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Mass-Spectrometric Study on Ion-Molecule Reactions of CF_3^+ with Nitrogen-Containing Benzene Derivatives, Pyridine, Pyrrole, and Acetonitrile at Near-Thermal Energy

Masaharu Tsuji,* Masato Aizawa,† Hiroki Ujita, and Yukio Nishimura

Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816

†Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

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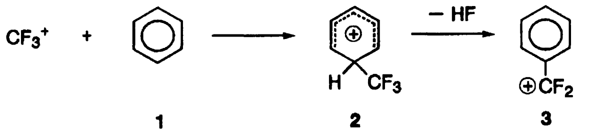
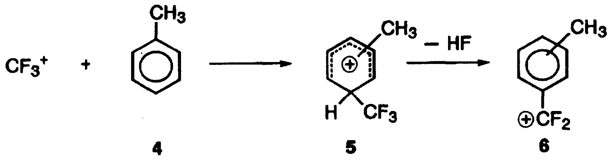
The gas-phase ion-molecule reactions of CF_3^+ with nitrogen-containing benzene derivatives (C_6H_5Y : Y= NH_2, NO_2, and CN), pyridine, pyrrole, and acetonitrile have been studied at near-thermal energy using an ion-beam apparatus. The major product channels are charge transfer for aniline (71.7±0.5%), O^- abstraction for nitrobenzene (91.7±0.5%), electrophilic addition leading to initial adduct ions for benzonitrile (97.5±0.8%), acetonitrile (100%), and pyridine (94.8±0.4%), and electrophilic addition followed by HF elimination for pyrrole (80.0±1.4%). The reaction mechanism is discussed based on product ion distributions and theoretical calculations of the energies of reaction pathways.

We have recently developed a new type of ion-beam apparatus for studying gas-phase ion-molecule reactions at near-thermal energy.[1,2] A flowing-afterglow ion source was coupled with a low-pressure reaction chamber. One advantage of our beam apparatus is that secondary ion-molecule reactions and collisional stabilization of long-lived intermediates can be greatly reduced because of low operating pressures (ca. 10^{-3} Torr, 1 Torr = 133.322 *Pa*) and the short distance between a reagent gas inlet and a sampling orifice (3 cm). The other advantage is that the reactant ion is completely thermalized before it enters the low-pressure reaction chamber. These advantages enabled us to obtain information about the primary ion-molecule reactions at near-thermal energy, which is often difficult to obtain using conventional flow-tube experiments operated at high pressures (0.1—1.0 Torr). Our beam apparatus has been successfully applied to the ion-molecule reactions of Ar^+, CO_2^+, and ArN_2^+ with simple aliphatic hydrocarbons and halogenated methanes.[1—4]

Our mass-spectrometric study has recently been extended to a study on ion-molecule reactions of a typical superacid, CF_3^+, with aromatic molecules in order to clarify the reactivities of carbocations for aromatic molecules in the gas phase completely free from a solvent. In preceding papers,[5,6] the product ion distributions have been reported for benzene, toluene, and anisole. The major product channels for benzene and toluene without highly reactive substituents were electrophilic addition followed by HF elimination (Schemes 1 and 2). The branching ratios of **3** and **6** were found to be 93.4±2.2 and 84.3±2.4%, respectively. As a minor product channel, hydride transfer (HT) occurs for benzene with a branching ratio of 6.6±2.2%, while both HT and charge transfer (CT) take place for toluene with branching ratios of 7.9±2.0 and 7.8±1.5%, respectively. By substituting a methoxy group with highly reactive lone-pair electrons to the benzene ring, more product channels were found to be open. The major product channels for anisole were electrophilic addition to lone-pair electrons of the oxygen atom, leading to **8**, **9**, and **10** with branching ratios of 15.4±2.4, 16.7±3.0, and 17.8±2.7%, respectively, and the electrophilic addition to the benzene ring followed by loss of HF leading to **12** with a branching ratio of 35.7±4.3% (Scheme 3).

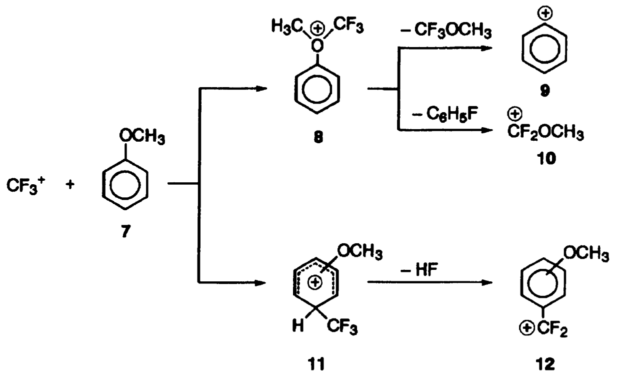


Scheme 1.



Scheme 2.

