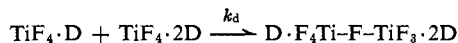


where  $k_t$  is a second-order rate constant. Applying the steady-state approximation to  $[\text{TiF}_4 \cdot \text{D}]$  gives<sup>8</sup>

$$\frac{1}{\tau} = \frac{k_1 k_t}{k_{-1} + k_t} \quad (2)$$

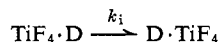
Fluorine equivalence could also occur *via* a bridged intermediate



For this scheme  $\tau$  would be given by

$$\frac{1}{\tau} = \frac{k_1 k_d [\text{TiF}_4 \cdot 2\text{D}]}{k_{-1} [\text{D}] + k_d [\text{TiF}_4 \cdot 2\text{D}]} \quad (3)$$

A third possibility is that upon dissociation a non-rigid five-coordinate species is formed.<sup>9,10</sup> This intermediate would undergo an inversion or series of anharmonic vibrations<sup>11</sup> to scramble the fluorines



For this scheme  $\tau$  is given by

$$\frac{1}{\tau} = \frac{k_1 k_i}{k_{-1} [\text{D}] + k_i} \quad (4)$$

The mechanism involving dissociation and inversion is the only one in agreement with the experimental data. Equation 4 requires that excess base will increase the average lifetime of a fluorine-19 spin state, causing the triplets to coalesce at a higher temperature. The concentration of the complex should not effect  $T_c$ . The experimental data are compatible with these requirements.

Since the proposed mechanism requires an exchange of donor molecules between the complex and the solution, the proton nmr spectra of  $\text{TiF}_4 \cdot 2\text{DEF}$  solutions were studied at ambient temperature as a function of the concentration of excess N,N-diethylformamide. The resonance of the formyl protons in each of these solutions is a single peak. The chemical shift of this resonance is a weighted average of the formyl proton shifts of the coordinated and uncoordinated donor molecules, showing that a fast donor exchange is occurring. The chemical shift (15 cps at 60 Mc) between the formyl peaks of solutions containing only  $\text{TiF}_4 \cdot 2\text{DEF}$  and those containing only DEF indicates that the rate constant for dissociation,  $k_1$ , is larger than  $2(15\pi/\sqrt{2})$  ( $=67 \text{ sec}^{-1}$ ) at ambient temperature.<sup>12</sup> A value for  $k_1$  can be obtained from  $\text{F}^{19}$  nmr experiments since eq 4 reduces to

$$\frac{1}{\tau} = k_1 \quad (5)$$

as  $[\text{D}]$  approaches zero. If the equilibrium constant of the dissociation is small, a value of  $370 \text{ sec}^{-1}$  at  $0^\circ$  is obtained for  $k_1$  from the triplet coalescence of  $\text{TiF}_4 \cdot 2\text{DEF}$  solutions to which no excess donor was added.

**Acknowledgment.** Support of this work by the Air Force Materials Laboratory, Research and Tech-

(8) Equation 2 applies to any mechanism in which fluorine equivalence is achieved by attack of the five-coordinate species with a donor molecule.

(9) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

(10) E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966).

(11) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(12) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1957).

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## Reaction of Carbon Atoms with Benzene

Sir:

While the reactions of atomic carbon with aliphatic hydrocarbons are now quite well outlined,<sup>1</sup> no clear picture has emerged of their interaction with aromatic systems. Most of the literature<sup>2-6</sup> on the subject is restricted to hot carbon atom reactions in the condensed phase and, furthermore, is limited to investigation of only a few products accounting for a relatively small fraction of the total yield. In an attempt to delineate some of the principal features involved, the present communication has a wider scope, including the first reported results of studies of thermal and hot carbon atoms reacting in the gas phase as well as a more complete analysis of products formed in condensed systems.

Free carbon atoms in the form of  $^{11}\text{C}$  (20.5 min) were produced by the Yale heavy ion and electron accelerators by nuclear techniques described elsewhere.<sup>7</sup> Such atoms are translationally "hot" species in one of the low-lying ( $^3\text{P}$ ,  $^1\text{D}$ ,  $^1\text{S}$ ) electronic states. In certain experiments, they were cooled to thermal energies by the addition of excess neon moderator.

Products were formed on a tracer scale ( $\approx 10^8$  molecules), separated by gas chromatography, and radioassayed by flow proportional counting.<sup>8</sup> Both the purity and the identity of the products were confirmed by establishing that they had identical elution properties with known carriers on at least two columns having different separating properties. External monitoring<sup>7</sup> of the number of carbon atoms produced in gas-phase experiments made it possible to establish absolute yields of identified products and provide an estimate of polymeric material.

