Ion–Molecule Reactions of CF_3^+ with Simple Unsaturated Aliphatic Hydrocarbons at Near-Thermal Energy

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Ion-molecule reactions of CF_3^+ with C_2H_2 , C_2H_4 , and C_3H_6 have been studied at near-thermal energy (0.05 eV) by using an ion beam apparatus. Initial product ion distributions and reaction rate constants were determined and compared with previous beam and selected ion flow tube (SIFT) data. The CF_3^+/C_2H_2 reaction produces exclusively the electrophilic adduct $C_3H_2F_3^+$ ion. For C_2H_4 and C_3H_6 , hydride abstraction and electrophilic addition followed by HF elimination or fluoride transfer occur in parallel. The branching ratios of the former and latter reactions are 0.29 ± 0.04 : 0.71 ± 0.06 for the CF_3^+/C_2H_4 reaction and 0.07 ± 0.02 : 0.93 ± 0.07 for the CF_3^+/C_2H_4 systems, the lack of the HF elimination channel in the CF_3^+/C_2H_2 reaction, whereas the lack of the initial adduct ion in the CF_3^+/C_2H_4 reaction, is attributed to the different stability of the intermediate adduct ions for HF elimination. The reaction rate constants were 0.45×10^{-9} , 1.3×10^{-9} , and 1.6×10^{-9} cm³ s⁻¹ for C_2H_2 , C_2H_4 , and C_3H_6 , respectively, which correspond to 46%, 120%, and 130% of calculated rate constants from Langevin theory or a parametrized trajectory model. Although there are significant discrepancies in the product ion distributions between the present beam experiment and the previous beam data, the product ion distributions and the reaction rate constants obtained here are in reasonable agreement with the previous SIFT data.

Introduction

The study on ion-molecule reactions of CF_3^+ with alkynes and alkenes is significant for understanding the reaction mechanism of carbocations, which are important intermediates in organic reactions.¹ The ion-molecule reactions of CF_3^+ with C_2H_4 and C_3H_6 have been first studied by Stanney et al.² by using a triple quadrupole mass spectrometer. Their experiments were performed at different olefin pressures in the $(1-10) \times$ 10^{-6} Torr range (1 Torr = 133.3 Pa). It was found that the relative ion currents of product ions depended strongly on the olefin pressure. They reported that the CF3+/C2H4 yielded $C_2H_4F^+$ (44%), $C_3H_3F_2^+$ (23%), $C_2H_3^+$ (19%), and $C_3H_5^+$ (15%), while the CF_3^+/C_3H_6 reaction gave $C_2H_4F^+$ (49%), $\begin{array}{cccc} C_{3}H_{6}^{+} & (14\%), \ C_{3}H_{5}^{+} & (11\%), \ C_{3}H_{7}^{+} & (11\%), \ C_{4}H_{7}^{+} & (4\%), \\ C_{3}H_{4}F^{+} & (3\%), \ C_{3}H_{6}F^{+} & (3\%), \ \text{and} \ C_{2}H_{3}F_{2}^{+} & (3\%). \end{array}$ observations of the $C_3H_5^+$ ion in the CF_3^+/C_2H_4 reaction and the $C_3H_7^+$ and $C_4H_7^+$ ions in the CF_3^+/C_3H_6 reaction suggest that secondary ion-molecule reactions were not completely eliminated in their measurements. Since the recombination energy of CF_3^+ (9.25 \pm 0.04 eV,³ \leq 8.9 eV⁴) is lower than the ionization potential of C₃H₆ (9.73 eV),⁵ the following chargetransfer (CT) channel is endothermic:

$$CF_{3}^{+} + C_{3}H_{6} \rightarrow C_{3}H_{6}^{+} + CF_{3}$$
 (1)

$$\Delta H = 0.48 \text{ eV} \text{ or} \ge 0.83 \text{ eV}$$

However, they found $C_3H_6^+$ with a branching ratio of 14% in the CF_3^+/C_3H_6 reaction, indicating that the reactant CF_3^+ ion possessed at least an excess energy of 0.48 eV as internal and/ or translational energies in their experiments. On the basis of the above findings, it seems difficult to deduce the initial distributions of ionic products at thermal energy from their data.

