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Mass-Spectrometric Study on Ion-Molecule Reactions of CF_3^+ with PhX (X = F, Cl, Br, I) at Near-Thermal Energies

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The branching ratios of product ions for the reactions of CF_3^+ with PhX (X = F, Cl, Br, I) have been determined by using an ion-beam apparatus. The main reaction channels are electrophilic addition to a benzene ring, followed by HF and HX elimination, and X^- abstraction reaction leading to phenyl cation. Charge transfer reaction leading to the parent cation was found only for PhI with the lowest ionization potential. Semi-empirical MNDO calculations of heats of formation of various intermediates and products were carried out to explore possible reaction mechanisms.

We have recently made systematic mass-spectrometric studies on ion-molecule reactions of a typical superacid, CF_3^+, with aromatic molecules in order to clarify the reactivity of carbocations for aromatic molecules in the gas phase. In our previous papers,[1—7] product ions and their branching ratios have been reported for monosubstituted benzenes carrying an amino, cyano, nitro, alkyl, hydroxy, alkoxy, or carbonyl group, pyridine, pyrrole, furan, or thiophene. In this paper, the results for monohalogenated benzenes PhX (X = F, Cl, Br, I) are reported. The initial branching ratios are determined from mass spectrometric analyses of the product ions. Semi-empirical MNDO calculations of heats of formation of possible intermediates and products are used to explore reaction mechanisms. The results obtained are compared with those for the CH_3^+/PhX (X = F, Cl) reactions reported by Morrison et al.[8]

Experimental

The experiments were performed on an ion-beam apparatus. The apparatus and its operation have been described previously.[9,10] In brief, ground-state $Ar^+(^2P_{3/2})$ ions were generated by a microwave discharge of high-purity Ar gas in a quartz flow tube. The reactant CF_3^+ ions were formed by the thermal-energy CT reaction of Ar^+ with CF_4. After being completely thermalized by collisions with Ar buffer gas, the reactant CF_3^+ ions were expanded into a low pressure chamber through a nozzle. The reagent gases were 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 by using a quadrupole mass spectrometer. Operating pressures were 0.5—1 Torr (1 Torr = 133.322 Pa) in the ion-source chamber, $1.5—2.5\times10^{-3}$ Torr in the reaction chamber, and $0.8—2.0\times10^{-5}$ Torr in the mass analyzing chamber. The partial pressures of the sample gases were $< 1\times10^{-5}$ Torr in the reaction chamber and $< 1\times10^{-6}$ Torr in the mass analyzing chamber. By using the same method as that reported previously,[3—7] average center-of-mass translational energies of the CF_3^+–PhX (X = F, Cl, Br, I) pairs under a typical Ar pressure in the flow tube (1.0 Torr) were evaluated to be 63, 65, 69, and 72 meV, respectively. Thus, the present experiments were carried out at only slightly hyperthermal energies.

The heats of formation are known for the reactant ion, reagent, and some stable products obtained in this work.[11] However, there are many species whose ΔH_f values are unknown. These values were calculated by using the semi-empirical MNDO method (MOPAC Ver. 6.0) in order to describe the potential-energy diagrams.

Results and Discussion

Mass Spectrum and Product Ion Distributions. Figures 1(a)—(d) show mass spectra obtained from the ion-molecule reactions of CF_3^+ with PhX (X = F, Cl, Br, I), where (A^+–HX) represents a product ion formed by the elimination of HX from an initial adduct ion A^+(= CF_3^+ + PhX). The most strong peaks are the reactant CF_3^+ ion with $m/z = 69$. The $C_6H_5^+$ ion with $m/z = 77$ and the (A^+–HX) ions with $m/z = 145$ are found in all spectra. Besides these ions, the (A^+–HF) ions are found for PhCl and PhBr. Their peaks consist of two isotopic components of ^{35}Cl (76%) and ^{37}Cl (24%) and ^{79}Br (51%) and ^{81}Br (49%). The (A^+–HX) ion is equal to the (A^+–HF) ion for X = F, so that the two elimination processes can not be distinguished for PhF. Although the (A^+–HF) ion is absent for PhI, the parent $C_6H_5I^+$ ion is detected. The observed product ions and their branching ratios are given in Table 1. It is clear from Table 1 that the total branching ratios of (A^+–HF) and (A^+–HX) are comparable with that of $C_6H_5^+$ for PhX (X = F, Cl, Br). The branching ratio of (A^+–HX) increases with increasing the mass of X for PhX (X = Cl, Br, I).

