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CARBON IONS AND ATOMS

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ABSTRACT

This is an account of the development and results of research on the chemical effects of impinging a beam of accelerated $^{14}\text{C}^+$ ions on solid hydrocarbon targets, principally benzene. The instrument used is a capillary-arc type of "chemical accelerator". The major ^{14}C -labeled products from benzene irradiations are benzene, toluene, cycloheptatriene, phenylacetylene, diphenylmethane, biphenyl, phenylcycloheptatriene, and benzaldehyde (benzaldehyde's oxygen is derived from residual air in the evacuated system). These products account for about 35% of the ions striking the benzene--many other labeled products are apparent on gas chromatograms, but are not identified. The yields of known products, and the distributions in them of ^{14}C have been studied as functions of the kinetic energy of the irradiating ions--from 5,000 to 2 eV. These studies have led to proposals for the mechanisms of formation of the observed products.

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Reactions of Accelerated Carbon Ions and Atoms

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How can a carbon-14 ion, accelerated by an electrostatic field, strike a benzene molecule in such a way as to yield a ^{14}C -labeled benzene product? This is one of the intriguing questions that led us into studies of the chemical consequences of impinging a beam of carbon ions or atoms upon an organic target. From the standpoints of the statistician, the physicist, and the organic chemist the appearance of the benzene- ^{14}C seems an unlikely result--yet it happens. Along with recounting what we know about this ^{12}C - ^{14}C replacement reaction, this Account will relate other factors that drew us into this field of research. Among them are that we wanted (1) to learn what we could about the carbon chemistry that takes place at energies beyond those reachable by thermal and photochemical techniques, (2) to look for the possible appearance of new, that is to say, unknown, carbon compounds, and (3) to look into the possibility of obtaining useful amounts of labeled (tracer) organic compounds.

Carbon beam research may also have a relevance to chemical evolution and the origin of life. As is well known, the Earth is steadily irradiated by high energy carbon atoms in cosmic rays, and such irradiation was doubtless also taking place in prebiological times. It is quite possible that the emergence of life on our planet depended upon some key organic reaction or reactions that were promoted by the high energy carbons. For any real understanding of this possibility we need to investigate energetic-carbon reactions in our laboratories.

The "Hot-Atom" Chemistry of Carbon

Our research with carbon beams is closely related to the many studies that have been carried out in the recoil-, or "hot-atom" chemistry of carbon. This research has followed the ultimate fate of an energetic carbon atom formed in nuclear reactions; the usual ones employed have been $^{14}\text{N}(n,p)^{14}\text{C}$ and $^{12}\text{C}(n,2n)^{11}\text{C}$. Such studies began as far back as 1941¹ and were later extensively pursued in the laboratories of Wolf,² Wolfgang,³ and Voigt.⁴ The carbon isotopes produced in the above reactions are radioactive, a property that facilitates the identification of the product into which the recoiling carbon is built after it penetrates an organic target. In recent years the $^{12}\text{C}(n,2n)^{11}\text{C}$ reaction has become the favored one because fewer neutrons are needed to get a given number of recoiling carbons. Radiation damage to the system under study is thereby minimized.

The ^{14}C from the above nuclear reaction is born with about 45 KeV of kinetic energy, the ^{11}C with about 1.1 MeV. It is apparent that almost all this energy must be disposed of before the carbon can enter into chemical-bond formation with a target molecule. What happens is random fragmentation along the path of the recoiling carbon atom until it slows down to a kinetic energy of about 50 eV. Here it is possible for the carbon to pick up hydrogen atoms from target molecules, becoming, successively, CH, CH₂, and CH₃. New carbon-carbon bonds are probably not formed until the recoil carbon has been slowed to something less than 10 eV. The main results and the postulated mechanisms of carbon-recoil chemistry are summarized in the excellent review of A. P. Wolf.²

Carbon Beam Studies--Early Experiments

An extension, or companion, of the carbon recoil work is to accelerate a beam of carbon ions in an electromagnetic device. Such a beam, which

also may consist of isotopic carbon, may then be directed onto any target of interest. Carbon-14 beam studies were first reported by Giacomello in 1954.⁵ He and his associates used an electromagnetic separator to direct a beam of $^{14}\text{C}^+$ ions (intensity about 10^{-9} amp, kinetic energy about 30 KeV) onto solid organic targets such as stearic acid and cholesterol. Although severe problems were encountered in purifying the very small amounts of labeled products, the author reported the formation of ^{14}C -labeled stearic acid and cholesterol. Subsequent work by this group indicated the formation of ^{14}C -labeled organic acids on the irradiation of paraffin with $^{14}\text{CO}_2^+$ and of calcium oxalate- ^{14}C on the irradiation of CaCO_3 with $^{14}\text{CO}^+$.

Ion beam studies have an attractive advantage over recoils in that, in principle, the ions' kinetic energy can be controlled (by electrostatic deceleration devices) before the target is struck. This minimizes radiation damage to target molecules, thus minimizing the complications arising from ^{14}C reactions with target-molecule fragments.

Our first experiments were done on a conventional analytical mass spectrometer whose target section was replaced by a cold trap. During an irradiation, target molecules were steadily condensed on the surface of the trap, which was maintained at -160° . Labeled carbon dioxide ($^{14}\text{CO}_2$) was introduced steadily into the ion source; and from it we obtained an approximately 10^{-9} amp beam of singly charged carbon ions ($^{14}\text{C}^+$). A one-hour's operation of this beam deposited approximately two nanocuries, about 4,000 disintegrations per minute (dpm), on the target. Several hours of irradiation provided sufficient radioactivity to permit some product identifications.

The target molecule we chose to study, and the principal one we have investigated to the present time, was benzene. This molecule was selected

because it is resistant to radiation decomposition and because its purification could be carried out with high efficiency by means of the then-new technique of gas chromatography. At the time we undertook this work (1956) we had no idea how interesting benzene was to become as a target molecule.

Several hours of irradiation, followed by gas chromatography on several different types of columns, established benzene- ^{14}C as a product of the $^{14}\text{C}^+$ ion irradiation.⁶ We discovered that about 2% of the ions that struck the target became incorporated into the labeled benzene product. Since labeled toluene had earlier been reported as a product of the reaction of recoiling carbon-14 with benzene,⁴ we added carrier toluene to our irradiated benzene target. Subsequent gas chromatographic purification established that another 1% of our $^{14}\text{C}^+$ ions were incorporated into the toluene- ^{14}C product.⁶ At the time we had no notion of the fate of the remaining 97% of the ions that reached the target.

