Reactions of Halomethanes with γ-Alumina Surfaces. 2. X-ray Photoelectron and Temperature-Programmed Reaction Spectroscopic Studies

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The reactions of CF_3Cl, CF_2Cl_2, $CFCl_3$, and CCl_4 with γ-alumina powders have been studied using temperature-programmed reaction (TPR) and X-ray photoelectron (XPS) spectroscopies. In the TPR experiments, powder samples that had been dehydroxylated by heating to 1000 K in vacuum were dosed at 100 K with halomethanes and then gradually heated. Desorbing species were monitored as a function of substrate temperature using a line-of-sight quadrupole mass spectrometer. Hydrogen chloride and halomethyl fragments, which are indicative of halomethane dissociative chemisorption, were observed to desorb at temperatures below 150 K. Carbon dioxide began to desorb between 240 and 320 K; the onset temperature of CO_2 desorption correlated inversely with the degree of chlorination of the compound. The CO_2 most likely arises from CO_n (carbonate and/or formate) species which are formed via the low-temperature dissociative chemisorption of the halomethanes. Repeated heating and dosing of the alumina sample resulted in a drop in CO_2 production, implying that surface active sites become depleted. *In situ* XPS analysis of heat-treated powders that had been dosed at 150 K with chlorofluoromethanes revealed the presence of both organic and inorganic forms of fluorine. Powders dosed at 200 K had much lower organic halogen coverages. Halogen uptake probabilities, which are estimated to be ∼10^{-5} from the data, increased as the degree of chlorination of the halomethane increased. These results indicate that chlorofluoromethane compounds will probably decompose on alumina solid-propellant rocket motor exhaust particles in the stratosphere, forming adsorbed Al−X (X = F, Cl) and CO_n species and releasing gas phase HCl and CF_xCl_y fragments. However, the impact of these processes on global stratospheric halomethane and ozone concentrations is likely to be minimal.

I. Introduction

The studies reported in this and the preceding paper[1] were motivated by a concern about the potential impact of alumina solid-propellant rocket motor (SRM) exhaust particles on stratospheric chemistry. The infrared absorption spectroscopy experiments described in the preceding paper focused on elucidating the mechanism of dissociative chemisorption of halomethanes on heat-treated γ-alumina surfaces at temperatures characteristic of the lower stratosphere (∼200 K). The very high surface area of the alumina powder and its transparency throughout much of the mid-infrared greatly facilitated the task of detecting adsorbates using FTIR spectroscopy. However, as a result of the absorption of bulk aluminum oxide in the 800−1000 cm⁻¹ region and the lack of detector sensitivity below 800 cm⁻¹, it was not possible for us to observe absorption features associated with Al−X or O−X (X = F, Cl) bonds. More significantly, because of the broadness of the adsorbate infrared absorption features and the lack of absorption coefficients for adsorbate vibrational modes, it was not possible to determine relative or absolute reaction probabilities for the halomethane compounds studied.

In addition, the IR absorption experiments provided no information about reaction products that are released into the gas phase. Such information is crucial, however, to assessing the impact of surface-mediated decomposition of halomethanes on SRM−alumina particles on the stratospheric ozone cycle. In fact, previous X-ray photoelectron spectroscopy (XPS) studies

conducted in our laboratory[2] suggested that, under certain conditions, halogen-containing species are evolved from γ-alumina surfaces exposed to halomethane compounds at stratospheric temperatures. The identities of these desorbing species could not be ascertained from these experiments.

Two sets of experiments were conducted in order to expand upon our IR absorption spectroscopic results. In one, *in situ* X-ray photoelectron spectroscopy was used to detect halogen atoms bonded to the γ-alumina surface after dosing alumina powders with halomethanes at fixed temperatures. XPS allows one to determine the elemental composition of a surface at coverages as low as a fraction of a monolayer. In addition, since the photoelectron emission cross sections of the different elements are known, XPS possesses an intrinsic calibration standard, allowing one to determine absolute coverages of atoms on a surface. Thus, it was possible to determine approximate halomethane−alumina reaction probabilities at temperatures relevant to the stratosphere.

In the other set of experiments, the gas phase products of halomethane reactions with γ-alumina were identified using temperature-programmed reaction spectroscopy (TPRS). In these studies, the surface was first dosed with halomethane molecules at a temperature that was sufficiently low that most, if not all, of the molecules physisorbed but did not react. The sample was then slowly heated at a constant rate to promote diffusion of the adsorbed molecules and reaction with the surface. As the sample was heated, the desorbing species were monitored using a quadrupole mass spectrometer. The mass-to-charge ratios (*m/e*) and gas phase concentrations of the desorbing species were then measured as a function of sample heating time and thus temperature.

The results of these experiments confirm the conclusions of our IR studies[1] that chlorofluoromethane compounds and CCl_4

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dissociatively chemisorb on dehydroxylated γ-alumina powders at temperatures below 150 K. The likely surface reaction intermediates are CO_n ($n = 2, 3$) species. The results of our IR studies, together with the present results, are used to present a more complete picture of the halomethane−alumina reaction mechanism and to evaluate the potential impact of SRM particle reactions on stratospheric chemistry.

