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REACTIONS OF ACCELERATED $^{14}C^{+}$ IONS WITH BENZENE

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Abstract

A specially constructed isotope separator has been used for the purpose of irradiating organic compounds with a beam of singly-charged C^{14} ions of approximately one microampere.

Earlier work has shown that C^{14}-labeled benzene and toluene are produced in a ratio of 2 : 1 by the irradiation of solid benzene with the carbon ions. This finding has been confirmed with the new isotope separator, and the work has been extended with the aid of a gas chromatograph in which mass peaks and radioactivity peaks may be recorded simultaneously. Labeled cycloheptatriene was also found to be an invariable product of these irradiations. In addition to the labeled benzene, toluene, and cycloheptatriene, approximately twelve other radioactive products have been observed, but none of them have yet been identified. In the case of the labeled toluene, it was found that only about 87% of its radioactivity was in the methyl group.

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1. Introduction

The work described in this report is an outgrowth of the studies that have been made at several laboratories on the interactions of recoiling carbon atoms on organic molecules (1,2,3). In the recoil work, an organic compound containing nitrogen, or having dissolved in it a nitrogen-containing compound, is irradiated with neutrons in a reactor. The $N^{14}(n,p)C^{14}$ reaction provides the recoiling carbon-fourteen atoms. In the present work we have substituted C^{14} ions accelerated by a mass spectrometer, or isotope separator, for the recoiling carbon atoms born in a nuclear reactor. Effects of accelerated carbon-fourteen ions on organic targets have been reported earlier from laboratories in Italy (4) and the United States (5).

Earlier work has shown some of the effects of irradiating solid benzene with $^{14}C^{+}$ ions (5). In the present work, further details of this system have been determined through the use of (a) an isotope separator giving a far more intense beam (approx. 1 μamp) of carbon

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ions and (b) a gas chromatograph in which mass peaks and radioactivity peaks are simultaneously recorded. The present paper records (a) the state of our knowledge of the distribution of labeled products from $^{14}C^{+}$-irradiated benzene, (b) the effect of a variation of the energy of the impinging ions on that distribution, and (c) the distribution of radioactivity between the methyl group and the ring of toluene formed from the irradiated benzene.

2. Experimental Part

Isotope Separator. A low-voltage capillary arc type of isotope separator was constructed for this work. Details of the ion source of this instrument are shown in Figure 1. The arc chamber is made of stainless steel, and is water-cooled with low-conductivity water flowing through a small glass heat exchanger. The anode and cathode assemblies are constructed of tantalum and steel respectively. The cathode filament is a strip of rhenium metal. In order to strike an arc, the gas that is the source of the $^{14}C^{+}$ ($C^{14}O_2$) is admitted to the arc chamber (which operates at a pressure of about 10^{-3} mm) and the voltage between the anode and cathode is set at 500 volts. The filament current is then increased until an arc is established. The voltage is then reduced to about 50 while the filament current is increased. The arc current is usually between one and two amperes during an irradiation. The ions are extracted by a 5 kv negative potential on the extracting electrode. The focusing electrode, mounted inside the extraction electrode on insulator standoffs, focuses the divergent beam to a diameter of about 3 mm. The narrowed,

accelerated beam moves through the slit into the trajectory tank between the pole pieces of an electromagnet. The pumping system associated with the isotope separator maintains the instrument at a pressure of 10^{-5} - 10^{-6} mm.

In Figure 2 is shown a schematic diagram of the target end of the isotope separator. Upon emerging from the trajectory tank, the ion beam passes through a fine grid of copper wire. The purpose of this grid is to provide an opportunity of decelerating the ions, by means of a repelling voltage, to any desired energy. The ions then impinge on the solid benzene target. The benzene (previously purified by gas chromatography) is admitted into the target chamber through the valve-controlled inlet shown at the bottom of Figure 2. The benzene is admitted continuously during an irradiation. In most experiments, the benzene vapor flow was controlled so that about 0.06 ml. was frozen onto the target area (about 60 cm^2) per hour. The target area was maintained at about -160° by means of a slurry of isopentane. At this temperature, benzene has a vapor pressure of about 10^{-6} mm.

During most of the work reported here, a beam of $^{14}C^+$ ions of a few tenths of a microampere was directed onto the benzene target. The chemical erosion effects of the $C^{14}O_2$ on the rhenium filament are such that this filament lasts only about two hours. It must, therefore, be replaced if an irradiation is to continue. In the present work, the total $^{14}C^+$ beam varied from 0.045 to 2.03 μamp hours. This corresponds to from 1.0×10^{15} to 4.5×10^{16} ions of C^{14}.