Ion Accelerator

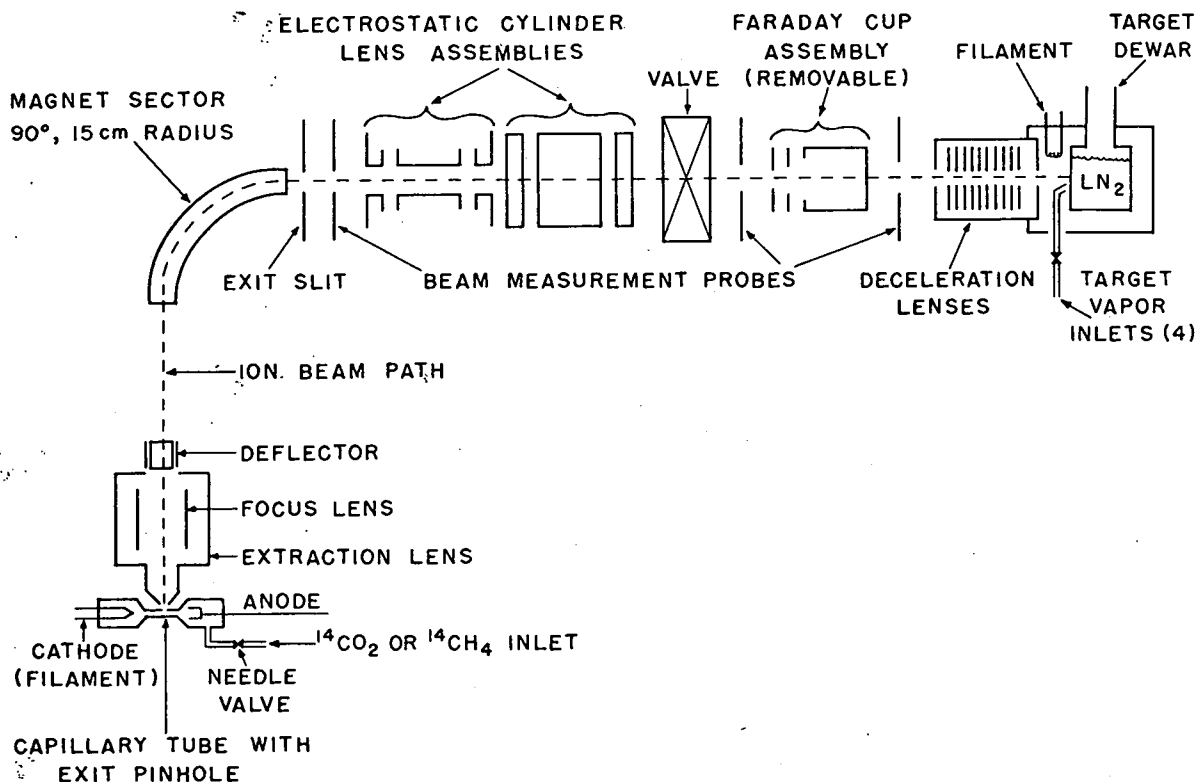
The interesting early results engendered in us the desire to have available much more intense beams than could be obtained with a conventional mass spectrometer. Consequently, our early collaborator, the late Frederick L. Reynolds, designed a new instrument that would deliver a $^{14}\text{C}^+$ ion beam of approximately 1 μ amp. (Hereafter we will refer to this instrument as our "ion accelerator"; it is an example of the kind of instrument later referred to by R. Wolfgang as a "chemical accelerator".^{7,8}) With many additions and modifications, the ion accelerator has been in steady use to the present time. Its main features were described in detail in a paper in 1970,⁹ and are shown schematically in Figure 1.

The ion beam path is maintained at high vacuum during irradiations by 3 similar diffusion pumps, whose combined pumping speed is about

1500 liters/min. at 10^{-5} Torr. The first pump is connected near the ion source, the second at the chamber where the ion beam passes through the magnetic field, and the third at the target section. During irradiations the pressures in the ion source are a few microns, and in all other sections they are maintained between 10^{-5} and 10^{-6} Torr.

A beam is struck by admitting $^{14}\text{CO}_2$ (at about one $\mu\text{mole}/\text{min.}$) into the capillary-arc ion source (bottom left in Figure 1), passing a suitable current (0.5 amp) through the cathode filament, and building a suitable voltage (60-100 V.) between the anode and cathode. The ions formed in the capillary arc are accelerated toward the magnet by a 4-5 kilovolt positive potential on the ion source. The total ion beam (mostly $^{14}\text{CO}^+$ and $^{14}\text{CO}_2^+$) is about 100 μA ; of this, about 2 μA is $^{14}\text{C}^+$ in a beam whose cross-section area is about 1 cm^2 . Unless otherwise stated, all the results reported here were obtained by use of the $^{14}\text{C}^+$ beams. However, we found that, in the 5,000-15 eV energy range, the yields and distributions of products was essentially the same with a $^{14}\text{CO}^+$ beam as with the $^{14}\text{C}^+$ beam. Apparently the $^{14}\text{CO}^+$ is broken up before the ^{14}C reaches the terminal "hot spot", where the ultimate chemistry takes place.

The target molecules are purified by gas chromatography before use. In all our ion accelerator work we have continued the practice of a steady condensation of target molecules on the Dewar (see Fig. 1) during an irradiation. The area of the condensed target is about 2 cm^2 . In our early work the Dewar was maintained at -160° (isopentane slush) as we were afraid of the effects of condensing $^{14}\text{CO}_2$, from the ion source, along with the target molecules. This temperature was later abandoned in favor of the more convenient -196° , made possible by improvements in beam alignments (passage through narrow slits), efficiency of $^{14}\text{C}^+$ production from $^{14}\text{CO}_2$, and in pumping arrangements. Condensation of $^{14}\text{CO}_2$ on the target is now



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Figure 1. Schematic drawing of the $^{14}\text{C}^+$ accelerator.

a negligible factor. Most of the work summarized here was done at -196° .

