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Gas-phase ion/molecule reactions in C_2F_4

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Abstract

Gas-phase ion/molecule reactions in tetrafluoroethylene (C_2F_4) were studied with a pulsed electron beam mass spectrometer. When a few Torr of major gas, N_2, containing 1–10 mTorr C_2F_4 was ionized by 2 keV electrons, CF_3^+ and $C_2F_4^+$ were formed as major ions. CF_3^+ reacted with C_2F_4 rapidly to form $C_3F_7^+$. The cluster ion $C_3F_7^+(C_2F_4)$ started to appear below ~280 K. In the clustering reactions of $C_3F_7^+$ with C_2F_4, the equilibria could not be observed but the cluster ions $C_3F_7^+(C_2F_4)_n$ were found to grow very slowly at the expense of the smaller cluster ions $C_3F_7^+(C_2F_4)_{n-1}$. The rate constant of reaction $C_2F_4^+ + C_2F_4 = C_3F_5^+ + CF_3$ was measured to be $(1.5 \pm 0.5) \times 10^{-11}$ cm^3/molecule s and found to be temperature-independent in the range of 310–180 K. The thermochemical stabilities of $X^-(C_2F_4)_n$ ($X^- = F^-$, Cl^- and Br^-) were measured. A peculiar behavior in reaction of F^- with C_2F_4 was observed. Two isomers for $F^-(C_2F_4)$ were predicted.

Keywords: High-pressure mass spectrometry; Cluster ion; Tetrafluoroethylene; Halide ion

1. Introduction

Fluorocarbon plasma is an indispensable tool for SiO_2 etching in ULSI manufacturing. In the selective etching of SiO_2, fluorocarbon plasma plays a key role in preferential formation of protective fluorocarbon polymer film on Si and Si_3N_4 surfaces. In addition, fluorocarbon film prepared by plasma-enhanced chemical vapor deposition (CVD) has attracted increasing interest as one of the most promising materials for interlayer dielectrics because of its low dielectric constant. These plasma process technologies with fluorocarbon gases require a deeper understanding of the chemical reactivities of these fluorocarbons. In our previous work, gas-phase ion/molecule reactions in CF_4 [1,2], C_3F_6 [3], c-C_4F_8 [4], and C_5F_8 [5], were studied in detail. The interactions between positive ions and C_3F_6 or C_5F_8 are weak and mainly electrostatic. In contrast, C_3F_6 and C_5F_8 have high reactivities toward the negative ions. This general trend is due to the perfluoro effect, i.e., the energy level of LUMO (π^*) is lowered by the F-atom substitution and the charge transfer from the negative ions to the π^* orbital becomes more favorable.

C_2F_4 has attracted deep interest as an alternative for the plasma etching of SiO_2 as it dissociates readily to form the etching fragment CF_2. SiO_2 etching has been performed using CF_4, C_2F_6, c-C_4F_8, etc. These molecules have extremely high global warming potentials (GWP). In contrast, the atmospheric lifetime of C_2F_4 was calculated to be only 1.9 days [6] due to the high reactivity of C_2F_4 with the OH radical. Samukawa et al. [7] proposed a new radical control (selective radical generation) method for high-performance SiO_2 patterning using non-perfluorocarbon gas mixture, CF_3I and C_2F_4, in ultrahigh frequency (UHF) plasma. This method enables independent control of polymerization and etching through the selective generation of CF_3 and CF_2 radicals in CF_3I/C_2F_4 gas mixture plasma. Thus it could accomplish both a high etching rate and also high etching selectivity during SiO_2 contact hole formation. Despite the importance of C_2F_4 for the semiconductor fabrications, investigation on the ion/molecule reactions in C_2F_4 was relatively scarce [8,9–15]. The present paper provides data for the reactivities of C_2F_4 in the positive and negative ion/molecule reactions.

2. Experimental

The experiments were made with a pulsed electron beam high-pressure mass spectrometer [16,17]. The major gas N_2 at

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a few Torr was purified by passing it through a dry ice acetone cooled 5Å molecular sieve trap. The reagent gas, C_2F_4 (5% in N_2, Daikin Industries, Ltd.), and halide-ion forming gases (NF_3 for F^-, CCl_4 for Cl^-, CH_2Br_2 for Br^- and CH_3I for I^-) were introduced into the major gas through stainless steel capillaries (1 m long × 0.1 mm inner diameter). The sample gas was ionized by a pulsed 2 keV electron beam. The ions produced in the field-free ion source were sampled through a slit made of razor blades and mass analyzed by a quadrupole mass spectrometer (ULVAC, MSQ-400, $m/z = 1$–550).

When C_2F_4 was introduced in the ion source, the wall of the ion source was quickly contaminated by the radiation products. The charging became serious in less than 1 h of operation and thus laborious repetitive cleaning of the ion source was necessary in order to obtain reasonably reliable data. The charging was suppressed only to some extent when the wall of the ion source was coated with colloidal graphite.

