Bull. Chem. Soc. Jpn., ***69***, *1055—1063 (1996)*

Mass-Spectrometric Study on Ion–Molecule Reactions of CF_3^+ with Monosubstituted Benzenes Carrying a Carbonyl Group at Near-Thermal Energies

Masaharu Tsuji,* Masato Aizawa,† 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

(Received October 6, 1995)

The gas-phase ion–molecule reactions of CF_3^+ with five monosubstituted benzenes carrying a carbonyl group (PhCOX: X = H, CH_3, C_2H_5, OCH_3, OC_2H_5) have been studied at near-thermal energies using an ion-beam apparatus. The major product channel for PhCHO, $PhCOCH_3$, and $PhCOOCH_3$ is electrophilic addition to the O-atom leading to initial adduct ions, which are 80.3—95.0% of the total product ions. Although no initial adduct ions are observed for $PhCOC_2H_5$ and $PhCOOC_2H_5$, major product ions are formed by electrophilic addition to the O-atom followed by dissociation and molecular eliminations. The reaction mechanism is discussed based on product ion distributions and semi-empirical calculations of the energies of intermediates and products. The results obtained are compared with reported ion-cyclotron-resonance data for aliphatic carbonyl compounds.

We have recently started a systematic mass-spectrometric study 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 completely free from a solvent.[1—5] In a recent paper,[5] results for monosubstituted benzenes carrying a hydroxy or alkoxy group were reported. The most favorable product channel for PhOH and PhROH (R = CH_2, CH_2CH_2, $CHCH_3$) was electrophilic addition to the O-atom followed by CF_3OH elimination due to a cleavage of Ph–O and R–O bonds. For the reaction with PhOH, electrophilic addition to the ring followed by HF elimination competes with this process, because electron-donating properties of the OH group strongly promotes the addition to the ring. For the reaction with $PhOC_2H_5$, a similar resonance effect of the OC_2H_5 group probably promotes the ring addition followed by C_2H_4 and C_2H_4 + HF eliminations. Since such an effect disappears by an insertion of the alkyl groups between Ph and OH, the corresponding channels were absent for PhROH (R = CH_2, CH_2CH_2, $CHCH_3$). As minor product channels, charge transfer (CT) was found for PhOH, $PhOCH_3$, and $PhOC_2H_5$. The lack of CT for $PhCH_2CH_2OH$ and $PhCH(OH)CH_3$ could be explained by higher ionization potentials (IP) than the recombination energy of CF_3^+ (≤ 8.90 eV). Although the IP value of $PhCH_2OH$ is lower than the recombination energy of CF_3^+, the CT channel could not be found.

In this work, ion-molecule reactions of CF_3^+ with PhCOX (X = H, CH_3, C_2H_5, OCH_3, OC_2H_5) were studied to examine the reactivity of monosubstituted benzenes with an aldehyde, ketone, or ester group. All of these reagents have highly reactive lone-pair electrons on the oxygen atom. Therefore, not only electrophilic attack of CF_3^+ on a benzene ring but also that on a substituent is possible. The reaction mechanism is discussed based on product ion distributions and semi-empirical calculations of potential energies of reaction pathways. The results obtained are compared with previous data on the reactions of CF_3^+ with aliphatic aldehydes, ketones, and esters obtained by using an ion-cyclotron resonance (ICR) method.[6,7]

Experimental

The ion-beam apparatus used in this study was identical with that reported previously.[1—5,8,9] 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 in the Ar afterglow.[8] They 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. The reactant and product ions were analyzed through an orifice using a quadrupole mass spectrometer. Operating pressures were 0.5—1.0 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 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] 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^+–PhCHO, CF_3^+–$PhCOCH_3$, CF_3^+–$PhCOC_2H_5$, CF_3^+–$PhCOOCH_3$, and CF_3^+–$PhCOOC_2H_5$ pairs were evaluated to be 545, 539, 533, 533, and 529 m s^{-1}, corresponding to average center-of-mass translational energies of 64, 66, 67, 67, and 68 m eV, respectively. Therefore, the present experiments were done at only slightly hyperthermal energies. In this experiment, the sample gas pressures were too low to be controlled by using a mass flowmeter. Therefore, it was difficult to determine the reaction rate coefficients. The vapor pressure of PhCOOH was so low that no product ion could be detected in the present measurement.

The heats of formation are known for the reactant ion, reagents, and some stable products obtained in this work.[11,12] However, there are many species the ΔH° values of which are unknown. These values were calculated by using a semi-empirical MNDO method (MOPAC Ver. 6.0) to describe the potential-energy diagram of the reaction pathways. A reasonable agreement between calculated and experimental ΔH° values of typical neutral species and ions[5] suggested that MNDO calculations were useful to discuss the reaction pathways.