In the present work, ion-molecule reactions of CF_3^+ with C_6H_5Y (Y=NH_2, NO_2, and CN), CH_3CN, C_5H_5N, and C_4H_4NH were studied in order to examine the effects of nitrogen-containing substituents in benzene derivatives and a nitrogen atom in heterocyclic aromatic molecules. All of these reagents have highly reactive



Scheme 3.

lone-pair electrons on the nitrogen atom, or a negative charge on the oxygen atom. The results obtained are compared with recent studies concerning the reactions of $CF_3{}^+$ with $C_6H_5NO_2$ by chemical ionization mass spectrometry (CI/MS)[7] and with NH_3, $(CH_3)_nNH_{3-n}$ (n=1—3) and $C_nH_{2n}NH$ (n=2—5) by an ion-cyclotron-resonance method.[8]

Experimental

The ion-beam apparatus used in the present study was similar to that reported previously.[1,2] 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 CT reaction of Ar^+ with CF_4 with a rate coefficient of $(6.7\pm2.6)\times10^{-10}$ $cm^3\,s^{-1}$.[1] 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 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 were analyzed using an ULVAC MSQ400 quadrupole mass spectrometer. The 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 sample gases were $<1\times10^{-5}$ Torr in the reaction chamber and $<1\times10^{-6}$ Torr in the mass-analyzing chamber.

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 $m\,s^{-1}$ from known relations.[10] 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 the same as that of the Ar carrier. Assuming a Boltzmann distribution of 300 K for reagent molecules and a perpendicular direction between the ion-beam and the reagent, the relative velocities of the $CF_3{}^+$–$C_6H_5NH_2$ $CF_3{}^+$–$C_6H_5NO_2$, $CF_3{}^+$–CH_3CN, $CF_3{}^+$–C_6H_5CN, $CF_3{}^+$–C_5H_5N, and $CF_3{}^+$–C_4H_4NH pairs were evaluated to be 553, 537, 394, 547, 554, and 576 $m\,s^{-1}$, corresponding to average center-of-mass translational energies of 63, 66, 52, 64, 62, and 58 meV, respectively. Therefore, the present experiments were carried out at only slightly hyperthermal energies. The reaction time between $CF_3{}^+$ and the reagents was estimated to be $<5\times10^{-5}$ s by using the velocity of the $CF_3{}^+$ beam and the distance between the reagent gas inlet and the sampling orifice.

In our previous study on the ion-molecule reactions of $CF_3{}^+$ with C_2H_2, C_2H_4, and C_3H_6,[9] not only the product ion distribution, 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 control by using a mass flowmeter. Therefore, it was difficult to determine the reaction rate coefficients.

Results and Discussion

Aniline and Nitrobenzene: For the $CF_3{}^+$ + $C_6H_5NH_2$ reaction, the following four product channels are observed:

$$CF_3{}^+ + C_6H_5NH_2 \longrightarrow C_7H_6NF_2{}^+ + HF, \qquad (1a)$$

$$\longrightarrow C_6H_5NH_2{}^+ + CF_3, \qquad (1b)$$

$$\longrightarrow C_6H_5{}^+ + CF_3NH_2, \qquad (1c)$$

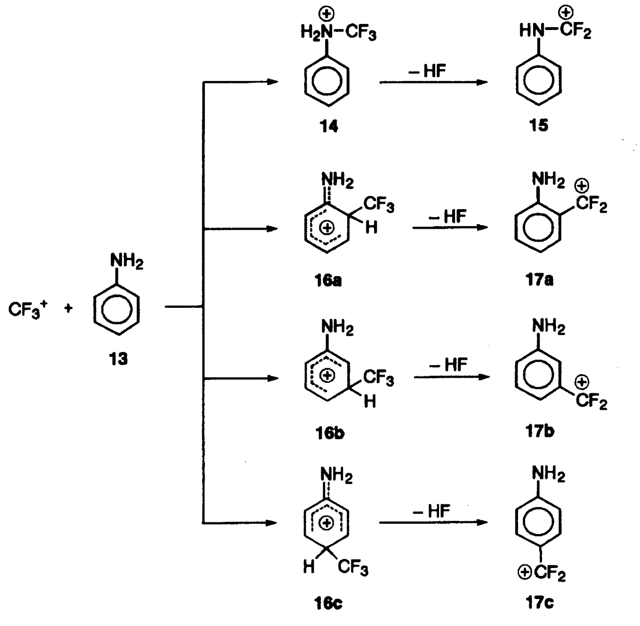
$$\longrightarrow CF_2NH_2{}^+ + C_6H_5F. \qquad (1d)$$

The branching ratios of each process are given in Table 1. Although the initial adduct ion was observed for the reaction with $C_6H_5OCH_3$ (15.4±2.4%),[6] it was absent for the reactions with C_6H_6 and $C_6H_5CH_3$.[5] The lack of an initial adduct ion for $C_6H_5NH_2$ agrees with the results for the latter aromatic hydrocarbons and for nitrogen-bases, such as NH_3, $(CH_3)_nNH_{3-n}$ (n=1—3), and $C_nH_{2n}NH$ (n = 2—5).[8] For the reactions with C_6H_6, $C_6H_5CH_3$, NH_3, $(CH_3)_nNH_{3-n}$ (n=1—3), and $C_nH_{2n}NH$ (n=2—5), the electrophilic addition followed by HF elimination was a dominant product channel in most cases.[5,8] The electrophilic $CF_3{}^+$-addition/HF-elimination process leading to $C_7H_6NF_2{}^+$ is also found for $C_6H_5NH_2$ with a branching ratio of 21.4±0.5%. The formation of $C_7H_6NF_2{}^+$ proceeds through the addition of the reactant $CF_3{}^+$ ion to lone-pair electrons of the nitrogen atom, or to π electrons of the benzene ring followed by loss of HF (Scheme 4). It is known that the electrophilic addition of $CH_3{}^+$, $C_2H_5{}^+$, CH_2Cl^+, and $CHCl_2{}^+$ to aniline occurs dominantly on the substituent, whereas that of H^+ takes place on the benzene ring from the measurements of mass-analyzed ion kinetic energy spectra.[11,12] Since the reactivity of $CF_3{}^+$ is expected to be similar to that of chlorinated methane ions, isomer **15** may also be a major adduct in the $CF_3{}^+$ reaction. In order to examine this prediction, the potential energies of the $CF_3{}^+$-addition/HF-elimination pathways were evaluated from reported thermochemical data[13] and calculated ΔH° values of four $C_7H_7NF_3{}^+$ and $C_7H_6NF_2{}^+$ ions. Theoretical values were obtained by using a semiempirical MNDO method (MOPAC Ver. 6.0). The results obtained are shown in Fig. 1. The ΔH° values of the $C_7H_7NF_3{}^+$ adduct ions are higher than those of the $C_7H_6NF_2{}^+$+HF products for all cases. Therefore, the adduct ions will completely decompose to $C_7H_6NF_2{}^+$+HF, which is consistent with the experi-