The ratio of incoming ions to target molecules is approximately 10^{-4} . Consequently, once a labeled product molecule is formed, it is very unlikely for it to interact with a second $^{14}\text{C}^+$ ion, or with any other labeled species. Positive-charge buildup on the surface of the target is prevented by an accompanying flow of electrons from the filament that is shown near the target (see Figure 1).

Identification and Degradation of Products

At the conclusion of an irradiation (usually of 1-2 hours' duration) the solid target is scraped, under a dry N_2 atmosphere, into a rubber septum-stoppered flask. After the contents of the flask are melted, appropriate carrier amounts of known or suspected products are added, and aliquot portions are analyzed by gas-liquid partition chromatography (glpc) on an instrument that records both mass (thermal conductivity cells) and radioactivity (proportional counter) detection. Confirmations of identities are made by rechromatography on different substrates, and by specific chemical reactions on the material appearing in separately trapped peaks. For experiments in which we are interested in volatile products, such as acetylene, the target area is brought to room temperature and the products pumped out into an external cold trap. Details of these procedures are available.¹⁰

Products Formed on Carbon-Ion Irradiations of Benzene

Our early experiments with the new ion accelerator were reported in 1961.^{11,12} The appearance of benzene- ^{14}C and toluene- ^{14}C in irradiated benzene was confirmed, and slightly higher yields were observed. In addition, we degraded the toluene- ^{14}C product and found that only 86% of its radioactivity was in the methyl group. The "scrambling" of activity into the ring showed clearly that toluene was not formed entirely by a simple insertion of the energetic ^{14}C into a C-H bond of the benzene. A very similar methyl/ring activity distribution had already been reported by Wolf¹³ for ^{14}C -recoil produced toluene- ^{14}C . The similarities in these results emphasized the complimentary nature of the carbon-recoil and carbon-beam studies. In addition, it became apparent that our ion beam

could be looked upon as an atomic beam because of the ion's large cross section for electron capture,^{14,15} making charge neutralization an immediate result of the ion's reaching the benzene matrix. In some of our later work we showed that our ions could be neutralized, before they reached the benzene target, without appreciable change in either absolute or relative yields of products.¹⁰

The activity in the ring of toluene had led Suryanarayana and Wolf¹⁶ to propose an energetic C₇ ring (resulting from the insertion of the recoiling carbon into a C-C bond) as an intermediate on the way to toluene. This suggestion led us to search for, and to find, cycloheptatriene-¹⁴C as a product of our beam irradiations of benzene. Its yield was about 2% of the irradiating ¹⁴C⁺ ions. Later carbon-recoil work established the appearance of cycloheptatriene as a product (from benzene) in that system, too.^{17,18}

During the next several years, a total of 13 labeled hydrocarbons were identified as products of the ¹⁴C⁺ beam irradiations of benzene. These products, and their approximate yields (based on the number of ions striking the benzene) are summarized in Table I.

In addition, we know that minor amounts of styrene (approx. 0.1%) are formed in these irradiations. Other possible labeled products that were sought, but not found, were benzocyclopropene, cyclooctatetraene, 2-phenyltoluene, methylcycloheptatriene, bicyclo[2.2.1]heptadiene-2,5, and spiro[6.6]tridecahexaene.

Another identified product (yields varying from 2-5%) is benzaldehyde-¹⁴C, the oxygen coming from residual air in the high-vacuum system. Small amounts of tropone and phenol may also be formed. The subject of the O-containing products is a complex one; in this Account we are focusing our attention on the formation of the labeled hydrocarbon products.

Table I

 ^{14}C -Products (and Yields) from Irradiations of Benzene with 5 KeV $^{14}\text{C}^+$ Ions

<u>Product</u> (C_6 or higher)	<u>Yield, %</u>	<u>Product</u> (C_5 or lower)	<u>Yield, %</u>
Benzene	4.2	Acetylene	5.0
Toluene	1.3	Allene	<0.1
Cycloheptatriene	3.3	1,2-Butadiene	"
Diphenylmethane	2.4	1,3-Butadiene	"
Phenylacetylene	2.1	1-Butyne	"
Phenylcycloheptatriene	6.3	Propyne	"
Biphenyl	2.1		

Of all the ions that strike the benzene target, we have been able to account for about 88% of them on our glpc traces, and about 30% have been accounted for as the above compounds. There are many radioactivity peaks on our chromatograms, but they are almost all, individually, of very low yield (0.1% or less). Some labeled polymeric material is formed during our irradiations, but it is as yet uncharacterized.

The numerous labeled products highlight the complexity of the system. The products with molecular weights lower than benzene are probably formed, at the end of the energetic carbon's track, where they can interact with fragments of a benzene molecule, that, a few angstroms back on the track, was disintegrated by effects of the carbon's passage. However, it is to be noted that the total yield of these products (acetylene excepted) is very low, an indication that random, "radiation damage" effects play no large role in our product formations. Acetylene is probably formed, as is discussed later with respect to the phenylacetylene product, by the pickup

by a fast carbon of another carbon from a struck benzene molecule to give a reactive C_2H_x fragment.

Of more interest to us are the C_6 , and higher molecular weight products, listed in the left column of Table I. Again, the complexity of our system is apparent. It is probable that routes leading to one or another product result from (a) the spin state of the energetic carbon as it interacts with the benzene to form the initial C_7 intermediate, (b) the number of hydrogens the carbon has picked up before the C_7 is formed, (c) the internal energy of the C_7 , and (d) the availability of benzene fragments in the neighborhood of the C_7 . The formation of phenylacetylene shows that yet another process is taking place: the preliminary formation of a C_2 fragment that then interacts with benzene in a C_8 -forming mechanism.

Further insight into these processes were sought (as described below) by studies of the effects of changes in the $^{14}C^+$ ion's energy on product yields and on the distribution of ^{14}C in the product molecules.

Effect of $^{14}C^+$ Kinetic Energy on Benzene-Product Formation

After we had developed a reasonable method of decelerating our ions before they reached the target,⁹ we determined the effects of different energies on the yields of our major hydrocarbon products.^{10,19,20} The results of these determinations are shown in Table II.