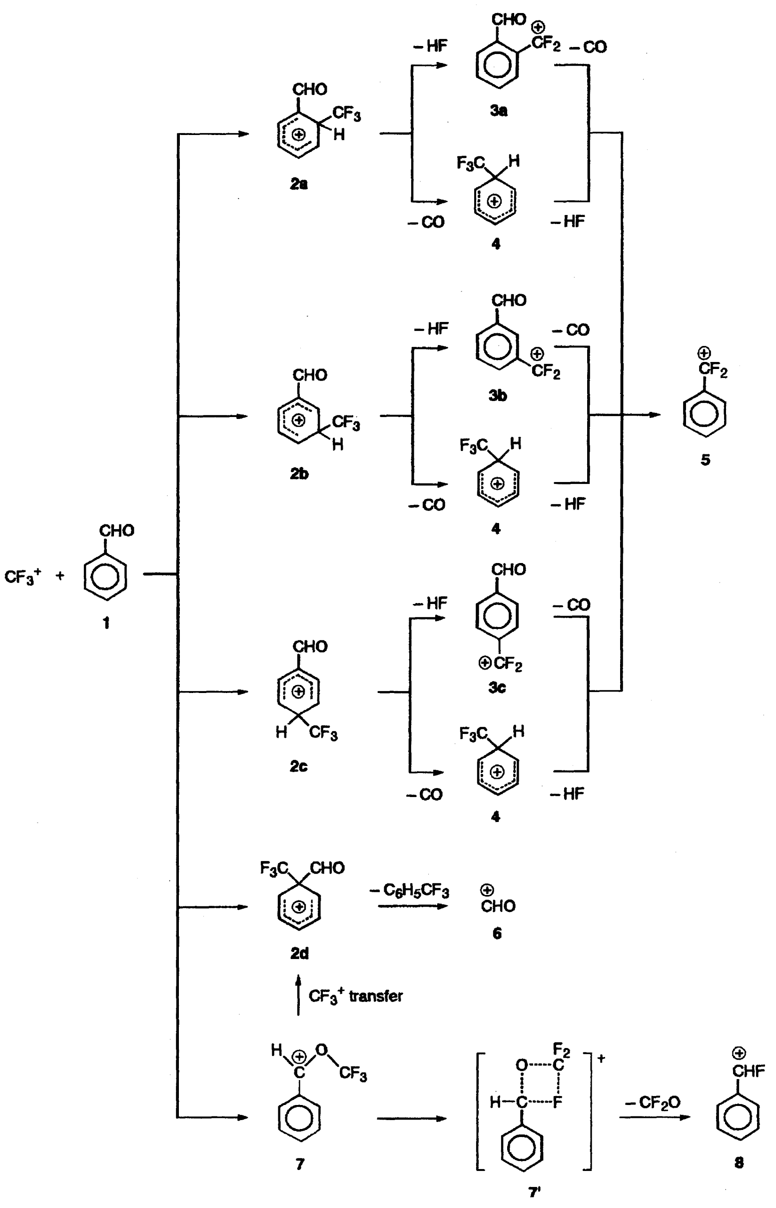
Results and Discussion

Benzaldehyde: The observed product channels and their branching ratios are summarized in Table 1. For the reaction with PhCHO, five product channels (1a)—(1e) were observed. The most outstanding feature is the appearance of the initial adduct $C_8H_6OF_3^+$ ion with a high branching ratio. It can be formed through electrophilic attack of CF_3^+ either on the ring or the substituent, as shown in Scheme 1. The electron-withdrawing effect of the CHO group will suppress the formation of Wheland-type adduct ions **2a**—**2c**, while a high reactivity of the lone-pair electrons on the oxygen atom will yield O-adduct ion **7**, preferentially. We have recently found that the initial ring adduct $C_7H_6F_3^+$ ion, formed in the CF_3^+/C_6H_6 reaction, decomposes completely by loss of HF.[1,4] Therefore, it is highly likely that ring-adduct ions **2a**—**2c**, formed in the CF_3^+/PhCHO reaction, also decompose completely into **3a**—**3c** by loss of HF. On the basis of the above findings, the initial adduct ion will be O-adduct ion **7**. In order to examine the validity of this prediction, the potential energies of the CF_3^+-addition/molecular-elimination pathways were evaluated (Fig. 1). Since there will be no energy barrier for the formation of the initial adduct ions, the relative formation rates of initial adduct ions will be governed thermochemically. It is clear from Fig. 1 that O-adduct ion **7** is much more stable than ring-adduct ions **2a**—**2c**, which may easily undergo HF elimination. These facts support our prediction that **7** is the initial adduct ion.

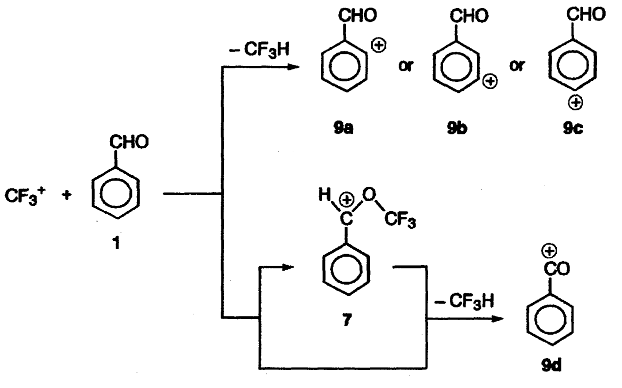
As minor product ions, $C_7H_5F_2^+$, $C_7H_6F^+$, $C_7H_5O^+$, and CHO^+ were found. The most probable reaction mechanism for the formation of these ions is shown in Schemes 1 and 2. The $C_7H_5F_2^+$ ion (**5**) is formed by loss of HF and CO from ring-adduct ions **2a**—**2c**, while the $C_7H_6F^+$ ion (**8**) is produced by loss of CF_2O from substituent-adduct ion **7**. Although the formation of the initial adduct ion is governed thermochemically, the branching ratios of elimination pathways from the adduct ions will be controlled kinetically. It should be noted that initial adduct ion **7** is preferentially formed, though the ΔH° value of **7** is higher than those of **8**+CF_2O and **9d**+CF_3H (Figs. 1 and 2). The formation of **8** via four-center intermediate **7′** is kinetically unfavorable because of the existence of a high energy barrier between **7** and **8**. Some energy barrier will also exist for the decomposition of **7** with loss of CF_3H. Therefore, only a small part of **7** will decompose into **8** and **9d**. Since the branching ratios of processes (1a)—(1e) are independent of the PhCHO and Ar pressures under the present experimental conditions, collisional stabilization by the PhCHO and Ar atoms will be insignificant for the formation of **7**. A radiative association process, as found for the thermal-energy reactions of NO^+ with such bases as 2-butanone and 3-pentanone[13] may take part in the stabilization of **7**.

Table 1. Product Ion Distributions in Ion–Molecule Reactions of CF_3^+ with Aromatic and Aliphatic Carbonyl Compounds at Near-Thermal Energies

