# Reactions of Accelerated Carbon-14 with Benzene. Degradation of Toluene and Its Mechanism of Formation[1]

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We have totally degraded the toluene product obtained from impinging 5000 and 4000 eV $^{14}C^+$ ions on solid benzene at −196°. The radioactivity distributions were essentially equivalent to that of toluene obtained in carbon recoil experiments. The ring/methyl activity ratios were also determined for toluenes from irradiations at various energies down to 5 eV. While the yield of toluene decreased drastically below 100 eV, the ring/methyl activity ratio remained constant, changing only when the energy of the incident ions were lowered to 5 eV. It is suggested that bare carbon atoms, as well as $CH_2$, are important species leading to toluene formation.

## Introduction

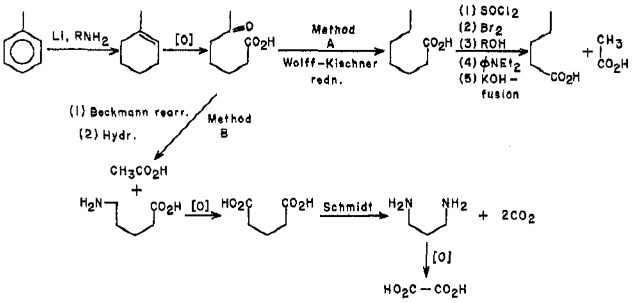
The present work was undertaken to add to our knowledge of how accelerated carbon ions and atoms interact with benzene to form (among other products) toluene. The first work of this kind, using recoiling $^{14}C$ atoms, was that of Wolf, *et al.*,[2] who showed that 15% of the activity of the toluene produced from benzene was in the ring of the toluene. A subsequent study by Visser, *et al.*,[3] revealed that the toluene's methyl, $C_1$, $C_2$, $C_3$, and $C_4$ activities were 85.7, 7.65, 3.68, 2.00, and 0.99%, respectively. Mullen then reported that the toluene-$^{14}C$ from the reaction of kinetically hot $^{14}C^+$ with benzene showed a similar ring/Me activity distribution.[4] Mullen's work was recently repeated and corroborated by us.[5] In reactions of recoiling carbon atoms with organic compounds, hot methylene has usually been postulated as the reactive species for the formation of synthesis products.[6] (A "synthesis" product has one or more carbons than the target molecule.) Since photolytically generated $^{14}CH_2$ gave toluene which was exclusively labeled at the methyl group,[7] it was assumed that, in the recoil-carbon work, a hot methylene must be involved and that a structure such as an excited norcaradiene was responsible for the incorporation of the activity in the aromatic ring.[8]

In the present paper, we report an examination of the above mechanism by total and partial degradations of toluene-$^{14}C$ obtained upon striking solid benzene with $^{14}C^+$ ions of various kinetic energies.

## Experimental Section

Toluene-$^{14}C$ was degraded by the two methods shown below.

Method A was essentially that used by Moore and Wolf in the degradation of their ethylbenzenes.[9] The activities in $C_{Me}$ and $C_1$ were determined by the Schmidt degradation of acetic acid obtained from the Beckmann rearrangement of the oxime of 6-ketoheptanoic acid, followed by the hydrolysis of the product. (This is the first step of "method B.") We also found that the alternative method, B, was easier for the total degradation of toluene. Partial degradations (ring/Me activity distributions) were carried out by oxidation to benzoic acid, followed by the Schmidt degradation.



Details of the irradiations, of the separations and purifications of the toluene, and of the degradations are described elsewhere.[5,10,11]

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[1] Abstracted in part from the Ph.D. Thesis of T. H. Lin, UCRL-19335, University of California, Berkeley, 1969, and based on work supported by the U. S. Atomic Energy Commission.

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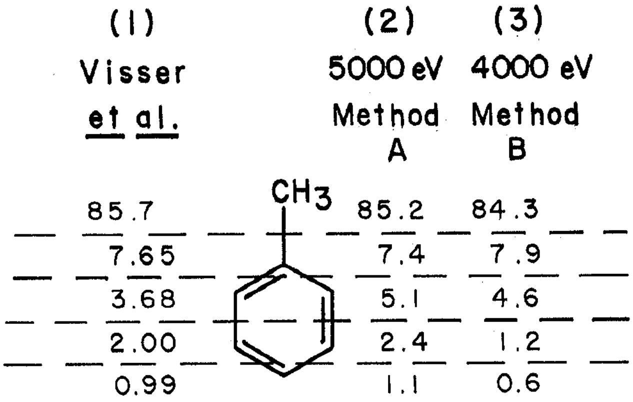

Figure 1. Distributions of radioactivity in toluene-$^{14}C$ formed from benzene and (1) recoiling $^{14}C$ atoms, (2) 5000-eV $^{14}C$ ions, and (3) 4000-eV $^{14}C$ ions. Methods A and B refer to different degradation routes (see text).