The data of Table II show a product-formation insensitivity to energy in the 5,000-100 eV range. This, of course, is not surprising since any kind of chemical bond formation is not to be expected until the fast carbon is slowed down to a kinetic energy of not more than 50 eV. Kinetic theory leads us to expect that above a carbon-beam energy of 100 eV, the yields and kinds of products would indeed be independent of the energy. This is

Table II

Yields of Labeled Hydrocarbons from Benzene--Effect of Varying the
Energy of the Irradiating $^{14}\text{C}^+$ Ion

Energy eV	Products*						
	Benz.	Tol.	CHT	$\phi\text{C}\equiv\text{CH}$	$\phi-\phi$	$\phi\text{CH}_2\phi$	ϕCHT
5,000	3.4	1.0	2.5	1.6	1.3	1.5	5.3
1,500	5.7	1.3	2.9	2.3	2.3	2.5	5.5
500	4.8	1.0	1.8	2.2	1.7	1.9	5.5
100	5.7	1.1	2.2	3.1	2.9	3.8	6.6
15	2.7	0.2	0.9	0.5	1.2	3.6	10.3
5	3.9	0.2	0.5	0.3	1.7	2.6	10.8
2	3.5	0.2	0.9	0.2	5.5	2.9	13.0

*Benz. = benzene, Tol. = toluene, CHT = 1,3,5-cycloheptatriene,
 $\phi\text{C}\equiv\text{CH}$ = phenylacetylene, $\phi-\phi$ = biphenyl, $\phi\text{CH}_2\phi$ = diphenylmethane,
 ϕCHT = 7-phenyl-1,3,5-cycloheptatriene.

because the distribution of collision-energies below 50 eV is expected to be similar for all carbon beam energies above approximately 100 eV.²¹

Below 100 eV we find a continued more-or-less constant yield for both benzene and diphenylmethane, while the toluene, cycloheptatriene, and phenylacetylene yields decrease by factors of 5, 3, and 8 respectively. In contrast, as one goes from 100 eV to 2 eV the yields of biphenyl and phenylcycloheptatriene increase by factors of about 4 and 2.5 respectively. Interpretations of these data will be made in the light of the degradation results that are presented below.

Distribution of Activity in Products from the $^{14}\text{C}^+$ Irradiation of Benzene

The ultimate fate of the irradiating ^{14}C , that is, the position where

it appears in a product molecule, tells us much about the mechanisms leading to that product. The results of such degradations on the products obtained in 5,000 eV irradiations are given in Figure 2. The details of the chemical degradations are recorded elsewhere.²²

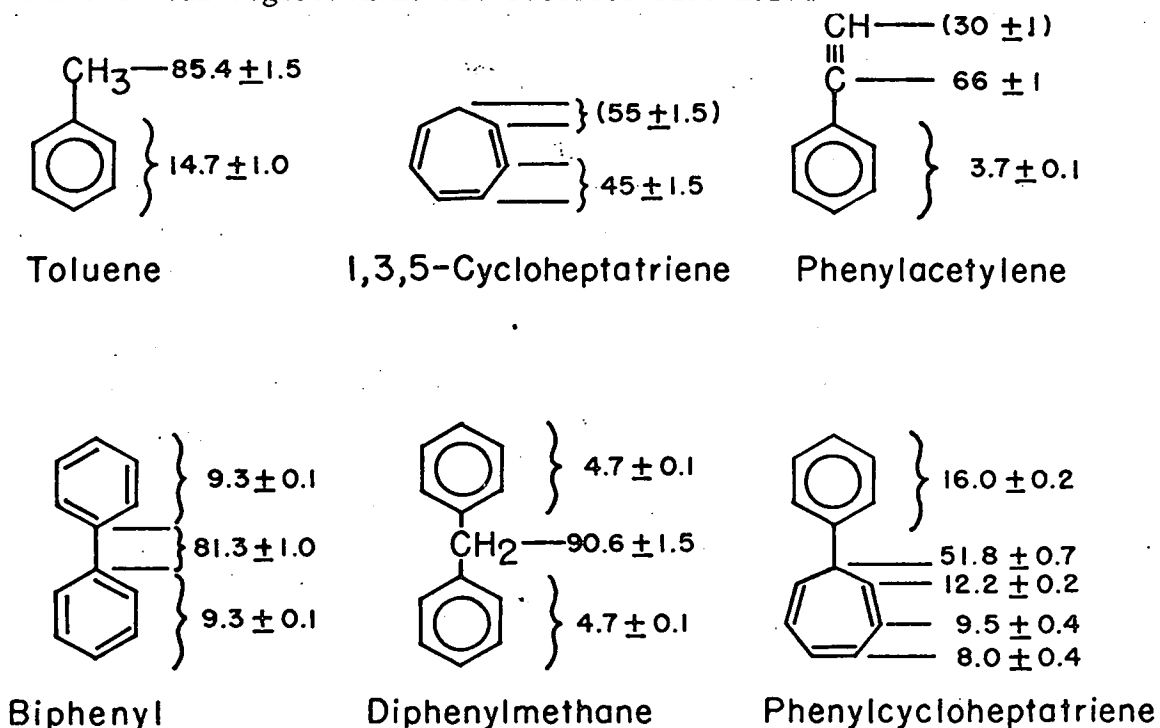


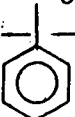

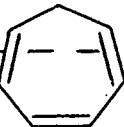











Figure 2. Distribution of ^{14}C in major products formed by the irradiation of solid benzene with 5 KeV $^{14}\text{C}^+$ ions.

Recently, degradations were performed on the major hydrocarbon products formed, in some cases, from $^{14}\text{C}^+$ ions whose kinetic energy was only 2 eV. The results are presented in Table III, with the 5 KeV data included for comparison.