Table 1. Product Ion Distributions in Ion-Molecule reactions of CF_3^+ with Benzene Derivatives, Pyridine, Pyrrole, and Acetonitrile at Near-Thermal Energy

Reagent	Product ion	Reaction mechanism	Branching ratio/% This work	Branching ratio/% CI/MS[a)]
$C_6H_5NH_2$	$C_7H_6NF_2^+$	EA[b)]	21.4±0.5	
	$C_6H_5NH_2^+$	CT[c)]	71.7±0.5	
	$C_6H_5^+$	EA	3.9±0.1	
	$CF_2NH_2^+$	EA	3.0±0.1	
$C_6H_5NO_2$	$C_6H_5NO_2^+$	CT	0	3
	$C_6H_5NO^+$	O^- abstraction	91.7±0.5	69
	$C_6H_5^+$	NO_2^- abstraction	8.3±0.5	28
C_6H_5CN	$C_8H_5NF_3^+$	EA	97.5±0.8	
	$C_8H_4NF_2^+$	EA	2.5±0.8	
C_5H_5N	$C_6H_5NF_3^+$	EA	94.8±0.4	
	$C_6H_4NF_2^+$	EA	5.2±0.4	
C_4H_4NH	$C_5H_4NF_2^+$	EA	80.0±1.4	
	$C_4H_4NH^+$	CT	20.0±1.4	
CH_3CN	$CH_3CNCF_3^+$	EA	100.0	

a) Chemical ionization mass spectrometry (Ref. 7) b) Electrophilic addition. c) Charge transfer.



Scheme 4.

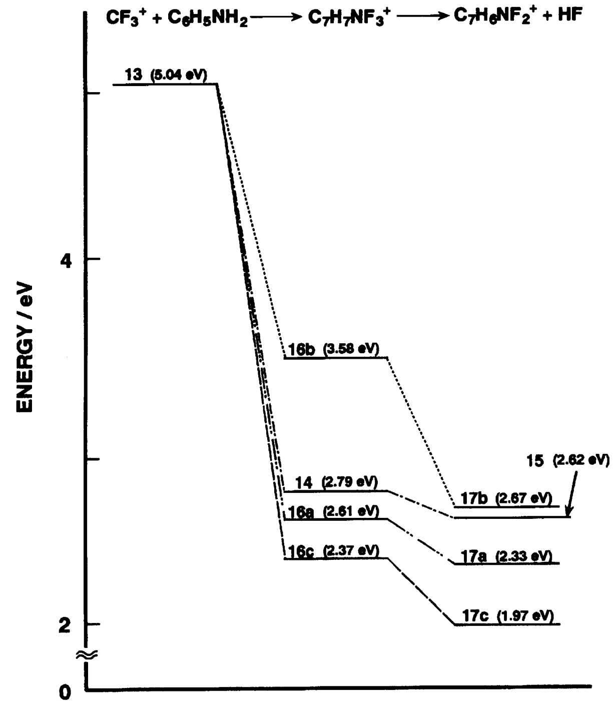


Fig. 1. MNDO potential-energy diagram for the $CF_3^+ + C_6H_5NH_2$ system. The energy of the reactant system is obtained from thermochemical data in Ref. 13.

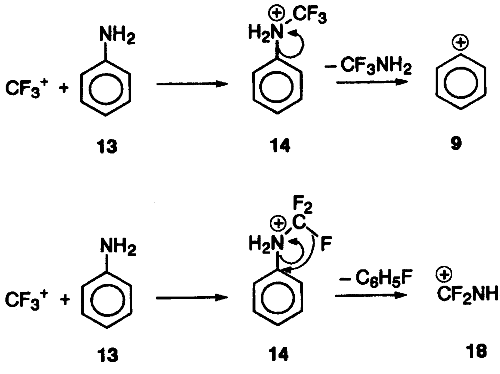
mental observation. Since adduct ions **16a** and **16c** are more stable than **16b**, the formation of **17a** and **17c** may be more favorable than that of **17b**. Although the potential energies of electrophilic addition/HF elimination pathways through **16a** and **16c** are lower than that through **14**, there are no significant difference in the energies among the three adduct ions. Therefore, not only ring adducts (**17a**, **17c**), but also substituent adduct **15**, may be formed, though their branching fractions could not be determined in the present study.