Eastman Kodak benzene, thiophene free, Fisher Spectrograde benzene, and 99.999% zone-refined benzene (purchased from J. Hinton, Valparaiso, Fla.) were all used without further purification except for meticulous degassing on a vacuum line. All three samples gave similar results within the experimental error. Matheson oxygen and research grade neon were used and were at least 99.5% pure.

(1) (a) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965), and references therein; (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 210 (1964), and references therein.

(2) (a) A. G. Schrodt and W. F. Libby, *J. Am. Chem. Soc.*, **78**, 1267 (1956); (b) J. Sprung, S. Winstein, and W. F. Libby, *ibid.*, **87**, 1812 (1965).

(3) (a) B. Suryanarayana and A. P. Wolf, *J. Phys. Chem.*, **62**, 1369 (1958); (b) A. P. Wolf, *Ann. Rev. Nucl. Sci.*, **10**, 259 (1960); (c) A. P. Wolf, "Chemical Effects of Nuclear Transformations," Vol. II, International Atomic Energy Association, Vienna, 1961, p. 3.

(4) A. F. Voigt, Hot Atomic Chemistry Symposium, Purdue University, Lafayette, Ind., April 1-2, 1966.

(5) The reactions of accelerated  $\text{C}^+$  ions have been studied by Lemmon and Mullen. See "The Chemical Interactions of Accelerated Carbon-14 Ions with Benzene," by R. T. Mullen, Ph.D. Thesis, University of California, Berkeley, Calif., 1961. Some similarities to the work with nucleogenic carbon atoms were observed.

(6) A. P. Wolf, private communication; cf. also ref 3c.

(7) J. Dubrin, C. MacKay, M. Pandow, and R. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964).

(8) R. Wolfgang and C. MacKay, *Nucleonics*, **16**, No. 10, 69 (1958); R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

Table I. Yields of  $^{11}\text{C}$ -Labeled Products from Reactions of  $^{11}\text{C}$  and Benzene<sup>a</sup>

| Product <sup>b</sup>           | Gas phase<br>Yields as % total $^{11}\text{C}$ atoms |   |                                   | Condensed phase<br>Relative yields <sup>c</sup> |                              |
|--------------------------------|--|---|-----------------------------------|---|------------------------------|
|                                | Benzene,<br>7 cm                                     | Benzene,<br>6.65 cm<br>oxygen,<br>0.35 cm | Benzene,<br>4.0 cm<br>neon, 76 cm | Benzene,<br>liquid<br>(25°)                     | Benzene,<br>solid<br>(-195°) |
| Carbon monoxide }<br>Methane } | 4.0 ± 0.2  | 11.0 ± 1.2 <sup>d</sup>                   | 2.0 ± 1.3                         | 0.9 ± 0.1                                       | 0.7 ± 0.1                    |
| Acetylene                      | 7.4 ± 0.2  | 6.7 ± 0.9                                 | 1.9 ± 0.4                         | 18.4 ± 1.6                                      | 14.8 ± 1.4                   |
| Vinylacetylene                 | 0.2 ± 0.1  | 0.3 ± 0.1                                 | 0.2 ± 0.1                         | 2.5 ± 0.4                                       | 3.7 ± 1.6                    |
| Diacetylene                    | 5.3 ± 0.5  | 6.1 ± 0.6                                 | 1.7 ± 0.1                         | 7.6 ± 0.1                                       | 2.7 ± 0.3                    |
| Benzene                        | 2.3 ± 0.2  | 2.6 ± 0.4                                 | 0.4 ± 1.0                         | 6.4 ± 0.8 <sup>e</sup>                          | 12.3 ± 0.9                   |
| Toluene                        | 0.5 ± 0.1  | 0.5 ± 0.1                                 | 0.3 ± 0.1                         | 7.3 ± 0.9 <sup>e</sup>                          | 7.7 ± 0.9                    |
| Tropylidene                    | <0.1   | <0.1                                      | 0.6 ± 0.2                         | 8.4 ± 2.1                                       | 16.8 ± 3.3                   |
| Polymer                        | 80 ± 7   | 73 ± 5                                    | 93 ± 2                            |   |                              |

