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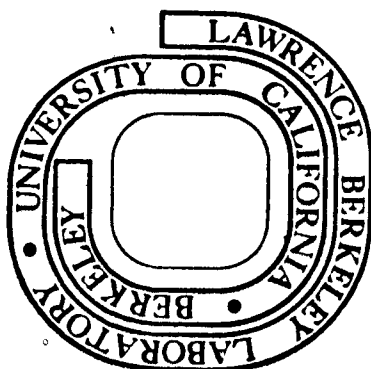
W. R. Erwin, B. E. Gordon, L. D. Spicer, and
R. M. Lemmon

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IRRADIATION OF BENZENE WITH $^{14}\text{CH}^+$ AND $^{14}\text{CH}_3^+$ IONSW. R. Erwin, B. E. Gordon, L. D. Spicer,¹ and R. M. Lemmon

Contribution from the Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

Abstract: Solid benzene at -196°C was irradiated with $^{14}\text{CH}^+$ and $^{14}\text{CH}_3^+$ ions at 10 eV kinetic energy. Yields were determined for the labeled hydrocarbon products: benzene, toluene, cycloheptatriene, diphenylmethane, biphenyl, and phenylcycloheptatriene. The radioactivity distributions between the ring and the methyl group of the toluene product were also determined. These results have been compared to those previously obtained with $^{14}\text{C}^+$ and $^{14}\text{CH}_2^+$ ions. The comparisons have provided both insight into the reaction mechanisms and a tentative estimate of the distribution of the species ($^{14}\text{CH}_x$) that react with the benzene.

In a recent report² we described the principal differences observed when solid benzene is irradiated with $^{14}\text{CH}_2^+$ in place of $^{14}\text{C}^+$ ions. This work was carried out to gain information on whether the $^{14}\text{C}^+$ ion picks up hydrogen before the carbon-carbon bond forming interaction with benzene, or whether the initially formed C_7H_6 intermediate then abstracts hydrogen from an adjacent benzene molecule. Our major observations and conclusions from the $^{14}\text{CH}_2^+$ work were (a) labeled benzene yields appeared to be about the same as with $^{14}\text{C}^+$ --this led us to surmise that methylidene (CH) radicals might be intermediates in a postulated bicyclo C_7 intermediate in the mechanism leading to labeled benzene, (b) the high yields of toluene and cycloheptatriene pointed to similarities to known reactions of benzene with photolytically produced methylene, (c) in contrast to $^{14}\text{C}^+$ results, $^{14}\text{CH}_2^+$ ions produced high yields of labeled toluene and cycloheptatriene, and (d) also in contrast to the $^{14}\text{C}^+$ results, the $^{14}\text{CH}_2^+$ irradiations produced toluene that had no measurable activity in the ring.

In the present report we describe extensions of our studies by irradiations of benzene with $^{14}\text{CH}^+$ and $^{14}\text{CH}_3^+$ ions.

Experimental Section

Most of the experimental details have been described in a recent paper and in the literature cited therein.³ All the irradiations reported in this paper were carried out at a kinetic energy of 10eV. The ion source gas, $^{14}\text{CH}_4$, specific activity 62.7 mCi/mmole, was obtained from the New England Nuclear Co., Boston, Mass. Methane gives good beams of C^+ and CH_3^+ (about one μamp) in our carbon-ion accelerator⁴, but poor beams of CH^+ and CH_2^+ (about 0.1 μamp). The low intensities of the methylidene and methylene beams have been a major impediment in this work. The radioactivity in peaks emerging from the gas chromatograph were determined either by direct counting in a proportional tube connected to a multichannel analyzer, or by trapping and subsequent counting in a liquid scintillation solution.

The toluene radioactivity distribution was determined by adding carrier toluene to the target benzene, isolating the toluene by gas-liquid chromatography (GLC) on Carbowax-20M, trapping the emerging peak in glacial acetic acid that contained additional carrier, and oxidizing the toluene to benzoic acid with CrO_3 and sulfuric acid. The benzoic acid was converted to its silyl ester and the latter was rigorously purified by GLC on an SE-30 column. The ester's specific activity was determined by liquid scintillation counting, after which it was decarboxylated via the Schmidt reaction⁵ to aniline (which contains the toluene ring's activity) and CO_2 (which contains the methyl activity). The latter was trapped and analyzed for both mass and radioactivity after passage through a Poropak R GLC column. The residual sulfuric acid solution, which contained the aniline, was analyzed for radioactivity by liquid scintillation counting.

