Kinetic Energy Dependence of the Reactions of O^+ and O_2^+ with CF₄ and C_2F_6

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Guided ion beam techniques are used to measure cross sections as a function of kinetic energy for reaction of O^+ and O_2^+ with CF_4 and C_2F_6 . The predominant ions formed in these fluorocarbon systems correspond to dissociative charge-transfer reactions, with small amounts of FCO⁺ and F₂CO⁺ being formed. The thresholds and shapes of dissociative charge-transfer cross sections are explained in terms of vertical ionization to various electronic states of CF_4^+ and $C_2F_6^+$. In the O⁺ reactions, fluoride transfer to form CF_3^+ in the CF_4 system and $C_2F_5^+$ in the C_2F_6 system is also observed at thermal energies. The formation of carbon oxyfluoride ions in these systems is postulated to occur by insertion of the oxygen ions into C-F bonds of the fluorocarbon molecules. From the $O_2^+ + CF_4$ and $O^+ + C_2F_6$ systems, $\Delta_f H(F_2CO^+)$ is determined. The relationship of these reactions to plasma deposition and etching is discussed.

Introduction

Use of fluorocarbon and fluorocarbon/oxygen plasmas in etching processes is becoming widespread. Etch characteristics of Ta and Si surfaces resulting from these plasmas have been investigated by a number of methods.¹⁻⁴ For example, reactive ion beam etching studies indicate that plasmas containing C_2F_6 and C_3F_8 give high etch selectivity for SiO₂ to Si of 10 to 1, while the selectivity obtained with CF_4 is less than 2 to $1.^2$ This is substantiated by another study which found that rf discharges in pure CF₄ tend to etch Si and SiO₂ at comparable rates.⁵ It has been demonstrated that fluorine atoms produced in the discharge are the primary etchant of Si,⁶ while F atoms are found to react with SiO_2 only very slowly.⁷ Another reactive species, CF₃ radicals, are abundant in fluorocarbon plasmas and known to chemisorb on silicon,⁸ but they cannot etch silicon alone because of the presence of the carbon atom.⁹ The active etchant for SiO_2 is unclear, but species such as CF_3 , CF_3^+ , ¹⁰ CF_2 , ¹¹ CF_2^+ , ⁶ and others have been proposed as having some effect. Additionally, plasma reactive sputter etching studies show that surface bombardment by ions such as CF_x^+ has an essential role in selective etching of SiO₂.³ It has also been shown that the relative reactivity of CF_x^+ ions with SiO₂ is proportional to x^{12} Thus CF_3^+ and CF_2^+ contribute significantly more to the etching process than do CF⁺ or C⁺

Although fluorocarbon gases are used extensively in these etching systems because of their low toxicity, unsaturates such as $C_x F_{2x}$ in the discharge can scavenge free F atoms and, in unfavorable cases, can lead to polymer or residue formation.⁶ The role of oxygen additions to these plasmas has thus been found to be twofold. First, O_2 and O atoms react with unsaturates which helps eliminate polymerization and recombination reactions and thereby enhances formation of F atoms, which serves to increase the $Si:SiO_2$ etch selectivity. Further, these reactions lead to stable, volatile carbon-containing species such as CO, CO₂, FCO, and F_2CO , thereby decreasing carbonaceous deposits on the etched surface. The second function of oxygen additions is O_2 or Oreactions with the surface being etched. Such reactions can inhibit etching of SiO₂ or Si₃N₄ layers by occupying active sites on these surfaces⁶ and can act to remove carbonaceous layers from Si.¹³ Both types of reactions aid the selective etching of Si over SiO₂.

For CF_4/O_2 plasmas, the maximum F concentration and the maximum etch rate for Si occurs for addition of only $\sim 12\%$ oxygen.¹⁴ In contrast, almost no increase in F concentration is observed when oxygen is added to a C_2F_6 plasma since formation of two CF₃ radicals is energetically favored over other processes, such as production of F atoms.¹⁵ Similar results have been obtained for the etching of tantalum surfaces. In CF_4/O_2 plasmas, the Ta etch rate is high and linearly proportional to the F radical concentration. In contrast, for C_2F_6/O_2 plasmas, the overall Ta

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etch rate is somewhat smaller and independent of F concentration.¹ This indicates that a plasma species other than F atoms is important in Ta etching and that there is a substantial difference in the gas-phase chemistry between these two systems.

In a CF₄ plasma, the primary ions observed are CF_3^+ and CF^+ although CF_2^+ , C^+ , and F^+ are also present in substantial con-centrations.¹⁶ The principal ions observed in a CF_4 plasma containing 25% O_2 are, in order of decreasing intensity, CF_3^+ FCO⁺, CF₂⁺, CO⁺, CF⁺, CO₂⁺, F⁺, O⁺, C⁺, F₂⁺, and F₂CO^{+, 17} These ions, through reactions with other radicals and molecules and via collisions with surfaces, can be a source of the active etching radicals F, CF_3 , and CF_2 . It has been speculated that many of these ions are formed via reactions of atomic or molecular oxygen ions or metastables with CF₄.¹⁸

Recent work in our laboratory has focused on ion-molecule reactions related to CF_4 ,¹⁹ SiF₄,^{20,21} SiCl₄,²² and SiH₄,²³⁻²⁵ plasma systems. In the reactions of rare-gas ions with CF_4 ¹⁹ and SiH₄,²⁵ the energy dependence of the cross sections for fragmentation products was easily understood by considering the energies necessary for vertical transitions to various electronic states of CF₄⁺.