After an irradiation, the target area was closed off from the rest of the instrument and allowed to come to room temperature. The benzene was distilled into an external, cold trap. A mixture of carrier hydrocarbons (benzene, toluene, cycloheptatriene, and occasionally some alkanes) was then admitted into the target chamber, from which they were distilled into the same trap holding the target benzene. The combined material in the trap was then subjected to gas chromatography.

Gas Chromatography. The gas chromatography (gas-liquid partition chromatography) was performed on a Wilkens "Aerograph". The column was 155 cm. (five ft.) in length and 6.3 mm. in diameter. It was filled with crushed fire-brick that was coated with "Apiezon" (a high-boiling hydrocarbon mixture). The carrier gas was pure methane, the column temperature 70°, and the gas flow rate was 28 cc. per min. The effluent gas, after passing through the detecting thermal-conductivity cell, flowed through a 16 cc. proportional counter tube (also heated to 70°) similar to one recently described (6,7). The proportional counter was connected through a scaler (which also provided the counter's power supply) to a Nuclear-Chicago Model 1620B ratemeter, and the output of the ratemeter was connected to a Leeds and Northrup dual-pen "Speedomax" recorder. The other pen of the recorder was controlled by the Wheatstone bridge potential from the gas chromatograph's thermal-conductivity cells. Consequently, the dual-pen recorder gave a simultaneous record of both mass peaks and radioactivity peaks from the gas chromatograph. The lower limit of C^{14} radioactivity detection by the proportional tube was about 200 disintegrations per minute.

Toluene Degradation. C^{14}-labeled toluene formed from the benzene irradiations was degraded only as far as a determination of the amounts of activity in the methyl group and in the ring. The toluene was oxidized by $KMnO_4$ solution to benzoic acid which was, in turn, converted to aniline and CO_2 via the Schmidt reaction. The radioactivity in the CO_2 was determined by ionization chamber methods, and that in the aniline (which was brought to constant specific radioactivity by gas chromatography) was determined by liquid scintillation counting.

3. Results and Discussion

There are many variables, some controllable, some only partly so, and some essentially uncontrollable, that are encountered in the operation of the isotope separator. Among these variables may be mentioned the following:

1. Energy of the impinging ions
2. Intensity of the ion beam
3. Amount of beam spreading before the ions strike the target
4. Dilution of $^{14}C^+$ ions with other mass-14 ions (e.g., N^{14})
5. Rate of benzene input
6. Build-up of repelling charges on the benzene surface
7. Adsorption of micro amounts of labeled products on surfaces inside the isotope separator
8. Treatment of target mixture after irradiation and prior to chromatography.

These variables have, so far, operated to prevent the duplication of results on a quantitative basis. Experiments are now in progress that are aimed at better control over these variables.

In Figure 3 are presented the results of a typical record of mass peaks and activity peaks after a $^{14}C^{+}$ irradiation of benzene. In this particular experiment, the energy of the impinging ions was 5 kv. during about one-third of the irradiation, and 90 e.v. during the rest of the irradiation (with about the same beam intensities). As would be expected, most of the results here are intermediate between experiments where the ion energy was entirely at 5 kv. and those where the ion energy was entirely at 90 e.v. The activity trace (solid line) shows at least three major peaks emerging from the column before benzene (whose maximum occurs at about 7 minutes). In all of the experiments so far done, the major portion (roughly 90%) of the radioactivity emerges from the gas chromatograph ahead of benzene. We have found major differences in this "pre-benzene" area from experiment to experiment. For example, not only is the general appearance of the area (that is, the kind and quantity of the different compounds) changed by the particular conditions of the carbon-ion irradiations, but it is also changed by post-irradiation treatment (e.g., time of standing and exposure to oxygen). Some of the compounds in this area disappear on treatment with bromine, and some do not. The very early peaks of the "pre-benzene" area may include such compounds as CO_2, methane, ethane, ethylene, and acetylene (i.e., compounds that travel through our columns at about the same rate as air). Beyond the area of these compounds, and before benzene is reached, one finds other peaks that contain, presumably, C_3, C_4, and C_5 hydrocarbons. However, none of these compounds have yet been identified.

