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Mass-Spectrometric Study on Ion-Molecule Reactions of CF_3^+ with Furan and Thiophene at Near-Thermal Energies

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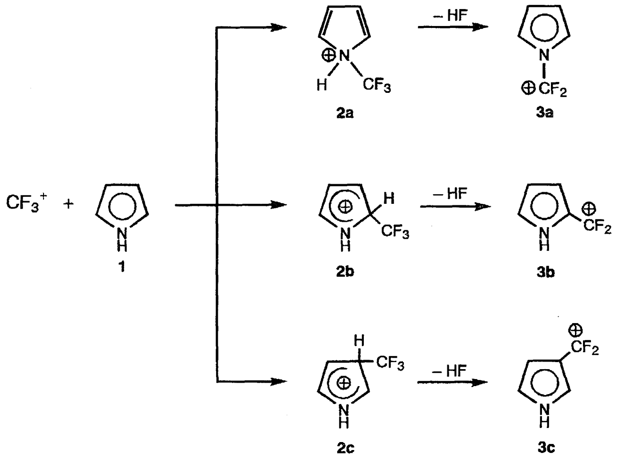
The branching ratios of product ions for the reactions of CF_3^+ with furan and thiophene were determined by using an ion-beam apparatus. The main reaction channels proceed via α- and β-trifluoromethylated intermediates (C-adducts), followed by HF elimination, CO elimination, and CO+HF elimination for furan, and followed by HF elimination for thiophene. Semiempirical MNDO calculations of heats of formation of various intermediates and products were carried out to explore possible mechanisms. It was concluded that the CO and CO+HF eliminations for furan occur through a cleavage of a C–O skeletal bond of the C-adducts. The lack of CO and CO+HF elimination channels for thiophene was explained by the fact that the ring-opening and ring-contraction channels are energetically closed.

Pyrrole, furan, and thiophene are all π-electron-rich five-membered heterocyclic compounds. The characteristic reaction of these molecules with electrophilic reagents in solutions is the electrophilic substitution which takes place at α-carbon preferentially.[1] However, in a superacid solution, the substitution is complicated because even pyrrole with a weak basicity is forced to protonate.[2] Thus, the gas-phase electrophilic reactions of these molecules have been of interest to understand the intrinsic reactivity of heterocyclic compounds.

Recently, we have initiated systematic mass-spectrometric studies on ion-molecule reactions of a Lewis superacid, CF_3^+, with aromatic molecules in order to clarify the reactivity of carbocations for aromatic molecules in the gas phase completely free from any solvent. In our previous papers,[3—7] product ions and their branching ratios have been reported for monosubstituted benzenes, pyridine, and pyrrole. The major product channel for pyrrole was electrophilic CF_3^+ addition to a C=C bond and/or a lone-pair of an N-atom, followed by HF elimination (Scheme 1). The total branching ratios of **3a**–**3c** were found to be 80±1.4%. As a minor product channel, charge transfer (CT) was as well found with a branching ratio of 20±1.4%. As the intermediates in the CF_3^+-addition/HF-elimination pathway, an N-adduct, namely N-trifluoromethylated intermediate (**2a**), and C-adducts, namely α- and β-trifluoromethylated intermediates (**2b** and **2c**), were possible. In the gas-phase ion-molecule reactions, the formation of the initial adduct ion is energetically favorable due to an electrostatic interaction between the ion and the dipole of a neutral molecule.[8,9] Moreover, since collisional stabilization is greatly reduced under our low-pressure experimental conditions (1.5—2.5×10^{-3} Torr), the formation processes of the initial adduct ions will undergo a thermodynamic control.



Scheme 1.

Semiempirical MNDO calculations of potential energies of intermediates demonstrated that the C-adducts (**2b** and **2c**) are more stable than the N-adduct (**2a**). It was therefore concluded that the CF_3^+-addition/HF-elimination pathway would dominantly proceed through the C-adducts (**2b** and **2c**).