Mechanisms of Product Formation

Toluene. As was mentioned earlier, the appearance of activity in the ring of toluene shows that its formation is not the result of a simple insertion of the energetic ^{14}C (or ^{14}CH or $^{14}\text{CH}_2$) into a C-H bond of the benzene, followed, if necessary, by a pick-up of one or two hydrogen atoms

Table III
Product Activity Distributions (%) as a Function of $^{14}\text{C}^+$ Energy

Energy Product	5 KeV	31 eV	6 eV	5 eV	4.5 eV	3 eV	2 eV
CH_3 	85	83	86	63	76	92	94
	13	12	15	41		10	6
	55*	70*		66*			
	45	30		34			
CH_2 	91			76		87	
	9			18		11	
CH 	30			33			30
	66			62			63
	4			4			6
	16			22		9	
	52			57		85	
	30			19		6	
	9		8			0	0
	81		84			100	100
	9		8			0	0

*Activity determined by difference only

from the surroundings. This result is in contrast with the known photochemical reaction of $^{14}\text{CH}_2$ (from photolyzed $^{14}\text{CH}_2\text{N}_2$) with benzene, in which all the activity in the toluene product is in the methyl group.²³

The involvement of hot methylene (i.e., $:\text{CH}_2$ with at least a few volts of kinetic and/or internal energy) has often been postulated in the interpretation of carbon-recoil reactions with benzene and with other targets.^{2,16} However, more recent reports from the laboratories of Voigt¹⁸ and Wolf,²⁴ based on studies of the appearance of acetylene- ^{11}C , have emphasized the role of bare carbon atoms in the initial product-forming interaction with benzene and other hydrocarbon targets. Our finding that the toluene yield greatly decreases somewhere between $^{14}\text{C}^+$ ion energies of 100 and 15 eV (see Table II) indicates an involvement of $^{14}\text{CH}_2$ radicals. At the lower energies there would be a decreased chance for the irradiating carbon to pick up hydrogens in sequence to form the assumed $^{14}\text{CH}_2$ precursor; thus, the diminished yield. Although we prefer to think of $^{14}\text{CH}_2$ as the precursor to toluene because of the analogy with the known reactions of photolytically- and thermally-produced CH_2 with benzene,^{23,25} the precursor could also be the ^{14}CH radical. Its insertion into a benzene C-H bond would give a benzyl radical, $\text{C}_6\text{H}_5^{14}\text{CH}_2$ ---the reaction would end by the abstraction of a hydrogen atom from the surroundings. We believe that the methyl radical, $^{14}\text{CH}_3$, is not involved in any major way in our system, mostly because methane is only a minor product (<0.2%) in the carbon-recoil chemistry of benzene.¹⁸

Assuming that $^{14}\text{CH}_2$ is the major reacting species at high irradiating energies (above 15 eV), we can visualize the formation of toluene and cycloheptatriene via mechanisms based on the one proposed by Suryanarayana and Wolf in 1958.¹⁶ A hot methylene can insert into a C-H bond of benzene, giving the intermediate I in Figure 3. Then, the indicated proton and electron rearrangements (upper route) would give a toluene product with

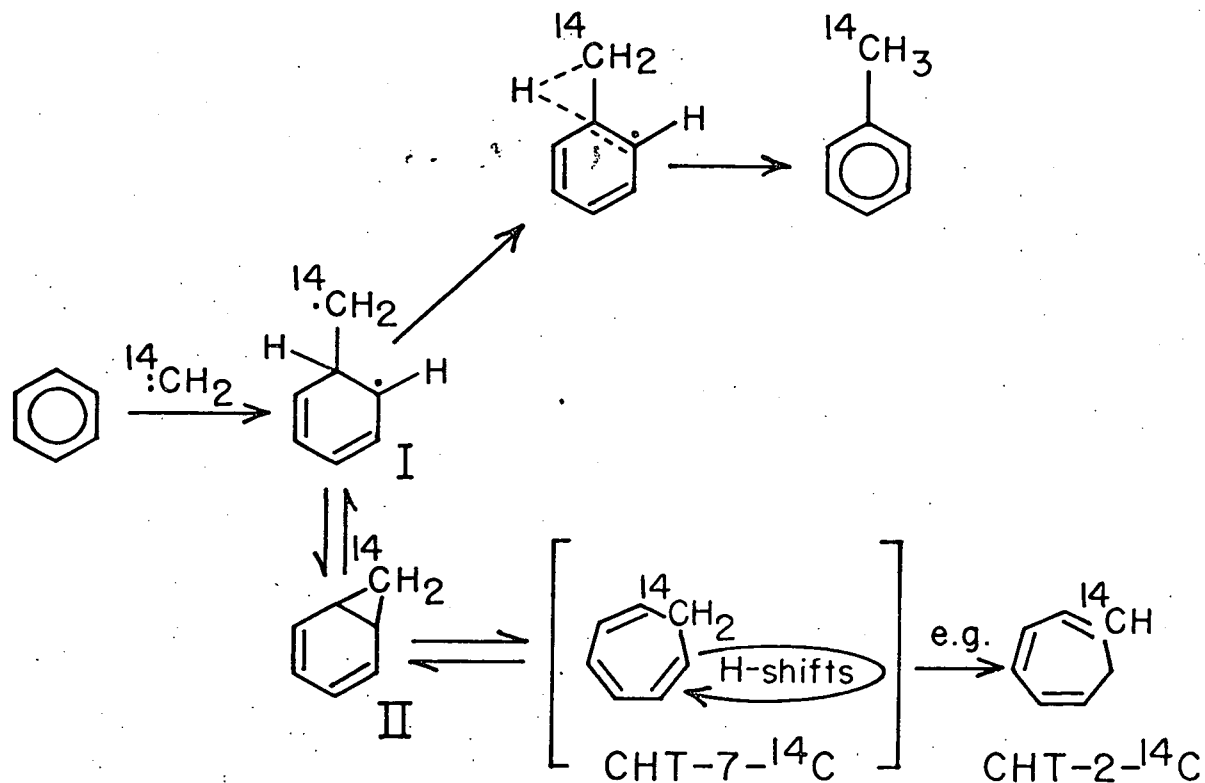


Figure 3. Mechanism for production of labeled toluene and cycloheptatriene from reactions of energetic ^{14}C -labeled methylene with benzene.

the label entirely in the methyl group. However, a C-C bond insertion, represented by adduct II, followed by electronic shifts, would give cycloheptatriene-7- ^{14}C (the "CHT-7- ^{14}C " of Figure 3). This mechanism, particularly if it involved an energy-rich methylene, could cause isomerization of the cycloheptatriene--and thermal isomerizations of cycloheptatriene are well known.²⁶⁻²⁸ The back reaction, through intermediate II, would give ring-labeled toluene. It would, of course, require more isomerizations in the C_7 ring to produce toluene-3- or 4- ^{14}C than toluene-1- or 2- ^{14}C . In fact, in both the recoil-carbon and carbon-beam experiments (at 5,000 eV--no ring degradations at lower energies have been performed) the toluene

ring labeling diminishes as one moves away from the methyl group.^{29,30} However, one would expect, and the data so indicates, that above a certain $^{14}\text{C}^+$ energy, the ring/methyl activity distributions (as well as the distribution in the ring) would be the same. Probably no $^{14}\text{CH}_2$ is formed until the irradiating $^{14}\text{C}^+$ ion's kinetic energy has been reduced to 50 eV or less; consequently, our experiments at 5,000 eV to 31 eV have given toluene with the same activity distribution.