Reaction Mechanism. The formation mechanism of (A^+–HX) is shown in Scheme 1. The (A^+–HF) ions **2a**—**2c**

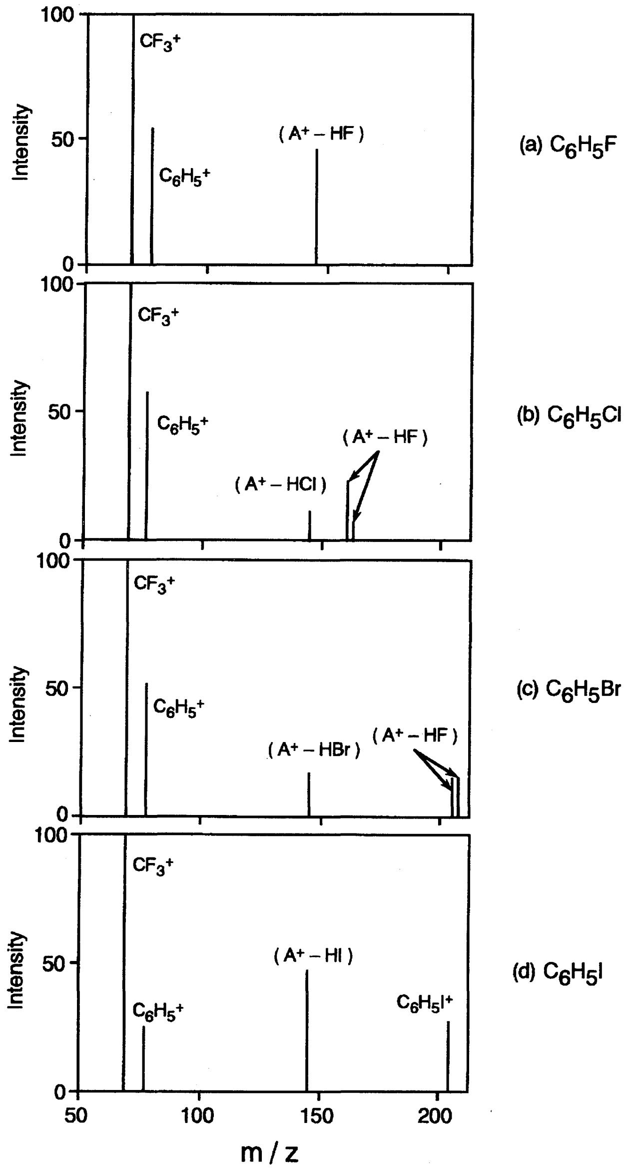


Fig. 1. Mass spectra of the CF_3^+/PhX (X = F, Cl, Br, I) reactions.

are formed through electrophilic addition to a benzene ring with a loss of HF. Possible structures of (A^+–HX) are **3a**—**3c** and **4a**—**4c**. The former ions are produced through a direct HF elimination from σ-complexes **1a**—**1d**, while the latter ions are produced through the HX elimination accompanied by F^- transfer. The phenyl cation **5** is produced via X^- abstraction from PhX, as shown in Scheme 2.

Figures 2, 3, 4, and 5 show potential-energy diagram of reaction pathways of Schemes 1 and 2 obtained from the thermochemical data of CF_3^+, Ph^+, PhX, HF, and HX[11] and calculated ΔH_f values of the other intermediates and products. From the energy diagrams, the following reaction mechanisms are deduced.

