Reactions of Halomethanes with γ-Alumina Surfaces. 1. An Infrared Spectroscopic Study

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The reactions of several atmospherically relevant halomethane compounds (CF_3Cl, CF_2Cl_2, $CFCl_3$, and CCl_4) with heat-treated γ-alumina powders have been investigated using *in situ* Fourier transform infrared absorption spectroscopy in an attempt to assess the impact of alumina exhaust particles from solid-propellant rocket motors on stratospheric chemistry. Infrared spectra revealed that heating the powders to 1000 K in vacuum promotes dehydroxylation of the alumina surface and formation of a new surface site which is proposed to consist of clusters of Al^{3+} and O^{2-} ions. The heat-treated powders were dosed at 100 K with halomethanes and then gradually heated to promote reaction; infrared spectra were recorded as a function of temperature. Several absorption features in the $1300-1850$ cm^{-1} region of the spectra were observed that were common to all of the compounds studied. These features, which appear at temperatures as low as 120 K, are attributed to adsorbed carbonate, bicarbonate, and/or formate species (CO_n, $n = 2,3$), indicating that halomethanes dissociatively chemisorb on heat-treated γ-alumina at temperatures below that of the lower midlatitude stratosphere. These CO_n species are apparently stable to temperatures in the range $250-400$ K, depending on the degree of chlorination of the halomethane compound. Pyridine preexposure experiments revealed that coordinatively unsaturated Al^{3+} sites that are formed during the heat treatment are essential to the low-temperature dissociative chemisorption process. The Al_xO_y ion-cluster sites formed as a result of heat treatment as well as residual OH groups also participate in the surface chemistry.

I. Introduction

Approximately 30 wt % of the exhaust from the solid-propellant rocket motors (SRMs) associated with U.S. Titan and Space Shuttle vehicles is composed of submicron- to micron-sized γ- and α-aluminum oxide particles.[1] The growing concentration of SRM−alumina particles in the stratosphere[2] has raised concern about their potential impact on the ozone cycle. Although some modeling studies have considered the heterogeneous chemical reactions of atmospheric reservoir species (e.g., $ClONO_2$ and N_2O_5) on ice- or sulfuric acid-coated SRM- exhaust particles,[3,4] little attention has been paid to the possibility of gas phase atmospheric species reacting directly with alumina surfaces.

Considering that alumina surfaces contain a variety of acid−base sites that react with compounds such as halogenated hydrocarbons,[5−14] SRM-exhaust particles could very well promote the decomposition of important trace species in the stratosphere. Our recent investigations into the chemistry of halomethanes on aluminum oxide surfaces at temperatures characteristic of the lower stratosphere have been motivated by an interest in this issue.[15] Of primary concern to us was the fact that since halomethane photolysis is the rate-limiting step in the entire halogen-catalyzed ozone depletion cycle, surface-mediated processes that promote carbon−halogen bond cleavage could potentially have a profound impact on the ozone cycle.

In previous experiments, we found that CF_2Cl_2 and CF_2Br_2 dissociatively chemisorb on heat-treated single-crystal α-aluminum oxide (sapphire) at 210 K.[15] In the present study, we have extended our investigations to the reactions of a series of homologous halomethane compounds, CF_3Cl, CF_2Cl_2, $CFCl_3$,

and CCl_4, on γ-alumina powders. CF_2Cl_2 and $CFCl_3$ are the two most abundant chlorofluorocarbon (CFC) compounds in the stratosphere.[16] To complement our previous studies, which utilized X-ray photoelectron spectroscopy to identify adsorbates and determine reaction probabilities, we have employed Fourier transform infrared spectroscopy to monitor the extent of surface hydroxylation and to obtain mechanistic information about the dissociative chemisorption process. In the following paper,[17] we present results on the same systems using X-ray photoelectron and temperature-programmed reaction spectroscopy to quantify the reactive uptake of halomethanes by γ-alumina and to identify species that are evolved into the gas phase as a result of reaction. Our results indicate that dissociative chemisorption occurs on heat-treated alumina surfaces at temperatures below 150 K for all of the compounds studied and that surface sites generated by preheating the powders to 1000 K are likely responsible for the low-temperature reactivity of these compounds. The results of both papers will be utilized to address the potential impact of SRM particles on stratospheric chemistry.

