Surface Chemistry and Radiation Chemistry of Trifluoroiodomethane (CF₃I) on Mo(110)

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The surface-induced and electron-induced chemistry of trifluoroiodomethane (CF₃I), a potential replacement for chlorofluorocarbons (CFCs) and chlorofluorobromocarbons (halons), were investigated under ultrahigh vacuum conditions ($p \sim 1 \times 10^{-10}$ Torr) on Mo(110). Results of temperature-programmed desorption (TPD) experiments indicate that dissociative adsorption of CF₃I leads only to nonselective decomposition on Mo-(110), in contrast to reactions of CF₃I on other metal surfaces. Desorption of CF₃ radicals and atomic iodine was detected mass spectrometrically during low-energy (10–100 eV) electron irradiation of four monolayer thick films of CF₃I condensed at 100 K. Results of postirradiation temperature-programmed desorption experiments were used to identify CF₂I₂, C₂F₅I, C₂F₆, C₂F₄I₂, and CFI₃ as electron-induced reaction products of CF₃I. Except for CFI₃, all of these electron-induced reaction products of CF₃I have been previously identified in γ -radiolysis studies, supporting our earlier claim that temperature-programmed desorption experiments conducted following *low-energy* radiation, including radical–radical reactions.

1. Introduction

The surface chemistry and radiation chemistry of trifluoroiodomethane (CF₃I) have recently come under increased scrutiny because CF₃I is being considered for many important industrial applications. The attractiveness of trifluoroiodomethane may be attributed to its excellent chemical and physical properties as evidenced by near-zero ozone-depletion potential (ODP), extremely low global warming potential (GWP),¹ good long-term stability at ambient conditions,² and relatively low toxicity.³ CF₃I may eventually replace CF₄, a gas with a high global warming potential, in semiconductor device fabrication because recent studies have demonstrated that CF3I can be used for plasma treatment of silicon dioxide,⁴ an important fabrication process which involves the etching of silicon surfaces with a mixture of energetic neutrals, ions, and electrons. Because CF₃I has been extensively promoted as an alternate fire suppression agent to Halon 1301 (CF₃Br), a potent ozone-depleting halon, the photon-induced degradation of CF₃I has become an important area of study.5 Radiation-induced dissociation of adsorbed CF₃I has recently been shown to be a facile method for the fluorination of diamond surfaces,⁶⁻⁸ a potentially important process in diamond thin film applications. Although CF₃I was recently rejected for use as a coolant for particle detectors in the large hadron collider (LHC) at CERN due to its chemical instability when exposed to ionizing radiation,9 CF₃I, especially as a component in mixtures, has been endorsed as a highperformance, environmentally sound refrigerant for other industrial uses.¹⁰ On the basis of the results of pulse radiolysis studies, it was concluded that CF₃I is the most promising candidate for an electron-beam initiated atomic iodine laser.¹¹

In contrast to the reactions on Mo(110) we will describe here, reactions of CF_3I on other metal surfaces yield gaseous reaction products containing at least one C-F bond, the strongest single bond that carbon forms. Desorption of CF₄ has been reported in the reactions of CF₃I on Ni(111)¹² and Ru(001).^{13,14} CF₃ radical desorption has been observed during the reaction of CF₃I on Ag(111),^{15–17} Ni(100),^{18,19} Ni(111),¹² Pt(111),²⁰ and Ru-(001).¹³ CF₂ fragments desorb during temperature-programmed desorption of CF₃I on Pt(111),²⁰ Ni(111),¹² and Ru(001).^{14,13} Following adsorption of CF₃I on Cu(111), cleavage of a single C-F bond in adsorbed CF₃ results in the selective formation of adsorbed CF₂ moieties whose subsequent coupling yields gaseous C₂F₄.²¹

