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Comparisons of electron impact ionization and ion chemistries of CF_3Br and CF_3I

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Abstract

Comparisons of the electron impact ionization and of the ion–molecule reactions for CF_3Br and CF_3I are made from a study of the two compounds using Fourier-transform mass spectrometry. The ionization of the compounds over the energy range from threshold to 70 eV produces primarily the molecular ion and 6 fragment ions, with the dominant ion from CF_3Br being CF_3^+ and, from CF_3I, CF_3I^+. The total cross sections at 70 eV are 8.3 ± 0.8 and $9.0 \pm 0.9 \times 10^{-16}$ cm^2 for CF_3Br and CF_3I, respectively. These results appear to be the first for the molecules. The ion–molecule reactions in the two compounds are similar, with CF^+ and X^+ ($X = $ Br or I) being the most reactive ions ($k \sim (8–13) \times 10^{-10}$ cm^3 s^{-1}). Ar^+ reactions with the two compounds are also studied. Results of our study on the ion kinetics are compared with those from previous studies by other groups. (Int J Mass Spectrom 208 (2001) 127–133) © 2001 Elsevier Science B.V.

Keywords: Ionization; Dissociative; Ion chemistry

1. Introduction

CF_3Br had been widely used as a fire suppressant in the past 50 years and as an etching gas in many plasma applications. Now its uses are greatly restricted by law because of its significant contribution to stratospheric ozone depletion due to its long lifetime in the troposphere and its ready photodissociation by short wavelength ultraviolet light in the stratosphere. In the search for halon alternatives during the past years, CF_3I has become a leading replacement agent, in either the fire suppression or plasma assisted fabrication applications [1–6]. A comparison of the chemistries of these two compounds, in terms of ionic as well as neutral processes, and in terms of gas-phase collisions as well as surface interactions, is therefore of interest and importance. There is a limited amount of information about the basic physical/chemical mechanisms of the two compounds' applications. In the fire suppression by CF_3Br the chemical effectiveness is considered to be mainly due to Br radicals [7]. In the etching of SiO_2 using CF_3I, it is reported that whereas CF_2 radicals are the main gas precursors for deposition of the fluoropolymer that is useful to protect any adjacent Si, ions including CF_3^+ are important in the reactive ion etching of SiO_2 [5].

This article presents cross sections of the electron

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impact ionization of CF_3Br and CF_3I, and the kinetics of gas-phase reactions between the ions derived from the two compounds and the parent molecules. Although the ionization cross sections of the two compounds are reported for the first time, the gas-phase ion–molecule reactions, of CF_3I in particular, have been an object of several studies by different groups in the past decades [8–11]. However, there are numerous differences among the results reported from different groups. Some of these differences have been explained by the different experimental methods in which ions are formed and reacted under varied conditions resulting in various internal-state distributions of ions and reaction mechanisms [9,11]. In our study the experimental technique differs from the others in either (1) the gas pressure is low (10^{-7} Torr) so only bimolecular processes are important, or (2) the reactant ions to be studied are isolated from each other so the reactant–product relationship and the product branching ratios can be determined less ambiguously. On the other hand, our rates are for the ions as formed by electron impact or from charge transfer. The ions are nascent and have energy distributions that are relevant to plasma processing and ignition models.

2. Experimental

All experiments are performed on a modified Extrel Fourier-transform mass spectrometer (FTMS) which was equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and had a 2 tesla superconducting magnet [12]. The theory and methodology of FTMS have been well documented in the literature [13–15]. In this experiment CF_3Br (99%, GL Service) or CF_3I (99%, Aldrich) is mixed with argon (99.999%, Matheson Research Grade) with a ratio of about 1:1 to a total pressure of ~800 Torr, as determined by capacitance manometry. The mixture is admitted through a precision leak value into the FTMS system. Ions are formed by electron impact in the trapping cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiates the cell with a few hundred picocoulombs of low-energy electrons. The motion of the ions is constrained radially by the superconducting magnetic field and axially by an electrostatic potential (1 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 stored waveform inverse Fourier transform (SWIFT) [16–18] applied to two opposing trap faces which are parallel to the magnetic field. Following cyclotron excitation, the image currents induced on the two remaining faces of the trap are amplified, digitized and Fourier analyzed to yield a mass spectrum. In some experiments ions are selected using SWIFT [18] for further kinetic studies.

