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Proton Exchange in Gas-Phase Isopropylation of Benzene and Toluene

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Abstract: 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 found that the isopropylbenzene (IPB) produced by the attack of the $i-C_3H_7^+$ ions derived from propane to benzene involves IPB- d_1 , - d_2 , - d_3 , and - d_4 as well as IPB- d_0 and - d_5 , and the relative yields of these IPBs increase with increasing degree of the H–D exchange. The result suggests that the proton exchange between the rings of the intermediate complexes, $C_3H_7C_6H_6^+$ and $C_3H_7C_6D_6^+$, and of the reactant benzene molecules occurs. The degree of the H–D exchange decreases with increasing temperature. The H–D exchange during the isopropylation has also been studied in propane–toluene and propane–benzene–toluene systems. The reversible π complex formation between the intermediate complexes and the reactant aromatic molecules followed by the proton exchange has been proposed.

Introduction

In previous papers we reported results for the electrophilic aromatic substitution occurring in gas-phase radiolysis.^{1,2} In the reaction the intermediate complex, an arenium ion, formed by the attack of a gaseous ion to an aromatic molecule, exists as a free ion with excess vibrational energy, and interesting features which differ from those in the analogous catalytic reaction in solution (Friedel–Crafts reaction) have been observed. One of them was the thermodynamically controlled isomer distribution of substituted products, which has been revealed by the dominant formation of meta isomers in the isopropylation and benzylation of alkylbenzenes.^{1a,b,c}

In the catalytic reaction in solution a counterion acts as a proton acceptor to the intermediate complex giving a neutral product. However, the fate of the intermediate complex in the gas-phase reaction has not been clear, and it is of interest to elucidate the mechanism of the electrophilic aromatic substitution in the absence of a counterion. During the course of our

investigations on this subject it was found that the proton exchange between the rings of the intermediate complex and of the reactant benzene occurs in the isopropylation of benzene.³ In the present study the proton exchange reaction in the isopropylation of benzene and toluene has been investigated in detail in order to obtain information about the fate of the intermediate complex in the gas-phase electrophilic aromatic substitution. The results of the present study have also provided significant information about the gas-phase ion–molecule reactions in aromatic systems which have been studied by many workers using mass and ion cyclotron resonance spectrometric techniques.⁴

Experimental Section

Materials. Benzene and toluene obtained from Wako Pure Chemical Industrial Co. were purified by the usual method. After the extensive distillations using a spinning-band column, the reagents were dried over a sodium mirror and stored in Pyrex tubes equipped with break-seals. Benzene- d_6 and toluene- d_8 , obtained from Merck Co.,

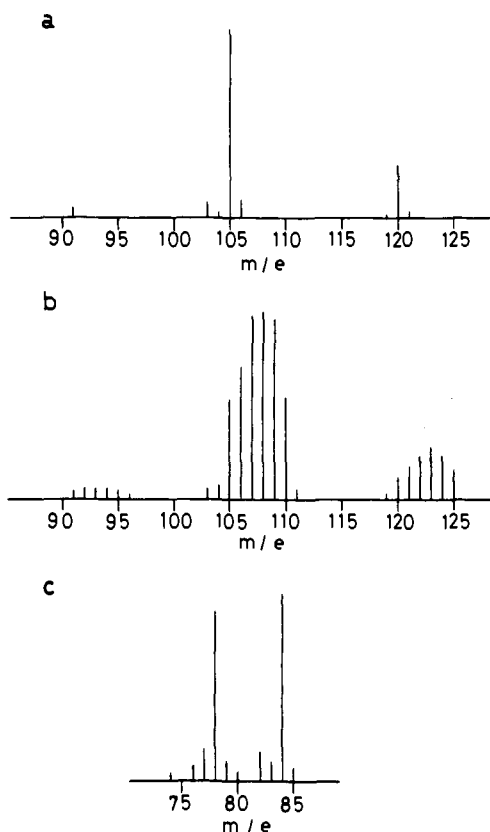


Figure 1. Mass spectra of (a) authentic isopropylbenzene, (b) isopropylbenzene produced in the radiolysis of the C_3H_8 (100 mm)- C_6H_6 (5 mm)- C_6D_6 (5 mm) mixture at room temperature, and (c) the reactant benzene remaining after the radiolysis. The m/e values of the parent ions are $C_3H_7C_6H_5^+$, 120; $C_3H_7C_6D_5^+$, 125; $C_6H_6^+$, 78; and $C_6D_6^+$, 84.