Morris et al.⁶ have recently studied ion-molecule reactions

of CF_3^+ with C_2H_2 , C_2H_4 , and C_3H_6 at 300 and 525 K by using a variable-temperature SIFT method. They found that the CF_3^+ reactions all include some hydride transfer, except for the reaction with C_2H_2 , which is a condensation (association) process leading to $C_3H_2F_3^+$. In addition to hydride transfer, elimination of HF was observed in the reactions of CF_3^+ with C_2H_4 and C_3H_6 . A negative temperature dependence was found for the rate constants between 300 and 525 K.

In the present study, ion-molecule reactions of CF_3^+ with C_2H_2 , C_2H_4 , and C_3H_6 have been investigated at near-thermal energy by using a low-energy ion beam apparatus. One advantage of our beam apparatus is that the contribution from collisional relaxation of long-lived intermediates and secondary ion-molecule reactions can be greatly reduced because of low operating pressures and a short distance between a reagent gas inlet and a sampling orifice (3 cm). The other advantage is that the reactant CF_3^+ ion beam is completely thermalized before it enters the reaction zone. The initial product ion distributions and reaction rate constants are determined and compared with the previous beam and SIFT data. The reaction mechanism for the formation of various ionic products is discussed.

Experimental Section

The low-energy ion beam apparatus used in the present study was similar to that used for the ion-molecule reactions of Ar⁺, CO_2^+ , and ArN_2^+ with simple aliphatic hydrocarbons.⁷⁻⁹ In brief, a mixture of the ground-state $Ar^+(^2P_{3/2,1/2})$ ions and the metastable $Ar(^{3}P_{0,2})$ atoms was generated by a microwave discharge of high-purity Ar gas in a quartz flow tube.¹⁰ There are two spin-orbit states, $Ar^+(^{2}P_{3/2})$ and $Ar^+(^{2}P_{1/2})$, with recombination energies of 15.76 and 15.92 eV, respectively. The lack of the upper $Ar^+(^{2}P_{1/2})$ component and the presence of the lower $Ar^+(^{2}P_{3/2})$ one in the Ar flowing afterglow were confirmed by observing ArF(B-X,D-X) excimers resulting from the spin-orbit state selective $Ar^+(^{2}P_{1/2,3/2}) + SF_6^-$ ionic

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recombination reaction.^{11,12} The metastable $Ar({}^{3}P_{0,2})$ atoms were quenched by the addition of a sufficient amount of CF₄. The CF₃⁺ ions were produced by the thermal energy CT reaction of Ar^{+} with CF₄:

$$\operatorname{Ar}^{+}({}^{2}\mathrm{P}_{3/2}) + \operatorname{CF}_{4} \xrightarrow{k_{2}} \operatorname{CF}_{3}^{+}(\tilde{X}) + \mathrm{F} + \mathrm{Ar} + 1.13 \text{ eV}$$
 (2)
 $k_{2} = (6.6 \pm 3.9) \times 10^{-10} \text{ cm}^{3} \text{ s}^{-1} {}^{13,14}$

Since only CF_3^+ is formed by the Ar^+/CF_4 reaction, a pure CF_3^+ ion beam can be obtained without mass selection. After being completely thermalized by collisions with the buffer Ar gas, with reactant CF_3^+ ions were expanded into a low-pressure chamber through a molybdenum nozzle (2 mm in diameter) centered on the flow tube.

The reagent gas was kept at a constant mass flow and injected into the reaction zone from a stainless steel orifice placed 5 cm downstream from the nozzle. The reactant and product ions were sampled through a molybdenum orifice (2 mm in diameter) placed 3 cm further downstream and analyzed using an ULVAC MSQ400 quadrupole mass spectrometer. The mass spectra were averaged using a Kenwood DCS-8200 digital storage oscilloscope and the data stored in a microcomputer. Operating pressures were 0.7-1.2 Torr in the flowing-afterglow ion source chamber, $(2.0-4.0) \times 10^{-3}$ Torr in the reaction chamber, and $(0.8-2.0) \times 10^{-5}$ Torr in the mass analyzing chamber. The partial pressures of reagent gases were $\leq 1 \times 10^{-5}$ Torr in the reaction chamber and $\leq 1 \times 10^{-6}$ 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, a relative translational temperature of 69 K, and a final velocity of 487 m s⁻¹ from known relations.¹⁵ Assuming a Boltzmann distribution of 300 K for reagents and a perpendicular crossing of the reactant ion beam and a reagent molecule, the relative velocities of the $CF_3^+-C_2H_2$, $CF_3^+-C_2H_4$, and $CF_3^+-C_3H_6$ pairs were evaluated to be 694, 681, and 623 m s⁻¹, corresponding to average center-of-mass translational energies of 0.047, 0.048, and 0.053 eV, respectively. Thus, the experiments were carried out at only slightly hyperthermal energies.