It should be noted that, in addition to their relevance to stratospheric chemistry, reactions of halomethanes with metal oxides are of interest lately as a possible means of disposing of stockpiles of CFCs whose production has been banned by international treaty.[18]

II. Experimental Section

The experiments were carried out in a cryopumped ultrahigh-vacuum chamber equipped with a variable temperature sample manipulator, an external Fourier transform infrared (FTIR) spectrometer, and a quadrupole mass spectrometer. The base pressure in the chamber after bakeout was $\sim 1 \times 10^{-10}$ Torr.

We chose to concentrate on $γ$-Al_2O_3 as the substrate because it is more abundant than $α$-Al_2O_3 in the SRM exhaust plume[1b,c] and is generally more reactive than α-alumina.[19] The γ-alumina powder (Johnson Matthey) had a nominal purity of 99.97%, a

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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.[20] 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 ∼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. The sample temperature was measured with two pairs of chromel/alumel thermocouples spot-welded or clamped to the Mo mesh. No temperature gradient was measured across the Mo platen.

Infrared spectra were obtained in transmission mode using a MIDAC (Model 2400) FTIR spectrometer coupled with a liquid nitrogen-cooled HgCdTe detector (with a low-frequency cutoff of ∼800 cm^{-1}). A series of mirrors steered the IR beam through the UHV chamber and focused it to a 5 mm spot at the sample holder. The beam steering/focusing optics were configured to maximize light collection. Coaligned holes in the platen and the radiative heater (7 mm diameter) allowed the focused infrared beam to pass through the sample. The IR beam path outside the ultrahigh-vacuum system was continuously purged with either dry N$_2$ or air that is free of water vapor and CO$_2$. However, despite this purging, water vapor was still present in some cases. The spectra presented were obtained with 2 cm^{-1} resolution and averaged over 100 scans.

Prior to dosing the pressed powder samples with halomethane compounds, the samples were heated under vacuum to remove physisorbed water and hydrocarbon impurities and chemisorbed hydroxyl groups. The heat treatment was as follows: 770 K for 2 h, 920 K for 30 min, 1000 K for 15 min, and 920 K for 1 h. Independent X-ray photoelectron spectroscopic studies carried out in our laboratory[17] indicate that no observable carbon or halogen remains on the powder surface after such heat treatment. IR spectra of the heat-treated samples indicated that all of the physisorbed water and most of the hydroxyl groups were removed from the powder surface, in agreement with previous studies.[5,21−25]

The halomethane compounds studied were CF$_3$Cl (Aldrich, 99+%), CF$_2$Cl$_2$ (Aldrich, 99+%), CFCl$_3$ (Matheson, 99.9+%), and CCl$_4$ (Aldrich, 99.9+%). In some experiments, the powder samples were dosed with pyridine (Aldrich, 99.9%, HPLC grade) prior to being exposed to halomethane. Vapor samples of these compounds were purified using several freeze/thaw cycles before being introduced into a ballast of known volume in the gas delivery manifold. The alumina powder samples were dosed using an effusive multichannel capillary array beam doser.[26] The molecular effusion rate was controlled by the pressure in the gas manifold (8−10 Torr) and the orifice diameter (30 μm). A 1 cm o.d., 0.5 mm thick glass multichannel capillary array disk (Galileo) mounted in front of the orifice collimated the gas beam (capillary diameter 10 μm). During gas exposure, the alumina samples were positioned ∼7 mm away from the disk. The gas exposures (per dose) in these experiments, determined from the measured pressure drop in the gas manifold and a calculated geometry factor,[26] were ∼1 × 10^{19} molecules cm^{-2}. The pressure in the chamber rose to the 10^{-7} Torr range during dosing, depending on the cryogenic pumping speed for the particular halomethane being used.

Typically, the alumina samples were dosed at a temperature of 100 K. Spectra of the clean, heat-treated alumina samples were measured at 100 K prior to dosing. Immediately before dosing, the samples were quickly heated to 1000 K to desorb
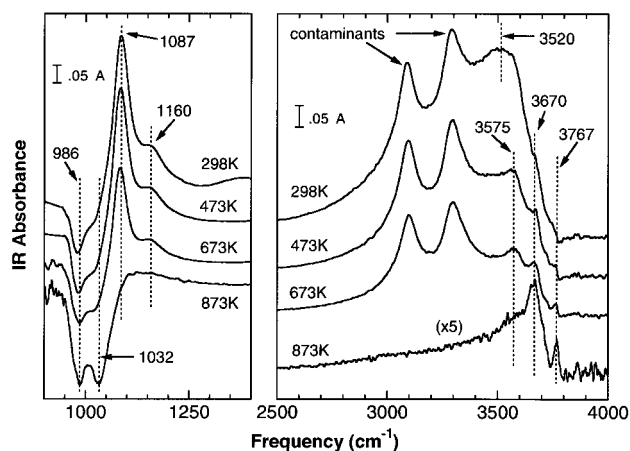