Results

The yields of the major labeled products obtained on irradiating benzene with $^{14}\text{CH}^+$ and $^{14}\text{CH}_3^+$ ions at 10eV are shown in Table I. For comparison we include earlier data obtained with $^{14}\text{C}^+$ and $^{14}\text{CH}_2^+$ ions at 5 and 10eV.

Table I. Percent Yields of Products From Ions at 5 and 10 eV
Irradiating Species and Energy

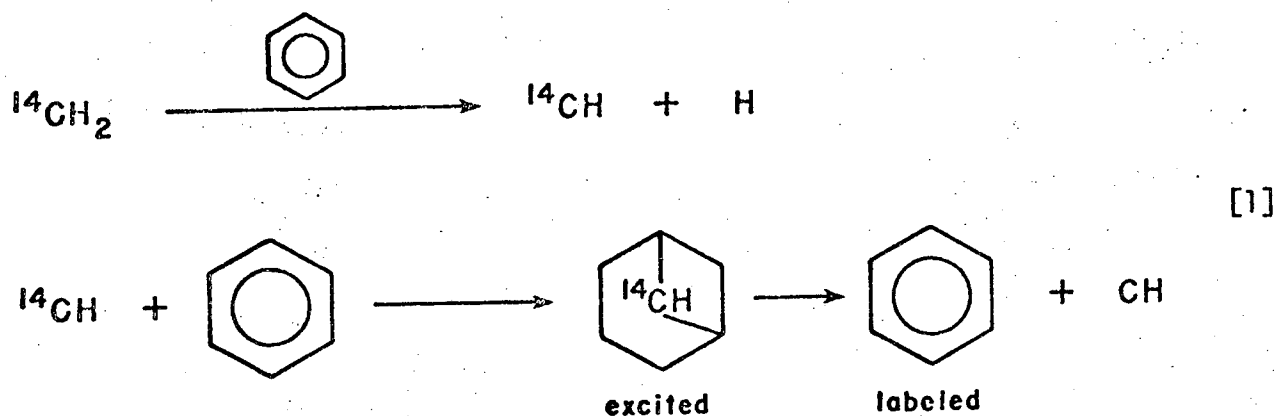
<u>Product</u>	C^+		CH^+	CH_2^+		CH_3^+
	5eV	10eV	10eV	5eV	10eV	10eV
Benzene	4	4	7.6	1.5	3.3	1.5
Toluene	0.2	0.2	1.4	18	21	35
CHT ^a	0.5	0.5	4.2	51	36	5
$\phi\text{C}\equiv\text{CH}$	0.3	0.5 ^b	<0.5	<0.5	<0.5	<0.1
ϕCHO	-	14	19	5	10	2
ϕ_2	1.5	1.5	5	1	^d	<0.1
$\phi_2\text{CH}_2$	3	2	3	1	6	6
ϕCHT	11	10	6	1		<0.1
Total yield ^c	20.5	18.7	27.2	73.5	66.3	47.5

^aCHT = 1,3,5-cycloheptatriene, ^bat 15eV, ^cnot including ϕCHO , ^dThese 3 products were not adequately separated on the GLC column.

Toluene degradations were carried out on the target material from two irradiations with $^{14}\text{CH}_3^+$ and two with $^{14}\text{CH}^+$, all at 10eV. The $^{14}\text{CH}_3^+$ results showed that no measurable radioactivity was incorporated into the ring of toluene. This result is the same as that previously found in the $^{14}\text{CH}_2^+$ irradiations², and is in contrast to the toluene product obtained on irradiation of benzene with $^{14}\text{C}^+$ ions. With these ions, from 5,000 down to 10eV, we have always found about 85% of the toluene's activity in the methyl groups, and the remaining approximately 15% in the ring. At 5eV this ratio becomes about 60/40, and at 2eV it is 94/6.⁶ The $^{14}\text{CH}^+$ irradiation gave a toluene product with about 10% of its radioactivity in the ring.