If $^{14}\text{CH}_2$ were the only intermediate involved in product-forming reactions with benzene, we would expect a steady decrease of ring activity as we reduced the energy of the irradiating carbon. Instead, however, at approximately 5 eV there is a dramatic increase in the ring activity. At the same time, toluene yields have dropped by a factor of 5 (see Table II) when the irradiating carbon's energy was reduced from 100 to 15 eV. Therefore, at 5 eV we presume that the principal reacting species is the bare carbon atom. We further presume that this is the maximum kinetic energy at which this species can interact with the benzene without the disintegration of the C_7H_6 intermediate.²⁰ Adduct formation is expected to require a substantial conversion of kinetic into internal energy, causing decomposition of the adduct unless its internal energy is only a little above bond energies (≈ 5 eV).¹⁹ Consequently, at 5 eV we have a maximum energy available for the scrambling of activity into the ring of toluene. At carbon ion energies below 5 eV the ring activity sharply diminishes, and at 2 eV we seem to be rapidly approaching a situation where all the activity will be in the toluene's methyl group.

The mechanisms for a bare carbon insertion into benzene would be quite similar to that depicted in Figure 3. The only difference would be the pick-up of hydrogen atoms after the intermediates (corresponding to I and II, but with 2 less hydrogens) were formed.

Further support for a mechanism involving the interaction of bare carbon atoms with benzene comes from experiments in which $C_6H_5CH:$ was generated in benzene solution by the photolysis of styrene oxide. The formation of toluene was firmly established by glpc analysis.³⁰ In addition, toluene and cycloheptatriene have been reported as products of the reaction of carbon vapor with benzene.³¹

Cycloheptatriene. As we indicated above, in discussing mechanisms for toluene's formation, routes to toluene and cycloheptatriene must be closely related. The yields of both these compounds decrease as the irradiating carbon ion energies are reduced below 100 eV. Both compounds are major products of the thermal reactions of methylene with benzene.^{25,32} In addition, the mass-spectrometric fragmentation patterns of the two compounds are remarkably similar; electron impact gives the same $C_7H_7^+$ (tropylium) ion from both compounds.³³

However, unlike the situation for toluene, the cycloheptatriene-formation data (Tables II and III) require no hypothesis of bare-C, or CH, interactions with benzene. The degradation data at 5 eV shows no sudden shift, as it does for toluene, in the activity distribution.³⁴ Consequently, it appears that the cycloheptatriene product, at all energies so far studied, may come precominantly from the interactions of $^{14}CH_2$ with the benzene.

Phenylacetylene. Like those of toluene and cycloheptatriene, the yields of phenylacetylene decrease as the carbon beam's energy is brought below 100 eV. It appears that the incoming carbon can strip another carbon from a disintegrating benzene molecule to form a $^{14}C_2$ or $^{14}C_2H$ fragment, which subsequently interacts with another benzene molecule to form the phenylacetylene product. The lower the incoming carbon's translational energy, the lower the chance to form the C_2 or C_2H fragment, and the lower the yield of this compound.

The fact that the 96% of activity in the acetylenic carbons is not equally distributed between them indicates that the C_2 fragment is either "electronically" or "chemically" unsymmetrical. That is, a $^{14}C-^{12}C$ adduct might have more electronic energy in the ^{14}C , thus making that carbon the more likely to participate in the bond formation with the benzene. Or, the carbon stripped from a benzene molecule might carry its hydrogen with it, giving a $^{14}C-^{12}CH$ fragment; this species might then react with benzene before it could become a symmetrical intermediate such as $\begin{array}{c} H \\ \diagup \quad \diagdown \\ C-C \end{array}$, which would, of course, be equally labeled in both carbons.

Diphenylmethane. Like toluene, diphenylmethane shows a maximum activity in the benzene rings for irradiations carried out at 5 eV. The reasonable interpretation is that the diphenylmethane and toluene are formed from the same intermediate, perhaps a benzylidene (phenylcarbene) radical ($C_6H_5CH\cdot$). Hydrogen abstractions by this radical would give toluene; a reaction (C-H bond insertion) with a nearby benzene molecule might give the diphenylmethane (see Figure 4). The same explanation for maximum ring activity from 5 eV irradiations would hold for diphenylmethane as well as for toluene. However, unlike toluene, the yield of diphenylmethane does not diminish as the incoming carbon ion's kinetic energy goes to very low values. The data of Table II show diphenylmethane's yield to be at least as high at 2 eV as it was at several hundred or thousand eV. We think that the explanation for this difference from the toluene data must await the time when we can carry out $^{14}CH^+$, $^{14}CH_2^+$, and $^{14}CH_3^+$ irradiations.