This work				Ref. 7			
Reagent	Product	Branching ratio/%		Reagent	Product	Branching ratio/%	
C_6H_5CHO	$C_8H_6OF_3^+$	84.9±2.7	(1a)	CH_3CHO	$C_2H_4F^+ + CF_2O$	100	(6)
	$C_7H_5F_2^+ + HF + CO$	5.0±0.7	(1b)	C_2H_5CHO	$C_3H_6F^+ + CF_2O$	6	(7a)
	$C_7H_6F^+ + CF_2O$	8.4±1.8	(1c)		$C_3H_5^+ + CF_2O + HF$	94	(7b)
	$C_7H_5O^+ + CF_3H$	1.3±0.4	(1d)				
	$CHO^+ + C_6H_5CF_3$	0.4±0.1	(1e)				
$C_6H_5COCH_3$	$C_9H_8OF_3^+$	95.0±0.9	(2a)	CH_3COCH_3	$C_3H_6F^+ + CF_2O$	75	(8a)
	$COCH_3^+ + C_6H_5CF_3$	5.0±0.9	(2b)		$C_3H_5^+ + CF_2O + HF$	25	(8b)
$C_6H_5COC_2H_5$	$C_9H_{10}F^+ + CF_2O$	15.6±1.5	(3a)	$CH_3COC_2H_5$	$C_4H_8F^+ + CF_2O$	3	(9a)
	$C_9H_9^+ + CF_2O + HF$	53.9±3.0	(3b)		$C_4H_7^+ + CF_2O + HF$	87	(9b)
	$C_6H_5CO^+ + CF_3C_2H_5$	18.1±3.1	(3c)		$CH_3CO^+ + CF_3C_2H_5$	9	(9c)
	$C_7H_7^+ + CF_2O + HF + C_2H_2$ and/or $C_7H_7^+ + CF_2O + C_2H_3F$	8.4±0.6	(3d)				
	$COC_2H_5^+ + C_6H_5CF_3$	4.0±0.7	(3e)				
$C_6H_5COOCH_3$	$C_9H_8O_2F_3^+$	80.3±1.7	(4a)	CH_3COOCH_3	$CH_3CO^+ + CF_3OCH_3$	100	(10)
	$C_6H_5CO^+ + CF_3OCH_3$	4.7±0.7	(4b)				
	$COOCH_3^+ + C_6H_5CF_3$	15.0±1.4	(4c)				
$C_6H_5COOC_2H_5$	$C_6H_5CO^+ + CF_3OC_2H_5$	94.5±0.9	(5a)	$HCOOC_2H_5$	$HCO^+ + CF_3OC_2H_5$	90	(11a)
	$C_2H_5^+ + C_6H_5COOCF_3$	5.5±0.9	(5b)		$CF_3COOH_2^+ + C_2H_4$	10	(11b)



Scheme 1.



Scheme 2.

The minor CHO^+ ion (**6**) is produced via unimolecular decomposition of *ipso*-adduct ion **2d** (Scheme 1). Since the potential energy of **2d** is higher than *ortho*-, *meta*-, and *para*-adduct ions **2a**—**2c** (Fig. 1), the formation of the former adduct ion will be unfavorable. This prediction is inconsistent with the experimental finding that the electrophilic attack of CF_3^+ occurs exclusively on the *ipso* position. It is highly likely that **2d** is not produced through a direct attack on the *ipso* position but through a CF_3^+ transfer from O-adduct ion **7**. Three mechanism could be invoked in the formation of the $C_7H_5O^+$ ion (**9a**—**9d**), including a direct H^- abstraction from the ring and the substituent, or alternatively, the unimolecular dissociation of excited **7** with loss of CF_3H (Scheme 2). The electron-withdrawing properties of the CHO group promote the hydride-transfer process, while highly stable benzyl-type cation **9d** is formed by the hydride transfer from the substituent. In order to examine the relative importance of the three pathways, an MNDO potential-energy diagram for the formation of **9a**—**9d** is calculated. The results obtained are shown in Fig. 2. On the basis of MNDO calculations, the potential energies of **9a**—**9c**+CF_3H formed through the H^- abstraction from the benzene ring are slightly

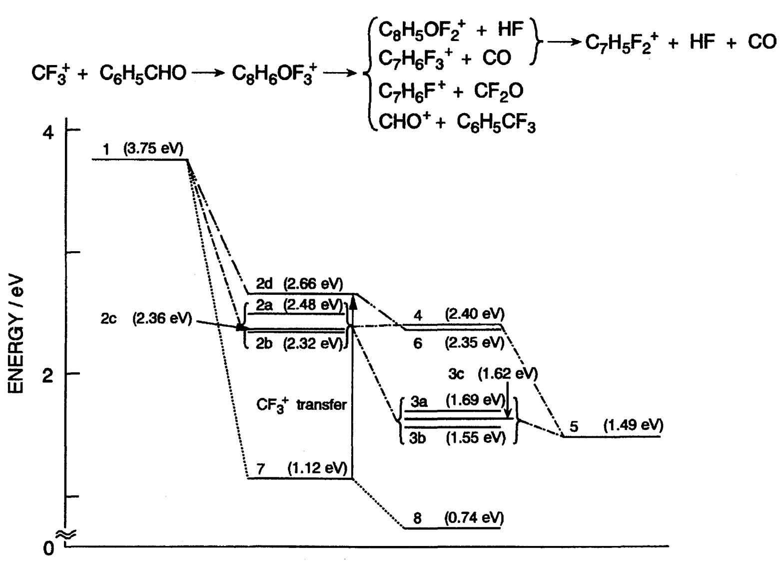


Fig. 1. A potential-energy diagram for the electrophilic CF_3^+-addition/dissociation pathways in the CF_3^++PhCHO system.

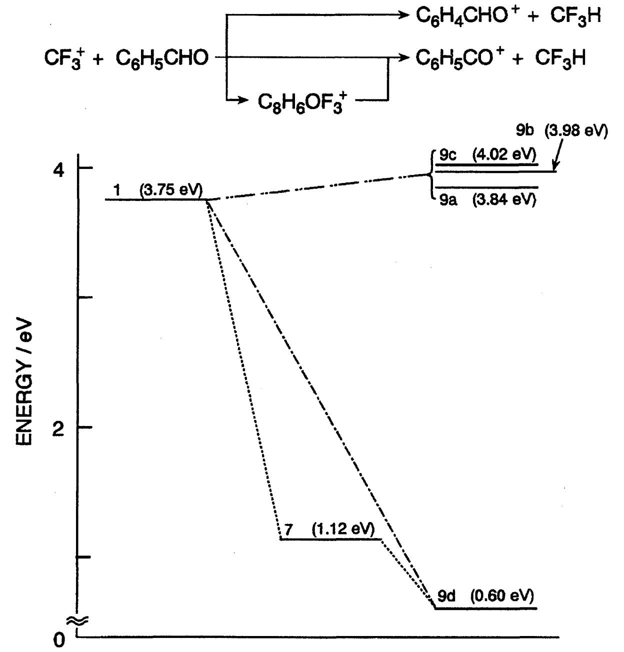
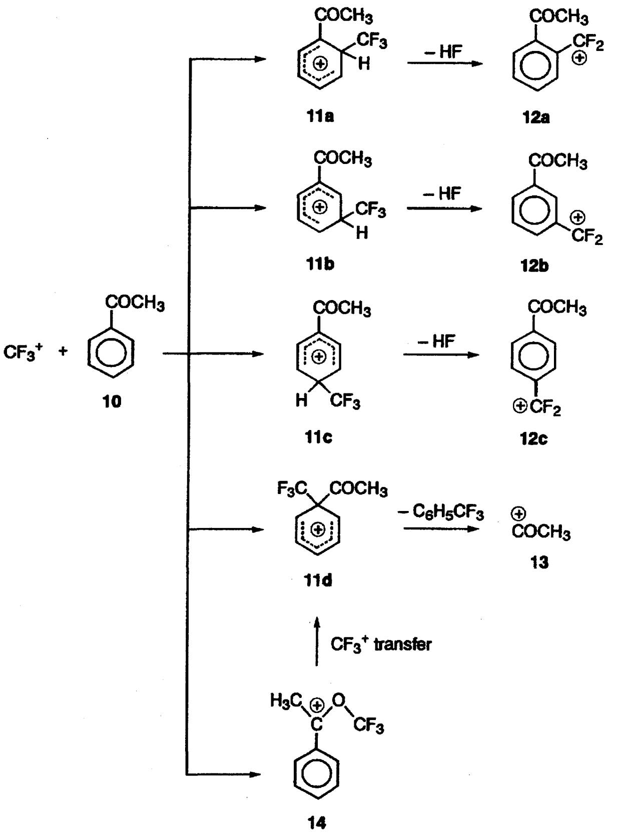