Germany, were used without purification except drying by a sodium mirror; the deuterium contents of the benzene- d_6 and toluene- d_8 were 99.5 and 99.6%, respectively. Propane obtained from Takachiho Shoji Co. was purified by several trap to trap distillations through sodium mirrors and stored in a storage bulb.

Procedures. The irradiation cells were Pyrex cylinders of ~ 120 mL in volume with a break-seal. After the cells were evacuated at a pressure of $\sim 10^{-6}$ mm for ~ 24 h with periodic heating by a hand torch, the propane vapor from the storage bulb was dried by passing through a sodium mirror and introduced into the cells at a pressure of 100 mm. The pressure of the sample was measured by a mercury manometer. Then, a known amount of the aromatic reagent, dried similarly, was introduced into the cells, in which propane was condensed at $-196^\circ C$, by a trap to trap distillation, and the cells were sealed.

The samples were irradiated with γ rays from a 7000-Ci ^{60}Co source at a dose rate of 4.1×10^{15} eV/h- μmol for propane. After irradiation, the cell was sealed to a high vacuum line, and the break-seal was ruptured after evacuation. The propane was pumped off at $-120^\circ C$, and then the residual liquid fraction was collected into a capillary. The liquid fraction was submitted to a directly coupled gas chromatograph-mass spectrometer (Hitachi RMS-4 mass spectrometer) in order to determine the deuterium distributions in the substituted product and the residual aromatic reagent.

Results

C_3H_8 (100 mm)- C_6H_6 (5 mm)- C_6D_6 (5 mm) Mixture. As is previously reported,^{1c} in the gas-phase radiolysis of propane containing a small amount of benzene the dominant product is isopropylbenzene (IPB) formed by the electrophilic substitution of benzene by an i - $C_3H_7^+$ ion which is known to be the major product ion from propane.⁵ In the present study the gas-phase radiolysis of the C_3H_8 - C_6H_6 - C_6D_6 mixture was carried out in order to investigate the H-D exchange during the substitution. The mass spectrum of the IPB produced in

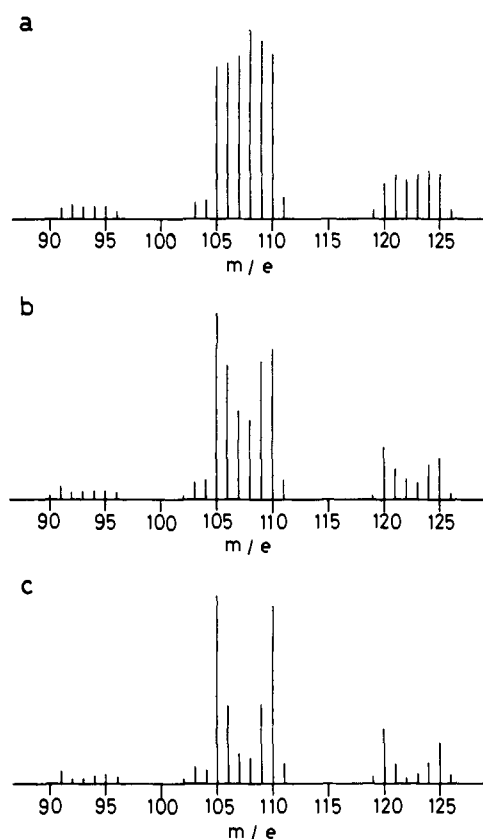


Figure 2. Mass spectra of isopropylbenzene produced in the radiolysis of the C_3H_8 (100 mm)- C_6H_6 (5 mm)- C_6D_6 (5 mm) mixture at higher temperatures: (a) $75^\circ C$, (b) $130^\circ C$, and (c) $185^\circ C$.

