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STRUCTURE AND REACTIVITY OF ORGANIC IONS IN GAS-PHASE RADIOLYSIS. VII. PROTON EXCHANGE REACTION IN ELECTROPHILIC AROMATIC SUBSTITUTION

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In the gas-phase radiolysis of a C_3H_8(100 mm)-C_6H_6(5 mm)-C_6D_6(5 mm) mixture, it has been shown that isopropylbenzene (IPB) formed by the attack of i-$C_3H_7^+$ ions to benzene consists of IPB-d_1, -d_2, -d_3, and -d_4 as well as IPB-d_0 and -d_5, indicating that a proton exchange between an intermediate complex and benzene molecules has occurred.

In previous papers of this series we reported results for the electrophilic aromatic substitution observed in the gas-phase radiolysis.[1,2] The most important feature of the gas-phase reaction compared with the analogous catalytic reaction in solution (Friedel-Crafts reaction) was the thermodynamically controlled isomer distribution of substituted products. Such a result has been attributed to the fact that an intermediate complex formed by the attack of a gaseous ion to an aromatic molecule exists as a free ion with excess vibrational energy and easily isomerizes to the most stable structure. Thus, in order to clarify the specific mode of the gas-phase electrophilic aromatic substitution it is important to obtain information on the behavior of the intermediate complex, benzenonium ion. In the present paper we wish to describe a proton exchange reaction of the intermediate complex with aromatic molecules and to explore the reaction mechanism of the gas-phase electrophilic aromatic substitution.

As is previously reported, in the gas-phase radiolysis of propane-benzene-O_2 mixtures, the dominant product is isopropylbenzene (IPB) formed by the reaction of an i-$C_3H_7^+$ ion from propane with benzene.[1b] In the present study a C_3H_8(100 mm)-C_6H_6(5 mm) C_6D_6(5 mm) mixture was irradiated by ^{60}Co γ rays at room temperature,[3] and the mass spectra of produced IPB and reactant benzene were determined with a directly coupled

gas chromatograph-mass spectrometer (Hitachi RMS-4 mass spectrometer), both of which are shown in Figures 1a and 1b, respectively. The dose rate and the total dose were 5.3×10^{15} eV/hr·μmol and 1.3×10^{17} eV/μmol for propane, respectively, and the conversion of benzene to IPB was 1.9%.

