Mass-Spectrometric Study on Ion–Molecule Reactions of CF_3^+ with PhX [X=H, CH_3, and C_2H_n (n=1,3,5)] at Near-Thermal Energy

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The gas-phase ion-molecule reactions of CF_3^+ with benzene, toluene, ethylbenzene, styrene, and ethynylbenzene have been studied at near-thermal energy using an ion-beam apparatus. The major product channels are electrophilic addition followed by HF elimination for benzene (93.4±2.2%), toluene (84.3±2.4%), and ethynylbenzene (76.9±0.9%). The dominant product channels for ethylbenzene are electrophilic addition followed by C_2H_4 and C_2H_4+HF eliminations (78.9±4.7%), while those for styrene are electrophilic addition followed by one or two HF eliminations and $C_2H_2F_2$ elimination (91.7±5.4%). Only ethynylbenzene gives an initial adduct ion with a small branching ratio of 6.2±0.4%. As minor product channels, hydride transfer occurs for benzene (6.6±2.2%) and toluene (7.8±1.5%), and charge transfer takes place for toluene (7.9±2.0%), styrene (8.3±1.4%), and ethynylbenzene (6.2±0.4%). The reaction mechanisms are discussed on the basis of product ion distributions and semi-empirical calculations of potential energies of reaction pathways.

There has been continuing interest in the reactions of carbocations with unsaturated molecules because of their importance in organic reactions and polymer syntheses.[1] In order to clarify the ion–molecule reactions of carbocations with unsaturated hydrocarbons in the gas phase, we have recently studied the ion–molecule reactions of a typical superacid, CF_3^+, with acetylene, ethylene, and propylene at near-thermal energy by using an ion-beam apparatus.[2] The initial product ion distributions and reaction rate coefficients were determined. Only electrophilic addition to a C≡C triple bond was found for the reaction with C_2H_2.

$$CF_3^+ + C_2H_2 \rightarrow C_2H_2CF_3^+ \quad (100\%) \qquad (1)$$

For the reaction with C_2H_4, the following four product channels were found.

$$CF_3^+ + C_2H_4 \rightarrow C_3H_3F_2^+ + HF \quad (62\pm3\%) \qquad (2a)$$

$$\rightarrow C_2H_3^+ + CF_3H \quad (29\pm4\%) \qquad (2b)$$

$$\rightarrow CHF_2^+ + C_2H_3F \quad (7\pm2\%) \qquad (2c)$$

$$\rightarrow CH_2F^+ + C_2H_2F_2 \quad (2\pm1\%) \qquad (2d)$$

Electrophilic addition followed by molecular elimination [channels (2a), (2c), and (2d)] and hydride transfer [channel (2b)] were found for C_2H_4. On the basis of semi-empirical calculations of potential energies for the electrophilic CF_3^+-addition/HF-elimination pathways, the lack of the HF elimination channel in the CF_3^+/C_2H_2 reaction was attributed to the formation of a $CHFC\dot{H}CF_2^+$ isomer ion (which is more stable than the $C_3HF_2^+$+HF products) by F^- transfer from the initial adduct $CHCHCF_3^+$ ion. The lack of the initial adduct ion in the CF_3^+/C_2H_4 reaction was explained by the instability of the adduct $C_3H_4F_3^+$ ion for HF elimination. The reaction rate coefficients for the three simple unsaturated aliphatic hydrocarbons amounted to ≥46% of the total collision rate coefficients estimated from either the Langevin theory or the parameterized trajectory model.

The ion–molecule reactions of CCl_3^+ with benzene, toluene, ethylbenzene, and styrene have been studied in the gas phase by Virin et al.[3—5] at low operating pressures of 10^{-4}—10^{-2} Torr (1 Torr=133.322 Pa) and by Stone and Moote[6] at high operating pressures of 1—3 Torr. Only electrophilic addition followed by an HCl elimination process (3a) has been found for the CCl_3^+/C_6H_6 reaction at 10^{-4}—10^{-2} Torr, while not only process (3a), but also an initial electrophilic-addition process (3b) has been found at 1—3 Torr due to collisional stabilization of the initial adduct ion.

$$CCl_3^+ + C_6H_6 \rightarrow C_7H_5Cl_2^+ + HCl \qquad (3a)$$

$$\rightarrow C_7H_6Cl_3^+ \qquad (3b)$$

The $CCl_3^+/PhCH_3$ and CCl_3^+/PhC_2H_5 reactions at 10^{-4}—10^{-2} Torr provided only the electrophilic CCl_3^+-addition/HCl-elimination products.

$$CCl_3^+ + C_6H_5CH_3 \rightarrow C_8H_7Cl_2^+ + HCl \quad (4)$$

$$CCl_3^+ + C_6H_5C_2H_5 \rightarrow C_9H_9Cl_2^+ + HCl \quad (5)$$

Although the CCl_3^+/PhC_2H_3 reaction has not been studied at low pressures, the following three product channels have been found at 1—3 Torr.

$$CCl_3^+ + C_6H_5C_2H_3 \rightarrow C_7H_6Cl^+ + C_2H_2Cl_2 \quad (63\%) \quad (6a)$$

$$\rightarrow C_9H_8Cl_3^+ \quad (31\%) \quad (6b)$$

$$\rightarrow C_9H_7Cl_2^+ + HCl \quad (6\%) \quad (6c)$$

A reaction scheme of the dominant process (6a), which proceeds through electrophilic addition to the substituent followed by $C_2H_2Cl_2$ elimination, has been proposed.[6]

In the present study, the ion-molecule reactions of CF_3^+ with benzene, toluene, ethylbenzene, styrene, and ethynylbenzene have been investigated using an ion-beam apparatus. The reaction mechanisms are discussed based on the initial product ion distributions and semi-empirical calculations of heats of formation of product ions. The results obtained are compared with the previous data for the reactions of CF_3^+ with unsaturated hydrocarbons[2] and those of CCl_3^+ with benzene, toluene, ethylbenzene, and styrene.[3—6] Preliminary results for benzene and toluene have already been communicated,[7] although no theoretical approach to explain the reaction mechanism has been presented.