Fig. 2. A potential-energy diagram for the CF_3^+ + PhCHO→$C_7H_5O^+$+CF_3H reaction.



Scheme 3.

higher than that of the reactant system, while the energy of **9d**+CF_3H is much lower than that of the reactant system due to the high stability of benzyl-type cation **9d**. It is therefore concluded that $C_7H_5O^+$ is formed by either direct hydride transfer from the substituent or decomposition of substituent-adduct ion **7**.

Methyl Phenyl Ketone: The reaction pathway becomes more simple for $PhCOCH_3$ and only two product channels (2a) and (2b) were observed, as shown in Table 1. The $C_9H_8OF_3^+$ ion can be formed via an attack of CF_3^+ on the ring and/or the substituent, as shown in Scheme 3. The electron-withdrawing effect of the $COCH_3$ group will suppress the formation of Wheland-type adduct ions **11a**—**11c**, while a high reactivity of the lone-pair electrons on the oxygen atom will yield O-adduct ion **14**, preferentially. An MNDO potential energy diagram for the electrophilic-addition/molecular-elimination-pathways is shown in Fig. 3. Benzyl-type adduct ion (**14**) is much more stable than the ring adduct ions (**11a**—**11c**), and the ring adduct ions are unstable for the HF elimination, as in the case of PhCHO. It is therefore concluded that the initial adduct ion is **14**.

The minor $COCH_3^+$ ion (**13**) is formed through the unimolecular decomposition of *ipso*-adduct ion **11d** (Scheme 3).

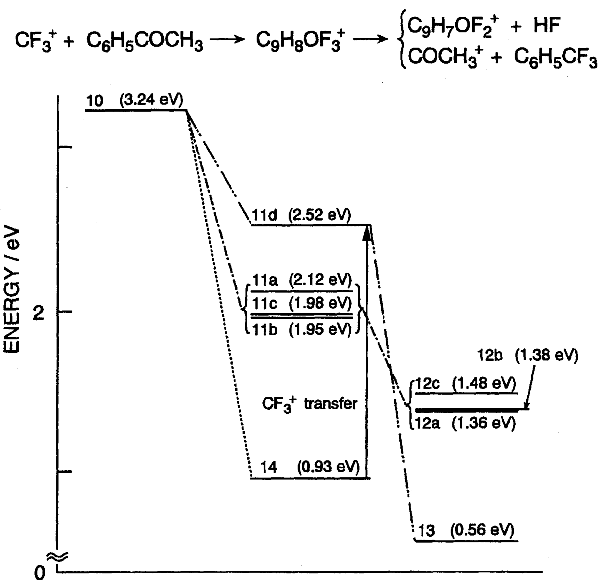


Fig. 3. A potential-energy diagram for the electrophilic CF_3^+- addition/dissociation pathways in the CF_3^+ + $PhCOCH_3$ system.

On the basis of the potential-energy diagram shown in Fig. 3, the potential energy of **13** + $PhCF_3$ is lower than that of O-adduct ion **14**. Ring adduct ions **11a**—**11c** are unstable for the HF elimination, as found for the other aromatic molecules. Therefore, the formation of **12a**—**12c** is expected, if **11a**—**11c** are formed. The lack of **12a**—**12c** led us to conclude that the electrophilic-addition pathway leading to **11a**—**11c** is closed for $PhCOCH_3$ because the electron-withdrawing properties and the high reactivity of the lone-pair electron in the $COCH_3$ group promote the substituent as only the reactive site. The formation of *ipso*-adduct ion **11d** is thermochemically most unfavorable, as shown in Fig. 3. Therefore, the formation of **13** probably proceeds through a CF_3^+ transfer from the excited states of **14** to **11d**.

Ethyl Phenyl Ketone: Five product channels (3a)—(3e) were observed with the branching ratios given in Table 1. A possible reaction mechanism is shown in Scheme 4. In order to obtain information about the CF_3^+-addition/molecular-elimination pathways, a potential-energy diagram was evaluated from reported and calculated ΔH° values of the reactants and products (Fig. 4). The most outstanding feature is the lack of an initial adduct ion, which was a dominant product ion for PhCHO and $PhCOCH_3$. The major product channels are electrophilic addition to the O-atom of the carbonyl group followed by eliminations of CF_2O, CF_2O+HF, and $CF_2O+HF+C_2H_2$(or C_2H_3F), leading to $C_9H_{10}F^+$, $C_9H_9^+$, and $C_7H_7^+$, respectively. These ions occupy 77.9±5.1% of the total product channels. This shows that the elimination of CF_2O via four-center intermediate **19′** occurs preferentially by the substitution of the C_2H_5 group. The $C_7H_7^+$ ion can be formed through **20**→**21**→**22** and **20**→**22**, as shown in Scheme 4. The cation **21** is formed as a major ion and the potential energy of **22** is much higher than that of **20** (Fig. 4). These facts led us to conclude that the formation of **22** occurs exclusively from the former process.

