Ion chemistry in trifluoromethane, CHF$_3$

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Abstract

Cross sections for dissociative ionization of trifluoromethane by electron impact have been measured using Fourier-transform mass spectrometry. Four fragment ions, CHF_2^+, CF_3^+, CF_2^+, and CF^+ are observed, with a total cross section of $3.4 \pm 0.4 \times 10^{-16}$ cm^2 at 60 eV. CF_x^+ ($x = 1 - 3$) ions react with neutral CHF$_3$ to yield CHF_2^+ with rate coefficients of 3.9 ± 0.5 and $2.1 \pm 0.4 \times 10^{-10}$ cm^{3}s^{-1} for $x = 2$ and 3, respectively. The rate of cationic polymerization is less than 7×10^{-13} cm^{3}s^{-1} and the anions F$^-$ and CF$_3^-$ have yields less than 3×10^{-20} cm^2 between 30 and 60 eV. © 1997 Published by Elsevier Science B.V.

1. Introduction

Trifluoromethane (CHF$_3$) has emerged as an ozone-friendly replacement for halocarbon etching gases that are used in semiconductor fabrication [1]. Its electron impact ionization [2-6], attachment [7-15], and ion–molecule reactions [16,17,19-23] have been reported. As part of our systematic study of ion plasma chemistry using Fourier-transform mass spectrometry [24-28] we report here the cross sections for electron impact ionization and attachment and rates for ion–molecule reactions of CHF$_3$. The present data support analysis of discharge chemistry in CHF$_3$ plasmas and, on a more fundamental level, bear directly on the partitioning between dissociation into neutral and charged fragments following electron impact with this simple molecule.
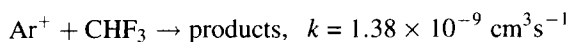
2. Experimental

Trifluoromethane (CHF$_3$, 98+%, Aldrich) was mixed with argon (99.999% Matheson Research Grade) with a ratio (CHF$_3$: Ar) in the range of 1 : 4 to 4 : 1, and admitted through a precision leak valve into a modified Fourier-transform mass spectrometry (FTMS) system that has been described in detail elsewhere [29]. Ions are formed by electron impact in a cubic ion cyclotron resonance (ICR) trap cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiates the trap with a few hundred picocoulombs of low-energy electrons. The motions of the ions are constrained radially by a superconducting solenoidal magnetic field (≈ 2 T) and axially by a nominal electrostatic potential (≈ 2 V) applied to the trap faces that are perpendicular to the magnetic field. Ions of all mass-to-charge ratios are simultaneously and coherently excited into cyclotron orbits using a stored waveform [30] applied to two opposing trap faces that are parallel to the magnetic field. Following cyclotron

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excitation, the image currents induced on the two re-maining faces of the trap are amplified, digitized, and Fourier analyzed to yield a mass spectrum.

Calculation of cross sections from the mass spectra requires knowledge of the gas pressure, the electron beam current, and the number of ions produced. These calibration issues have been described previously [29,31]. The ratios of $CH_xF_y^+$ to Ar^+ intensities give cross sections relative to those for argon ionization [32,33] since the CHF_3 : Ar pressure ratio is quantified by capacitance manometry of the gas mixture. The absolute CHF_3 pressure at the ICR trap that is needed for ion–molecule kinetic analysis is inferred from the decay of Ar^+ and the rate coefficient for the reaction

$$Ar^+ + CHF_3 \rightarrow products, \quad k = 1.38 \times 10^{-9} \ cm^3 s^{-1}$$

reported by Bowers et al. [22].

The distribution of electron energies in the trap, based on solution of Laplace's equation for the experimental geometry, is roughly Gaussian with a full width at half maximum of 0.5 eV due to the electrostatic trapping bias [29]. The mean energy of the irradiating electrons is accurate to ± 0.2 eV based on comparison of noble gas ionization thresholds with spectroscopic data. We fit the cross section data to a heuristic but parsimonious functional form:

$$\sigma(\epsilon - T) = A \tanh \frac{\pi(\epsilon - T)}{\alpha} e^{-k(\epsilon - T)},$$

where σ is the cross section, ϵ is the electron energy, T is the appearance potential, A scales the amplitude, k characterizes the higher energy behavior of σ, and α quantifies $d\sigma/d\epsilon$ near threshold.

Ion–molecule reactions are probed by introducing a delay between the formation of an ion ensemble and measurement of its mass spectrum. The product of reagent pressure and reactant time that we study is motivated by the product of ambipolar diffusion times and pressures typically encountered for plasma etching of semiconductors.