Experimental

The ion-beam apparatus used in the present study was similar to that reported previously.[2,7] 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. CF_3^+ ions were produced by the thermal-energy CT reaction of Ar^+ with CF_4.[8] 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 nozzle. 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—1.0 Torr 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,[2,7] the relative velocities of the CF_3^+–C_6H_6, CF_3^+–$PhCH_3$, CF_3^+–PhC_2H_5, CF_3^+–PhC_2H_3, and CF_3^+–PhC_2H pairs under a typical Ar pressure in the flow tube (1.0 Torr) were evaluated to be 564, 553, 545, 546, and 547 $m\,s^{-1}$, respectively corresponding to average center-of mass translational energies of 60—64 meV. Therefore, the present experiments were carried out at only slightly hyperthermal energies.

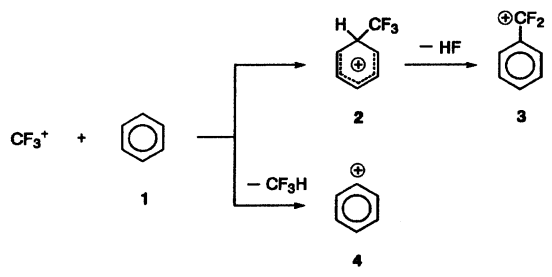
In our previous study on the ion–molecule reactions of CF_3^+ with C_2H_2, C_2H_4, and C_3H_6,[2] not only the product ion distributions, but also the reaction rate coefficients were determined by measuring the dependence of the reactant ion intensity on the sample flow rate. In the present experiment, the sample gas pressures were too low to determine the reaction rate coefficients.

The heats of formation are known for the reactant ion, reagents, and some stable products obtained in this work.[9] However, there are many species whose $\Delta H°$ values are unknown. These values were calculated by using a semi-empirical MNDO method (MOPAC Ver. 6.0) in order to describe potential-energy diagrams. The $\Delta H°$ values of $C_6H_5^+$ and C_6H_5F were calculated in order to estimate the uncertainties of the calculated values. The calculated values for $C_6H_5^+$ and C_6H_5F are 1185 and -106 $kJ\,mol^{-1}$, which are in reasonable agreement with reported experimental data of 1142 and -116 $kJ\,mol^{-1}$, respectively.[9] It is thus concluded that the MNDO values are useful to discuss the reaction pathways.

Results and Discussion

Benzene and Toluene: The observed product channels and their branching ratios are summarized in Table 1. For the reaction with benzene, electrophilic addition followed by HF elimination (7a) and hydride transfer (7b) were found. The reaction mechanism of processes (7a) and (7b) is shown in Scheme 1. Although we have reported that a positive charge in **3** is localized on a carbon atom of the benzene ring, it was found to be dominantly localized in the carbon atom of the CF_2 substituent on the basis of an MNDO calculation of the charge density. Therefore, the latter dominant structure is shown in Scheme 1. We have predicted that the lack of initial adduct ion **2** is due to its instability for HF elimination by analogy with the theoretical calculation of the electrophilic CF_3^+-addition/HF-elimination pathways in the CF_3^+/C_2H_4 reaction.[2] In order to examine the validity of this prediction, the potential energy of the CF_3^+-addition/HF-elimination pathway was evaluated from the reported thermochemical data[9] of CF_3^+, C_6H_6, and HF and calculated $\Delta H°$ values of $C_7H_6F_3^+$ and $C_7H_5F_2^+$ (Fig. 1). The $\Delta H°$ value of initial adduct ion **2** is higher than that of **3**+HF by ca. 0.9 eV. Therefore, the elimination of HF from **2** occurs completely, which is consistent with our previous prediction.

The potential energy diagram for the minor HT process (7b) is also shown in Fig. 1. By using reported thermochemical data,[9] the HT process is exoergic only by



Scheme 1.

Table 1. Product Ion Distributions in Ion-Moleucle Reactions of CF_3^+ and CCl_3^+ with Aromatic and Aliphatic Hydrocarbon at Near-Thermal Energy