Although the major product channels proceed through four-center intermediate **19′**, small amounts of the $PhCO^+$ and $COC_2H_5^+$ ions are formed. One possible mechanism for the formation of the $PhCO^+$ ion (**9d**) is a simple displacement reaction from PhCO to CF_3 through the attack of CF_3^+ to the PhCO–C_2H_5 bond, as reported for reactions with aliphatic carbonyl compounds.[7] The other possible mechanism is the elimination of $CF_3C_2H_5$ from **19**. Although **9d** is formed from $PhCOC_2H_5$, it is not produced from $PhCOCH_3$. This may be due to the fact that the elimination channel of CF_3CH_3 from **14** is closed because the energy barrier for the

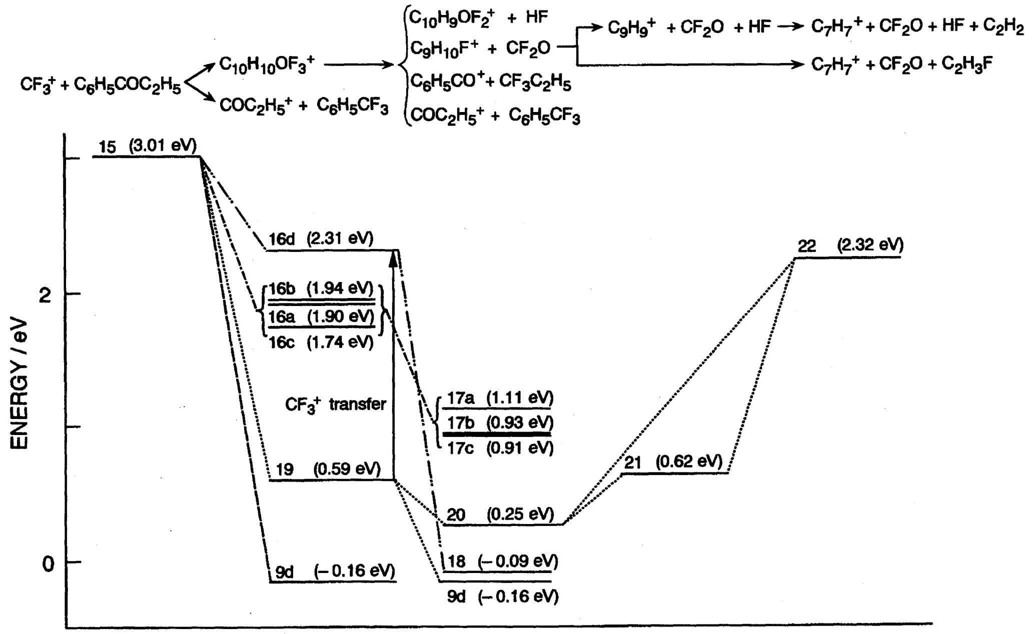
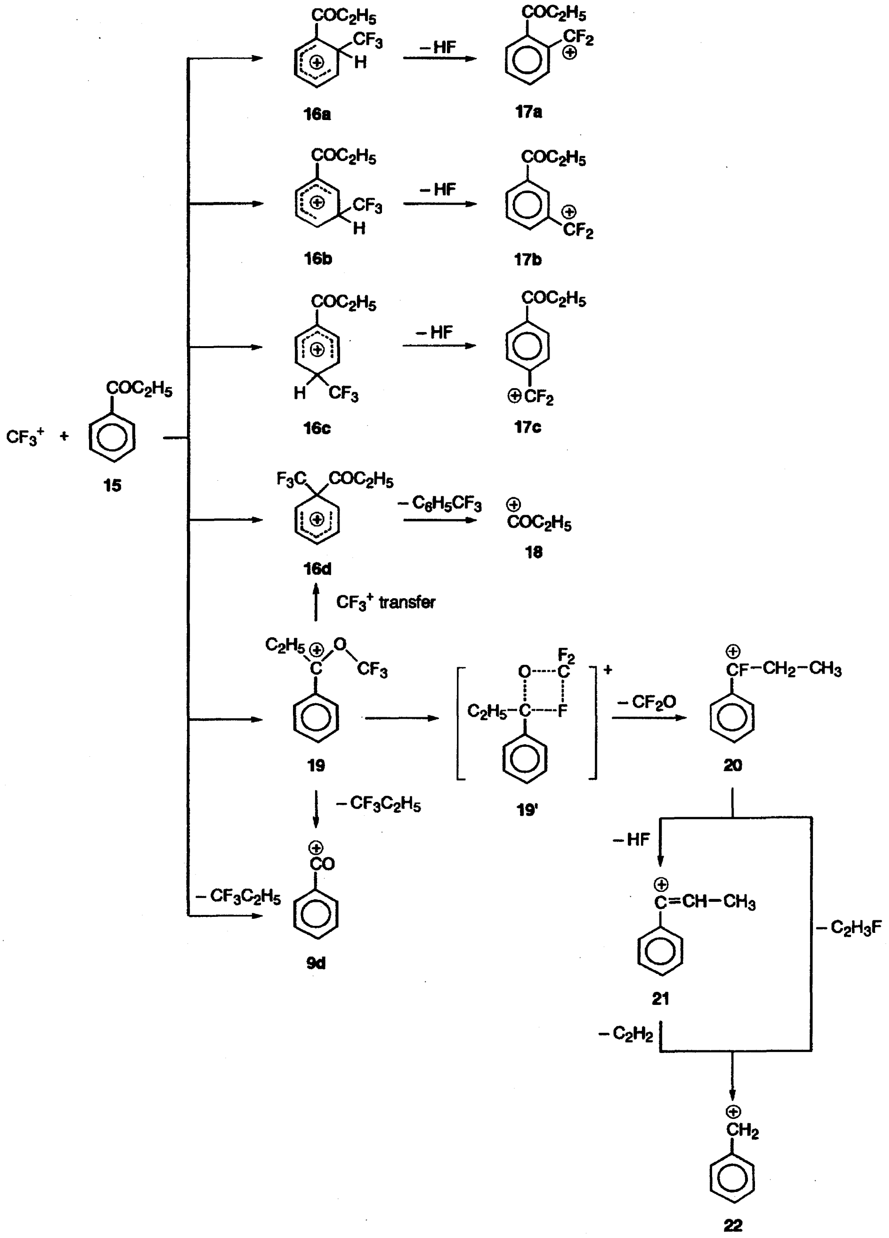