3. Results and discussion

3.1. Positive-mode ion/molecule reactions

The ions CF_3^+ and $C_2F_4^+$ were formed when a few Torr N_2 major gas containing 1–15 mTorr C_2F_4 was ionized by a 2 keV electron irradiation. These ions were mainly formed by the charge transfer reactions (2) and (3).

$$N_2^+ + N_2 + M \rightarrow N_4^+ + M \tag{1}$$

$$N_4^+ + C_2F_4 \rightarrow C_2F_4^+ + 2N_2 \tag{2}$$

$$N_4^+ + C_2F_4 \rightarrow CF_3^+ + CF + 2N_2 \tag{3}$$

The ratio of the intensities of ions $[C_2F_4^+]/[CF_3^+]$ right after the electron pulse was about 7/3.

Fig. 1 displays the temporal profiles of ions observed after the electron pulse in 3.9 Torr N_2 containing 13.0 mTorr C_2F_4 at 308.0 K. In order to increase the ion intensities, the electron pulse width of 170 μs was used. Thus, the kinetics of ion molecule reactions in Fig. 1 is more or less blurred due to the rather long electron pulse. In Fig. 1, the primary ions CF_3^+ and $C_2F_4^+$ are found to react with C_2F_4 to form $C_3F_7^+$ and $C_3F_5^+$, respectively, in agreement with previous work [9–11,15].

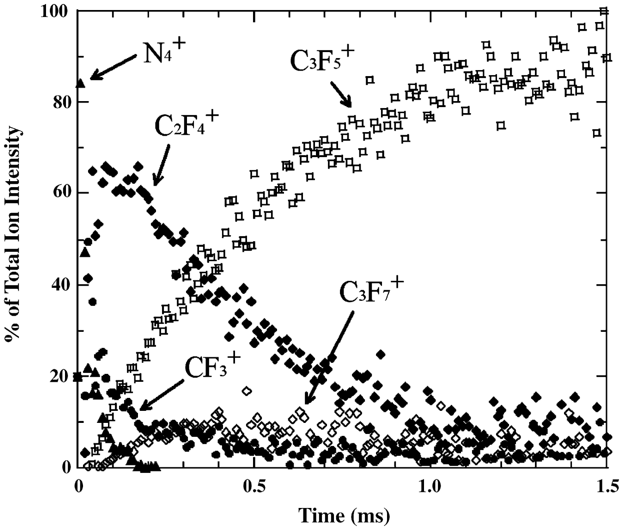

Fig. 1. Temporal profiles of ions observed after the electron pulse in 3.9 Torr N_2 containing 13.0 mTorr C_2F_4 at 308.0 K. The width of the electron pulse is about 170 μs.

$$CF_3^+ + C_2F_4 \rightarrow C_3F_7^+ \tag{4}$$

$$C_2F_4^+ + C_2F_4 \rightarrow C_3F_5^+ + CF_3 \tag{5}$$

Reliable experimental data for the heats of formation of fluorinated molecules and ions are rather scarce. Bauschlicher and Ricca calculated the heats of formation for C_nF_m, $C_nF_m^+$, CHF_m, and CHF_m^+[18]. By using computed heats of formation at 298 K (kcal/mol) of CF_3 (−111.99), CF_3^+ (101.98), C_2F_4 (−161.69), $C_2F_4^+$ (75.25), $C_3F_5^+$ (10.63), $C_3F_7^+$ (isomer: $F_2C(CF_2)CF_3^+$) (−99.19), $C_3F_7^+$ (isomer: $F_3C(CF)CF_3^+$) (−85.58), the enthalpy changes of reaction (4) is calculated as −38.78 kcal/mol for the product ion, $C_3F_7^+(F_2C(CF_2)CF_3^+)$, and −25.17 kcal/mol for the product ion, $C_3F_7^+(F_3C(CF)CF_3^+)$, and −14.92 kcal/mol for reaction (5). That is, reactions (4) and (5) are highly exothermic.

In Fig. 1, CF_3^+ decays and is converted to $C_3F_7^+$ during the electron pulse. This suggests that CF_3^+ has a high reactivity toward C_2F_4. We have made some effort to measure the rate constants for reaction (4). However, no reliable data could be obtained due to the weak ion intensity of CF_3^+. It should be noted that the ion intensities of CF_3^+ and $C_3F_7^+$ become nearly time-independent after about 0.4 ms. Apparently, this seems to argue against the occurrence of reaction (4) as reported previously [9–11,15]. This contradiction is explicable by the further reaction of $C_3F_7^+$ with C_2F_4 to regenerate CF_3^+[15].

$$C_3F_7^+ + C_2F_4 \rightarrow CF_3^+ + C_4F_8 \tag{6}$$

Reactions (4) and (6) together constitute a catalytic cycle, i.e., dimerization of C_2F_4 to form C_4F_8 catalyzed by CF_3^+[15]. The rate constants for reactions (4) and (6) were measured to be $k_4 = 2.8 \times 10^{-11}$ and $k_6 = 2.0 \times 10^{-11}$ cm^3/s, respectively, at 300 K [15]. Assuming the steady-state concentration for CF_3^+ and $C_3F_7^+$, the ratio of the steady-state intensities $I[C_3F_7^+]/I[CF_3^+]$ is estimated to be $2.8 \times 10^{-11}/2.0 \times 10^{-11} = 1.4$ at 300 K. This is in fair agreement with the ratio of $I[C_3F_7^+]/I[CF_{3+}] \approx 1.9$ in Fig. 1 measured at 308.0 K.