(1) Since the formation of (trifluoromethy)phenyl cations **3a**—**3c** is endoergic, they can be excluded from possible products. It is therefore concluded that the structures of (A^+–HF) and (A^+–HX) are **2a**—**2c** and **4a**—**4c**, respectively.

(2) Initial adduct ions have been observed in the reactions

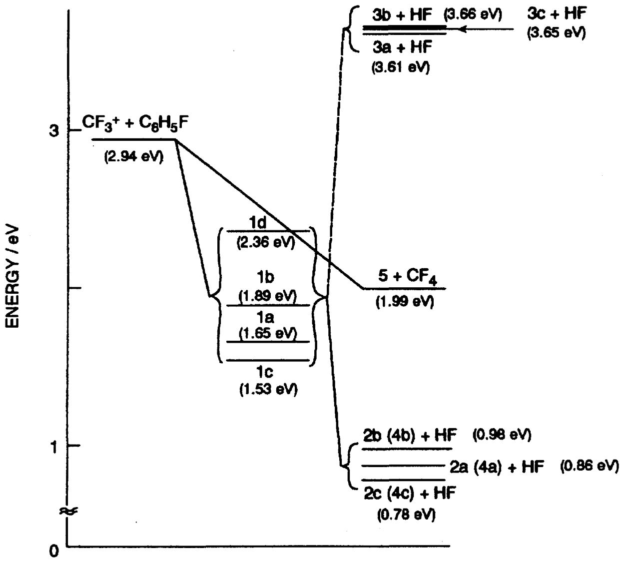


Fig. 2. A potential-energy diagram for the electrophilic CF_3^+-addition followed by HF elimination pathways in the CF_3^++PhF system.

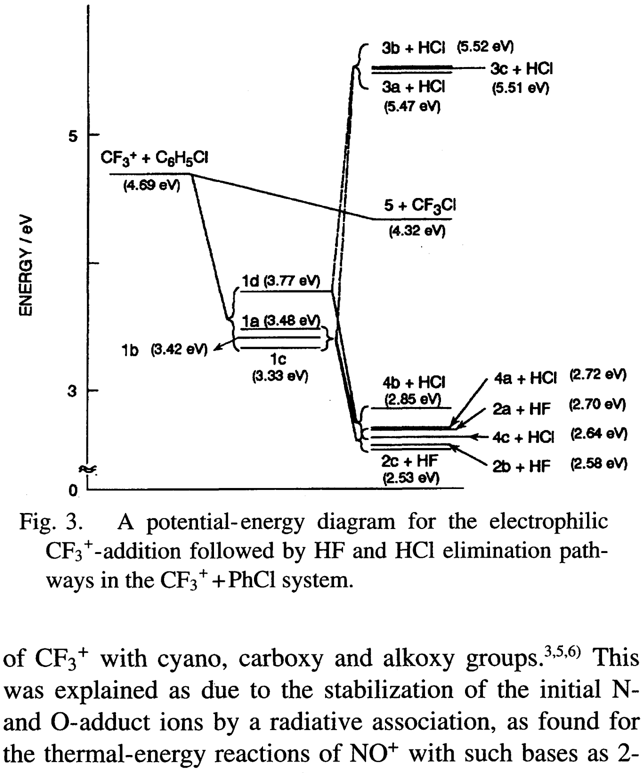


Fig. 3. A potential-energy diagram for the electrophilic CF_3^+-addition followed by HF and HCl elimination pathways in the CF_3^++PhCl system.