In the experiment recorded in Figure 3, a low-boiling petroleum ether (consisting mostly of n-pentane and n-hexane), benzene, toluene, and cycloheptatriene were added as carriers. In the mass trace (dashed line) peaks of pentane and hexane and two minor alkanes may be seen in the "pre-benzene" area. None of these peaks coincide with radioactivity peaks. However, in this experiment, as in all so far done, the mass peaks and radioactivity peaks for benzene, toluene, and cycloheptatriene coincide very well and there is no doubt of the identity of these radioactive products. In this experiment the ratio of radioactivity of benzene : toluene : cycloheptatriene is 1 : 0.68 : 0.73. However, this ratio has varied widely over our experiments. Benzene has always had (with but one exception out of ten experiments) the greatest amount of activity of these three compounds. The cycloheptatriene radioactivity peak disappears on treatment of the target mixture with Br_2. The benzene and toluene peaks are unaffected.

We have made estimates of the fractions of the total number of carbon ions striking the benzene target that appear as labeled benzene, toluene, and cycloheptatriene. This fraction for benzene has varied from 0.46 to 1.92 %, for toluene from 0.20 to 0.94 %, and for cycloheptatriene from 0.24 to 1.96 %. Here again, the variables in our irradiation conditions lead to considerable differences in the total amount of activity appearing in a given compound for a given number of ions striking the benzene target.

In one experiment, the amount of activity in the methyl group and in the ring of the toluene was measured. The value for the methyl group was found to be 87 $\pm$ 5 % and for the ring carbons 16 - 25 % of

the total activity in the toluene. (The methyl group activity, measured as $C^{14}O_2$, is a secure figure. The ring activity, measured as aniline, was so little above background radioactivity that a considerable error was possible in its measurement.) The distribution we have found for the toluene radioactivity is quite similar to that which has been reported for toluene formed from the recoil-carbon irradiation of benzene (2), and for benzalaniline formed from azobenzene (1). The similar fractions appearing, in each case, in the ring carbons and in the exocyclic carbon lead to the suspicion that a similar mechanism may be operating in all three cases.

In an early carbon-ion irradiation of benzene, we found a fairly sharp radioactivity peak from a gas chromatogram (silicone substrate) that coincided very well with the known position of ethyl benzene, m-xylene, and p-xylene (these three C_8 hydrocarbons are not separated under the particular chromatographic conditions used). This peak contained a large fraction (about 60%) of the total target activity (i.e., activity recorded in the proportional counter). It was at first believed that C_8 compounds, if such indeed were formed, were due to a very slow rate of benzene input to the target area. However, all subsequent experiments, including those where the rate of application of benzene to the target was very slow during the irradiation, failed to reveal any radioactivity in the area of C_8 hydrocarbons. In addition, in no other experiment have we ever detected any radioactivity peak (of any kind) emerging from the gas chromatograph later than cycloheptatriene. Therefore, we believe that the earlier result was an artifact and that, in fact, no detectable amounts of C_8 hydrocarbons are formed during the benzene irradiations.

At least one of the peaks in the "pre-benzene" area of the radioactivity trace disappears on treatment of the mixture with aqueous hydroxide. It therefore appears that at least one carboxylic acid is formed during the irradiation. It is probable that this formation is the result of a reaction between an excited hydrocarbon debris species in the target area with unchanged $C^{14}O_2$ from the ion source. Such a reaction is similar to carboxylation reactions with $C^{14}O_2$ that have been reported earlier (8,9).

A change in the energy of the impinging ions from 5,000 to 90 e.v. appears to increase the amount of radioactivity in the "pre-benzene" area and to decrease the amounts of labeled benzene, toluene, and cycloheptatriene. Assuming that this observation stands the test of further experiments, the following suggestions may be made: (1) The lower-energy irradiation should give a lower concentration of benzene debris fragments. Perhaps some of these fragments act as scavengers that interfere with the reactions leading to the "pre-benzene" compounds. (2) In the case of the decrease in radioactivity appearing in benzene, toluene, and cycloheptatriene, it may be imagined that these labeled compounds are formed principally by epithermal reactions, and thus that their formation would be mostly unaffected by the presence of scavengers. We know that essentially all of the 90 e.v. ions strike the benzene target (from comparisons with the activities achieved in the 5 kv. irradiations). However, it is quite probable that static charge will build up on the benzene surface during an irradiation, and that this charge will further reduce the

kinetic energy of the 90 e.v. ions. Thus, these ions may actually be striking the benzene at an energy of only a few electron volts, making epithermal reactions less probable.

The present state of our knowledge of the products formed on the $^{14}C^{+}$ ion irradiation of benzene may be summarized as follows:

(1) Labeled benzene, toluene, and cycloheptatriene are always formed, each of them in amounts varying from a few tenths of a percent to two percent of the total number of ions striking the benzene.