The measurement of the rate constants for reaction (5) was straightforward because of the slow decay of $C_2F_4^+$ as shown in Fig. 1. Fig. 2 shows the temperature dependence of the rate constants for reaction (5) measured in the range of 310–118 K. Although the data points are rather scattered due to the difficulty in maintaining the steady-state experimental conditions (i.e., charging of the ion source), the rate constants are found to be temperature-independent down to ∼180 K. It was confirmed that the second-order rate constants for reaction (5) were independent on the change of the C_2F_4 pressure in the range of 1–13 mTorr, i.e., reaction (5) is first-order with the C_2F_4 pressure. The average value of the rate constants in Fig. 2, 1.5×10^{-11} cm^3/molecule s, is in good agreement with previous

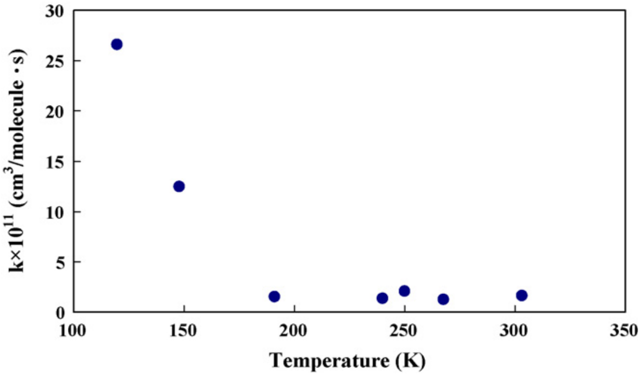

Fig. 2. Temperature dependence of the rate constants for reaction (5), $C_2F_4^+ + C_2F_4 = C_3F_5^+ + CF_3$, measured in the temperature range of 310–118 K.

values of 1.5×10^{-11} cm^3/molecule s determined by Anicich and Bowers [11] and of 2.0×10^{-11} cm^3/molecule s determined by Morris et al. [15]. It is worth noting that the obtained rate constant for reaction (5) is much smaller than that for reactions (7.1)–(7.3) of 7.3×10^{-10} cm^3/molecule s [19].

$$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3 \quad (45\%) \tag{7.1}$$

$$C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H \quad (21\%) \tag{7.2}$$

$$C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+ \quad (34\%) \tag{7.3}$$

That is, fluorine substitution of ethylene leads to a marked decrease of the rate constant. Anicich and Bowers [11] performed detailed isotopic labeling studies utilizing C_2D_4, *cis*- and *trans*-CDFCDF. They found that the most dramatic effect observed in the ion chemistry of the fluoroethylenes is most probably the methylene switching reactions that occur without any trace of hydrogen scrambling. They suggested that the mechanism for reactions appears to include the formation of a "four-centered" complex that can symmetrically cleave to form either the original reactants or ethylenic products in which the methylene groups have been switched without hydrogen scrambling.

The value of the rate constant measured in Fig. 2 is temperature-independent in the range of 190–308 K. The value of the rate constant of 1.5×10^{-11} cm^3/molecule s is about two orders of magnitude smaller than the collision rate. The small value suggests the entropy barrier for the reaction coordinate. Sterically hindered ion/molecule reactions proceeding through locked-rotor, low-entropy intermediates has been examined by Meot-Ner and co-workers [20,21]. Slow kinetics in hindered systems results because, in a large fraction of the collisions, steric effects prevent close approach of the reactive centers. With decreasing temperature, the formation of the tight intermediate required for the reaction becomes increasingly favorable. In general, the reactions exhibit large negative temperature coefficients (up to $k = CT^{-8.7}$) [21]. The rates become slower and the temperature dependences steeper with increasing steric hindrance. Interestingly, however, the rate constants for reaction (5) are temperature-independent in the range of 308–190 K in Fig. 2. This means that the general trend predicted by Meot-Ner and co-workers [20,21] cannot be applied to reaction (5). We conjecture that this might be due to the existence of isomers for the intermediate complexes, $C_2F_4^+\cdots C_2F_4$ in addition to the "four-centered" intermediate (i.e., π complex) predicted by Anicich and Bowers [11]. One candidate for the isomer may be the σ complex in which the F atom of neutral C_2F_4 attacks the cationic center of $C_2F_4^+$. With decreasing the temperature, the formation of the σ complex may become increasingly more favorable due to the smaller entropy barrier. The further speculation may not be profitable without the solid theoretical background. The detailed theoretical study on the structures of the isomers is highly needed.