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TABLE I: Heats of Formation at 298 K^a

A	$\Delta_{\rm f} H({\rm A}), {\rm eV}$	$\Delta_{\rm f} H({\rm A}^+), {\rm eV}$	A	$\Delta_{\rm f} H({\rm A}), {\rm eV}$	$\Delta_{\rm f} H({\rm A^+}), {\rm eV}$
0	2.582 (0.001)	16.200 (0.001)	CF,	-2.12 (0.13)	9.28 (0.13)
Ö,	0.000	12.071 (0.001)	FCO	-1.82 (0.17)	6.94 (0.36)
F	0.823 (0.003)	18.311 (0.003)	F ₂ CO	-6.63 (0.02)	6.37 (0.15)
ŌF	1.13 (0.09)	13.88 (0.09)	ĊF,	-4.81 (0.043)	3.74 (0.07) ^c
Ô₅F	0.13 (0.02)	12.75 (0.20)	CF₄	-9.688 (0.013)	. ,
OF,	0.255 (0.017)	13.36 (0.02)	C,F,	-9.24 (0.04)	~0.0
CF	2.64 (0.09)	11.76 (0.09)*	C_2F_6	-13.92 (0.05)	-0.52 (0.05)

"Ion heats of formation are calculated by using the stationary electron convention. Values from the literature which use the convention that the electron is a monatomic gas should be decreased by 0.064 eV at 298 K. Unless otherwise noted, values are taken from ref 33. ^bDyke, J. M.; Lewis, A. E.; Morris, A. J. Chem. Phys. 1984, 80, 1382. Based on the threshold for the reaction, $Kr^{+}(^{2}P_{3/2}) + CF_{4} \rightarrow CF_{3}^{+} + F + Kr$. Fisher, E. R.; Armentrout, P. B. Int. J. Mass Spectrom. Ion Processes 1990, 101, R1.

In the present study, we examine the reactions of O^+ and O_2^+ with CF_4 and C_2F_6 in order to investigate the importance of these ion-molecule reactions in fluorocarbon/ O_2 plasmas and to further investigate the previously observed^{19,25} coupling of translational and internal energy in dissociative charge-transfer (CT) reactions.

Previous work on these reactions is rather limited. The reaction of O⁺ with CF₄ has been studied by Richter and Lindinger at thermal energies,²⁶ and the excitation cross section in collisions of O_2^+ with \widetilde{CF}_4 has been measured to be less than 5×10^{-20} cm² at a laboratory energy of 1800 eV.²⁷ In addition, no emission was observed from this reaction in the wavelength region 2000-8000 Å.²⁷

Experiment

General. The ion beam apparatus and experimental techniques used in this work are described in detail elsewhere.²⁸ The molecular and atomic oxygen ions are produced as described below. The O_2^+ and O^+ ion beams are each mass analyzed, decelerated to the desired translational energy, and injected into an rf octopole ion beam guide,²⁹ which passes through the reaction cell containing the neutral reactant gas. The neutral pressure is sufficiently low, 0.01-0.07 mTorr, that multiple ion-molecule collisions are improbable. The transmitted reactant and product ions drift out of the gas chamber to the end of the octopole, where they are extracted and analyzed in a quadrupole mass filter. Ions are detected by a secondary electron scintillation ion counter using standard pulse counting techniques. Raw ion intensities are converted to absolute reaction cross sections as described previously.²⁸

Laboratory ion energies (lab) are converted to energies in the center-of-mass frame (CM) by using the conversion E_{CM} = $E_{iab}M/(m + M)$, where m is the ion mass and M is the neutral molecule mass. Unless stated otherwise, all energies quoted in this work correspond to the CM frame. The absolute zero and the full width at half-maximum (fwhm) of the ion kinetic energy distribution are determined by using the octopole beam guide as a retarding potential analyzer.²⁸ The uncertainty in the absolute energy scale is $\pm 0.05 \text{ eV}$ (lab). The distribution of ion energies has an average fwhm of 0.3 eV (lab) for both O₂⁺ and O⁺. **Ion Source.** The O⁺ and O₂⁺ ions are formed in their ground

electronic and vibrational states by using a recently constructed flow tube (FT) ion source.³⁰ This flow tube (either 50 or 100 cm in length) operates at a pressure of 0.4-0.7 Torr with a helium flow rate of 3500-7000 standard cm³/min. In this source, He⁺ and He* are formed by microwave discharge. Further downstream, these species interact with the reagent gas to form O⁺ and O_2^+ ions [appearance energy (AE) of $O^+ = 18.8 \pm 0.4 \text{ eV}$,³¹ and ionization energy (IE) of $O_2 = 12.071 \pm 0.001 \text{ eV}^{32.33}$] through charge transfer or possibly Penning ionization.

Primary cooling of the O_2^+ ions is obtained by self-quenching collisions with the O_2 reagent gas. This is because electronically excited metastable ions of O_2^+ are rapidly deexcited in collisions with $O_2 [k = 3.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}]$,³⁴ and vibrationally excited O_2^+ ions are also rapidly quenched by $O_2 [k = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}].^{35}$ The internal energy content of the O_2^+ ions is evaluated in several ways which have been discussed in detail previously.³⁶ Based on these tests, the O_2^+ ion beams used for these experiments are >99.9% ground $O_2^{+(2}\Pi_g, v=0)$. For O⁺ beams, the FT source has been shown to produce beams composed of >99.9% ground-state ⁴S ions.³⁷ This is determined by using the reaction of O⁺ with N_2 as a diagnostic for the amount of excited-state O⁺ in the beam, as described elsewhere.38

Ion Collection Efficiency. For charge-transfer (CT) and dissociative CT reactions, products may be formed through a long-range electron jump such that little or no forward momentum is transferred to the ionic products.³⁹ In such instances, it is possible that up to 50% of these ions may have no forward velocity in the laboratory and will not drift out of the octopole to the detector. Such slow product ions that do traverse the octopole may be inefficiently transmitted through the quadrupole mass filter.²⁸ Exothermic or nearly thermoneutral reaction channels, in particular, can be subject to these effects. Nevertheless, results reported here were reproduced on several occasions and the cross-section magnitudes shown are averaged results from all data sets. Based on reproducibility, the uncertainty in the absolute cross sections is estimated as $\pm 30\%$ in both the O₂⁺ and O⁺ systems.