Electron-induced reactions of CF₃I have been previously investigated. The role of dissociative electron attachment in the desorption of negative ions during the electron irradiation of condensed and gaseous CF₃I has been carefully delineated.^{22–24} Both CF₂I₂ and C₂F₃I have been identified in postirradiation (with 100 eV electrons) temperature-programmed desorption experiments of CF₃I multilayers on Ag(111).²⁵ The desorption of CF₃ and I[–] during photolysis of CF₃I on Ag(111) has been attributed to hot electrons produced at the Ag(111) surface by the incident photons.²⁶ Low energy electron diffraction (LEED) and electron-stimulated desorption ion angular distribution (ESDIAD) have been used to probe the electron-induced dissociation of CF₃I on Ru(001).²⁷ Results of postirradiation temperature-programmed desorption experiments demonstrate carbon–carbon coupling in CF₃I multilayer films on Ni(100).¹⁹

We report the use of temperature-programmed desorption experiments to investigate the surface chemistry of CF_3I on Mo-(110) under ultrahigh vacuum conditions. In addition, we report the use of isothermal electron-stimulated desorption experiments to study the *neutral* species desorbed during the interactions of low-energy (10–100 eV) electrons with multilayer adsorbed films of CF₃I on Mo(110). Such studies have previously been shown to provide detailed information regarding the dynamics of electron-induced condensed phase reactions relevant to radiation chemistry and physics.^{28–30} We also report on the results of postirradiation temperature-programmed desorption

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studies of multilayer films of CF₃I on Mo(110). We have previously demonstrated that temperature-programmed desorption experiments conducted following *low-energy* electron irradiation of multilayer thin films provide an effective method to investigate the effects of *high-energy* radiation, including ion–molecule and radical–radical reactions.³¹

2. Experimental Section

Experiments were performed in a custom-designed stainless steel ultrahigh vacuum chamber with a base pressure of 1×10^{-10} Torr described in detail previously.³¹ The Mo(110) single crystal can be cooled to 100 K with liquid nitrogen and heated to 800 K radiatively or to 2200 K by electron bombardment. The crystal temperature was measured by a tungsten—rhenium, W-5% Re vs W-26% Re, thermocouple spot-welded to the edge of the crystal. The Mo(110) crystal was cleaned in situ with oxygen followed by heating briefly to 2200 K, exceeding the desorption temperature of oxygen and sulfur. The carbon coverage after repeated oxygen cleaning cycles was determined to be less than the Auger detection limit. Low energy electron diffraction was used to verify the surface structure of the Mo(110) single crystal.

Trifluoroiodomethane (Synquest Labs; lot assay > 99% pure) was used without further purification. In situ mass spectrometry was used to verify the absence of potential contaminants such as hexafluoroethane. Direct dosers with precision leak valves allowed for controlled deposition at normal incidence of the CF₃I onto the Mo(110) crystal surface at 100 K to obtain multilayer coverages of approximately four layers prior to electron-stimulated desorption and postirradiation temperature-programmed desorption experiments. Film thickness was estimated based on temperature-programmed desorption experiments. One monolayer (1 ML) is defined as the maximum exposure of CF₃I that does not yield a multilayer peak.

The UTI model 100 C quadrupole mass spectrometer is enclosed by a shield with a 1/8 in. diameter aperture to optimize detection of the molecules desorbing directly from the center of the crystal during temperature-programmed desorption and isothermal electron-stimulated desorption experiments. Although up to 100 masses could be monitored under a multiplexing arrangement, typically only 10 masses were sampled during a single experiment.

The mass spectrometer filament or the LEED electron gun was used to irradiate the CF₃I thin films. All electron irradiation experiments were conducted with the crystal grounded. At an ionization energy setting of 70 eV, the mass spectrometer filament provides an electron flux of $\sim 2 \times 10^{13}$ cm⁻² s⁻¹ (lower limit because scattered electrons are not counted) with an energy of 55 eV at the grounded sample surface. Because the LEED electron gun, with an electron flux of $\sim 3 \times 10^{13}$ cm⁻² s⁻¹, provides a relatively monochromatic electron beam, the LEED electron gun was used to perform electron-stimulated desorption experiments as a function of electron energy. As described below, the LEED electron gun was also used to verify that the species desorbing during electron irradiation were neutral and not positively charged ions. During electron-stimulated desorption experiments carried out with the LEED electron gun, the shutter in front of the mass spectrometer ionizer was moved to allow the mass spectrometer to sample the entire UHV chamber. All electron-stimulated desorption experiments were conducted at a surface temperature of ~ 100 K.