Results and Discussion

A. Product Ion Distribution. According to the SIFT data of Morris et al.,⁶ the reaction of CF_3^+ with C_2H_2 occurs by condensation (association),

$$CF_3^+ + C_2H_2 + He \rightarrow C_3H_2F_3^+ + He$$
 (3)

He buffer gas was included in the reaction because the above reaction is a clustering reaction. Reaction 3 was studied as a function of pressure, and the second-order rate constants were independent of pressure. They reported therefore that the reaction was in the high-pressure limit for association reactions, but the lack of pressure dependence did not rule out the possibility of a contribution from radiative association.

In order to examine the contribution from the third-body buffer gas, the CF_3^+/C_2H_2 reaction is studied here under the single-collision condition. Figure 1 shows semilogarithmic plots of the reactant and product ion currents vs C_2H_2 flow rate in the CF_3^+/C_2H_2 reaction. Only the $C_3H_2F_3^+$ ion resulting from the electrophilic addition is found, as in the case of the highpressure SIFT experiment. The detection of the $C_3H_2F_3^+$ adduct ions at low pressure suggests that the third-body atom does not



Figure 1. Variation in the reactant and product ion currents with C_2H_2 flow for the CF_3^+/C_2H_2 reaction. The standard $CF_3^+/n-C_4H_{10}$ decay curve is given for comparison. The reagent flow rate is shown in units of cm³/min at a standard state (sccm). A nonlinear curve is obtained by fitting data points to the function $y = ax^b$, where a and b are constants.

participate in the reaction, and the association occurs by the two-body reaction

$$CF_3^+ + HC \equiv CH \rightarrow CF_3CH = CH^+$$
 (4)

This finding is consistent with the lack of pressure dependence of the reaction rate constant observed in the SIFT experiment over the He pressure range 0.26-0.99 Torr⁶ and good agreement of the reaction rate constant between the present low-pressure beam experiment and the high-pressure SIFT one, as will be shown in section B.

Thermochemical data of $C_3H_2F_3^+$ and $C_3HF_2^+$ ions are absent. Therefore, ΔH° values of various C₃H₂F₃⁺ and C₃HF₂⁺ isomers are calculated by using a MINDO/3 method (MOPAC version 6.0) in order to examine the formation mechanism of the $C_3H_2F_3^+$ adduct ion without further HF elimination. The results obtained are shown in Figure 2a. It should be noted that the formation of $C_3HF_2^+$ + HF is energetically possible in the CF₃^{+/} C₂H₂ reaction. However, there are two stable isomers of $C_3H_2F_3^+$ whose ΔH° values are smaller than those of four $C_3^ HF_2^+$ + HF product channels. Thus, the following pathway may predominantly contribute to the lack of HF elimination. The negative temperature dependence of the reaction rate constant found in the SIFT study of Morris et al.⁶ suggests that the CF_3^+/C_2H_2 reaction leading to the $C_3H_2F_3^+$ adduct ion has no activation barrier. After the initial formation of adduct ion A, more stable isomers B and C are formed by fast migration of a fluorine atom. Since the energy differences between initial adduct ion A and isomers B and C are large, isomers B and C are expected to be in electronically excited states or in high vibrationally excited levels of the ground electronic states. The electronically excited states either radiatively decay into the ground states or relax to ground states via internal conversion, while the high vibrationally excited levels of the ground states relax to lower vibrational levels via internal conversion because $C_3H_2F_3^+$ is a relatively large molecule with a number of acceptor vibrational modes. Since elimination of HF from isomers B and C in the ground electronic states is energetically forbidden, only the adduct ion will be formed in the CF_3^+/C_2H_2 reaction. According to this mechanism, intermediate adduct ion A is expected to be isomerized completely to stable forms B and/or C.



Figure 2. MINDO/3 potential energy diagram (a) for the $CF_3^+ + C_2H_2$ system and (b) for the $CF_3^+ + C_2H_4$ system.

In the CH_3^+/C_2H_2 reaction, only the electrophilic addition followed by loss of H_2 has been found,¹⁶

$$CH_3^{+} + C_2H_2 \xrightarrow{k_5} C_3H_3^{+} + H_2 + 1.5 \text{ eV}$$
 (5)

 $k_5 = (1-1.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1.16}$

where ΔH°_{298} values are calculated by using thermochemical data listed in refs 17 and 18. On the other hand, no further dissociation of the adduct $C_3H_2F_3^+$ ion by losing H_2 or HF was found in the CF_3^+/C_2H_2 reaction, indicating the different reactivity of the two typical carbocations for C_2H_2 .