<sup>a</sup> Errors indicate the standard deviation obtained from several measurements. <sup>b</sup> Other volatile products found in very small yields (<0.4% absolute) in gas-phase studies were ethane, ethylene, allene, methylacetylene, 1,3-butadiene, and some unidentified  $\text{C}_7$  compounds. Two other volatile products having a total volatile yield of 2.9 and 3.7% in the liquid and solid phases, respectively, are as yet unidentified, but have boiling points and bonding properties very similar to that of benzene. <sup>c</sup> Expressed as per cent total volatile  $^{11}\text{C}$  labeled yield. Absolute yields were not determined in condensed phase. However, both Wolf<sup>9</sup> and Voigt<sup>4</sup> give 2.3% as the absolute toluene yield in the liquid phase. <sup>d</sup> Includes 1.6%  $^{11}\text{C}$ -labeled carbon dioxide. <sup>e</sup> Addition of 0.003% diphenylpicrylhydrazyl (DPPH) as scavenger caused no significant change in yield.

Results are shown in Table I. Benzene:toluene:tropylidene yield ratios are in reasonable agreement with those of Wolf and co-workers,<sup>3a,6</sup> with the exception of the reported benzene:toluene ratio in unscavenged benzene,<sup>3a</sup> and also agree with the most recent values of Voigt, *et al.*<sup>4</sup> Two  $\text{C}_4$  products not previously identified, vinylacetylene and diacetylene, were found in relatively high yields.

The new gas-phase data provide the most striking features. Absolute yields of volatile ( $\text{C}_1$ - $\text{C}_7$ ) products are always low, and polymeric material is correspondingly dominant. When the carbon atoms are thermalized by neon, this tendency is even more pronounced, with the lighter products almost disappearing altogether.

A primary conclusion is that atomic carbon is extremely reactive with benzene. This is indicated by an increase in the absolute yield of carbon monoxide of only about 5% when 5 mole % oxygen is added. The reactivity of benzene is, therefore, comparable to that of oxygen, which, in turn, is similar to that of the alkenes. (See Table II of ref 9.) It is not surprising that atomic carbon adds readily to benzene. Several stable adducts with  $\pi$ -bonded configurations, including that of the "open-sandwich" type, can be readily conceived, and others resulting from carbon atom insertion into the C-H bonds are also possible (see Figure 1).

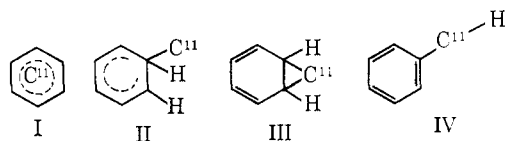
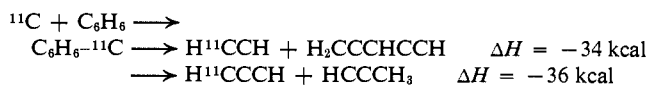


Figure 1. Some possible configuration of  $^{11}\text{C}$ - $\text{C}_6\text{H}_6$  adducts: (I)  $\pi$ -bond complex; (II, III) double bond additions; (IV) C-H bond insertion.

Adducts formed by carbon atoms with alkenes, such as ethylene<sup>9</sup> and cyclopentadiene,<sup>10</sup> frequently fragment to form stable compounds, but this appears to be more difficult in the benzene case. Such processes are energetically possible, even for benzene adducts formed by thermal carbon atoms, *e.g.*<sup>11</sup>

(9) J. Dubrin, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4747 (1964).

(10) T. Rose, C. MacKay, and R. Wolfgang, *ibid.*, **88**, 1064 (1966).



However, analogous reactions with alkenes are not only considerably more exoergic but, more important, require much less extensive internal rearrangement. Thus, the probability of fragmentation of the  $\text{C}_6\text{H}_6\text{-}^{11}\text{C}$  adduct is unusually low even when a hot carbon atom provides extra driving energy. When the carbon atom has been thermalized, such processes become almost negligible. Since there is no stable  $\text{C}_7\text{H}_6$  molecule to which the adducts may easily rearrange, they must eventually undergo bimolecular reaction. In view of their nature, addition of the intermediates to benzene to form polymer should readily occur. This propensity for forming polymers had previously been noted in aromatic systems<sup>2a,12</sup> and is obvious in the results of this work.

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(11) The energetics for the reactions are calculated using data of M. Cowperthwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962).

(12) A. P. Wolf and R. C. Anderson, *J. Am. Chem. Soc.*, **77**, 1608 (1955).

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### An Octahedral Complex Containing Three Four-Membered Chelate Rings

Sir:

1,3-Diphenyltriazene (I) (commonly referred to as diazoaminobenzene and abbreviated as Hdpt) forms a series of metal derivatives which have a structural form very closely related to that observed for copper-(II) acetate monohydrate.<sup>1,2</sup> For example, the crystal