In this work, the ion-molecule reactions of CF_3^+ with furan and thiophene have been studied in order to gain a better understanding of the intrinsic reactivity of heterocyclic compounds. The initial branching ratios are determined from mass-spectrometric analysis of the product ions. Semiempirical MNDO calculations of heats of formation of possible intermediates and products are used to explore possible reaction mechanisms. The results obtained are compared with our previous data for pyrrole.[5]

Experimental

The experiments were performed on an ion-beam apparatus. The apparatus and its operation have been described previously,[3—7] thus only details pertinent to the present study will be given. Ground-state $Ar^+(^2P_{3/2})$ ions were generated by a microwave discharge of high-purify 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] the relative velocities of the CF_3^+–C_4H_4O and CF_3^+–C_4H_4S pairs under a typical Ar pressure in the flow tube (1.0 Torr) were evaluated to be 575 and 559 $m\,s^{-1}$, corresponding to average center-of-mass translational energies of 59 and 61 meV, respectively. Thus, the present experiments were carried out at only slightly hyperthermal energies.

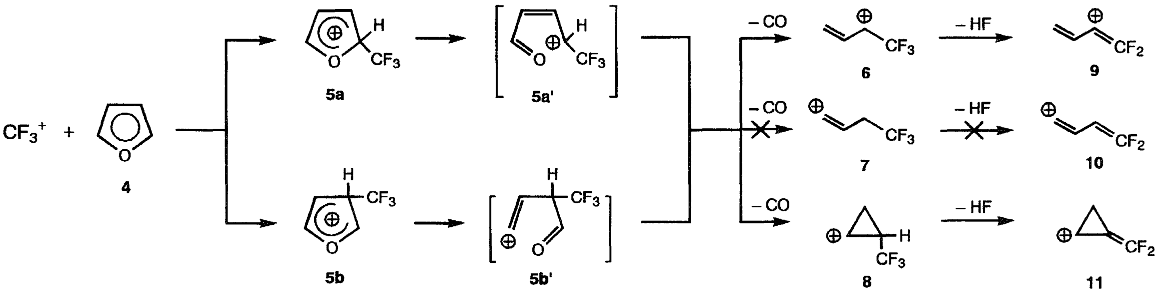
The heats of formation are known for the reactant ion, reagent, and some stable products obtained in this work.[10] However, there are many species whose ΔH_f values are unknown. These values were calculated by using the semiempiricial MNDO method (MOPAC Ver. 6.0) in order to describe the potential-energy diagrams.