In the CF_3^+/C_2H_4 and CF_3^+/C_3H_6 reactions described below, ionic products resulting from hydride abstraction are found. The lack of C_2H^+ in the CF_3^+/C_2H_2 is attributable to the endothermicity of the hydride abstraction reaction:

$$CF_3^+ + C_2H_2 \rightarrow C_2H^+ + CF_3H - 3.8 \text{ eV}$$
 (6)

Figure 3a shows the dependence of reactant and product ion currents on C_2H_4 flow rate in the CF_3^+/C_2H_4 reaction, where $C_3H_3F_2^+$, CHF_2^+ , CH_2F^+ , $C_2H_5^+$, and $C_2H_3^+$ are found as ionic products. In order to examine whether these ionic products result from the primary reaction or some secondary reactions, the dependence of branching ratios of each product ion on C_2H_4 flow rate is obtained from raw data shown in Figure 3a. The results obtained are shown in Figure 3b. With decreasing C_2H_4 flow rate, the branching ratio of $C_2H_3^+$ increases, whereas that of $C_2H_5^+$ decreases and becomes zero at zero C_2H_4 flow rate. The variation in the branching ratios is small for $C_3H_3F_2^+$, CHF_2^+ , and CH_2F^+ . On the basis of these facts and known product channel of the $C_2H_3^+/C_2H_4$ reaction,¹⁶ it is concluded that the following primary and secondary reactions participate



Figure 3. Variation in (a) the reactant and product ion currents and (b) the branching ratio of ionic products with C_2H_4 flow for the CF_3^+/C_2H_4 reaction. Nonlinear curves are obtained by fitting data points to the functions $y = ax^b$, where a and b are constants.

in the formation of the product ions,

$$CF_3^{+} + C_2H_4 \rightarrow C_3H_3F_2^{+} + HF$$
 (7a)

$$\rightarrow CHF_2^+ + C_2H_3F \tag{7b}$$

$$\rightarrow CH_2F^+ + C_2H_2F_2 \tag{7c}$$

$$\rightarrow C_2 H_3^{+} + CF_3 H + 0.35 \text{ eV}$$
 (7d)

$$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2 + 0.35 \text{ eV}$$
 (8)

The reaction rate constant of process 8 has been measured to be 3.8 \times $10^{-10}~cm^3~s^{-1.16}$

By extrapolating C_2H_4 flow rate to zero, the initial branching ratios of each product ion are determined for the CF3+/C2H4 reaction. The results are compared with the previous beam data of Stanney et al.² and the SIFT data of Morris et al.⁶ in Table 1. There are significant differences in the product ion distribution between the two beam data sets. The $C_2H_4F^+$ ion, which is the most abundant ion in their beam data, is absent in the present beam data. The branching ratio of C₃H₃F₂⁺, which occupies 23% in their data, amounts to $62 \pm 3\%$ in our data. The secondary $C_3H_5^+$ ion, which occupies 15% in their beam data, cannot be detected in our beam data. Although we do not know the exact reason for such great discrepancies between our experiment and their measurements, some unknown secondary reactions took place significantly in their experiments probably due to high operating pressures and a long reaction zone.

TABLE 1: Product Ion Distributions in Ion-MoleculeReactions of CF_3^+ with Unsaturated Aliphatic Hydrocarbonsat Thermal Energy

		branching ratio (%)					
		bear	n	SIFT			
		this work		ref 6			
reagent	product ion	0.05 eV	ref 2 ^a	300 K	525 K		
C_2H_2	$C_{3}H_{2}F_{3}^{+}$	100		100	100		
C2H4	$\begin{array}{c} C_{3}H_{3}F_{2}^{+} \\ C_{2}H_{3}^{+} \\ CHF_{2}^{+} \\ CH_{2}F^{+} \\ C_{2}H_{4}F^{+} \\ C_{3}H_{5}^{+} \end{array}$	$ \begin{array}{r} 62 \pm 3 \\ 29 \pm 4 \\ 7 \pm 2 \\ 2 \pm 1 \end{array} $	23 19 44 15	70 30	86 14		
C₃H₀	$\begin{array}{c} C_2 H_4 F^+ \\ C_4 H_5 F_2^+ \\ C_4 H_4 F^+ \\ C_3 H_5^+ \\ C_3 H_6^+ \\ C_3 H_7^+ \\ C_4 H_7^+ \\ C_4 H_7^+ \\ C_3 H_4 F^+ \\ C_3 H_6 F^+ \\ C_2 H_3 F_2^+ \end{array}$	58 ± 2 26 ± 3 9 ± 2 7 ± 2	49 11 14 11 4 3 3 3	77 17 7	84 10 6		

^{*a*} From Table 2 in ref 2.