Following electron irradiation (electron fluence of $\sim 2 \times 10^{15}$ cm⁻²), temperature-programmed desorption experiments were conducted to identify radiolysis products. Since the crystal is

TPD of CF₃I on Clean Mo(110)



Figure 1. Low temperature thermal desorption data of CF_3I on Mo-(110) in the absence of electron irradiation demonstrating the multilayer and monolayer desorption of CF_3I at ~130 and ~160 K, respectively.

close to the mass spectrometer filament during temperatureprogrammed desorption experiments, the crystal was negatively biased (-100 V) prior to each thermal desorption experiment to prevent further electron-induced reactions. As the surface was heated from 100 to 700 K via radiative heating at \sim 7 K/s, temperature-programmed desorption data were collected with the mass spectrometer and the thermocouple, both of which were interfaced to a computer.

Charging of the thin film during irradiation may change the incident electron energy. To reduce the effect of surface charging, film thickness was minimized to decrease the distance to the conducting metal surface. Surface charging may result in an uncertainty of a few electronvolts in our energy scale.

3. Results and Discussion

3.1. Surface Chemistry of CF₃I on Mo(110). Results of temperature-programmed desorption experiments demonstrate that multilayers of CF₃I desorb at \sim 130 K followed by the monolayer at ~ 160 K (Figure 1). The very small CF₃I desorption peak at \sim 145 K is very similar to a desorption peak attributed to the influence of atomic iodine on monolayer CF₃I desorption from Pt(111).²⁰ During a comprehensive search of fragments up to m/z = 300, no gaseous reaction products were detected in low temperature (up to 700 K) thermal desorption experiments. Results of subsequent high temperature (up to 1400 K) thermal desorption experiments (data not shown), demonstrate the desorption of atomic iodine (m/z = 127 but not m/z= 254) as a broad peak at ~1100 K and atomic fluorine (m/z= 19 but not m/z = 38) as two very broad overlapping peaks at \sim 900 K and \sim 1200 K. Oxygen titration experiments (data not shown), following low temperature thermal desorption experiments, demonstrate the presence of adsorbed atomic carbon, providing additional evidence for the nonselective decomposition of CF₃I into its atomic constituents. In contrast to reactions on other metal surfaces from which C-F-containing species desorb, as described previously, dissociative adsorption of CF_3I on Mo(110) results in the facile and total cleavage of the very strong C-F bond. However, nondissociative adsorption of CF₃I on Mo(110) is a significant competing process as evidenced by the monolayer peak at ~ 160 K (Figure 1).

3.2. Isothermal Electron Stimulated Desorption of CF₃I. Isothermal electron-stimulated desorption experiments were



Figure 2. Isothermal experiment depicting the desorption of CF₃I, CF₃ radicals, and atomic iodine during 55 eV electron irradiation of CF₃I (four layers) initiated at $t \sim 13$ s. The mass spectrometer filament was used as the irradiation source to produce an incident electron flux of 1.6×10^{13} cm⁻² s⁻¹. The unusual time dependence of the I⁺ signal is due to an upward sloping background signal.

conducted to investigate the desorption of radiolysis products *during* electron irradiation. These experiments were conducted as follows: while the surface temperature was kept constant at ~ 100 K, the mass spectrometer signal was monitored as a function of time as the CF₃I-covered crystal was rotated to face the mass spectrometer (or LEED gun). As described in detail below, desorption of trifluoroiodomethane (CF₃I), iodine (I), and trifluoromethyl radicals (CF₃) occurs when the crystal comes into alignment with the mass spectrometer filament (or LEED gun).

On the basis of the relative CF₃I mass spectral intensities found in temperature-programmed desorption data (Figure 1), CF₃I fragments account for only a fraction of the desorption intensities for m/z = 127, 69, 50, and 31 in the electronstimulated desorption experiments (Figure 2). Hence we conclude that one or more species, in addition to CF₃I, must desorb during electron irradiation of CF₃I thin films.