	Reactant ion					
	CF_3^+ (Our work)[a]			CCl_3^+ (Refs. 3—6)		
Reagent	Product	Branching ratio/%		Product	Branching ratio/%	
C_6H_6	$C_7H_5F_2^+$+HF	93.4±2.2	(7a)	$C_7H_5Cl_2^+$+HCl	100	(3a)
	$C_6H_5^+$+CF_3H	6.6±2.2	(7b)			
$C_6H_5CH_3$	$C_8H_7F_2^+$+HF	84.3±2.4	(8a)	$C_8H_7Cl_2^+$+HCl	100	(4)
	$C_6H_5CH_3^+$+CF_3	7.9±2.0	(8b)			
	$C_7H_7^+$+CF_3H	7.8±1.5	(8c)			
$C_6H_5C_2H_5$	$C_7H_6F_3^+$+C_2H_4	29.5±2.3	(9a)	$C_9H_9Cl_2^+$+HCl	100	(5)
	$C_7H_5F_2^+$+C_2H_4+HF	49.4±2.4	(9b)			
	$C_2H_5^+$+$C_6H_5CF_3$	21.1±1.4	(9c)			
$C_6H_5C_2H_3$	$C_9H_7F_2^+$+HF	33.7±2.3	(10a)	$C_9H_8Cl_3^+$	31	(6b)
	$C_9H_6F^+$+2HF	18.2±2.1	(10b)	$C_9H_7Cl_2^+$+HCl	6	(6c)
	$C_7H_6F^+$+$C_2H_2F_2$	39.8±1.0	(10c)	$C_7H_6Cl^+$+$C_2H_2Cl_2$	63	(6a)
	$C_6H_5C_2H_3^+$+CF_3	8.3±1.4	(10d)			
$C_6H_5C_2H$	$C_9H_6F_3^+$	16.9±0.7	(11a)			
	$C_9H_5F_2^+$+HF	76.9±0.9	(11b)			
	$C_6H_5C_2H^+$+CF_3	6.2±0.4	(11c)			
CH_4	No reaction					
C_2H_6	$C_2H_5^+$+CF_3H	100	(16)			
C_2H_4	$C_3H_3F_2^+$+HF	62±3	(2a)			
	CHF_2^++C_2H_3F	7±2	(2c)			
	CH_2F^++$C_2H_2F_2$	2±1	(2d)			
	$C_2H_3^+$+CF_3H	29±4	(2b)			
C_2H_2	$C_3H_2F_3^+$	100	(1)			

a) Data for C_2H_n (n=2,4,6) are obtained from Ref. 2 and that for CH_4 is obtained from Ref. 11.

0.45 eV.

$$CF_3^+ + C_6H_6 \rightarrow C_6H_5^+ + CF_3H + 0.45\ \text{eV} \quad (7b)$$

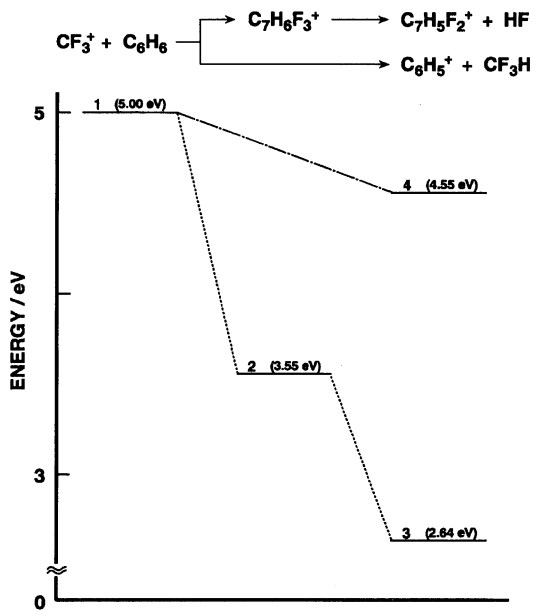
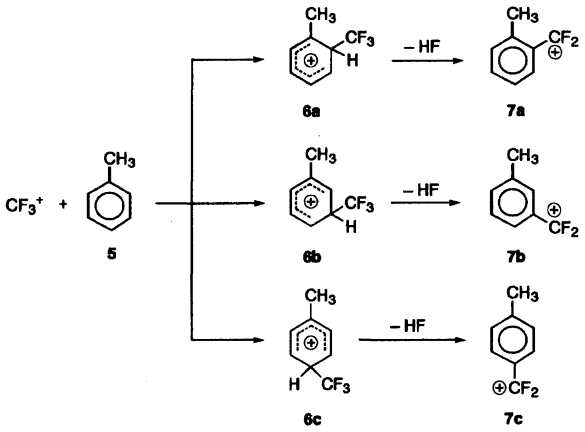


Fig. 1. A potential-energy diagram for the electrophilic CF_3^+-addition/HF-elimination and hydride-transfer pathways in the CF_3^++C_6H_6 system.

This implies that HT process (7b) proceeds through a much higher energy surface than that of the major electrophilic CF_3^+-addition/HF-elimination pathway (7a).

For the reaction with toluene, besides electrophilic addition followed by HF elimination (8a) and hydride transfer (8c), as found for the CF_3^+/C_6H_6 reaction, CT process (8b) was observed with the branching ratios given in Table 1. The possible reaction mechanism of process (8a) is shown in Scheme 2. *Ortho*-, *meta*-, and *para*-$C_8H_7F_2^+$ isomers (**7a**—**7c**) can be formed through electrophilic CF_3^+-addition/HF-elimination. We have predicted that more stable *ortho*- and *para*-isomers (**7a**, **7c**) will be the dominant product $C_8H_7F_2^+$ ion due to electron-donating inductive effects of the CH_3 group.[2] The lack of adduct ions **6a**—**6c** was predicted to be due to a lower stability of the initial adduct ions for the HF elimination.[2] In order to examine the validity of the above prediction, a potential-energy diagram was obtained by using reported and calculated $\Delta H°$ values (Fig. 2). The energies of **7a**—**7c**+HF are lower than those of **6a**—**6c** by 0.66—0.90 eV. Therefore, the lack of **6a**—**6c** is attributed to their instability for HF elimination, which agrees with our previous prediction.