The integrated peak intensities, which are proportional to the number of ions in the trapping cell [15], are used to establish the cross sections, as described previously [12,19]. The intensity ratios of the ions from CF_3Br (or CF_3I) to Ar^+ give cross sections relative to those for argon ionization [20] since the pressure ratio of CF_3Br (or CF_3I) to Ar is known. As a cross check, and for ion–molecule kinetic analyses, the gas pressure is calibrated using accumulated gas pulses from a pulsed valve and a spinning rotor friction gauge (MKS Instruments model SRG2, Burlington, MA) with the vacuum chamber sealed off from the pumps. The electron current is collected on a Faraday cup and recorded with a digital oscilloscope after passage of the electron beam through the ion trap. The quantitative relationship between the image current and the number of ions is based on an analysis of the image currents induced on the detection plates of the cubic ion cyclotron resonance cell. This analysis, is similar to those described in the literature [15].

3. Results and discussion

3.1. Electron impact ionization

Electron impact ionization on CF_3Br at energies from threshold to 70 eV produces molecular ions and six fragment ions, with a total ionization cross section reaching $8.3 \pm 0.8 \times 10^{-16}$ cm^2 at 70 eV. Cross-sections for each partial ionization channel are shown in Fig. 1. Trace amounts of $CFBr^+$ and F^+ (not shown

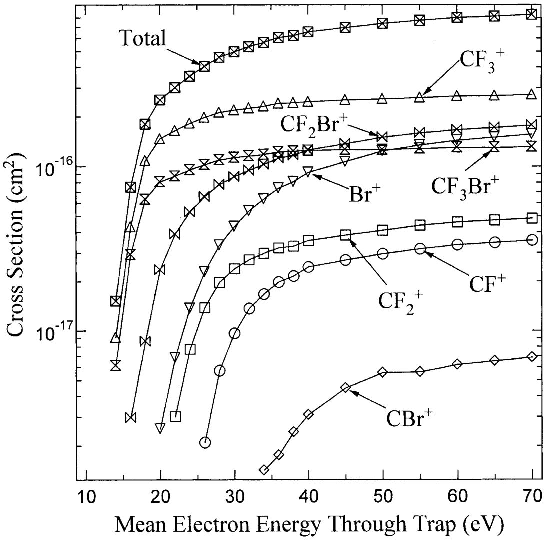

Fig. 1. Cross sections for electron impact ionization of CF_3Br.

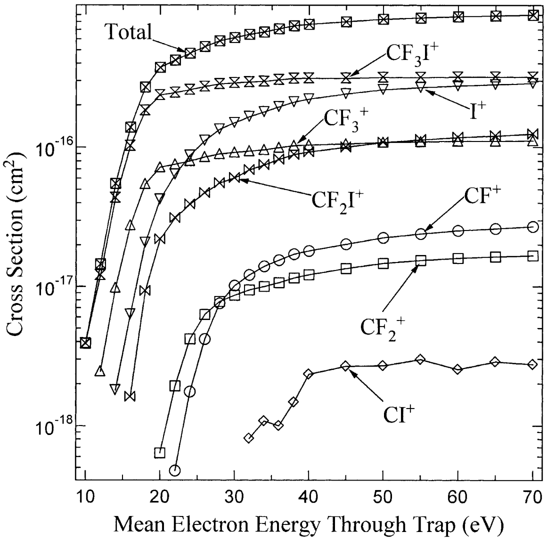

Fig. 2. Cross sections for electron impact ionization of CF_3I.

in Fig. 1) have been observed but the cross sections are less than 10^{-18} cm^2. CF_3^+ is the most abundant ion in the energy range studied. The appearance potentials of CF_3^+ (from CF_3Br) and CF_3Br^+ are rather close, being 12.2 and 12.3 eV [21], respectively, and the Jahn-Teller distortion effect results in an increased probability of the molecular ion dissociating to from CF_3^+, which makes CF_3Br^+ less abundant than CF_3^+ even at energies near threshold. At energies above 15 eV, a second dissociation channel forming CF_2Br^+ becomes available. In brief, the neutral radicals produced by the electron impact ionization at energies from the threshold to 20 eV are expected to be primarily Br and, second, F atoms, as they are the counter partners of the ionic products CF_3^+ and CF_2Br^+, respectively.