In contrast to significant differences between the two beam data sets, the present beam data are in reasonable agreement with the recent SIFT data, except for the detection of small amounts of CHF_2^+ and CH_2F^+ ions in the present beam experiment. The ΔH°_{298} values for processes 7b and 7c are evaluated to be 0.22 and 0.38 eV, respectively, by using the ΔH°_{298} values in ref 18. It is unlikely that these ions are formed by a high-energy Maxwell tail at a collision energy of 0.05 eV. Since the formation of $CF_3^+ + F$ from the Ar⁺/CF₄ CT reaction is 1.13 eV exothermic, CF_3^+ can initially possess an excess energy of <1.13 eV. This excess internal and/or translational energies will be thermalized by collisions with the buffer Ar and the source CF₄ gases in the discharge-flow ion source. Since the product ion distribution was independent of the Ar buffer gas pressure over the range 0.5-1.2 Torr and the CF₄ gas pressure over the range 0.01-0.05 Torr, the reactant CF_3^+ ion must be thermalized completely before it enters the low-pressure reaction chamber. Thus, the occurrence of reactions 7b and 7c in the present near-thermal experiment suggests that these processes are exothermic. The reported ΔH°_{298} value for C₂H₄ is expected to be more reliable than those of the other species in processes 7b and 7c. It seems therefore that the ΔH°_{298} value for CF_3^+ (399.0 kJ mol⁻¹) is underestimated and/or those for CHF_2^+ (611 kJ mol⁻¹), C_2H_3F (-133.8 ± 1.7 kJ mol⁻¹), CH_2F^+ (833 kJ mol⁻¹), or C₂H₂F₂ (-345 \pm 10 kJ mol⁻¹) are overestimated in ref 18. Although detailed experimental conditions have not been reported, Stanney et al.² also detected large amounts of CHF2⁺ and CH2F⁺ ions in their beam experiment (see Table 1 in ref 2). Thus, the possibility of the collisional deactivation of some long-lived intermediates leading to these two ions cannot be completely ruled out in the high-pressure SIFT experiment.

There are four product channels 7a-7d for the CF₃+/C₂H₄ reactions. Among them, direct hydride abstraction leads to pathway 7d. The reaction mechanisms of product channels 7a and 7c are represented in Schemes 1 and 2. The electrophilic addition followed by loss of HF results in reaction pathway 7a, while that followed by fluoride transfer results in reaction pathway 7c. Although the formation mechanism of CHF₂+ is not as definitive as that for C₃H₃F₂+ and CH₂F⁺, a probable

SCHEME 1

$$CF_3^+ + CH_2 = CH_2 \longrightarrow \begin{array}{c} \bigoplus \\ CH_2 - CH_7 CF_2 \\ H_2 - F_2 \end{array} \xrightarrow{\bigoplus} \begin{array}{c} \bigoplus \\ CH_2 - CH_7 CF_2 \\ H_2 - F_2 \end{array}$$

SCHEME 2

SCHEME 3

$$CF_{3}^{*} + CH_{2} = CH_{2} \longrightarrow \begin{array}{c} \bigoplus \\ CH_{2} - CH_{2} - CH_{2} \\ H \end{array} \xrightarrow{f} H \xrightarrow{f} H$$

mechanism is shown in Scheme 3. On the basis of the above results, the branching ratios of hydride abstraction and electrophilic addition followed by HF elimination or fluoride transfer are determined to be $29 \pm 4\%$ and $71 \pm 6\%$, respectively, in the CF₃⁺/C₂H₄ reaction.