Scheme 2.

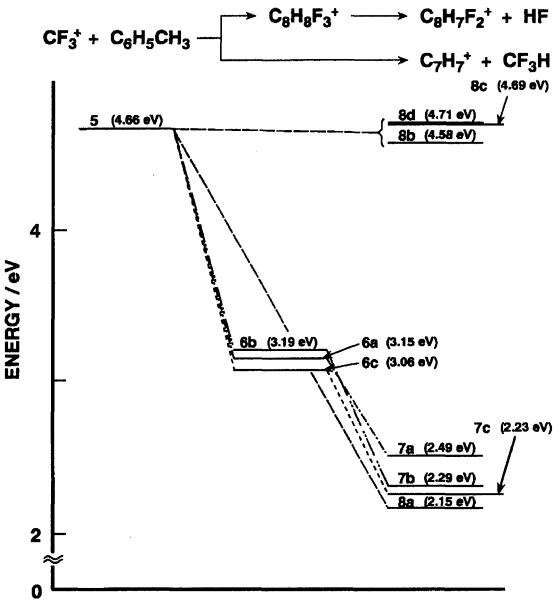
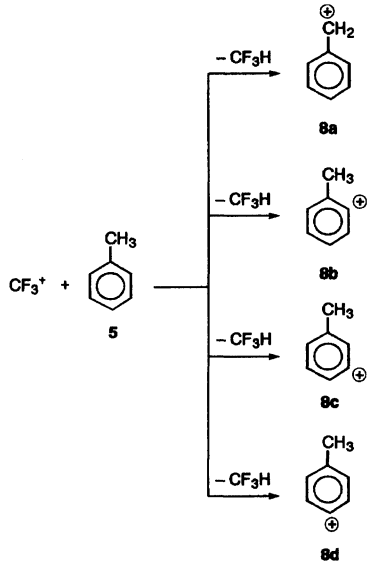


Fig. 2. A potential-energy diagram for the electrophilic CF_3^+-addition/HF-elimination and hydride-transfer pathways in the $CF_3^+ + C_6H_5CH_3$ system.

There are no significant differences in the $\Delta H°$ values among **6a**—**6c** and **7a**—**7c**, indicating no significant *ortho*- and *para*-selectivity probably due to weak inductive effects of the CH_3 group. This lack of *ortho*- and *para*-selectivity is inconsistent with our prediction.

H^- abstraction is possible both from the benzene ring and from the side CH_3 chain in process (8c), as shown in Scheme 3. Cipollini et al.[10] have reported that CF_3^+ may abstract a side-chain hydride ion from toluene based on the gas-chromatographic analysis of the final products. Although the electron-donating properties of the CH_3 group suppress hydride abstraction from the benzene ring, its branching ratio is nearly the same as that for benzene. Therefore, we assumed that H^- abstraction from toluene occurs predominantly at the side CH_3 chain.[2] Figure 2 shows an MNDO potential-energy diagram for the H^- abstraction pathway. Ac-



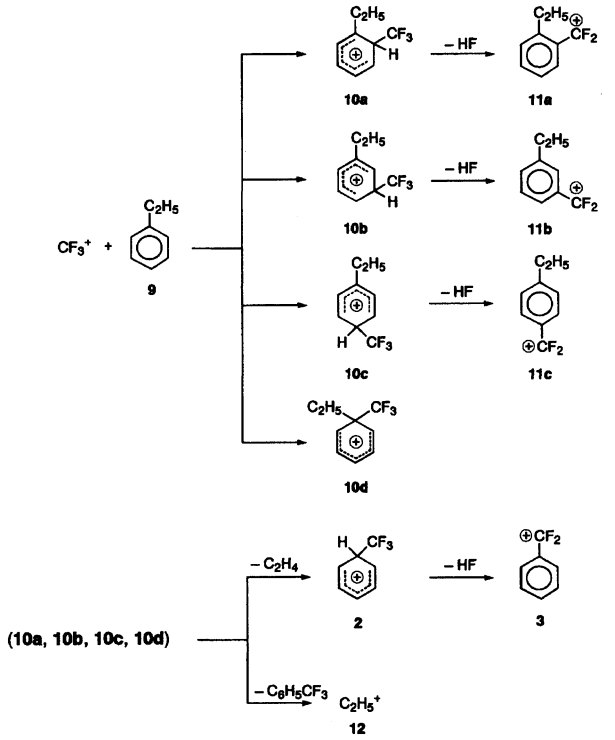
Scheme 3.

cording to theoretical calculations, the potential energies of **8b**—**8d**+CF_3H formed through H^- abstraction from the benzene ring are comparable with that of the reactant system, while the energy of **8a**+CF_3H is much lower than that of the reactant system. It is therefore reasonable to assume that the hydride abstraction predominantly occurs at the substituent. This conclusion supports our previous prediction.