The electron-donating resonance effects of the NH_2 group will enhance the formation of Wheland-type adducts (**16a**, **16c**), while a high reactivity of the lone-pair electrons on the nitrogen atom will yield N-adduct **14** preferentially. However, the branching ratio of the electrophilic $CF_3{}^+$-addition/HF elimination process, 21.4±0.5%, is found to be lower than those of the $CF_3{}^+$-addition and $CF_3{}^+$-addition/molecular elimination processes for C_6H_6 (93.4±2.2%), $C_6H_5CH_3$ (84.3±2.4%), and $C_6H_5OCH_3$ (85.6±12.4%).[5,6] It should be noted that the branching ratio of the parent $C_6H_5NH_2{}^+$ ion resulting from a simple CT, 71.7±0.5%, is much larger than those of C_6H_6 (0%), $C_6H_5CH_3$ (7.8±1.5%), and $C_6H_5OCH_3$ (14.4±1.8%). The lack of the CT channel for C_6H_6 is explained by a higher ionization potential of C_6H_6 (9.25 eV)[13] than the recombination energy of $CF_3{}^+$ ($\leq$8.90 eV).[13] The large branching ratio of the CT channel for $C_6H_5NH_2$ can be attributed to a lower ionization potential of $C_6H_5NH_2$ (7.72 eV) than those of $C_6H_5CH_3$ (8.82 eV) and $C_6H_5OCH_3$ (8.21 eV),[13] which provides a greater chance to produce various rovibrational levels of the ground state of $C_6H_5NH_2{}^+(\tilde{X}^2B_1)$ after CT. The preferential occurrence of the CT channel for $C_6H_5NH_2$ results in a great reduction of the probability of the competitive electrophilic addition channel.

The minor $C_6H_5{}^+$ and $CF_2NH_2{}^+$ ions must be formed through an attack of $CF_3{}^+$ on the lone-pair electrons of the nitrogen atom, followed by a loss of CF_3NH_2 or C_6H_5F (Scheme 5). Corresponding processes leading to $C_6H_5{}^+$ and $CF_2OCH_3{}^+$ have been found for $C_6H_5OCH_3$.[6] This suggests that substitution of the NH_2 and OCH_3 groups with lone-pair electrons to benzene induces similar product channels.

Although HT was observed as a minor product channel for C_6H_6 (6.6±2.2%) and $C_6H_5CH_3$ (7.9±2.0%),[5] it cannot be detected for $C_6H_5NH_2$. Taking account of the resonance form of aniline, a negative charge is developed in the benzene ring due to the electron-donating resonance effects of the amino group. This makes it difficult to abstract H^- from the benzene ring of aniline.

For the $CF_3{}^+ + C_6H_5NO_2$ reaction, the following two product channels have been observed:



Scheme 5.

$$CF_3{}^+ + C_6H_5NO_2 \longrightarrow C_6H_5NO^+ + CF_3O, \qquad (2a)$$

$$\longrightarrow C_6H_5{}^+ + CF_3NO_2. \qquad (2b)$$

The branching ratios of the two processes are given in Table 1 along with previous CI/MS data. Since the formation of $CF_3 + NO_2$ as a by-product of $C_6H_5{}^+$ is energetically inaccessible in Eq. 2b, CF_3NO_2 must be produced. The major process was found to be the O^- abstraction leading to a nitrosobenzene cation. This finding agrees with the CI/MS data reported by Vairamani and Saraswathi,[7] though its branching ratio obtained here is higher than their value. Although a small amount of the parent $C_6H_5NO_2{}^+$ ion was observed in their study, it was absent in the present study. The CT process leading to the parent $C_6H_5NO_2{}^+$ ion is endoergic, at least by 0.96 eV, using a recombination energy of $CF_3{}^+$ ($\leq$8.90 eV).[13] Therefore, direct electron-impact ionization and/or a high-energy ion must take part in the formation of the parent ion in their CI/MS experiment. The branching ratio of the $C_6H_5{}^+$ ion in the present study is smaller than their value by a factor of about 3. Since electron-impact ionization of $C_6H_5NO_2$ yields a large amount of $C_6H_5{}^+$, as reported by Vairamani and Saraswathi,[7] its large branching ratio in their study is probably due to such an unexpected reaction. Summing up the above facts, the branching ratios obtained here are more reliable than the previous CI/MS data, because only thermalized $CF_3{}^+$ ions can participate in the formation of the product ions in our measurements.

The most outstanding feature in the reaction pathways is that the reaction of $CF_3{}^+$ occurs only on the NO_2 substituent. The lack of electrophilic addition and the addition/HF-elimination channels can be attributed to the fact that the availability of a negative charge on the substituent along with the electron-withdrawing inductive and resonance effects of the NO_2 group promotes the substituent as the only reactive site. A positive charge is developed in the benzene ring as a resonance form of $C_6H_5NO_2$ due to strong electron-withdrawing effects of NO_2. Although the HT process will be a favorite product channel for $C_6H_5NO_2$ on the basis of this fact, no HT channel was detected. This suggests that the reactivity of the NO_2 substituent with a highly localized negative charge on the oxygen atom is much higher than that of the neutral hydrogen atoms of the benzene ring.