Results and Discussion

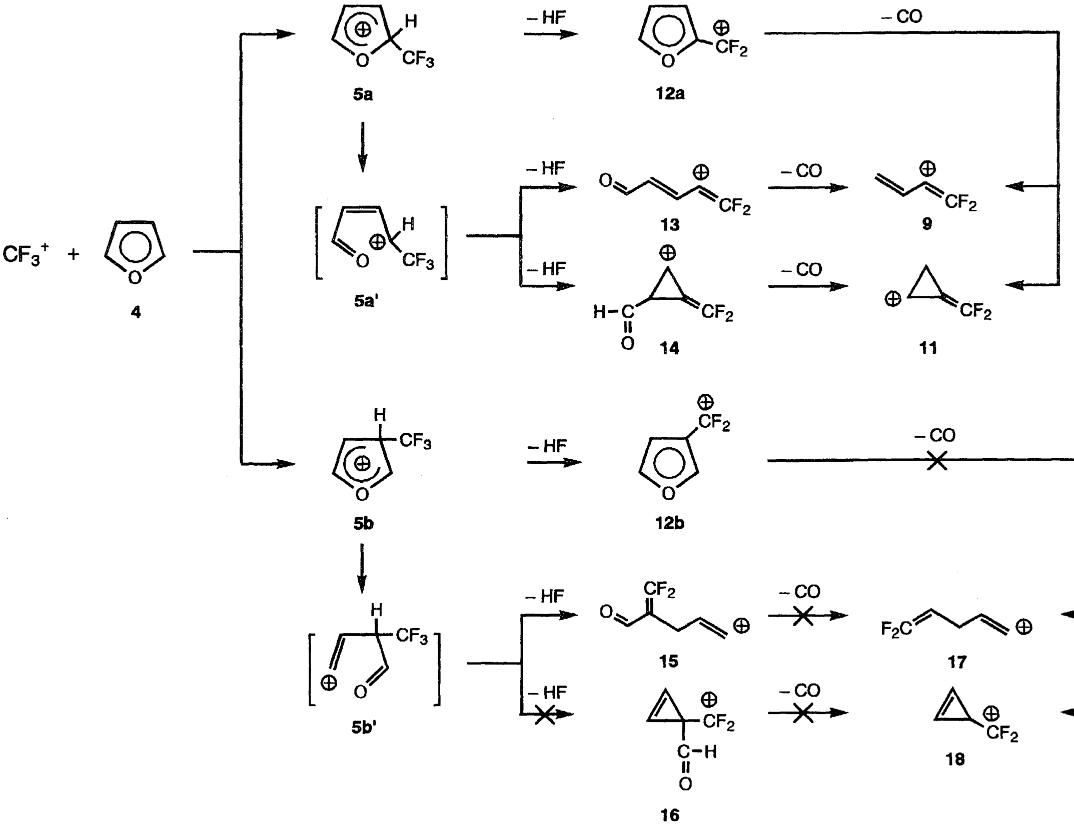
Furan. The determined product ions and their branching ratios for the reaction with furan are presented in Table 1. Since the initial adduct ion and electrophilic CF_3^+-addition/CO-elimination channel could be found, there exist significant differences in the product channels between furan and pyrrole. The major processes for furan are the electrophilic addition, followed by HF elimination (2b), CO elimination (2c), and CO+HF elimination (2d). Although the primary attack of CF_3^+ can occur both on a C=C bond and a lone-pair of the O-atom, it appears that these elimination channels proceed through the α- and/or β-trifluoromethylated intermediates (**5a** and **5b**), as shown in Scheme 2. A further cleavage of a C–O skeletal bond of the C-adducts is necessary for processes (2c) and (2d). It is well known that the C–O bond scission takes precedence over the C–C bond scission in furan.[11] Thus, we inferred that the CO elimination proceeds through the formation of the C-adduct isomers (**5a′** and **5b′**). On the other hand, the HF elimination can occur with or without the cleavage of the C–O bond, as given in Scheme 3. Since we can't discriminate whether the CO or HF elimination occurs at the first step, the two possible mechanisms are shown for the CO+HF elimination in Schemes 2 and 3. The formation of the three-membered ring has been proposed as the product channel of the $C_3H_3^+$ ion in the mass spectrum of furan obtained under the fast electron-

Table 1. Products and Their Branching Ratios for the Reactions of CF_3^+ with Furan, Thiophene, and Pyrrole at Near-Thermal Energies

Reagents		Products		Branching ratios/%
C_4H_4O	This work	$C_5H_4OF_3^+$	(2a)	12.6±0.8
		$C_5H_3OF_2^+$+HF	(2b)	30.8±1.1
		$C_4H_4F_3^+$+CO	(2c)	35.5±0.9
		$C_4H_3F_2^+$+CO+HF	(2d)	16.3±1.3
		$C_4H_4OF^+$+CF_2	(2e)	3.6±0.4
		$C_4H_3^+$+CF_3OH and/or $C_4H_3^+$+CF_2O+HF	(2f)	1.2±0.2
C_4H_4S	This work	$C_5H_3SF_2^+$+HF	(3a)	96.0±1.1
		$C_4H_4S^+$+CF_3	(3b)	4.0±1.1
C_4H_4NH	Ref. 5	$C_5H_4NF_2^+$+HF	(1a)	80.0±1.4
		$C_4H_4NH^+$+CF_3	(1b)	20.0±1.4



Scheme 2.



Scheme 3.

impact ionization.[11] Therefore, not only linear compounds but also cyclic ones can be formed in the elimination processes of CO, HF, and CO+HF, as shown in Schemes 2 and 3. In fact, the calculated ΔH_f values of the three-membered ions (**8**, **11**, and **14**) are either equal or nearly equal to those of the corresponding isomeric linear ions (**6**, **9**, and **13**) (see Fig. 1).