The most significant difference in the product channels between $PhCH_3$ and PhH is the occurrence of CT for $PhCH_3$. The occurrence of CT for $PhCH_3$ and the lack of CT for PhH are consistent with the facts that the recombination energy (RE) of CF_3^+ ($\leq$8.90 eV)[9] is lower that the ionization potential (IP) of PhH (9.25 eV),[9] while it is higher than the IP value of $PhCH_3$ (8.82 eV).[9]

Ethylbenzene: Three product channels (9a—9c) were observed in the CF_3^+/PhC_2H_5 reaction with the branching ratios given in Table 1. All pathways proceed through electrophilic addition followed by molecular elimination, where Ph–C_2H_5 bond scission occurs in all cases (Scheme 4). On the basis of our recent study on the reactions of CF_3^+ with aliphatic hydrocarbons,[2,11] the elimination of saturated C_2 hydrocarbons such as C_2H_6 and C_2H_5F has never been observed, while that of unsaturated hydrocarbons such as C_2H_4 and C_2H_3F is quite common. Therefore, it is highly likely that the by-product of $C_7H_5F_2^+$ is not C_2H_5F but C_2H_4+HF in process (9b).

The most outstanding feature is the lack of the electrophilic CF_3^+-addition/HF-elimination pathway, which is a major product channel for benzene and toluene. In order to obtain information about the CF_3^+-addition/molecular-elimination pathways, a potential-energy diagram was evaluated from reported and calculated $\Delta H°$ values of the reactants and products (Fig. 3). Since the energies of the HF elimination pathways are



Scheme 4.

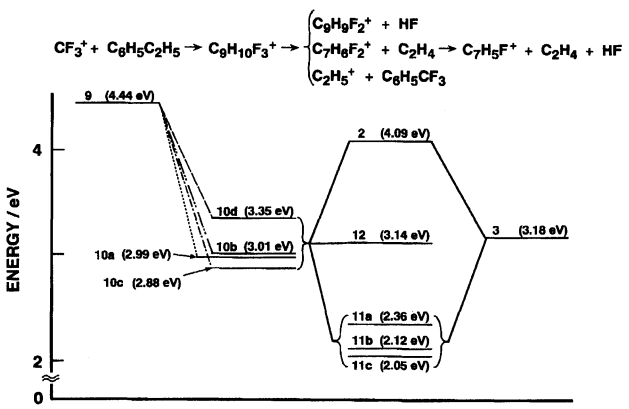


Fig. 3. A potential-energy diagram for the electrophilic CF_3^+-addition/molecular-elimination pathways in the $CF_3^+ + C_6H_5C_2H_5$ system.

lower than those of the C_2H_4 and C_2H_4+HF elimination pathways, **11a**—**11c** will be produced preferentially as in the cases of benzene and toluene. This is inconsistent with the experimental observation. If the elimination of HF occurs at the first step, stable ions **11a**—**11c** will be formed from **10a**—**10c**. Although **11a**—**11c**+HF are not produced, the formation of **3**+C_2H_4+HF is observed. The lack of **11a**—**11c** and the detection of **3** may be explained by the fact that the eliminations of C_2H_4 and $PhCF_3$ from **10a**—**10c** take precedence over that of HF, even though the potential energies of **2**+C_2H_4 and **12**+$PhCF_3$ are higher than those of **11a**—**11c**+HF. An alternative explanation is the selective formation of *ipso* isomer **10d** which decomposes completely into **2**+C_2H_4, **3**+C_2H_4+HF, and **12**+$PhCF_3$. The potential energy of **10d** is only slightly higher than those of **10a**—**10c** and the electron density of the 1-position carbon is slightly higher than those of the 2- and 3-position carbons in reagent **9** on the basis of MNDO calculations. It is therefore reasonable to assume that **10d** is formed preferentially. In order to determine the relative importance of the above two pathways, further detailed experimental and theoretical studies will be necessary.

It should be noted that the CT channel is closed for PhC_2H_5, though it is energetically open because the IP value of PhC_2H_5 (8.77 eV)[9] is lower than the RE of CF_3^+ ($\leq$8.90 eV). Although HT was observed as a minor product channel for PhH (6.6±2.2%) and $PhCH_3$ (7.9±2.0%), it could not be detected for PhC_2H_5. Since electron-donating inductive effects of the ethyl group enhance electrophilic addition to the ring, the competitive CT and HT channels will be suppressed.

Styrene: Four product channels (10a—10d) were observed in the CF_3^+/PhC_2H_3 reaction with the branching ratios given in Table 1. Since unsaturated bonds exist both in the ring and the substituent for styrene, electrophilic addition can occur at both reactive sites, as shown in Scheme 5. The potential-energy diagrams of processes (10a—10c) are shown in Figs. 4 and 5. Since the formation of **21** is endoergic, it can be excluded from the possible product ions. The absence of the initial adduct $C_9H_8F_3^+$ ions is consistent with their instability for HF elimination for all cases (**14a**—**14c**→**15a**—**15c**, **16**→**17**, and **23**→**24**). The most important $C_9H_7F_2^+$ ion will be **17** because its stability is highest. Although adduct ions **19** and **25** can be produced by F^- transfer from **16** and **23**, respectively, the potential energies of the former adducts are higher than those of the latter ones. Therefore, reaction pathways from adduct ions **19** and **25** to **20**, **22**, **24**, and **26** will be insignificant. It should be noted that the potential energy of **18**+HF is higher than that of precursor ion **17** by 1.1 eV. Therefore, precursor ion **17** must have at least 1.1 eV excess internal energy to elim-