A. Identification of Atomic Iodine. The presence of a desorption feature for m/z = 127 (and not for m/z = 254) that cannot be attributed to CF₃I alone indicates that atomic iodine (and not molecular iodine) desorbs during electron irradiation of CF₃I thin films (Figure 2).

B. Identification of CF₃ Radicals. To verify that desorption of positive ions such as CF₃⁺ did not contribute to the observed desorption features for m/z = 69, 50, and 31, isothermal electronstimulated desorption experiments were conducted with the LEED electron gun as the irradiation source. The desorption features disappeared in these experiments when the mass spectrometer ionization energy was reduced to ~15 eV, demonstrating that the observed ion signal is due to uncharged species. Because 15 eV is sufficient to ionize most radicals and neutral species, the inability to see a signal at 15 eV must be due to the poor ionization efficiency at this low energy rather than the ionization energy being below the ionization potential of the desorbed species. These results demonstrate that the electron-stimulated desorption signals at m/z = 69, 50, and 31 are solely due to neutral species.

Additional experiments were conducted to verify the identity of the desorbing neutral species. Because tetrafluoromethane (CF₄) does not have a parent peak at m/z = 88 in its mass spectrum, temperature-programmed desorption experiments were

Dependence of Yield on Electron Energy



Figure 3. Isothermal electron-stimulated desorption yield of CF_3 radicals, corrected for small variations in incident electron flux, plotted as a function of incident electron energy.

conducted with CF_4 to ascertain the CF_4 fragment intensities in our mass spectrometer. The relative $CF_3^+:CF_2^+:CF^+$ intensity ratios for CF_4 and electron-stimulated desorption experiments of CF_3I (after subtracting the CF_3I contribution) were found to be 100:12:6 and 43:100:87, respectively. Since these two ratios differ significantly, CF_4 alone cannot account for the desorption features observed during electron irradiation of CF_3I thin films. Our results are suggestive of CF_3 radical desorption, although we cannot rule out the concomitant desorption of CF, CF_2 , or CF_4 .

Additional evidence for the desorption of CF₃ radicals during electron irradiation of CF₃I is provided by a previously published mass spectrum of CF₃ radicals. The CF₃⁺:CF₂⁺:CF⁺ intensity ratio of CF₃ radicals produced in thermal desorption experiments was found to be 42:100:42,¹⁹ in good agreement with the ratio determined in the experiments described herein. This comparison is reasonable given the work of White and co-workers who have demonstrated that the fragmentation pattern of excited-state CF₃ radicals desorbed during photon irradiation of CF₃I is the same as that of ground-state CF₃ radicals produced in thermal desorption experiments.²⁶

The desorption of CF₃ radicals during electron irradiation of CF₃I thin films is also consistent with previous studies of radiation-induced decomposition of CF₃I. Excited-state CF₃ radicals have been previously postulated to account for the radiolysis products of CF₃I.³² CF₃ radicals are also produced during the infrared-multiphoton decomposition of CF₃I.^{33,34}

C. Dependence of Desorption Yield on Electron Energy. The electron energy dependence of the desorption yield (Figure 3) suggests electron impact excitation or ionization as the mechanism for the formation of the CF3 radicals. As the incident electron energy is increased from 10 to 100 eV, the electronstimulated desorption yield of CF3 radicals increases monotonically with electron energy. Because of the limitations of the electron gun, isothermal electron-stimulated desorption experiments were not conducted at incident electron energies below 10 eV, an energy regime where dissociative electron attachment is strongest. Moreover, the signal at higher energies may be due to dissociative electron attachment induced by very low energy (<10 eV) electrons resulting from ionization in the CF₃I film. However, the use of a four-monolayer thick film minimizes the possibility of energy loss due to multiple scattering followed by dissociative electron attachment at lower electron energy. On the basis of the results displayed in Figure 3, we suggest that dissociative electron attachment is not dominating in the observed production of CF_3 radicals and that the mechanism involves electronic excitation or ionization of the condensed CF_3I .

