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Hot-Atom Chemistry of Carbon-14 in Solid Benzene at Kinetic Energies at or below 5 eV

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The yields of seven major hydrocarbon products from the irradiation of solid benzene with accelerated carbon-14 ions were determined at very low kinetic energies, namely, down to 2 eV. The ultimate fate of the irradiating carbon ions was determined by chemical degradation of the products to reveal the percent of $^{14}C$ activity at a given position in the molecule. This work has shown (a) throughout the 5,000-2 eV energy range, an essentially constant yield of benzene (about 3-4% of the irradiating $^{14}C^+$ ions), (b) a decrease in the yields of toluene, cycloheptatriene, and phenylacetylene as one goes from 100 eV down to 2 eV, (c) an increase in the yields of phenylcycloheptatriene and biphenyl when the 5-2 eV energy range is reached, and (d) the appearance of maximum activity in the phenyl groups of toluene and diphenylmethane at about 5 eV. These results suggest the mechanisms involved in the formations of these products.
Introduction

Previous papers from this laboratory\(^1\text{-}^5\) have reported the principal chemical results obtained when a beam of accelerated \(^{14}\text{C}^+\) ions is impinged upon a target of solid benzene at \(-196^\circ\). As a function of the kinetic energy of the impinging ions, we determined the yields and (with the exception of benzene-\(^{14}\text{C}\)) the activity distributions of the major, labeled hydrocarbon products (toluene, cycloheptatriene, diphenylmethane, phenylacetylene, biphenyl, and phenylcycloheptatriene). The kinetic energy range studied was from 5,000 to 5 eV. These studies provided insight into the energetic states (both kinetic and internal), and into the extent of hydrogen-to-carbon attachment (C, CH, CH\(_2\), or CH\(_3\)), before the bond-forming event with the benzene molecule takes place.

Recent improvements in our carbon-ion accelerator have made it possible for us to reduce the kinetic energy of our impinging \(^{14}\text{C}^+\) ions down to about 2 eV. The lower energy region is important in order to minimize the hydrogen-attachments mentioned above, the internal energy of the initially formed C\(_7\) species, and radiation damage effects. This energy region also enables us to correlate better our energetic system with the known photochemistry and thermal chemistry of carbon and methylene with benzene. The present paper reports the observations that we have made in the 5-2 eV region, and summarizes the added information gained concerning the energetic reactions of carbon, and its hydrogen-containing adducts, with benzene. We also report some toluene and xylene irradiations that have provided further information on the mechanism of the benzene-\(^{14}\text{C}\) formation.
Experimental Section

Ion accelerator. The instrument used in these studies has been described in a recent publication. Since that paper appeared we have added probes for monitoring the ion beam position and shape, and have adjusted the position and angle of our decelerator lens system. These improvements have enabled us to reduce the $^{14}$C$^+$ beam's kinetic energy down to 2 eV; at this energy we still have an approximately 0.25 µamp current striking the target.

Irradiation conditions and analytical techniques. A one-hour's operation of the 0.25 µamp beam embeds about 0.6 µcuries of $^{14}$C in the benzene (which is added steadily to the target during the irradiation; a total of about 100 µ is used). A product formed in 1% yield of the incoming carbon ions would, therefore, contain about 6 nanocuries, or about 13,200 dpm. The ratio of incoming ions to benzene molecules in the target is about $10^{-4}$. At the conclusion of an irradiation the solid benzene target is scraped into a rubber-capped vial, to which hydrocarbon carriers are added, and from which aliquot portions are removed via syringe needles for subsequent radiogaschromatography. Details of the chromatographic techniques were given in an earlier publication.