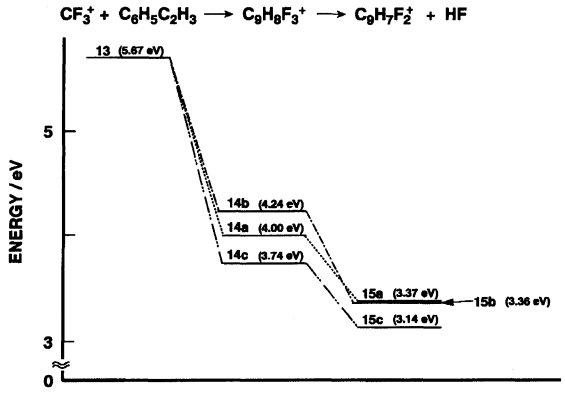
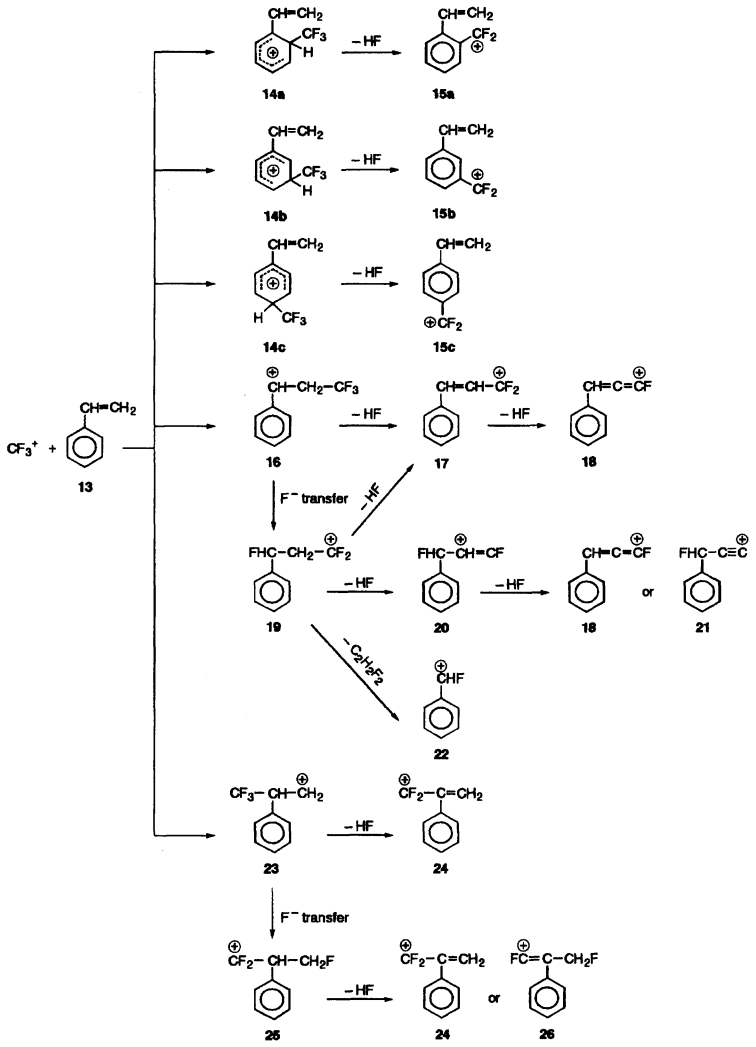


Fig. 4. A potential-energy diagram for the ring-addition/HF-elimination pathways in the $CF_3^+ + C_6H_5C_2H_3$ system.



Scheme 5.

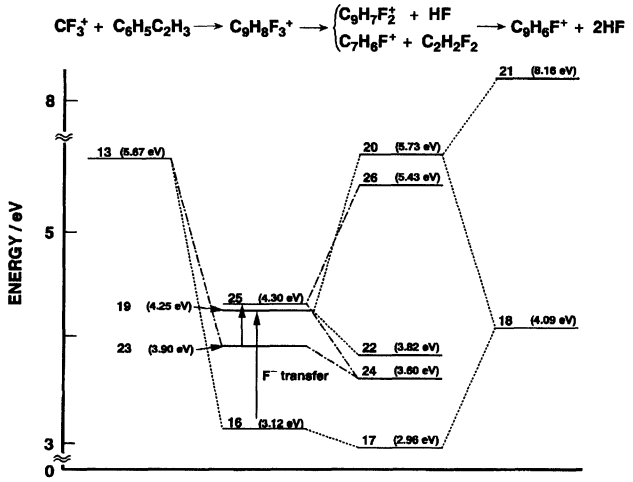
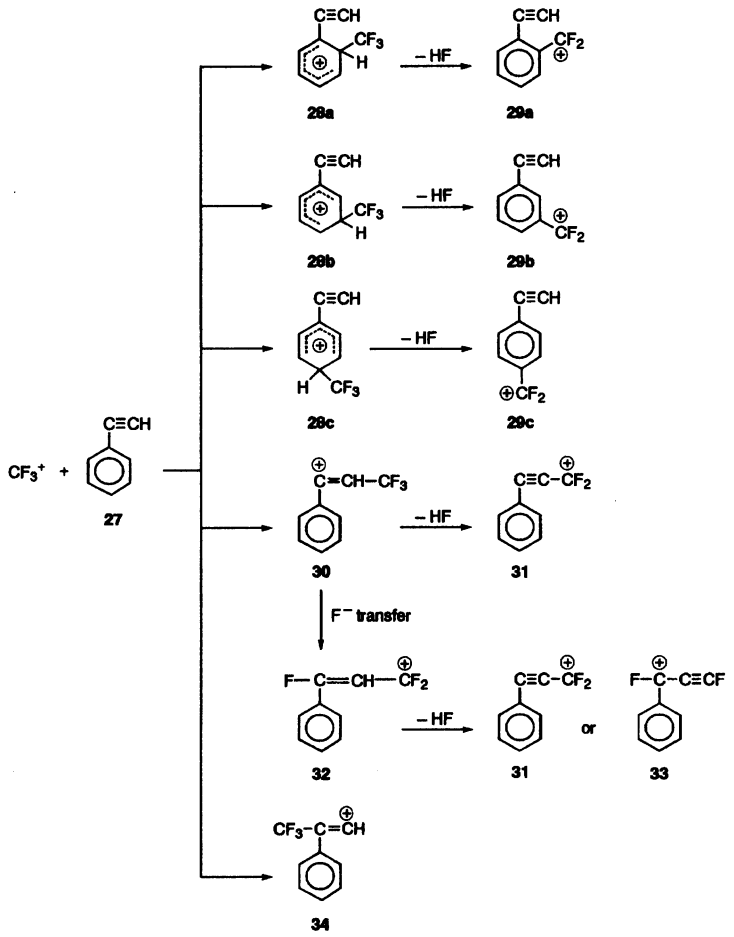