The dimer ion $C_2F_4^+(C_2F_4)$ started to appear below 150 K with 2.2 Torr N_2 major gas containing about 2 mTorr C_2F_4. Concomitantly, the decay rates of $C_2F_4^+$ became faster than those above 150 K. With decreasing the ion source temperature down to 118 K, $C_2F_4^+(C_2F_4)_2$ was also observed. The cluster ions with $n = 0$, 1 and 2 for $C_2F_4^+(C_2F_4)_n$ decay with nearly the same rate and they are completely converted to $C_3F_5^+$ and its cluster ions $C_3F_5^+(C_2F_4)_n$ almost right after the electron pulse. This suggests that the intracluster reaction to form $C_3F_5^+$ takes place in $C_2F_4^+(C_2F_4)_n$. It is likely that the cluster $C_2F_4^+(C_2F_4)_n$ has the four-centered bond complex as a core that leads to the formation of $C_3F_5^+$.

The associated ion $C_3F_7^+(C_2F_4)$ started to be observed when the ion source temperature was decreased below 280 K and CF_3^+ became too weak to be detected after the electron pulse. The equilibria between $C_3F_7^+(C_2F_4)_{n-1}$ and $C_3F_7^+(C_2F_4)_n$ were not observed but $C_3F_7^+(C_2F_4)_n$ was slowly formed at the expense of $C_3F_7^+(C_2F_4)_{n-1}$ up to $n = 3$. The slow formation of higher-order associated ions suggests either that the rates of the clustering reactions are slow due to the steric hindrance (i.e., existence of the entropy barrier in the reaction coordinate) or that the reaction of $C_3F_7^+(C_2F_4)_{n-1}$ with C_2F_4 is irreversible and the ion $C_3F_7^+(C_2F_4)_n$ is not a mere cluster ion but rather the covalently bound molecular ion. The fact that the associated ions are not observed at higher temperature means that the energy barriers for the association reactions are negative. Thus the observed associated ions are likely to be weakly bound cluster ions. The observed slow clustering reactions are quite similar to the results observed for the reactions of $C_2F_4^+$ and $C_3F_6^+$ with C_3F_6 [3]. These ions form cluster ions with C_3F_6 only at lower temperature region. The presence of entropy barriers are likely for the formation of these cluster ions, i.e., there are several isomeric structures for cluster ions and there is an entropy bottle neck for the formation of the most stable isomer.

In our previous work [3], the $C_2F_4^+$ ion was found to be unreactive and only formed cluster ions with C_3F_6. In contrast, $C_2F_4^+$ reacts with C_2F_4 to form $C_3F_5^+$ as shown in Fig. 1. The substitution of F in C_2F_4 with CF_3 apparently decreases the reactivity for C_3F_6 due to the inductive and hyperconjugation effects.

The ion $C_3F_5^+$ formed by reaction (5) was found to be chemically inert toward C_2F_4. This is due to the charge dispersal in $C_3F_5^+$. The $C_3F_5^+$ forms the cluster ion $C_3F_5^+(C_2F_4)$ below 150 K. The ratio of the ion intensities $[C_3F_5^+\cdots C_2F_4]/[C_3F_5^+]$ observed at 148 K was measured to be about 1/10 with C_2F_4 pressure of 2.2 mTorr. If the entropy change for the clustering

Table 1
Experimental ($\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$) and calculated thermochemical data for the gas-phase clustering reactions of halide ions (X^-) with C_2F_4 and C_3F_6[a]

	$n=1$		$n=2$		$n=3$		$n=4$	
	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
$CCl_3^+ + CCl_4 = CCl_3^+(CCl_4)$	6.1 ± 0.3	15 ± 3						
$Cl^-(C_2F_4)_{n-1} + C_2F_4 = Cl^-(C_2F_4)_n$	≥10	25[b]	6.6 ± 0.5	16 ± 5	6.3 ± 0.5	19 ± 5	6.0 ± 0.5	20 ± 5
$Cl^-(C_3F_6)_{n-1} + C_3F_6 = Cl^-(C_3F_6)_n$	12.6 ± 0.3	25 ± 3	9.6 ± 0.3	23 ± 3	8.9 ± 0.3	25 ± 3		
$Br^-(C_2F_4)_{n-1} + C_2F_4 = Br^-(C_2F_4)_n$	7.1 ± 0.5	16 ± 5	6.0 ± 0.5	17 ± 5				
$Br^-(C_3F_6)_{n-1} + C_3F_6 = Br^-(C_3F_6)_n$	9.9 ± 0.3	19 ± 3	8.3 ± 0.3	22 ± 3				

$\Delta H^\circ_{n-1,n}$ is in kcal/mol and $\Delta S^\circ_{n-1,n}$ is in cal/mol K (standard state, 1 atm).
[a] Ref. [1].
[b] Entropy value assumed.

reaction, $C_3F_5^+ + C_2F_4 \rightleftarrows C_3F_5^+(C_2F_4)$, is arbitrarily assumed to be 20 cal/mol K, the enthalpy change for the clustering reaction is roughly estimated to be ~6 kcal/mol. This estimated bond energy is much smaller than that of $C_3F_5^+(C_3F_6)$ (9.2 ± 0.3 kcal/mol) [3]. This means that the nucleophilicity of C_2F_4 is considerably smaller than that of C_3F_6.