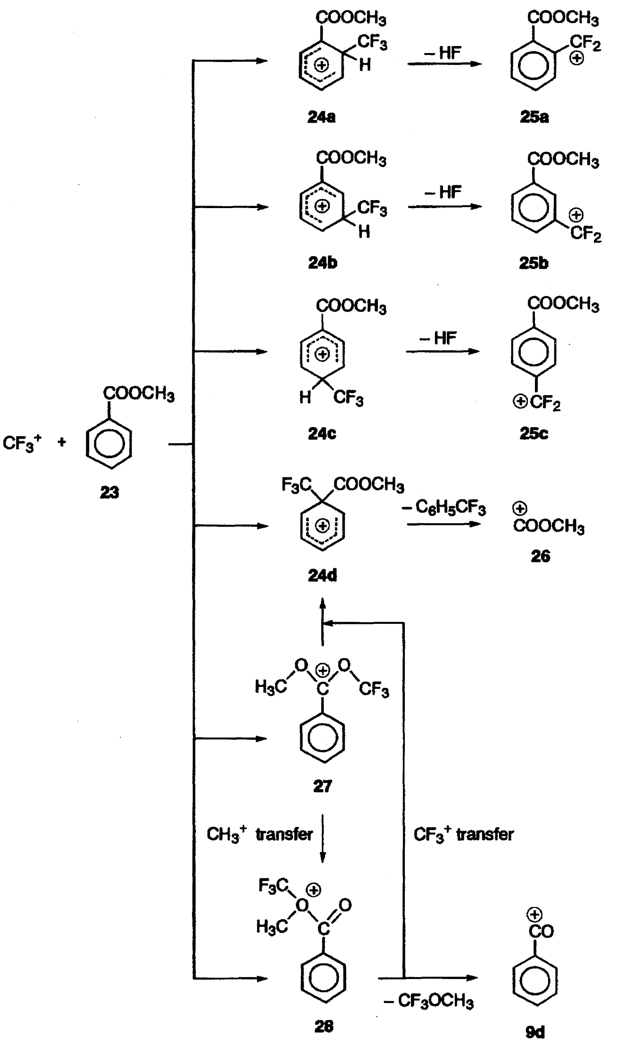
Fig. 4. A potential-energy diagram for the electrophilic CF_3^+-addition/dissociation pathways in the CF_3^+ + $PhCOC_2H_5$ system.



Scheme 4.

elimination of CF_3CH_3 is high. The $COC_2H_5^+$ ion (**18**) is probably formed via *ipso*-adduct ion **16d**. Although the formation of *ortho-*, *meta-*, and *para*-adduct ions (**16a**—**16c**) is thermochemically more favorable than that of **16d**, no evidence of their formation was found. It is therefore reasonable to assume that the formation of **16d** occurs through a CF_3^+ transfer from O-adduct ion **19**. On the basis of the above facts, electrophilic attack of CF_3^+ takes place selectively on the O-atom in the substituent because the electron-withdrawing properties of COC_2H_5 suppress the formation of Wheland-type adduct ions.

Methyl Bezoate: The $CF_3^+/PhCOOCH_3$ reaction gives three product channels (4a)—(4c) given in Table 1. The most probable reaction processes are shown in Scheme 5. The major product channel is the electrophilic addition leading to the initial adduct ion, as found for PhCHO and $PhCOCH_3$. In addition to three ring-adducts ions **24a**—**24c**, two substituent-adduct ions **27** and **28** can be produced as possible candidates of the adduct $C_9H_8O_2F_3^+$ ion. On the basis of semi-empirical calculations, the substituent-adduct ions (**27**, **28**) are much more stable than the ring-adduct ions (**24a**—**24c**), as shown in Fig. 5. It is therefore reasonable to assume that the observed initial adduct ion is **27** and/or **28**. In this study, we found that large fractions of initial adduct ions are formed by the attack of CF_3^+ on the O-atom of the carbonyl group. On the other hand, a small amount of initial adduct ion has been observed by the attack of CF_3^+ on the O-atom of the methoxy group in our previous study.[2] On the basis of these findings, both **27** and **28** cannot be excluded from the possible candidates for the initial adduct ion, though **28** is thermochemically more favorable than **27**. The potential-energy diagram for the ring-addition/HF-elim-



Scheme 5.