Phenylcycloheptatriene. This product seems obviously related to the diphenylmethane. The first would result from a $C_6H_5CH\cdot$ insertion into a benzene C-C bond, the second into a benzene C-H bond (see Figure 4). Stabilization of the postulated benzylidene by C-C bond insertion seems,

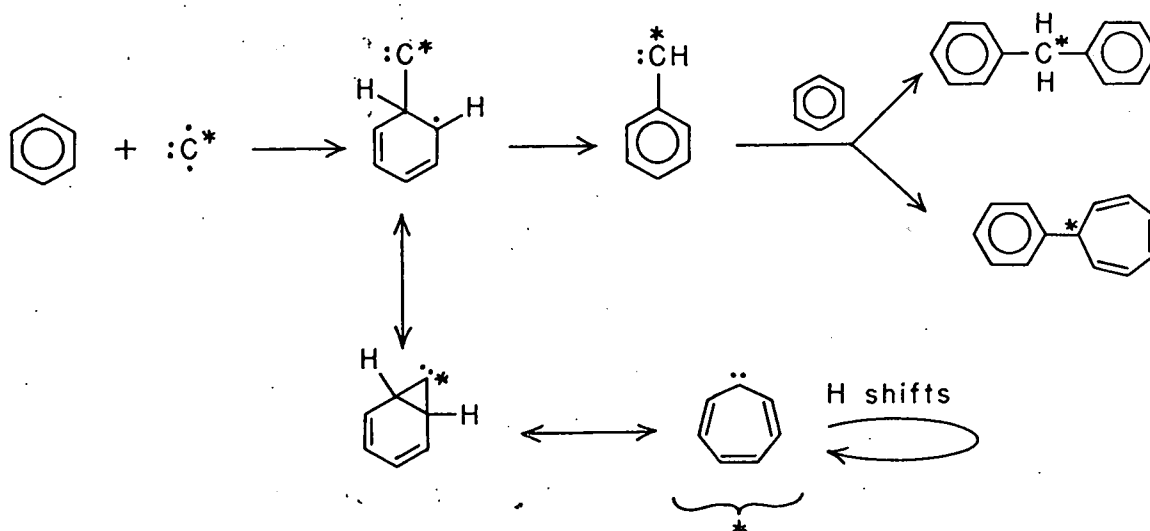


Figure 4. Mechanisms for production of labeled diphenylmethane and phenylcycloheptatriene from reactions of energetic carbon ($:\dot{C}^* = {}^{14}\dot{C}$) with benzene.

for reasons not understood, particularly efficient at low irradiating energies--the yields of phenylcycloheptatriene are particularly high at 5 eV (10.8%) and 2 eV (13.0%).

As reviewed earlier in the discussions of toluene- and cycloheptatriene-forming mechanisms, hydrogen shifts in an intermediate cycloheptatrienyl radical would explain the appearance of radioactivity in the phenyl groups. The 5 and 3 eV data for these two products show very similar amounts of radioactivity in the phenyl groups, indicating a common precursor as the mechanism of Figure 4 postulates. This approximate equality of phenyl group activities does not seem to hold for the 5,000 eV irradiation (9 and 16%). However, a higher-energy irradiation would be less likely to give a single precursor.

In the 3 eV experiment (the lowest energy for which we have phenylcycloheptatriene degradation data) we have the highest (86%) concentration of radioactivity in the 7-position of the cycloheptatriene ring. This result is in accord with the mechanism of Figure 4. The incoming carbon

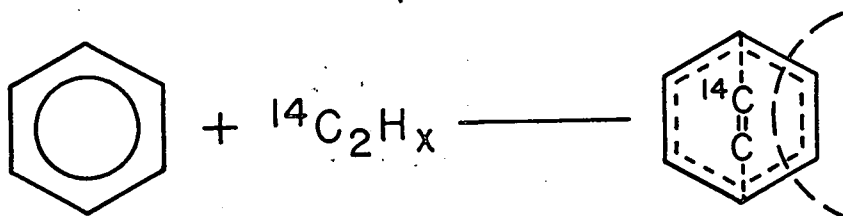
would, at 3 eV, carry the least translational energy. The least internal energy would then be available to accomplish the "H shifts" in the cycloheptatrienyl radical.

Biphenyl. The formation of biphenyl- ^{14}C is probably closely related to the mechanism by which labeled benzene appears (see below). The 100% labeling in the C_1 position(s) in the 2- and 3-eV experiments are the first examples of specific labeling in any product obtained in carbon-recoil or accelerated-carbon experiments. These low-energy results indicate that the new, labeled C_6 ring reacts with another molecule of benzene (to form biphenyl), making use of the excess vibrational or electronic energy in the ^{14}C atom, but without transferring that energy to another carbon atom of the C_6 ring. The biphenyl is the second product (in addition to phenylcycloheptatriene) whose yield rises as we go to the very low irradiation energies. We do not yet understand why this should be so.

Benzene. The most intriguing problem we have had since the onset of this work is how the benzene itself becomes labeled. A direct, inelastic (or "billiard-ball") collision, by which a ^{12}C , or ^{12}CH would be replaced by a ^{14}C has never been a serious contender as an explanation for the appearance of benzene- ^{14}C . There are several reasons for this: (1) For a high kinetic energy (above 100 eV) carbon, the collision would have to be direct (as opposed to glancing) in order for the necessary, nearly-complete momentum transfer to take place. Classical mechanical calculations show that it would be statistically impossible to obtain the observed 3-6% yield of benzene- ^{14}C .³⁵ (2) At energies below 100 eV the "billiard-ball" mechanism becomes increasingly probable; however, in ^{11}C -recoil experiments on benzene it was found that the addition of 10^{-3} mole fraction of a radical scavenger, which couldn't affect such a mechanism, decreased the benzene- ^{11}C yield from 4.6 to 2.9%.¹⁶ Phase and temperature

effects on the benzene yield were also reported.^{16,17} (3) Contrary to "billiard-ball" expectations, the yield of CD_3T (from recoiling tritium on CD_4) is lower than that of CH_3T from CH_4 .^{35,36} (4) Even for atoms of very similar masses (e.g., ^{81}Br and ^{82}Br) the cross sections for billiard-ball displacements is expected to be very small.³⁵

The appearance of both acetylene and phenylacetylene as products of our benzene irradiations led to the idea that a bicyclo C_8 intermediate might be involved in the route to labeled benzene:



The C_8 adduct could then split out the indicated two-carbon species to give labeled benzene. Such a mechanism could also give benzene- ^{14}C from the irradiation of toluene or o-xylene, but not from p-xylene. We recently tested this mechanism by irradiating, separately, toluene and the two xylenes at -196° with $10\text{-eV } ^{14}C^+$ ions.²⁰ The results are shown in Table IV. Where no data appears it means that no radioactive "peak" was visible on the radiogaschromatographic tracing. The percent yield figures result from the addition of carriers to the target material after the irradiation, the trapping of the carriers at the end of the glpc column, and the liquid-scintillation counting of the trapped "peaks".