In the presence of CCl_4 in the reagent gas, the CCl_3^+ ion was observed with a high abundance. In the present work, the temperature dependence of equilibrium constants for clustering reaction (8) was also measured.

$$CCl_3^+ + CCl_4 \rightleftarrows CCl_3^+(CCl_4) \quad (8)$$

The obtained thermochemical data are summarized in Table 1.

3.2. Negative-mode ion/molecule reactions

In the measurements of negative-mode ion/molecule reactions in C_2F_4, the charging of the ion source was much more serious than that of the positive-mode ion/molecule reactions, and great care was taken to obtain reliable experimental data.

When a few Torr of N_2 containing about 10 mTorr of C_2F_4 was irradiated by 2 keV electron beam, no negative ions could be detected. This indicates that the vertical electron affinity of C_2F_4 is zero or negative in agreement with the theoretical prediction by King et al. [22].

In our previous work [3], gas-phase clustering reactions of halide ions (X^-) with C_3F_6 were studied. The polymerization reaction of C_3F_6 initiated by F^- was observed. Instead, the halide ions Cl^-, Br^- and I^- were found to form cluster ions with C_3F_6. Thermochemical stabilities of $X^-(C_3F_6)_n$ ($X^- = Cl^-$, Br^-, and I^-) have been determined [3]. A slight charge transfer in the complex $Cl^- \rightarrow C_3F_6$ results in the fairly strong bond energy (12.6 ± 0.3 kcal/mol) for the cluster.

In this work, clustering reactions of halide ions ($X^- = F^-$, Cl^-, and Br^-) with C_2F_4, reaction (9), were measured and the comparative study on the thermochemical stabilities of $X^-(C_2F_4)_n$ and $X^-(C_3F_6)_n$ was made.

$$X^-(C_2F_4)_{n-1} + C_2F_4 \rightleftarrows X^-(C_2F_4)_n \quad (9)$$

Firstly, reaction (9) with $X^- = F^-$ will be described. Fig. 3a and b shows the temporal profiles of $F^-(C_2F_4)_n$ with $n = 0$–2 at 238 and 305 K, respectively. It should be noted that the ions F^- and $F^-(C_2F_4)$ show the same decay rates after the electron pulse. This suggests that the equilibrium between F^- and $F^-(C_2F_4)$ is established rather quickly after the electron pulse. In Fig. 3a and b, F^- and $F^-(C_2F_4)$ are seen to be converted gradually to $F^-(C_2F_4)_2$. The formation of $F^-(C_2F_4)_2$ from $F^-(C_2F_4)$ is apparently irreversible.

King et al. determined the molecular structures and total energies of C_2F_n and $C_2F_n^-$ ($n = 1$–6) by several independent density functional theory (DFT) [22]. The bond dissociation energy of $C_2F_5^-$ to form $C_2F_4 + F^-$ is calculated to be ~35 kcal/mol. This value predicts the ratio of the ion intensities for $[F^-\cdots C_2F_4]/[F^-]$ to be ~10^{25} in Fig. 3b at 305 K. The observed ratio of ion intensities $[F^-\cdots C_2F_4]/[F^-]$ in Fig. 3b is calculated to be 3 taking into consideration of the ion collection time and the transmission coefficients of ions for the quadrupole mass spectrometer. If the complex $F^-\cdots C_2F_4$ has the bond energy of ~35 kcal/mol, the fluoride ion F^- should be completely converted to $F^-(C_2F_4)$. The appearance of F^- and the apparent establishment of equilibrium for reaction (9) with $n = 1$ at 238 and 305 K suggest the presence of much loose complex for $F^-\cdots C_2F_4$. We conjecture that there are two isomers for $F^-(C_2F_4)$, i.e., one is loosely bound and the other is tightly bound. The latter may react with C_2F_4 to form the dimer, $F^-(C_2F_4)_2$. The possible reaction mechanisms may be summarized as follows:

$$F^- + C_2F_4 \rightleftarrows [F^-\cdots C_2F_4]^* \overset{M}{\rightleftarrows} F^-(C_2F_4)(a) \quad \text{(loose complex)} \quad (10)$$

$$F^-(C_2F_4)(a)\ \text{(loose complex)} \rightarrow F^-(C_2F_4)(b)\ \text{(tight complex)} \quad (11)$$

$$F^-(C_2F_4)(b) + C_2F_4 \rightleftarrows [F^-(C_2F_4)(b)\cdots C_2F_4]^* \rightarrow F^-(C_2F_4)_2 \quad (12)$$

The intermediate collision complex $[F^-\cdots C_2F_4]^*$ may be stabilized by the collision with a third body (M) as a weak electrostatic complex (a). The complex (a) may be collisionally activated and regenerate the original species F^- and C_2F_4. The growth of $F^-(C_2F_4)_2$ at the expense of $F^-(C_2F_4)$ in Fig. 3a and b means

