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STRUCTURE AND REACTIVITY OF ORGANIC IONS IN GAS-PHASE RADIOLYSIS. IX. PROTON EXCHANGE REACTION IN METHANE-BENZENE MIXTURE

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In the gas-phase radiolysis of a CH_4(100 mm)-C_6H_6(5 mm)-C_6D_6(5 mm) mixture, an H-D exchange was observed in reactant benzene; the G value of the H-D exchanged benzenes was 69. The result has been attributed to the proton exchange reaction of the $C_6H_7^+$ ion with reactant benzene.

During the course of our investigations on the electrophilic aromatic substitution observed in the gas-phase radiolysis, it was suggested that the intermediate complex, benzenonium ion, exchange its proton with reactant aromatic molecules. The conclusion has been based on the result that in the radiolysis of a C_3H_8(100 mm)-C_6H_6(5 mm)-C_6D_6 (5 mm) mixture, isopropylbenzene, which is formed by the reaction of i-$C_3H_7^+$ ions derived from propane with benzene,[1] consisted of $C_3H_7C_6H_5$, $C_3H_7C_6H_4D$, $C_3H_7C_6H_3D_2$, $C_3H_7C_6H_2D_3$, $C_3H_7C_6HD_4$, and $C_3H_7C_6D_5$.[2] In the present study the radiolysis of a CH_4(100 mm)-C_6H_6 (5 mm)-C_6D_6(5 mm) mixture was examined in order to obtain further information on the proton exchange reaction between benzenonium ions and benzene molecules. In the high pressure mass spectrometry of methane the major product ions at higher pressures are CH_5^+ and $C_2H_5^+$,[3] which react with an aromatic hydrocarbon to yield a protonated aromatic ion along with a relatively small amount of an ethyl ion adduct.[4] It is expected that in the gas-phase radiolysis of a methane-benzene mixture these ionic reactions are important,

$$CH_4 \rightsquigarrow CH_5^+,\ C_2H_5^+ \qquad (1)$$

$$CH_5^+ \text{ (and } C_2H_5^+) + C_6H_6 \longrightarrow C_6H_7^+ + CH_4 \text{ (and } C_2H_4) \qquad (2)$$

$$C_2H_5^+ + C_6H_6 \longrightarrow C_2H_5C_6H_6^+ \qquad (3)$$

and the reaction 3 leads to the formation of ethylbenzene (EB).[5]

The experimental procedures were the same as those in the previous study.[2] The mixture was irradiated by a ^{60}Co γ ray source at room temperature, and the dose rate and the total dose were 2.0×10^{15} eV/hr·μmole and 4.8×10^{16} eV/μmole for methane, respectively After the irradiation, the mass spectra of produced EB and reactant benzene were measured and shown in Figures 1a and 1b, respectively. Figure 1a indicates that EB-d_1, -d_2, -d_3, and -d_4 are formed as well as EB-d_0 and -d_5, and the relative yields of these EB's increase in the order EB-d_0,-d_5 < EB-d_1,-d_4 < EB-d_2,-d_3. This result is similar to that for isopropylbenzene produced in the C_3H_8-C_6H_6-C_6D_6 mixture.[2]

On the other hand, as is shown in Figure 1b, the H-D exchange also occurred in reactant benzene to a certain extent in contrast with the case of the propane system, where reactant benzene almost exclusively consisted of C_6H_6 and C_6D_6.[2] The H-D exchanged