Figure 1 shows a potential-energy diagram of processes (2b), (2c), and (2d) obtained from the thermochemical data of CF_3^+, C_4H_4O, HF, and CO, and calculated ΔH_f values of $C_5H_4OF_3^+$, $C_4H_4F_3^+$, $C_5H_3OF_2^+$, and $C_4H_3F_2^+$. Reaction pathways of Schemes 2 and 3 are on the right and left sides of the figure, respectively. Since the formation of **7**+CO is energetically inaccessible, the $C_4H_4F_3^+$ ion will be **6** and/or **8**. On the other hand, the formation of **16**+HF is endothermic, and **12a** and **12b** are much more stable than **13**, **14**, and **15**. Therefore, the $C_5H_3OF_2^+$ ion will be **12a** and/or **12b**. Possible candidates of the $C_4H_3F_2^+$ ion are **9**, **11**, and

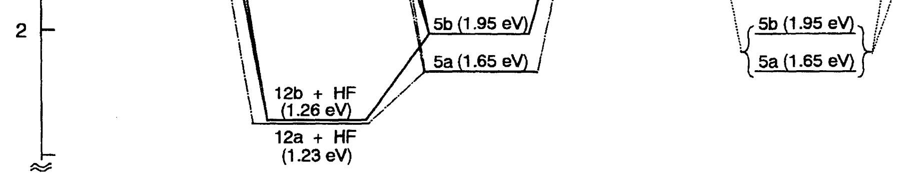


Fig. 1. A potential-energy diagram for the electrophilic CF_3^+-addition followed by CO, HF, and CO+HF elimination pathways in the CF_3^++C_4H_4O system. The heats of formation of reactants, HF, and CO are obtained from Ref. 10 and those of **5a**, **5b**, **6**—**11**, **12a**, **12b**, and **13**—**18** are calculated by a semiempirical MNDO method.

17. Since the formation of **17**+CO+HF is energetically inaccessible, the $C_4H_3F_2^+$ ion will be **9** and/or **11** with the same ΔH_f value. The occurrence of the HF+CO elimination suggests that **5a** and **5b**, excited by the exothermicity of their formation processes, have internal energies of at least 1.84 and 1.54 eV to eliminate HF and CO.

The HF elimination retaining the five-membered ring (**5a**→**12a**+HF and **5b**→**12b**+HF) proceeds through a much lower energy surface than all of the CO eliminations in which the stable aromatic ring must be decomposed. On the basis of this fact, the HF elimination channel will be favorable, as in the case of pyrrole.[5] However, the branching ratios of the two elimination processes are comparable. This suggests that there exists a comparable energy barrier between the HF and CO elimination channels from the C-adducts (**5a** and **5b**) and these elimination channels undergo the kinetic control.

A further outstanding feature for the reaction with furan is the detection of the initial adduct $C_5H_4OF_3^+$ ion. Hitherto, we have found that N-adducts and ring-adducts, formed in the CF_3^++C_4H_4NH and PhX (e. g., X = H, CH_3, NH_2 etc.) reactions, decompose by a loss of HF.[3—7] Moreover, it was concluded that the C-adducts (**5a** and **5b**), formed in the reaction with furan, have sufficient internal energies to decompose by a loss of HF. On the basis of the above findings, it is reasonable to assume that the initial adduct $C_5H_4OF_3^+$ ion is O-adduct (**19**) resulting from the hetero O-atom attack (Scheme 4). Since the branching ratios of product ions were independent of the reagent gas pressure in the reaction chamber, collisional stabilization of the energized **19** ion will be insignificant. A radiative association, as found for the thermal-energy reaction of $Si(CH_3)_3^+$ with such oxygenated organic compounds as acetone[12] and 2-methylfuran,[13] may take part in the stabilization of **19**. In our previous studies of reactions of CF_3^+ with monosubstituted benzenes having an O atom in the substituent,[4,6,7] similar initial adduct ions have been found from $PhOCH_3$, PhCHO, $PhCOCH_3$, and $PhCOOCH_3$ with branching ratios of 15.4±2.4, 84.9±2.7, 95.0±0.9, and 80.3±1.7%, respectively. The potential energy of the O-adduct was higher than those of the ring C-adducts for $PhOCH_3$, which gives a small amount of the initial adduct ion.[4] On the other hand, the potential energies of initial O-adducts were lower than those of the ring C-adducts for PhCHO, $PhCOCH_3$, and $PhCOOCH_3$, which yield large amounts of initial O-adduct ions.[7] Here, we found that the branching ratio of the initial adduct ion for furan was relatively small, as in the case of $PhOCH_3$. The potential energy of the O-adduct (**19**) is higher than those of the C-adducts (**5a**, **5b**), as shown in Fig. 2. Thus, the small branching ratio of the initial O-adduct ion must be due to its instability in comparison with the C-adduct ions.

