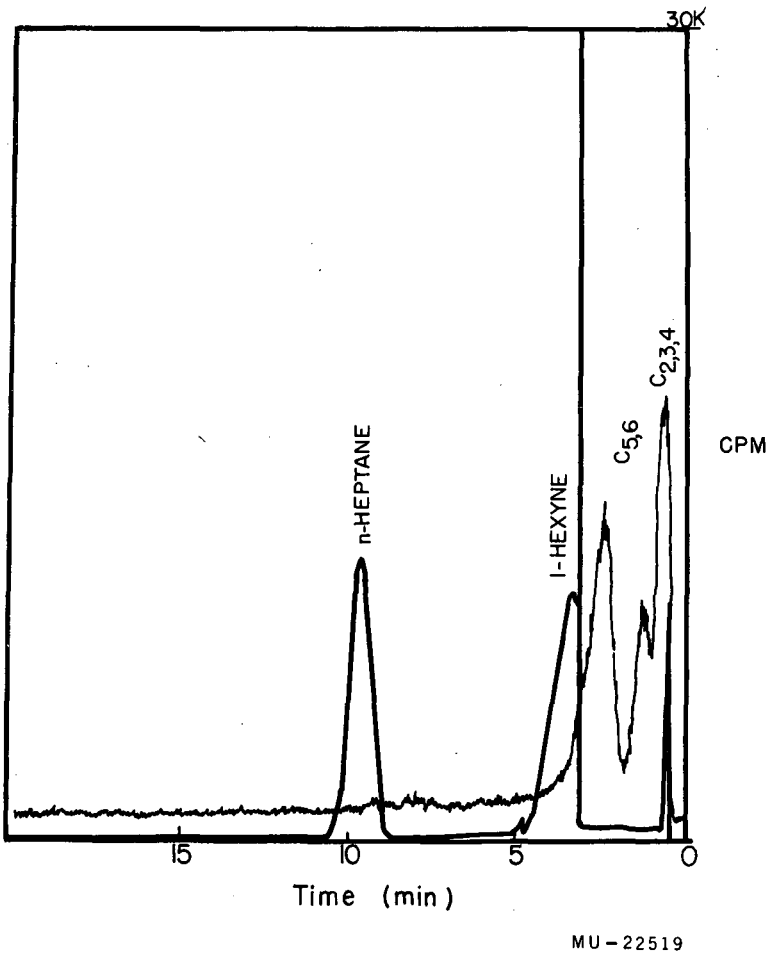


Fig. 74. B14: AP-L analysis of products of 1-hexyne irradiation. Conditions are the same as for the analysis of benzene, toluene, and cycloheptatriene.

IV. DISCUSSION AND CONCLUSIONS

A. Discussion of the Results of the Yield Determinations of Benzene, Toluene, and Cycloheptatriene: Energy and Yield

1. The Energy-Density Effect

If the inverse dependence of product yields on ϵ, the energy density, had been observed at only one ion energy, it would have been interpreted as probably meaning that these three products are formed by a reaction of the ^{14}C species in some form with benzene, as such, and that yield increased with decreasing energy density because of the resulting decrease in the concentration of free radicals, ions, and highly reactive molecules, which we will lump all together under the title of debris or fragments. The ^{14}C species would then have a greater probability of reacting with benzene, and a smaller proportion of the intermediates formed--if indeed any of these reactions do go through many steps--would be scavenged by the debris.

If this were true, then reduction of ion energy would affect the yield only in so far as it affected the energy density. This was, in fact, the result which was anticipated upon irradiation with low-energy ions--a large increase in yield of benzene, toluene, and cycloheptatriene. Precisely the opposite effect was found, however, dependence on ion energy *per se* occurring which was strong enough to overcome the reduction in energy density, resulting in a large net decrease in yield for all three of these compounds. In view of this, the interpretation of the effect of energy density at a constant ion energy must be revised and considerably limited.

These facts can best be interpreted by regarding the yield of a given compound as being proportional to the product of two probability factors, one giving the probability of formation of the first, or of a critical intermediate, depending only on E, and being associated with phenomena occurring in the track of an individual ^{14}C species; the other being the probability that such an intermediate, once formed, will survive to become a stable product molecule, this last factor

depending only on ϵ, and being a property of the irradiated volume as a whole. Furthermore it seems likely that the fate of a highly reactive intermediate, perhaps itself a free radical, is decided not while the sample is a solid at -160° but rather during the time when the sample is warmed up and is melted or sublimed immediately prior to collection. The effect of ϵ on Y at a given E, therefore, provides no detailed information regarding the reactions involved in any sequence, but it does strongly suggest that in all cases discrete labile intermediates exist, and that these intermediates must further react with benzene to become stable products and that competing scavenging reactions occur between the intermediates and the debris. We know with certainty in the case of benzene and toluene, and with lesser probability for cycloheptatriene, that we must consider intermediates and not the final product because of the expected small extent of destruction incurred by the benzene as a whole as judged by the radiation chemistry of benzene.[58] That is to say, the same effect would occur in principle, but would be small beyond observation were the destruction of benzene-^{14}C as such involved. Toluene as such is likewise relatively radiation-resistent,[58] but cycloheptatriene might well be scavengable in its final form. This could, in fact, explain the greater dependence of the cycloheptatriene yield on ϵ relative to that of benzene and toluene, which are comparable to each other.

Before proceeding further, it is perhaps worth while to indicate the type of intermediate and follow-up reactions the author has in mind, on a purely speculative basis, in this discussion. In the case of toluene, for example, we visualize something like a C_7H_6 species having the skeleton of toluene, perhaps, but needing to pick up two hydrogens to become stable toluene. Although one does not expect free hydrogen atoms to be existing for long times in the irradiated sample, it is perhaps possible that species exist from which hydrogen abstraction would be easier than from benzene. We shall now show that in order for the ϵ effect to exist, at least some of the follow-up reactions of the intermediate must occur with benzene. This is so because if the

necessary follow-up reactions occurred only with fragments, and destruction also occurred only by reaction with fragments, the two would vary in the same proportion as ϵ varied. Perhaps this is sufficiently obvious to merit no further discussion, but it can be more explicitly shown.

If the follow-up reactions of a given intermediate occur only with F, the fragments, the following three reactions are of product-determining importance, where I is a reactive intermediate, F is a generalized fragment, P is a product molecule, X is some side product in general, and the k's are rate constants.

$$I + F \xrightarrow{k_1} P , \tag{R1}$$

$$I + F \xrightarrow{k_2} X , \tag{R2}$$

$$F + F \xrightarrow{k_3} X . \tag{R3}$$

The rate of change of P, I, and F with time are given by the following equations:

$$\frac{d(P)}{dt} = k_1 (I)\ (F) , \tag{1}$$

$$\frac{d(I)}{dt} = -\ (k_1 + k_2)\ (I)\ (F) , \tag{2}$$

$$\frac{d(F)}{dt} = -\ k_3 (F)^2 . \tag{3}$$

In Eq. (3), the rate of disappearance of F due to reaction with I is ignored because of the much greater concentration of F. Integration of Eq. (3) between t = t and t = 0 gives

$$(F) = (F)_0 / (1 + k_3 (F_0)\ t) , \tag{4}$$

where $(F)_0$ is the initial fragment concentration. Substitution of this value for F in Eq. (2) and integration between t = t and t = 0 gives

$$(I) = (I)_0 \left[1 + k_3 (F)_0 t\right] -\ (k_1 + k_2) / k_3 , \tag{5}$$

where $(I)_0$ is the initial concentration of I. Finally, substitution of the equations for F and I given in Eqs. (4) and (5) into Eq. (1), followed by integration between $t = \infty$ and $t = 0$, gives

$$(P)f/(I)_0 = k_1/(k_1 + k_2) , \tag{6}$$

where $(P)_f$ is the final concentration of the product. The Ratio of $(P)_f$ to $(I)_0$ is the survival factor, i.e., that factor whose effect on the yield we directly observe by variation of ϵ at constant E. The result expressed in Eq. (6) is in agreement with our initial expectation: the fraction of intermediate surviving to become product is independent of the initial fragment concentration, which is assumed to be directly proportional to ϵ, depending only upon the rate constants involved in the reaction of I with F to give product on the one hand, and side product on the other.

We were fortunate in the foregoing argument to encounter integrals that were soluble in closed form. Upon addition of a step allowing reaction of I with benzene to give product, we find that our luck does not hold. Addition of Reaction R1', where B indicates benzene, and modification of the rate equations for P and I, gives

$$I + B \xrightarrow{k'_1} P , \tag{R1'}$$

$$\frac{d(P)}{dt} = k_1(I)\,(F) + k'_1\,(I) , \tag{1'}$$

$$\frac{d(I)}{dt} = -k_1(I)\,(F) - k_2(I)\,(F) - k'_1\,(I) , \tag{2'}$$

results in no change in the integrated equation for F, and still allows I to be determined as a function of time and F_0, but the final equation giving $(P)_f$ contains an intractable integral. Although the dependence of yield on ϵ cannot be calculated in this case, at least by the author, it is nevertheless clear that some dependence on ϵ does indeed exist.

Before yielding completely in the fact of mathematical difficulty, one finds it interesting to re-examine Eq. (5) of the preceding argument, because the ratio of the concentration of I at time t to the initial

concentration of I has a dependence on F_0 of the same form as was noted for the dependence of yield on ϵ. Writing $F_0 = c\epsilon$, where c is a constant, one may rewrite Eq. (5) to give

$$\frac{(I)}{(I)_0} = \left[1 + k_3 c\epsilon t\right]^{-\left(\frac{k_1+k_2}{k_3}\right)} . \tag{7}$$

Under what physical circumstances, then, may the left-hand side of Eq. (7) be conceivably interpreted as related to the final yield of a product? It has already been shown that if I reacts with F and only with F to give P, the final yield must be independent of ϵ. It was argued earlier that a reactive intermediate, and not a relatively unreactive product molecule, must be involved in the survival phase, giving the ϵ effect. It is believed that that argument is quite compelling, especially for benzene and toluene, but it is interesting to observe that if it were wrong and if all that were involved here were survival of a finished product, we could then substitute P for I in Eq. (7), dropping k_1 because no constructive fragment reactions would then occur, giving

$$\frac{(P)}{(P)_0} = \left[1 + k_3 c\epsilon t\right]^{-k_2/k_3} . \tag{8}$$

In Eq. (8), P goes to 0 as t goes to infinity, but for the present argument there is no necessity to make t go to infinity--it need go only to some definite value, for example, to the time when all the sample has sublimed off the target cold finger. If t could be assigned some definite value for a series of experiments, then $(P)/(P)_0$ would be directly proportional to the yield and the yield would vary with ϵ in the manner observed, the exponents being the ratio of the rate constants involved, and having nothing to do with the order of the overall process.

Although this argument is rather strained, the agreement of the form of Eq. (8) with that observed for the ϵ effect is sufficiently

suggestive to require more specific justification for our refusal to accept destruction of stable product, such as benzene-^{14}C, as an explanation of the ϵ effect. The G value for pure liquid benzene upon irradiation with 1.5-Mev electrons is 0.8; that is, 0.8 benzene molecule is permanently altered for every 100 ev of energy absorbed.[57] In Table X ϵ, the ev absorbed per molecule in the portion of the benzene irradiated by the ion beam, is listed. If the G value in our work is near that cited for pure liquid benzene, then the total decomposition of benzene in the 5000-v irradiations ranges from a few tenths of a percent to about 9%, and is less than 2% for all irradiations save B6. The fraction of benzene-^{14}C molecules once formed that is destroyed by reaction with debris can be no greater, therefore, than 1 or 2%, in all cases but one. Increase of ϵ from 1 to 2 would, at the most, result in the destruction of around 2% of the benzene-^{14}C rather than 1%. The effect would not be noticeable. A much larger, and clearly evident, effect is noticed. Hence, labile intermediates, not benzene itself, must be involved. The same argument holds for toluene[58] and, perhaps also, for cycloheptatriene. No information regarding the latter is available.

There is yet another avenue of speculation open to us concerning Eq. (7), one which is, perhaps, as unlikely as the preceding but at least contains no elements which we strongly feel are precluded. If reaction of I with F to give P either does not occur at all, or occurs to only a minor extent, we may drop k_1 from the exponent of the right-hand side of Eq. (7). Further, if when the sample is warmed prior to product collection the reactions involving F—F with I and F with F—run their course to a large part before the constructive steps going from I to P occur, then the ratio of (I) to $(I)_0$ at a fairly well-defined time, or, more likely, temperature, would be directly related to the over-all probability of the survival of I. This would require a large difference in the activation energies of the reactions involving F relative to those involved in the reactions of I to give product.

This, however, is not unreasonable, for reactions involving I might well be radical recombinations or addition reactions having relatively small activation energies, whereas reactions of I to give product might well involve bond breaking or rearrangement, therefore having relatively high activation energies. Possible product-forming reactions would be hydrogen abstraction, by I, from benzene, or intramolecular rearrangement of I to give P. The time factor in Eq. (7) would then be associated with either the time required for the fragment reactions to burn themselves out, or the time to reach a temperature at which product-forming reactions can rather sharply cut in. The rate constants appearing in Eq. (7) would be temperature-dependent, and the experimentally determined exponent would reflect the average of the constants over the temperature range where intermediate-destroying reactions occurred. If all this were true, then the ratio of (I) to $(I)_0$ at t, the cut-in or cutout time, would be the fraction of the intermediates that survived the destructive phase, and the yield of a given product would then be directly proportional to that ratio, and we could write for the yield of a given compound at a given ion energy

$$Y = a\left[1 + ck_3\epsilon t\right]^{-k_2/k_3} = a\left[1 + b\epsilon\right]^{-k_2/k_3}, \qquad (9)$$

where a is the proportionality constant in the equation relating Y and $(I)/(I)_0$, and b is k_3ct. It will be recalled that the equation found to approximately describe the dependence of Y on ϵ for the 5000-v irradiations was

$$Y_i = a_i\epsilon^{-n_i}. \qquad (10)$$

In this model, then, we picture the "freezing in" at -160° of the intermediates and fragments after their formation in the ion track. Upon warming of the sample, after irradiation, a brush fire of reactions due to the trapped radicals and other highly reactive species occurs, which rapidly burns itself out, after which the surviving

intermediates may proceed at a relatively leisurely pace to become stable product molecules. The intermediates need not themselves be radicals, but must be highly susceptible to attack by radicals or other highly reactive species. In his review article on radiation chemistry Willard discusses many of the elements contained in the preceding model. Since it is unlikely that paraphrasing his comments would add to their clarity we quote directly in part from that discussion.[59]

"Evidence for the 'freezing-in' of photochemically produced C_2H_5 and I radicals has been provided by Norman and Porter who showed that there is no coloration produced when a dilute solid solution of C_2H_5I in hexane is irradiated at -195°C with ultraviolet light, but that if the solid is warmed following irradiation, I_2 color appears.[60] Similarly, when a solid solution of I_2 in hexane is irradiated, the I_2 color fades as a result of the conversion of I_2 molecules to colorless, frozen-in I atoms, but returns when the system is warmed sufficiently for the atoms to diffuse to each other.... Mador has observed that 0.1 mm thick films of CH_3I subjected to 10^{19} quanta/cm^2 of 2537 A light at 4°K developed a red color which may be due to CH_3 radicals, and on warming to 40°K disintegrate violently in a manner which is attributed to exothermic radical recombination reactions.[61] A similar violet release of stored energy, following irradiation of acrylamide and related monomers with gamma rays at -18°C has been reported by Mesrobian and co-workers.[62] When the samples were heated to room temperature following irradiation, polymerization proceeded rapidly, heating the sample sufficiently to cause it to 'explode.' "

Speculation on the nature of the details of the ϵ effect has been carried as far as is reasonable to go on the basis of the evidence we have gathered. We do not regard the above model as compelling or even probable, but it is possible. Two broad aspects of this interpretation, however, are regarded as being strongly suggested: (a) The ϵ effect is associated only with the destruction of intermediates

formed in the track and has little or no effect on the probability of formation of the first intermediates in the track; and (b) at least in the case of benzene and toluene, labile intermediates, not the eventual product molecules, are involved in the destructive phase. Although it is not essential to this broad interpretation of the ϵ effect, it seems reasonable to assume that destruction is well separated in time from the initial track event, probably occurring when the temperature of the sample is raised prior to product collection. Before we consider how well our interpretation of the ϵ effect can be reconciled with related experiments using recoil techniques, we wish to proceed to a consideration of the effect due to E, the ion energy.