Hence we propose three possible routes to the formation of CF_3 radicals.

1. Electron impact excitation (not followed by dipolar dissociation):

$$CF_3I \rightarrow CF_3I^* \rightarrow {}^{\bullet}CF_3 + I^{\bullet}$$
 (1)

2. Electron impact ionization followed by fragmentation:

$$CF_3I \rightarrow CF_3I^+ + e^- \rightarrow I^+ + {}^{\bullet}CF_3 + e^-$$
 (2)

3. Electron impact ionization followed by ion-molecule reaction

$$CF_3I^+ + CF_3I \rightarrow CF_3I_2^+ + {}^{\bullet}CF_3$$
(4)

D. Cross Section Measurement. The total effective degradation cross section (σ_{eff}) of condensed phase CF₃I for electroninduced processes including electron-induced desorption was calculated from results of isothermal electron-stimulated desorption experiments. The cross section analysis assumes that CF₃ derives exclusively from CF₃I and not from any of the products. The mass spectrometer signal as a function of time for m/z = 69 (CF₃⁺) was fitted to the following equation to obtain the total effective degradation cross-section:

$$Y = Y_0 \mathrm{e}^{-\sigma_{\mathrm{eff}}Ft} \tag{5}$$

where *Y* and *Y*₀ are the mass spectrometer signal at time *t* and t = 0 respectively, and *F* is the electron flux. The electron flux is given by F = I/Ae where *I* is the incident electron current, *A* is the area of the electron beam incident on the crystal, and *e* is the charge of an electron. The measured electron flux is a lower limit because scattered electrons are not counted. The effective total degradation cross section for condensed phase CF₃I at incident electron energy of 70 eV was calculated to be $\sigma_{\text{eff}} = 3 \times 10^{-16} \text{ cm}^2$. This value is of the same order of magnitude as the gas-phase CF₃I electron impact ionization cross section of $9.0 \pm 0.9 \times 10^{-16} \text{ cm}^2$ at an electron energy of 70 eV.³⁵

3.3. Postirradiation Temperature-Programmed Desorption Experiments. Results of postirradiation temperature-programmed desorption experiments were used to identify CF_2I_2 , CFI_3 , C_2F_5I , $C_2F_4I_2$, and C_2F_6 as radiolysis products of CF_3I as described in detail below.

A. Identification of Radiolysis Products. The electroninduced reaction products were identified by comparing fragments found at a given temperature in the thermal desorption data to those found in known mass spectra.^{36,37} When monitoring mass fragments such as CF⁺, CI⁺, CFI⁺, and CF₂I⁺ that were also fragments of CF₃I, the crystal was heated to \sim 160 K, above the desorption temperature of CF₃I, following irradiation, to remove the multilayers and monolayer of CF₃I before conducting temperature-programmed desorption experiments. This procedure allowed for the detection of radiolysis product desorption peaks at temperatures above 160 K that would have been too small to detect in the presence of the large CF₃I multilayer and monolayer peaks. In identifying the radiolysis products, the results of the postirradiation temperatureprogrammed desorption experiments were also compared to previously identified γ -radiolysis products³⁸⁻⁴⁴ of CF₃I: I₂, CF₄, C₂F₆, CF₂I₂, C₂F₅I, and C₂F₄I₂. To further verify the identifica-

Post-Irradiation TPD of CF₃I



Figure 4. Postirradiation (40 eV electrons at a fluence of 2×10^{15} cm⁻²) temperature-programmed desorption data of CF₃I multilayers (four layers) showing the desorption of C₂F₆, C₂F₅I, CF₂I₂, C₂F₄I₂, I₂, and CFI₃.

tion of radiolysis products, the desorption temperature and boiling point trends of the radiolysis products were also compared.