Both $C_4H_4OF^+$ and $C_4HF_2^+$ are possible as the product ion with a mass-to-charge ratio (*m*/*z*) of 87. However, the formation processes of the latter $C_4HF_2^+$ ion by losses of H_2CO and HF from the C-adducts are closed energetically.

$$CF_3^+ + C_4H_4O$$

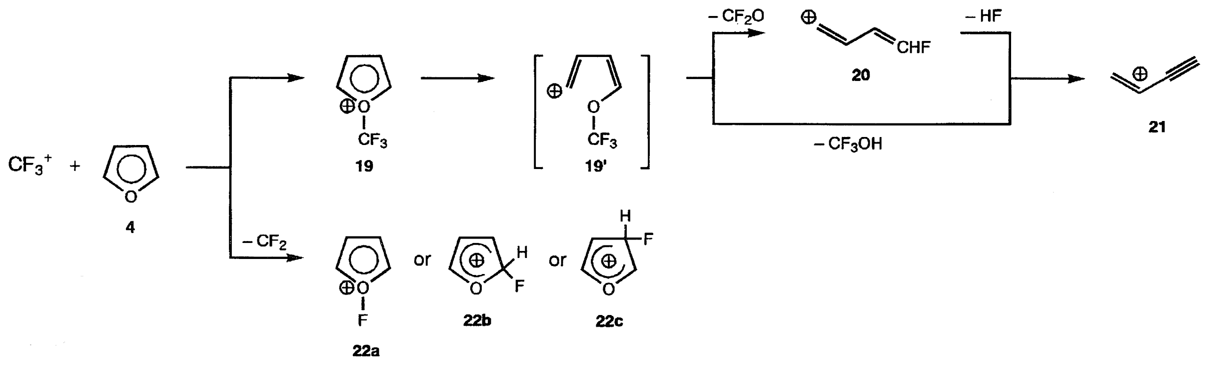
$$\rightarrow CH{\equiv}C{-}\overset{\oplus}{C}{=}CF_2 + H_2CO + HF - 1.73\ \text{eV} \quad (4a)$$

$$\rightarrow \overset{\oplus}{C}{\equiv}C{-}CH{=}CF_2 + H_2CO + HF - 4.18\ \text{eV} \quad (4b)$$

Therefore, the $C_4HF_2^+$ ion was excluded from the possible candidates. Among the three possible $C_4H_4OF^+$ ions (**22a**, **22b**, and **22c**), shown in Scheme 4, only the formation of **22b** is energetically allowed, as shown in Fig. 2. Therefore, the minor $C_4H_4OF^+$ ion was concluded to be **22b**. The F^+ transfer proceeds through a higher energy surface than those in the electrophilic addition to the ring C- and O-atoms. This will be one reason for the small branching ratio of the $C_4H_4OF^+$ ion.

The most probable pathway and a potential-energy diagram for the formation of the $C_4H_3^+$ ion is shown in Scheme 4 and Fig. 2, respectively. For the formation of $C_4H_3^+$, not only CF_3OH elimination but also the elimination of CF_2O+HF is possible. Actually, the latter elimination process has been found in the reaction of CF_3^+ with such aldehydes and ketones as CH_3CHO and CH_3COCH_3.[14] The O-adduct (**19**) is less stable than the C-adducts (**5a** and **5b**). This will be a major reason for the smallest branching ratio of the $C_4H_3^+$ ion.

Thiophene. The experimentally determined product ions and their branching ratios are presented in Table 1. The reaction with thiophene becomes simple, and electrophilic addition, followed by HF elimination (3a), and CT (3b), were found. Although the reactivity of CF_3^+ for thiophene is significantly different from that of furan, it resembles that of pyrrole (see Table 1). The mechanisms for the processes



Scheme 4.