the radiolysis at room temperature at an irradiation time of 24 h is shown in Figure 1. In this figure the mass spectra of authentic IPB and of the reactant benzene remaining after the radiolysis are also shown. The mass spectrum of the product (Figure 1b) reveals that IPB- d_1 , - d_2 , - d_3 , and - d_4 are formed as well as IPB- d_0 and - d_5 (that is, intermolecular H-D exchanges occur) and that the relative yields are in the order IPB- d_0 , - $d_5 < IPB-d_1$, - $d_4 < IPB-d_2$, - d_3 . It can be considered that the H-D exchange is restricted to the aromatic ring since the IPB containing more than five deuterium atoms is not formed. On the other hand, the reactant benzene almost exclusively consists of C_6H_6 and C_6D_6 after the radiolysis (Figure 1c).

The relative intensities of the peaks in the mass spectrum of the product did not change with irradiation time from 3 to 24 h, while the yield increased linearly with irradiation time, indicating that the H-D exchange occurs in the course of the substitution process. Thus, it can be concluded that the proton exchange between the rings of the intermediate complex, $C_3H_7C_6H_6^+$ (1a) or $C_3H_7C_6D_6^+$ (1b), and of the reactant benzene occurs prior to the formation of the neutral product. The much smaller degree of the H-D exchange in the remaining benzene can be attributed to the low conversion of benzene to IPB under the experimental conditions; the conversion was 1.5% at the irradiation time of 24 h.

The effect of temperature on the H-D exchange in the product was investigated at temperatures up to $185^\circ C$, and the result is shown in Figure 2. The mass spectra indicate that the H-D exchange is suppressed by elevating temperature. On the other hand, the yield of the product was not affected by temperature; the G value of IPB was 0.92 ± 0.03 in the temperature range studied.

The proton exchange reaction during the isopropylation was further studied in the gas-phase radiolysis of mixtures con-

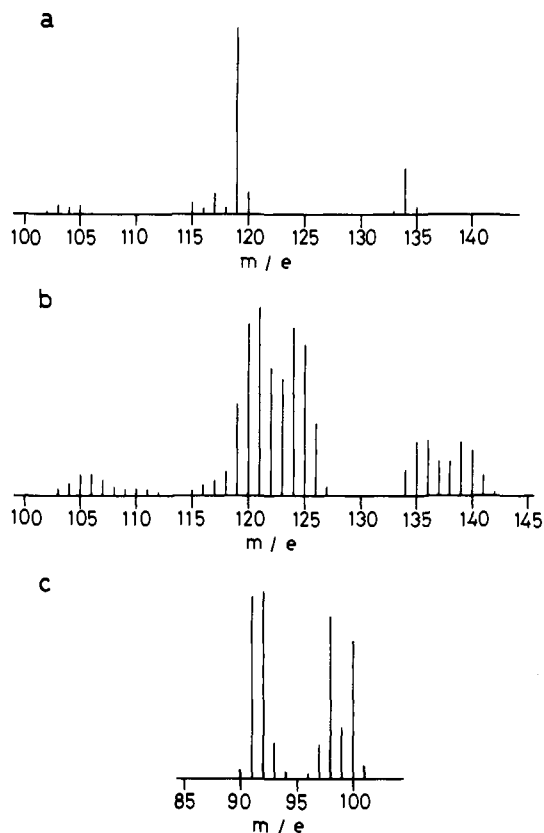


Figure 3. Mass spectra of (a) authentic isopropyltoluene, (b) isopropyltoluene produced in the radiolysis of the C_3H_8 (100 mm)- $CH_3C_6H_5$ (5 mm)- $CD_3C_6D_5$ (5 mm) mixture, and (c) the reactant toluene remaining after the radiolysis. The m/e values of the parent ions are $C_3H_7(CH_3)C_6H_4^+$, 134; $C_3H_7(CD_3)C_6D_4^+$, 141; $CH_3C_6H_5^+$, 92; and $CD_3C_6D_5^+$, 100.

taining toluene as an aromatic reactant at room temperature and an irradiation time of 24 h.