Fig. 5. A potential-energy diagram for the substituent-addition/molecular-elimination pathways in the $CF_3^+ + C_6H_5C_2H_3$ system.

inate the second HF molecule. The occurrence of the CT channel leading to the parent $PhC_2H_3^+$ ion is consistent with the fact that the IP of styrene (8.43 eV)[9] is lower than the RE of CF_3^+ ($\leq$8.90 eV).

Ethynylbenzene: Three product channels (11a—11c) were observed in the $CF_3^+/C_6H_5C_2H$ reaction with the branching ratios listed in Table 1. The most outstanding feature of the CF_3^+/PhC_2H reaction is the detection of a small amount of the initial adduct $C_9H_6F_3^+$ ion, which was absent for the other four aromatic hydrocarbons studied here. The formation of the three ring adducts **28a**—**28c** and two substituent adducts **30** and **34** are possible (Scheme 6). Although the formation of these adduct ions is energetically accessible, as shown in a potential-energy diagram (Fig. 6), substituent adduct **30** is the most stable. Since F^- transfer from **30** gives the more stable adduct ion **32**, a fast F^- transfer from **30** to **32** will take place preferentially. It should be noted that the potential energy of substituent adduct **32** is lower than those of **31**+HF and **33**+HF, while ring adducts **28a**—**28c** are unstable for HF elimination, as found for the other aromatic hydrocarbons. It was therefore concluded that the initial adduct $C_9H_6F_3^+$ ion is substituent adduct **32** and the



Scheme 6.

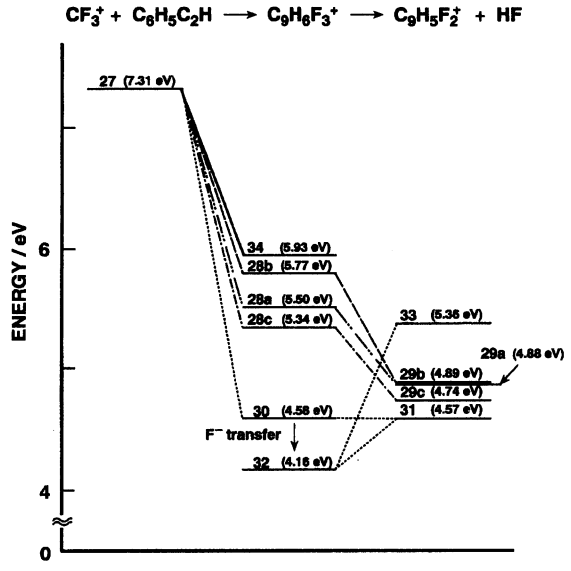


Fig. 6. A potential-energy diagram for the electrophilic CF_3^+-addition/HF-elimination pathways in the $CF_3^+ + C_6H_5C_2H$ system.

$C_9H_5F_2^+$ ion is ring adducts **29a**—**29c** with small energy differences. The occurrence of the CT channel is consistent with the fact that the IP of ethynylbenzene (8.81 eV)[9] is lower than the RE of CF_3^+ ($\leq$8.90 eV).

Comparison with the Related Data: If CF_3^+ attacks substituents of aromatic hydrocarbons, similar reaction pathways will appear between aromatic hydrocarbons and simple aliphatic hydrocarbons. Two reaction systems are compared in Table 1. Since no reaction occurs for CH_4 and only HT takes place for C_2H_6, the reactivity of CF_3^+ for CH_4 and C_2H_6 is different from that for $PhCH_3$ and PhC_2H_5. The lack of HT and CT channels for CH_4 and a CT channel for C_2H_6 can be attributed to energy constraints.

$$CF_3^+ + CH_4 \rightarrow CH_3^+ + CF_3H - 0.77 \text{ eV} \quad (12a)$$

$$CF_3^+ + CH_4 \rightarrow CH_4^+ + CF_3 \quad (\Delta H^\circ \geq 3.61 \text{ eV}) \quad (12b)$$

$$CF_3^+ + C_2H_6 \rightarrow C_2H_6^+ + CF_3 \quad (\Delta H^\circ \geq 2.62 \text{ eV}) \quad (13)$$

The large difference between saturated aliphatic hydrocarbons (CH_4, C_2H_6) and aromatic hydrocarbons ($PhCH_3$, PhC_2H_5) arises from the existence of a highly reactive site in the ring for the aromatic hydrocarbons.