Acetonitrile and Benzonitrile: Meerwein et al.[14] have obtained N-alkyliminium salts from nitrile–Leweis acid complexes and alkyl halides in solution:

$$\text{R–C}\equiv\text{N} + SbCl_5 + R'Cl$$
$$\longrightarrow \left\{ \text{R–C}\equiv\overset{+}{\text{N}}\text{–R}' \longleftrightarrow \text{R–}\overset{+}{\text{C}}\text{=N–R}' \right\} SbCl_6{}^-. \qquad (3)$$

($R=CH_3$, C_6H_5; $R'=C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$, $C_6H_5CH_2$)

For the gas-phase CF_3^+/CH_3CN reaction, only the electrophilic addition has been found at low CH_3CN pressures below 1×10^{-5} Torr:

$$CF_3^+ + CH_3C{\equiv}N \longrightarrow \left\{ CH_3C{\equiv}\overset{+}{N}{-}CF_3 \longleftrightarrow CH_3\overset{+}{C}{=}\overset{\cdot\cdot}{N}{-}CF_3 \right\}. \qquad (4)$$

The selective addition of CF_3^+ to the C≡N triple bond of CH_3CN agrees with the selective formation of the adduct ions in solution. At high sample gas pressures, besides the $CH_3CNCF_3^+$ adduct ion, the CH_4CN^+ ion resulting from the following secondary reaction appeared:

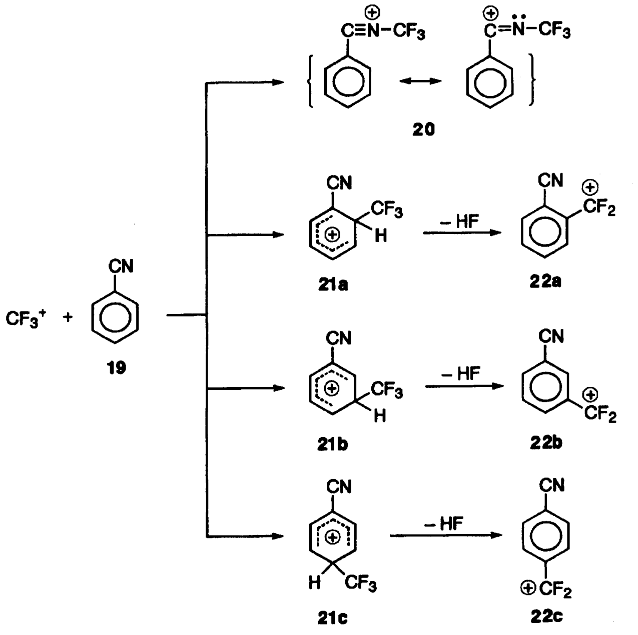
$$CH_3CNCF_3^+ + CH_3CN \longrightarrow CH_4CN^+ + CH_2CNCF_3. \qquad (5)$$

For the $CF_3^+ + C_6H_5CN$ reaction, the following two product channels are found:

$$CF_3^+ + C_6H_5CN \longrightarrow C_8H_5NF_3^+, \qquad (6a)$$

$$\longrightarrow C_8H_4NF_2^+ + HF. \qquad (6b)$$

The branching ratios are given in Table 1. The preferential formation of the initial adduct ion, as in the case of CH_3CN, implies that the electrophilic addition is also a dominant process for benzene derivative with a cyano group. This finding is consistent with the reactions between nitrile-Lewis acid complexes and alkyl halides in solution. Although a similar adduct ion has been found for anisole (15.4±2.4%),[6] the corresponding adduct ions are absent for benzene, toluene, aniline, and nitrobenzene. The CF_3^+ ion can attack both the C≡N substituent and the benzene ring to yield adducts **20** and **21a**—**21c**, respectively (Scheme 6). Isomer **20** will be a major adduct, because strong electron-withdrawing effects of the CN group prevent the reagent from forming Wheland-type isomers **21a**—**21c**. This prediction is consistent with the theoretical calculations of the energies of the electrophilic addition pathways (Fig. 2), where the energy of the substituent-addition pathway is much lower than those of the ring-addition ones. The theoretical calculations suggest that Wheland-type adduct ions **21a**—**21c** are too unstable to be detected, so that the addition reactions are always accompanied by HF elimination, as found for C_6H_6 and $C_6H_5CH_3$.[5] Therefore, adduct ions **21a**—**21c** can be excluded from the possible $C_8H_5NF_3^+$ ion. On the basis of the above results, it is concluded that all of the adduct $C_8H_5NF_3^+$ ion is **20**.



Scheme 6.