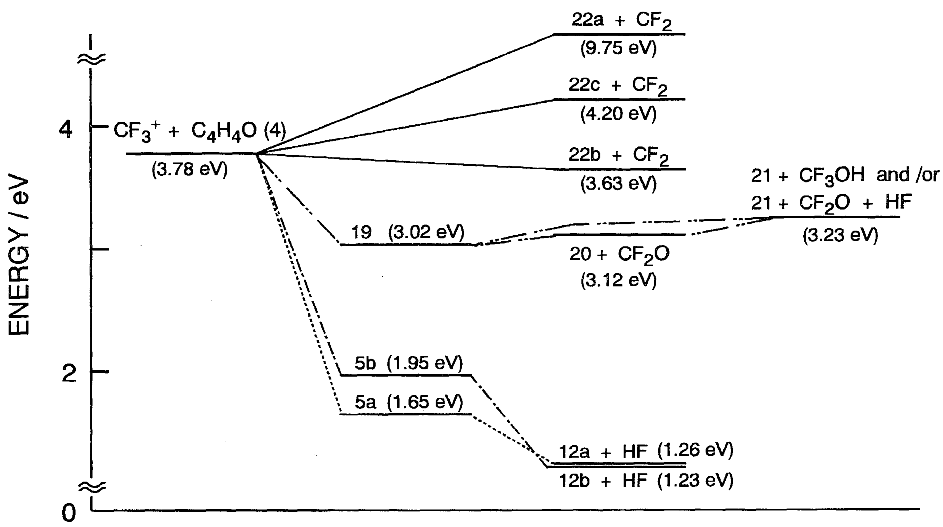
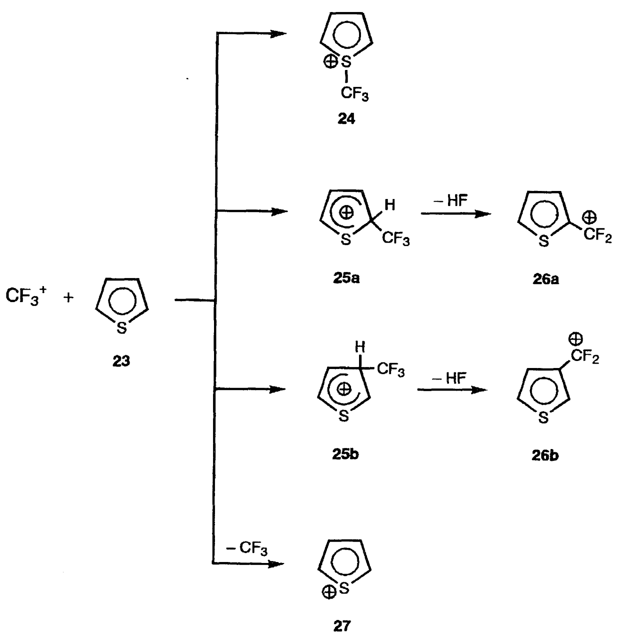


Fig. 2. A potential-energy diagram for the electrophilic $CF_3{}^+$-addition followed by HF, CF_2O+HF, and CF_3OH elimination pathways, and the formation of the $C_4H_4F^+$ ion in the $CF_3{}^+$+C_4H_4O system. The heats of formation of reactants, CF_2, CF_2O, CF_3OH, and HF are obtained from Ref. 10 and those of **5a**, **5b**, **12a**, **12b**, **19**—**21**, and **22a**—**22c** are calculated by a semiempirical MNDO method.

(3a) and (3b) are shown in Scheme 5. Since thiophene has no hydrogen atom bonded to a hetero S-atom, the intermediate ions of the reaction (3a) must be the C-adducts (**25a** and **25b**). These C-adducts could not be detected, as found for the case of the $CF_3{}^+$+C_4H_4NH reaction.[5] The lack of the intermediate ions in the $CF_3{}^+$+C_4H_4NH reaction has been explained as due to their instability for HF elimination on the basis of the theoretical calculations of the potential energies.[5] In order to examine whether the same explanation was applicable to the present system, the potential energies of the $CF_3{}^+$-addition/HF-elimination pathways were evaluated from the reported thermochemical data of $CF_3{}^+$ and HF, and from calculated ΔH_f values of $C_5H_4SF_3{}^+$ and $C_5H_3SF_2{}^+$ (Fig. 3). As shown in Fig. 3, the C-adduct ions (**25a** and **25b**) are less stable than **26a**+HF and **26b**+HF by 0.64 and 0.77 eV, respectively. Therefore, the elimination of HF from **25a** and **25b** will occur completely. The internal energies of cations **25a** and **25b**, arising from the exothermicity of their formation processes, would enhance the HF elimination.