The most outstanding feature of the CF_3^+/C_2H_4 reaction is the lack of the adduct ion and the preferential formation of $C_3H_3F_2^+$ through HF elimination from the adduct ion. Since thermochemical data of related ions are absent, ΔH° values of two $C_3H_4F_3^+$ adduct ions and two $C_3H_3F_2^+$ + HF products are calculated, as shown in Figure 2b. It is clear from Figure 2b that the ΔH° values of the two intermediate $C_3H_4F_3^+$ adduct ions are higher than those of the two $C_3H_3F_2^+$ + HF products. Thus, the adduct ions decompose completely. The lack of the adduct ion in the CF_3^+/C_2H_4 reaction can be explained by the instability of intermediate adduct ion A and its isomer B formed by fluoride transfer for HF elimination.

The CF₃⁺/C₃H₆ yields C₄H₅F₂⁺, C₄H₄F⁺, C₄H₉⁺, C₄H₇⁺, C₂H₄F⁺, C₃H₇⁺, and C₃H₅⁺, as shown in Figure 4a. With decreasing the reagent gas flow, the branching ratios of C₄H₄F⁺ and C₂H₄F⁺ increase, while those of C₄H₉⁺, C₄H₇⁺, and C₃H₇⁺ decrease and approach zero at zero flow rate. The branching ratios of C₄H₅F₂⁺ and C₃H₅⁺ are essentially independent of C₃H₆ flow rate. On the basis of the above findings, the following primary reactions are responsible for the formation of C₄H₅F₂⁺, C₄H₄F⁺, C₂H₄F⁺, and C₃H₅⁺:

$$CF_3^+ + C_3H_6 \rightarrow C_4H_5F_2^+ + HF$$
(9a)

$$\rightarrow C_4 H_4 F^+ + 2HF \tag{9b}$$

$$\rightarrow C_2 H_4 F^+ + C_2 H_2 F_2 + 1.1 \text{ eV}$$
 (9c)

$$\rightarrow C_{3}H_{5}^{+} + CF_{3}H + 1.7 \text{ eV}$$
 (9d)

On the other hand, the $C_4H_4F^+/C_3H_6$ and/or $C_2H_4F^+/C_3H_6$ reactions participate in the formation of $C_4H_9^+$, $C_4H_7^+$, and $C_3H_7^+$. Among them, the following secondary ion-molecule reaction will be most important:

$$C_2H_4F^+ + C_3H_6 \rightarrow iso-C_3H_7^+ + C_2H_3F + 0.20 \text{ eV}$$
 (10)

The initial product ion distribution obtained from Figure 4b is given in Table 1 along with the previous beam and SIFT data. Significant discrepancies are found between the two beam data sets. In our beam data, the $C_4H_5F_2^+$ and $C_4H_4F^+$ ions, which are absent in their beam data, are detected with branching ratios of $26 \pm 3\%$ and $9 \pm 2\%$, respectively. They found the secondary $C_3H_7^+$ and $C_4H_7^+$ ions and the parent $C_3H_6^+$ ion, whose formation is at least 0.48 eV endothermic. Although these ions occupy 29% of the total product ions in their data,



Figure 4. Variation in (a) the reactant and product ion currents and (b) the branching ratio of ionic products with C_3H_6 flow for the CF_3^+/C_3H_6 reaction.

SCHEME 4

$$CF_3^+ + CH_3 - CH = CH_2 \longrightarrow CH_3 - CH - CH_2 CH_2 - CH_3 - CH - CH = CF_2 + HF$$

SCHEME 5

$$CF_3^* + CH_3 - CH = CH_2 \longrightarrow CH_3 - CH - CH_7 CF_2 \longrightarrow CH_3 - CH - CH_7 CF + HF$$

 $H \longrightarrow F$ $H \longrightarrow F$

----> CH₃-CH-C≡CF + 2HF

SCHEME 6

 $CF_3^* + CH_3 - CH = CH_2 \longrightarrow (H_3 \oplus H_2) (H_2 \oplus H_2) (H_2) (H_2) (H_2) (H_2) (H_2) (H_2)$

they cannot be found in our measurement. The $C_3H_4F^+$, $C_3H_6F^+$, and $C_2H_3F_2^+$ ions, which occupy 9% of the total product ions in their data, cannot be detected in our measurement. In contrast to the significant discrepancies between the two beam data sets, our beam data are in good agreement with the SIFT data, except for the detection of $C_4H_4F^+$ in the present experiment. The lack of this ion in the SIFT experiment may be due to the deactivation of long-lived intermediates by collisions with the buffer He gas.