2. The Ion-Energy Effect

Although the yields of benzene, toluene, and cycloheptatriene increase with decreasing energy density when the radiation is carried out at constant ion energy, a large decrease in the yield of these three compounds occurs upon reduction of the ion energy. This effect, due to E, has been interpreted as being intimately associated with the track of a given ion, manifesting itself through events occurring in and close to the track during or very shortly after the track is formed. Granting this for the moment, what does this phenomenon tell us about the mechanisms of the reactions which eventually lead to ^{14}C-labeled benzene, toluene, and cycloheptatriene?

Let us first consider what we need to know to completely describe a given mechanism. First and foremost, we must know the reacting species involved: Is the ^{14}C species charged or neutral? Is it still a bare carbon atom or has it picked up one or more hydrogen atoms? Is it electronically or vibrationally excited at the time it undergoes a given reaction? Does the primary reaction leading to a given product involve reaction of the ^{14}C species with benzene in its ground state, or when electronically or vibrationally excited, or does reaction involve a fragment generated in the track by the passage of the energetic ^{14}C species? Is such a fragment aromatic or aliphatic?

Is it a radical? Is it an ion? Is it electronically or vibrationally excited? If a series of intermediates is involved, what is their nature and what reaction must they undergo to become stable products? Secondly, what are the energetics: Does a primary reaction require the ^{14}C species to have tens of electron volts kinetic energy, or several electron volts kinetic energy, or does it occur after the ^{14}C species has been thermalized?

Surely we cannot begin to answer this awesome array of questions from our simple observation that yield decreases with decreasing ion energy. We can, however, exclude a few possibilities, and when this fact is added to some of the results of recoil experiments, we can speculate on a bit firmer base than was heretofore available on the nature of the primary events.

That decreasing yield with decreasing ion energy could occur as a result of the ion energy's falling below an activation energy threshold seems extremely unlikely in the energy range we have investigated. As has been pointed out by Hornig, Levy, and Willard, conservation of energy and momentum fixes the maximum fraction of the kinetic energy of an incident particle that can go into internal energy of a complex resulting from a completely inelastic collision, the fraction being $M_2/(M_1 + M_2)$, where M_2 is the mass of the struck molecule and M_1 is the mass of the incident particle.[63] For a ^{14}C atom striking benzene and remaining with it in an activated complex, 85% of the kinetic energy would be available and would have to go into internal energy, 15% remaining as kinetic energy of the complex. A ^{14}C atom with 90 ev kinetic energy engaging in an inelastic collision with a benzene molecule would cause 76 ev to go into internal energy, and the complex would be left with about 13 ev kinetic energy.

Even if such a huge activation energy were required, one would hardly expect chemical coherence to persist following the collision. Taking from steacie the heat of formation of benzene from the elements in their standard state as -24 kcal/mole, the heat of sublimation of

graphite as 141 kcal/mole, and the dissociation energy for H_2 as 103 kcal/mole,[64] we calculate that the dissociation energy of benzene into atomic hydrogen and gaseous carbon atoms is 49 ev. So it is reasonable to assert that a complex formed by a completely inelastic collision of a 90- or even of a 45-ev ^{14}C atom with benzene could not dissipate either its internal energy or its kinetic energy without the occurrance of severe molecular dissociation. Furthermore, if an activation energy threshold were involved, one would expect a relatively sharp cutoff energy to occur, but we observe an apparently steady decrease in yield in going from 5000 through 90 to 45 ev.

It is not argued here that high-energy events cannot be product-determining. We are merely arguing that completely inelastic--that is, sticking collisions--in the range 45 to 90 ev and up cannot be expected to lead directly to C_6 or C_7 ^{14}C-labeled products. On the other hand, one way in which the decrease in yield of benzene-^{14}C with decreasing ion energy can be rationalized is through the billiard ball collision process of Libby,[26] and Miller, Gryder, and Dodson,[27] which was described in the Introduction.

According to this view, it will be recalled, completely elastic head-on or near-head-on collision between the energetic particle and an atom of like mass is pictured, energy transfer being complete or nearly so, resulting in the ejection of the struck atom and the caging of the thermalized radioatom in the immediate vicinity of the resulting molecular fragment. The combination of the radioatom and the fragment would lead to a labeled product. This hypothesis was proposed for recoiling radiohalogen atoms in organohalide medium, and its application to the present case is less attractive because it would require a ring-closure step following combination of the stopped ^{14}C species with the remaining C_5 fragment. However, activity does get into the benzene ring in some manner, and the billiard ball hypothesis cannot be excluded solely on the grounds of improbability of ring fission followed by re-formation of the ring. Furthermore, the probability of

such a head-on collision's occurring would be weakly dependent on the total number of collisions made in the energy range where hard-sphere collision is the primary mode of energy loss, that is, from 5000 to 6000 ev down to 10 ev or so.[17] Hence, the probability of head-on collision would, in principle, increase with increasing ion energy.

The maximum fraction of the incident particle's kinetic energy that can be transferred to the struck particle is given by $4 M_1 M_2/(M_1 + M_2)^2$, where M_1 is the mass of the incident particle and M_2 is the mass of the struck particle. When a ^{14}C atom impinges upon a ^{12}C atom a maximum of 99.4% of the initial kinetic energy can therefore be given to the struck ^{12}C. If a CH unit were ejected, with mass equal 13, then in a head-on collision 99.9% of the ^{14}C's kinetic energy could be transferred to the ^{12}CH species, so this model could therefore be applied to the formation of benzene-^{14}C at least over the last 1000 to 2000 ev of the 5000-ev range. It cannot, however, be applied to the formation of toluene-^{14}C or cycloheptatriene-^{14}C in any straightforward manner, since only 24.8% of the incident particle's kinetic energy can be transferred to a hydrogen atom in a head-on collision. There would be little chance of the ^{14}C species' remaining in the immediate vicinity of the phenyl species resulting from the collision. When it became apparent that the billiard ball hypothesis could not account for all the products formed in recoil halogen experiments, Friedman and Libby[65] and Fox and Libby[66] gave increased emphasis to a second type of energy transfer involving inelastic collisions between the recoiling particle and the solvent molecules as a whole, the resulting dissociation of the excited solvent molecules providing a variety of radicals, etc., with which the recoiling species could then react. This type of energy loss was assumed to become important at about the 10-ev region, and was called epithermal, in contrast to the so-called "hot" billiard-ball-type processes occurring in the several-hundred-ev region.

As was mentioned in the Introduction, the billiard ball hypothesis, even as extended by the addition of epithermal processes, was criticized by several workers on a variety of grounds. One of the most important was the argument by Willard that "the assumption that momentum transfer events which a recoil atom experiences in the liquid or solid phase are identical with those between isolated atoms in the gas phase must be far from correct."[67] An alternative "random fragmentation" hypothesis by Willard is very attractive to us for the rationalization of the observed dependence of product yield on ion energy.[67] Developed primarily for recoiling halogen atoms in the liquid phase, its essential argument is that a recoiling halogen atom of several hundred ev initial energy loses its recoil energy in a relatively small volume, breaking bonds in an indiscriminate fashion in the immediate vicinity of its first few collisions. After its energy has been reduced below that required for the breaking of bonds, the radiohalogen atom is trapped in a region of very high local radical concentration, in a so-called "brush heap" or "nest" of radicals. Reaction with these fragments can then occur, either while the radiohalogen still possesses kinetic energy well above thermal or after it has been thermalized by repeated collision. The feature of this hypothesis which is essential to the suggestion that will be made in regard to the ion-energy effect we have observed is the short range postulated for the recoiling atom and the essential homogeneity, or intercommunication, of the debris-laden track formed by the passage of the recoiling atom.

It has already been argued that the lowest ion energy used in the present work is far too high to allow use of a threshold energy effect to explain the decreasing yield with decreasing ion energy. It further follows that if the critical step in the formation of any of the products of interest involved a reaction of a ^{14}C atom with an unexcited benzene molecule, either after the ^{14}C atom had been thermalized or while it still possessed considerable kinetic energy (but not enough

to cause loss of chemical coherence, say, a maximum of 10 or at the most 20 ev), there would be no ion energy dependence, for a ^{14}C atom would have the same chance of undergoing such a reaction whether its initial energy were 45 or 90 ev or 5000 ev. It has been suggested that the billiard ball hypothesis can be invoked to explain the dependence of the yield of benzene-^{14}C on ion energy, but that this hypothesis does not seem applicable to the formation of toluene-^{14}C or cycloheptatriene-^{14}C.

We are therefore forced to conclude that the dependence of the yield of toluene and cycloheptatriene, and perhaps also of benzene, on ion energy is associated with the probability that the ^{14}C atom (a) encounters a suitable fragment or excited benzene molecule in its track after it has been slowed down to the point where chemical reaction is feasible, or (b) encounters hydrogen atoms, or species that are better hydrogen donors than ground-state benzene, in its track after it has been reduced in energy to the point where hydrogen abstraction is probable. That is, if the critical reaction leading to any of these three products involves atomic ^{14}C, then that reaction cannot also involve unexcited benzene, and if it were essential to a given reaction that the ^{14}C species be hydrogenated to a greater or lesser extent, then that requirement alone could give rise to a dependence on the debris density in the track. In that case, reaction of the CH or CH_2 species with ground state benzene would not be excluded. It is by no means certain that the nature of the ^{14}C species, whether it is C or CH, for example, is of critical product-determining importance, but it could be and, indeed, very likely is.

It may now be seen why it is essential to this view that the range of the ^{14}C atom be short, or, more fundamentally, that the track formed by its passage be essentially continuous and intercommunicating. If the end of a track were remote from a earlier portion, a ^{14}C species coming to rest at the track end would find itself in much the same environment as another ion of widely different initial energy. It is for

this reason that it is felt that our results are compatible with Willard's random-fragmentation hypothesis.

It is implicit in the conclusion just drawn that either (a) some reaction of the ^{14}C species with unexcited benzene occurs--leading to products other than benzene, toluene, and cycloheptatriene--or (b) it is necessary for the ^{14}C species to find a proper fragment before it drops below a certain energy. Since it seems reasonable to assume that the number of each kind of fragment produced in the track depends directly on the initial ion energy, there would be no net effect of ion energy on product distribution unless one of the two conditions mentioned above existed.

It would, of course, be surprising if no reaction of the ^{14}C species with unexcited benzene occurred. But it should be emphasized that even if all the reaction were with fragments, the dependence of the yield of the three compounds of interest on ion energy could still be seen, provided the fragment reactions leading to them required energies well above thermal while other fragment reactions leading to other products could occur when the ^{14}C species was thermalized.

It must be remembered that we have investigated only three ion energies, and in particular have jumped from 5000 ev down to 90 ev. It cannot, therefore, be asserted that the whole track formed by a 5000-ev ^{14}C ion is important in determining the chemical fate of that species. It may be that the area of track homogeneity, or that portion of the total track volume important in product determination, is but a small fraction of the entire 5000-ev track. If such were the case, it might be found that little or no decrease in yield would occur by reduction of ion energy until the ion energy fell to, say, a few hundred ev.

In his recent review article Wolf presents a picture of the track of a recoiling ^{14}C atom in which it is suggested that "the last few hundred ev are lost in a very small volume with about 25 to 50 ev being associated with the terminal hot spot. Since these last few

hundred ev are released in a relatively small volume, hot spots or molten zones may overlap and provide additional reactive sites for the attenuated fragment."[12] He further states, however, that the range from 5000 to 6000 ev, where hard-sphere collisions become important, to the end of the track is quite uncertain, and it seems to us safe to conclude that the validity of picturing the entire track made by a 5000-ev particle as an essentially continuous blob cannot, at present, be decided one way or the other.

Since the detailed nature of the tracks has assumed such a key role in the present discussion, it is fitting to linger on this point a bit longer. Let us consider what other workers in this field have proposed in this matter, for the nature of the track is at the very heart of hot atom chemistry, and has repeatedly been the subject of discussion and speculation.

At one extreme, Libby has proposed that the recoiling atom of 10,000 ev initial kinetic energy can come to rest after traveling as little as 6 A from its birthplace.[26] This result is obtained for ionic crystals, and assumes that the mean free path between successive hard-sphere collisions is of the order of the mean ionic spacing in the crystal. If the crystal contains ions of the same mass as the recoiling species, only eight collisions would be required to reduce it from 10,000 ev to about 5 ev. All the recoil energy would then be deposited in a very small volume, creating a liquid-like drop containing a dozen ions or so. The hot droplet would then transmit its thermal energy to the crystal wall surrounding it until it solidified.

Although this model was proposed for a recoil event in an inorganic ionic crystal, its essential elements would still hold for a molecular crystal. The main differences would be a somewhat longer range and less firm lattice wall surrounding the hop droplet.

Disagreeing with the Libby model, Yankwich has proposed another,[17] based on the equations of Seitz and Kohler.[68] Using recoiling ^{14}C in Be_3N_2 as an illustration, Yankwich points out that a recoiling ^{14}C species with an initial energy of about 45,000 ev would, at first, lose energy primarily by small-angle Rutherford scattering, losing, on the average, less than 1 ev per collision. Occasionally, a struck atom would receive enough energy (approx 25 ev) to be displaced from its site. The average energy transferred in such an event would be about 200 ev. Over the energy range where Rutherford scattering dominates, the mean free path is of the order of 10 A. After traveling perhaps several hundred Angstroms from its birthplace, the recoiling ^{14}C is reduced to about 6 kev energy, at which point the collisions become hard-sphere in character.

Yankwich agrees with Libby that the efficiency of energy transfer in the range of hard-sphere collision is high, but argues that the mean free path between collisions is much larger than the mean ionic separation until the recoiling atom is almost at rest. Hence, even though five or six collisions suffice to reduce the energy from 6000 ev to about 25 ev the distance covered in that energy range is relatively large. Yankwich states that as long as the mean free path is large compared with the mean ion separate, movement is diffusion-like, and only about 25 to 50 ev will be associated with the terminal hot spot, about 25 ev being the energy required to displace an ion from its lattice site.

Yankwich points out that in the Libby model, in which all the energy is dissipated in a very small volume, about 150 ions would be raised to a temperature of 10^7 °K and would cool with a time constant of about 10^{-9} sec, long enough for diffusion to occur. Polyatomic ions would be demolished by the high transient temperature.