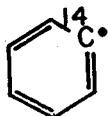
Discussion

In accord with a previously published mechanism² that we used to explain the production of labeled benzene from $^{14}\text{CH}_2^+$, we now find that our highest yields of the benzene come from $^{14}\text{CH}^+$ irradiations. The mechanism is

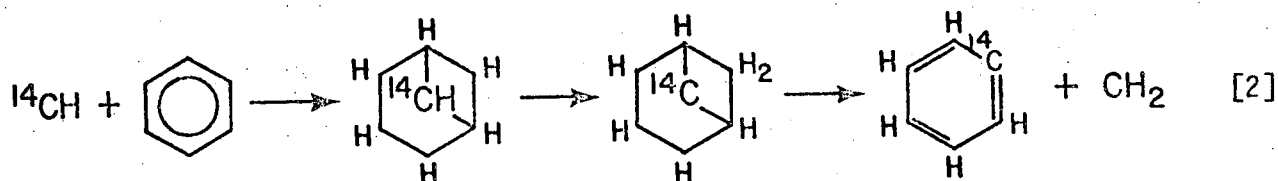


Evidence for a 7-membered intermediate has been found in gas-phase mass spectral studies of C^+ reactions with benzene.⁷ In addition, this mechanism is in agreement with a higher yield of benzene from $^{14}\text{CH}_2^+$ ions at 10eV than from the same ions at 5eV. At the lower energy a lower probability of stripping off a hydrogen atom to produce methylidene radical is expected. This postulate is also useful in explaining the observation that, of the four irradiating ions that we have used, methyl appears the least effective in producing labeled benzene.

The high yield of labeled biphenyl from the $^{14}\text{CH}^+$ irradiations was not expected. If the excited intermediate in (1) ejects a CH, it becomes labeled benzene without generating a phenyl radical. In contrast, the intermediate from $^{14}\text{C}^+$ reaction,



is expected to react with a neighboring benzene molecule either to abstract hydrogen or to form labeled biphenyl. If $^{14}\text{CH}^+$ is the primary reactant that produced biphenyl as the data suggest, hydrogen migration either before or during the secondary reaction most likely occurs with the expulsion of a methylene. This is shown in reaction 2 (non-bonding electrons are omitted).



The yields of toluene rise with increased numbers of hydrogens on the irradiating carbon, that is, they are the highest of all with methyl. That methylene is an effective producer of toluene (by simple C-H bond insertion, as is indicated by the toluene's radioactivity distribution) is not surprising. That methyl is even more effective, is surprising although alkylation of arenes with CH_3^+ is strongly exothermic⁸ and has been observed previously in the liquid phase.⁹ We expect to be able to determine whether hydrogen is lost from the benzene or from the methyl ion by (1) irradiating benzene with CD_3^+ ions, followed by a GC/MS examination of the toluene product and/or (2) irradiating tritiated benzene with CH_3^+ ions and comparing the specific activities of the benzene target with the toluene product.

It is also noteworthy that, in contrast to toluene, cycloheptatriene yields are as expected, that is, they reach a maximum with methylene irradiations. This difference is probably explained on the basis that the main route to cycloheptatriene is through C-C bond insertions, whereas toluene can be formed by both C-C and C-H bond insertions (reference 3, p. 70).

The $^{14}\text{C}^+$ ions, and to a lesser extent, the $^{14}\text{CH}^+$ ions can give a toluene product that is partially ring labeled. Methylene and methyl ions give toluene that is only methyl-group labeled. We interpret this to mean that the "bare carbon" (^{14}C) gives ring-labeled toluene by insertion into a benzene C-C bond. We presume that $^{14}\text{CH}^+$ irradiations lead to the ring labeled product through the CH-bridged bicyclo intermediate in reaction (2) above.