Collision Cross Sections. The collision cross section, σ_{col} , for ion-molecule reactions at low energies is predicted by the Langevin-Gioumousis-Stevenson (LGS) model⁴⁰

$$\sigma_{\rm LGS} = \pi e (2\alpha/E)^{1/2} \tag{1}$$

where e is the electron charge, α is the polarizability of the target molecule, and E is the relative kinetic energy of the reactants. Many exothermic reaction cross sections follow this type of energy dependence, although deviations are commonly seen.⁴¹ In this work, we use $\alpha(CF_4) = 2.92 \text{ Å}^{342}$ and $\alpha(C_2F_6) = 5.0 \text{ Å}^{3,43}$

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ENERGY (eV, Lab)





Figure 1. Variation of product cross sections with translational energy in the laboratory frame of reference (upper scale) and the center-of-mass frame (lower scale) for the reaction of O⁺ with CF₄. The dashed line shows the collision cross section, given by the maximum of σ_{HS} or σ_{LGS} $[\alpha(CF_4) = 2.92 \text{ Å}^3]$. Arrows indicate the ΔIE values listed in Table III for the CF_4^+ states labeled.

At high kinetic energies, σ_{col} for CT reactions is better represented by the hard-sphere limit, $\sigma_{\rm HS} = \pi R^2$. We estimate that $\sigma_{\rm HS}(O^+/CF_4) = 22 \text{ Å}^{2,44} \sigma_{\rm HS}(O_2^+/CF_4) = 32 \text{ Å}^{2,45} \sigma_{\rm HS}(O^+/C_2F_6)$ = 37 Å^{2,46} and $\sigma_{\rm HS}(O_2^+/C_2F_6) = 50 \text{ Å}^{2,47}$ In this work, $\sigma_{\rm col}$ is taken to be the maximum of σ_{LGS} and σ_{HS} .

Threshold Analysis. The threshold regions of the experimental reaction cross sections can be analyzed by using the empirical model in eq 2. Here, E_{T} is the reaction endothermicity, σ_0 is an

$$\sigma(E) = \sigma_0 (E - E_{\rm T})^n / E \tag{2}$$

energy-independent scaling factor, and n is an adjustable parameter. This form has been derived as a model for translationally driven reactions⁴⁸ and has been found to be quite useful in describing the shapes of endothermic reaction cross sections and in deriving accurate thermochemistry for a wide range of systems.^{20,49,50} The parameters n, σ_0 , and E_T are allowed to vary freely to best fit the data as determined by nonlinear least-squares analysis. Errors in threshold values are determined by the variation in E_{T} for the various models applied to several data sets and the absolute uncertainty in the energy scale, $\sim 0.04 \text{ eV}$.

Heats of formation used in deriving thermochemical results are given in Table I. We assume that the neutral reactants and the



Figure 2. Variation of product cross sections with translational energy in the laboratory frame of reference (upper scale) and the center-of-mass frame (lower scale) for the reaction of O_2^+ with CF₄. Arrows indicate the ΔIE values listed in Table III for the CF_4^+ states labeled.

products formed at the threshold of an endothermic reaction are characterized by a temperature of 300 K in all degrees of freedom. Thus, we make no correction for the energy available in internal modes of the neutral reactant. Furthermore, eq 2 implicitly assumes that there are no activation barriers in excess of the endothermicity. This assumption is generally true for ion-molecule reactions and has been explicitly tested a number of times.^{50,51}

Results

 $O^+ + CF_4$. Results for the reaction of $O^+ + CF_4$ are shown in Figure 1. At the lowest energies, the total cross section matches σ_{LGS} but then declines as $E^{-0.85\pm0.05}$, faster than the behavior predicted by the LGS model of eq 1. At energies greater than \sim 2.0 eV, the cross section levels off at about 10 Å², mimicking the behavior of σ_{col} . The decline in σ_{tot} at high energies (above 30 eV) may be due to a decrease in ion collection efficiency.

The ionic products observed in reaction of O⁺ with CF₄ (Figure 1) are given in reactions 3-6, along with their heats of reaction

$$O^+ + CF_4 \rightarrow CF_3^+ + OF \qquad \Delta H = -1.64 \pm 0.11 \text{ eV}$$
 (3)

$$\rightarrow CF_2^+ + O + 2F$$
 $\Delta H = 7.00 \pm 0.13 \text{ eV}$ (4)

$$\rightarrow CF^+ + O + 3F$$
 $\Delta H = 10.30 \pm 0.09 \text{ eV}$ (5)

$$\rightarrow FCO^+ + 3F \qquad \Delta H = 2.90 \pm 0.36 \text{ eV} \tag{6}$$

as calculated from the literature heats of formation given in Table I. Formation of the molecular ion CF_4^+ is not observed at any energies. Process 3, formation of CF_3^+ , is favored over the other products at all energies. At the lowest energies, the CF_3^+ cross section increases monotonically as the energy decreases, indicating an exothermic process. This must be due to fluoride transfer, reaction 3, since formation of separated O + F atoms is endothermic by 0.63 ± 0.05 eV. The observation of this exothermic process is consistent with the relative fluoride affinities of O⁺ and CF_3^+ , 4.27 ± 0.12 and 2.62 ± 0.11 eV, respectively.⁵²

All other ions observed are formed in highly endothermic processes (Figure 1). For CF_2^+ production, the apparent threshold is \sim 8.0 eV, well above the thermodynamic threshold for reaction 4. Cross sections for both CF⁺ and FCO⁺ have similar apparent thresholds of $\sim 11 \text{ eV}$. This is close to the threshold for reaction

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5 but considerably higher than the thermodynamic threshold for reaction 6.

 $O_2^+ + CF_4$. Results for reaction of O_2^+ with CF_4 are shown in Figure 2. Above 15 eV, the total cross section reaches a constant value of about 3 Å², ~10% σ_{HS} . CF_4^+ is not observed at any energies. Formation of CF⁺ is also not observed in this system due to considerable mass overlap from the O_2^+ beam. Reaction channels 7–10 all display reaction thresholds, typical of endothermic processes.