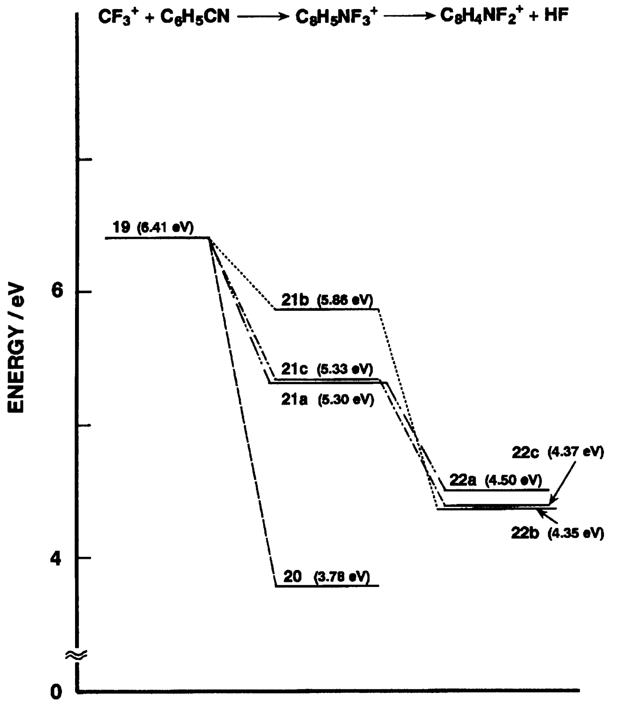


Fig. 2. MNDO potential-energy diagram for the $CF_3^+ + C_6H_5CN$ system. The energy of the reactant system is obtained from thermochemical data in Ref. 13.

It should be noted that a small amount of $C_8H_4NF_2^+$ is formed. This ion must arise from the loss of HF from Wheland-type intermediates **21a**—**21c**, indicating that the electrophilic addition occurs not only to the CN substituent but also to the ring. The small branching ratio of $C_8H_4NF_2^+$ can be attributed to a higher reactivity of CF_3^+ for the CN group and a great reduction of the probability of the electrophilic addition to the ring due to the electron-withdrawing effects of the CN group. Burinsky and Campana[12] have found that the electrophilic addition of CH_3^+ to benzonitrile occurs both to the substituent and the ring with a high propensity for the former by using the mass-analyzed ion kinetic energy spectrometry. The present findings for the $CF_3^+ + C_6H_5CN$ reaction agree with their results for the $CH_3^+ + C_6H_5CN$ reaction.

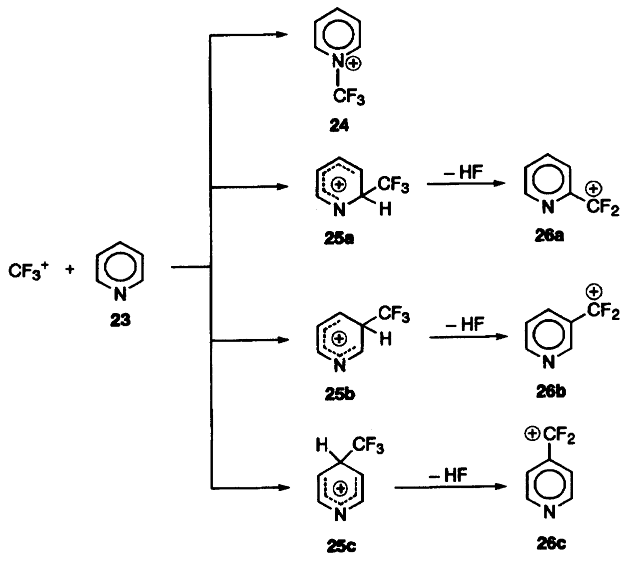
The CT channel cannot be detected for acetonitrile and benzonitrile. It is explained by higher ionization potentials of CH_3CN (12.19 eV)[13] and C_6H_5CN (9.62 eV)[13] than the recombination energy of CF_3^+ ($\leq$8.90 eV). Taking account of the resonance form of benzonitrile, a positive charge is developed in the benzene ring. Although the HT channel for benzonitrile will be enhanced compared with that for benzene on the basis of this fact, the HT channel was found to be closed. This can be explained by the fast electrophilic addition to the substituent and the ring, which will reduce the probability of the competitive HT channel.

Pyridine and Pyrrole: The following two product channels are observed in the $CF_3^+ + C_5H_5N$ reaction:

$$CF_3^+ + C_5H_5N \longrightarrow C_6H_5NF_3^+, \qquad (7a)$$

$$\longrightarrow C_6H_4NF_2^+ + HF. \qquad (7b)$$

The branching ratios are given in Table 1. The most outstanding feature is the preferential formation of the initial adduct $C_6H_5NF_3^+$ ion. Although similar initial adduct ions have been found for CH_3CN and C_6H_5CN, they could not be detected for $C_6H_5NH_2$ and $C_6H_5NO_2$, and such amines as NH_3, $(CH_3)_nNH_{3-n}$ (n=1—3), and $C_nH_{2n}NH$ (n=2—5).[8] The electrophilic addition can occur both on lone-pair electrons of the nitrogen atom and on π electrons of the aromatic ring to yield adducts **24** and **25a**—**25c**, respectively (Scheme 7). Figure 3 shows a potential energy-diagram of the electrophilic addition/HF elimination processes obtained from the MNDO calculations. It is clear that the formation of ring and substituent adducts is energetically possible. However, the potential energy of N-adduct ion **24** is much lower than those of Wheland-type adduct ions **25a**—**25c**, because electron-withdrawing inductive effects of nitrogen greatly suppress the formation of the latter adducts. The potential energies of ring adducts **25a**—**25c** are higher than those of $C_6H_4NF_2^+ + HF$ products **26a**—**26c**. Thus, adduct ions **25a**—**25c** are expected to decompose completely into **26a**—**26c**, as found for benzene and aniline. On the basis of the above facts, the $C_6H_5NF_3^+$ and $C_6H_4NF_2^+$ ions observed here are attributed to **24** and **26a**—**26c**, respectively. This shows that almost all electrophilic addition (94.8±0.4%) occurs on the N atom, while a small amount of the addition (5.2±0.4%) occurs on the C atom. The small branching ratio of the latter addition can be attributed to a higher reactivity of CF_3^+ for the lone-pair electrons of the nitrogen atom and a great reduction of the probability of electrophilic addition to the ring due to the electron-withdrawing inductive effects of the nitrogen atom. Among three minor isomers **26a**—**26c**, most stable **26b** will be a major $C_5H_4NCF_2^+$ ion, though the possibility of the formation of **26a** and **26c** cannot be excluded because of small energy differences among **26a**, **26b**, and **26c**.