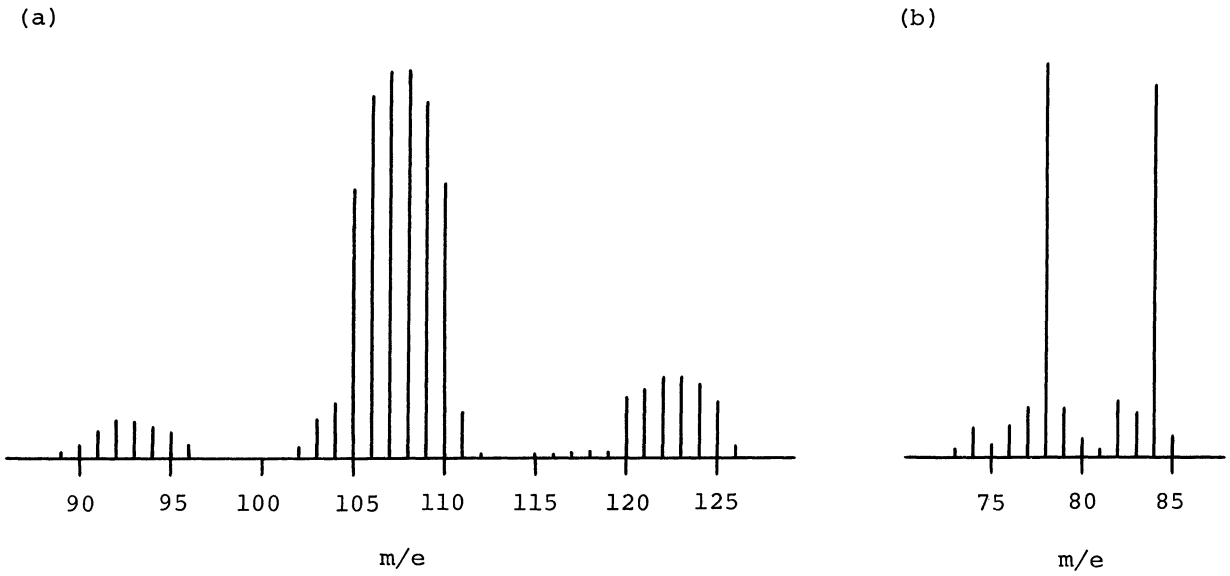

Figure 1. The partial mass spectra of (a) isopropylbenzene and (b) reactant benzene in the gas-phase radiolysis of a C_3H_8(100 mm)-C_6H_6(5 mm)-C_6D_6(5 mm) mixture.

The mass spectra in Figure 1 indicate that IPB-d_1, -d_2, -d_3, and -d_4 are formed as well as IPB-d_0 and -d_5, that is, an intermolecular H-D exchange has occurred, while reactant benzene almost exclusively consists of C_6H_6 and C_6D_6. The degree of the H-D exchange in produced IPB showed no dose effect within the range 1.3×10^{16} to 1.3×10^{17} eV/μmol, indicating that the H-D exchange occurs in the transition state of the substitution reaction. The experiment with a C_3H_8(100 mm)-C_6D_6(10 mm) mixture was also carried out, and in this case IPB-d_5 was almost exclusively formed. On the basis of these results it can be concluded that the H-D exchange occurs between the rings of the intermediate complex, isopropylbenzenonium ion, and reactant benzene; the much smaller degree of H-D exchange in reactant benzene may be attributed to the low conversion of benzene to IPB in the experimental condition. Considering the formation of the highly exchanged IPB's such as IPB-d_2 and -d_3, the following mechanism of the H-D exchange can be proposed.

$$C_3H_7^+ + C_6H_6 \longrightarrow \underset{(I)}{C_3H_7C_6H_6^+} \qquad (1)$$

$$I + C_6H_6 \longrightarrow \underset{(II)}{[C_3H_7C_6H_6^+ \cdot C_6H_6]} \quad (2)$$

$$II \rightleftharpoons \underset{(III)}{[C_3H_7C_6H_5 \cdot C_6H_7^+]} \quad (3)$$

Thus, the initially formed complex (I) attacks another benzene molecule to yield the π complex (II), and the proton is exchanged between the rings during the equilibrium reaction (3). The relative yields of the IPB's, $C_3H_7C_6H_5$, $C_3H_7C_6H_4D$, $C_3H_7C_6H_3D_2$, $C_3H_7C_6H_2D_3$, $C_3H_7C_6HD_4$, and $C_3H_7C_6D_5$, were approximately determined to be 1.0, 1.3, 1.4, 1.4, 1.3, and 1.0, respectively, from the mass spectrum (Figure 1a). Such higher yields of the H-D exchanged IPB's compared with those of IPB-d_0 and -d_5 indicate that the complex (I) exchanges its proton with more than one benzene molecule.[4] On this basis it may be considered that the complex (II) further reacts with another benzene molecule after the proton exchange occurred and loses the original one,

$$II + C_6H_6' \longrightarrow \underset{(II')}{[C_3H_7C_6H_6^+ \cdot C_6H_6']} + C_6H_6 \quad (4)$$

and the resulting complex (II') undergoes the proton exchange in the same manner as II.

It is reported that in Friedel-Crafts isopropylation only slight hydrogen exchange occurs unless a strong acid catalyst is used.[5] Thus, the exhaustive H-D exchange observed in the present study is attributable to the specificity of the gas-phase electrophilic aromatic substitution, that is, the intermediate complex is certainly excited and longlived because the attack of a gaseous free ion to an aromatic molecule is largely exothermic, and deactivating solvent molecules and a counter ion which acts as a proton acceptor are absent.