Results of postirradiation temperature-programmed desorption experiments of CF₃I are shown in Figure 4. Desorption peaks for $m/z = 100 (C_2F_4^+)$ and 119 $(C_2F_5^+)$ at ~129 K were assigned to C₂F₆. The absence of the parent peak m/z = 138 $(C_2F_6^+)$ at ~129 K is consistent with a previously published mass spectrum of C₂F₆.³⁷ Desorption peaks for mass fragments $m/z = 246 (C_2F_5I^+), 227 (C_2F_4I^+), 119 (C_2F_5^+), and 100 (C_2F_4^+)$ observed at ~ 165 K were assigned to C₂F₅I. Desorption peaks for mass fragments m/z = 285 (CFI₂⁺), 266 (CI₂⁺), 254 (I₂⁺), 177 (CF₂I⁺), 158 (CFI⁺), 139 (CI⁺), 31 (CF⁺) detected at \sim 193 K were assigned to CF_2I_2 . The presence of the fragment m/z =254 (I_2^+) is consistent with published³⁶ and unpublished,⁴⁵ mass spectra of CF₂I₂. Although the mass fragments m/z = 285 and 266 are absent in published mass spectra,^{37,36} these fragments are present in an unpublished mass spectrum⁴⁵ of CF₂I₂. Desorption peaks for mass fragments m/z = 254 (I₂⁺), 227 (C₂F₄I⁺), 100 (C₂F₄⁺), and 81 (C₂F₃⁺) at \sim 213 K were assigned to C₂F₄I₂. Desorption features for mass fragments m/z = 285(CFI₂⁺), 158 (CFI⁺), and 139 (CI⁺) at \sim 233 K were identified as CFI₃ and not CF₂I₂ because a peak was absent for the mass fragment m/z = 177 (CF₂I⁺) at ~233 K. A mass spectrum of CFI3 was not available for direct comparison. The parent peaks of CFI₃ (m/z = 412), CF₂I₂ (m/z = 304), and C₂F₄I₂ (m/z =354) could not be monitored because the UTI model 100C mass spectrometer is only capable of monitoring mass fragments up to 300. Previous γ -radiolysis studies of CF₃I have identified CF₂I₂, C₂F₅I, C₂F₄I₂, and C₂F₆ as radiolysis products of CF₃I.³⁸⁻⁴⁴ Our identification of CFI₃, however, represents a new finding.

The results of postirradiation temperature-programmed desorption experiments discussed above do not provide evidence for CF₄, a previously known γ -radiolysis product of CF₃I.^{38-40,43} The failure to identify CF₄ as a radiolysis product of CF₃I may be attributed to a combination of three factors: (1) CF₄ does not have a parent peak (m/z = 88) in its mass spectrum, (2) the other mass spectral fragments (CF₃⁺, CF₂⁺, CF⁺, and F⁺) of CF₄ are also fragments of CF₃I.³⁷ and (3) CF₄ has a lower desorption temperature than CF₃I.

The boiling point trend parallels the desorption temperature trend for the radiolysis products, providing additional evidence for the identification of CF₂I₂, C₂F₅I, C₂F₄I₂, CFI₃, and C₂F₆. The boiling points of CF₃I and its radiolysis products are as follows: C₂F₆ (195 K)³⁷ < CF₃I (250.6 K)³⁷ < C₂F₅I (286 K)³⁷ < CF₂I₂ (374 K)⁴⁵ < C₂F₄I₂ (386 K)³⁷ < CFI₃ (477.5 K).⁴⁶ The increase in boiling points is consistent with the increase in desorption temperatures: C₂F₆ (~129 K) < CF₃I (~132 K) < C₂F₅I (~165 K) < CF₂I₂ (~193 K) < C₂F₄I₂ (~215 K) < CFI₃ (~233 K).

Additional postirradiation temperature-programmed desorption experiments to probe the dependence of product yield on electron energy and electron fluence are currently underway.

B. Postulated Mechanisms for CF₃I Radiolysis. Radical– radical reactions play a central role in the radiation chemistry of CF₃I. As described previously, we have identified both CF₃ and I radicals in electron-stimulated desorption experiments. Formation of •CF₂I radicals has been hypothesized previously in γ -radiolysis studies of liquid and gas-phase CF₃I^{39,40} and electron-induced chemistry of adsorbed CF₃I.^{19,25} Formation of difluorocarbene (:CF₂) has been previously postulated in the radiolysis of CF₃I.³⁸ Below we postulate several reaction mechanisms, involving the aforementioned intermediates, to explain the radiolysis of CF₃I.