Figure 1. Infrared absorption spectra of γ-alumina powder as the sample is heated to sucessively higher temperatures. The spectra are referenced to the spectrum of the sample powder after it had been heated to 1000 K.

any condensed background molecules and then cooled to 100 K. Following halomethane exposure, a spectrum of the dosed surface was recorded. The samples were then gradually heated (∼5 K/s) to a series of temperatures. After heating to a temperature of interest, the sample was cooled back to 100 K where IR spectra were recorded. A final spectrum measured after heating the sample to 1000 K served as a reference for background subtraction. In other experiments, halomethane exposure and IR probing were carried out at several fixed temperatures. IR spectra obtained in these experiments did not differ qualitatively from those obtained when the surface was dosed at 100 K and subsequently heated to the same fixed temperatures.

III. Results

A. Dehydroxylation of Al$_2$O$_3$ Powders. In ambient air, water vapor dissociatively chemisorbs on aluminum oxide surfaces to form adsorbed hydroxyl ions. On the γ-alumina surface, there are at least five chemically distinct OH species which have varying degrees of Brønsted acid character.[24] Heating the surface promotes desorption of chemisorbed OH through the reaction:

$$2OH^-_{ads} \rightarrow H_2O + O^{2-}_{ads}$$
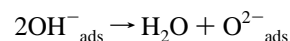
The surface hydroxyl concentrations monotonically decrease as the aluminum oxide surface is heated above room temperature.[24] Removal of hydroxyl ions from γ-alumina is thought to be essentially complete at ∼1200 K ; however, both experimental and modeling studies suggest that the minimum achievable hydroxyl coverage is a few percent.[5,21−25,27] At sufficiently high temperatures, this dehydroxylation process exposes coordinatively unsaturated (cus) Al^{3+} ions as well as O^{2-} ions that act as Lewis acids and bases, respectively. Evidence suggests that clusters of ions, vacancies, and strained Al−O bonds are formed on the Al$_2$O$_3$ surface as a result of the dehydroxylation process and that these defect sites are responsible for the enhanced reactivity of heat-treated alumina.[22,24,28]

In an effort to simulate the very hot environment of the rocket exhaust plume experimentally, we heated the alumina powder samples in the present study prior to exposing them to halomethane compounds. After the pressed alumina sample was mounted in the high-vacuum chamber, an IR spectrum was recorded with the sample at 298 K (Figure 1). The alumina sample was then heated to several higher temperatures: 473,

673, and 873 K. After heating to each temperature, the sample was kept at that temperature for 10 min and was then cooled back to room temperature before recording a spectrum. All spectra are referenced to a spectrum taken after the sample was heated to 1000 K. Therefore, the presence of adsorbed species is indicated by an increased absorption of infrared light at characteristic frequencies.

The loss of both adsorbed water and hydroxyl groups from the γ-alumina surface as a function of heating temperature is demonstrated in Figure 1. The absorption features at 3100 and 3300 cm^{-1} that were observed at 298 K suggest the presence of adventitious hydrocarbons; the absorption at 3520 cm^{-1} is probably due to coordinatively bonded water.[29] Heating resulted in the decrease and eventual disappearance the water and hydrocarbon absorptions. The absorption band at 3575 cm^{-1} at 473 K probably arises from H-bonded OH groups.[25,29] The features in the 3600–3800 cm^{-1} region are due to stretching modes of isolated hydroxyl groups bonded to Al^{3+} ions;[22,24] we attribute the peaks at 1160 and 1087 cm^{-1} to surface OH bending modes.[30,31] The spectra indicate that the surface still had a significant number of OH groups after heating to 673 K. In the 873 K spectrum, the two hydroxyl group absorption features observed at 3767 and 3670 cm^{-1} have decreased markedly in intensity. The peak at 3575 cm^{-1} has become unresolvable. Thus, heating the powder to 873 K removed water and other trace contaminants as well as a significant fraction of surface OH groups. Since the spectra are referenced to a 1000 K spectrum, Figure 1 indicates that heating to 1000 K resulted in further depletion of a small number of OH groups. Further heating to 1200 K (data not shown) leads to no observable change in the hydroxyl region of the spectra.