In the Yankwich model, on the other hand, in which only 25 to 50 ev is associated with the terminal hot spot, about 5 ions in the immediate vicinity of the stopped ^{14}C would be raised to a temperature of about 10^5 °K, and the time constant for the ensuing decrease in temperature would be very short, about 10^{-12} sec, which would be

too short for diffusion to occur, hence too short for any true liquid-like disorder to set in.

Yankwich points out that on the basis of the Seitz-Kohler model--i.e., Yankwich's model--one would expect no dependence of the chemical fate on the initial recoil energy, because only a small portion of the recoil energy would be available in the terminal hot spot. On the basis of the Libby model, however, one would expect to see dependence of chemical fate on initial recoil energy, because all the energy is dissipated in a very small volume, and the relaxation time is long enough to allow diffusion before resolidification ensues.

We are, of course, happy to accept this criterion, using it to argue that the results of this work support the Libby model, or something very close to it. If future work with the isotope separator, filling in the energy gap that we have left between 5000 ev and 90 ev, showed a steady decrease of yield of benzene et al. throughout the entire energy range, it would be felt that the Libby model as interpreted by Yankwich must be far closer to the truth than the Seitz-Kohler model, as championed by Yankwich.

Purely by chance, the maximum ion energy used in the work reported herein was 5000 ev. Hence, investigations confined to the energy range 5000 ev on down would put us completely within the range of hard-sphere collisions as defined by Yankwich. Therefore, it matters little to us whether a hard-sphere collision becomes important at 10,000 ev or at 6000 ev. What is important is the mean free path of the ^{14}C atom from 5000 ev on down, where both models are in agreement that hard-sphere collision is the major mode of energy loss.

As discussed earlier, Willard in his random-fragmentation theory questions the importance of elastic collisions at all in the condensed phase, arguing that for initial recoil energies of several hundred ev the recoiling atom would not travel far from its birthplace but would lose energy by inelastic processes, breaking bonds left and

right in its immediate vicinity in an indiscriminate manner. It seems to us that if the Libby model of energy loss, as interpreted by Yankwich, were modified just a little (when applied to molecular organic crystals), so that complete carnage did not result in the hot spot, the net results of the process proposed by Libby and of that by Willard would be much the same, both yielding a small volume of transiently high debris concentration, in or near which the radioatom finds itself after it has slowed down to the point where it can enter chemical combination.

To be sure, these are supposedly conflicting models, and they do differ completely in the mode of energy loss, but they provide the same picture of general molecular disruption in the immediate vicinity of the radioatom. Perhaps we are missing the point, but it seems to us that if there is any conflict it is between the billiard-ball-collision hypothesis of Libby and the over-all model of energy loss of Libby, at least as interpreted by Yankwich. If the energy of a recoiling radioatom is lost, on the average, in a very short distance, then an atom displaced by a head-on collision with a radioatom of like mass will not sail off to the next county, leaving the stopped radioatom and the molecular fragment in peace to unite at their leisure, but will itself be stopped within a few molecular diameters, and the stopped radioatom should be enveloped in the ensuing hot spot.

Perhaps this conflict arises from the fact that we are carrying over the details of Libby's argument concerning the range from an ionic crystal to a molecular crystal such as benzene. If elastic collisions are of primary importance in energy loss, then passage of a ^{14}C atom through a medium containing a sizable fraction of atoms of considerably different mass, such as hydrogen, should result in a considerably longer range than the approx 6 A obtained from consideration of collision with ions of the same mass as the recoiling atom and more closely spaced than are atoms in a molecular crystal. Indeed the difference expected between the rate of energy loss in a molecular crystal and that in an ionic one would provide us with just the

"softening" of the Libby model that we would like to see. We could then have complete loss of energy in a relatively small volume, a transiently high debris concentration, and sufficient time for the slowed-down ^{14}C to diffuse through the mass of debris it had created, but avoid the complete molecular dissociation visualized by Yankwich as a consequence of the Libby model in an ionic crystal.

When Yankwich stated that a necessary consequence of the Seitz-Seitz-Kohler model was independence of chemical fate on initial recoil energy he cited the work of Schuler in support of the Seitz-Kohler model. Schuler had found that the yield of organically bound radioiodine from iodine recoil in alkyl iodides was independent of the method of activation of the iodine, hence independent of the initial recoil energy of the iodine.[69] In more recent work, however, McCauley and Schuler report the occurrence of an initial recoil energy effect on product distribution in hydrocarbon-iodine systems where both the (n, γ) and the (n, 2n) reactions were used to form radioiodine.[70] In the first case the recoil energy of the iodine is in the range 100 to 1000 ev, depending on the initial energy of the neutron, and in the second case it is of the order of 100,000 ev. A 15% greater yield of organically bound iodine from the cyclohexane-iodine system was found for the process giving the higher recoil energy. A similar energy effect was found for the alkyl bromide systems, despite the fact that no such effect was found for alkyl iodides.

These workers felt that in those cases where yields of certain products increase with increasing recoil energy, greater local disruption was responsible for the increase. Willard's "brush heap" or "random fragmentation" hypothesis allows an energy dependence to be explained if "a significant probability exists that as a result of diffusion processes the activated atom may react with a fragment produced at some distance from the site of final thermalization." This is precisely the only general explanation we can offer for the observed decrease in the yield of benzene, toluene, and cycloheptatriene with decreasing ion energy in our work.

A lack of constancy in the effect of initial recoil energy on product distribution seems to be the rule in recoil chemistry. Willard, for example, reports that various pure alkyl iodides give the same organic yield despite differences in the energy of the neutrons used.[28] On the other hand, Capron and Crevecoeur found that the organic yield of bromine-80 differed from that of bromine-80m when bromobenzene was irradiated with neutrons and that, furthermore, the ratio of the organic retentions of the two isomers differed with the energy of the neutrons.[71] This effect was ascribed to differences in the recoil energies of the two isomers. In work already mentioned, Wolf and Suranayana found higher yields of benzene and toluene-^{11}C from 1-Mev ^{11}C recoil in benzene than was found for 45-kev ^{14}C recoil in benzene-2-methylpyrazine solutions,[13] but it is certainly not clear that this difference is due to the recoil energy. Other factors such as the absence of a strong γ field and of a nitrogen source in the ^{11}C work may be affecting the results.

3. Energy of Reaction

It has been suggested that the observed decrease in yield of benzene, toluene, and cycloheptatriene upon decrease of ion energy from 5000 ev to 90 and 45 ev furnishes some limited information about the nature of the reactants involved, or, rather, allows us to eliminate reaction of atomic carbon with ground-state benzene in the case of the three compounds of interest. Further, it is argued that this effect suggests that at least a significant fraction of the energy of a 5000-ev $^{14}C^{+}$ ion is deposited in a relatively small volume at the end of the track.

It would seem, on the other hand, that the data we have gathered provide no information whatsoever about the energy range in which any of the reactions of interest occur, that is, we have no way of distinguishing reactions occurring when the ^{14}C species possesses several or 10 or so ev kinetic energy from those occurring after the

^{14}C atom is reduced to the temperature of its immediate surroundings.

In principle the isotope separator would be expected to be a potent tool for the determination of energy thresholds, but in this study case the yields of the compounds we have been following fall so sharply with decreasing energy that it would not be possible to note a sharp threshold if one occurred at, say, 10 or 20 ev. Of course if the yields of some compounds decreased with decreasing ion energy, then the yields of other compounds must increase, and, in principle, if a relatively high-energy threshold existed for a compound whose yield increased with decreasing ion energy, it should be easily seen.

It is not clear, however, how well the energy of the ion beam can be controlled at very low energies by the present method. The possibility of an accumulation of charge in the irradiated benzene exists and has, indeed, been a source of considerable concern to us. The 45-v irradiation was performed not to obtain a third ion energy point but to assure us that the ions used in a 90-v irradiation actually had more than 45 ev when they hit the target, the reasoning being that if 45-ev ions managed to hit the target, then the potential on the target cannot be greater than 45 v, and ions with 90 v initial energy must have at least 45 v left when they strike the benzene surfaces.

The remarks made earlier in this discussion concerning the improbability of an energy threshold's existing as high as 90 v holds equally well for 45 v. Since we have no reason to believe the energy of the ions in the 90- and 45-ev irradiations was significantly less than their nominal value, we feel justified in regarding them as bona fide 90- and 45-ev runs. It may well be, though, that difficulty will be encountered in attempting to irradiate with ions of 10 ev or so, which is, of course, the energy range where thresholds would be expected to be found. It may be possible to deliver nominally 10-ev ions to a target, but reasonably accurate knowledge of the true ion energy at the time it hits the target may be quite difficult to obtain.

4. Further Discussion of the Energy-Density Effect

We wish to reserve final comments on the interpretation that has been made of the energy-density effect until after the effect due to ion energy *per se* has been discussed, because clearly the interpretation of one effect depends upon the interpretation given to the other. It may be that we have speculated a good deal more about the meaning of these two effects than is warranted by the few data we have collected regarding them. On the other hand, we have tried to clearly distinguish those comments which were purely speculative from those few broad generalizations which were felt to be strongly indicated when both effects were considered together.

The effect of ion energy on yield, which we have observed at three ion energies, is undoubtedly capable of shedding more light on the fundamental processes occurring than is the energy-density effect, although the latter is of value in that it clearly demonstrates the existence of labile intermediates in the reaction sequences leading to benzene and toluene and perhaps to cycloheptatriene.

A more detailed investigation of the ion energy effect, on the other hand, over the entire range between 5000 and 90 v has the potential of providing direct experimental evidence for the validity of the Seitz-Kohler model of the ^{14}C track as described by Yankwich in the article previously mentioned. This would be of fundamental importance to the field of recoil chemistry. It is our feeling that the importance we have given to the concentration of debris in the ion track and the ability of the $^{14}C^{+}$ ion to come into contact with that debris conflicts in no way with any experimental fact we are aware of in the field of recoil chemistry. If it conflicts with some of the ideas now prevalent in this area it is also in good accord with others. This has been discussed at length. This interpretation is not novel. McCauley and Schüler, as mentioned earlier, reached the same conclusion after observing a considerably smaller effect in hydrocarbon-iodine recoil work.

Our observation of the energy-density effect, however, does not to our knowledge have any comparable analog in the recoil field. Evidence for the freezing in of radicals generated in solids at low temperatures and their rapid recombination upon warming of the solid has already been cited. The effect of thermal annealing on the product distribution in crystals following irradiation is well known. Quoting Harbottle and Suttin, "since recoil atoms in solids generally undergo recombination reactions during post-irradiation annealing, the reactions in the hot zone evidently are quenched by cooling before they have gone to completion."[72] This is essentially the effect that we supposed was involved in the energy-density effect, the trapping of intermediates formed in the track along with fragments likewise produced in the primary process. When the sample is warmed the fragments recombine rapidly as soon as they have a chance to diffuse about, destroying some of the labile intermediates in the process.

Probably the nearest analog in recoil experiments to the energy-density effect we have observed is found in those recoil experiments in which the effect of variation of the associated γ flux on product formation was investigated. Several workers have shown that large variation in the γ flux has little or no effect on product distribution in a variety of recoil reactions. It has been argued very convincingly by Levey and Willard that the free radicals produced by the γ flux can have little effect on the primary reactions occurring in the track of a recoil particle, since irradiation level of 5000 r per hour would provide a steady-state free-radical concentration of only about 10^{-11} mole fraction, whereas a stopped recoil atom exists in a volume element where the transient free-radical concentration is of the order of 10^{-3} mole fraction.[73] They further cite evidence indicating that stable products containing the radioatom would not be expected to be affected by the γ flux.

The mere fact that the primary events and the stable products are not expected to be affected by a γ flux does not mean, however,

that any relatively long-lived intermediates that might be involved in the sequence leading from primary event to stable product would be indifferent to the generation, at a rapid rate, of free radicals in the system.

It would seem then that experiments showing no effect of variation of γ flux on product distribution would be in conflict with our interpretation of the energy density effect which we observed. This need not be the case for a large variety of reasons. In the first place we may note that not all such tests of the importance of γ flux have been negative, although the preponderance certainly seems to lie in that direction. What is more to the point is the possibility that the physical differences between the manner of carrying out our isotope-separator experiments and that employed in the recoil technique is so great that comparison of the two is precluded in regard to this question.

In this work we irradiated a solid at a low temperature, whereas most of the recoil experiments are concerned with the irradiation of liquids at room temperature. But the most important difference is that in this work a given volume element of target is not subjected to further radiation after the primary process has occurred, since we are continuously laying down a fresh surface of benzene on the target. In the recoil work a steady flux of neutrons and γ rays permeates the irradiated sample; that is, in the recoil case, steady-state conditions prevail, whereas in this work we physically isolated the products of the primary track events from subsequent ion impingement.

Because of this and because of the low temperature used, we may well have separated primary and secondary processes in time to an extent not approached in the recoil experiments in the liquid phase under steady-state conditions. It may be that in the recoil experiments in the liquid phase the entire process leading to a stable product occurs rapidly in time and in the immediate vicinity of the primary track, no freezing in or quenching occurring in the liquid phase. In that case, the whole process would be affected only by the recoil energy, that is,

by the debris concentration in the track, and would be indifferent to the over-all radical concentration in the solution as a whole. On the other hand, if relatively long-lived intermediates are involved in some cases, it may be that saturation effects are being observed over the entire range of γ flux investigated.[12] At any rate, one can, of course, not expect to have all products affected in the same way by variation of energy density, or by variation of ion energy--if variation of any parameter causes the yield of some products to decrease, obviously the yield of other products must increase. Every product in every chemical system must be treated as a unique case, and only if one has good reason for believing that a given product in a given system is formed by a given set of reactions can one predict beforehand the way in which the yield of that product will vary with variation of the important experimental parameters.

B. Nature of the Reactions Leading to ^{14}C-Labeled Benzene, Toulene, and Cycloheptatriene

It has been argued that the primary steps in the reactions leading to ^{14}C-labeled benzene, toluene, and cycloheptatriene must in some fashion involve the availability of fragments formed in the ion track. By fragments we mean anything other than unexcited benzene, and so in making this conclusion contribute very little to the knowledge of the critical reactions. The primary steps could equally well involve benzene in its first excited electronic state, a long-lived triplet,[74] or some aliphatic fragment. All the dependence could be due to the need of the ^{14}C species to have acquired a certain number of hydrogen atoms before the necessary first steps can be taken. The ease with which a ^{14}C atom may acquire atoms may well depend on the debris concentration. One or more of these reactions could require the presence of a species only slightly different from benzene itself, say a phenyl radical, or a benzene ion. We have no way of deciding between these various possibilities in the present work.

Let us see, then, if the knowledge of the radiation chemistry of benzene sheds any light on this subject.

1. Radiation Chemistry of Benzene

In his timely book on the radiation chemistry of organic compounds, Swallow discusses the present state of the knowledge of the radiation chemistry of benzene.[75] The most striking feature of the radiation chemistry of benzene is its high resistance to radiation. In the liquid phase, -G for monomer to polymer is 0.75, while +G for gas is only 0.055. Less than one benzene molecule, on the average, is permanently altered for every 100 ev of ionizing radiation in the liquid phase. The gas consists almost exclusively of acetylene and hydrogen. The polymer is poorly characterized. It is a viscous yellow liquid containing aliphatic double bonds; its molecular weight increases as irradiation proceeds, reaching 430 at about 10^3 mrad; it is a complex mixture, containing abou 10% biphenyl. Phenylcyclohexadiene and phenylcyclohexene have also been identified. High-molecular-weight products include hydrogenated terphenyls. No cyclic compounds with noncyclic substituents have been found.