Scheme 5.

A potential-energy diagram for minor CT process (3b) is also shown in Fig. 3. By using reported thermochemical data,[10] the CT process is exoergic only by 0.03 eV. This implies that CT process (3b) proceeds through a much higher energy surface than that of major electrophilic $CF_3{}^+$-addition/HF-elimination pathway (3a).

The most outstanding feature in the reaction of $CF_3{}^+$ with thiophene is that ring-opening and ring-contraction channels could not be found. As in the case of furan, it is known that the C–S bond scission takes precedence over the C–C bond scission in thiophene under the fast electron-impact ionization.[11] Therefore, if the ring opening and ring contraction of C-adduct ions (**25a** and **25b**) occur, **25a** and **25b** may show the similar elimination pathways, as found for furan. The losses of CS and CS+HF from **25a** and **25b** give the same products as found for furan in Schemes 2 and 3. On the other hand, the loss of HF produces **13′**, **14′**, **15′**, and **16′** ions, as shown in Fig. 4, which correspond to **13**, **14**,**15**, and **16** ions for furan. In order to examine the origin of the different reactivities, we calculated the heats of the reaction of the CS and/or HF eliminations leading to the ring-opening and ring-contraction products from the thermochemical data of $CF_3{}^+$, C_4H_4S, CS, and HF, and calculated ΔH_f values of $C_4H_4F_3{}^+$, $C_5H_3SF_2{}^+$, and $C_4H_3F_2{}^+$. The results obtained are shown in Table 2. It is clear from Table 2 that all of the CS and/or HF elimination processes are endothermic by 0.28—2.60 eV. It was therefore concluded that the CS and/or HF elimination channels leading to the ring-opening and ring-contraction products are closed energetically for thiophene.

Reaction Mechanism of $CF_3{}^+$ with Furan, Thiophene, and Pyrrole. The reaction pathways observed are summarized in Table 3 along with our previous result on pyrrole.[5] Mechanisms are classified into an electrophilic reaction, a

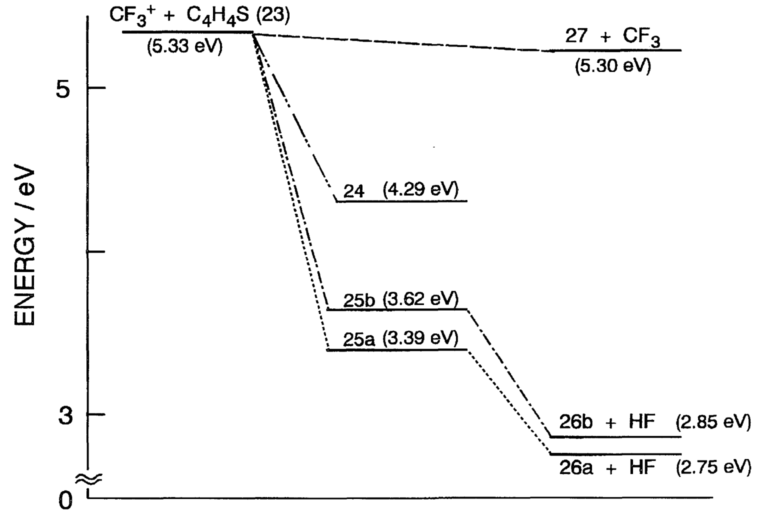


Fig. 3. A potential-energy diagram for the electrophilic CF_3^+-addition/dissociation pathways in the $CF_3^+ + C_4H_4S$ system. The heats of formation of reactants, CF_3, and HF are obtained from Ref. 10 and those of **24**, **25a**, **25b**, **26a**, **26b**, and **27** are calculated by a semiempirical MNDO method.