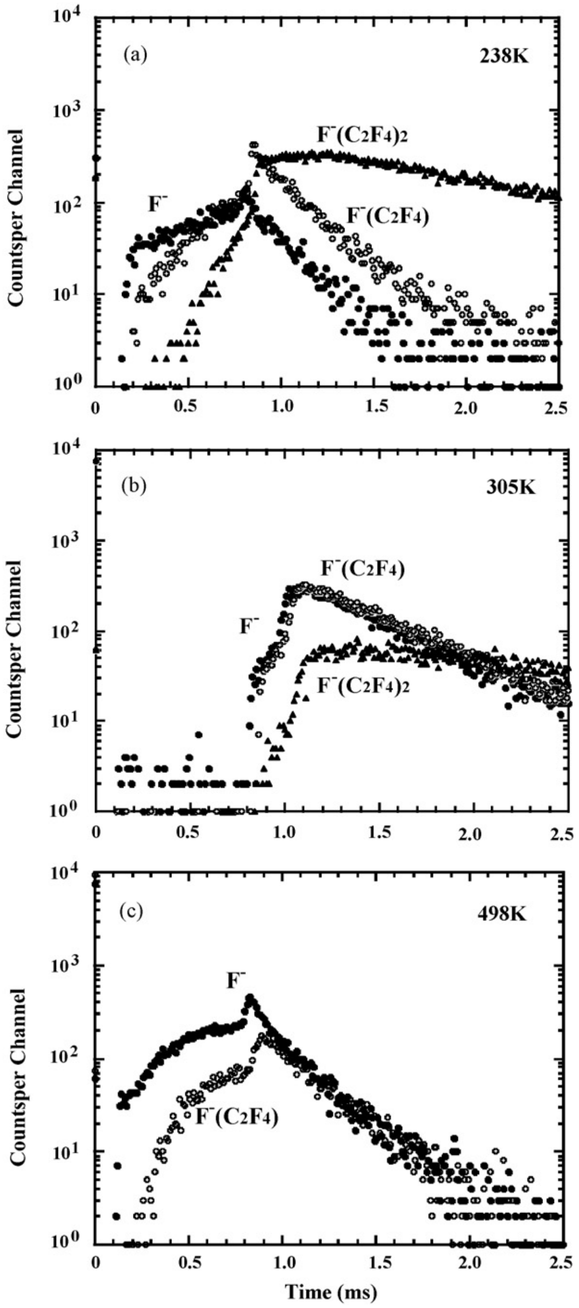

Fig. 3. (a) Temporal profile of $F^-(C_2F_4)_n$ with $n = 0–2$ observed in 3.4 Torr N_2, 1.8 mTorr C_2F_4, and 28 mTorr of NF_3 at 238 K. The collection times for F^-, $F^-(C_2F_4)$, and $F^-(C_2F_4)_2$ are 300, 180, and 180 s, respectively. (b) Temporal profile of $F^-(C_2F_4)_n$ with $n = 0–2$ observed in 3.4 Torr N_2, 1.8 mTorr C_2F_4, and 11 mTorr of NF_3 at 305 K. The collection times for F^-, $F^-(C_2F_4)$, and $F^-(C_2F_4)_2$ are all 60 s. (c) Temporal profile of $F^-(C_2F_4)_n$ with $n = 0$ and 1 observed in 3.7 Torr N_2, 1.2 mTorr C_2F_4, and 28 mTorr of NF_3 at 498 K. The collection times for F^- and $F^-(C_2F_4)$ are 60 and 75 s, respectively.

that the terminal product $F^-(C_2F_4)_2$ is not a mere electrostatic complex but a tightly bound complex with a semicovalent-bond character. The $F^-(C_2F_4)_2$ may be the F^--initiated polymerized product. Interestingly, the trimer ion $F^-(C_2F_4)_3$ was not detected down to 240 K. This indicates that the negative charge in the tightly bound complex $F^-(C_2F_4)_2$ is dispersed due to the semi-covalent bond formation. Namely, the polymerization reaction terminates with $n = 2$ for $F^-(C_2F_4)_n$.

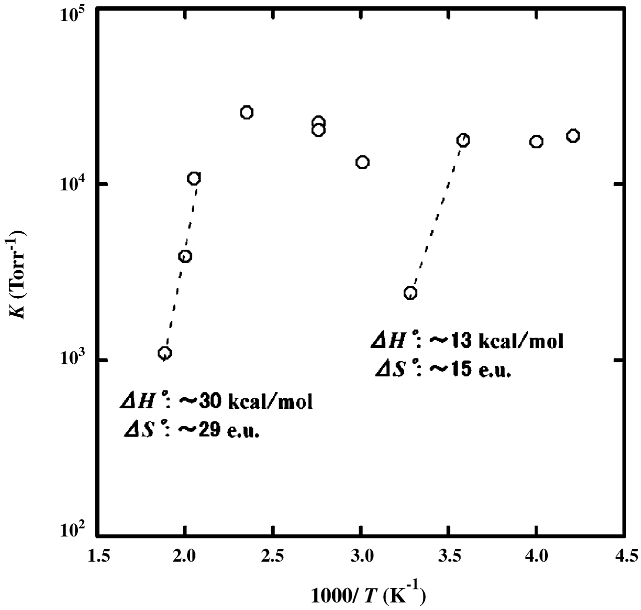

Fig. 4. van't Hoff plots for clustering reactions, $F^- + C_2F_4 = F^-(C_2F_4)$.