II. Experimental Section

The temperature-programmed reaction spectroscopic (TPRS) experiments were carried out in an ultrahigh-vacuum chamber equipped with an *in situ* line-of-sight quadrupole mass spectrometer. The base pressure in the chamber after bakeout, maintained by a cryopump, was $\sim 1 \times 10^{-10}$ Torr. During halomethane exposure and thermal desorption, the pressure in the chamber rose to $\sim 10^{-7}$−10^{-8} Torr, depending on the vapor pressure of the compound studied.

The γ-Al_2O_3 powder (Johnson Matthey) had a nominal purity of 99.97%, a particle size of 3 μm, and a nominal surface area of 100 m^2 g^{-1}. Powder samples were prepared according to the method of Yates and co-workers.[3] Alumina powder (3−10 mg) was pressed into a 1 cm^2 piece of molybdenum mesh (Buckbee-Mears) with a hydraulic press (12 000 psi). The mesh has an open area of $\sim 64\%$. The pressed powder samples were clamped onto a molybdenum platen screwed into the base of a double-walled, vacuum-insulated liquid nitrogen-cooled cryostat. The sample temperature could be regulated from 100 to 1000 K by means of a pyrolytic boron nitride radiative heater mounted behind the Mo platen. Temperatures were measured with two pairs of chromel/alumel thermocouples spot-welded or clamped to the Mo mesh. The heating rate of the sample in these experiments was approximately 5 K s^{-1}. The uncertainty in the temperature of the sample, which is due uncertainty in the thermocouple voltage-to-temperature conversion as well as to temperature gradients across the mesh, is estimated to be $\sim \pm 5$ K.

The samples were heat-treated in vacuum according to the procedure described in the preceding paper[1] to remove impurities and to dehydroxylate the surface. The preceding paper also describes the preparation of the halomethane compounds and the dosing procedure. The gas doses used in these experiments were the same for all four compounds. The doses ($\sim 1.2 \times 10^{17}$ cm^{-2}) were ~ 50 times lower than those used in the IR absorption experiments; the lower exposure lessened the likelihood of adsorbing multilayers. Since the sticking probabilities of the different compounds are not known, it was not possible to adjust the doses for the four different compounds so that the resulting coverages were identical.

An Extrel quadrupole mass spectrometer was used to monitor the mass-to-charge ratios (m/e) of the desorbing halomethane molecules and reaction products as a function of sample temperature. The mass-dependent signal from the Channeltron particle multiplier (Galileo) was recorded in a pulse counting mode. Individual pulses were amplified and converted to TTL pulses by a discriminator (MIT) and routed to 4 MHz counters on a LabMaster data acquisition board (Scientific Solutions) interfaced to a personal computer. The LabMaster board was also used to control the setting of the mass filter and monitor the temperature of the powder samples.

Great care was taken to minimize background signal from halomethane molecules adsorbed on surfaces other than the powder sample. In particular, using a double-walled, vacuum-insulated cryostat minimized the surface area from which halomethane molecules could desorb during heating. Furthermore, the electron bombardment ionizer was surrounded by a

stainless steel shroud with a collimating aperture smaller than that of the powder sample. When the sample was heated, the distance between the sample and the collimating aperture was kept at less than 1 cm in order to maximize signal collection. In addition, control experiments were performed on bare Mo mesh without any alumina powder. None of the reactions observed with the alumina powder were seen with the bare mesh alone.

The XPS experiments were performed in a separate ultrahigh-vacuum apparatus (base pressure $\approx 10^{-9}$ Torr). The apparatus consists of two contiguous chambers: one is used to dose the powders with gases, and the other is used for surface analysis. The dosing chamber is pumped by a turbomolecular pump and a liquid nitrogen cold trap. A gold-plated copper shield is attached to the liquid nitrogen reservoir and surrounds the pressed powder sample during heating and dosing. The samples are clamped onto a molybdenum platen with heating and cooling capabilities (150−1100 K); the platen is attached to a linear motion feedthrough manipulator. The surface analysis chamber, which is separated from the dosing chamber by a gate valve and is pumped by an ion pump, contains the X-ray photoelectron spectrometer.

The XPS analyses were performed using a PHI 15 keV, Mg Kα X-ray source and a PHI 15-255 GAR double pass cylindrical mirror electron energy analyzer operated at a band-pass energy of 50 eV. Depending on the experiment being performed, fluorine (1s), chlorine (2p), aluminum (2p), oxygen (1s), and carbon (1s) spectra were measured. The spectra were fit using a combination of Gaussian and Lorentzian functions. The halogen uptake data reported are integrated F(1s) and Cl(2p) peak intensities normalized to the integrated Al(2p) peak intensity. All reported electron binding energies are referenced to the O(1s) peak at 531.0 eV.

Heat-treated γ-alumina powder samples were prepared as described in ref 1, except that a pressure of 2800 psi was used to press the powders into the molybdenum mesh and the preheating protocol was modified slightly to 770 K for 2 h, 920 K for 30 min, and 1000 K for 30 min. Sufficient powder was used to cover the metal mesh completely so that the mesh itself was not exposed to gases or to X-rays. Our XPS results indicated that the heat treatment produced powders that were free of adsorbed carbon and halogen. Dosing was carried out using a multichannel capillary array source as described in the preceding paper. The halomethane gas dose used in the XPS studies was $\sim 7 \times 10^{18}$ molecules cm^{-2}, slightly lower than those used in the infrared absorption studies.[1] No XPS experiments were performed using CCl_4 because of the likelihood of X-ray-induced damage of the samples (see below).