Based on the yields of Table I, a rough estimate can be made of the relative amounts of the four species, CH_{0-3} or their neutralized counterparts (see Table II, footnote a) that undergo a bond-forming (i.e., stable product forming) interaction with benzene when the irradiating species is C^+ , CH^+ , CH_2^+ , or CH_3^+ . Such estimates are presented in Table II. They follow directly from the following hypotheses: (1) that CHT comes primarily from CH_2^+ and that the ratio of toluene to CHT found in CH_2^+ irradiations represents the relative reactivities of CH_2^+ to give these products, (2) that from the above assumption the amount of CHT formed from CH^+ via a pick up of one hydrogen, and the amount of toluene formed from CH_3^+ by loss of hydrogen, can be determined, (3) that in CH^+ irradiations benzene, biphenyl, diphenylmethane, and phenylcycloheptatriene are formed directly via CH^+ reaction, and (4) that from the yields of these latter products derived from hydrogen pickup by C^+ to form CH^+ , and from hydrogen elimination from CH_2^+ to form CH^+ , can be determined. While the data provide evidence that diphenylmethane

can also arise from a CH_2^+ or CH_3^+ intermediate, we are not able to suggest a reasonable mechanistic route for its formation from these species. Nevertheless, such a reaction would avoid the unfavorable consequence outlined below in which hydrogen atoms are lost from CH_2^+ and would alter the figures reported in Table II in a minor way.

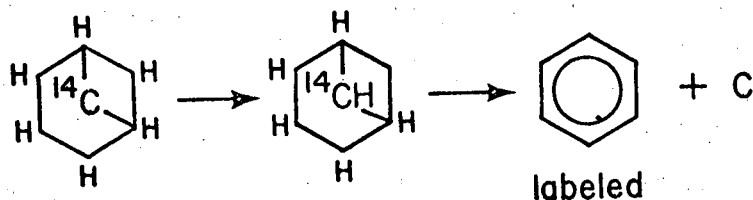
Although, as will be explained below, the above hypotheses are not firmly established, they lead to the rough approximations presented in Table II. These approximations indicate that at 10 eV (1) C^+ picks up hydrogen almost as readily as it inserts in benzene. Such pick ups may occur via direct abstraction or by a insertion-decomposition reaction either into the ring, or as has been reported previously for recoil produced carbon atoms, into a C-H bond.¹⁰ (2) CH^+ reacts primarily by insertion, but prefers hydrogen pickup over elimination, (3) CH_2^+ also reacts primarily by insertion with only a small percentage of the methylene ions losing a hydrogen, and (4) CH_3^+ loses one or two hydrogens but also reacts readily to methylate benzene. It is also apparent both from Table I and Table II that the most reactive ion in producing the insertion products observed at 10 eV is CH_2^+ followed, in order, by CH_3^+ , CH^+ , and C^+ .

Table II. Estimated Distribution of Species Reacting With Benzene Derived From Initial Ion Beams of C^+ , CH^+ , CH_2^+ , and CH_3^+ at 10eV Translational Energy

Ion Beam	Reacting Species ^a , Percent			
	C	CH	CH ₂	CH ₃
C^+	10	8	<1	-
CH^+	<1	24	4	-
CH_2^+	-	9	57	-
CH_3^+	-	8	8	32

^aCharge neutralization is expected to be the first result when these ions reach the benzene matrix--see refs. 11 and 12.

The data of Table I leave no doubt that CH_2 is the most efficient species for forming CHT, and that CH is the most efficient species for forming benzene. However, this does not necessarily mean that the bare ^{14}C atom must pick up a hydrogen before the interaction that leads to the labeled benzene product. In fact, our previous studies^{6,13} have shown that the yields of labeled benzene, toluene, and CHT from $^{14}C^+$ irradiations are essentially constant through the translational energy range of 10eV to 2eV. Consequently, an alternative interpretation might postulate similar bicyclo C_7 intermediates like that in (1) arising from the initial reaction of C^+ , CH^+ , or CH_2^+ with benzene. In each case, labeled benzene and biphenyl would be produced following intramolecular hydrogen transfer when needed--as, for example, in reaction (2) or



How important the suggested intramolecular hydrogen transfers are may be determined by future experiments using $^{14}\text{CH}_x^+$ beams at 5eV, or lower, kinetic energy.

A problem with the intramolecular hydrogen shift mechanism lies in the experimental results which support the energetically unfavorable conclusion that C is more readily expelled than CH from the C_7 intermediate, and CH is more readily expelled than CH_2 . Such a mechanism yields labeled ^{14}CH fragments from C^+ and $^{14}\text{CH}_2$ fragments from CH^+ , but in lower quantities than estimated in Table II. Here, as in the previous interpretation, there is no mechanistic explanation for the high yield of diphenylmethane in the methyl irradiations.

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