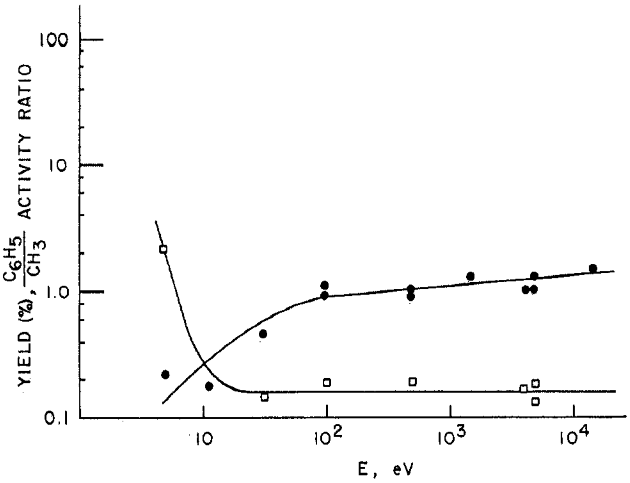

Figure 2. The yields of toluene-$^{14}C$ (□) and the toluene ring/Me activity distributions (●), plotted as a function of the kinetic energy of the $^{14}C^+$.

## Results

Toluene-$^{14}C$ from 5000 and 4000 eV $^{14}C^+$ beams was degraded *via* methods A and B, respectively. The results are shown in Figure 1, along with those from a $^{14}C$-recoil experiment (Visser, *et al.*).[3] Close similarity to the latter results is apparent.

As has been previously reported, the partial degradation of toluene-$^{14}C$ obtained from irradiations at various $^{14}C^+$ energies showed no apparent change in the ring/Me activity ratio at energies above 31 eV.[12] However, a drastic increase in the ring activity was found in 5-eV irradiations. A plot of ring/Me activities *vs.* that of the ion energies is presented in Figure 2. A plot of the toluene-$^{14}C$ yield[5] is also included.

## Discussion

The activity distributions reported here (Figure 1), and those reported by Visser and Wolf in their study of the recoil-$^{14}C$ chemistry of benzene, indicate that the hot carbon species that interacts with the benzene is the same in both the recoil-$^{14}C$ and the accelerated $^{14}C^+$ systems. In addition, it is to be expected, as we have previously inferred from the work of other authors, that our accelerated ions are rapidly neutralized upon entering the benzene matrix;[5] therefore, our system may also be taken as a study of carbon atom reactions.

The formation of toluene from the reactions of recoiling carbon atoms with benzene has been shown to be a hot reaction.[8] Although the involvement of hot methylene is usually postulated in the interpretation of carbon-recoil results,[6,8] there is as yet no direct evidence that indicates at which stage the two hydrogen atoms are picked up, *i.e.*, before or after the carbon's bonding to the benzene. One of the reasons for the assumption of a hot methylene was that the three hexanes (from *n*-pentane and recoiling $^{14}C$) and the ethylbenzene and the three xylenes (from toluene and recoiling $^{14}C$) were formed in the statistical ratio expected from indiscriminate insertion of $CH_2$ into the C–H bonds of the target molecule.[6] The observation that about 15% of the activity of toluene (from benzene and recoiling $^{14}C$) was in the ring was believed to have been caused by the excess kinetic energy of the hot methylene intermediate. The more recent study of Williams and Voigt, however, revealed that the products from toluene and xylenes were not statistically distributed,[13] and their work emphasizes the role of bare carbon atoms in the formation, from benzene, of acetylene, ethylene, and higher olefins. The scrambling of activity into an unexpected part of the synthesis product molecule may also be suggestive of the participation of a species other than methylene, *e.g.*, CH or C.