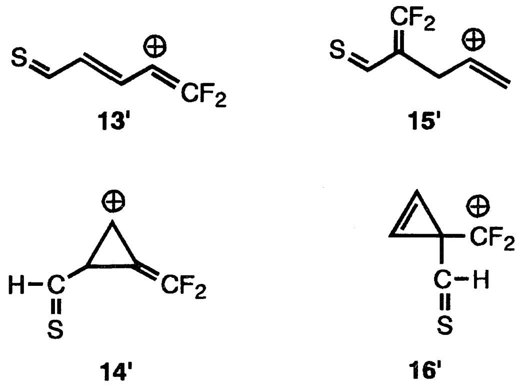


Fig. 4. Product ions, which are substituted an O-atom of **13**, **14**, **15**, and **16** ions for a S-atom, formed by a loss of HF from C-adducts (**25a** and **25b**).

Table 2. The Heats of Reaction for the Ring-Opening and Ring-Contraction Reactions of CF_3^+ with Thiophene

Products[a]	ΔH_f°/eV[b]
6+CS and **8**+CS	1.41
7+CS	2.60
9+CS+HF and **11**+CS+HF	2.08
10+CS+HF and **17**+CS+HF	2.54
13′+HF	0.28
14′+HF	0.78
15′+HF	0.41
16′+HF	1.93

a) Refer to Schemes 2 and 3, and Fig. 4. b) The heats of formation of reactants, CS, and HF are obtained from Ref. 10 and those of **6**—**11**, **17**, and **13′**—**16′** are calculated by the MNDO method.

charge transfer, and the other [2(e) for furan]. Here, we concluded that the electrophilic reaction of CF_3^+ with pyrrole would proceed largely through the α- and β-trifluoromethylated intermediates on the basis of their high thermochemical stability.[5] Although the primary electrophilic attack can occur on a C=C bond and a lone pair of a hetero atom, the attack of CF_3^+ toward furan, thiophene, and pyrrole largely occurs on a C=C bond. These results are consistent with those of the electrophilic substitution in solutions.[1] Angelini et al.[15,16] have investigated the gas-phase methylation of furan, thiophene, and pyrrole by $CH_3FCH_3^+$ from the γ-radiolysis of CH_3F. From the gas chromatographic analysis of the irradiation products, it was concluded that both O- and S-methylated intermediates isomerize to the α- and β-methylated intermediates. Similar isomerization from the O-adduct (**19**) and the S-adduct (**24**) to the energetically fa-

Table 3. Mechanisms for the Reactions of CF_3^+ with Furan, Thiophene, and Pyrrole at Near-Thermal Energies

Reagents	I. P./eV[a]		Branching ratios of each reaction/%		
			Electrophilic reaction	Charge transfer	The other
C_4H_4O	8.88	This work	82.6±3.3 (C=C[b]), 13.8±1.0 (O[c])		3.6±0.4
C_4H_4S	8.87	This work	96.0±1.1 (C=C)	4.0±1.1	
C_4H_4NH	8.21	Ref. 5	80.0±1.4 (C=C and/or N[d])	20.0±1.4	

a) Ionization potential (Ref. 10). b) Attack on a C=C bond. c) Attack on a lone pair of O-atom. d) Attack on a lone pair of N-atom.

vorable C-adducts might take place preferentially under our low-pressure experiments (Figs. 2 and 3). This is consistent with the fact that most of the product ions are formed via the C-adducts.

For thiophene and pyrrole with lower ionization potential (IP) than the recombination energy (RE) of CF_3^+ ($\leq$8.9 eV), the CT process was found as a minor channel. Although the IP of furan is slightly lower than the RE of CF_3^+, no CT process was observed. This may be attributed to the higher reactivity of CF_3^+ for the furan ring.

Conclusion

The present mass-spectrometric study demonstrated that the main reactions of CF_3^+ with furan and thiophene proceed via α- and β-trifluoromethylated intermediates, followed by molecular eliminations. With furan, the major elimination channels were HF elimination retaining the ring, and CO and CO+HF eliminations accompanied by the opening of the ring. With thiophene, only the HF elimination retaining the ring was observed. The different elimination processes between furan and thiophene were attributed to the fact that the ring-opening and ring-contraction channels are energetically open only for furan.

The reaction of CF_3^+ with furan suggested that α- and β-trifluoromethylated intermediates have at least internal energies of 1.5 eV and an energy barrier exists for the HF elimination. The initial adduct ion was observed only for furan. It would be an O-trifluoromethylated intermediate ion, formed by a radiative association.

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