III. Results and Discussion

A. TPRS Experiments. Heat-treated γ-alumina samples were cooled to 100 K and then dosed with CF_3Cl, CF_2Cl_2, $CFCl_3$, and CCl_4. Our IR measurements[1] indicate that at this temperature these compounds physisorb on the powder surface. The dosed γ-alumina samples were then heated at ~ 5 K s^{-1}, and desorbing species were monitored in real time. Typical TPRS spectra for CF_2Cl_2 on γ-alumina are shown in Figure 1.

Desorption features corresponding to fragments of CF_2Cl_2 were observed to peak at ~ 125 K: CF ($m/e = 31$), Cl ($m/e = 35$), CCl ($m/e = 47$), CF_2 ($m/e = 50$), CFCl ($m/e = 66$) and CF_2Cl ($m/e = 85$). No CF_2Cl_2 ($m/e = 120$) was observed. These desorption features are due either to electron bombardment-induced dissociation of the parent molecule in the ionizer of the mass spectrometer or to CF_xCl_y fragments formed as a result of surface-mediated decomposition of CF_2Cl_2. Since the ratio of CF_2Cl to CF was about 10 times lower than that observed as

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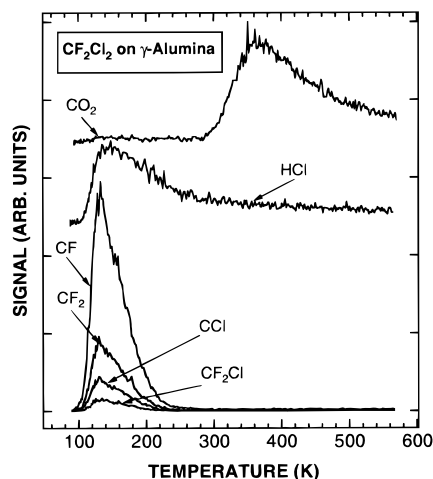
Figure 1. Temperature-programmed reaction (TPR) spectra for γ-alumina powder that has been dosed with CF_2Cl_2 at 100 K. Recorded spectra of some desorbing species are not shown for clarity. (The spectra are offset arbitrarily from one another.)
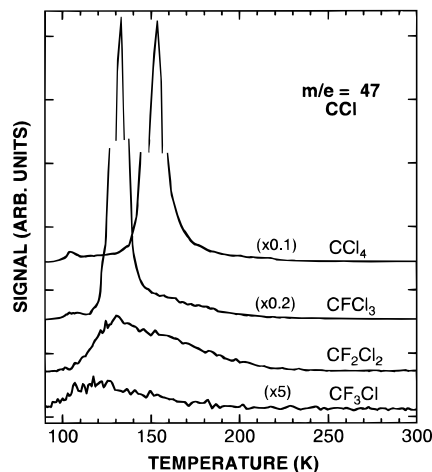

Figure 2. TPR spectra of $m/e = 47$ (CCl) for all four compounds studied. Spectra for $CFCl_3$ and CCl_4 are truncated; the peaks of these spectra, scaled as noted, are appended.

Figure 3. TPR spectra of $m/e = 44$ (CO_2) for all four compounds studied.

a result of cracking of gas phase CF_2Cl_2, it is likely that a large fraction of the desorbing species are indeed halomethyl fragments that are formed via the dissociative chemisorption of CF_2Cl_2 on γ-alumina.

A feature corresponding to $m/e = 36$ was also observed to peak at ~125 K; however, its temperature profile differed distinctly from those of the CF_xCl_y fragments (Figure 1). We attribute this feature to HCl. This is a significant observation since it indicates that C–Cl bonds are broken during the adsorption of CF_2Cl_2. The formation of HCl presumably involves reaction with residual OH groups on the heat-treated alumina surface.

In addition to the desorption features at 125 K, a broad feature was observed at ~350 K from CO_2 ($m/e = 44$). The CO_2 most likely arises from the desorption of CO_n ($n = 2, 3$; formate and/or carbonate) species which are formed via the low-temperature dissociative chemisorption of CF_2Cl_2 (and other halomethanes) on γ-alumina, as described in the preceding paper.[1] Control experiments ruled out the possibility of simple background contamination as the source of CO_2, since no CO_2 desorption was observed from clean γ-alumina held at low temperatures in the chamber in the absence of CF_2Cl_2 exposure. The broadness of the temperature profile of the $m/e = 44$ peak ($\Delta T \approx 150$ K) presumably reflects the heterogeneity of the powder surface and the consequent variability in the binding energy of the adsorbates.

Overall, the TPRS results for CF_3Cl, $CFCl_3$ and CCl_4 on γ-alumina surfaces are similar to those for CF_2Cl_2. Spectra of CCl ($m/e = 47$) are plotted for all four compounds in Figure 2. Given the heterogeneity of the powder surface and the uncertainty in the adsorbate coverages, it is difficult to assign features of the TPR spectra to specific adsorbate phases (i.e., physisorbed or chemisorbed monolayer). However, the presence of small desorption peaks between ~105 and 112 K for the two most condensable compounds, $CFCl_3$ and CCl_4, suggests that physisorbed multilayers are formed under the dosing conditions of these experiments.