Scheme 7.

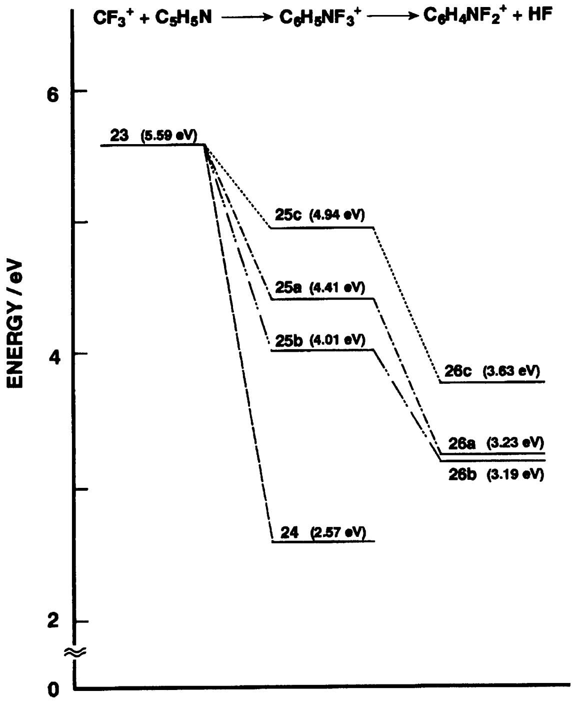


Fig. 3. MNDO potential-energy diagram for the $CF_3^+ + C_5H_5N$ system. The energy of the reactant system is obtained from thermochemical data in Ref. 13.

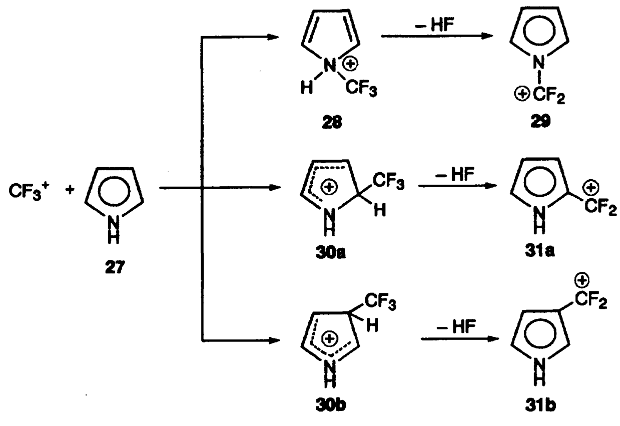
The lack of CT channel leading to the parent $C_5H_5N^+$ ion is explained by a higher ionization potential of pyridine (9.25 eV)[13] than the recombination energy of CF_3^+ ($\leq$8.90 eV). Taking account of the resonance form of pyridine, a positive charge is developed in the pyridine ring due to the electron-withdrawing properties of the nitrogen atom. Although the HT channel for pyridine will be enhanced compared with that for benzene on the basis of this fact, the HT channel was found to be closed. It can be explained by the fast electrophilic addition of CF_3^+ to the lone-pair electrons of the nitrogen atom and to the ring π electrons.

The following two product channels are observed in the $CF_3^+ + C_4H_4NH$ reaction:

$$CF_3^+ + C_4H_4NH \longrightarrow C_5H_4NF_2^+ + HF, \qquad (8a)$$

$$\longrightarrow C_4H_4NH^+ + CF_3. \qquad (8b)$$

The branching ratios are given in Table 1. Although the initial adduct ion has been detected for pyridine, it was not detected for pyrrole. The major product channel is the electrophilic CF_3^+-addition/HF-elimination, as in the case of aniline. The electrophilic addition can occur both on lone-pair electrons of the nitrogen atom and on a C=C double bond of the ring to yield adducts **28**, and (**30a**, **30b**), respectively (Scheme 8). Figure 4 shows a potential-energy diagram of the electrophilic addition/HF elimination processes obtained from semiempirical calculations. It should be noted that intermediates **30a** and **30b** are much more stable than **28**. Therefore, it is highly likely that the observed $C_5H_4NF_2^+$ ion is **31a** and/or **31b**. We have concluded that the electrophilic addition occurs dominantly on the carbon atom for pyrrole and on the nitrogen atom for pyridine on the basis of the product ion distributions and the theoretical calculations. This conclusion is consistent with electrophilic reactions for these two typical heteroaromatic molecules in solution.[15]



Scheme 8.