Our finding of a drastic increase in the toluene's ring/Me activity distribution at 5 eV is also suggestive of the involvement of a species other than methylene. Rose, *et al.*,[14] reported that atomic carbon (from $^{11}C$ recoil) was extremely reactive with benzene. Several stable adducts, including $\pi$-bonded configurations, double bond additions, and C–H bond insertions, were postulated. Our recent paper also assumed the formation of benzylidene and cycloheptatrienilidene and/or norcaradienilidene[10] as the precursors for two of our major products, diphenylmethane and phenylcycloheptatriene. It seems reasonable to expect that these precursors would abstract hydrogens from the reaction medium, benzene, to form toluene and cycloheptatriene. In fact, even thermal carbon vapor is reported to give these products with benzene.[15] Skell

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(11) T. H. Lin, "The Chemical Interactions of Accelerated Carbon-14 Ions and Atoms with Benzene," Ph.D. Thesis, UCRL-19335, University of California, Berkeley, 1969.

(12) H. M. Pohlit, W. R. Erwin, T. H. Lin, and R. M. Lemmon, *J. Phys. Chem.*, **75**, 2555 (1971).

(13) R. L. Williams and A. F. Voigt, *ibid.*, **73**, 2538 (1969).

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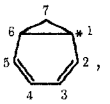
(15) J. L. Sprung, S. Winstein, and W. F. Libby, *ibid.*, **87**, 1812 (1965).

and Engel[16] reported that parent-molecule-plus-$CH_2$ (*i.e.*, "synthesis") products were obtainable in high yield in the reaction of thermal carbon vapor with hydrocarbons; in their system it was demonstrated that no methylene was involved. To support this mechanism, we have photolytically generated $C_6H_5CH$: in benzene solution by the photolysis of styrene oxide. The formation of toluene was firmly established by glpc analysis. We therefore believe that bare C atoms, as well as methylene, are reacting directly with benzene.

Another argument that favors the notion that methylene is not the major species involved in the ring labeling of toluene is the following. A methylene route to ring labeling is presumed to involve (after intramolecular hydrogen shifts) such norcaradiene structures as



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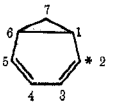

, etc.

Such structures can only give more $C_2$-labeled toluene than $C_1$-labeled. However, the data of Figure 1 show that $C_1$ is the more highly labeled. These results indicate that a route through methylene is not the principal one in the ring labeling, although it may be for the methyl labeling.

It is possible that the relative populations of the various carbon spin states, the ground state $^1S$ or the excited $^1D$ and $^3P$ states, may decide the yield and radioactivity distributions of the toluene product. However, the high ring/Me activity ratio in the 5-eV experiment is apparently not the result of the $^{14}C^+$ ion reacting with the benzene before the ion becomes neutralized. Recent results in our laboratory, the subject of a forthcoming publication, have (1) confirmed the 5-eV result and (2) shown that, when the irradiating ion's kinetic energy is reduced to 3 or 2 eV, the ring/Me activity ratio diminishes to about 0.1.

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(16) P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **88**, 4883 (1966).

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# Sorption Properties of Activated Carbon

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Adsorption–desorption isotherm data were obtained for 15 organic vapors on a BPL grade, PAC, activated carbon. Isotherm data in the form of log $W$ as a function of $\epsilon^2$ for each adsorbate were given to a Univac 1108 computer to determine the characteristic curve equation by means of regression analysis ($W$ = volume of adsorbed vapor, $\epsilon$ = adsorption potential). Equations in the form of the Dubinin–Polanyi equation for fine grained carbon were obtained for each adsorbate. Structural constants for the adsorbent and affinity coefficients for the adsorbates were calculated from the coefficients of these equations. Affinity coefficients calculated from the experimental data were then compared to theoretical values in order to test the predictive ability of the characteristic curve equation.

## Introduction

*Predictive Isotherm Equations.* The ability to predict adsorption isotherms for a given adsorbent from a knowledge of the physical properties of the adsorbate has long been an important objective in solid surface–gas interaction research. Kummer in 1946 studied the relation of Polanyi's adsorption potential to molecular polarizability.[1] In 1947, Dubinin and his coworkers first suggested that the following equations could be used for predicting adsorption isotherms[2]

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(2) (a) M. M. Dubinin and E. D. Zaverina, *Zh. Fiz. Khim.*, **23**, 1129 (1949); (b) M. M. Dubinin, E. D. Zaverina, and L. V. Radushkevich, *ibid.*, **21**, 1351 (1947).