As in the case of CF_2Cl_2, HCl desorption accompanied CF_xCl_y desorption for $CFCl_3$ and CCl_4. In the case of CF_3Cl, the signal-to-noise for $m/e = 36$ was too low to discern a peak. The HCl desorption profiles are always broader than the corresponding CF_xCl_y desorption profiles. CO_2 desorption was also observed for these three compounds. The CO_2 desorption temperatures decrease with increasing chlorination of the halomethane
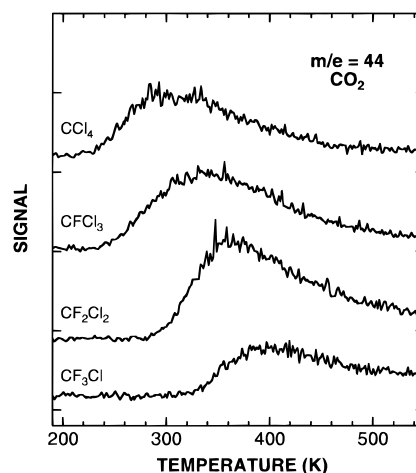
compound (Figure 3) with the onset of desorption decreasing from 370 K for CF_3Cl to 240 K for CCl_4. No desorption peaks were observed for any aluminum halide or oxyhalide species from any of the compounds studied.

The observed trend in CO_2 desorption temperatures correlates well with our IR absorption studies,[1] which indicate that the temperatures at which surface CO_n species appear and disappear decrease with increasing chlorination. A possible explanation for the trend in CO_n appearance temperatures which was discussed in the preceding paper[1] relates to systematic changes in the energetics of C–X bond dissociation (X = Cl, F) with degree of chlorination; namely, C–X (X = Cl, F) bond dissociation energies decrease with increasing chlorination. We would therefore expect C–X dissociation, and hence CO_n formation, to occur at lower temperatures for CCl_4 than for CF_3Cl.

However, the IR results indicate that adsorbed CO_n species are always formed below 170 K, well below the temperatures at which CO_2 begins to desorb. In addition, desorption of HCl and halomethyl fragments is complete before the onset of CO_2 desorption. These results suggest that the rate of CO_2 desorption is not limited by the rate of halomethane dissociative chemisorption and that the observed differences in CO_2 desorption temperatures are therefore not due to differences in the energetics of C–X bond breakage.

We therefore propose two possible explanations for the trend in CO_2 desorption temperature with degree of halomethane

chlorination. First, it is unlikely that all of the C−X bonds dissociate at low temperature. In particular, the stronger C−F bonds may remain fully or partially intact until the onset of CO_2 desorption. As we will show below, our XPS results indicate that at 200 K some C−F bonds remain intact. Therefore, the increase in C−F bond dissociation energy with decreasing chlorination could account for the trend in CO_2 desorption temperatures. Second, the energy of interaction of the adsorbed CO_n with the halogenated surface may vary with the degree of fluorination of the surface. Since the Lewis acidity of fluorinated alumina is greater than that of chlorinated alumina,[4,5] CO_n intermediates may interact more strongly with a fluorinated surface than with a chlorinated surface. Assuming that some of the surface sites neighboring the CO_n intermediate are halogenated, CO_2 would desorb at a higher temperature from a CF_3Cl-dosed surface than from a CCl_4-dosed surface.

As noted above, the TPRS results for the two most condensable compounds, $CFCl_3$ and CCl_4, indicate the presence of physisorbed multilayers. It is possible that the presence of multilayers may affect the observed results. In particular, at multilayer coverages bimolecular reactions become more likely. However, the IR[1] and TPRS results indicate no significant differences among the reactive products of the four different compounds studied. Clearly, there are competing processes occurring as the temperature of the sample is raised. Physisorbed multilayers desorb and molecules also diffuse into the pores of the sample and react. Note, however, that the most condensable compound, CCl_4, shows evidence of reaction below 150 K[1] so the presence of physisorbed molecules does not impede the adsorbate−surface reaction and does not seem to change the resulting adsorbed or desorbed products. Regarding the shape of the desorption peaks associated with $CFCl_3$ and CCl_4, although the narrow components probably reflect the desorption of physisorbed molecules, there are also broad bases to the peaks that are similar in shape to the peaks seen for CF_2Cl_2 and CF_3Cl. Again, we believe that desorption of physisorbed molecules competes with diffusion and reaction with the surface.

Depletion of Surface Sites on γ-Alumina. To obtain further insight into the mechanism of halomethane dissociative chemisorption and to assess the potential for catalytic decomposition of halomethanes on γ-alumina, we performed experiments in which γ-alumina was repetitively dosed at 100 K with CF_2Cl_2 and then heated to 573 K while monitoring the desorption products. Product yields were determined by integrating the desorption peak areas. Since all of the CF_2Cl_2 doses were of the same magnitude, and the experiments were carried out consecutively under exactly the same conditions, a plot of the CO_2 yield against the number of CF_2Cl_2 dose cycles is a measure of the surface reactivity.