(2) A considerable amount of radioactivity (about 90% of the activity appearing in the proportional counter) is incorporated into compounds more volatile than benzene. About half of these compounds appear to be C_3, C_4, and C_5 hydrocarbons, but none of them have yet been identified.

(3) On changing the energy of the impinging ions from 5,000 e.v. to 90 e.v., we find increased amounts of activity in compounds of lower molecular weight than benzene, and decreased amounts of radioactivity in benzene, toluene, and cycloheptatriene.

(4) Of the radioactivity in the toluene, about 87% is in the methyl group and the remainder in the ring.

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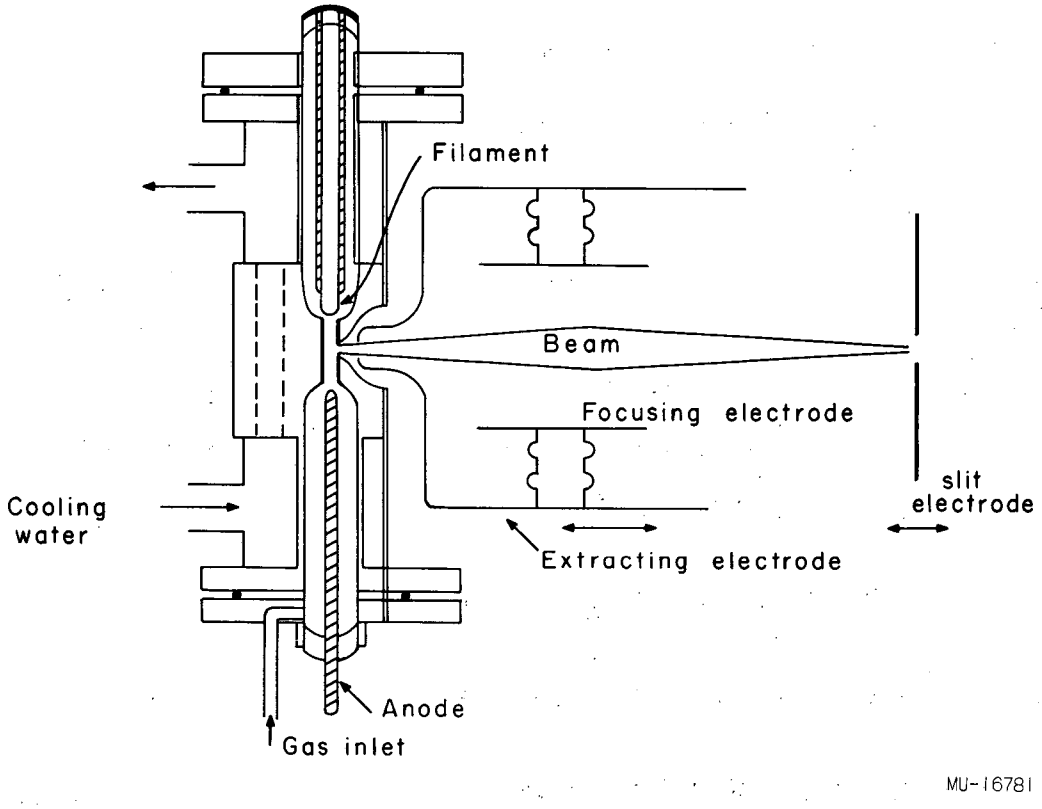

Figure 1. Details of the ion source of the isotope separator.