Four product channels 9a-9d are found for the CF_3^+/C_3H_6 reaction. Among them, $C_3H_5^+$ results from direct hydride abstraction 9d. The reaction mechanism of product channels 9a-9c is shown in Schemes 4-6, respectively. The electrophilic addition followed by one or two HF elimination results in reaction pathways 9a and 9b, while that followed by fluoride transfer results in reaction pathway 9c. Pathways 9a-9cproceed through the same secondary intermediate carbocation. If a primary carbocation is formed in the initial electrophilic **SCHEME 7**

$$CF_3^+ + CH_3 - CH = CH_2 \longrightarrow H_2 \overset{\oplus}{\underset{CH}{\longrightarrow}} \overset{F}{\underset{CH}{\longrightarrow}} CF_2 \longrightarrow \overset{\oplus}{\underset{CH_2F}{\oplus}} + CH_3CH = CF_2$$

addition, CH_2F^+ will be produced via Scheme 7. The lack of CH₂F⁺ implies that only the stable secondary carbocation is formed as an intermediate adduct ion. On the basis of the above results, the branching ratios of the hydride abstraction and the electrophilic addition followed by HF elimination or fluoride transfer are estimated to be $7 \pm 2\%$ and $93 \pm 7\%$, respectively, in the CF_3^+/C_3H_6 reaction. Outstanding features of the $CF_3^+/$ C_3H_6 reaction in comparison with those in the CF_3^+/C_2H_4 reaction are the low branching ratio of the hydride abstraction, the occurrence of two HF eliminations from the adduct ion, and the lack of CH_2F^+ and CHF_2^+ . As an intermediate adduct ion, only the primary carbocation is formed in the CF_3^+/C_2H_4 reaction, while more stable secondary one is produced in the CF_3^+/C_3H_6 reaction. Thus, one reason for the high branching ratio of electrophilic addition for C₃H₆ is attributed to a higher stability of the intermediate adduct ion. Although ionic product resulting from losing one HF molecule from the adduct ion is found in the CF_3^+/C_2H_4 reaction, not only one HF elimination but also two HF eliminations from the adduct ion occur in the CF_3^+/C_3H_6 reaction. This may be due to the fact that two HF elimination processes are energetically closed for C₂H₄. The lack of CH_2F^+ in the CF_3^+/C_3H_6 reaction can be explained as due to the instability of the primary intermediate carbocation, as discussed above.

B. Rate Constants. Figures 1, 3a, and 4a show semilogarithmic plots of CF_3^+ ion current vs a reagent flow rate. Total rate constants $k_{C_mH_n}$ are determined from the decay of CF_3^+ , which is governed by the pseudo-first-order rate law,

$$I(CF_3^+) = I_0(CF_3^+) \exp(-k_{C_nH_n}[C_mH_n]t)$$
(11)

Here, $I_0(CF_3^+)$ represents the initial CF_3^+ ion current and t is the reaction time. Because of the difficulty in evaluating the accurate t value, the $k_{C_mH_n}$ value is evaluated by reference to the rate constant of the CF_3^+/n -C₄H₁₀ reaction ($k_{C_mH_n}$), which has been determined to be (7.5 ± 0.7) × 10⁻¹⁰ cm³ s⁻¹ by Lias et al.,¹⁹

$$k_{C_m H_n} = k_{C_m H_n} \frac{\ln\{I(CF_3^+)/I_0(CF_3^+)\}_{C_m H_n}}{\ln\{I(CF_3^+)/I_0(CF_3^+)\}_{C_4 H_{10}}} \frac{[C_4 H_{10}]}{[C_m H_n]}$$
(12)

The decay of CF_3^+ upon addition of $n-C_4H_{10}$ under the same experimental conditions is also shown in Figures 1, 3a, and 4a. The slower decay of CF_3^+ for C_2H_2 and the faster decay of CF_3^+ for C_2H_4 and C_3H_6 than that for $n-C_4H_{10}$ imply that the rate constant for C_2H_2 is smaller than that for $n-C_4H_{10}$, while those for C_2H_4 and C_3H_6 are larger than that for $n-C_4H_{10}$. The rate constants obtained from slopes in each figure are summarized in Table 2 along with reported data for saturated hydrocarbons and recent SIFT data for unsaturated hydrocarbons. A good agreement is found for the k_{obs} value of C_2H_2 between the present beam data and the SIFT data at 525 K (0.068 eV). Although the k_{obs} values for C₂H₄ and C₃H₆ obtained here are slightly larger than the SIFT data, the same tendency is found between C_2H_4 and C_3H_6 . The k_{obs} value for C_2H_2 is lower than those for C_2H_4 and C_3H_6 . This can be explained by the fact that only the electrophilic addition without further dissociation is open as product channels for the former reagent, while hydride transfer as well as electrophilic addition followed by HF elimination or fluoride transfer occurs for the latter reagents. All three reactions studied here are faster than