We believe that the two negative features at 1032 and 986 cm^{-1} in the 873 K spectrum (Figure 1) arise from clusters of Al^{3+} and O^{2-} ions of variable stoichiometry (Al$_x$O$_y$) on the surface of the heat-treated alumina. (The negative absorption indicates that the surface coverage at 1000 K is larger than that at 873 K.) These absorptions are higher in frequency than the lattice modes of bulk (860 cm^{-1})[32] and plasma-grown (940 cm^{-1})[30,31] Al$_2$O$_3$. As noted above, clusters of ions and vacancies are created as a result of heating alumina to 1000 K. Our results suggest that these defect sites are involved in the low-temperature reactions of halomethanes on dehydroxylated γ-alumina (see below).

It is difficult to determine quantitatively the fraction of OH groups remaining after heating because the OH absorption features are not well resolved. As noted above, previous results indicate that 10% or less of the hydroxyl groups remain behind after heating in vacuum to 1000 K. However, we have evidence from the halomethane exposure experiments (see below) that indicates that the remaining OH groups indeed participate in the surface chemistry. (However, no difference in reactivity was observed between powders heated to 1000 and 1200 K, indicating that a limiting OH coverage has been reached at 1000 K.) Although we denote the heat-treated surface as "dehydroxylated", the extent of dehydroxylation is uncertain.

B. Decomposition of Halomethanes on γ-Alumina Surfaces. Heat-treated γ-alumina samples were cooled to 100 K and then dosed with ∼1 × 10^{19} molecules cm^{-2} of halomethane. Under these exposure conditions, all of the compounds condensed on the powders to form multilayer "ices". (Although similar gas doses were used for each of the compounds, their sticking coefficients are expected to differ significantly from one another.) Sharp and narrow absorption features were observed in the 1000–1200 cm^{-1} region of the spectra of the fluorinated compounds that are due to C−F stretching modes
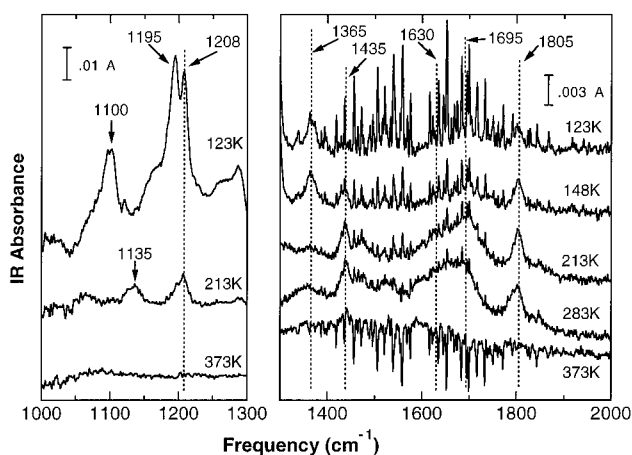

Figure 2. IR absorption spectra of γ-alumina dosed with CF$_3$Cl at 100 K and subsequently heated to higher temperatures. Spectra are referenced to spectrum of powder that has been heated to 1000 K after dosing. Noise is due to incomplete subtraction of gas phase H$_2$O.
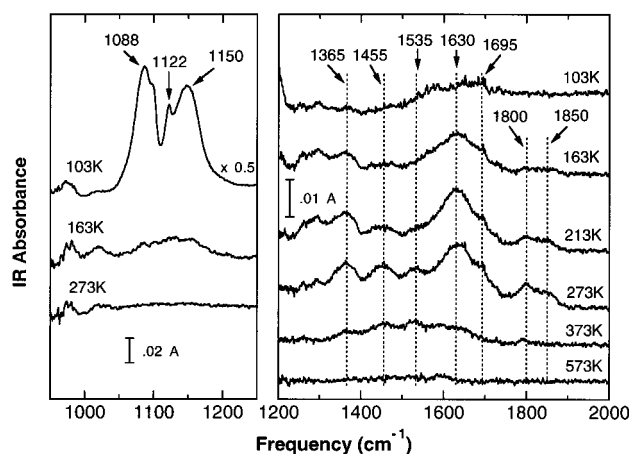
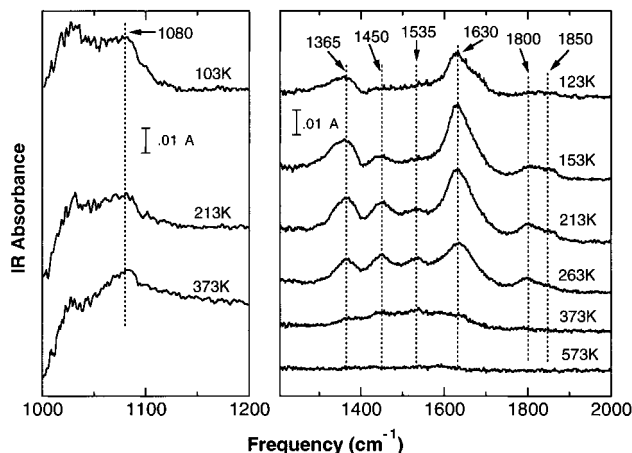