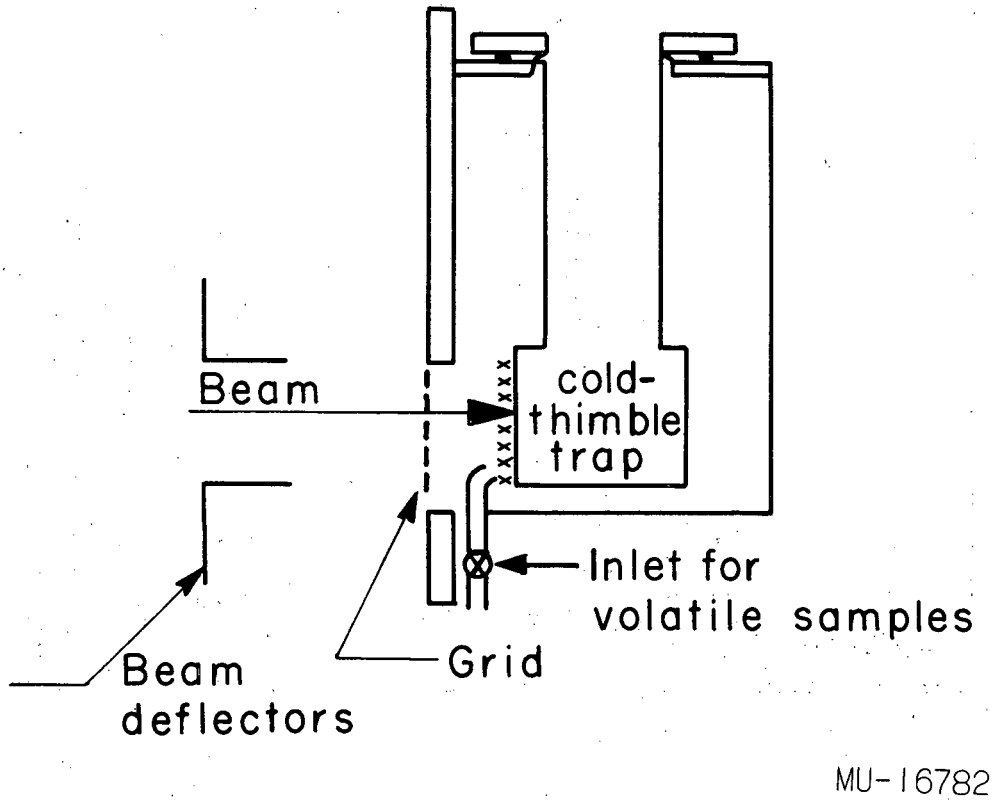

Figure 2. Details of the target end of the isotope separator.

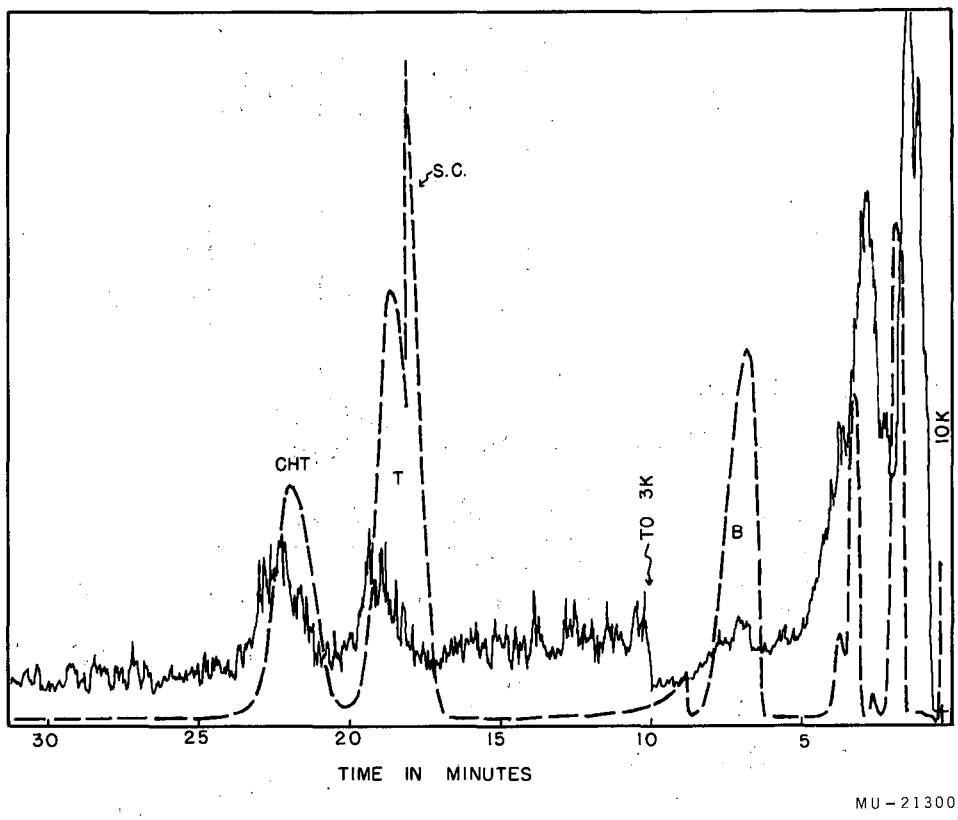

Figure 3. Mass (dashed line) and radioactivity (full line) record of the gas-chromatographic separation of the products of the $^{14}C^{+}$ irradiation of benzene.

Legend: CHT = cycloheptatriene, T = toluene, B = benzene, 10K and 3K signify 10,000 counts/min. and 3,000 counts/min full-scale deflection on the radioactivity record, S.C. = scale change on the mass record.

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