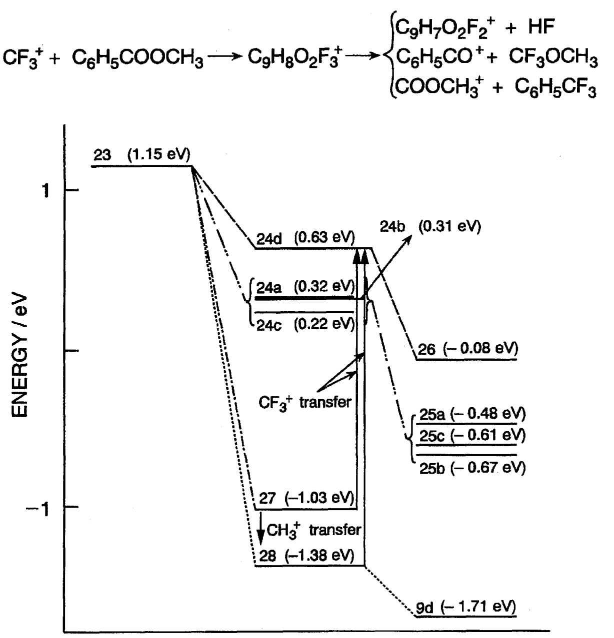


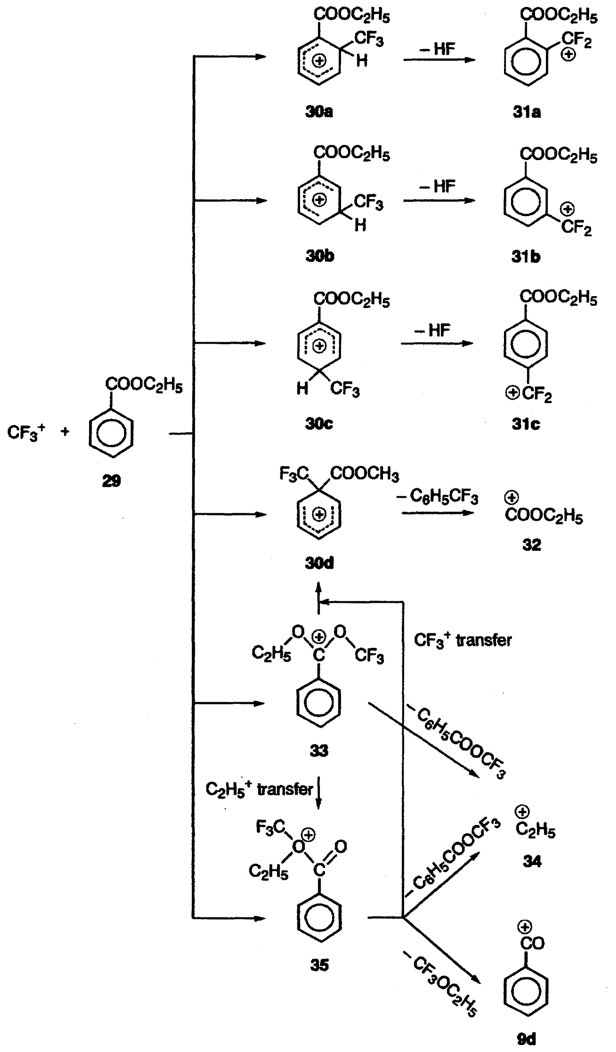
Fig. 5. A potential-energy diagram for the electrophilic CF_3^+- addition/dissociation pathways in the CF_3^+ + $PhCOOCH_3$ system.

ination-pathway (Fig. 5) demonstrates that **24a**—**24c** will be decomposed completely by loss of HF. Thus, the lack of **25a**—**25c** implies that the substitution of the highly reactive electron-withdrawing CH_3COO group to the benzene ring promotes the substituent as the only reactive site, as in the case of $PhCOCH_3$.

The $COOCH_3^+$ ion (**26**) is formed through *ipso*-adduct ion **24d**. It is clear from Fig. 5 that ring-adduct ions **24a**—**24c** are too unstable for the HF elimination. Therefore, **25a**—**25c** will be formed through thermochemically favored **24a**—**24c**, if electrophilic addition takes place to the benzene ring. However, no evidence of the formation of ring-adduct ions **24a**—**24c** could be found. It is therefore expected that **24d** is formed via more stable substituent adduct ions **27** and/or **28** in the excited states. The formation of the $PhCO^+$ ion (**9d**) proceeds through the unimolecular decomposition of the most stable oxonium ion **28**, as shown in Scheme 5. The precursor ion **28** can be formed via either direct electrophilic addition or a $C_2H_5^+$ transfer from **27**.

Ethyl Benzoate: A possible reaction mechanism in the $CF_3^+/PhCOOC_2H_5$ is shown in Scheme 6. Two product channels (5a) and (5b) are found with the branching ratios given in Table 1. The major product channel is the electrophilic addition to the O-atom in the ethoxy group followed by loss of $CF_3OC_2H_5$, leading to the $PhCO^+$ ion (**9d**). The minor product channel for the reactions with $PhCOOC_2H_5$ was the formation of the $C_2H_5^+$ ion (**34**), which proceeds through the electrophilic addition to the O-atom in either the ethoxy group or the carbonyl group followed by the unimolecular decomposition of the O–C_2H_5 bond. There are significant differences in the product channels between $PhCOOCH_3$ and $PhCOOC_2H_5$. The most outstanding difference is the lack of the initial adduct ion for $PhCOOC_2H_5$. The formation of $PhCO^+$, which was a minor product channel for $PhCOOCH_3$, becomes a major product channel for $PhCOOC_2H_5$. These findings may be explained by the fact that the $C_2H_5^+$ transfer from **33** is faster than the CH_3^+ transfer from **27**. The observation of $C_2H_5^+$ from $PhCOOC_2H_5$ supports this explanation. In this study, we found that O-adducts resulting from the reactions with aromatic carbonyl compounds with an ethyl group (**19**, **33**, **35**) decompose completely, while the decomposition of those with a methyl group (**14**, **27**, **28**) is inefficient. This difference arises from the fact that efficient dissociation pathways of the O-adducts are opened by the substitution of the more stable C_2H_5 group.

Although the $COOCH_3^+$ ion was formed with a branching ratio of 15.0±1.4% for $PhCOOCH_3$, the corresponding $COOC_2H_5^+$ ion could not be observed for $PhCOOC_2H_5$. These results imply that the reaction mechanism strongly depends on the alkyl group attached to the PhCOO group. No evidence of ring-addition channels was found. The potential energies of the ring-adduct ions are higher than the substituent ones, as shown in Fig. 6. The electron-withdrawing properties of the $COOC_2H_5$ group will suppress the electrophilic addition to the ring. These facts along with



Scheme 6.

a high reactivity of the $COOC_2H_5$ group will promote the substituent as the only reactive site.

Comparison with the ICR Study on Aliphatic Carbonyl Compounds: For comparison, the ICR data of Ausloos et al.[7] for aliphatic carbonyl compounds are given in Table 1. The major product channels for CH_3CHO, C_2H_5CHO, CH_3COCH_3, and $CH_3COC_2H_5$ are the electrophilic attack on the lone-pair electron of the O-atom followed by loss of CF_2O or its further decomposition by loss of HF. Ausloos et al.[7] reported that these reactions proceed through four-center intermediates, as shown in Schemes 1 and 4 for the cases of PhCHO and $PhCOC_2H_5$ (**7**′, **19**′). For the reaction with $CH_3COC_2H_5$, a small amount of the CH_3CO^+ ion is formed. Ausloos et al.[7] predicted that it is produced through a displacement reaction:

$$CF_3^+ + RCOR' \rightarrow RCO^+ + CF_3R', \qquad (12)$$

where $R=CH_3$ and $R'=C_2H_5$. Since the major product channel for the aromatic compounds is the formation of the initial adduct ion, there is a great difference in the major product channels for RCHO and $RCOCH_3$ between aromatic and aliphatic compounds. For the cases of PhCHO and $PhCOCH_3$, initial O-adduct ions are stabilized by the resonance effects of the phenyl group, while such a stabilization of O-adduct ion is absent for the aliphatic aldehydes and ketones. Therefore, the initial O-adduct ions are preferentially formed in the aromatic compounds. Although hydride-transfer channel is open for PhCHO, it is closed for aliphatic aldehydes. It can also be explained by the formation of a highly stable benzyl-type cation for PhCHO.