Since electrophilic addition to the substituent occurs as a major product channel for aromatic hydrocarbons with a multiple bond in the substituent, the reactivity for PhC_2H_3 and PhC_2H becomes similar to that for C_2H_4 and C_2H_2. However, there are great differences in the subsequent molecular-elimination processes. Not

Table 2. Reaction Mechanism of CF_3^+ with Aromatic Hydrocarbons at Near-Thermal Energy

Reagent	IP/eV [a]		Branching ratio of each reaction/%		
			Electrophilic addition	Hydride transfer	Charge transfer
C_6H_6	9.25	Ref.2	93.4±2.2(R) [b]	6.6±2.2	
$C_6H_5CH_3$	8.82	Ref.2	84.3±2.4(R)	7.8±1.5	7.9±2.0
$C_6H_5C_2H_5$	8.77	This work	100(R)		
$C_6H_5C_2H_3$	8.43	This work	0—33.7±2.3(R), 58.0±3.1—91.7±5.4(S) [c]		8.3±1.4
$C_6H_5C_2H$	8.81	This work	0—76.9±0.9(R), 16.9±0.7—93.8±1.6(S)		6.2±0.4

a) Ionization potential (Ref. 9). b) Addition to benzene ring. c) Addition to substituent.

just one, but two HF eliminations occur for PhC_2H_3, while only one HF elimination takes place for C_2H_4 probably due to an insufficient excess internal energy to eliminate the second HF molecule. Although the initial adduct ion is formed from PhC_2H, its branching fraction is much smaller than that for C_2H_2. The major process for PhC_2H was the electrophilic CF_3^+-addition/HF-elimination process, which was not observed for C_2H_2. This difference probably arises from the existence of a highly reactive site in the ring, which is responsible for the CF_3^+-addition/HF-elimination process.

The reactions of CF_3^+ with PhH, $PhCH_3$, PhC_2H_5, and PhC_2H_3 are compared with those of the CCl_3^+ reactions in Table 1. The dominant reaction pathway for PhH and $PhCH_3$ is similar between the two reactions. In both reactions, the major product channel is the electrophilic CX_3^+-addition/HX-elimination (X=F, Cl) pathway. The HT and CT channels are energetically closed in the CCl_3^+ reactions due to the low RE of CCl_3^+ (7.80 eV)[9] and a high $\Delta H°$ value of HCl (−0.96 eV)[9] in comparison with that of HF (−2.82 eV).[9]

$$CCl_3^+ + C_6H_6 \rightarrow C_6H_6^+ + CCl_3 - 1.81 \text{ eV} \quad (14a)$$

$$CCl_3^+ + C_6H_6 \rightarrow C_6H_5^+ + CHCl_3 - 3.11 \text{ eV} \quad (14b)$$

$$CCl_3^+ + C_6H_5CH_3 \rightarrow C_6H_5CH_3^+ + CCl_3 - 3.00 \text{ eV} \quad (15a)$$

$$CCl_3^+ + C_6H_5CH_3 \rightarrow C_6H_5CH_2^+ + CHCl_3 - 1.10 \text{ eV} \quad (15b)$$

There is a significant difference between the two reactions for PhC_2H_5. Only the electrophilic CCl_3^+-addition/HCl-elimination pathway is open in the CCl_3^+ reaction, whereas the corresponding pathway is closed in the CF_3^+ reaction. The main product channels are electrophilic addition followed by C_2H_4 and C_2H_4+HF eliminations. The higher available energy of CF_3^+ will induce the C_2H_4-elimination pathway, which takes precedence over the single HF-elimination pathway.

The major product channel for PhC_2H_3 is similar between the two reactions, in which the electrophilic CX_3^+-addition/$C_2H_2X_2$-elimination occurs with the highest probability. The available energy of CF_3^+ is higher than that of CCl_3^+. Therefore, not only electrophilic addition followed by one HF elimination, but also that followed by two HF eliminations is detected in the CF_3^+/PhC_2H_3 reaction. The higher RE of CF_3^+ induces the CT channel, though its branching ratio is small. Although the initial adduct $C_9H_8Cl_3^+$ ion was found in the CCl_3^+/PhC_2H_3 reaction, its measurement was carried out at high pressures of 1—3 Torr.[6] Therefore, low-pressure experiments, where the effects of collisional stabilization are insignificant, will be required for further detailed comparison.

Conclusion

The gas-phase ion-molecule reactions of CF_3^+ with five fundamental aromatic hydrocarbons have been studied at near-thermal energy. The branching ratios of electrophilic addition to the ring and substituent, HT, and CT are summarized in Table 2. The gas-phase reactions of CF_3^+ with benzene derivatives generate two product channels: (1) mostly electrophilic attack on the benzene ring for reagents without a highly reactive substituent (e.g. benzene, toluene, and ethylbenzene) and (2) electrophilic attack on the substituent for reagents with a multiple bond (e.g. styrene and ethynylbenzene). There are large uncertainties in the branching ratios between the ring adducts and the substituent adducts. In order to reduce such uncertainties, further experimental studies, such as isotopic experiments, will be required. Although the HT process was found for benzene and toluene, it was absent for the other four aromatic hydrocarbons studied here. This was attributed to the higher reactivity of CF_3^+ for multiple bonds in the ring and/or substituents. For all molecules with lower ionization potentials than the RE of CF_3^+ ($\leq$8.90 eV) except for ethylbenzene, the CT process was found as a minor channel.

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