Degradations. The chemical degradations were performed by procedures whose main details have been reported earlier. However, several significant improvements were made in these procedures, as follows:

1. In the oxidation of labeled products (toluene, diphenylmethane, phenylacetylene, and phenylcycloheptatriene) to benzoic acid, the excess chromic acid was destroyed with aqueous Na$_2$SO$_3$ instead of with methanol. Subsequently, the reaction mixture was not taken to dryness, but instead
was extracted by ether for 5 hr in a liquid-liquid extractor. This change reduced losses of the volatile benzoic acid and increased its yield from about 55% to 75%, an improvement especially valuable for toluene and phenylacetylene, whose yields from the $^{14}C^+$ beam are only about 0.2%.

(2) The crude benzoic acid was purified by silination with bis(tri-methylsilyl)-trifluoroacetamide, followed by GLC (SE-30, 5% on DMCS Chromosorb W, 70/80 mesh, 1/4" x 10', He flow 100 cc/min). The silyl benzoate peak was trapped in a mixture of water-acetone-NaOH (slight excess of the hydroxide). The ester hydrolysis was fast, and evaporation of the solvent gave dry sodium benzoate suitable for the subsequent Schmidt reaction. The recovery of the benzoate (as the Na salt from the GLC operation) was 99%. This almost quantitative purification is especially good for eliminating traces of acetic acid (the solvent for the CrO$_3$ oxidation). Any such traces would decrease the specific activity of the $^{14}CO_2$ coming from the Schmidt reaction on the benzoic acid.

(3) The phenyl-ring activity was determined by bubbling gaseous HCl thru the aniline-in-ether solution coming from the Schmidt reaction, and the ether was then evaporated to dryness in a stream of dry N$_2$. An excess of dry diethylamine (60 λ to 1 λ of aniline) was added, with good stirring, to the dry aniline hydrochloride. The aniline-in-diethylamine solution was injected into the GLC column with a Flath-Lundin filter syringe (Hamilton Co.) that retains the solid particles of Et$_2$NH.HCl.

(4) In our previous work, in which benzophenone was an intermediate in the degradation of diphenylmethane, we used benzene as the solvent in the reaction between benzophenone and hydrazoic acid. However, since
small amounts of aniline may be formed by reaction with benzene, we abandoned that solvent and, in its place, used trichloroacetic acid; we followed the reaction conditions of Smith, and achieved a benzanilide yield of 92%. The benzanilide was hydrolyzed by an overnight refluxing with KOH in an alcohol-water solution, from which, after dilution with water, the aniline (85% yield) was extracted with ether.

(5) The values of the mass peaks on the GLC columns were determined by a digital integrator (Hewlett-Packard Model 3370A). Relationships between mass and peak areas were determined by previous injections into the GLC columns of known amounts of a particular compound.

**Toluene and xylene irradiations.** In an attempt to learn more about the interesting processes that lead to labeled benzene, we also irradiated (separately) solid toluene, o-xylene, and p-xylene at -196°, with a 10-eV $^{14}$C$^+$ beam; we then determined the yields of labeled benzene, toluene, ethylbenzene, styrene, methyl styrenes, and the xylenes.

**Results**

**Activity distributions.** The degradation results are recorded in Table I. For comparison, we have included some previous results that were obtained at 5 eV, and at higher, kinetic energies. Because of small analytical and counting errors the results do not necessarily add up to 100%.

**Yields.** The product yields as a function of energy are recorded in Table II. Yield is defined as the percent of the activity, in an aliquot portion of the target, that appears in the GLC peak of the product. We believe that these yield determinations are valid to within ±25%.
Table I: Product Activity Distributions (%) as a Function of $^{14}\text{C}^+$ Energy