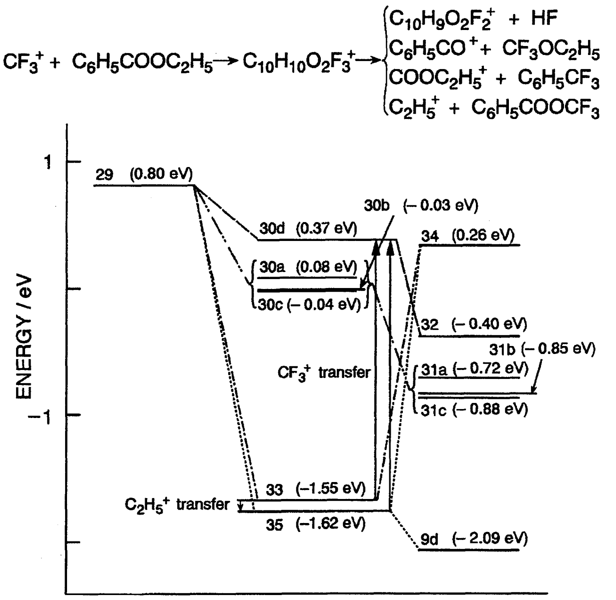


Fig. 6. A potential-energy diagram for the electrophilic CF_3^+- addition/dissociation pathways in the CF_3^+ + $PhCOOC_2H_5$ system.

In contrast with the results for RCHO and $RCOCH_3$, the main product channel for $RCOC_2H_5$ is the same between the aromatic and aliphatic compounds; a four-center reaction followed by loss of CF_2O and CF_2O+HF occupies the dominant product channel for both compounds. We found here that the major product channel for $PhCOOCH_3$ is the electrophilic addition to the O-atoms of the substituent. This result is sharply contrasted with the ICR data for CH_3COOCH_3, in which a displacement reaction occurs preferentially. This significant difference can be explained by the stabilization of the benzyl-type cation due to the resonance effects of the phenyl group. Although there is a large difference in the dominant reaction pathway between aromatic and aliphatic $RCOOCH_3$ compounds, the major product channel is identical for $RCOOC_2H_5$. The electrophilic addition to the O-atom in the ethoxy group followed by the unimolecular decomposition of the $RCO–OC_2H_5$ occurs preferentially for both cases. Summing up these results, the product channels in the reactions of CF_3^+ with aromatic and aliphatic carbonyl compounds depend strongly on the substituent.

Conclusion

The gas-phase ion-molecule reactions of CF_3^+ with mono-substituted benzenes carrying a carbonyl group have been studied at near-thermal energies. The branching ratios of electrophilic addition to ring and substituent, displacement

Table 2. Reaction Mechanism of CF_3^+ with Aromatic and Aliphatic Carbonyl Compounds at Near-Thermal Energies

		Branching ratio of each reaction/%		
Reagent	Ionization potential/eV[a]	Electrophilic addition	Displacement reaction	Hydride transfer
C_6H_5CHO	9.49	5.4±0.8(R),[b] 93.3±4.5—94.6±4.9(S)[c]		0—1.3±0.4
$C_6H_5COCH_3$	9.29	5.0±0.9(R), 95.0±0.9(S)		
$C_6H_5COC_2H_5$	9.16	4.0±0.7(R), 77.9±5.1—96.0±4.0(S)	0—18.1±3.1	
$C_6H_5COOCH_3$	9.32	15.0±1.4(R), 85.0±2.4(S)		
$C_6H_5COOC_2H_5$	8.90	100(S)		

a) Ref. 12. b) Addition to benzene ring. c) Addition to lone-pair electrons of oxygen on substituents.

reactions, and hydride transfer are summarized in Table 2. The electrophilic addition to the ring or the substituent was classified based upon the final position of F atoms. The most favored product channel was the electrophilic addition to the O-atom in the substituent with and without further decomposition and molecular elimination. These processes occupy 77.9—100% of the total product channel. As a minor product channel, the displacement reaction takes place for $PhCOC_2H_5$ and hydride transfer occurs for PhCHO. No CT channel was found. The IP values of these five compounds studied here are shown in Table 2. The lack of CT channel for PhCHO, $PhCOCH_3$, $PhCOC_2H_5$, and $PhCOOCH_3$ is consistent with higher IP values than the recombination energy of CF_3^+ ($\leq$8.90 eV).

The authors are grateful to Mr. Hiroki Ujita in our institute for his helpful discussion. This work was supported by a Grant-in-Aid for Scientific Research No. 06453026 from the Ministry of Education, Science, Sports and Culture, the Iwatani Naoji Memorial Foundation, and the Showa Shell Sekiyu Foundation for Promotion of Environmental Research.

References

1) M. Tsuji, M. Aizawa, and Y. Nishimura, *Chem. Lett.*, **1995**, 211.

2) M. Tsuji, M. Aizawa, and Y. Nishimura, *J. Mass Spectrom. Soc. Jpn.*, **43**, 109 (1995).

3) M. Tsuji, M. Aizawa, H. Ujita, and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, **68**, 2385 (1995).

4) M. Tsuji, M. Aizawa, and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, **68**, 3497 (1995).

5) M. Tsuji, M. Aizawa, and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, **69**, 147 (1996).

6) J. R. Eyler, P. Ausloos, and S. G. Lias, *J. Am. Chem. Soc.*, **96**, 3673 (1974).

7) P. Ausloos, S. G. Lias, and J. R. Eyler, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 261 (1975).

8) M. Tsuji, T. Funatsu, H. Kouno, Y. Nishimura, and H. Obase, *J. Chem. Phys.*, **96**, 3649 (1992).

9) M. Tsuji, H. Kouno, K. Matsumura, T. Funatsu, Y. Nishimura, H. Obase, H. Kugishima, and K. Yoshida, *J. Chem, Phys.*, **98**, 2011 (1993).

10) J. B. Anderson in "Molecular Beams and Low Density Gas Dynamics," ed by P. P. Wegener, Dekker, New York (1974), Vol. 4, p. 1.

11) H. M. Rosenstock, K. Draxl, G. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Suppl. 1 (1977).

12) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data*, **17**, Suppl. 1 (1988).

13) G. Weddle and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Processes*, **134**, 73 (1994).