Electron impact ionization on CF_3I produces a similar set of ions corresponding to those from CF_3Br, but the relative order of the ion abundances is different. Fig. 2 presents the partial ionization cross sections of CF_3I, showing that the molecular ion CF_3I^+ dominates over the whole energy range. Compared to CF_3Br, the ionization threshold is lower and the total ionization cross section is slightly greater, reaching $9.0 \pm 0.9 \times 10^{-16}$ cm^2 at 70 eV. The most abundant fragment ion at energies below 20 eV is still CF_3^+, followed by I^+ and CF_2I^+, and therefore the corresponding neutral radical products are I, CF_3, and F, in the order of decreasing importance. CF_3^+ and I^+ appear to be the products of two competing dissociation channels via the cleavage of CF_3–I bond in the molecular ion. At energies near threshold, CF_3^+ prevails because it has a lower ionization potential than I^+ [22], complying with Stevenson's rule that states that the positive charge will remain on the fragment of lower ionization potential [23]. Data in Fig. 2 show that in the higher energy range, I^+ has greater intensities than CF_3^+, which may be due to the formation of I^+ by more extensive fragmentation of the molecular rather than a simple CF_3–I bond cleavage, and therefore it is simplified that as the collisional energy increases, the neutral partner of the I^+ product may not be simply CF_3.

3.2. Gas-phase ion–molecule reactions

Table 1 presents the kinetics of the reactions of ions derived from CF_3Br or CF_3I with their parent molecules (CBr^+ and CI^+ are not included because they have too small intensities to be studied), which are compared with the results from other studies. Also included in the table are Ar^+ reactions with the two

Table 1

Rate coefficients (k, in 10^{-10} cm^3/s) and ionic products (branching ratios shown in the parentheses) of the gas-phase reaction between the ions derived from CF_3Br and CF_3I with their parent molecules; the reactions of Ar^+ with these compounds are also included; in this work the reactant ions have not been thermalized prior to their reactions

Reactant ions	Hsieh et al. [8]	Berman and Beauchamp [9]	Morris et al. [10,11]	This work
With CF_3Br				
CF^+			$k = 12$ CF_2Br^+ (100)	$k = 3.2$ CF_3^+ (30) CF_2Br^+ (70)
CF_2^+			$k = 12$ CF_3^+ (22) CF_2Br^+ (78)	$k = 9.9$ CF_3^+ (35) CF_2Br^+ (20) CF_3Br^+ (45)
CF_3^+			$k = 4.3$ CF_2Br^+ (100)	$k = 0.81$ CF_2Br^+ (100)
Br^+				$k = 9.8$ CF_3^+ (50) CF_3Br^+ (50)
Ar^+			$k = 13$ CF_3^+ (25) CF_2Br^+ (75)	$k = 11$ CF_3^+ (20) CF_2Br^+ (80)
With CF_3I				
CF^+			$k = 16$ CF_2I^+ (100)	$k = 5.8$ CF_3^+ (35) CF_2I^+ (65)
CF_2^+			$k = 14$ CF_2I^+ (24) CF_3I^+ (76)	$k = 13$ CF_3^+ (30) CF_3I^+ (70)
CF_3^+	$k = 4.8$ CF_2I^+ (100)	$k = 2.5$ CF_2I^+ (68) CF_3I^+ (32)	$k = 8.7$ CF_2I^+ (100)	$k = 1.9$ CF_2I^+ (100)
I^+	$k = 7.4$ CF_3^+ (47) CF_3IT (53)	$k = 2.9$ CF_3I^+ (72) I_2^+ (28)	$k = 8.7$ CF_3^+ (63) CF_2I^+ (5) CF_3I^+ (26) I_2^+ (6)	$k = 8.2$ CF_3^+ (20) CF_2I^+ (5) CF_3I^+ (70) I_2^+ (5)
Ar^+			$k = 16$ CF_3^+ (11) CF_2I^+ (68) I^+ (20)	$k = 14$ CF_3^+ (7) CF_2I^+ (90) I^+ (3)