TABLE 2: Observed and Calculated Rate Constants of Ion-Molecule Reactions of CF_3^+ with Unsaturated Aliphatic Hydrocarbons and Dipole Moments and Polarizabilities of C_mH_n

	$k_{\rm obs} \ (10^{-9} \ {\rm cm^3 \ s^{-1}})$							
	beam		SIFT					
	this work	ICR	ref 6		$k_{calc}{}^a$		dipole	
reagent	0.05 eV	ref 2	300 K	525 K	$(10^{-9} \text{ cm}^3 \text{ s}^{-1})$	$k_{\rm obs}/k_{\rm calc}$	moment ^b (D)	$a^{b}(A^{3})$
C_2H_2	0.45 ± 0.1		0.95 ± 0.2	0.50 ± 0.1	0.98	0.46 ± 0.10	0	3.33
C_2H_4	1.3 ± 0.3		0.98 ± 0.2	0.71 ± 0.2	1.1	1.2 ± 0.3	0	4.25
C_3H_6	1.6 ± 0.2		1.2 ± 0.3	$>1.0 \pm 0.3$	1.2	1.3 ± 0.2	0.366	6.26
C_2H_6		0.37 ± 0.03			1.1	0.34 ± 0.03	0	4.47
C_3H_8		0.59 ± 0.07			1.1	0.54 ± 0.06	0.084	6.29
$n-C_4H_{10}$		0.75 ± 0.07			1.2	0.63 ± 0.06	0.050	8.20

^a Calculated from Langevin or parametrized trajectory theory.²⁰⁻²² ^b Reference 23.

those for such saturated aliphatic hydrocarbons as C_2H_6 , C_3H_8 , and *n*- C_4H_{10} , as shown in Table 2. Although only the hydride abstraction takes place for saturated hydrocarbons,¹⁹ higher reactive electrophilic addition reactions occur for unsaturated hydrocarbons. Thus, the larger k_{obs} values must be obtained for C_2H_2 , C_2H_4 , and C_3H_6 .

Total rate constants of thermal energy ion-molecule reactions have been evaluated by using the Langevin theory for nonpolar molecules with no dipole moment²⁰ and the parametrized trajectory model for polar molecules with permanent dipole moments.^{21,22} Since the dipole moments of aliphatic hydrocarbons are either zero or small (see Table 2), theoretical values from the trajectory model are close to the Langevin rate constants. The k_{calc} values increase in the order of C₂H₂, C₂H₄, and C₃H₆, as shown in Table 2, being in agreement with the experimental data. The ratio of the observed and calculated rate constants serves as a measure for the efficiency of a reaction. The k_{obs}/k_{calc} ratios for C₂H₂, C₂H₄, and C₃H₆ are ≥ 0.46 , indicating that the ion-molecule reactions of CF₃⁺ with C₂H₂, C₂H₄, and C₃H₆ take place with high efficiencies.

Summary and Conclusion

Ion-molecule reactions of CF_3^+ with C_2H_2 , C_2H_4 , and C_3H_6 have been investigated at near-thermal energy by using an ion beam apparatus. The initial product ion distributions and reaction rate constants were determined and summarized in Tables 1 and 2, respectively. For reaction with C₂H₂, only $C_3H_2F_3^+$ resulting from electrophilic addition was found. For the reaction with C₂H₄, hydride abstraction and electrophilic addition followed by HF elimination or fluoride transfer occur with the branching ratios of 0.29 ± 0.04 : 0.71 ± 0.06 . For the reaction with C₃H₆, hydride abstraction and electrophilic addition followed by one and two HF eliminations and fluoride transfer take place with the branching ratios of $0.07 \pm 0.02:0.93 \pm 0.07$. The lack of CH_2F^+ led us to conclude that only primary carbocation is formed as an initial electrophilic adduct ion in the CF_3^+/C_3H_6 reaction. The total rate constants amount to \geq 46% of the collision rate constants estimated from either the Langevin theory or the parametrized trajectory model, indicating high efficiencies of the present reaction systems. In order to clarify the reaction mechanisms of CF3⁺ with unsaturated hydrocarbons, further detailed experimental studies and theoretical calculations of reaction pathways will be necessary.

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