As shown in Figure 4, the yield of CO_2 decreased sharply after the first CF_2Cl_2 exposure. After three doses, the amount of desorbed CO_2 reached a minimum and leveled off. At the same time, the $m/e = 85$ signal (CF_2Cl, a mass fragment that we associate with desorption of the undissociated parent molecule) increased. This result indicates that the surface reactive sites that are responsible for CO_2 production become depleted as a result of CF_2Cl_2 dissociative chemisorption. We speculate that the coordinatively unsaturated (cus) Al^{3+} sites that are formed during the initial heat treatment are deactivated due to the formation of Al−X bonds. Without these cus-Al^{3+} sites, CF_2Cl_2 adsorbs nondissociatively. In addition, oxygen cluster sites, formed during heat treatment and implicated in the halomethane reactions, also become depleted. (This is consistent with the IR results reported in the preceding paper.[1]) As a consequence, the CO_2 yield decreases.
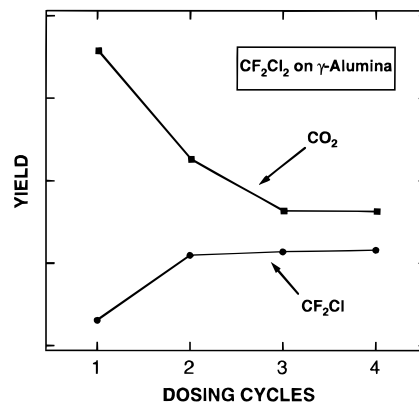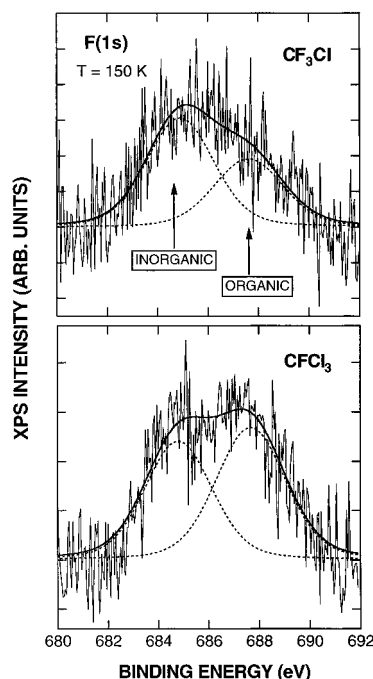

Figure 4. Yields of CO_2 ($m/e = 44$) and unreacted CF_2Cl_2 (as represented by CF_2Cl, $m/e = 85$) as a function of repetitive dosing and heating of γ-alumina powder. During each cycle, the sample was sequentially cooled to 100 K, dosed with CF_2Cl_2, and heated to 573 K while monitoring the desorbing species as a function of temperature.
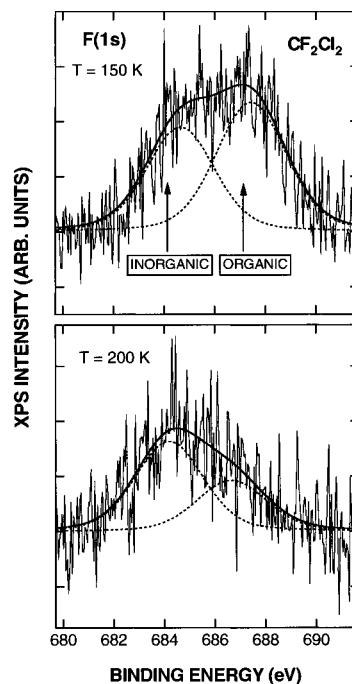
Figure 5. Fluorine(1s) X-ray photoelectron spectra of γ-alumina powder dosed with 7×10^{18} cm^{-2} CF_2Cl_2 at 150 K (top) and 200 K (bottom).

B. XPS Experiments. In order to determine the elemental composition of the γ-alumina surface after exposure to chlorofluoromethanes (CFMs) and to quantify the molecular adsorption probability, heat-treated γ-alumina powders were dosed with CFMs at fixed temperatures and subsequently probed with XPS. Figure 5 presents the fluorine (1s) spectra of γ-alumina dosed with CF_2Cl_2 at 150 and 200 K, respectively. Two resonances can be discerned in the F(1s) spectrum at 150 K (Figure 5a) peaking at binding energies of ∼685 and ∼688 eV; these correspond to the binding energies of F(1s) electrons in inorganic fluorides and in fluorinated hydrocarbons, respectively.[6] (The observation of two different fluorine-containing species was also noted in our studies of CF_2Cl_2 adsorption on single crystal α-aluminum oxide.[2]) Two F(1s) peaks are also observed for CF_3Cl and $CFCl_3$ at 150 K (Figure 6). At 200 K (a temperature typical of the lower stratosphere), a broad F(1s) peak is observed for all of the compounds which presumably comprises organic and inorganic components. The signal-to-noise is relatively low for these spectra for several reasons: the gas dose used was kept roughly equal to that used in the IR

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Figure 6. F(1s) spectra of γ-alumina at 150 K dosed with CF_3Cl (top) and $CFCl_3$ (bottom).