The resistance of benzene to ionizing radiation is commonly ascribed to its ability to absorb energy by electronic excitation in unlocalized π orbitals, insufficient energy accumulating in the vibrational modes of any single bond to cause disruption. It is further pointed out that since the ionization potential of benzene is only 9.2 ev, the apparent $C_6H_6^+$ ion can survive neutralization without subsequent dissociation.

Continuing to paraphrase Swallow, we find that the radiation chemistry of benzene is little better understood than is the recoil chemistry. Swallow states that only speculative mechanisms can be offered: "... since the role of such penomena as electron capture and ion molecule reactions is not known for this system. It is possible, however, to represent the main primary act as formation of excited benzene molecules, some of which give phenyl radicals and H atoms." Swallow further suggests that the H atoms would disappear primarily by

combination with benzene to give $C_6H_7^+$ radicals. "All types of radicals and excited benzene molecules may react together in various combinations to give the various polymers. Also, some of the radicals and excited molecules may react with normal benzene molecules, again giving polymers."

If the hot-atom chemistry of benzene is at all comparable to its radiation chemistry we are then led to consider a track environment consisting primarily of excited benzene molecules together with a few radicals such as $C_6H_5^+$ and $C_6H_7^+$ and, to a certain extent--since aliphatic double bonds are found in the polymer from the radiation chemistry of benzene-- aliphatic fragments from fission of the benzene ring. Since acetylene and hydrogen are minor products, we may also expect the presence, at least temporarily, of H atoms and acetylene or C_2 fragments in the track.

2. Toluene

In the formation of toluene-^{14}C there is one pair of facts, due to Wolf and his co-workers, which strikes us as being highly significant. Toluene-^{14}C formed from ^{14}C recoil in benzene-2-methylpyrazine solution is 88% methyl-labeled and 12% ring-labeled.[2] Toluene-^{14}C formed from ^{14}C recoil in aniline is found to be 86% methyl-labeled and 14% ring-labeled.[24] The essential equivalence of the ring methyl distribution of activity in toluene-^{14}C formed from two different parent compounds suggest to us that, to a high degree of probability, the same reaction is occurring in both cases, and that toluene-^{14}C is formed by a reaction of the ^{14}C species in some form with a fragment that can be obtained from both benzene and aniline. Interpreting these facts in this manner, we not only confirm our judgment regarding the importance of fragments in general, but--what is far more important--we also may exclude the direct participation of electronically or vibrationally excited benzene in the formation of toluene-^{14}C. Because the ring methyl distribution of activity in toluene-^{14}C produced by 5000-ev $^{14}C^+$ ions in this work is, within experimental error, the same as that found by

Wolf *et al.* for toluene-^{14}C formed in the recoil experiments, it may be concluded that the same process is occurring in all cases, as would be expected.

The essential equality of the ring methyl distribution of activity in toluene formed from aniline and toluene formed from benzene further suggests that the toluene arises not only by the same reaction in both cases but by only one reaction, which we have tacitly assumed heretofore. It is, of course, quite possible *a priori* that the ring methyl distribution is a reflection of two, or even more, different reactions leading to toluene-^{14}C. It seems very unlikely that two distinct reactions would occur to precisely the same relative extent in both aniline and benzene.

The reactive fragment that must be provided by both benzene and aniline need not be very exotic or far removed from benzene. The simplest possibility would be a phenyl species, a phenyl ion or a phenyl radical. The yield of toluene from aniline is only 0.744 %, while that from benzene through methylpyrazine is more than 2 %; the yields therefore differ in the expected direction if a species such as a phenyl radical is required for toluene formation.

It is most interesting to note that *o*-xylene-^{14}C, produced by ^{14}C recoil in toluene,[76] and toluene-^{14}C, prepared from toluidenes produced by ^{14}C recoil in aniline,[24] have essentially the same ring methyl distribution of activity as do toluene from benzene and toluene from aniline. Wolf has suggested that this may imply a common intermediate in all cases, but feels that the low yield of toluene from aniline conflicts with this hypothesis. We, on the other hand, are quite content with the low yield of toluene from aniline, but tend to be concerned with the high yield of 1.6 % for the toluidene from aniline.[24] In point of fact, however, yield *per se* is probably devoid of mechanistic significance, reflecting as it probably does a series of steps, only one of which may be important in determining the ring methyl distribution of activity.

Since it is beginning to appear to be a law of nature that toluene and toluene analogs must be 14% or so ring-labeled, it is comforting to note that toluene-^{14}C produced from ^{14}C recoil in toluene-2-methylpyrazine is found by Wolf and co-workers to be 89 % ring-labeled;[76] apparently a quite different process is occurring here.

Recently a complete ring degradation of toluene-^{14}C produced from ^{14}C recoil in benzene was made for Wolf[51] by Sixma and co-workers using the method of Sixma and Steinberg previously mentioned.[50] A curious, and so far unexplained, distribution was found. Of the 14.6 % of the total activity in the ring, 53 % was in the 1-carbon (that is, the carbon to which the methyl group was attached), 25 % was in the 2, 6 (ortho)-carbons, 14 % in the 3, 5 (meta)-carbons, and 7 % in the 4 (or para) carbon.

Presumably the activity in the toluene-^{14}C produced in this work is distributed in the same way. The results of the complete ring distribution provide the type of detailed information that is vital to an eventual understanding of the chemistry of the hot-atom chemical processes, and, as mentioned earlier, we had hoped in this work to develop and use techniques for ring degradation of toluene. We might have wished, however, for an activity distribution other than that found, for while we can at least imagine a sequence of reactions involving, say, a phenyl radical and a ^{14}C atom or $^{14}CH_2$ which could conceivably lead to the inclusion of one-seventh of the total activity randomly distributed in the ring, we are at a loss to rationalize the observed distribution of activity. Nor can this be done by imaging an aliphatic C_6 fragment as the reactive species, visualizing addition of a ^{14}C species to the C_6 fragment followed by ring closure to give toluene or the toluene skeleton. Here we would expect all the ring activity to be in the 2-position.

It is interesting to speculate on the nature of the ^{14}C species involved in the reaction leading to toluene-^{14}C. Photolysis of diazomethane in benzene yields both toluene and cycloheptatriene.[27] Since

this reaction is thought to involve methylene (carbene), it is natural to consider the possibility of ^{14}C-labeled toluene's arising from a reaction involving $^{14}CH_2$ in this work and in the ^{14}C recoil experiments in benzene. Lemmon and Strohmeier have conclusively demonstrated, however, that the toluene-^{14}C formed upon photolysis of ^{14}C-diazomethane in benzene is completely (> 99.8%) methyl-labeled,[78] whereas toluene-^{14}C produced from benzene in the hot-atom experiments is only 86 to 88 % methyl-labeled, and we have seen that there is good reason to believe that only one reaction sequence is involved in the hot-atom formation of toluene-^{14}C.

These workers conclude that the difference may be due to the lower energy of the carbene produced by the photolysis of diazomethane (about 5 ev), but we could also take this to mean that carbene is not involved in the hot-atom reactions, or, more likely, that benzene as such is not involved in the hot-atom reactions to give toluene, as we have argued, while it presumably is in the photochemical case. Although the work of Doering and others has created great interest in carbene, showing it to have remarkable properties (i.e., C-H bond insertion),[79] there would seem to be little justification for considering its possible role in these hot-atom processes to the exclusion of other equally probable carbon species.

In their studies of the hot-atom chemistry of ^{11}C in gaseous hydrocarbon systems, Wolfgang and co-workers have given emphasis to the role of carbon atoms as reacting species.[14] Although they find the yields and ratios of yields of some products to be in accord with the known behavior of carbene, these workers find that it is easier to explain the formation of many other products by postulating that atomic carbon can undergo CH bond insertion reactions and perhaps addition to C=C double bonds.

One would not expect toluene-^{14}C to be formed by a thermal combination of a phenyl radical and a ^{14}C methyl radical, as that should lead to a completely methyl-labeled toluene. It is not inconceivable,

on the other hand, that a sufficiently energetic encounter of these two radicals could lead to rearrangement via a seven-membered ring. This possibility is not in conflict with the finding by Wolf and Suryanarayana that the yield of toluene-^{11}C in benzene is unaffected by the presence of free-radical scavengers, for only thermal free-radical reactions would be affected.[13] The possibility that this or related reactions might involve a CH radical or ion has not been considered so far as we know, but there seems no a priori reason for neglecting it.

One of the most interesting potentialities of the isotope-separator technique is that it may furnish an answer to these questions concerning the nature of the ^{14}C species in a given reaction. By using methane-^{14}C as the source gas, irradiation may be carried out with CH, CH_2, or CH_3 ions. It may well be that the yield of some products, or, indeed, their formation at all, will be found to depend on the nature of the ^{14}C species.

As was mentioned in the Introduction, Wolf has found that although the yield of toluene-^{14}C from ^{14}C recoil in solutions of benzene and 2-methylpyrazine varies directly with the mole fraction of benzene, the yield of toluene-^{14}C from solutions of benzene and 3, 3'-diaminodipropylamine shows marked deviation from linearity, the toluene yield peaking to a maximum of about 3.25 % at about 30 mole % amine, whereas the extrapolated value for 0 mole % amine is about 2.25 %.[23] Wolf relates this behavior to the availability of hydrogen in the system.

This explanation is in good agreement with suggestions we have made in rationalizing the observed effect of energy density and ion energy on yield. Increased hydrogen availability could increase the yield by making it easier for the ^{14}C species to pick up necessary hydrogens--if any are needed before the reaction to give toluene occurs--or it could be related to the enhanced ability of a toluene intermediate to abstract necessary hydrogen in the later stages of the reaction sequence. Yet another possiblity is that the necessary reactant is $C_6H_7^{\cdot}$, which could be formed in greater amounts in spite of the decreasing benzene

mole fraction if the availability of hydrogen atoms increased faster than the availability of benzene acceptors fell off. Those possibilities associated with the formation of the first intermediate, rather than survival of succeeding intermediates, are more attractive to us because of the failure of the toluene yield to be affected by the presence of free-radical scavengers. On the other hand, although our results are interpreted as indicating the presence of frozen-in, or relatively long-lived, labile intermediates in the sequence leading to toluene, it should be remembered that these need not be free radicals.

3. Benzene

Unlike toluene, the yield of benzene-^{14}C in the benzene-aliphatic amine system was found by Wolf to be directly proportional to the mole fraction of benzene present. This would then indicate, according to the above discussion, that hydrogen availability is not important in the formation of benzene-^{14}C. Wolf and Suryanarayana found that the yield of benzene-^{11}C from recoiling ^{11}C in benzene was significantly reduced upon addition of diphenylpicrylhydrazyl to liquid benzene, indicating the participation, or intervention, of thermal free-radical reactions in the sequence leading to benzene-^{11}C.[13] They further found that the yield of benzene-^{11}C was reduced when irradiation was carried out in the solid phase.

We interpret our results as suggesting the participation of a fragment (in the broadest sense, as previously defined) in the initial step or steps leading to benzene, and, further, suggest that labile intermediates exist in the reaction sequence. Are these observations and interpretations mutually reconcilable, and is there a plausible reaction sequence to fit these facts? With the exception of the question of hydrogen availability, which takes a little hedging, the answer is "Yes."

If ^{14}C- or ^{11}C-labeled benzene resulted from a reaction of the radiocarbon species--say, as atomic carbon, with a straight-chain C_5 fragment by addition, or in a substitution reaction with a straight-chain C_6 fragment, followed by re-formation of the six-membered ring

to give benzene--these facts and interpretations could be accommodated. The requirement of the presence of a C_5 or a C_6 straight-chain fragment satisfies our interpretation of the ion energy effect. The resulting C_6 straight-chain species is a fitting candidate for our labile intermediate; if in the simplest, or most naive picture, it were a hexamethylyne diradical,[55] it would certainly be susceptible to destruction by dimerization or, from the point of view of benzene formation, by hydrogen abstraction, also, thereby agreeing with the radical scavenger effect observed by Wolf and Suryanarayana.

Decreasing yield upon change of irradiation phase from liquid to solid could be due either to the reduced ability of the C_6 intermediate to diffuse away from the high debris concentration in the track area, or to a hindrance of its ability to cyclize in the solid state.

If we picture a ^{14}C atom adding to a C_5H_5 fragment, then hydrogen abstraction must, of course, occur at some stage. It may be that hydrogen abstraction reactions are both beneficial and harmful to the production of labeled benzene, whereas radical dimerization reactions are purely destructive. If a straight-chain C_6H_5 fragment resulted from the primary step, abstraction of one more hydrogens might be necessary before cyclization or, at any rate, need not be harmful, while further abstraction would lead to products other than benzene.

There is no end to the "ifs" and "buts" possible here, but it seems fair to say that if the effect of the nitrogen source in the ^{14}C recoil work of Wolf is, indeed, limited solely to the question of hydrogen availability, there is ample room to maneuver around it in the foregoing suggestion. There is one set of facts from the ^{11}C work of Suryanarayana and Wolf which is not consistent with this general view. A progressive increase in the yield of benzene-^{11}C from irradiations of solid benzene was found as the temperature of the solid was decreased from 0° to -78° to -195°.

One would expect the ease of cyclization to decrease with

decreasing temperature. Perhaps other factors intervene to give a net increase. As Suryanarayana and Wolf suggest, perhaps the initial reactant is longer-lived at the lower temperatures, or perhaps the yield increase is a reflection of competing paths to the same end product.[13] It should be pointed out that these workers discuss the formation of benzene-^{11}C in terms of a reactive fragment in the damaged area, but are not to be held responsible for the speculative details given above.

In suggesting that benzene-^{14}C may be formed via cyclization of an aliphatic hydrocarbon, we are of course proposing nothing new in principle, the formation of benzene upon photolysis or pyrolysis of a large variety of hydrocarbons being well known. To cite a few examples: Benzene, among other things, is formed as a result of photolysis of acetylene with 1849-A light.[80] It is produced in the pyrolysis of 1,3-butadiene,[81] butene,[82] 1-heptyne and 1-hexyne (at a sufficiently high temperature),[83] 1,5-hexadiene,[84] and pentane,[85]

4. Cycloheptatriene

It was stated in the Introduction that we intended at the beginning of this work to look for activity in cycloheptatriene, as it was considered a likely and interesting product. There are two reasons for so considering it. Firstly, as mentioned earlier, it, along with toluene, is produced by photolysis of diazomethane in benzene. Secondly, incorporation of activity in the toluene ring leads one to suspect a seven-membered intermediate of a cycloheptatriene or tropylium ion or radical type in the reaction sequence leading to toluene. So far as we know, cycloheptatriene has not been found before in this field, so we have no information to supplement our own results concerning it.