 $O_2^+ + CF_4 \rightarrow CF_3^+ + O_2 + F$ $\Delta H = 2.18 \pm 0.07 \text{ eV}$ (7)

$$\rightarrow CF_2^+ + O_2^- + 2F \qquad \Delta H = 8.54 \pm 0.13 \text{ eV}$$
 (8)

 $\rightarrow FCO^+ + O + 3F \qquad \Delta H \ 9.61 \pm 0.36 \ eV \qquad (9)$

$$\rightarrow$$
 F₂CO⁺ + OF₂ $\Delta H = 4.24 \pm 0.15 \text{ eV}$ (10)

Similar to the $O^+ + CF_4$ system, the major product observed is CF_3^+ , formed in reaction 7. The cross section for CF_3^+ formation has a threshold of 3.6 ± 0.2 eV as determined by analysis with eq 2. This is higher than the thermodynamic threshold for reaction 7 but is lower than that for the alternatives, formation of OF + O as neutrals, 5.07 ± 0.11 eV, or 2O + F, 7.34 ± 0.07 eV. Similarly, the threshold measured for the CF_2^+ cross section by analysis with eq 2, $E_T = 10.6 \pm 0.2 \text{ eV}$, is well above the energy needed for process 8. In addition, this threshold does not correspond directly to the energies required for formation of 2OF at 9.14 \pm 0.16 eV, of O + OF₂ at 9.73 \pm 0.13 eV, of OF + F + O at 11.42 \pm 0.16 eV, or complete atomization at 13.70 \pm 0.13 eV. For formation of FCO⁺, the apparent threshold is $\sim 16 \text{ eV}$, although the value of E_T determined by analysis with eq 2 is considerably lower, 11.4 ± 0.2 eV. In either case, these values are considerably higher than the thermodynamic threshold for reaction 9.

In contrast, the apparent threshold for formation of $F_2CO^+ + OF_2$ is close to the thermodynamic threshold for process 10. Analysis of this cross section yields the eq 2 parameters $n = 1.48 \pm 0.12$, $E_T = 4.17 \pm 0.12$ eV, and $\sigma_0 = 0.03 \pm 0.01$. This threshold then leads to $\Delta_f H(F_2CO^+) = 6.30 \pm 0.12$ eV, in good agreement with the literature value (Table I). It is likely that the F_2CO^+ and CF_2^+ products compete with one another in this system since the F_2CO^+ cross section declines as that for the CF_2^+ cross section rises. This decline begins somewhat higher than the thermodynamic threshold for formation of $CF_2^+ + O + OF_2$, 9.73 ± 0.13 eV (Table I).

 $O^+ + C_2F_6$. Results for reaction of O^+ with C_2F_6 are shown in Figures 3 and 4. The major processes seen are reactions 11-16.

 $O^+ + C_2 F_6 \rightarrow C_2 F_5^+ + OF \qquad \Delta H = -1.15 \pm 0.10 \text{ eV}$ (11)

 $\rightarrow CF_3^+ + O + CF_3 \qquad \Delta H = -0.77 \pm 0.08 \text{ eV}$ (12)

 \rightarrow F₂CO⁺ + CF₃ + F $\Delta H = 0.10 \pm 0.08 \text{ eV}$ (13)

 $\rightarrow CF_2^+ + CF_3 + O + F \qquad \Delta H = 3.01 \pm 0.14 \text{ eV}$ (14)

 $\rightarrow CF^+ + CF_3 + O + 2F$ $\Delta H = 8.90 \pm 0.11 \text{ eV}$ (15)

→ FCO⁺ + CF₃ + 2F
$$\Delta H = 1.50 \pm 0.36 \text{ eV}$$
 (16)

Figure 3 shows an expanded view of the low-energy reactions. From the lowest energies to ~10 eV, the total cross section, σ_{tot} , follows σ_{col} closely. At the highest energies, σ_{tot} decreases significantly, although this may be due to poor ion collection efficiency at these energies. At the lowest energies, formation of CF₃⁺, process 12, is favored over formation of C₂F₃⁺, with a branching ratio of 72:28. The cross section for CF₃⁺ increases with decreasing energy, indicative of an exothermic process. Below ~2 eV, $\sigma(CF_3^+)$ decreases as $E^{-0.48\pm0.03}$, in good agreement with the predicted behavior of eq 1, while at higher energies, it levels out somewhat, mimicking σ_{col} .

somewhat, mimicking σ_{col} . The cross section for formation of $C_2F_5^+$ also increases monotonically as the kinetic energy decreases, indicating an exothermic reaction (Figure 3) consistent with the thermochemistry for reaction 11. This is reasonable as the fluoride affinity of O⁺ is



Figure 3. Variation of product cross sections for products formed at low energies in the reaction of O⁺ with C₂F₆ in the laboratory frame of reference (upper scale) and the center-of-mass frame (lower scale). The solid line represents the total cross section, and the dashed line represents the collision cross section, the maximum of σ_{HS} or σ_{LOS} [α (C₂F₆) = 5.0 Å³]. The solid line running through the F₂CO⁺ cross section is the eq 2 model with the parameters listed in the text. The arrows show the Δ IE values listed in Table III for the CF₄⁺ states labeled and for the threshold for formation of C₂F₅⁺ + O + F at 1.13 eV. For the A state, both the adiabatic and vertical values are shown.

greater than that for $C_2F_5^+$ (3.10 ± 0.09 eV).⁵² Between ~0.07 and 0.4 eV, $\sigma(C_2F_5^+)$ declines as $E^{-0.50\pm0.03}$, in good agreement with the predicted behavior of eq 1. At ~1.0 eV, the cross section actually rises and is then fairly constant out to high energies. Since the thermodynamic threshold for formation of separated O + F neutrals is 1.12 ± 0.04 eV, the second feature in $\sigma(C_2F_5^+)$ is probably due to formation of separated atoms as neutrals.

Although the cross section for process 13, formation of F_2CO^+ + $CF_3 + F$, is nonzero at the lowest energies (Figure 3), this process should be slightly endothermic based on the thermochemistry of Table I. Consistent with this are the observations that the cross section for F_2CO^+ declines more slowly than those of either CF_3^+ or $C_2F_5^+$ (Figure 3) and that the cross-section shape cannot be reproduced with $E_T = 0.0$ eV in eq 2. Indeed, analysis of this cross section with eq 2 yields the parameters n = 0.67 and $E_T = 0.03 \pm 0.02$ eV. This cross-section model is compared to the data in Figure 3. We have previously shown that we are able to accurately measure the thresholds for such near-thermoneutral reactions.^{53,54} From this threshold, we determine $\Delta_f H(F_2CO^+)$ = 6.30 ± 0.08 eV, in excellent agreement with the value derived above in the $O_2^+ + CF_4$ system and with the literature thermochemistry.