The effect of additives on the proton exchange reaction was investigated by adding 10 mm of O_2, NO, CO, N_2O, N_2, or Xe. The yield of IPB was not affected so much by the addition of these additives. However, when O_2, NO, CO, or N_2O was added, the proton exchange was almost completely inhibited, and only IPB-d_0 and -d_5 were formed; the mass spectrum of IPB produced in the presence of NO is shown in Figure 2. On the other hand, when N_2 or Xe was added, the mass spectrum of IPB was almost identical with that in the absence of the additive. Two explanations may be offered for this observation. First, and less likely, it may be suggested that O_2, NO, CO, and N_2O interact with the intermediate complex (I) and deactivate it while N_2 and Xe are inert to it. A second, and perhaps more likely, explanation is that in the presence of O_2, NO, CO, or N_2O

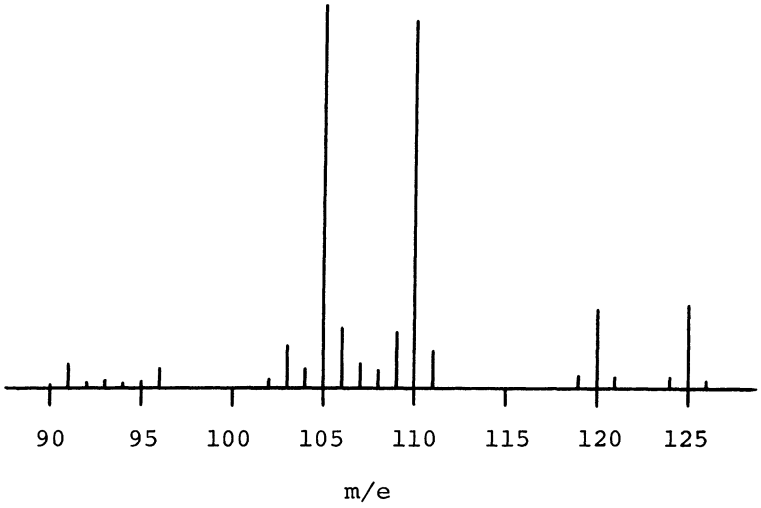

Figure 2. The partial mass spectrum of isopropylbenzene in the gas-phase radiolysis of a C_3H_8(100 mm)-C_6H_6(5 mm)-C_6D_6(5 mm)-NO(10 mm) mixture.

oxygenated products (H_2O, ROH, etc.) having large proton affinities are formed and abstract the proton from the intermediate complex before the proton exchange occurs. However, the precise mechanism of the inhibition of the proton exchange by the additives is obscure, and on this problem further investigations are required.

References and Notes

1) (a) Y. Yamamoto, S. Takamuku, and H. Sakurai, J. Amer. Chem. Soc., 91, 7192 (1969); (b) S. Takamuku, K. Iseda, and H. Sakurai, ibid., 93, 2420 (1971); (c) Y. Yamamoto, S. Takamuku, and H. Sakurai, Bull. Chem. Soc. Japan, 45, 255 (1972).

2) This subject has also been studied by other workers; (a) F. Cacace and E. Possagno, J. Amer. Chem. Soc., 95, 3397 (1973); (b) F. Cacace and P. Giacomello, ibid., 95, 5851 (1973).

3) The experimental procedures are the same as previously reported (see Ref. 1b). The effect of added O_2 on the yield of IPB was negligible and in this study any radical scavenger was not added.

4) If the proton exchange occurred between the complex (I) and only one benzene molecule, the sum of the yields of IPB-d_0 and -d_5 should be more than half of the total yield of IPB in the presence of equal amounts of C_6H_6 and C_6D_6.

5) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, J. Amer. Chem. Soc., 86, 1046 (1964).

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