Figure 3. Same as Figure 2 for CF$_2$Cl$_2$.

Figure 4. Same as Figure 2 for CFCl$_3$.

in condensed, multilayer films (Figures 2–4). Our sensitivity to absorptions which occurred below 950 cm^{-1} was limited significantly by the strong absorption of bulk alumina in the 800–1000 cm^{-1} region and by the detector cutoff frequency of 800 cm^{-1}. We were thus unable to observe any absorption features due to C−Cl stretches, which occur below 800 cm^{-1}.[33]

The dosed γ-alumina samples were then gradually heated; the resulting absorption spectra showed distinct changes as a function of heating temperature (Figures 2–5). First, the absorption features associated with condensed chlorofluoromethanes (1000–1200 cm^{-1}) decreased in intensity dramati-
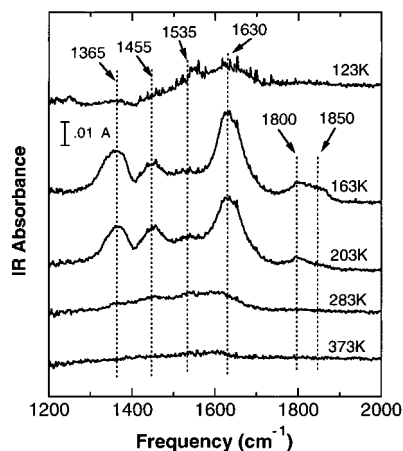
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Figure 5. Same as Figure 2 for CCl_4.

cally after heating slightly; by 200 K, only weak features were observed. At the same time, a number of new and broader absorption features appeared in the region of 1300–1850 cm^{-1}. These features, most of which are common to all of the compounds, increased in intensity as the sample was heated further, reaching maximum absorbance between 150 and 300 K. Further heating resulted in the decrease and eventual loss of all of the absorption features. A series of experiments were performed in which heat-treated powders were dosed at 200 K. Essentially identical spectra were obtained under these conditions as when the powders were dosed at 100 K and heated to 200 K.

The spectral changes observed in Figures 2–5 clearly indicate that the halomethanes react with γ-alumina at temperatures below 150 K. Although an accurate assignment of the new spectral features is difficult, they are not due to intact adsorbed halomethane molecules. Since most of the absorption features in the 1300–1850 cm^{-1} region are common to all of the compounds, including CCl_4, and since C–Cl vibrational frequencies are typically observed below 800 cm^{-1}, we conclude that these features are not due to C–Cl or C–F vibrations. Al–X and O–X (X = F, Cl) species can also be ruled out as the cause since their vibrational frequencies are below 1000 cm^{-1}.[34]

We propose that these spectral features reflect the bonding of the carbon atom from the halomethane molecule with oxygen ions on the aluminum oxide surface. Previous IR spectroscopic studies of CO_2 adsorption on dehydroxylated transition alumina powders suggest that the absorption peaks observed between 1350 and 1650 cm^{-1} are most likely due to vibrational modes of adsorbed carbonate (CO_3^{2-}), bicarbonate (HCO_3), and/or formate (CO_2^-) ions (CO_n, n = 2, 3), with possible frequency shifts due to halogen atoms adsorbed on the surface and/or bonded to the carbon atom.[23,35–43] Indeed, almost all of the absorption features that we observe in the 1300–1650 cm^{-1} region correspond in frequency to absorptions seen for CO_2 adsorbed on dehydroxylated alumina. (See discussion of the tentative spectral assignments below.) Background CO or CO_2 adsorption was examined and found to be negligible.