<table>
<thead>
<tr>
<th>Energy Product</th>
<th>5 KeV</th>
<th>6 eV</th>
<th>5 eV</th>
<th>4.5 eV</th>
<th>3 eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>85</td>
<td>86</td>
<td>63</td>
<td>76</td>
<td>92</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>15</td>
<td>41</td>
<td></td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>91</td>
<td></td>
<td>76</td>
<td></td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>(CH$_2$)$_2$</td>
<td>9</td>
<td>18</td>
<td></td>
<td></td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>CH=C</td>
<td>30</td>
<td>33</td>
<td></td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CH=C</td>
<td>66</td>
<td>62</td>
<td></td>
<td></td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>4</td>
<td>7</td>
<td></td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>16</td>
<td>22</td>
<td></td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>57</td>
<td></td>
<td>85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>19</td>
<td></td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>9</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>84</td>
<td></td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>9</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II: Product Yields as a Function of Energy

<table>
<thead>
<tr>
<th>Product</th>
<th>% Yield at indicated energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 KeV</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.0</td>
</tr>
<tr>
<td>Cycloheptatriene</td>
<td>2.5</td>
</tr>
<tr>
<td>4C≡CH</td>
<td>1.6</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>1.3</td>
</tr>
<tr>
<td>4CH₂Φ</td>
<td>1.5</td>
</tr>
<tr>
<td>4cycloheptatriene</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Irradiation of toluene, o-xylene, and p-xylene. The products, and their yields, obtained on the separate irradiations of these solid targets (at -196°) with 10-eV $^{14}$C$^+$ ions are given in Table III.

Discussion

As we have discussed previously, \(^3\) we interpret the decreases in yields of toluene and cycloheptatriene below 100 eV as reflecting a diminished opportunity for the incoming carbon-14 atom $^9$ to pick up hydrogens to form CH or CH$_2$ $^{10}$ before the bond-forming interaction with a benzene molecule. The toluene yields, apparently, reflect the involvement of CH$_2$, CH, and C in the reactions leading to toluene at energies above 5 eV, but only C for reactions at or below that energy. However, our
Table III: Labeled-Product Yields (%) from $^{14}$C-Irradiated Toluene, o-Xylene, and p-Xylene

<table>
<thead>
<tr>
<th>Product</th>
<th>Toluene</th>
<th>o-Xylene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.3</td>
<td>&lt;0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.0</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Styrene</td>
<td>17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methylstyrene</td>
<td>-</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.3</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>m' + p-Xylene</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>-</td>
<td>-</td>
<td>2.2</td>
</tr>
</tbody>
</table>

interpretations regarding toluene are circumscribed by the formation of an oxygenated product, benzaldehyde (from the residual, $10^{-6}$ Torr, $O_2$ in our instrument). At 10 eV or lower energy, the benzaldehyde yields appear to be inversely related to those of toluene. The implications of scavenging-by-oxygen processes, and of changes in the target's temperature, will be the subject of a forthcoming paper.

The cycloheptatriene yield appears to rise as one goes from 5 eV to 2 eV; however, we are less than certain that this is indeed true. As we surmised previously, the diminished yield of phenylacetylene at 5 eV must reflect a diminished opportunity for a C-stripping reaction leading to a reactive $C_2H_x$ fragment; our 2 eV result recorded here adds strength to that suggestion.
We interpret the increased yields of phenylcycloheptatriene and biphenyl, as one goes from 5 eV to 2 eV irradiations, as being due to the lessened internal energy that a reactive intermediate must dispose of in order to avoid decomposition before the product-forming reaction with a benzene molecule.

The yield of labeled benzene has stayed remarkably constant throughout the entire 5,000-to-2 eV energy range. It continues to intrigue us how such a low kinetic energy (2 eV) \(^{14}\text{C}\) can replace a \(^{12}\text{C}\) to form a new, labeled benzene molecule. Our present hypothesis is that there must be an excited \(C_7\) intermediate such as

\[
\begin{array}{c}
\text{1} \\
\text{6} \\
\text{5} \\
\text{4} \\
\text{3} \\
\text{2}
\end{array}
\]

(11)

Similar intermediates have been proposed by Rose et al., who studied the interactions of energetic \(^{11}\text{C}\) with benzene and observed many of the products discussed here. Without, for the moment, specifying anything about hydrogen-atom and electronic redistributions, we can visualize such an excited intermediate splitting out carbon-2 to produce the new, labeled product. A partial test of this notion has been carried out in our irradiations (results reported in Table III) of toluene and xylenes. Benzene-\(^{14}\text{C}\) is formed from toluene but is a negligible, if not non-existent, product from the xylenes. This is in accord with the above formulation, and also in accord with the results obtained in carbon-recoil studies.\(^{12}\) Also in accord is the higher yield of toluene (0.8%) from xylene, compared to that of benzene (0.3%) from toluene.