C_3H_8 (100 mm)- $CH_3C_6H_5$ (5 mm)- $CD_3C_6D_5$ (5 mm) Mixture. The H-D exchange was also observed in the isopropylation of toluene.⁶ The mass spectrum of the produced isopropyltoluene (IPT) is shown in Figure 3 together with the mass spectra of authentic IPT and of the reactant toluene remaining after the radiolysis. The mass spectra of IPTs shown in the figure are those of meta isomer; in the gas-phase isopropylation of toluene the meta isomer comprises ~60% of the produced IPT, and the mass spectra of the other isomers were similar to that of the meta isomer. The mass spectrum of the product (Figure 3b) indicates that all of the IPTs containing less than eight deuterium atoms are formed. It seems reasonable to assume that the H-D exchange does not occur in the methyl group of the product as well as in the isopropyl group. Thus, the IPTs produced via the proton exchange are considered to be $C_3H_7(CH_3)C_6H_4$ (M^+ , m/e 134), $C_3H_7(CH_3)C_6H_3D$ (135), $C_3H_7(CH_3)C_6H_2D_2$ (136), $C_3H_7(CH_3)C_6HD_3$ (137), and $C_3H_7(CH_3)C_6D_4$ (138), which are produced from the intermediate complex, $C_3H_7(CH_3)C_6H_5^+$ (IIa), and $C_3H_7(CD_3)C_6D_4$ (141), $C_3H_7(CD_3)C_6D_3H$ (140), $C_3H_7(CD_3)C_6D_2H_2$ (139), $C_3H_7(CD_3)C_6DH_3$ (138), and $C_3H_7(CD_3)C_6H_4$ (137), which are produced from the intermediate complex, $C_3H_7(CD_3)C_6D_5^+$ (IIb). The mass spectrum also shows that the relative yields are in the orders $C_3H_7(CH_3)C_6H_4 < C_3H_7(CH_3)C_6H_3D < C_3H_7(CH_3)C_6H_2D_2$ and $C_3H_7(CD_3)C_6D_4 < C_3H_7(CD_3)C_6D_3H < C_3H_7(CD_3)C_6D_2H_2$; that is, they increase with increasing degree of the H-D exchange; $C_3H_7(CH_3)C_6HD_3$ and $C_3H_7(CD_3)C_6H_4$ and $C_3H_7(CH_3)C_6D_4$ and $C_3H_7(CD_3)C_6DH_3$ have the same mass numbers, 137 and 138, respec-

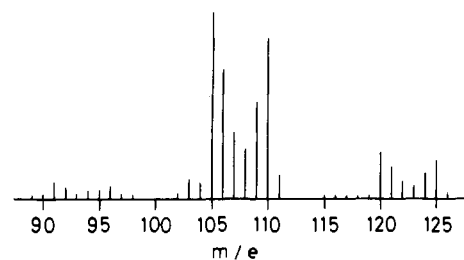


Figure 4. Mass spectra of isopropylbenzene produced in the radiolysis of the C_3H_8 (100 mm)- C_6H_6 (2.5 mm)- C_6D_6 (2.5 mm)- $CH_3C_6H_5$ (2.5 mm)- $CD_3C_6D_5$ (2.5 mm) mixture.

tively; and the relative yields of these IPTs are not known from the mass spectrum.

The degree of the H-D exchange in the reactant toluene after the radiolysis is negligibly small (Figure 3c) as well as that in the reactant benzene remaining after the radiolysis of the C_3H_8 - C_6H_6 - C_6D_6 mixture (Figure 1c).

C_3H_8 (100 mm)- C_6H_6 (2.5 mm)- C_6D_6 (2.5 mm)- $CH_3C_6H_5$ (2.5 mm)- $CD_3C_6D_5$ (2.5 mm) Mixture. The proton exchange reaction was investigated in the presence of benzene and toluene by measuring the mass spectra of the IPB and IPT produced in the gas-phase radiolysis of the propane-benzene-toluene mixture. As is shown in Figure 4, the degree of the H-D exchange in the IPB is apparently smaller than that in the case of the C_3H_8 - C_6H_6 - C_6D_6 system (Figure 1b). On the other hand, the mass spectrum of the IPT was almost identical with that in the C_3H_8 - $CH_3C_6H_5$ - $CD_3C_6D_5$ system (Figure 3c). In order to elucidate the effect of the partial pressure of benzene on the H-D exchange in the IPB, the radiolysis of a C_3H_8 (100 mm)- C_6H_6 (2.5 mm)- C_6D_6 (2.5 mm) mixture was carried out, and it was found that the mass spectrum of the IPB hardly differs from that of the product in the C_3H_8 (100 mm)- C_6H_6 (5 mm)- C_6D_6 (5 mm) system. Thus, the results suggest that the proton exchange during the isopropylation of benzene is suppressed by the addition of toluene, while that during the isopropylation of toluene is not affected by the addition of benzene.