At higher kinetic energies, we also observe formation of small amounts of CF_2^+ , CF^+ and FCO^+ (Figure 4). Both CF_2^+ and FCO^+ are formed at energies well above the thermodynamic thresholds for the reactions given in processes 14 and 16, while CF^+ is formed with an apparent threshold near the thermodynamic threshold for reaction 15.

 $O_2^+ + C_2F_6$. Only three reaction products are observed in this system, processes 17-19 (Figure 5). Above ~10 eV, the total

$$O_2^+ + C_2F_6 \to CF_3^+ + CF_3 + O_2 \qquad \Delta H = 0.78 \triangleq 0.10 \text{ eV}$$
(17)

$$\rightarrow C_{2}F_{4}^{+} + F + O_{2}$$
 $\Delta H = 2.67 \pm 0.06 \text{ eV}$ (18)

$$\Rightarrow CF_2^+ + CF_3 + F + O_2 \qquad \Delta H = 7.14 \pm 0.15 \text{ eV}$$
(19)

⁽⁵³⁾ Ervin, K. M.; Armentrout, P. B. J. Chem. Phys. 1987, 86, 2659.
(54) Loh, S. K.; Fisher, E. R. Lian, L.; Schultz, R. H.; Armentrout, P. B. J. Phys. Chem. 1989, 93, 3159. Fisher, E. R.; Armentrout, P. B. J. Phys. Chem. 1990, 94, 1674.



Figure 4. Variation of product cross sections with translational energy in the laboratory frame of reference (upper scale) and the center-of-mass frame (lower scale) for the reaction of O⁺ with C₂F₆. The dashed line shows the collision cross section, the maximum of $\sigma_{\rm HS}$ or $\sigma_{\rm LGS}$ [α (C₂F₆) = 5.0 Å³].



Figure 5. Variation of product cross sections with translational energy in the laboratory frame of reference (upper scale) and the center-of-mass frame (lower scale) for the reaction of O_2^+ with C_2F_6 . Arrows indicate the ΔIE values listed in Table IV for the $C_2F_6^+$ states labeled.

cross section is fairly constant at about 10 Å², ~20% $\sigma_{\rm HS}$. Similar to the O₂⁺ + CF₄ system, we do not observe formation of CF⁺ due to mass overlap with the O₂⁺ beam. The cross sections for all three of these products display endothermic behavior. The apparent thresholds for $\sigma(CF_3^+)$ and $\sigma(C_2F_5^+)$ are nearly identical at ~3.0 eV. For CF₃⁺, this threshold is much higher than the thermodynamic threshold for reaction 17, while for C₂F₅⁺, the observed threshold is close to the thermodynamic threshold for reaction 18. $\sigma(C_2F_5^+)$ rises faster than $\sigma(CF_3^+)$ such that it is the larger cross section between ~5 and 8 eV (Figure 5). Formation of CF₂⁺ is seen at higher kinetic energies, with an apparent threshold of ~11 eV, significantly higher than the thermodynamic threshold for process 19.

Discussion

Reaction Rates. Cross sections at low kinetic energies can be converted to thermal reaction rate constants for the exothermic reactions as described previously.⁵⁵ These rate constants are given

TABLE II: Reaction Rate Constants at 298 Ka

system	product	present work	previous	LGS
$\begin{array}{c} O^+ + CF_4 \\ O^+ + C_2F_6 \end{array}$	total (CF_3^+) CF_3^+ $C_2F_5^+$ F_2CO^+	$\begin{array}{c} 1.3 \pm 0.4 \\ 0.89 \pm 0.26 \\ 0.33 \pm 0.10 \\ 0.06 \pm 0.02 \end{array}$	1.0 ± 0.2^{b}	1.09
	total	1.3 ± 0.4		1.38

^aAll rates in units of 10^{-9} cm³ s⁻¹. ^bReference 26, assumed 20% error.

TABLE III:	Adiabatic and	Vertical	Ionization	Energies	for CF	•
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orbital	adiab	vert	ΔIE(O) ^b	$\Delta IE(O_2)$
X^2T_1	≤14.24 ^c	16.2	$2.2 (0.4)^d$	3.7 (0.4) ^d
A^2T_2	17.1	17.4	3.6 (0.2)	5.2 (0.2)
B ² E	18.3	18.5	4.8 (0.1)	6.3 (0.1)
$C^{2}T_{2}$	21.7	22.1	8.3 (0.2)	9.8 (0.2)
$D^2 A_1$	25.1	25.1	11.5	13.0

^a Except where noted, values (in eV) are taken from ref 56. ^b Δ IE-(A) = IE(orbital) – IE(A) where IE(orbital) is the mean of the adiabatic and vertical values and the uncertainties (in parentheses) show the spread in these values. ^cThis adiabatic IE is the appearance energy for CF₃⁺ + F from CF₄ as calculated from the information in Table I. ^dThese uncertainties (in parentheses) represent the width of this band in the photoelectron spectrum of ref 56.