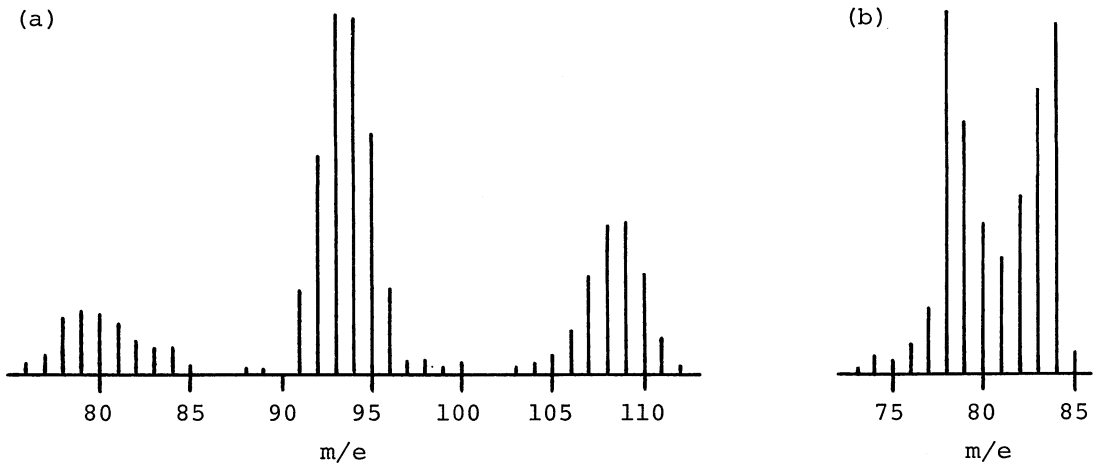
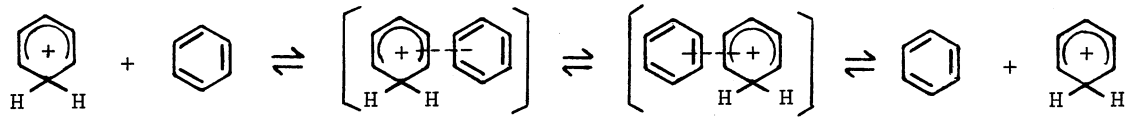


Figure 1. The partial mass spectra of (a) ethylbenzene and (b) reactant benzene in the gas-phase radiolysis of a CH_4(100 mm)-C_6H_6(5 mm)-C_6D_6(5 mm) mixture.

benzenes, C_6H_5D, $C_6H_4D_2$, $C_6H_3D_3$, $C_6H_2D_4$, and C_6HD_5, amounted to about 58% of reactant benzene, and their total G value was estimated to be 69, indicating that the exchange is a chain reaction. Since the conversion of benzene to EB was very low, 0.40%, in this experiment, it can be considered that the formation of the H-D exchanged benzenes by a reaction of an intermediate complex of the ethylation with benzene is not important. Thus, the result suggests that the proton exchange occurs between the $C_6H_7^+$ ion formed by the reaction 2 and benzene molecules as follows.



The difference in the H-D exchange in reactant benzene between the methane and propane systems is attributable to the fact that in the former the protonated benzene is the most abundant ion, while in the latter the protonation of benzene by the $C_3H_7^+$, the most abundant ion derived from propane at higher pressures, is of limited significance as is shown in a mass spectrometric study.[6]

References and Notes

1) S. Takamuku, K. Iseda, and H. Sakurai, J. Amer. Chem. Soc., 93, 2420 (1971).
2) Y. Yamamoto, S. Takamuku, and H. Sakurai, Chem. Lett., 849 (1974).
3) See for example, F. H. Field and M. S. B. Munson, J. Amer. Chem. Soc., 87, 3289 (1965).
4) M. S. B. Munson and F. H. Field, ibid., 89, 1047 (1967).
5) In the gas-phase radiolysis of a CH_4(100 mm)-C_6H_6(10 mm) mixture, ethylbenzene was formed with a G value of 0.47, and the yield was not reduced by the addition of a radical scavenger, NO. The ethylation of aromatic hydrocarbons has also been studied in other systems; see ref. 1 and Y. Yamamoto, S. Takamuku, and H. Sakurai, Bull. Chem. Soc. Japan, 45, 255 (1972).
6) L. I. Bone and J. H. Futrell, J. Chem. Phys., 47, 4366 (1967).

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