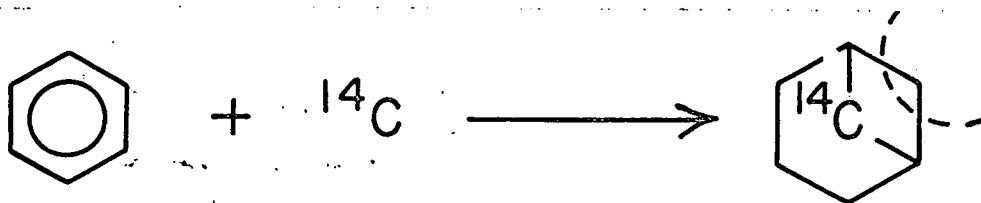
The failure to find labeled benzene from o-xylene (the traces of activity in the o-xylene are ascribable to blpc-column contamination) indicates that the C_8 mechanism above is not operating. In addition, we sought, but were unable to find, bicyclo[2.2.2]octane ("barrelane") after catalytic hydrogenation of an irradiated benzene target.³⁷

Table IV

Labeled-Product Yields (%) from ^{14}C -Irradiated
Toluene, o-Xylene, and p-Xylene

Product	Toluene	o-Xylene	p-Xylene
Benzene	0.3	0.03	0.01
Toluene	1.0	0.4	0.8
Ethylbenzene	0.8	-	-
Styrene	17	-	-
Methylstyrene	-	11	14
o-Xylene	0.3	0.8	-
m + p-Xylene	1.1	-	-
p-Xylene	-	-	2.2

Some kind of a C_7 -adduct mechanism remains as a possible route to labeled benzene, for example:



This mechanism, which does not specify hydrogen-atom and electron distributions, would be compatible with the data of Table IV (benzene- ^{14}C from toluene irradiations, but not from either xylene; toluene- ^{14}C obtained from both xylenes). It is also compatible with results that have been obtained in carbon-recoil studies.¹⁸ Also in accord with the C_7 mechanism are the higher yields we observed of toluene (0.8 and 0.4%) from the xylenes, compared to that of benzene from toluene (0.3%). Intermediates similar to the one above have been proposed by Rose *et al.*,¹⁷ who studied the interactions of recoiling ^{11}C with benzene and observed many of the products

discussed here. However, a search for bicyclo[2.2.1]heptadiene-2,5 in our irradiated benzene was unsuccessful--although not too much weight should be attached to that result because the excited C_7 adduct depicted above might be quite different from that particular bicyclo heptadiene.

Other Compounds Irradiated

In addition to our principal target, benzene, and the toluene and xylenes, we have carried out irradiations of 1-hexyne, cyclohexane, β -carotene, and morphine. The latter two natural products were irradiated (with a 2 KeV $^{14}C^+$ beam) in the early days of this research to test the feasibility of using an ion beam to obtain ^{14}C -labeled natural products for use as tracers in metabolic studies. We quickly learned that such compounds are indeed labeled by the ion beam, but that purification problems are very severe due to the large number of labeled products that are formed. Probably most, if not all, the possible monomethyl analogs (cf. toluene from benzene) are present, and their physical and chemical properties are extremely close to those of the parent carotene or morphine.

In more recent work, our interest in the possible use of the ion beam as a useful ^{14}C labeling device was rekindled. We observed, as reported above, that the yield of benzene- ^{14}C (from benzene) stayed fairly constant even when the ion beam's energy was reduced to 2 eV; at the same time, the yield of the monomethyl derivative, toluene, diminished as the beam's energy was reduced. Consequently, at the 2 eV energy we tried an irradiation of cyclohexane, a compound that has only one monomethyl derivative, and whose energetic-carbon chemistry, we hoped, might be simpler than benzene's. However, we were disappointed to find that, in spite of the low irradiation energy, many labeled derivatives were formed. We now believe that a kinetic energy even lower than 2 eV must be employed (and we hope to do this) if

we are to achieve useful labeling without a plethora of other, unwanted labeled products. Further hopes regarding labeled tracers are raised by the specific (100% in the C_1 s) labeling found in the biphenyl product from benzene (see Table III) irradiated at 3 and 2 eV. This result implies that by proper adjustments in beam energies, and by proper choices of targets (including mixtures), we may achieve not only labeled, but specifically labeled, tracers.

Future Directions

A new ion source has been constructed for us by Mr. Kenneth Ehlers of the Lawrence Laboratory. This source also produces ions in an arc plasma. However, the ion extraction orifice is in the anode itself, and this feature should give us a lessened "spread" of energies at a given ion energy. That, in turn, should give us better energy control in the important below-5 eV region, and may aid us in achieving controllable energies below 2 eV. In addition, the new ion source appears to be a superior one in handling CH_4 as the source gas. Consequently, we hope soon to be able to effect irradiations with $^{14}CH^+$, $^{14}CH_2^+$, and $^{14}CH_3^+$ ions. This may enable us to settle some of the problems, recounted above, about the time at which hydrogens are picked up by intermediates.

The advent of "total effluent" gas chromatographic-mass spectrometric (GC-MS) techniques, enabling the investigator to detect and identify 1-10 nanograms of organic compounds,³⁹ provides a method that should lead to a considerable advance in our ion beam studies. A one-hour's operation of our μ pump beam of $^{14}C^+$ gives (for example, in the case of toluene, at a 0.2% yield) 4×10^{13} molecules, which equals 6 nanograms. Consequently, the new GC-MS technique appears about as sensitive for detecting products,

and has a far greater potentiality (through the mass spectra) for product identification. We can, therefore, use $^{13}\text{C}^+$ instead of $^{14}\text{C}^+$ as our irradiating ion, and we can hope to identify many more of the products of our irradiations. Among these as yet unidentified products we may expect unusual benzene isomers (and their methyl and phenyl derivatives) such as benzvalene, Dewar benzene, fulvene, prismane, and bicyclopropenyl^{40,41}--the first three of which have already been successfully handled via GC-MS techniques.⁴²

We also intend to use the new technique to reveal the fate of the "secondary" carbons, that is, the carbon atoms ejected from the benzene, or from another target, by the irradiating carbons. With the ^{14}C technique described in this Account, the fate of ejected ^{12}C s is unknown. However, the GC-MS method should enable us to irradiate benzene- ^{13}C with $^{12}\text{C}^+$ ions and to identify the compounds into which the ^{13}C is incorporated.

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