Three different reaction channels can be proposed for the formation of CF_2I_2 . The ${}^{\bullet}CF_2I$ radicals could abstract an iodine atom from molecular iodine (eq 6)⁴⁷ or CF_3I (eq 7),³⁹ or react with atomic iodine (eq 8).³⁹

$$^{\bullet}\mathrm{CF}_{2}\mathrm{I} + \mathrm{I}_{2} \rightarrow \mathrm{CF}_{2}\mathrm{I}_{2} + ^{\bullet}\mathrm{I}$$
(6)

$${}^{\bullet}\mathrm{CF}_{2}\mathrm{I} + \mathrm{CF}_{3}\mathrm{I} \to \mathrm{CF}_{2}\mathrm{I}_{2} + {}^{\bullet}\mathrm{CF}_{3}$$
(7)

$${}^{\bullet}\mathrm{CF}_{2}\mathrm{I} + {}^{\bullet}\mathrm{I} \to \mathrm{CF}_{2}\mathrm{I}_{2} \tag{8}$$

 C_2F_5I could be formed by a carbene insertion reaction (eq 9) or a radical-radical reaction (eq 10):

$$:CF_2 + CF_3I \to C_2F_5I \tag{9}$$

$$^{\bullet}\mathrm{CF}_{2}\mathrm{I} + ^{\bullet}\mathrm{CF}_{3} \rightarrow \mathrm{C}_{2}\mathrm{F}_{5}\mathrm{I}$$
(10)

 $C_2F_4I_2$ may be formed by the dimerization of two •CF₂I radicals (eq 11) or by a carbene insertion reaction (eq 12).

$$^{\bullet}CF_{2}I + ^{\bullet}CF_{2}I \rightarrow C_{2}F_{4}I_{2}$$
(11)

$$:CFI + CF_3I \rightarrow C_2F_4I_2 \tag{12}$$

 CFI_3 may be formed from :CFI reacting with CF_3I (or I_2) in two steps abstracting an iodine atom in each step.

$$:CFI + CF_3I \rightarrow {}^{\bullet}CFI_2 + {}^{\bullet}CF_3$$
(13)

$$^{\bullet}CFI_2 + CF_3I \rightarrow CFI_3 + ^{\bullet}CF_3$$
(14)

 CF_3 radicals may dimerize (eq 15)^{39} or react with CF_3I (eq 16)^{47} to form $C_2F_6.$

$$^{\bullet}\mathrm{CF}_{3} + ^{\bullet}\mathrm{CF}_{3} \rightarrow \mathrm{C}_{2}\mathrm{F}_{6} \tag{15}$$

$${}^{\bullet}\mathrm{CF}_{3} + \mathrm{CF}_{3}\mathrm{I} \rightarrow \mathrm{C}_{2}\mathrm{F}_{6} + {}^{\bullet}\mathrm{I}$$
(16)

Additional experiments probing the dependence of radiolysis product yield on electron energy and electron fluence are necessary to obtain a better understanding of the electroninduced reaction mechanisms of CF_3I .

4. Conclusion

The surface chemistry and radiation chemistry of trifluoroiodomethane (CF₃I), a potential replacement for chlorofluorocarbons (CFCs) and chlorofluorobromocarbons (halons), were investigated under ultrahigh vacuum conditions. In contrast to reactions on other metal surfaces, dissociative adsorption of CF₃I leads only to nonselective decomposition on Mo(110). Lowenergy electron-induced reactions of CF₃I produce gas-phase CF₃ radicals during electron-stimulated desorption experiments. Postirradiation thermal desorption studies demonstrate that CFI₃, CF₂I₂, C₂F₆, C₂F₅I, and C₂F₄I₂ are electron-induced radiolysis products of CF₃I. Our results demonstrate that temperatureprogrammed desorption experiments conducted following *lowenergy* electron irradiation of multilayer thin films provide an effective method to investigate the effects of *high-energy* radiation, including radical–radical reactions.

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