compounds. The reactant ions are generated by 50 eV electron impact ionization on a mixture of CF_3Br or CF_3I with Ar. Each of the reactant ions is separated from the others by rf excitation to eject all of the unwanted ions out of the trapping cell, followed by a varying reaction time to study the reaction kinetics of the selected ion. The rate coefficients listed in the table are accurate to within ±20%, based on the uncertainty in the pressure measurements. The relative rate coefficients are more accurate, however, with the uncertainties estimated to be ±10%. The ion chemistries in both of the compounds are similar: CF_2^+ and X^+ ($X =$ Br or I) are the most reactive ions, CF^+ and CF_3^+ are relatively less reactive, and CF_2X^+

and CF_3X^+ are basically unreactive. We noted that a small portion of CF_3Br^+ undergoes collision-induced dissociation yielding CF_3^+, due to the internally energetic ions that have sufficient energy to permit bond breaking. After CF_3Br^+ is trapped for 0.3 s under the gas pressure of $\sim 10^{-7}$ Torr, no more reaction producing CF_3^+ is observed, because the CF_3Br^{+*} excited ion population has been reduced to a negligible amount by a combination of reactive collisions and collisional/radiative quenching. In Table 1, the reactions of CF_3^+ have the lowest reaction rates. It was found that semilogarithmic plots of the CF_3^+ reactions show a linear CF_3^+ decay up to 0.5 s reaction time when about 30% of CF_3^+ has been consumed. At longer reaction time CF_3^+ is found to continue reacting but the data at that time were not used to define the reaction rate because, at these long times, the ion signal has been reduced to a value too small to be quantitatively meaningful. There is a slow loss of ions due to collisional diffusion across the magnetic field [19]. The CF_3^+ reactions, however, are believed to be caused by the excited state(s) of the ion, as suggested by the endothermicities of the following reaction equation that are calculated using the heats of formation of the ground state ions:

$$CF_3^+ + CF_3X \rightarrow CF_2X^+ + CF_4$$

The reaction heats are 26.2 and 16.1 kJ/mol for $X =$ Br and I, respectively, based on the thermochemical data from [24]. If the heat of formation for CF_3^+ is taken to be the recently published values, 360.8 [25] or 407.5 kJ/mol [26], the endothermicities are even greater. Other equations for the CF_3^+ reaction (i.e. in which different neutral products are formed) are possible but they are more endothermic than the previous equation. We have experimental evidence, as mentioned in the following suggesting that at least ground state CF_3^+ is unreactive. The CF_3^+ reactivities given above suggest that long-lived excited state(s) of CF_3^+ having a rather low collisional quenching rate are formed by the electron impact ionization of CF_3Br or CF_3I.

The difference among the results from different studies shown in Table 1, in terms of the reaction rates and product branching ratios, are believed to be mainly due to different experimental conditions that result in different ion internal energies and/or ion–molecule reaction mechanisms. At the pressure of $\sim 10^{-7}$ Torr the reactant ions generated from the electron impact ionization do not experience enough collisions to be thermalized before being reacted with their parent molecules. A comparison of our results with the [selected ion flow drift tube] (SIFDT) experiments of Morris et al. in Table 1 appears to demonstrate that the reactant ions in our experiments have some population of excited states. CF^+ and CF_3^+ are shown in the study by Morris et al. to have significant negative temperature dependences of reaction rates [10], which may be the explanation of lower reaction rates were observed because of the more energetic ions. In our experiments, we also observed that as a function of the reaction time the product percentage of CF_3^+ decreases and the percentage of CF_2X^+ increases. Although the changes of the percentages may be partly due to the secondary reaction of CF_3^+ as discussed later, it may be that the branching ratios of the reactions forming CF_3^+ and CF_2X^+ change as functions of the reaction time because of the reactant ions are being thermalized. The thermalized reactant ions may have the reaction branching ratios more or less in line with the data of Morris et al. Secondary reactions have been observed for some ions. For example, I^+ reacts with CF_3I to yield CF_3^+ among other products, which, when isolated from other ions and allowed to collide with CF_3I, is found to react producing CF_2I^+. However, CF_3^+ derived from the Ar^+ reactions with CF_3X is not found to undergo secondary reactions with CF_3X, which may be an indicator that at least ground state CF_3^+ is unreactive with CF_3X.