TABLE IV: Adiabatic and Vertical Ionization Energies for C₂F₆^a

or	bital	adiab	vert	ΔIE(O) ^b	$\Delta IE(O_2)^b$	
X	$^{2}A_{1g}$	≤12.85 ^c	14.3	$0.3 (0.4)^d$	$2.0 (0.4)^d$	
A	² E	15.4	16.4	2.3 (0.5)	3.8 (0.5)	
В		16.8	17.1	3.3 (0.2)	4.9 (0.2)	
С		~17.8	18.2	4.4 (0.2)	5.9 (0.2)	

^a Values (in eV) estimated from spectra in refs 57 and 58. ^b Δ IE(A) = IE(orbital) – IE(A) where IE(orbital) is the mean of the adiabatic and vertical values and the uncertainties (in parentheses) show the spread in these values. ^cThis adiabatic IE is the appearance energy for CF₃⁺ + CF₃ from C₂F₆ as calculated from the information in Table I. ^dThese uncertainties (in parentheses) represent the width of this band in the photoelectron spectrum of ref 57.

in Table II where it can be seen that totals agree with the LGS rate constants within experimental error. The only system that has been studied previously to yield a reaction rate constant is the $O^+ + CF_4$ system. Richter and Lindinger $(RL)^{26}$ used drift tube techniques to determine a value that is in good agreement with the value derived here (Table II). At kinetic energies between 1.8 and 4.0 eV, RL also observed formation of FCO⁺ and CF⁺. Although we observe these products (Figure 1), we do so only at energies above ~10 eV. This discrepancy indicates that the O⁺ ions in RL's experiments may not have been completely thermalized or that secondary reactions were occurring.

Kinetic Energy Dependence of Cross Sections. Much of the behavior displayed in the present CF_4 and C_2F_6 systems can be explained by dissociative charge-transfer (CT) reactions. In all four systems, reaction thresholds for many of these processes are well above their thermodynamic thresholds, in direct contrast to typical behavior for most endothermic ion-molecule reactions.⁴¹ In previous work on reactions of rare-gas ions with CF_4 and SiH_4 ,^{19,25} we found that dissociative CT processes were controlled by vertical ionization processes. It is thus possible that similar behavior is being observed here. These vertical processes can be quantified in the present systems by examining the photoelectron spectra (PES) of CF_4 and C_2F_6 . Table III lists vertical and adiabatic IEs for CF_4 from the UV PES of Brundle, Robin, and Basch.⁵⁶ Table IV lists IEs for C_2F_6 from the UV PES of Simm, Danby, and Eland⁵⁷ and the threshold photoelectron-photoion

⁽⁵⁵⁾ Rate constants are derived from cross-section data by using methods described in ref 28.

⁽⁵⁶⁾ Brundle, C. R.; Robin, M. B.; Basch, H. J. Chem. Phys. 1970, 53, 2196.

⁽⁵⁷⁾ Simm, I. G.; Danby, C. J.; Eland, J. H. D. Int. J. Mass Spectrom. Ion Processes 1974, 14, 285.

coincidence data of Inghram, Hanson, and Stockbauer.⁵⁸ Also listed in these two tables are ΔIE values, the difference between IEs of the neutral molecules and those of molecular and atomic oxygen.

Vertical transitions are often characterized in terms of Franck-Condon factors. There has been a great deal of work on the importance of these factors and energy resonances in charge-transfer reactions between atomic ions and small molecules at thermal energies.⁵⁹⁻⁶² It is generally accepted that, for a thermal energy reaction to be efficient, the molecular ion must have an energy level that is resonant with the recombination energy of the approaching ion and that this resonant energy level must possess a favorable Franck-Condon factor.⁵⁹ Such factors, however, have not been thoroughly explored at hyperthermal energies.

Carbon Tetrafluoride. In both CF_4 systems, formation of CF_4^+ is not observed at any energies and formation of CF3⁺ dominates the reactivity at nearly all energies (Figures 1 and 2). This result is partially explained by noting that the stable region of the CF_4^+ ground state is not accessible by a vertical transition from the CF₄ molecule. Rather, the region of the X^2T_1 state of CF_4^+ which is accessible via a vertical transition, as well as the A^2T_2 and B^2E states of CF_4^+ , all predissociate to $CF_3^+ + F_1^{63}$ In addition, the C^2T_2 and D^2A_1 states of CF_4^+ are observed to radiate to the lower lying states,^{64,65} which can then dissociate.

The appearance of product cross sections in the $O^+ + CF_4$ system can be better understood by using these ideas. As noted above, despite the nonresonant nature of the $O^+ + CF_4$ reaction, formation of OF as the neutral in reaction 3 allows for production of CF_3^+ via an efficient exothermic process. While this reaction could account for the CF_3^+ product seen at all energies, it is also possible that dissociative CT contributes at elevated energies as has been seen for reactions of rare-gas ions with CF₄.¹⁹ Such a process is probably not efficient until the vertically accessible ionization region to form $CF_4^+(X^2T_1)$ at ~16 eV, over 2 eV higher than IE(O). This may explain why the cross section for CF_3^+ stops decreasing when this vertical excitation energy is reached at $\Delta IE = 2.2 \pm 0.4 \text{ eV}$ (Table III) and then remains constant until further dissociation channels become available. In the intermediate energy region, O⁺ could produce the A^2T_2 and B^2E states of CF_4^+ , but, as noted above, these also form CF_3^+ exclusively.

Formation of the CF_2^+ product, reaction 4, has an apparent threshold of ~8.0 eV (Figure 1), close to ΔIE for the C^2T_2 band of CF_4^+ (Table III). In the reactions of CF_4 with rare-gas ions,¹⁹ the thresholds for formation of CF_2^+ also occur at the ΔIEs for the C^2T_2 state. Also, the apparent threshold for reaction 5 occurs at ~11 eV, near ΔIE for the D²A₁ band of CF₄⁺. Thus, high energy dissociative CT reactions of atomic oxygen ions with CF4 may be controlled by vertical excitations to various electronic states of the CF_4^+ ion, leading to fragmentation thresholds well above the thermodynamic values.

These ideas can also be applied to the $O_2^+ + CF_4$ system. Molecular oxygen ions (IE = 12.071 eV) are also not resonant with the X^2T_1 band of CF_4^+ , consistent with the endothermic nature of the reaction between O_2^+ and CF_4 (Figure 2). Rather, formation of CF₃⁺ is observed as soon as a vertical transition to the X^2T_1 band becomes energetically accessible at $\Delta IE = 3.7 \pm$ 0.4 eV, in contrast to the thermodynamic threshold for reaction 7 of 2.18 \pm 0.07 eV. Likewise, formation of CF₂⁺ is observed

(65) Aarts, J. F. M.; Mason, S. M.; Tuckett, R. P. Mol Phys. 1987, 60, 761.

with a threshold corresponding most closely to ΔIE for the C²T₂ band at 9.8 \pm 0.2 eV, although the agreement here is not outstanding. Fluoride transfer to form O_2F is not seen in the O_2^+ system because the fluoride affinity O_2^+ (1.14 ± 0.09 eV)⁵² is much less than that of CF_3^+ .