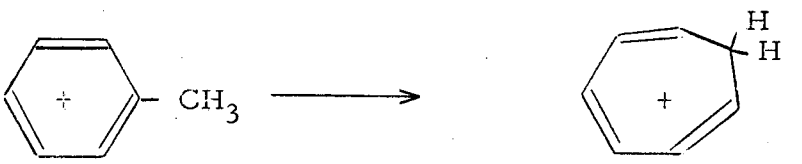
It is, of course, possible that cycloheptatriene in this work is formed in the same way as it is in the photolysis of diazomethane in benzene. On the basis of a partial degradation, Juppe and Wolf have recently reported that cycloheptatriene-^{14}C, formed by photolysis of diazomethane in benzene, contains little or no activity in the 4-5 carbons, a finding consistent with the expectation of exclusive methylene

labeling. A similar degradation of cycloheptatriene-^{14}C produced by ^{14}C ion irradiation of benzene, or by ^{14}C recoil in benzene, would be of great value in determining the similarity of photochemical and hot-atom synthesis.

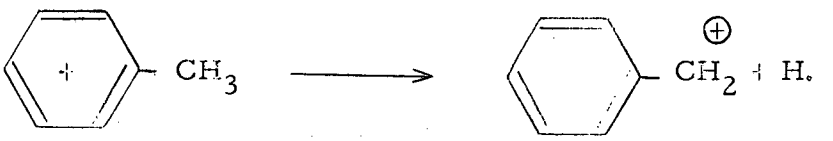
It is important to note in this regard that Juppe and Wolf have shown that the activity in photolytically produced cycloheptatriene-^{14}C is not appreciably randomized, if at all, by electron irradiation. This result encourages us to believe that the application of the partial degradation by Juppe and Wolf to cycloheptatriene formed in the hot-atom cases might allow a distinction between the photochemical and hot-atom syntheses, if they are indeed different. Whether a complete degradation would be required to make such a distinction would of course depend on the actual distribution of activity in the hot-atom case.

Rylander, Myerson, and Grubb have demonstrated that the $C_7H_7^+$ ion formed by electron bombardment of toluene in the ion source of a mass spectrometer is symmetrical, all the hydrogens being equivalent, as shown by selective deuteration.[87] They conclude that the $C_7H_7^+$ ion cannot have the benzyl structure but is very probable a tropylium ion, taking the resonance energy of the benzene ring at about 41 kcal, resonance stabilization of the benzyl radical at 0 to 24 kcal, and resonance energy of the tropylium ion based on molecular orbital calculation at 60 kcal, they point out that the tropylium ion should be more stable than the benzyl ion by -5 to +19 kcal. Before we conclude that our cycloheptatriene may result from formation of a benzyl ion which then rearranges to tropylium and, eventually, goes on to cycloheptatriene, we must note two points brought out by these workers. One is that rearrangement from benzyl ion to tropylium ion has not been observed in solution--perhaps, according to Rylander *et al.*, because benzyl ion can be stabilized by solvation or else disappears in a bimolecular process, whereas in the gas phase tropylium ion is the favored form. The second point is more important. Not only are all the hydrogens of $C_7H_7^+$ equivalent, indicating the tropylium ion

structure, but also equivalence of all the hydrogens of the initial toluene is achieved before the first hydrogen is lost, that is, the deuterium-to-protium ratio in the $C_7H_7^+$ ion is essentially the same for methyl-deuterated toluene as it is for ring-deuterated toluene. Position of ring deuteration likewise has no effect on the mass spectrum, leading these investigators to conclude that rearrangement occurs before, or during, bond cleavage. Benzyl ion or benzyl radical does not first form and then rearrange to tropylium. In ethyl benzene, on the other hand, no rearrangement is observed prior to the formation of the $C_7H_7^+$ ion, although that ion is itself again shown to be tropylium and not benzyl. Rylander et al. suggest that for toluene the step in the sequence



occurs more rapidly than



It would seem implicit in this suggestion that the methylene hydrogens of the cycloheptatriene cation are lost in the same proportion as the CH hydrogens.

Thus it is seen that although benzyl ion rearranges to tropylium ion in the gas phase, it is not known to do so in the condensed phase, but we are left with the possibility that a toluene ion may rearrange to give a cycloheptatriene ion, although analogous rearrangement in the condensed phase is apparently unknown.

There seems to be no suggestion from the photolysis or pyrolysis of toluene that the benzyl radical undergoes any rearrangement.

Indeed, Szwarc has found the benzyl radical to be very stable, undergoing essentially no side reactions and disappearing mainly as dibenzyl.[88]

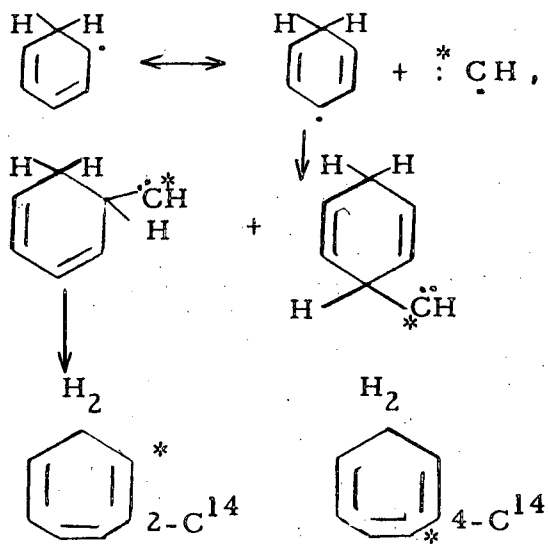
Let us now reverse our viewpoint and consider the possibility of rearrangement of cycloheptatriene to give toluene. As is well known, cycloheptatriene is nonaromatic, possessing only 6.7 kcal/mole resonance energy,[89] whereas the benzene ring is stabilized by around 35 kcal/mole;[90] the standard heat of formation of cycloheptatriene vapor at 25°C is +43 kcal/mole,[91] whereas that of toluene is +12 kcal/mole.[92] Rearrangement of cycloheptatriene to toluene is therefore possible. Lemmon and Strohmeier, however, found no detectable rearrangement upon heating cycloheptatriene in a Pyrex tube at 130° for 50 hours.[78] Likewise, no toluene was detected after cycloheptatriene was irradiated in sealed tubes with light from a sunlamp for 60 hours, or from an ultra violet lamp for the same time. One-half percent rearrangement could have been detected.

It is of course always possible that thermodynamically allowed processes occur in energy-rich hot-atom events which are not observed under milder conditions. It is obvious that one cannot exclude a possibility merely because it is unknown under photolytic or pyrolytic conditions. It is not so obvious, but equally true in principle, that reactive species known to be important in the radiation chemistry of a given substance are not necessarily important in its hot-atom chemistry. Differences may arise because of large variation in the average rate of energy transfer in the two cases. Even within the field of radiation chemistry results are sometimes found to depend upon the type of radiation because of differences in linear energy transfer.[93] Nevertheless, it seems wisest to emphasize in one's speculative considerations that which is known to be important in related areas.

In that spirit we suggest that cycloheptatriene-^{14}C may be formed in this work by the reaction sequence shown in Fig. 75. Reaction is postulated to occur between a ^{14}CH radical and a C_6H_7 radical. A ^{14}C atom may either combine with atomic hydrogen or abstract

$$^{*}:C: + [H\cdot] \longrightarrow {}^{*}:CH, \qquad (A)$$

$$C_6H_6 + H\cdot \longrightarrow C_6H_7\cdot, \qquad (B)$$



and (or)

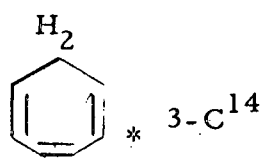


Fig. 75. A speculative mechanism for the formation of cyclo-heptatriene-^{14}C.

hydrogen from benzene or another fragment to give the CH radical; C_6H_7 radical is formed by combination of benzene and atomic hydrogen.

Taking the methylene carbon of the C_6H_7 radical as a reference point, one would expect reaction to occur at both the ortho and para carbons--perhaps, but not necessarily, in 2:1 ratio. Cycloheptatriene may be formed by the equivalent of two electron-pair shifts with no nuclear rearrangement. Cycloheptatriene produced by ortho addition may be 2-labeled or 3-labeled or both. That resulting from para addition would be 4-5 labeled. No activity should be in the methylene carbon.

This scheme is purely speculative, yet it has some merit. We have seen that Swallow gives Reaction B considerable weight, along with phenyl production, in the rationalization of the radiation chemistry of benzene.[93] Geib and Harteck conclude that Reaction B is the primary process occurring in the photolysis of benzene at liquid air temperature.[94]

We must confess that the CH radical is chosen primarily because we feel it has been sadly neglected and wish to give it its place in the sun. Moreover, it allows a simple mechanism to be written, further gain or loss of hydrogen being unnecessary. In chosing CH we allow both reactants to at least potentially depend upon the track fragment concentration for formation, which could account for the greater dependence of the yield of cycloheptatriene on ion energy than was found for benzene or toluene. The unrearranged adduct or cycloheptatriene itself, or both, could be labile (i.e., scavengable) species indicated as present in the cycloheptatriene sequence according to our interpretation of the energy-density effect on yield.

The chief merit of this suggestion is that it may be tested, perhaps critically by experiment. Cycloheptatriene possesses four distinct kinds of carbon atoms: the methylene or 1 carbon, the 2-7 carbons, the 3-6 carbons, and the 4-5 carbons. If the sequences shown in Fig. 75 are correct, activity would not be found in the 1-carbon; it could lead to labeling in all the CH carbons, perhaps to an equal

extent in each. One would certainly expect addition to occur at both the ortho and para positions. If it went only ortho, however, activity would not be found except in the 2- or 3-carbons (or both), whereas para addition alone would give 4-labeled cycloheptatriene. In any event, no activity would appear in the methylene carbon.

As mentioned earlier, Juppe and Wolf have partially degraded cycloheptatriene-^{14}C produced by photolysis of diazomethane in benzene. In this method, cyclopropane dicarboxylic acid anhydride is eventually made from cycloheptatriene; the anhydride contains five of the seven-cycloheptatriene carbons, lacking, according to Juppe and Wolf, carbons 4-5. Since they found that essentially no activity was lost in going to the anhydride, it seemed reasonable to assume that the photolytic cycloheptatriene is 1-labeled, although 2- or 3-labeling was not precluded.

We do not state that the reaction scheme we have pictured in Fig. 75 and the reaction or reactions occurring in the photolysis of diazomethane in benzene are the only ways in which cycloheptatriene-^{14}C could be produced in this work. It is certainly not unlikely, for example, that a symmetrical seven-membered intermediate, such as the tropylium ion, is involved—in which case random labeling would result. Let us therefore consider to what extent the partial degradation by Juppe and Wolf could help us decide among these various possibilities.

Let us list the three possibilities mentioned above, and their respective labeling criteria:

(a) photochemical synthesis--all the activity should remain in the anhydride;

(b) sequence suggested in Fig. 75--all the activity could remain in the anhydride, but we would expect some to be lost with the 4-5 carbons;

(c) any sequence involving a symmetrical intermediate--5/7 of the activity should remain the anhydride.

We see that if all the activity remained in the anhydride, then upon application of the partial degradation to cycloheptatriene produced in this work, (c) would be precluded, (a) would be strengthened, and (b) weakened, but no conclusive decision between (a) and (b) could be made.

If the anhydride did not contain all the activity, (a) would be precluded. If it had other than 5/7 of the cycloheptatriene activity, beyond the limit of experimental error, then (c) would be eliminated, and (b) would be consistent with that distribution. If 4/6 of the activity remained in the anhydride, (b) would receive considerable support, for that distribution would result from indiscriminate attack at the ortho and para positions of $C_6H_7\cdot$ in case (b), regardless of the way the ortho adduct rearranges. It would doubtless be difficult, but we should think possible nevertheless, to distinguish between 4/6 and 5/7 residual activity, the latter being that demanded by (c).

This partial degradation, then, can give results consistent with each case, but not exclusively. It can preclude cases (a) and (c), but cannot preclude (b). Obviously a complete degradation is required to allow one to make a clear distinction between these possibilities. Case (b) demands no 1-carbon activity. Case (a) could result in a compound entirely 1-labeled; it could not be randomly labeled, and surely has at least some methylene activity. If a complete degradation were available, we would therefore be able to clearly distinguish these possibilities. In particular, if no 1-carbon activity were found, the participation of the $C_6H_7\cdot$ radical, as an aromatic entity, would seem very likely.

It is implicit in the foregoing discussion that the methylene carbon of the $C_6H_7\cdot$ radical maintains its identity throughout the sequence leading to cycloheptatriene, and that no further rearrangement of cycloheptatriene occurs. Our belief, or rather hope, that this is the case in hot-atom chemistry, is encouraged by the finding by Juppe and Wolf that the activity in cycloheptatriene-^{14}C from photolysis of diazomethane in benzene ". . . was not appreciably randomized (if at all)"

upon electron irradiation.[86] The precision of the degradation results caused them to set an upper limit of 10 % randomization.

As always, we must remind ourselves that the fact that randomization does not occur in radiation chemistry does not mean that it is absent in hot-atom chemistry, particularly when the only cycloheptatriene seen in the latter case has certainly been involved in the hot-atom process. We do not stress this to hedge our bet, however. If activity were found in the 1-position, we would simply regard our suggestion as wrong, just as we would regard the photochemical analog as not occurring if activity were found in the 3- and 4-carbons.

As discussed earlier, we are hopeful that isotope-separator irradiation of benzene with $^{14}CH^+$, $^{14}CH_2^+$, and perhaps $^{14}CH_3^+$ ions will perhaps shed some light on the nature of the ^{14}C species as it undergoes the first step leading to benzene, toluene, or cycloheptatriene.

C. Discussion of the Prebenzene Investigation

There is, mercifully, very little that can be said about the origin of the prebenzene compounds. As before, we would like to know the reactions and reacting species participating in their formation, as well as the energetics of their formation. We can form no judgment on either count.

The question of reaction divides itself into two categories:

(a) reaction of ^{14}C as anything from atomic carbon to methyl with fragments formed by ion impact. Reaction could be either addition or substitution.

(b) reaction of ^{14}C in some form with benzene itself, two or more fragments being formed in a concerted reaction or as a result of dissociation of the adduct.

It is easy to visualize these prebenzene compounds as arising from addition reactions of the ^{14}C species to acetylene and other unsaturated benzene fragments. We have seen that acetylene is a product of the radiolysis of benzene.[57] Reaction of carbene with

acetylene by CH bond insertion would lead directly to methyl-labeled propyne; for example, Scott and Steacie found that C-2, C-3, C-4, and C-5 hydrocarbons were present in small amounts when benzene was photolyzed at high temperature in the presence of T ($^3P_1$) mercury atoms.[96] Figure 76 shows the cracking pattern of benzene vapor upon bombardment with 70-ev electrons in the ion source of a mass spectrometer.[97] If ions or radicals of the type seen in the mass spectra also appeared in the track in hot-atom work, they would furnish the kind of unsaturated species which could lead by addition reaction with ^{14}C species to the unsaturated prebenzene compounds we have identified.

Wolfgang et al. found as products of ^{11}C recoil in gaseous propane all the prebenzene compounds we have identified.[14] It is interesting to note that the ratio of propane to allyne in their work is about 2:1, the same ratio, approximately, that we observe in the present work. That no C-2 activity was found in our prebenzene compounds could mean that reaction with fragments, if it does occur, goes by addition rather than substitution.