C_3H_8 (100 mm)- C_6H_6 (5 mm)- $CD_3C_6D_5$ (5 mm) and C_3H_8 (100 mm)- C_6D_6 (5 mm)- $CH_3C_6H_5$ (5 mm) Mixtures. In order to clarify the above results, the gas-phase radiolysis of these mixtures was carried out, and the degree of the H-D exchange in the products was investigated. The results are shown in Figures 5 and 6. The mass spectra of the IPBs produced in these systems are shown in Figures 5a and 5b, and the superposition of these mass spectra is in Figure 5c, in which the peak height is shown as the sum of the relative intensities of the individual peaks of the mass spectra in Figures 5a and 5b. The result for the IPT is similarly shown in Figure 6; the mass spectra of the IPTs produced in these systems are shown in Figures 6a and 6b, and the superposition of these mass spectra is in Figure 6c. In the presence of benzene and toluene the proton exchange between the intermediate complexes, I ($C_3H_7C_6H_6^+$ and $C_3H_7C_6D_6^+$) and II ($C_3H_7(CH_3)C_6H_5^+$ and $C_3H_7(CD_3)C_6D_5^+$), and both the reactants, benzene and toluene, should occur. The H-D exchange in the IPB shown by the superposed mass spectrum (Figure 5c) is due to the proton exchange between the intermediate complex I and toluene. The superposed mass spectrum is almost identical with the mass spectrum of the IPB produced in the C_3H_8 - C_6H_6 - C_6D_6 - $CH_3C_6H_5$ - $CD_3C_6D_5$ system (Figure 4). Such a result indicates that in the presence of benzene and toluene the proton exchange between the intermediate complex I and benzene hardly occurs, while in the propane-benzene system the exhaustive proton exchange occurs as is shown in Figure 1b; that is, the H-D exchange in the IPB produced in the C_3H_8 - C_6H_6 - C_6D_6 - $CH_3C_6H_5$ - $CD_3C_6D_5$ system is almost exclu-

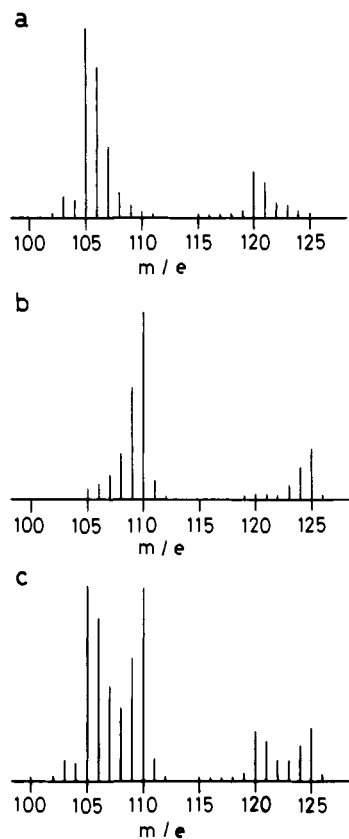


Figure 5. Mass spectra of isopropylbenzene produced in the radiolysis of (a) the C_3H_8 (100 mm)- C_6H_6 (5 mm)- $CD_3C_6D_5$ (5 mm) and (b) C_3H_8 (100 mm)- C_6D_6 (5 mm)- $CH_3C_6H_5$ (5 mm) mixtures, and (c) the superposition of these mass spectra.