For both of these systems, a possible explanation for the delay in the dissociative CT reaction thresholds is that the lack of resonance between O^+ ions or ground-state O_2^+ ions and any of the electronic states of CF_4^+ produces a slow onset and delayed reaction thresholds for high-energy dissociative charge-transfer reactions. Further, since these processes involve successive loss of F atoms, the probability is low that each F atom will depart with no momentum and leave all the interaction energy available for further dissociation. Thus, a kinetic shift is observed.

Hexafluoroethane. Similar to the CF4 systems, formation of the molecular ion in the C_2F_6 systems is not observed. This concurs with the observation that no $C_2F_6^+$ parent ions have been observed by means of photon⁵⁸ or electron impact⁶⁶ mass spectrometry. This observation is due to the unstable nature of $C_2F_6^+$ ions. Photofragmentation studies indicate that the X^2A_{1g} state of $C_2F_6^+$ dissociates to form exclusively CF_3^+ , while the A^2E state dissociates primarily to $C_2F_5^{+,57}$ This indicates that the A²E excited state does not undergo internal conversion to the ground state before decomposition. At higher energies, the B and C states fragment primarily to CF_3^+ , although formation of CF_2^+ and CF^+ is also seen.

This specific dissociation behavior can be understood since the $X^{2}A_{1g}$ and $A^{2}E$ states of $C_{2}F_{6}^{+}$ result from removal of an electron from very different molecular orbitals. The X²A_{1g} ground state of $C_2F_6^+$ corresponds to the loss of an electron from an essentially C-C σ -bonding orbital on the molecule, the 4a_{1g} orbital.⁵⁷ In contrast, the A²E first excited state of $C_2F_6^+$ corresponds to loss of an electron from an e_u or e_g orbital, largely associated with the π -levels of the fluorine atoms.

These observations can now be used to help explain the cross sections of Figures 3 and 4. In the $O^+ + C_2F_6$ system, CT to form $C_2F_6^+(X^2A_{1g})$ is near resonant (Table IV). Thus, the reaction efficiency is high at all energies and favors formation of CF_3^+ over $C_2F_5^+$ at the lowest energies by more than a factor of 2. Indeed, this preference is found even though the fluoride-transfer reaction 11 is more exothermic than reaction 12. As the kinetic energy increases, $C_2F_5^+$ formation rather than CF_3^+ formation is pre-ferred. The increase in the cross section for $C_2F_5^+$ and the concomitant decrease in that for CF_3^+ (Figure 3) occur at energies near the thermodynamic threshold for production of $C_2F_5^+ + O$ + F, 1.13 ± 0.04 eV, and near the onset for a vertical transition to $C_2F_6^+(A^2E)$, ~1.8 eV (Table IV). The observation that $\sigma(C_2F_5^+)$ is larger than $\sigma(CF_3^+)$ from ~1.5 eV to the highest kinetic energies is consistent with the observation that photoionization of C_2F_6 favors $C_2F_5^+$ over CF_3^+ production at energies where both the X^2A_{1g} and A^2E states are accessible.⁵⁸

Similar ideas can be applied to the $O_2^+ + C_2F_6$ reaction system. Here, the O_2^+ ions are not resonant with the ground state of $C_2F_6^+$, and the fluoride affinity of $O_2^+ < C_2F_5^+$, such that O_2F is not formed in this reaction. Thus, we observe no reactivity at thermal energies. As the kinetic energy is increased, we observe formation of CF_3^+ and $C_2F_5^+$ with approximately the same threshold (Figure 5). This threshold corresponds somewhat to ΔIE for the A²E state of $C_2F_6^+$, consistent with the observation that from threshold to ~9 eV the cross section for $C_2F_5^+$ formation is greater than that for CF_3^+ formation. At higher energies, CF_3^+ dominates over $C_2F_5^+$ by about a factor of 4. This is consistent with the photoionization results that show that the higher lying excited states of $C_2F_6^+$ preferentially dissociate to $CF_3^+ + CF_3^{.57}$

In both $C_2F_6^+$ systems, we observe formation of dissociative CT products with thresholds well above the ΔIE values of Table IV. These include formation of CF_2^+ and CF^+ in the O⁺ system and formation of CF_2^+ in the O_2^+ system. It is possible that these thresholds correspond to a $C_2 \tilde{F_6}^+$ excited state that has not yet been measured. Using the apparent thresholds for the CF_2^+

⁽⁵⁸⁾ Inghram, M. G.; Hanson, G. R.; Stockbauer, R. Int. J. Mass Spectrom. Ion Processes 1980, 33, 253.

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(61) Bowers, M. T.; Elleman, D. D. Chem. Phys. Lett. 1972, 16, 486.
(62) Mauclaire, G.; Derai, R.; Fenistein, S.; Marx, R. J. Chem. Phys. 1979, 70, 4017. Derai, R.; Mauclaire, G.; Marx, R. Symp. At. Surf. Phys. 1982, 278.

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product ion, we can approximate the IE for this state. In the O⁺ system, the apparent threshold for CF_2^+ (10–11 eV) leads to IE = 24–25 eV, and in the O₂⁺ system, we find IE = 23–24 eV. For comparison, the D²A₁ state of CF₄⁺ has a similar ionization energy of 25.1 eV (Table III). As noted above, however, it is also possible that we are simply observing a kinetic shift in these reactions.

Formation of Carbon Oxyfluoride Ions. In both CF₄ systems and in the O⁺ + C₂F₆ system, the observation of FCO⁺ and F₂CO⁺ as product ions indicates that these reactions are more than just simple dissociative CT processes as was seen in the Rg⁺ + CF₄ systems.¹⁹ In all cases, the carbon oxyfluoride ions are formed in very inefficient reactions (Figures 1-4) via mechanisms that are not transparent. We presume that these species have the structures O=C⁺-F and F₂C=O⁺.