We did not intend to quantitatively analyze the prebenzene compounds, and the yield estimates we have made are extremely rough. No consistent trend of yield with variation of energy density or ion energy is noticeable. Indeed, the relation of yield to ion energy has been inconsistent. Perhaps this is a reflection of incomplete collection of these compounds, as no carrier was added, or perhaps it reflects the unjustified grouping of all the prebenzene compounds together in these considerations.

We would certainly expect these compounds as such, as well as any intermediates leading to them, to be extremely susceptible to scavenging and incorporation into polymer. It would therefore not be surprising to see a large increase in prebenzene activity at the lower-energy irradiations, since the energy density is considerably reduced. In the first 90-v irradiation, there does appear to be an increase in prebenzene activity even when possible $^{14}CO_2$ contribution is discounted,

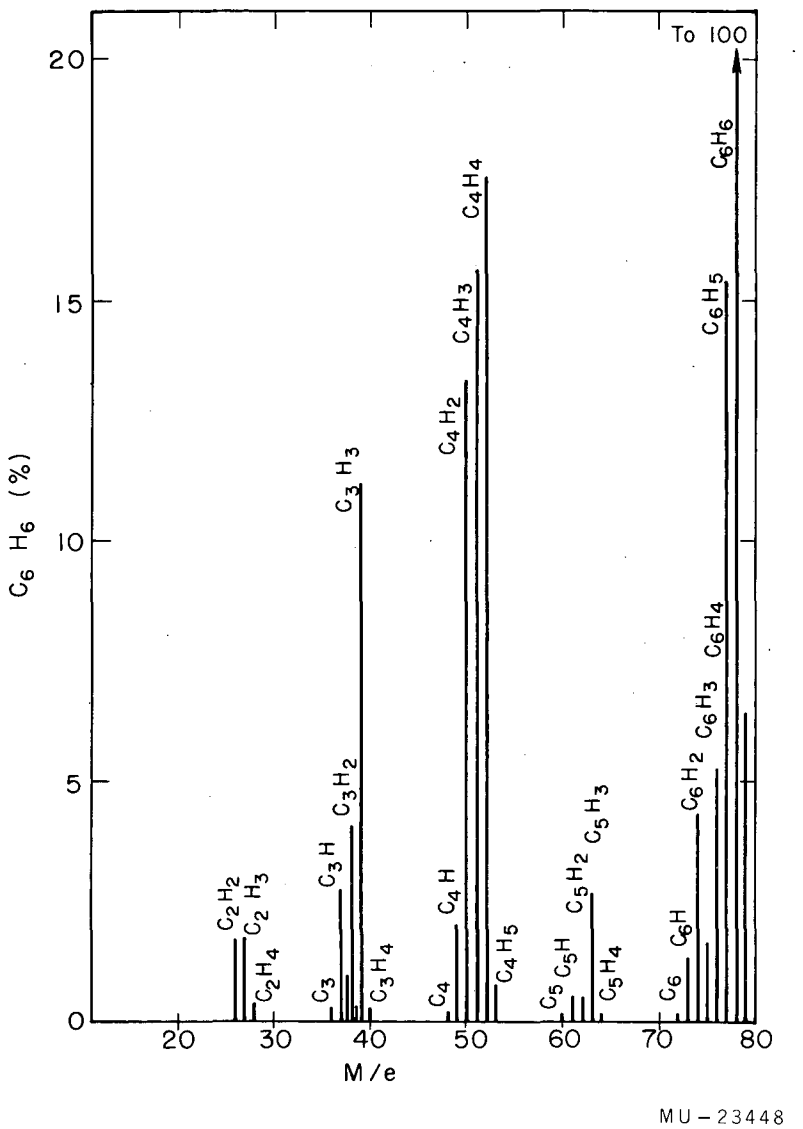


Fig. 76. Mass spectrum of benzene vapor bombarded with 70-ev electrons.

but in B12 and B13 (90 and 45 ev respectively) there is essentially little or no difference in the prebenzene activity compared with B11 at 5000 ev. B13, actually, is somewhat lower in prebenzene activity. If the decrease in ion energy balances the benefits of decreased energy density, it does not do so in a consistent fashion.

We have no reason to exclude the possibility of direct reaction with benzene to give these fragments. Such reactions might or might not be dependent upon ion energy, depending upon the energy range over which they occurred.

The results of the 1-hexyne irradiation cannot be interpreted as deciding the nature of the reactant in the benzene irradiations. The mere fact that little or no activity was seen in the C-7 or even the C-6 region following ^{14}C ion irradiation of 1-hexyne certainly does not mean that addition to acetylene or other alkynes or alkyne precursors cannot occur in the irradiation of benzene. It may be, in the benzene case, that radicals or ions or excited compounds are involved. It may be that in the hexyne irradiation the parent compound could not compete with reactions involving more reactive species, such as radicals. As suggested in Results, addition to the hexyne triple bond might have occurred readily, the products, however, being left in an excited state and unable to lose their excess internal energy by collision or radiation in time to avoid dissociation. Another possibility is that the adduct might have been an ion which could not dissipate the excitation energy generated by neutralization without dissociation. Unfortunately, it seems clear that the 1-hexyne irradiation is of little value in understanding the formation of the prebenzene compounds in the benzene irradiation.

Progress in regard to the prebenzene group has been limited solely to the qualitative identifications of some of the components in the C-3 and C-4 areas.

V. SUMMARY AND CONCLUSION

Our limited goal for this work, as described in Introduction, was to investigate the effect of ion energy on the yields of benzene, toluene, and cycloheptatriene, if indeed they were found. In addition to that, we wished to at least qualitatively identify any other products that might appear.

We have found cycloheptatriene for the first time. We have found a dependence of yield on ion energy. We have at least qualitatively identified some of the other products appearing: allene, propyne, 1,3-butadiene, 1-butyne, 1,2-butadiene, 1- and (or) isobutyne, and trace amounts of n-butane, are all considered, to at least a fair degree of security, as having been identified. Propane is considered to have been indirectly identified.

Thinking of ion energy as primarily a means to vary the total energy density in the sample, we were surprised to find that energy density *per se* does indeed affect the yields, but that ion energy *per se* has a separate and reverse effect. It is suggested that the effect due to ion energy must be associated with the track of an individual ion. Therefore, fragment density in the track, having a product-determining effect, is distinct from and in opposition to the role played by the energy density in the sample as a whole. We have seen that this interpretation implies that a sizable fraction, if not all, of the fragments generated by the passage of the ion must be accessible to the cooled-off ^{14}C species. It can be argued that if future experiments show a steady decrease in the yields of benzene, toluene, and cycloheptatriene with decreasing ion energy over the range 5000 to 45 ev, then the 100-A or so range attributed to a 5000- or 6000-ev ^{14}C ion by Yankwich[17] (through the equations of Seitz and Kohler[68]) must be considerably too long, and that the energy-loss models by Willard[67] and by Libby[26] must be closer to the truth.

From the results of our ring methyl degradation of toluene-^{14}C, it appears that the reaction sequence giving toluene in the $^{14}C^{+}$

ion irradiation of benzene is the same as that occurring in ^{14}C recoil in benzene. Using the degradation data amassed by Wolf and his co-workers at Brookhaven National Laboratory, we have limited the possible reactions leading to toluene to a fragment which can be provided in common by benzene, aniline, and toluene. We are unable to suggest a mechanism that would account for the observed ring distribution of activities found by Wolf for toluene-^{14}C from benzene.

It appears possible to visualize a reaction leading to benzene that can be reconciled with virtually all the observations made by us and others in regard to it. In addition to the obvious possibility that cycloheptatriene-^{14}C arises in this work in the same way as in the photolysis of diazomethane in benzene, we have suggested an alternative reaction sequence which would lead to a unique distribution of activity in cycloheptatriene. We should be able to decide between these two possibilities, and any other sequence which would involve a symmetrical seven-membered intermediate, by a complete degradation of cycloheptatriene. A partial degradation is available and we are hopeful that a complete one can be devised.

It is customary at this point for one to state that additional study is required in this problem, whatever the problem may be. Doubtless this claim is always well justified. It is clear, however, that in the present case this traditional assertion carries more than the usual amount of force. We have obtained a great deal of verbiage out of relatively little data. The conclusions we have made, the speculations we have indulged in, are for the most part capable of being tested by further experiment. We are confident that most of them will be tested in better conceived and better executed experiments providing more precise and more copious data. If they should all survive, we would be amazed and delighted. But if they all should fall, the most worth-while aspect of this work would still remain, for it lies in a technique, a tool—the isotope separator.

The thing conclusively demonstrated in this work is that the isotope separator is indeed capable of fulfilling its obvious potential. To be sure, isotope-separator irradiations have been carried out before, and we are indebted to Giacomello and his associates for their pioneering demonstration of the feasibility of the technique.[3-6] But in this work, for the first time, the unique abilities of the isotope separator were utilized.

From a preparative standpoint, it is hard to imagine a situation in which the isotope separator could compete with the facility and relative economy of recoil labeling, but, as an investigative tool, the isotope separator can control important parameters and avoid some difficulties the control and avoidance of which are inherently difficult in recoil labeling. The isotope separator, on the other hand, has difficulties and limitations of its own, as has been brought out from time to time in this dissertation, and it is this writer's view that the isotope-separator technique and the recoil technique complement each other quite nicely.

It seems clear that the only route to secure knowledge of a mechanism lies in the degradation of labeled products. This approach has been emphasized by Wolf and Anderson and others, and is today the subject of intensive effort by Wolf and his co-workers. When the results of such degradations are pooled with the information obtained from the isotope separator, we are truly hopeful that considerable progress will be made in the future in understanding these hot-atom processes.

ACKNOWLEDGMENTS

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Special acknowledgment is due Dr. Richard M. Lemmon, with whom I was in constant contact throughout this work, and whose guidance, encouragement, and tolerance are much appreciated. They were not only invaluable, they were essential to me. Because Dr. Lemmon and Professor Calvin translated their appreciation of the potential of the isotope separator into action, we have this valuable tool today.

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Appendix I

THE PRINCIPLE OF ION SEPARATION IN THE ISOTOPE SEPARATOR

The principle by which monoenergetic ions are separated in a homogeneous magnetic field according to their ratio of mass to charge is well known and may be found in almost any elementary physics text or discourse on electricity and magnetism. It is presented here for the convenience of the reader and to illustrate how even the simplest consideration of the equations of motion can be of use to the nonexpert in choosing the operating conditions of a machine such as the isotope separator.

Since all the ions are accelerated through a potential drop, V, the kinetic energy of an ion is given by

$$1/2\ mv^2 = Ve, \tag{I-1}$$

and the equation of motion of a moving ion in a magnetic field is given by

$$\vec{F} = \frac{e}{c}\ \vec{v} \times \vec{B}, \tag{I-2}$$

where n = ion mass in grams, v = ion velocity in cm/sec, V = accelerating voltage in stat volts, e = ion charge in stat coulombs = 4.8×10^{-10} esu/charge, B = magnetic flux density in gauss, c = speed of light in cm/sec = 3×10^{10} cm/sec, r = radius of curvature of ion in cm.

The vector product in Eq. (I-2) indicates that the force on an ion moving in a magnetic field is in a direction perpendicular to the plane defined by the direction of the ion and the direction of the magnetic field. In our case the ion trajectory and field are at right angles, so that the magnitude of the centripetal force on an ion is given by

$$F = \frac{B \cdot e \cdot v}{c}\ . \tag{I-3}$$

Since the direction of the force acting on an ion moving in a uniform magnetic field is always at right angles to the ion trajectory, an ion must follow a circular path while in the magnetic field, and the centripetal force in Eq. (I-3) must be balanced by a centrifugal force,

$$\frac{B \cdot e \cdot v}{c} = \frac{mv^2}{r}. \qquad \text{(I-4)}$$

Elimination of the ion velocity v from Eqs. (I-1) and (I-4) gives

$$r = \frac{c}{B} \left(2 V \frac{m}{e}\right)^{1/2}. \qquad \text{(I-5)}$$

Thus it is seen from Eq. (I-5) that for B and V constant the radius of curvature of an ion, r, depends only on m/e. In order for ions of a given m/e to be extracted, B and V must be chosen to allow the ions to pass through the trajectory tank and through the exit slit--that is, the desired ions must have a radius of curvature equal to that of the trajectory tank of the isotope separator. In our case, V is held constant at about 5000 v, equal to 16-2/3 stat volts, and r must equal 15 cm for extraction. Putting these values in Eq. (I-5) gives

$$B = 6.80 \times 10^2 \left(\frac{M}{n}\right)^{1/2} \text{ gauss}, \qquad \text{(I-6)}$$

which gives the strength of the magnetic field needed to separate and extract ions of mass number M and charge number n.

For $^{14}C^+$, B = 2540 gauss.

In practice, factors such as angular divergence, finite beam width, and energy spread cause an analyzed beam of ions to have considerable width, and the resolving power of a separator depends on the magnitude of these factors. (In Ref. 98 there is a simple and clear discussion of these considerations.)

Even though Eq. (I-5) is highly idealized when applied to an actual ion beam, it can be used to give some limiting values for operational considerations. For a given value of B and V, Eq. (I-5) can

be simplified to

$$r = kM'^{1/2} , \qquad \text{(I.-7)}$$

where

$$M' = \frac{M}{n} .$$

The horizontal displacement of infinitely thin ion beams of mass-to-charge ratio M' and M' + ΔM' is just equal to the difference in the radius of curvature of these two ion beams for a 90-deg-sector magnet, and this can be calculated from Eq. (I-7), giving

$$\Delta r = k(M' + \Delta M')^{1/2} - kM'^{1/2}$$

$$= kM'^{1/2} \left(1 + \frac{\Delta M'}{M'}\right)^{1/2} - kM'^{1/2} . \qquad \text{(I.-8)}$$

Since we are interested in cases in which $\Delta M'/n$ is considerably less than unity, we may use the binomial expansion, dropping all terms of second and higher order in $\Delta m'/M'$, giving

$$\Delta r = \frac{k\Delta M'}{2M'^{1/2}} = \frac{r}{2} \frac{\Delta M'}{M'} , \qquad \text{(I.-9)}$$

the well-known equation for mass dispersion. Equation (I-9) can be used to obtain a limiting value for changes such as were made in exit-slit width, as discussed in II. A. 2. b. In that case, we were interested in the horizontal displacement at the exit slit of ion beams of M' = 13 and 15 from the $^{14}C^{+}$ beam of M' = 14. With r = 15 cm, Eq. (I-9) gives

$$\Delta r = \frac{15}{2} \times \frac{1}{14} = 5.4 \text{ mm} . \qquad \text{(I-10)}$$

This told us that the maximum exit-slit width that could be used under ideal conditions was 10.8 mm; anything larger than that would allow

passage of the adjacent ion beams through the exit slit, assuming that the $^{14}C^{+}$ beam passes through the center of the slit. Since the width of the exit slit used in the later irradiations was 9.5 mm, we would expect complete resolution if the ion beams were indeed infinitely thin. It was therefore feasible to try the 9.5-mm slit, observing empirically how the actual width of the ion beams affected the resolution. As was mentioned earlier, the resolution obtained was found to be acceptable. (See Figs. 10 and 11.)