Figure 7. (a) Total uptake of fluorine on γ-alumina for the three compounds studied as measured by the integrated F(1s) intensity at 150 and 200 K. (b) Uptake of fluorine normalized to the number of F atoms per incident molecule.

experiments, the halomethane chemisorption probability is low (see below), and the data collection times were kept short to minimize X-ray-induced damage to the halomethane adsorbates (see below).

Most of the Cl(2p) spectra at both temperatures exhibit one broad peak with a maximum at $\sim$199 eV. Although assigning Cl(2p) features to inorganic or organic species is difficult because the signal-to-noise ratio is low and spin$-$orbit splitting of the Cl(2p) level broadens the observed XPS peak, we believe that this feature is due predominantly to an inorganic chloride species. According to Wagner et al.,[6] the Cl(2p) binding energies in inorganic chlorides and chlorinated organic compounds are $\sim$198 and 200$-$201 eV, respectively. Cl(2p) spectra for $CFCl_3$ at 150 K show a strong photoelectron peak at 200 eV, which is undoubtedly due to organic chlorine. Thus, we conclude that the resonances peaking at $\sim$199 eV can be attributed primarily to inorganic Cl species. However, the broadness of these Cl(2p) peaks suggests that organic Cl species are also present and are contributing to the XPS signal.

Our observation of inorganic halides in the present experiments confirms our earlier conclusion that chlorofluoromethane compounds dissociatively chemisorb on γ-alumina at temperatures below 150 K. In particular, these results demonstrate that halogen atoms bond directly to surface sites. We believe that the organic halogen species that we observe are adsorbed intact molecules and/or intermediates in the dissociative chemisorption process that convert to CO_n (carbonate and/or formate) ions as the temperature is raised. The TPRS results presented above support this conclusion. In particular, the drop in the organic halogen coverage between 150 and 200 K correlates with the halomethyl desorption seen in the TPRS experiments. The XPS results indicate, however, that some C$-$F bonds remain intact at 200 K. Note that the approximate halogen uptake probabilities that we calculate (see below) indicate that the halogen coverages are submonolayer at 150 K for all three compounds. Therefore, it is unlikely that there are physisorbed molecules on the surface at this temperature.

X-ray-generated photoelectrons can lead to C$-$X (X = halogen) bond cleavage in adsorbed haloalkanes.[7] In the present
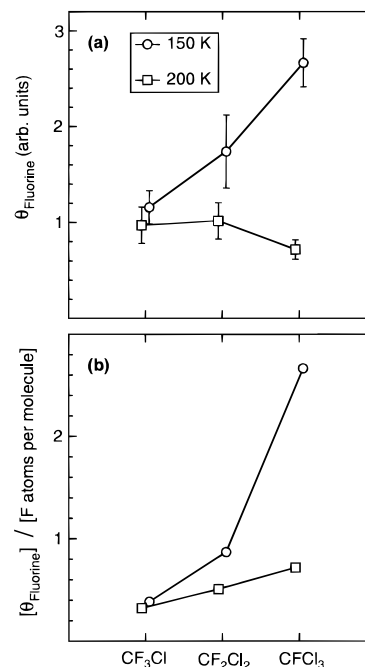
experiments, every effort was made, within signal-to-noise constraints, to minimize exposure of the dosed samples to X-rays. For CF_2Cl_2 and CF_3Cl, little if any (0$-$10%) loss of halogen atoms occurred during the course of an XPS analysis run ($\sim$8$-$12 min). For $CFCl_3$, X-ray exposure was limited to $\sim$7 min; the errors in the measured halogen coverages introduced as a result of X-ray exposure are estimated to be on the order of 10%. No experiments were conducted with CCl_4 because of the likelihood of severe X-ray-induced artifacts.

Carbon(1s) spectra were recorded, but the features were quite broad and the signal-to-noise ratios were low (as a result of the low photoemission cross section of carbon). Peaks could sometimes be observed in the C(1s) spectra at $\sim$285 and $\sim$290 eV that probably were due to unsubstituted organic carbon and halogenated/oxygenated organic carbon, respectively.[6] However, it is difficult to draw definitive conclusions regarding the carbon uptake from these spectra.

Halogen Uptake. The uptake of fluorine and chlorine by γ-alumina can be determined by integrating the F(1s) and Cl(2p) XPS spectra. In order to account for small variations in the position of the sample manipulator with respect to the X-ray gun and detector from run to run, the integrated halogen intensity is normalized to the Al(2p) intensity, which is not expected to change as a result of gas exposure. Uptake results for fluorine and chlorine at 150 and 200 K are plotted in Figures 7, 8, and 9. The points represent averages of data from at least three experimental runs.