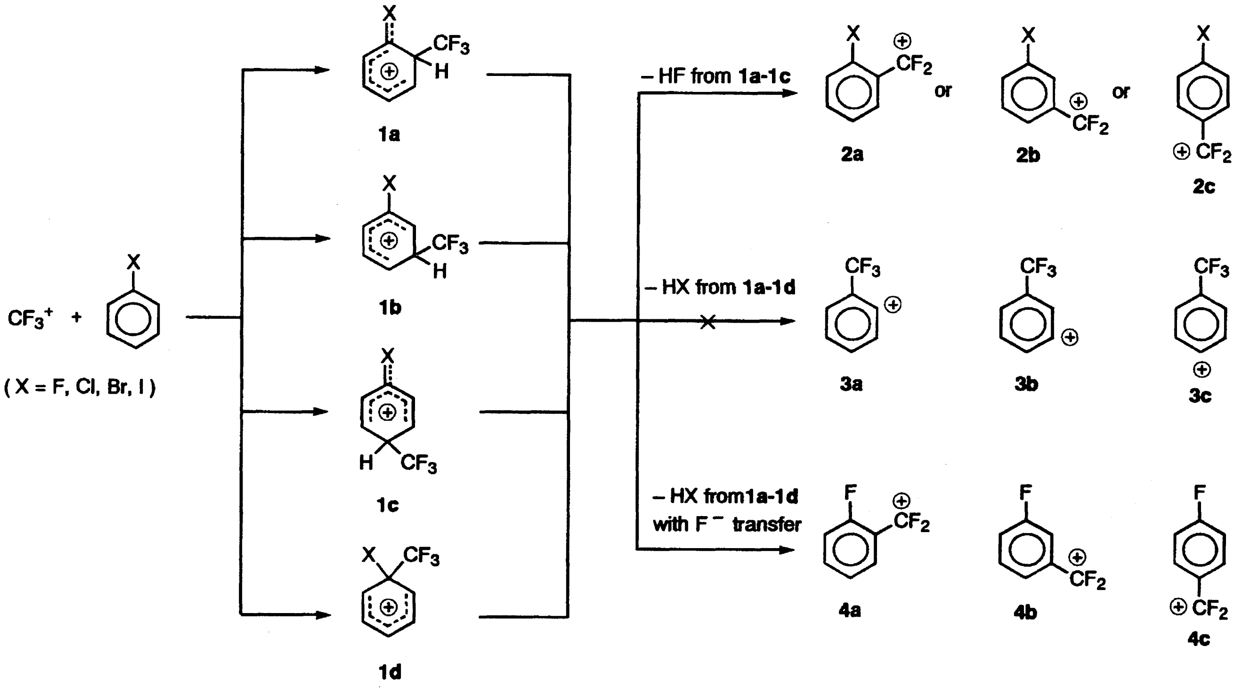
of CF_3^+ with cyano, carboxy and alkoxy groups.[3,5,6] This was explained as due to the stabilization of the initial N- and O-adduct ions by a radiative association, as found for the thermal-energy reactions of NO^+ with such bases as 2-butanone and 3-pentanone.[12] In the present study, no initial adduct ions could be detected, indicating such a radiative association process is insignificant for σ-complexes **1a**—**1d**. It is clear from Figs. 2, 3, 4, and 5 that about 0.6—1.7 eV is released in the formation of σ-complex through the electrophilic addition. These excess energies are used to eliminate HX and HF molecules from the σ-complexes in the present reaction system.

(3) For the reactions with PhX (X = Cl, Br, I), the energies of **4a**—**4c**+HX become high in comparison with those of **2a**—**2c**+HF with increasing the mass of X. Therefore,

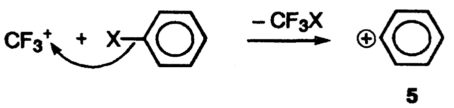
Table 1. Products and Their Branching Ratios for the CF_3^+/C_6H_5X (X = F, Cl, Br, I) and CH_3^+/C_6H_5X (X = F, Cl) Reactions