Appendix II

DERIVATION OF THE PROPERTIES OF AN ACTIVITY TRACE FROM A GIVEN MASS TRACE

For the purpose of qualitative identification of radioactive compounds by means of GLC-PC it is sufficient to know only the expected displacement in time of the maximum of an activity trace from the maximum of the corresponding mass trace. It is interesting, however, to derive in detail the expected shape of an activity trace from a given mass trace in terms of the operating parameters of the GLC-PC unit.

In their paper describing the first use of an internal-flow proportional counter in conjunction with gas-liquid chromatography, Wolfgang and Rowland derived the expression for the average counting rate of a sample, assuming a rectangular mass trace and a counter volume so small compared with the volume of effluent gas carrying the radioactive compound that the activity trace was also rectangular, i.e., constant with time during the time of passage. We will proceed here to derive the actual shape of an activity trace from realistic mass traces.

In the following discussion we shall assume:

a. The hot filament in the thermal-conductivity cell which gives rise to the mass trace is a true differential detector.

b. The flow rate of carrier gas (in cc/min) is constant from the thermal-conductivity cell through the proportional counter, and no turbulence occurs.

c. The sensitive volume of the counter is uniformly efficient throughout.

d. The recorder responds immediately to the mass and activity signals--a rather unrealistic assumption in the case of the activity traces in this work, where the ratemeter time constant was 2 sec.

It is well known and easily shown that the total area under a mass trace is directly proportional to the total amount of sample that

has passed the mass detector. Let M = the response of the mass detector as a function of time; M at a given instant is directly proportional to the concentration of the emerging compound in a differential volume of carrier gas surrounding the filament at that instant. We have

$$M = kc, \tag{II-1}$$

where k is a constant for a given compound and c is the concentration of the compound in, say, μmole/cc of carrier gas. The amount of sample passing the detector in a time interval dt is equal to the differential volume of gas passing in that time, dv, times the instantaneous composition of the gas, c. We can write

$$dn = cdv, \tag{II-2}$$

where n = μmoles;

$$dv = fdt, \tag{II-3}$$

where f = flow rate of carrier gas in cc/min;

$$dn = fcdt. \tag{II-4}$$

From Eq. (II-1) we obtain

$$dn = \frac{f}{k} \; Mdt. \tag{II-5}$$

The number of μmoles passing the detector between time t_2 and time t_1 is

$$\Delta n = \frac{f}{k} \int_{t_1}^{t_2} Mdt. \tag{II-6}$$

The total amount of sample passing by the detector is

$$n_{total} = \frac{f}{k} \int_{0}^{\infty} Mdt. \tag{II-7}$$

Let the instantaneous response of the proportional counter be A, which is given by

$$A = eSn, \tag{II-8}$$

where e = efficiency of the counter,

S = specific activity of the compound, in dpm/μmole

n_c = μmoles of sample in the counter at a given instant.

To calculate A as a function of time we must therefore know n_c as a function of time, which, in turn, requires knowledge of M as a function of time.

Let t = 0 when the first portion of the sample enters the mass detector. The total amount of sample in the proportional counter at a given time, n_c, is equal to the total amount of compound that has entered the counter from t = 0 to t = t, minus the amount that has left the counter in the time interval t = 0 to t = t. In the most general case the volume of gas carrying the sample is greater than the sensitive volume of the counter, and the time interval during which the samples are in the counter can be conveniently divided into three portions: the first is that period when the counter is filling but not emptying; the second is when the counter is both filling and emptying; and the third is when the counter is only emptying. In the less common case, in which the volume of gas carrying the sample is less than the counter volume, there is no period during which the sample is both leaving and entering the counter. There is instead a period during which the sample is neither entering nor leaving the counter. This case is easier to treat but less useful.

<u>Case 1</u>. $V_S > V_c$,

where V_S = volume of gas carrying the sample,

V_c = volume of counter.

Period I -- Filling:

Range: $0 \leqslant t \leqslant \frac{V_c}{f} + t_d$,

where t_d = the time required for passage between the mass detector and the beginning of the proportional counter;

$$A_I = eSn_c = \frac{eSf}{k} \int_0^{t-t_d} Mdt = k' \int_0^{t-t_d} Mdt .$$

When $t = V_c/f + t_d$, the sample begins leaving the counter.

Period II -- Filling and Emptying:

Range: $V_c/f + t_d \leqslant t \leqslant V_s/f + t_d$;

$$A_{II} = k' \int_0^{t-t_d} Mdt - k' \int_0^{t-V_c/f - t_d} Mdt,$$

$$A_{II} = k' \int_{t-V_c/f - t_d}^{t-t_d} Mdt.$$

When $t = V_S/f + t_d$, the counter stops filling.

Period III -- Emptying:

Range: $(V_S/f + t_d) \leqslant t \leqslant (V_S/f + V_c/f + t_d)$;

$$A_{III} = k' \int_0^{V_S/f} Mdt - k' \int_0^{t-V_c/f - t_d} Mdt ;$$

$$A_{III} = k' \int_{t - \frac{V_c}{f} - t_d}^{V_S/f} Mdt.$$

When $t = \frac{V_S}{f} + \frac{V_c}{f} + t_d$, all the sample has left the counter.

Case 2 $V_S < V_c$

Period I -- Filling:

Range: $0 \leqslant t \leqslant \frac{V_S}{f} + t_d$;

$$A_I = k' \int_0^{t-t_d} M dt.$$

where $t = \frac{V_S}{f} + t_d$, all the sample has entered the counter and none has yet left.

Period II--Plateau:

Range: $\frac{V_S}{f} + t_d \leqslant t \leqslant \frac{V_c}{f} + t_d$;

$$A_{II} = k' \int_0^{V_S/f} M dt = \text{constant}.$$

When $t = \frac{V_c}{f} + t_d$, the sample begins to leave the counter.

Period III -- Emptying:

Range: $\frac{V_c}{f} + t_d \leqslant t \leqslant \frac{V_c}{f} + \frac{V_S}{f} + t_d$;

$$A_{III} = k' \int_0^{V_S/f} M dt - k' \int_0^{t - V_c/f - t_d} M dt;$$

$$A_{III} = k' \int_{t - \frac{V_c}{f} - t_d}^{V_S/f} M dt.$$

When $t = \frac{V_c}{f} + \frac{V_S}{f} + t_d$, all the sample has left the counter.

These equations are of use only if the function M is known. A rectangle is never a good approximation to an actual mass trace, but a triangle is a fair approximation and a Gaussian shape is better yet.

Using the equations derived for Case 1, we calculated the activity traces expected from a triangular mass trace and a Gaussian mass trace. It should be emphasized that what is of interest here is the shape of the activity trace relative to the mass trace; the magnitude of either trace is arbitrary, depending upon the value assumed for the amount and specific activity of the compound, the efficiency of the counter, and the sensitivity of the mass detector.

Triangular Mass Trace

Let $\frac{V_S}{f}$, the width in time of the mass trace, be W. Then from

$$t = 0 \text{ to } t = W/2, \quad M = M_{max} \times \frac{t}{W/2} = 2\frac{M_{max}}{W}\, t,$$

and from

$$t = W/2 \text{ to } t = W, M = M_{max} \frac{(W - t)}{W/2} = 2\, M_{max} \frac{(W - t)}{W} .$$

Here M is simple to integrate, but Calculation of A is cumbersome because M must be treated in two parts. The expressions giving A during the several periods are as follows:

I -- Filling:

Range: $0 \leq t \leq \frac{V_c}{f} + t_d$;

$$A_I = k' \int_0^{t-t_d} \frac{2M_{max}}{W} t \, dt;$$

$$A_I = \frac{k'M_{max}}{W} (t - t_d)^2 .$$

In the following equations the final integrated expression only is given.

II -- Filling and Emptying:

(a) Only the first half of the mass trace involved

Range: $\frac{V_c}{f} + t_d \leqslant t \leqslant \frac{W}{2} + t_d$;

$$A_{II_a} = \frac{2k'M_{max} V_c/f}{W} \left[t - t_d + \frac{V_c}{2f} \right] .$$

(b) Both halves of the mass trace involved

Range: $W/2 + t_d \leqslant t \leqslant W/2 + V_c/f + t_d$;

$$A_{II_b} = \frac{2k'M_{max}}{W} \left[-t^2 + (W + \frac{V_c}{f} + 2t_d)\, t - (t_d^2 + \frac{W^2}{4} + 1/2 \left(\frac{V_c}{f}\right)^2 + Wt_d + \frac{V_c}{f} t_d) \right] .$$

(c) Only second half of mass trace involved

Range: $W/2 + V_c/f + t_d \leqslant t \leqslant W + t_d$;

$$A_{II_c} = \frac{2k'M_{max} V_c/f}{W} \left[- t + (W + \frac{V_c}{2f} + t_d) \right] .$$

III -- Emptying:

Range: $W + t_d \leqslant t \leqslant W + \frac{V_c}{f} + t_d$,

$$A_{II} = \frac{k'M_{max}}{W} \left[(t - \frac{V_c}{f} - t_d)^2 - 2W(t - \frac{V_c}{f} - t_d) + W^2 \right] .$$

The values of the several parameters chosen in the calculation of the activity curve shown in Fig. 77 were taken to be approximately those encountered in the analyses made in this work, and are as follows:

$$t_d = 1/4 \text{ min},$$

$$\frac{V_c}{f} = 1/2 \text{ min},$$

$$W = \frac{V_s}{f} = 3 \text{ min},$$

$$M_{max} = 20 \text{ arbitrary units},$$

$$k' = \frac{\epsilon Sf}{k} = 3/2 \text{ arbitrary units}.$$

There are several points worth noting about the activity trace from the triangular mass trace.

(a) The shape of the activity trace is obviously quite different from that of the mass trace.

(b) The activity trace rises quite slowly compared with the sharply rising triangular mass trace.

(c) The activity-trace maximum is displaced in time from the mass-trace maximum, and differentiation of the equation giving the activity trace during Period IIb shows that the displacement between the two maxima is equal to $t_d + V_c/2f$, as previously stated.

(d) The activity trace has the same width at its inflection point as the mass trace at its inflection point.

(e) The activity trace is V_c/f minutes wider at the base line than the mass trace.

Gaussian Mass Trace

If a mass trace is Gaussian in shape, we have

$$M = M_{max} \exp\left[-(t-t_m)^2/2\sigma^2\right], \qquad \text{(II-9)}$$

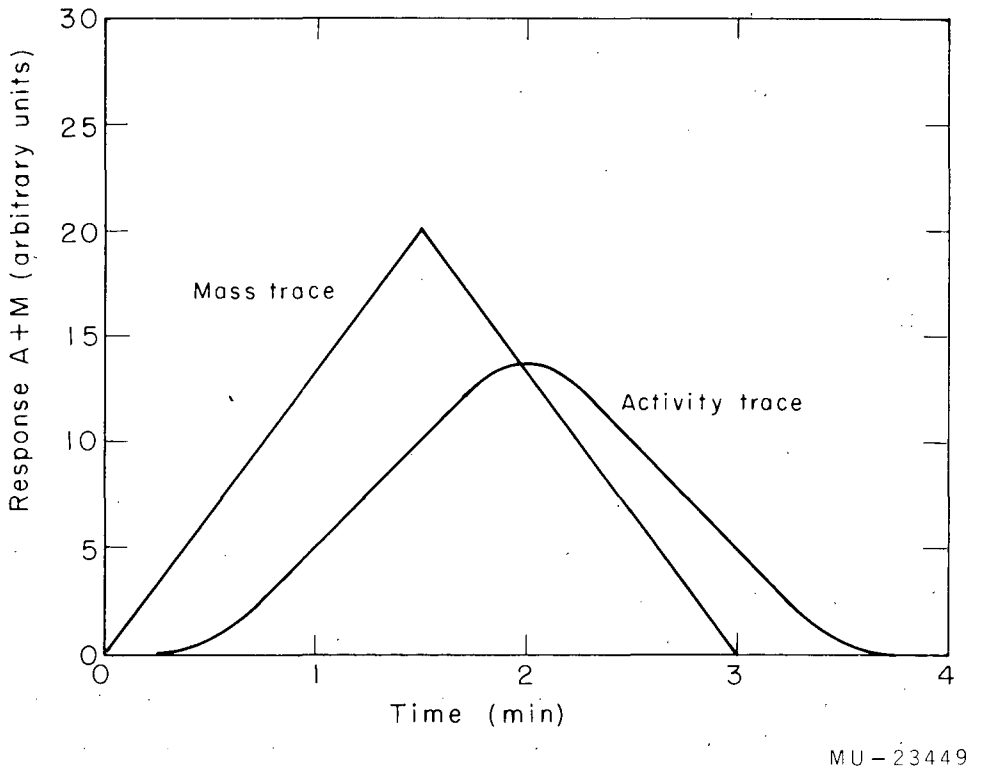

Fig. 77. Calculated shape and position of an activity trace produced by a triangular mass trace.

where t_m = the time at which the mass maximum appears σ = one-half the width of the Gaussian mass trace at its inflection point, which occurs at $M = M_{max}/\sqrt{e} = 0.606\ M_{max}$. The total amount of material responsible for the mass trace is given by

$$n_{total} = \int_{-\infty}^{+\infty} M dt = M_{max} \int_{-\infty}^{+\infty} \exp\left[-(t-t_m)/2\sigma^2\right] dt \qquad \text{(II-10)}$$
$$= (2\pi)^{1/2}\ \sigma\ M_{max}.$$

Since more than 99.7% of the total area under a Gaussian curve lies within

$$t-t_m/\sigma = \mu = \pm 3, \qquad \text{(II-11)}$$

we need not carry out our calculations much beyond three or four σ units. The Gaussian mass trace shown in Fig. 78 is modeled after the cycloheptatriene mass trace shown in the analysis of B8-1 in Fig. 33. The sensible duration of that trace is about 4.5 min, therefore t_m is taken here equal to 2.25 min. The half-width of the cycloheptatriene peak at its inflection point is 0.55 min, and that value is taken here for σ:

$$M = M_{max} \exp\left\{-(t-2.25)^2 / \left[2(0.55)^2\right]\right\} \qquad \text{(II-12)}$$
$$= \frac{n_T}{\sqrt{2} \times 0.55} \exp\left\{-(t-2.25)^2 / \left[2(0.55)^2\right]\right\}.$$

The values of

$$(1/\sqrt{2\pi}) \exp\left\{-(t-2.25)^2 / \left[2(0.55)^2\right]\right\}$$

as a function of

$$\mu = (t - 2.25)/0.55$$

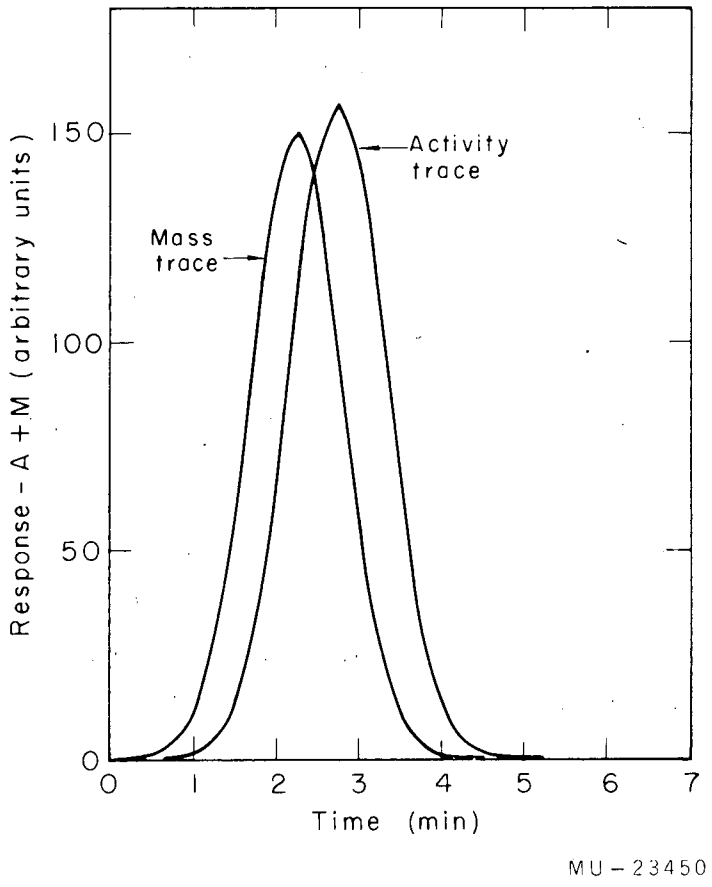

Fig. 78. Calculated shape and position of an activity trace produced by a Gaussian mass trace.

are obtained from standard probability tables [99] and are multiplied by 376 to give $M_{max} = 150$, an arbitrary choice.