3. Results and discussion

Electron impact ionization of CHF_3 yields CHF_2^+, CF_3^+, CF_2^+, and CF^+ from threshold to 60 eV. There is no discernible peak for the parent ion, CHF_3^+. This
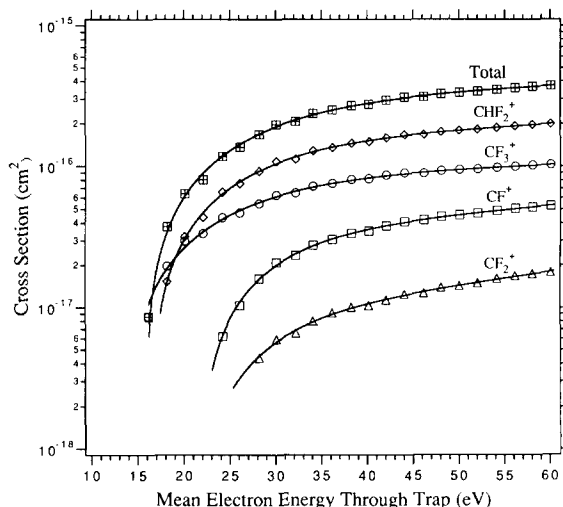

Fig. 1. Cross sections (cm^2) for ionization of CHF_3 by electron impact. Points represent experimental data, and solid lines are fits of the equation described in the text.

is consistent with recent calculations by Winstead and McKoy that show the molecular ion to be thermodynamically less stable than the dissociative ionization products [34]. The cross sections for each dissociative ionization process are shown in Fig. 1 and the coefficients for our functional fit are summarized in Table 1. The preeminent contribution of CHF_2^+ and CF_3^+ among the dissociative ionization products is consistent with most of the prior literature including studies by time-of-flight mass spectrometry [2] and a classical ICR instrument [19]. For example, we find excellent agreement with the 2 : 1 ratio of CHF_2^+ : CF_3^+ reported by time-of-flight experiments at 70 eV [2]. Two notable exceptions are the quadruopole mass spectrometry reports by Poll and Meischner [5] and Goto et al. [6]. In contrast to these quadrupole-based experiments, the FTMS sensitivity is demonstrably independent of ion mass and chemical composition. The ions are formed and detected by FTMS in the same spatial volume, obviating the ion optic and quadrupole transmission functions necessary for quadrupole cross section determination. Further, the image currents are determined by solution of Maxwell's equations in the trap; no ion current collection is required in FTMS. This avoids calibration factors associated with the collection efficiency and multiplier gain that contribute to the uncertainty of quadrupole experiments. Taken together with the results in Refs. [2,19] the present

Table 1
Fitting parameters for simple and dissociative ionization cross sections. Also shown are appearance potentials estimated from thermochemical data in the JANAF tables

Ion	A (cm^2)	k (eV^{-1})	α (eV)	T (eV)	JANAF T (eV)
CF$_3^+$	8.5×10^{-17}	-4.6×10^{-3}	63	13.7	13.8
CHF$_2^+$	1.4×10^{-16}	-8.0×10^{-3}	55	16.4	–
CF$_2^+$	8.0×10^{-18}	-2.1×10^{-2}	42	21.2	20.1 [a]
CF$^+$	3.2×10^{-17}	-1.3×10^{-2}	43	21.6	21.4 [b]

[a] Calculated for the reaction of: $CHF_3 + e^- \rightarrow CF_2^+ + H + F + 2e^-$.
[b] Calculated for the reaction of: $CHF_3 + e^- \rightarrow CF^+ + H + F_2 + 2e^-$.

data suggest that the basis for the CHF$_2^+$: CF$_3^+$ ratio of 3 : 5 presented in the EPA/NIH Mass Spectral Data Base ought to be revisited. [18].

The cross section for electron-impact dissociation of CHF$_3$ has been reported in classic experiments by Winters and Inokuti [4]. They found the total dissociation cross sections at 22 and 72 eV of 2.4 and 5.5×10^{-16} cm^2, respectively. Subtracting our dissociative ionization cross sections from these values gives an estimate of the balance between dissociation into charged radicals:

$$e + CHF_3 \rightarrow [CHF_3^*] + e \rightarrow C_xH_yF_z^+ + 2e$$
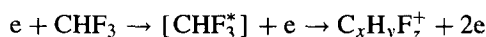
and dissociation into neutral radicals:

$$e + CHF_3 \rightarrow [CHF_3^*] + e \rightarrow C_xH_yF_z + e.$$
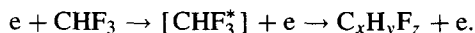
At 22 eV we find that neutral dissociation $\sigma \approx 1.6 \times 10^{-16}$ cm^2 is twice as probable as dissociative ionization, while at 72 eV the neutral channel, $\sigma \approx 2.1 \times 10^{-16}$ cm^2, is 60% as probable as the charged channel. These estimates of neutral dissociation cross sections are consistent with intuitive arguments advanced by Bethe and interpreted at low energies by Winters [4], as well as with quantum scattering calculations by Winstead and McKoy [34]. Our estimates of neutral dissociation are larger than values inferred from threshold ionization of radicals in the quadrupole experiments [6]; they are, in fact, over one hundred times larger at 22 eV and are sixteen times larger at 72 eV. We attribute these differences to nonlinearities in quadrupole mass spectrometric detection and the rapid change of the ionization cross sections of radicals with electron energy near threshold.