sively due to the proton exchange between I and toluene. Thus, it is considered that in the presence of benzene and toluene the intermediate complex I predominantly reacts with toluene rather than with benzene. The result also indicates that the proton exchange between I and toluene occurs to less extent than that between I and benzene in the propane-benzene system (Figure 1b). On the other hand, the degree of the H-D exchange in the IPT shown by the superposed mass spectrum (Figure 6c) is apparently smaller than that in the IPT produced in the C_3H_8 - C_6H_6 - C_6D_6 - $CH_3C_6D_5$ - $CD_3C_6D_5$ system, which was almost identical with that in the case of the C_3H_8 - $CH_3C_6H_5$ - $CD_3C_6D_5$ system (Figure 3b) as described above. Since the H-D exchange in the IPT shown by the superposed mass spectrum is due to the proton exchange between the intermediate complex II and benzene, the result indicates that the H-D exchange in the IPT produced in the C_3H_8 - C_6H_6 - C_6D_6 - $CH_3C_6H_5$ - $CD_3C_6D_5$ system is predominantly due to the proton exchange between II and toluene, that is, in the presence of benzene and toluene the proton exchange between II and benzene occurs to less extent than that between II and toluene. This is also attributable to the fact that the reactivity of the intermediate complex with toluene is higher than that with benzene as described above.

Discussion

The results obtained in the present study demonstrate that the proton exchange between the rings of the intermediate complex and of the reactant aromatic molecule occurs during the electrophilic isopropylation by the free ion in the gas phase. It has been reported that in Friedel-Crafts isopropylation only slight hydrogen exchange occurs unless a strong catalyst is used.⁷ Thus, the exhaustive H-D exchange observed in the present study is attributable to the specificity of the reaction by a free ion in the gas phase; that is, the intermediate complex

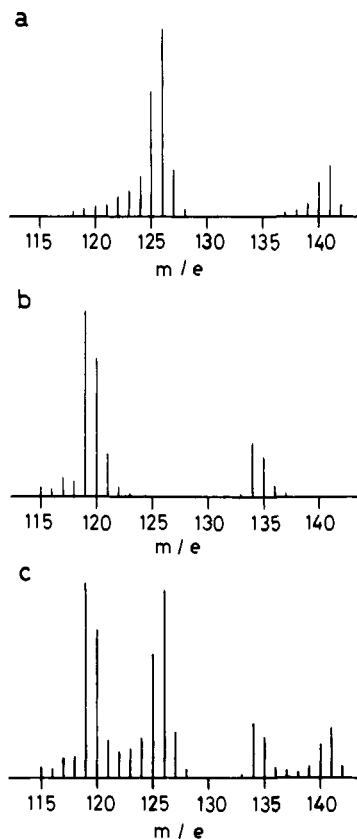
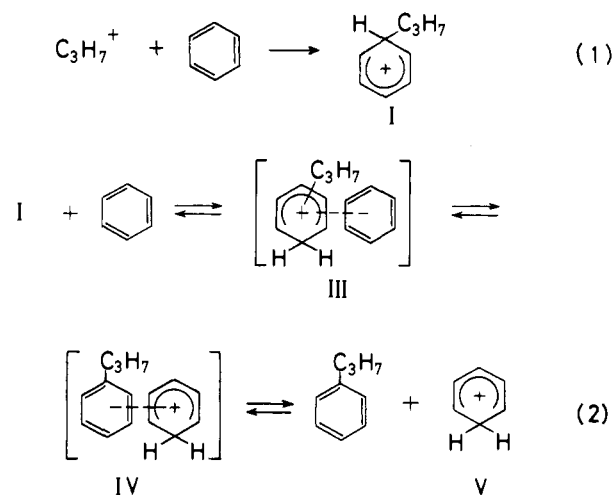


Figure 6. Mass spectra of isopropyltoluene produced in the radiolysis of (a) the C_3H_8 (100 mm)- C_6H_6 (5 mm)- $CD_3C_6D_5$ (5 mm) and (b) C_3H_8 (100 mm)- C_6D_6 (5 mm)- $CH_3C_6H_5$ (5 mm) mixtures, and (c) the superposition of these mass spectra.

is certainly excited and long-lived without a counterion which acts as a proton acceptor.