Reagent	CF_3^+ (This work)		CH_3^+ (Ref. 8)	
	8.9 eV		9.84 eV	
Ionization potential/eV[a]	Ionic product[b]	Branching ratio/%	Ionic product	Branching ratio/%
C_6H_5F	$(A^+\text{-}HF)$	45.6 ± 3.9	$(A^+\text{-}H_2)$	7
9.20	$C_6H_5^+$	54.4 ± 3.9	$(A^+\text{-}HF)$	3
			$C_6H_5F^+$	90
C_6H_5Cl	$(A^+\text{-}HF)$	30.5 ± 3.7	$(A^+\text{-}H_2)$	1
9.06	$(A^+\text{-}HCl)$	11.6 ± 1.5	$(A^+\text{-}HCl)$	14
	$C_6H_5^+$	57.8 ± 3.9	$C_6H_5Cl^+$	52
			$C_6H_5^+$	33
C_6H_5Br	$(A^+\text{-}HF)$	31.0 ± 2.4		
8.98	$(A^+\text{-}HBr)$	17.0 ± 1.3		
	$C_6H_5^+$	52.0 ± 3.7		
C_6H_5I	$(A^+\text{-}HI)$	47.3 ± 1.6		
8.69	$C_6H_5I^+$	27.6 ± 2.0		
	$C_6H_5^+$	25.1 ± 0.9		

a) Ref. 11. b) The $(A^+\text{-}M)$ ion represents an ion produced from the elimination of M from an initial adduct ion A^+.



Scheme 1.



Scheme 2.

the latter products with heavy X atoms are more favorable, if the reaction pathways are controlled thermochemically. However, irreversible elimination processes leading to **4a**—**4c** and **2a**—**2c** are expected to be controlled kinetically, where the height of activation barriers dominates the reaction pathways. In the present study, absolute values of activation barriers required for HX and HF eliminations could not be determined. However, the activation barriers for the HX elimination are expected to decrease with decreasing the dissociation energy of C–X: C–F (105 kcal mol^{-1}) > C–Cl (79 kcal mol^{-1}) > C–Br (67 kcal mol^{-1}) > C–I (57 kcal mol^{-1}).[13] Therefore, the branching ratios of **4a**–**4c** become large in comparison with those of **2a**–**2c** with increasing the mass of X.

(4) The X^- abstraction pathways leading to **5** compete with the electrophilic addition leading to σ-complexes

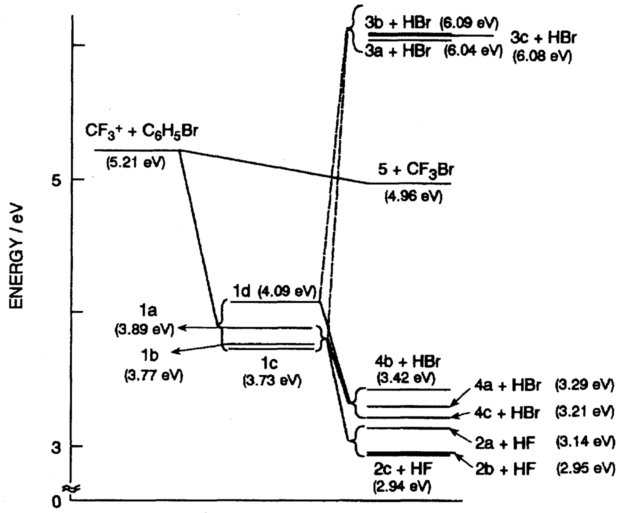


Fig. 4. A potential-energy diagram for the electrophilic CF_3^+-addition followed by HF and HBr elimination pathways in the CF_3^+ + PhBr system.

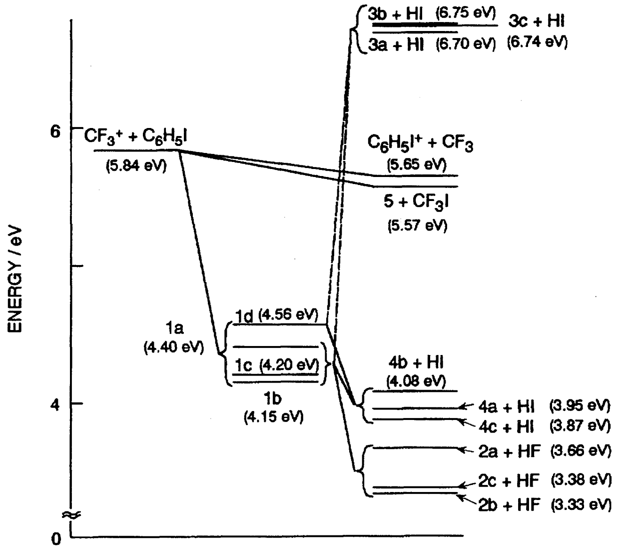


Fig. 5. A potential-energy diagram for the electrophilic CF_3^+-addition followed by HF and HI elimination pathways in the CF_3^+ + PhI system.