The negative ions F$^-$ and CF$_3^-$ are detected with cross sections less than 3×10^{-20} cm^2 in the elec-
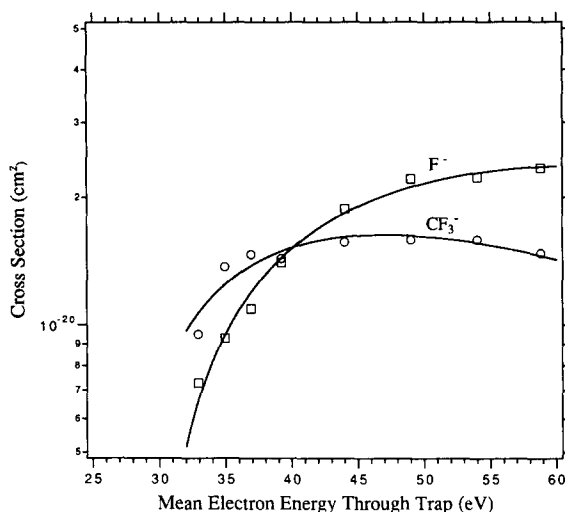

Fig. 2. Cross sections (cm^2) for negative ion formation by electron impact on CHF$_3$ from 30 to 60 eV.

tron energy range between 30 and 60 eV as shown in Fig. 2. The observed F$^-$ is due to ion pair formation, as first reported by Scheunemann et al. [14]. Our electron beam cannot probe energies below 10 eV, where Scheunemann and his coworkers observed feeble dissociative electron attachment resonances with peaks at 4.5, 10.1 and 12.3 eV [14]. The intensities of F$^-$ and CF$_3^-$ are unchanged by the introduction of a delay between negative ion formation and mass spectrum acquisition, indicating no reaction between these two ions and CHF$_3$. The formation of CF$_3^-$ above 25 eV is probably due, on energetic grounds, to polar dissociation as proposed by MacNeil and Thynne [9], $CHF_3 + e^- \rightarrow CF_3^- + H^+ + e^-$. Protons are not monitored directly in our positive ion experiments, but we titrate H$^+$ by ejecting all other ions and introducing a delay to probe for charge transfer products of the reactions:

$$H^+ + CHF_3 \rightarrow CH_aF_b^+ \quad (a = 0 - 2; b = 0 - 3).$$
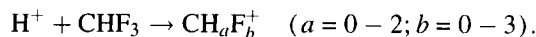
The failure to observe a positive product ion signal above our noise level is compatible with the very small cross section measured for the polar dissociation of CHF_3.

The ion-pair cross sections have high thresholds and feeble magnitudes, suggesting that the CHF_3 ought to be a poor attaching gas. However, the gas displays electronegative characteristics in plasma devices. For example, Haverlag et al. measure ratios of negative ion to electron densities in CHF_3 plasmas from 6 to 12 [15] and electron attachment in a pulsed afterglow has also been reported [12]. In these devices the gas residence times are long compared to the collisional time scales for electron impact dissociation, radical and ion chemistry, and surface reactions. Furthermore, negative ions are trapped by electrostatic sheaths in glow discharges, so the heterogeneous losses that constrain positive ion residence times are obviated. We propose, therefore, that negative ions reported in plasma devices using CHF_3 may arise primarily by attachment to radicals, excited species, and/or species at surfaces or from stable products of polymerization reactions.

We find that the principal product of dissociative ionization, CHF_2^+, is unreactive with the neutral parent gas while CF_x^+ ($x = 1 - 3$) react rapidly with CHF_3 to yield CHF_2^+. The reaction rate coefficients summarized in Table 2 are unchanged when the electron energy with which the reactant ions are formed is 20, 35, or 50 eV. The argon ion charge transfer reaction has two channels

$$Ar^+ + CHF_3 \rightarrow CF_3^+, \quad CHF_2^+$$
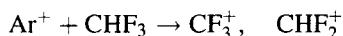
but favors the CHF_2^+ product by a factor of three.