In the $O^+ + CF_4$ reaction, FCO⁺ could be formed after insertion of O⁺ into a C-F bond leads to FOCF₃⁺. This intermediate could dissociate to produce CF_3^+ + OF or lose three F atoms to give FCO⁺. In the O_2^+ + CF₄ reaction, formation of F_2CO^+ is accompanied by formation of OF_2 as the neutral product. The simplest explanation for this reaction is insertion of the O₂⁺ molecule into a C-F bond of CF4 to form the intermediate FOOCF₃⁺. This type of insertion has been seen previously in the reaction of O_2^+ with CH_4 .^{36,67} Fluorine atom transfer could then lead to $F_2CO^+ \cdot OF_2$, which could dissociate to $F_2CO^+ + OF_2$ via cleavage of the O–O bond. The relative IEs of OF_2 and F_2CO indicate that formation of F_2CO^+ would be favored over OF_2^+ (Table I). Although the simplest pathway to formation of FCO⁺ would be loss of an F atom from F_2CO^+ , the shapes of $\sigma(FCO^+)$ and $\sigma(F_2CO^+)$ do not indicate that these two processes are directly competitive. Instead, FCO⁺ probably results directly from decomposition of the $FOOCF_3^+$ intermediate.

Both F_2CO^+ and FCO^+ are seen in the $O^+ + C_2F_6$ reaction. On the basis of thermochemical arguments, formation of F_2CO^+ must be accompanied by $CF_3 + F$ as neutrals. Two pathways are conceivable. Insertion of the O^+ ion into the C-C bond of C_2F_6 to form the intermediate $F_3COCF_3^+$ may be reasonable since

(67) Barlow, S. E.; Van Doren, J. M.; Depuy, C. H.; Bierbaum, V. M.; Dotan, I.; Ferguson, E. E.; Adams, N. G.; Smith, D.; Rowe, B. R.; Marquette, J. B.; Dupeyrat, G.; Durup-Ferguson, M. J. Chem. Phys. **1986**, 85, 3851. the C-C bond is the weakest in the molecule. This intermediate decomposes by cleavage of one of the C-O bonds to form F_3CO^+ , which can then lose an additional F atom to give F_2CO^+ . Alternatively, the O⁺ ion could insert into a more accessible C-F bond to form $F-OCF_2^+-CF_3$ which could then lose F and CF₃. Unlike the $O_2^+ + CF_4$ system, the cross-section data are consistent with the possibility that FCO^+ is formed via loss of a F atom from F_2CO^+ .

Relation to Plasma Systems. Many of the ions found in CF_4/O_2 plasmas (listed above) are also formed in the reactions studied here (Figures 1 and 2). Reactions of O⁺ and O₂⁺ with CF₄ produce primarily CF₃⁺ ions and OF and F radicals. Reactions of O⁺ and O₂⁺ with C₂F₆ produce CF₃⁺ and C₂F₅⁺ ions and CF₃, OF, and F radicals (Figures 3-5). Both O⁺ systems have efficiencies near the collision limit over extended ranges of kinetic energy while the O₂⁺ reactions are somewhat less efficient at elevated energies and do not occur at all at thermal energies. These results demonstrate that the ion-molecule reactions studied here, in particular those of O⁺, are possible sources of these reactive species in CF₄/O₂ and C₂F₆/O₂ plasmas.

As noted above, Martz, Hess, and Anderson found that the etch rate for Ta in a CF_4/O_2 plasma is dependent on the F concentration, whereas in a C_2F_6/O_2 plasma, no dependence on F atom concentration is observed.¹ These authors suggest that this difference could be the result of different gas-phase chemistry of these two systems. While they hypothesize that the difference centers on CF_2 , a possibility suggested by the present results is that an active species is CF_3^+ , a major ion produced in all four reaction systems studied here. In CF_4/O_2 plasmas, the increase in F concentration would reflect an increase in the CF_3^+ concentration since formation of CF_3^+ ions from CF_4 is accompanied by formation of F radicals. Conversely, in C_2F_6/O_2 plasmas, formation of CF_3^+ is accompanied by CF_3 formation, such that the etch rate would not be dependent upon the F concentration. Other active etchants are presumably present since the etch rate in CF_4/O_2 plasmas is higher than in C_2F_6/O_2 plasmas.¹

Acknowledgment. This work was supported by the Air Force Wright Aeronautical Laboratories. We thank Taejoon Han for performing preliminary experiments on the C_2F_6 systems.

Cage Effect on the Photodissociation of H₂O in Xe Matrices

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Photodissociation of H_2O in Xe matrices has been investigated by excitation in the first continuum (\tilde{A}^1B_1) by using dispersed synchrotron radiation. The dissociation threshold near 6.4 eV corresponds to a barrier of ~1.3 eV due to repulsive H-Xe pair interactions and is attributed to a prompt cage exit of the H atoms. The dissociation efficiency for crystalline samples does not depend on temperature in the 5-40 K range. An increase of the dissociation efficiency with temperature for noncrystalline samples up to the value of crystalline ones is caused by partial annealing. The dependence of dissociation efficiency on excess kinetic energy is well rationalized in terms of a model based on the mass dependence of energy exchange between the H fragment and the cage atoms that had been derived for the case of Ar and Kr matrices (*J. Chem. Phys.* 1990, 93, 3245).

Introduction

The photodissociation of H_2O (D_2O) embedded in Ar and Kr crystals has been investigated in a series of recent papers.¹⁻³ These studies are part of current general efforts aiming at a microscopic description of the effect of the cage on a molecule dissociating in a dense medium and on the transport of its fragments from the original reaction site to a final stable site. In refs 1 and 2,

we determined threshold energies and the energy dependence of relative quantum efficiencies for the permanent dissociation of $H_2O(D_2O)$ in Ar and Kr matrices excited in its first continuum (\tilde{A}^1B_1) . In ref 3, we reported on the absolute photodissociation

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