1a—1d. Although the energy of **5** + CF_4 is lower than the reactant by 0.95 eV, the energies of **5** + CF_3X (X = Cl, Br, I) are lower than the reactants by only 0.25—0.37 eV. The detection of **5** from PhX (X = Br, I) implies that high activation barriers are absent in the simple X^- abstraction pathways leading to **5**.

A Comparison with the Results for the CH_3^+/PhX (X=F, Cl) Reactions. It is of interest to compare the present results with those of a typical carbocation, CH_3^+, with a higher recombination energy (9.84 eV) than that of CF_3^+ (8.9 eV). For comparison, the reported branching ratios of the product ions in the CH_3^+/PhX (X = F, Cl) reactions are also given in Table 1. It is clear from Table 1 that dominant product channels of the CF_3^+/PhX (X = F, Cl) reactions are electrophilic addition/HF or HCl-elimination processes and the X^- abstraction reaction. The ionization potentials of PhX are shown in the first column of Table 1. No charge-transfer channel was found because the ionization potentials of PhX (X = F, Cl) are higher than the recombination energies of CF_3^+. On the other hand, the main product channel of the CH_3^+/PhX (X = F, Cl) reactions is charge-transfer leading to parent cations, because the recombination energy of CH_3^+ is higher than the ionization potentials of PhX (X = F, Cl).

In the CF_3^+/PhX (X = Cl, Br, I) reactions, the branching ratio of (A^+–HX) increases with increasing the mass of X. In the CH_3^+/PhX (X = F, Cl) reactions, the branching ratio of (A^+–HCl) is also larger than that of (A^+–HF). These results indicate that the branching ratio of (A^+–HX) in both reactions increases with increasing the mass of X, due to the decrease in the bond dissociation energy of C–X.

Conclusion

In this study, the ion-molecule reactions of CF_3^+ with PhX (X = F, Cl, Br, I) have been studied using a thermal-energy ion-beam apparatus. The reaction mechanisms are summarized in Table 2. In the present reaction system, three types of reaction processes are found. They are electrophilic attack on a benzene ring or a halogen atom and charge-transfer. Halogen atoms have both electron-withdrawing properties due to inductive effects and electron-releasing properties due to resonance effects.[14] The concurrence of electrophilic attack on a benzene ring and a halogen atom implies that both properties operate in the present reaction system. Similar substituent effects on the reaction mechanism has been found for PhOH and $PhOCH_3$,[5] in which electrophilic attacks on both the benzene ring and the substituent occur. The charge-transfer channel was only found for PhI. The lack of charge-transfer channels for PhF, PhCl, and PhBr is the lower recombination energy of CF_3^+ than their ionization potentials, as shown in

Table 2. Mechanisms for the CF_3^+/C_6H_5X (X = F, Cl, Br, I) Reactions

Reagent	Ionization potential/eV	Branching ratio of each reaction[a]/%	
		Electrophilic reaction	Charge transfer
C_6H_5F	9.20	54.4 (R[b]), 45.6 (S[c])	
C_6H_5Cl	9.06	42.1 (R), 57.8 (S)	
C_6H_5Br	8.98	48.0 (R), 52.0 (S)	
C_6H_5I	8.69	47.3 (R), 25.1 (S)	27.6

a) Experimental error is within ±10%. b) Electrophilic attack on a benzene ring. c) Electrophilic attack on a substituent.

Table 1.

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