The CF^+ reaction

$$CF^+ + CHF_3 \rightarrow CHF_2^+$$

occurs with a rate that increases with time as shown in Fig. 3. The mechanism of this reaction may involve electron transfer followed by dissociation yielding $CHF_2^+ + CF + F$, or it may involve transfer of F^- yielding $CF_2 + CHF_2^+$ as products. The time at which the rate increases is earlier when the Ar pressure is increased, indicating that the CF^+ formed by dissociative ionization is internally or translationally excited. The above accelerating reaction is identical whether
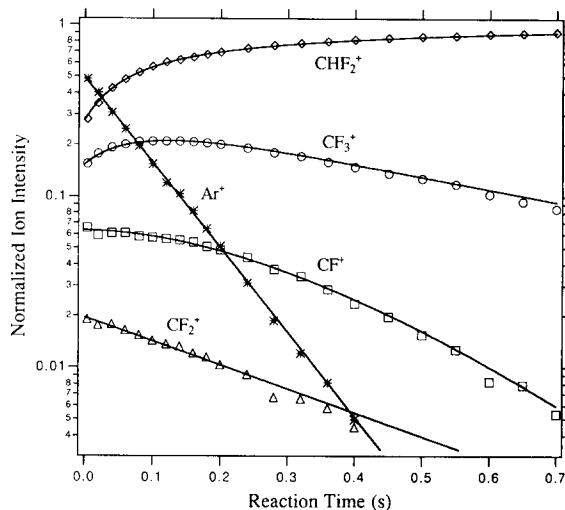

Fig. 3. Evolution of positive ion species produced by 35 eV electron impact at a mixture of CHF_3 and Ar (1 : 1) with a total pressure of 5.2×10^{-7} Torr. Points represent experimental data. Solid lines are fits of a kinetic model which gives the reaction rate coefficients presented in Table 2.

the reactant ion is formed by 35 or 50 eV electrons, with rapid conversion of CF^+ to CHF_2^+ occurring after a few tens of collisions with the argon buffer gas.

No higher molecular weight clusters are observed at CHF_3 pressures as high as 10^{-6} Torr and reaction times as long as 2 seconds, implying a rate coefficient for cationic polymerization that is less than 7×10^{-13} cm^{3}s^{-1}. Etching plasmas with pure CHF_3 or CHF_3 : Ar will have ion species distributions dominated by CHF_2^+ and CF_3^+, with precise ratios easily computed from the dissociative ionization cross-sections. These distributions will relax by reactions with CHF_3 to produce unreactive CHF_2^+ as the major ion species at modest partial pressures of trifluoromethane.

4. Conclusions

CHF_2^+, CF_3^+, CF_2^+, and CF^+ are formed by dissociative ionization of CHF_3 with a total cross section of $3.4 \pm 0.4 \times 10^{-16}$ cm^2 at 60 eV. No parent molecular ion is observed. The negative ions CF_3^- and F^- are observed with cross sections less than 3×10^{-20} cm^2 and nonresonant energy dependence between 30 and 60 eV. CF_x^+ ($x = 2, 3$) ions react with neutral CHF_3 to yield CHF_2^+ with rate coefficients of 3.9 ± 0.5 and

Table 2

Ion–molecule reaction rate coefficients in units of 10^{-10} cm^3s^{-1} for CHF_3. The first three columns of data are the present results with ions formed by dissociative ionization at different electron energies. Previously published rates are shown in the remaining columns

Reaction	20 eV	35 eV	50 eV	200 eV [a]	70 eV [b]	70 eV [c]
$CF_3^+ \rightarrow CHF_2^+$	1.9 ± 0.4	2.1 ± 0.4	2.1 ± 0.4	6.4	5.9	2.1
$CF_2^+ \rightarrow CHF_2^+$	...	3.9 ± 0.5	4.1 ± 0.5	9.3	9.2	...
$Ar^+ \rightarrow CHF_2^+$	10.3 ± 1.0	10.3 ± 1.0	10.3 ± 1.0			
$Ar^+ \rightarrow CF_3^+$	3.5 ± 0.4	3.7 ± 0.4	3.7 ± 0.4			

[a] Ref. [20].   [b] Ref. [16].   [c] Ref. [19].

$2.1 \pm 0.4 \times 10^{-10}$ cm^3s^{-1}, respectively. These rates are independent of the electron energy with which the reactant ions are formed. The reaction of CF^+ with CHF_3 also yields CHF_2^+, but the observation of an induction period suggests that the reactant is formed with excitation whose collisonal quenching facilitates the reaction. Ar^+ reacts with CHF_3 forming CHF_2^+ and CF_3^+, with rate coefficients of 10.3 ± 1.0 and $3.5 \pm 0.4 \times 10^{-10}$ cm^3s^{-1}, respectively.

Acknowledgements

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