For the derivation of the activity trace, we have the following.

I -- Filling:

Range: $0 \leqslant t \leqslant \frac{V_c}{f} + t_d$;

$$A_I = eSn_T \times \frac{1}{\sqrt{2\pi\sigma}} \int_0^{t-t_d} \exp\left\{-(t-2.25)/\left[2(0.55)^2\right]\right\}$$

$$= k'' F_N(t - t_d) = k'' F_N(t - 1/4);$$

when $k'' = eSn_T = 450$ in this construction, and in general,

$$F_N(t) = \frac{1}{\sqrt{2\pi\sigma}} \int_{-\infty}^{t} \exp\left[-(t-t_m)^2/2\sigma^2\right].$$

Since our $t = 0$ is 4σ units from the mean, t_m, it is a very good approximation to replace the zero in the lower bound of the above integral by $-\infty$. The values of $F_N(t)$ are taken from the standard probability tables [99] as a function of $= t-t_m/\sigma$.

II -- Filling and Emptying

Range: $\frac{V_c}{f} + t_d \leqslant t \leqslant W + t_d$,

where $W = \frac{V_s}{f}$, as before;

$$A_{II} = k'' \left[F_N(t-t_d) - F_N\left(t - \frac{V_c}{f} - t_d\right)\right].$$

In this construction $W = 4.5$ min, $t_d = 0.25$ min, and $V_c/f = 0.5$ min Therefore

$$A_{II} = 450 \left[F_N(t-0.25) - F_N(t-0.75)\right]$$

within the range

$$0.75 \leq t \leq 4.75 \text{ min.}$$

<u>III -- Emptying</u>

Range: $W + t_d \leq t \leq W + \frac{V_c}{f} + t_d$,

i.e., $4.75 \leq t \leq 5.25$;

$$A_{III} = k'' \left[F_N(W) - F_N\left(t - \frac{V_c}{f} - t_d\right) \right]$$

$$= 450 \left[F_N(4.5) - F_N(t-0.75) \right] .$$

Although the activity trace constructed here is not Gaussian, the difference between its shape and that of the mass shape is not striking. Indeed, as V_c/f becomes small compared with $V_s/f = W$, the shape of the activity trace approaches more and more closely the shape of the mass trace, that is, the proportional counter approaches differential detection as its volume becomes small compared with the volume of gas carrying the sample. Again the maximum of the activity trace is displaced by $V_c/f + t_d$ from the maximum of the mass trace. As was mentioned earlier in the discussion of the traces from this work, this is true in general for a symmetrical mass trace of any shape. It is also generally true that for a mass trace of any shape and degree of symmetry the activity trace will be broader in time than the mass trace by V_c/f.

BIBLIOGRAPHY

1. J. E. Willard, Ann. Rev. Phys. Chem. 6, 141 (1955).
2. A. P. Wolf, B. Gordon, and R. C. Anderson, J. Am. Chem. Soc. 78, 2657 (1956).
3. U. Croatto and G. Giacomello, Paper presented at the 45th meeting of the Italian Society for the Progress of Science, Naples, 1954.
4. B. Aliprandi, F. Cacace, and G. Giacomello, Ricerca Sci. 26, 3029 (1956).
5. B. Aliprandi and F. Cacace, Ann. Chem. 46, 1204 (1956).
6. B. Aliprandi, F. Cacace, L. Cieri, and R. Masironi, Radioisotopes in Scientific Research (Proc. 1st UNESCO Intern. Conf., Paris, 1957) Vol. 2 (Pergamon Press, Ltd., New York, 1958), pp. 146-153.
7. R. M. Lemmon, F. Mazzetti, F. L. Reynolds, and M. Calvin, J. Am. Chem. Soc. 78, 6414 (1956).
8. R. M. Lemmon, F. L. Reynolds, and F. Mazzetti, in Chemistry Division Quarterly Report, University of California Radiation Laboratory UCRL-3595, Oct. 1956, p. 5.
9. R. M. Lemmon, F. L. Reynolds, A. Coombs and M. Look, in Chemistry Division Quarterly Report, University of California Radiation Laboratory Report UCRL-3629, Jan. 1957, p. 25.
10. R. Wolfgang, T. Pratt, and F. S. Rowland, J. Am. Chem. Soc. 78, 5132 (1956).
11. M. Guillaume, Nature 182, 1592 (1958).
12. A. P. Wolf, Ann. Rev. Nuclear Sci. 10, 259 (1960).
13. B. Suryanarayana and A. P. Wolf, J. Phys. Chem. 62, 1369 (1958).
14. C. MacKay, M. Pandow, P. Polak, and R. Wolfgang, in Symposium on The Chemical Effects of Nuclear Transformations, International Atomic Energy Agency, Prague, 1960, Paper No. 51.
15. C. N. Turton, in Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958 (United Nations, Geneva, 1958), Paper 284.

16. H. A. Bethe and J. Ashkin, Passage of Radiations through Matter, in Experimental Nuclear Physics, ed. by E. Segrè (John Wiley and Sons, New York, N. Y., 1953), p. 167.

17. P. E. Yankwich, Can. J. Chem. 34, 301 (1956).

18. R. Muxart, Bull. soc chem. France, 1956, 1857.

19. A. P. Wolf, Radioisotopes in Scientific Research, (Proc. 1st UNESCO Intern. Conf., Paris, 1957) Vol. 2 (Pergamon Press, Ltd., New York, N. Y., 1958), pp. 114-135.

20. M. Zifferero, Ann. Chim. Rome 44, 563 (1954).

21. A. P. Wolf, R. C. Anderson, and C. S. Redvanly, Nature 176, 831 (1955).

22. A. G. Schrodt and W. F. Libby, J. Am. Chem. Soc. 78, 1267 (1956)

23. A. P. Wolf, Symposium on The Chemical Effects of Nuclear Transformations, International Atomic Energy Agency, Prague, 1960, Paper No. 14.

24. A. P. Wolf, unpublished work, cited in Refs. 12 and 23.

25. J. Y. Yang and A. P. Wolf, J. Am. Chem. Soc. 82, 3315 (1960).

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

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

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

29. G. Harbottle and N. Suttin, in Advances in Inorganic and Radiochemistry, Vol. 1 (Academic Press, Inc., New York, N. Y., 1959), p. 267.

30. A. P. Wolf, B. Gordon, and R. C. Anderson, J. Am. Chem. Soc. 78, 2657 (1956).

31. C. Brunello and R. Muxart, in Symposium on The Chemical Effects of Nuclear Transformations, International Atomic Energy Agency, Prague, 1960, Paper No. 29.

32. F. L. Reynolds, in Chemistry Division Semiannual Report, Lawrence Radiation Laboratory Report UCRL-8618, Jan. 1959, p. 76.

33. E. L. Yates, Proc. Roy. Soc. (London) A168, 148 (1938).

34. M. A. Tuve, O. Dahl, and L. R. Hafstad, Phys. Rev. 48, 241 (1935).

35. R. H. V. M. Dawton and M. L. Smith, in Electromagnetic Isotope Separators and Applications of Electromagnetically Enriched Isotopes, ed. by J. Kock (Interscience Publishers, Inc., New York, N. Y., 1958).

36. Ibid., p. 161.

37. M. G. Ingrahm and R. J. Hayden, in A Handbook on Mass Spectroscopy, Nuclear Science Series, Report No. 14 (NRC-USA), p. 43.

38. W. J. Moore, Physical Chemistry, 2nd. ed (Prentice-Hall, Inc. New York, N. Y., 1955), p. 166.

39. Int. Critical Tables 3, 207 (1928).

40. Int. Critical Tables 3, 208 (1928).

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

42. A. T. James and A. J. P. Martin, Biochem. J. 50, 679 (1952).

43. A. T. James, A. J. P. Martin, and G. H. Smith, Biochem. J. 52, 238 (1952).

44. A. E. M. Kilner, H. S. Turner, and R. J. Warne, in Proceedings of the Second Radioisotope Conference, Oxford, 19-23 July 1954 (Academic Press, Inc., New York, N. Y., 1954), p. 29.

45. R. B. Loftfield, J. Am. Chem. Soc. 73, 4707 (1951).

46. J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, J. Am. Chem. Soc. 78, 601 (1956).

47. Elton M. Baker, in Chemistry Division Quarterly Report, University of California Radiation Laboratory Report UCRL-3157, Sept. 1955, p. 51.

48. B. M. Tolbert, Ionization Chamber Assay of Radioactive Gases, University of California Radiation Laboratory Report UCRL-3499, March 1956, p. 23.

49. L. Reio and G. Ehrensvard, Arkiv Kemi 5, 301 (1953).

50. H. Steinberg and F. L. J. Sixma, Rec. trav. chim. 79, 679 (1960).

51. A. P. Wolf, Ring Degradation Data, presented orally at Symposium on The Chemical Effects of Nuclear Transformations, International Atomic Energy Agency, Prague , 1960.

52. F. Ullman and J. B. Uzbachian, Ber. deut. chem. Ges. 36, 1797 (1903).

53. Handbook of Chemistry and Physics, C. S. Hodgman, ed., 36th ed. (Chemical Rubber Publishing Co., Cleveland, Ohio, 1954-5), p. 779.

54. H. Wolf, "The Schmidt Reaction," Chapter 8 in Organic Reactions, Vol. 3, R. Adams, ed (John Wiley and Sons, Inc., New York, N. Y., 1946), pp. 307-336.

55. A. R. Jones, J. Chem. Phys. 32, 953 (1960).

56. A. van der Wiel, Nature 187, 142 (1960).

57. W. N. Patrick and M. J. Burton, J. Am. Chem. Soc. 76, 2626 (1954).

58. E. Collinson and A. J. Swallow, Chem. Rev. 56, 471 (1956).

59. Cf. Ref. 1, pp. 152-3.

60. I. Norman and G. Porter, Nature 174, 508 (1954).

61. I. L. Mador, J. Chem. Phys. 22, 1617 (1954).

62. R. B. Mesrobian et al., Nucleonics 12, No. 12, 62 (1954).

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

64. E. W. R. Steacie, Atomic and Free Radical Reactions, Vol. 1, 2nd Ed. (Reinhold Publishing Corp., New York, N. Y., 1954), Chapter III.

65. L. Friedman and W. F. Libby, J. Chem. Phys. 17, 647 (1959).

66. M. S. Fox and W. F. Libby, J. Chem. Phys. 20, 487 (1952).

67. J. E. Willard, cf. Ref. 28, p. 198.

68. F. Seitz and J. S. Kohler, "Displacement of Atoms During Irradiation," in Solid State Physics, Vol. 2, F. Seitz and A. Turnbull, eds. (Academic Press, Inc., New York, N. Y., 1956), p. 305.

69. R. M. Schuler, J. Chem. Phys. 22, 2026 (1954).

70. C. F. McCauley and R. M. Schuler, J. Phys. Chem. 62, 1364 (1958).

71. P. C. Capron and E. Crevecoeur, J. chim. phys. 49, 29 (1952).

72. G. Harbottle and N. Suttin, J. Phys. Chem. 62, 1344 (1958).

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

74. M. Mizushima and S. Koide, Busseiron Kenkyu 44, 102 (1951).

75. A. J. Swallow, Radiation Chemistry of Organic Compounds (Pergamon Press, New York, N. Y., 1960), Chapter V, pp. 124-146.

76. A. P. Wolf, B. Gordon, and B. Suryanarayana, unpublished work, cited in Refs.12 and 23.

77. W. von E. Doering and L. H. Knox, J. Am. Chem. Soc. 75, 297 (1953).

78. R. M. Lemmon and W. Strohmeier, J. Am. Chem. Soc. 81, 106 (1959).

79. W. von E. Doering and H. Prinzbach, Tetrahedron 6, 24 (1959).

80. M. Zelikof and M. Aschenbrand, J. Chem. Phys. 24, 1034 (1956).

81. M. T. Murphy and A. C. Duggan, J. Am. Chem. Soc. 71, 3347 (1949).

82. G. N. Maslyanskii and M. V. Veltistova, J. Chem. Chem. (USSR); 16, 2132 (1946).

83. R. Ya. Levina, E. A. Viktorova, and P. A. Akishin, Vestnik Noskov. Univ. 6, No. 12, Ser. Fiz.-Mat. i Estestven Nauk. No. 8, 71 (1951).

84. A. F. Plate and M. I. Batvev, Doklady Akad. Nauk S. S. S. R. 59, 1305 (1948).

85. N. I. Shuikin, E. A. Timoveeva, and V. M. Slodkikh, Izvest. Akad. Nauk S. S. S. R. 1955, 567; Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. S. S. R. (English Translation) 1955, 503.

86. G. Juppe and A. P. Wolf, J. Am. Chem. Soc. 83, 337 (1961).

87. P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Am. Chem. Soc. 79, 842 (1957).

88. M. Szwarc, J. Chem. Phys. 17, 431 (1949).

89. G. M. Badger, The Structure and Reaction of Aromatic Compounds (Cambridge University Press, New York, N. Y. 1954), p. 54.

90. M. J. S. Dewar, The Electronic Theory of Valence (Oxford University Press, Oxford, England, 1959), p. 35.

91. H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, J. Am. Chem. Soc. 78, 5469 (1956).

92. M. Szwarc, Chem. Rev. 47, 75 (1950).

93. Cf. Ref. 75, p. 126.

94. K. H. Geib and P. Harteck, Ber. deut. chem. Ges. 66B, 1815 (1933).

95. V. Alder and G. Jacobs, Chem. Ber. 86, 1528 (1953).

96. E. Y. J. Scott and E. W. R. Steacie, Can. J. Chem. 29, 233 (1951).

97. American Petroleum Institute Mass Spectral Catalogue, Mass Spectrum No. 1591, due to Imperial Chemical Industries, Ltd.

98. J. Koch, Ed., Electromagnetic Isotope Separators and Application of Electromagnetically Enriched Isotopes (Interscience Publishers, Inc., New York, N. Y., 1958), Part A, Chapter 2.

99. Biometrika Tables for Statisticians, Vol. I, E. S. Pearson and H. D. Hartley, eds. (Cambridge University Press, New York, 1958).

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