The mass spectrum of the IPB produced in the C_3H_8 - C_6H_6 - C_6D_6 system (Figure 1b) clearly shows that the relative yields increase with increasing degree of the H-D exchange. If the proton exchange occurred between the complex I and one benzene molecule, the sum of the yields of the H-D exchanged IPBs, IPB- d_1 , - d_2 , - d_3 , and - d_4 , should be less than half of the total yield because the mixture contains an equal amount of C_6H_6 and C_6D_6 . Thus, the result suggests that the proton exchange repeatedly occurs between the intermediate complex I and more than one benzene molecule. This can be successfully explained by the mechanism shown in eq 1 and 2



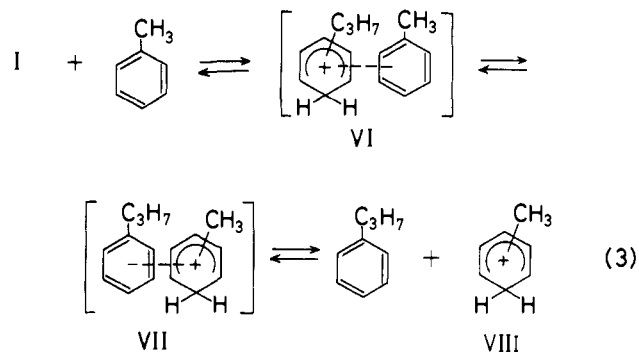
of the proton exchange reaction. The initially formed complex I attacks another benzene molecule to yield the π complex III,

and the proton exchange between the rings occurs during the equilibrium reaction between III and IV. Since the reactant benzene is in large excess of the product, IPB, the product hardly reacts with the arenium ion I or V once produced via the dissociation of IV. On the other hand, the complex I produced via the dissociation of III readily recombines with benzene, and the proton exchange repeatedly occurs between I and more than one benzene molecule. Thus, it is considered that the formation of the neutral product from the intermediate complex I is due to the proton transfer from I to the reactant benzene molecule via the reversible π -complex formation resulting in the intermolecular H-D exchange. The reversible π -complex formation between cations and neutral molecules has been studied in numerous systems including aromatic hydrocarbons by high pressure mass spectrometry.^{4g,h,8} It has been reported in the high pressure mass spectrometry of benzene in the presence of methane that the complex $C_6H_7^+ \cdot C_6H_6$ is not detected despite the large intensity of the $C_6H_7^+$ ion, which is produced by the reaction of CH_5^+ ion from methane with benzene.^{4h} On the other hand, the results of the present study suggest that arenium ions produce π complexes with neutral aromatic molecules in the gas-phase radiolysis. Such a difference in the results between the gas-phase radiolysis and the mass spectrometry may be attributed to the fact that the former is carried out at much higher pressure than the latter.

As is shown in Figure 2, the H-D exchange during the isopropylation of benzene is suppressed at higher temperatures. This result can be explained as follows. The proton transfer from the intermediate complex I to benzene is ~ 9 kcal/mol endothermic,^{4o,q} and the neutral product formation from I occurs more readily via the reversible π -complex formation at higher temperatures. Furthermore, the π complexes III and IV are considered to be more unstable at higher temperatures, as is commonly observed in the reversible π -complex formation by mass spectrometry.^{4g,h,8} Thus, the complex I gives the neutral product without the exhaustive proton exchange at higher temperatures.

The results obtained in the experiments with the mixtures containing both benzene and toluene suggest that the intermediate complexes, I and II, predominantly react with toluene rather than with benzene; that is, the reversible π -complex formation is sensitive to the basicity of the neutral aromatic molecule. The comparison of the mass spectra in Figures 1b and 5c reveals that the proton exchange between the intermediate complex I and toluene occurs to less extent than that between I and benzene. The reversible π -complex formation between I and toluene is shown in eq 3. Since the proton affinity of toluene is larger than that of benzene,⁴ⁱ the equilibrium 3 is displaced more to the right than the equilibrium 2; that is, the neutral product, IPB, is formed more readily in the equilibrium 3 than in the equilibrium 2, and the proton exchange between I and plural toluene molecules, which repeatedly occurs during the equilibrium $I + CH_3C_6H_5 \rightleftharpoons VI$, is limited.

Although the fate of the protonated aromatic reagents, V and VIII, is not clear at the present time, it seems reasonable



to assume that these ions produce the π complexes with the reactant aromatic molecules and then are neutralized.

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References and Notes

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