At 200 K, the total fluorine uptake is relatively constant for CF_3Cl and CF_2Cl_2 and drops for $CFCl_3$ (Figure 7a). However, the fluorine uptake normalized to the number of F atoms per molecule increases moderately with decreasing F atom content (Figure 7b). At 150 K, total fluorine uptake and uptake per impinging F atom are inversely proportional to the degree of fluorination of the CFM. Chlorine uptake also increases with increasing chlorination of the CFM (Figure 8). At 200 K, however, the chlorine uptake normalized to the number of Cl atoms per molecule is independent of degree of chlorination.
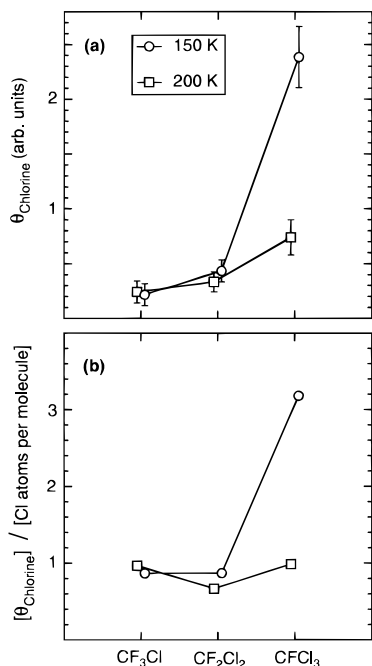
Figure 8. (a) Total uptake of chlorine on γ-alumina for the three compounds studied as measured by the integrated Cl(2p) intensity at 150 and 200 K. (b) Uptake of chlorine normalized to the number of Cl atoms per incident molecule.

Figure 9. Total fluorine uptake and uptake of organic and inorganic fluorine species for the three compounds at 150 K.

For all of the compounds, lowering the surface temperature enhances the halogen uptake.

The inverse correlation between halogen uptake and both surface temperature and the degree of fluorination is consistent with halogen uptake being limited by the initial sticking (i.e., molecular adsorption) probability of the compound. Sticking is enhanced at lower temperatures, and the more chlorinated compounds have lower vapor pressures and, consequently, higher sticking probabilities.

Chemisorption of halogen would also be enhanced for the more chlorinated compounds, owing to the change in the C−F and C−Cl bond dissociation energies (BDEs) with degree of chlorination. Both the C−F and C−Cl bonds weaken as the CFM becomes more chlorinated. Thus, the C−Cl BDE in $CFCl_3$ is lower than that in CF_3Cl by 13 kcal/mol (73 kcal/mol in $CFCl_3$ and 86 kcal/mol in CF_3Cl).[8] Likewise, the C−F BDE in $CFCl_3$ is lower than that in CF_3Cl by 21 kcal/mol (102 kcal/mol in $CFCl_3$ and 123 kcal/mol in CF_3Cl).[8] Thus, we expect more facile halogen uptake for $CFCl_3$ than for CF_3Cl.

Both the organic and inorganic components of the F(1s) spectra increase with increasing chlorination of the CFM (Figure 9). As noted above, the organic fluorine component may be due to adsorbed intact molecules and to fluorinated methyl radicals; the inorganic component is likely due to F atoms bonded directly to the surface. Both enhanced sticking of CFM molecules and more facile C−X bond breakage can work in concert to increase the organic and inorganic fluorine uptake with increasing degree of chlorination.

Since the number of CFM molecules per unit area impinging on the surface is known, we can obtain estimates of the halogen uptake probability, γ, by determining the absolute coverage of halogen atoms on the surface. Thus,

$$\gamma = \frac{\text{adsorbed halogen atoms cm}^{-2}}{4(\text{impinging molecules cm}^{-2})}$$

where the factor of 4 corresponds to the number of halogen atoms per molecule. The absolute coverage of fluorine atoms
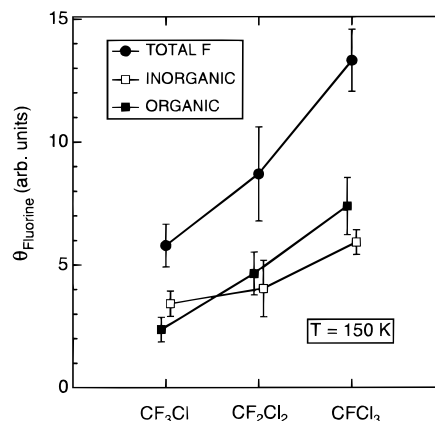
is estimated using a calibration factor obtained from previous XPS experiments conducted in this laboratory on the fluorination of self-assembled monolayers of *n*-alkanethiolates adsorbed on gold.[7] In those studies, absolute F atom coverages could be determined from the C(1s) spectra combined with the known absolute coverage of carbon atoms. Since the C(1s) binding energy in hydrocarbons shifts markedly with extent of fluorination, the fraction of carbon atoms that were fluorinated could be calculated. Knowing the number of carbon atoms per cm^2 from the number of carbon atoms per chain and the packing density of the chains, it was then possible to calculate the absolute coverage of F atoms. Thus, a calibration factor relating the F(1s) photoelectron count rate to the F atom coverage could be calculated.[9] This calibration factor was applied to the present data to obtain absolute F atom coverages on γ-alumina. Since the photoelectron emission cross sections of F(1s) and Cl(2p) differ from one another, Cl uptake values were calibrated using relative detection efficiencies for F and Cl derived from Wagner et al.[6]

A major source of uncertainty in γ, however, is the surface area of the powders viewed by the CMA detector of the X-ray photoelectron spectrometer. Since the escape depth of the photoelectrons is ~3 nm, only halogen atoms at the surface of the powder sample contribute to the XPS signal. However, there are pores both within and between the alumina particles into which CFM molecules can diffuse and react. We do not know how much of the pore surface area is visible to the detector. However, we assume that only the pore surface area that is within the line of sight of the detector is visible. Thus, the effective surface area of the powder is assumed to be essentially the geometrical area of the pressed powder sample.