By assuming equilibria between F^- and $F^-(C_2F_4)$, the temperature dependence of equilibrium constants is plotted as van't Hoff plots in Fig. 4 despite of the difficulty arising from the serious ion source charging. It was confirmed that the equilibrium constants for reaction (9) with $n = 1$ at 305 K is independent on the C_2F_4 pressure in the range of 0.38–2.6 mTorr. This indicates that the contamination of $F^-(C_2F_4)$(a) by $F^-(C_2F_4)$(b) is negligible at 305 K and below. We conjecture that the isomeric contaminant $F^-(C_2F_4)$(b) is quickly converted to $F^-(C_2F_4)_2$ below room temperature by reaction (12). At room temperature and below, the ratio of ion intensities $[F^-(C_2F_4)]/[F^-]$ become larger than 10 under the present experimental conditions. In such a case, the bending-over of the van't Hoff plots at lower temperature region (e.g., $3.6 > 1000/T$ in Fig. 4) cannot be avoided due to the collision-induced dissociation of the cluster ions outside the ion source (i.e., $F^-(C_2F_4)(a) \rightarrow F^- + C_2F_4$). This may explain the bending over of the van't Hoff plots below ~280 K ($1000/T = 3.6$). The straight line arbitrarily drawn using the two points at $1000/T = 3.25$ and $3.6\ K^{-1}$ gives $-\Delta H^\circ$ and $-\Delta S^\circ$ to be ~13 kcal/mol and ~15 cal/mol K, respectively. These values should be regarded as only very crudely estimated ones.

The equilibrium constants in Fig. 4 show an increase above room temperature and decrease at higher temperature. The increase of the equilibrium constants above room temperature is likely to the contamination of $F^-(C_2F_4)$(a) with $F^-(C_2F_4)$(b). Since the complex $F^-(C_2F_4)$(a) is loosely bound, the relative abundance of $F^-(C_2F_4)$(a) will become increasingly smaller than that of $F^-(C_2F_4)$(b) at higher temperature ($1000/T \geq 3$), i.e., $F^-(C_2F_4)$ observed above ~330 K may be mainly composed of $F^-(C_2F_4)$(b). As shown in Fig. 3a–c, the conversion rate of $F^-(C_2F_4)$ to $F^-(C_2F_4)_2$ becomes increasingly slower with increase of ion source temperature and the ion $F^-(C_2F_4)_2$ could not be detected above ~460 K (see Fig. 3c). Some finite lifetime is necessary for the activated complex $[F^-(C_2F_4)(b)\cdots C_2F_4]^*$ to form the tightly bound semi-covalent bond complex, $F^-(C_2F_4)_2$.

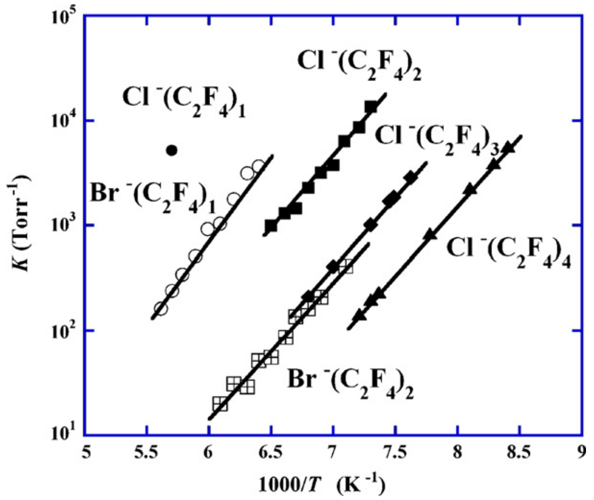

Fig. 5. van't Hoff plots for clustering reactions, $X^-(C_2F_4)_{n-1} + C_2F_4 = X^-(C_2F_4)_n$, $X^- = Cl^-$ and Br^-.

The tentatively drawn straight line ($1000/T \leq 2.1$) using three van't Hoff plots in the higher temperature region in Fig. 4 may give crude thermochemical values of $-\Delta H° = \sim 30$ kcal/mol and $-\Delta S°$ ~30 cal/mol K for reaction, $F^- + C_2F_4 = F^-(C_2F_4)$(b). The obtained $-\Delta H°$ is smaller than the theoretical values (~35 kcal/mol) [22].