The CT process was found as a minor product channel. The occurrence of CT channel is consistent with a lower ionization potential of pyrrole (8.21 eV)[13] than the recombination energy of CF_3^+ ($\leq$8.90 eV). The HT process was not detected for pyrrole. Since a negative charge is developed in the resonance form of pyrrole, the HT channel will be suppressed greatly.

Conclusion

The gas-phase ion-molecule reactions of CF_3^+ with five fundamental nitrogen-containing aromatic molecules and acetonitrile have been studied at near-

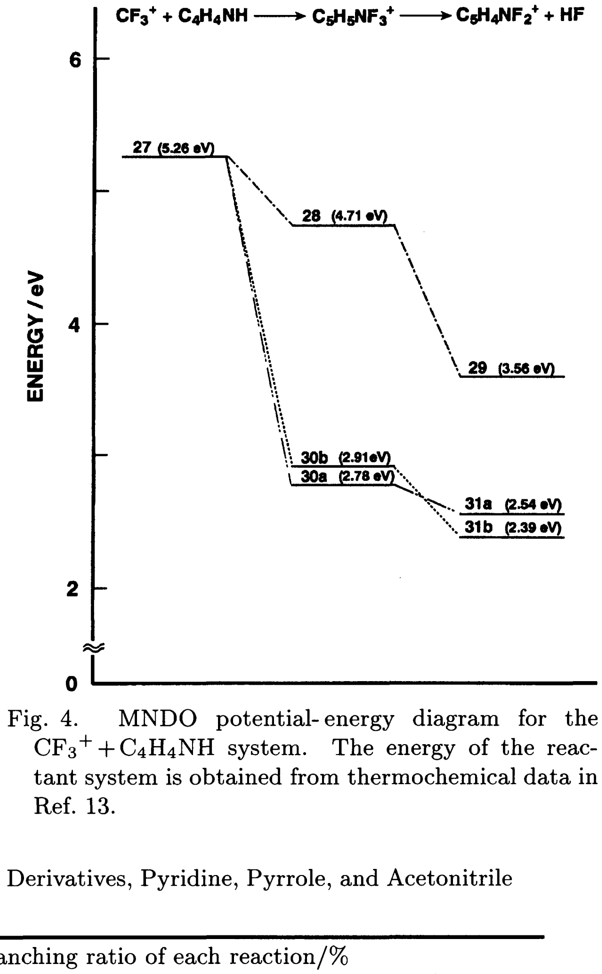


Fig. 4. MNDO potential-energy diagram for the $CF_3^+ + C_4H_4NH$ system. The energy of the reactant system is obtained from thermochemical data in Ref. 13.

Table 2. Reaction Mechanism of CF_3^+ with Benzene Derivatives, Pyridine, Pyrrole, and Acetonitrile at Near-Thermal Energy

Reagent	IP/eV[a)]		Branching ratio of each reaction/% Electrophilic addition	Hydride transfer	Charge transfer	The others
C_6H_6	9.25	Ref.5	93.4±2.2 (R)[b)]	6.6±2.2		
$C_6H_5CH_3$	8.82	Ref.5	84.3±2.4 (R)	7.9±2.0	7.8±1.5	
$C_6H_5OCH_3$	8.21	Ref.6	35.7±4.3 (R), 49.9±8.1 (S)[c)]		14.4±1.8	
$C_6H_5NH_2$	7.72	This work	0—21.4±0.5 (R), 6.9±0.2~28.3±0.7 (S)		71.7±0.5	
$C_6H_5NO_2$	9.86	This work				100
C_6H_5CN	9.62	This work	2.5±0.8 (R), 97.5±0.8 (S)			
C_5H_5N	9.25	This work	94.8±0.4 (N),[d)] 5.2±0.4 (C=C)[e)]			
C_4H_4NH	8.21	This work	80.0±1.4 (N and/or C=C)		20.0±1.4	
CH_3CN	12.19	This work	100 (N)			

a) Ionization potential (Ref. 13). b) Addition to benzene ring. c) Addition to substituent. d) Addition to nitrogen lone-pair. e) Addition to C=C bond.

thermal energy. The reaction pathways observed are summarized in Table 2 along with our previous results on benzene, toluene, and anisole. The gas-phase reactions of CF_3^+ with benzene derivatives generate product channels as follows: (1) mostly an electrophilic attack on a ring without highly reactive substituents (e.g. benzene and toluene), (2) an electrophilic attack on a substituent with lone-pair electrons and multiple bonds (e.g. anisole and benzonitrile), and (3) an attack on a negative charge (nitrobenzene). The dominant reactions of CF_3^+ with pyridine and pyrrole were an electrophilic attack to the heteroatom and to the carbon atom, respectively. On the basis of the present results, preferential σ-bond formation by trifluoromethylation occurs at polarizable centers of negative charge (i.e. lone-pair electrons and multiple bonds) in the gas-phase where polar heteroatoms are not solvated. For all molecules with lower ionization potentials than the recombination energy of CF_3^+ (≤ 8.90 eV), the CT process was found to compete with the above main reactions. The branching ratio of the CT channel increases with decreasing the ionization potential of the reagents. For aniline with the lowest ionization potential, the CT process becomes a dominant product channel. Although the HT process was found for such aromatic hydrocarbons as benzene and toluene, it was absent for the nitrogen-containing molecules studied here. This was attributed to the higher reactivity of CF_3^+ to high polarizable centers of negative charge.

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