These results also appear to rule out any significant \(\text{C}_2\)-adduct mechanism as a route to labeled benzene from the irradiation of benzene--
as might be suggested by the phenylacetylene product. In other words, benzene-$^{14}\text{C}$ might come from an excited adduct such as

![Diagram](image)

that would then split out the indicated two-carbon species to give labeled benzene. Such a mechanism could also give benzene-$^{14}\text{C}$ from o-xylene, but not from p-xylene. In fact, both xylenes give no detectable benzene (the difference between the "<0.03" and "<0.01" percent yields in Table III may be ignored--it has only to do with the background activity contaminations in our radiogaschromatographic equipment).

If labeled benzene is formed via the C$_7$ intermediate above, and if the postulated C$_1$ "bridge" attachments are unaffected by the presence of a methyl group, then we should expect that the irradiated toluene would give a toluene-$^{14}\text{C}$/benzene-$^{14}\text{C}$ product ratio of 5.0. We found 1.0/0.3 = 3.3. The same reasoning for the irradiated xylenes would give a xylene-$^{14}\text{C}$/toluene-$^{14}\text{C}$ product ratio of 2.0. We found for the two xylenes, respectively, 0.8/0.4 = 2.0, and 2.2/0.8 = 2.8. Our agreement with the expected results of "random C$_1$ bridge" attachments is, therefore, not as good as Williams and Voigt reported in their products from $^{11}\text{C}$ recoils striking aromatic targets. However, their targets were liquids, not solids, and it may be that out much lower energy (10 eV) carbons are showing some selectivities in their interactions with aromatic molecules.

The data of Table I show that the phenyl group activities for toluene, diphenylmethane, and phenylcycloheptatriene reach a maximum at about 5 eV.
In the case of toluene, for which we have carried out three irradiations of the benzene target at 5 eV (and others at 6, 4.5, 3, and 2 eV), there is no doubt whatever of the reality of this maximum. Our interpretation is that at 5 eV the predominant process leading to labeled toluene is the reaction with benzene of a bare (unhydrogenated) C atom, and that 5 eV gives the maximum internal energy that the intermediate, excited, C$_7$ species can accommodate without disintegration. That maximum internal energy would give a maximum of "activity scrambling", by processes such as those suggested earlier,$^{2,5}$ giving maximum labeling in the phenyl group. In contrast, an ion striking the benzene surface at 6 eV energy might not be able to interact to form a product intermediate until it had experienced an energy-degrading collision; thus a 6-eV ion beam can be looked upon as one that interacts at all energies between 6 and 0 eV. Corresponding arguments also apply to the phenyl activities in diphenylmethane and phenyl-cycloheptatriene.

The 100% labeling in the C$_1$ position(s) of biphenyl is an interesting result, and directly attributable to the low kinetic energies (2-3 eV) of our irradiating ions. To our knowledge, this is the first example of specific labeling in any product obtained in carbon-recoil or accelerated-carbon experiments. This result indicates 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.

Acknowledgments. This work was supported by the U. S. Atomic Energy Commission. We also express thanks for the technical assistance of Mr. Glenn A. Fisher.
References

(9) We believe that the ion is very rapidly neutralized on reaching the target. This question was discussed in reference 1.
(10) The low yields of methane from carbon-recoil studies on benzene (see reference 12) indicate that little CH₃ is formed.
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