King et al. predicted the 1A′ ground state for $F^-(C_2F_4)$(b), i.e., $C_2F_5^-$ [22]. The geometry of $C_2F_5^-$ is similar to that of hexafluoroethane with two valence electrons occupying a C_2F_6 bonding site. The experimental results obtained in this work suggest that there is a reverse barrier for dissociation for $C_2F_5^-$. Theoretical investigation for the isomeric structures for $F^-(C_2F_4)$ is highly necessary to clarify the peculiar behavior of the reactivity of F^- toward C_2F_4.

The temperature dependence of the equilibrium constants of reaction (9) for $X^- = Cl^-$ and Br^- as a function of temperature is shown as van't Hoff plots in Fig. 5. The obtained thermochemical data are summarized in Table 1. In Fig. 5, only a single point could be obtained for Cl^- with $n = 1$. The measurement of this equilibrium was extremely difficult because the intensity of $Cl^-(CCl_4)$ became much stronger than those of $Cl^-(C_2F_4)_n$ in the low temperature measurement and thus some part of Cl^- ion observed was produced outside the ion source by the collision-induced dissociation of $Cl^-(CCl_4)$, i.e., $Cl^-(CCl_4) \rightarrow Cl^- + CCl_4$. The strong appearance of $Cl^-(CCl_4)$ is due to the relatively large bond energy for $Cl^- \cdots CCl_4$ (13.4 kcal/mol) [23]. A single determination of an equilibrium constant shown in Fig. 5 for $Cl^-(C_2F_4)$ was made at the highest temperature for the appearance of the cluster ion $Cl^-(C_2F_4)$ with minimum CCl_4 introduction into the ion source and with the minimum electric field outside the ion source for the ion collimation. The enthalpy change for reaction (9) for Cl^- with $n = 1$ may be roughly estimated to be ~10 kcal/mol assuming that the entropy change is equal to that for the clustering reaction, $Cl^- + C_3F_6 \rightleftarrows Cl^-(C_3F_6)$; 25 cal/mol K [3]. This value could be underestimated because there may be still some contribution from Cl^- produced by the collision-induced dissociation of $Cl^-(CCl_4)$. The irregular decrease in bond energies for $Cl^-(C_2F_4)_n$ with $n = 1 \rightarrow 2$ ($\geq 10 \rightarrow 6.6 \pm 0.5$ kcal/mol in Table 1) suggests some charge transfer in the complex, $Cl^- \rightarrow C_2F_4$ as in the case of $Cl^- \rightarrow C_3F_6$ [3].

The van't Hoff plots for Br^- with $n = 1$ and 2 are shown in Fig. 5. Since the van't Hoff plots between $n = 1$ and 2 are close to each other and the values of $\Delta H°_{n-1,n}$ are rather n-independent in Table 1, the interaction between Br^- and C_2F_4 is mainly electrostatic in nature. The measurement for $X^- = I^-$ could not be made due to the weakening of the ion intensities at lower temperatures due to charging where the cluster ions $I^-(C_2F_4)_n$ started to appear.

4. Summary

Positive and negative ion/molecule reactions in C_2F_4 were studied. $CF_3{}^+$ and $C_2F_4{}^+$ were formed as major ions from the 2 keV electron irradiation on a few Torr N_2 major gas containing 1–10 mTorr C_2F_4. The association reaction of $CF_3{}^+$ with C_2F_4 to form $C_3F_7{}^+$ was observed. The regeneration of $CF_3{}^+$ by the reaction of $C_3F_7{}^+$ with C_2F_4 was reconfirmed [15]. The cluster ions $C_3F_7{}^+(C_2F_4)_n$ were formed below ~280 K but the equilibria for clustering reactions could not be observed, i.e., the higher-order cluster ions $C_3F_7{}^+(C_2F_4)_n$ grew slowly at the expense of smaller cluster ions $C_3F_7{}^+(C_2F_4)_{n-1}$. The rate constant for reaction, $C_2F_4{}^+ + C_2F_4 = C_3F_5{}^+ + CF_3$, was measured to be $(1.5 \pm 0.5) \times 10^{-11}$ cm³/molecule s and found to be temperature-independent in the range of 310–180 K. The presence of isomers for the intermediate complexes of $C_2F_4{}^+ \cdots C_2F_4$ was suggested. The bond energy of $C_3F_5{}^+ \cdots C_2F_4$ (~6 kcal/mol) is considerably smaller than that of $C_3F_5{}^+ \cdots C_3F_6$ (9.2 kcal/mol), i.e., the nucleophilicity of C_2F_4 is smaller than that of C_3F_6.

The vertical electron affinity of C_2F_4 was found to be negative. Two isomers for $F^-(C_2F_4)$ have been predicted, one is an electrostatic loosely bound complex and the other is a tightly bound semicovalent complex. The thermochemical stabilities for halide-ion clusters, $X^-(C_2F_4)_n$ ($X^- = Cl^-$ and Br^-), were determined. The bond energies for $X^-(C_2F_4)_n$ are smaller than those of $X^-(C_3F_6)_n$, i.e., the electrophilicity of C_2F_4 is smaller than that of C_3F_6.

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