One of the most significant differences between the SIFDT results and our FTMS results are the reactions of CF_2^+ with CF_3Br. Although we observed a significant fraction of the molecular ion CF_3Br^+, none was reported in the study by Morris et al. The explanation may be that under their experimental conditions either this ion is not formed or the ion is very weakly bound and is thermally dissociated. The situations in the reaction of CF_2^+ with CF_3I appears similar but with the evidence that the molecular ion is formed and being detected in both experiments. The branching ratio of CF_3I^+ reported in the FTMS experiments equals to the sum of the branching ratios of CF_3I^+ and CF_3^+ reported in the SIFDT experiments, again raising the possibility of thermal dissociation of the molecular ion.

The behaviors of the unreactive ions CF_2X^+ and CF_3X^+ when they are kinetically excited have been studied. CF_2X^{+*} ions are still not very reactive at a kinetic excitation energy range of approximately 1–6 eV (center-of-mass), producing only an insignificant amount of CF_3^+. At ~10 eV kinetic excitation energy,

$$CF_2Br^{+*} + CF_3Br \rightarrow CF^+ (8\%), CF_3^+ (26\%),$$
$$CF_3^+ (44\%), Br^+ (5\%), CF_3Br^+ (17\%)$$

$$CF_2I^{+*} + CF_3I \rightarrow CF^+ (3\%), CF_3^+ (354\%),$$
$$I^+ (18\%), CF_3I^+ (44\%)$$

In the prior equations only the ionic products are listed, with the branching ratios shown in parentheses. In the reaction of CF_2Br^+, the channel of producing Br^+ is identified to be a collision-induced dissociation whereas the channel of producing CF_3Br^+ is a charge-transfer mechanism, as determined by the isotopic pattern of the product ions. Kinetically excited CF_3X^{+*} (made in our experiment by rf exciting the ion after its selection) undergoes reactions more readily, producing exclusively CF_3^+ in the energy range of 1–12 eV.

4. Summary

Absolute ionization cross sections have been measured for CF_3Br and CF_3I Electron impact ionization on CF_3Br or CF_3I produces primarily the molecular ion and 6 fragment ions with a total ionization cross section at 70 eV of 8.3 ± 0.8 or 9.0 ± 0.9 × 10^{-16} cm^2, respectively. In CF_3Br, CF_3^+ is the principal ion over the energy range from threshold to 70 eV, whereas in CF_3I, the molecular ion CF_3I^+ is the most abundant. At low electron energies (from threshold to 20 eV), which are most relevant to processing plasmas, the most important dissociative ionization channel is the production of CF_3^+ and X radical ($X = Br$ or I) for both compounds. Other less important dissociative ionization processes at these low energies include the formation of CF_2X^+ and F radical. Among the ions derived from the ionization of the two compounds, CF_2^+ and X^+ are found to be the most reactive ions, while CF^+ and CF_3^+ are relatively less reactive, and CF_3X^+ and CF_2X^+ are basically unreactive. We consider that the CF_3^+ reactions may be caused by hard-to-quench long-lived excited state(s) of CF_3^+. Some of the product ions from the primary ion–molecule reactions undergo further reactions with the neutral molecules, forming mainly CF_2X^+. In brief summary, the electron impact ionization on these two compounds produces similar sets of ions, with slightly lower threshold and higher cross section for the total ionization of CF_3I compared to CF_3Br. The ion–molecule reactions in these two compounds are similar, the differences including the additional minor products in CF_3I reactions.

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