Mass Spectroscopic Studies on Ion-Molecule Reactions of CF_3^+ with Benzene and Toluene at Near-Thermal Energy

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Gas-phase ion-molecule reactions of CF_3^+ with C_6H_6 and $C_6H_5CH_3$ have been studied at near-thermal energy by using an ion-beam apparatus. The $C_7H_5F_2^+$(93.4±2.2%) and $C_6H_5^+$(6.6±2.2%) ions are produced for the reaction with C_6H_6, while the $C_8H_7F_2^+$(84.3±2.4%), $C_7H_8^+$(7.8±1.5%), and $C_7H_7^+$(7.9±2.0%) ions are formed for the reaction with $C_6H_5CH_3$.

The study on ion-molecule reactions of CF_3^+ with aromatic molecules is significant for understanding the reaction mechanism of carbocations, which are important intermediates in organic reactions.[1] Cipollini et al.[2] have measured final products of the gas-phase reactions of CF_3^+ with benzene derivatives in γ-radiolysis of CF_4–arene mixtures from the analysis of irradiated products by using gas chromatography. Since γ-radiolysis of CF_4–arene mixtures has been carried out at high total pressures of about 760 Torr, secondary reactions and collisional stabilization took part in the formation of the final products. In order to obtain information on initial product ions formed in ion-molecule reactions of CF_3^+ with aromatic hydrocarbons, we have performed here the first mass spectroscopic study on the reactions of CF_3^+ with benzene and toluene by using a low-pressure beam apparatus. On the basis of initial product ion distributions, the reaction mechanism is discussed.

The ion-beam apparatus used in the present study was similar to that reported previously.[3] In brief, the ground-state $Ar^+(^2P_{3/2})$ ions were generated by a microwave discharge of high purity Ar gas in a quartz flow tube. The CF_3^+ ions were produced by the thermal-energy charge-transfer (CT) reaction of Ar^+ with CF_4 with a rate coefficient of $(6.7 \pm 2.6) \times 10^{-10} cm^3 s^{-1}$.[4] After being completely thermalized by collisions with the buffer Ar gas, the reactant CF_3^+ ions were expanded into a low-pressure chamber through a molybdenum nozzle centered on the flow tube. The reagent gas was injected into the reaction zone from an orifice placed 5 cm downstream from the nozzle. The reactant and product ions were sampled through an orifice placed 3 cm further downstream and analyzed using a quadrupole mass spectrometer. Operating pressures were 0.5–1.2 Torr in the ion-source chamber, $(1.5–2.5) \times 10^{-3}$ Torr in the reaction chamber, and $(0.8–2.0) \times 10^{-5}$ Torr in the mass analyzing chamber. The partial pressures of reagent gases were $\leq 1 \times 10^{-4}$ Torr in the reaction chamber and $\leq 1 \times 10^{-6}$ Torr in the mass analyzing chamber. The detection limit of product ions in the mass spectrometer was 10^{-12} A.

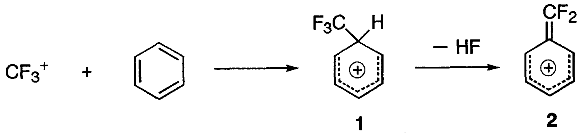
Under a typical Ar pressure in the flow tube (1.0 Torr), the Ar expansion was estimated to have a Mach number of 3.2 and a final velocity of 487 $m \cdot s^{-1}$ from known relations.[5] Since the difference in mass between Ar and CF_3^+ is small, the Ar/CF_3^+ velocity slip was negligibly small and the final CF_3^+ translational velocity was expected to be nearly that of the Ar carrier. Assuming a Boltzmann distribution of 300 K for reagents and a perpendicular direction between the ion-beam and the reagent gas, the relative velocities of the CF_3^+–C_6H_6, CF_3^+–$C_6H_5CH_3$ pairs were evaluated to be 564 and 553 $m \cdot s^{-1}$, corresponding to average center-of-mass translational energies of 60 and 63 meV, respectively. Therefore, the present experiments were carried out at only slightly hyperthermal energies.

For the reaction with benzene, electrophilic addition followed by HF elimination (1a) and hydride transfer (1b) are found with branching ratios of 93.4±2.2% and 6.6±2.2%, respectively:

$$CF_3^+ + C_6H_6 \longrightarrow C_7H_5F_2^+ + HF \qquad (1a)$$

$$\longrightarrow C_6H_5^+ + CF_3H + 0.45\ eV \qquad (1b)$$

Here, the ΔH° value for reaction (1b) is calculated from reported thermochemical data.[6] The $C_7H_5F_2^+$ ion must result from the following electrophilic addition followed by HF elimination.



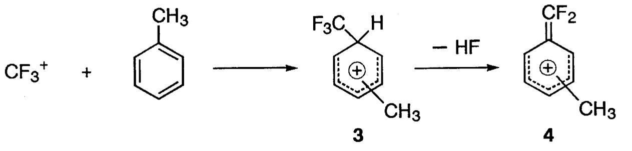
Scheme 1.