With this assumption, the halogen uptake probability at 200 K is calculated to be in the range $(0.4-1.0) \times 10^{-5}$ for the CFMs, depending on the degree of chlorination. Note, however, that the actual CFM−surface reaction probability is higher since halogen-containing species desorb from the surface below 200 K as fragments of CFM molecules and as HCl.

IV. Conclusions

Together with the infrared absorption results reported in the preceding paper,[1] the TPRS and XPS results reported here indicate that chlorofluoromethanes and CCl_4 dissociatively chemisorb on heat-treated γ-alumina surface at temperatures as low as ~120 K. Halomethyl fragments, which result from surface-mediated C−X (X = F, Cl) bond dissociation, desorb in the 120−200 K temperature range. HCl desorption is observed to accompany the halomethyl fragments, indicating

that CFMs react with residual OH groups on the surface and that C–Cl bonds are broken.

C–X bond rupture is accompanied by formation of surface Al–X and C–O bonds. CO_n ($n = 1,2$) (e.g., formate and carbonate) species are formed on the surface during this process. At temperatures between ~230 and ~300 K, CO_2 begins to desorb indicating that all of the C–X bonds have been broken. The temperatures at which CO_n appears and CO_2 begins to desorb decrease with increasing degree of chlorination of the compound. For CCl_4, CO_n species are observed below 150 K, and CO_2 begins to desorb at ~230 K.

Al_xO_y clusters and cus-Al^{3+} sites that are created as a result of heat-treating the surface are likely the active surface sites for CFM chemisorption. Repeated dosing and heating of the surface leads to depletion of these active sites, as manifested by decreased yield of CO_2, increased desorption of the parent compound, and loss of IR features associated with Al_xO_y clusters.

Halogen uptake by γ-alumina surfaces increases with increasing degree of chlorination of the halomethane and decreasing temperature, suggesting that uptake is governed by the initial sticking probability of the compound. The halogen uptake probability is estimated to be in the range $(0.4–1.0) \times 10^{-5}$ at 200 K. However, the uptake probabilities are only lower bounds to the actual overall molecular reaction probabilities since they do not account for products that desorb from the surface.

V. Implications for Stratospheric Chemistry

Our results clearly demonstrate that chlorofluoromethane compounds decompose on heat-treated γ-alumina surfaces at stratospheric temperatures. As we noted in an earlier paper,[2] dissociative chemisorption of halomethanes on SRM-exhaust particles in the stratosphere will shorten the lifetimes of these compounds relative to what they would be if photolysis were the only operative decomposition process. Any process that breaks C–Cl bonds can potentially increase the gas phase concentration of reactive chlorine, which can then promote the destruction of stratospheric ozone. Our temperature-programmed reaction experiments indicate that HCl and chlorofluoromethyl radicals are liberated from the alumina surface at very low temperatures after exposure to halomethanes. Such species can readily convert to Cl-containing radicals in the stratosphere which are capable of reacting with ozone. Thus, the release of chlorine-containing species from surface-mediated processes on SRM particles may indeed be a concern.

However, in order to assess the impact of SRM alumina particles on stratospheric chemistry, one must consider the surface reaction efficiency and the nature of the halomethane–alumina reaction. The halogen uptake probability on pressed γ-alumina powders has been found to be on the order of 10^{-5} at 200 K. The overall reaction probability is somewhat higher, but is probably less than 10^{-4}. Given the current estimate of the total surface area of SRM–alumina particles in the lower stratosphere (10^{-11} cm^2 cm^{-3}),[10] these reaction probabilities are sufficiently small that alumina surface-mediated decomposition is unlikely to affect the global lifetimes of chlorofluoromethanes in the stratosphere. However, localized depletion of CFMs may occur in the vicinity of the exhaust plume of a booster rocket where particle loading is much larger.[11]

In addition, our results indicate that the alumina surface must be activated through preheating in order that dissociative chemisorption can occur at stratospheric temperatures. SRM particles would be expected to be dehydroxylated when they are created in the rocket engine nozzle and reheated in the afterburning exhaust. Preliminary results from our laboratory and results from other groups[12–15] suggest that rehydroxylation at stratospheric temperatures and water vapor pressures is not a facile process. However, in order for CFM–alumina reactions to have a significant impact on stratospheric ozone concentrations, there needs to some means of regenerating surface reactive sites subsequent to dissociative chemisorption, thereby creating a catalytic cycle. The high flux of solar ultraviolet radiation in the stratosphere may possibly provide a photochemical mechanism for regenerating reactive surface sites. But, in the absence of such a catalytic cycle, the surface active sites would saturate over time. SRM particles could therefore have an effect on CFM and ozone levels in the immediate vicinity of the rocket plume but would not have any global impact. It should also be noted that chlorination of the SRM particle surface by HCl in the exhaust plume will probably influence its reactivity although the nature of this effect is not entirely clear at this time.

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