According to our recent study on the ion-molecule reactions of CF_3^+ with simple unsaturated aliphatic hydrocarbons,[7] only the initial adduct $C_3H_2F_3^+$ ion was found in the $CF_3^+ + C_2H_2$ reaction, while the initial adduct ion was absent in the $CF_3^+ + C_2H_4$ reaction. The major ion in the latter reaction is formed by elimination of HF from the adduct ion. On the basis of theoretical calculations of heats of formation of various isomers of adduct ions and their fragment ions formed through HF elimination, the difference between the above two reactions could be explained as a result of different stability of the intermediate adduct ions for HF elimination. By analogy with the above finding, the lack of initial adduct ion **1** may be also attributable to a higher stability of product ion **2** than that of adduct ion **1**. The available energy in the association leading to adduct ion **1** is gained by an electrostatic attraction between CF_3^+ and C_6H_6. The electrostatic energy between CF_3^+ and C_6H_6 was evaluated to be about 1 eV from the polarizability of benzene.[8] Thus, one reason for the lack of the adduct ion is the large additional available energy provided by the electrostatic attraction.

For the reaction with toluene, besides electrophilic addition followed by HF elimination (2a) and hydride transfer (2c), as found for the $CF_3^+ + C_6H_6$ reaction, CT process (2b) is observed. The branching ratios of (2a), (2b), and (2c) are evaluated to be 84.3±2.4%, 7.8±1.5%, and 7.9±2.0%, respectively.

$$\begin{aligned} CF_3^+ + C_6H_5CH_3 &\longrightarrow C_8H_7F_2^+ + HF, && (2a)\\ &\longrightarrow C_6H_5CH_3^+ + CF_3 && (2b)\\ &\longrightarrow C_7H_7^+ + CF_3H + 2.47\ \text{eV} && (2c) \end{aligned}$$

Process (2a) proceeds through the following reaction scheme.



Scheme 2.

Although *ortho-*, *meta-*, and *para-*$CH_3C_6H_4CF_2^+$ isomers can be formed in the CF_3^++$C_6H_5CH_3$ reaction, more stable *ortho-* and *para-*isomers due to electron-donating inductive effects of the CH_3 group will be the dominant product $CH_3C_6H_4CF_2^+$ ion. The lack of adduct ion **3** is probably attributable to the fact that product ion **4** is more stable than adduct ion **3**. By using the known polarizability and permanent dipole moment of toluene,[8] the electrostatic energy between CF_3^+ and $C_6H_5CH_3$ was estimated to be about 1 eV. The large electrostatic energy may support the complete elimination of HF from the adduct ion **3**.

The most significant difference between C_6H_6 and $C_6H_5CH_3$ is the occurrence of CT for $C_6H_5CH_3$ because of a lower ionization potential of $C_6H_5CH_3$ (8.82 eV) than that of C_6H_6 (9.25 eV).[6] The occurrence of CT (2b) at a collision energy of 63 meV suggests that the recombination energy (RE) of CF_3^+ is higher than 8.76 eV. Combining this data with a previous RE value ($\leq$ 8.90 eV) reported by Bombach et al.,[9] the RE value of CF_3^+ is estimated to be 8.76 eV $\leq$ RE(CF_3^+) $\leq$ 8.90 eV.

H^- abstraction is possible both from the benzene ring and from the side CH_3 chain in process (2c). Cipollini et al.[2] have reported that CF_3^+ may abstract a side-chain hydride ion from toluene based on the analysis of the final products. Although the electron-donating properties of the CH_3 group suppress the hydride abstraction from the benzene ring, its branching ratio is nearly the same as that for benzene. Therefore, it is reasonable to assume that H^- abstraction from toluene predominantly occurs at the side CH_3 chain, as reported by Cipollini et al.[2]

In summary, initial product ion distributions in ion-molecule reactions of CF_3^+ with benzene and toluene have been determined at near-thermal energy. Major product channels are electrophilic addition followed by HF elimination for both reagents. As minor product channels, hydride transfer occurs for benzene, while both hydride transfer and CT take place for toluene. Although Cipollini et al.,[2] have obtained α,α,α–trifluoromethylated products as final products of the CF_3^++ C_6H_6, $C_6H_5CH_3$ reactions, no direct evidence of the occurrence of a long-lived σ–complex from arene trifluoromethylation is available from the present study on the grounds of the analysis of the initial product ions obtained at low pressures. The stabilization of the initially hot adduct ions by collision with CF_4 probably occurred in their high-pressure experiments high pressures. The occurrence of hydride transfer and CT in the CF_3^++C_6H_6, $C_6H_5CH_3$ reactions is different from the product channels in the CF_3^++C_6H_6, $C_6H_5CH_3$ reactions at 0.1-10 mTorr,[10,11] where only electrophilic addition followed by HF elimination has been found.

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