The observation of adsorbed CO_n in our spectra indicates that halomethane compounds dissociatively chemisorb on heat-treated γ-alumina at low temperatures. The data are consistent with a chemisorption process involving the formation of multiple C–O bonds and consequent C–X (X = F, Cl) bond dissociation. We attribute the residual features observed in the 1000–1200 cm^{-1} region at ~200 K to C–F vibrational modes in adsorbed halomethyl fragments.[17,44] Below we will address in more detail the nature of the surface sites involved in these reactions.

The temperature dependence of the IR spectral features in the 1300–1850 cm^{-1} region (Figure 2–5) reveals that the onset temperature and thermal stability of CO_n species vary with the extent of chlorination of the molecules. For instance, in the case of CCl_4, the CO_n features appeared at 123 K and disappeared nearly completely after heating to 283 K (Figure 5), while with CF_3Cl, the CO_n features did not fully develop until 210–300 K and remained stable until ~400 K (Figure 2). We believe that this trend is related to the strengths of the C–Cl and C–F bonds in the different halomethanes (see Discussion). However, both CO_n- and Al_xO_y-related features (see below) diminish and eventually disappear upon heating, suggesting that heating leads to Al–O bond rupture and desorption of CO_n species (e.g., CO and CO_2). Temperature-programmed reaction experiments conducted in our laboratory have shown that gas phase CO_2 does indeed desorb from halomethane-dosed γ-alumina.[17] The desorption temperature depends on the degree of chlorination of the compound with the more highly chlorinated compounds evolving CO_2 at lower temperatures.

C. Assignment of Infrared Absorption Features. As noted above, most of the absorption features observed as a result of halomethane adsorption on deydroxylated γ-alumina correspond in frequency to absorptions seen when CO_2 is adsorbed on γ-alumina. In this section, we offer highly tentative assignments of the CO_n absorptions resulting from dissociative chemisorption of halomethanes based on past studies of CO_2 adsorption. It should be noted that the CO_n absorption frequencies are expected to be perturbed from the corresponding CO_2 frequencies as a result of the presence of halogen atoms co-adsorbed on the surface and/or bonded to the halomethane carbon atom (to form something akin to a halogenated carbonyl, formate, or carbonate species).

The peaks in our spectra (Figures 2–5) at 1365 cm^{-1} may suggest the presence of monodentate carbonate ions (structure **I**). (Note that these structures are simplified representations of CO_2 adsorbed on Al_2O_3.) For instance, Little has assigned a 1370 cm^{-1} band seen when CO_2 adsorbs on metal oxides to the symmetric stretch of the monodentate ion.[41,43] Parkyns attributed peaks at 1350 and 1530 cm^{-1} observed when CO_2 is adsorbed on alumina to monodentate carbonate ions.[23] We observe a very small feature at 1535 cm^{-1} for most of the compounds at temperatures above 200 K; however, the fact that it does not have the same temperature dependence as the 1365 cm^{-1} absorption feature argues against these two features arising from the same species. The feature that we observe between 1435 and 1455 cm^{-1} may correspond to one that appears in the range of 1450–1480 cm^{-1} in the CO_2/alumina spectrum that has been assigned to either uncoordinated or monodentate carbonate ions.[35,38,43] These assignments are rather tentative since formation of monodentate carbonate ions requires the rupture of at least two surface oxygen bonds, an energetically costly process.
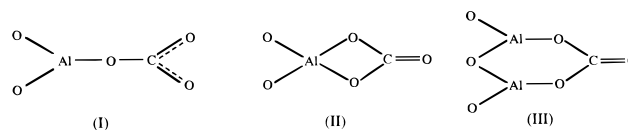
The ~1630 cm^{-1} feature that we observe for most of the compounds falls in the same frequency range (1630–1660 cm^{-1}) as the band in the CO_2/alumina spectrum that has been ascribed to bidentate carbonate ions (structure **II**).[13,35,41] The 213 K spectrum of the CF_3Cl-dosed sample shows a strong absorption feature at 1695 cm^{-1} and a shoulder at lower frequency. The reverse is true for CF_2Cl_2: a dominant feature

is observed at 1630 cm^{-1}, with a shoulder at $\sim$1695 cm^{-1}. With CFCl$_3$, the shoulder at $\sim$1695 cm^{-1} is less apparent, and in the case of CCl$_4$ this shoulder is not observed. On the basis of this trend, we speculate that the absorption at $\sim$1695 cm^{-1} arises from a carbonate species interacting with fluorine located at a neighboring site on the surface or from a fluorinated carbonate.

An absorption feature appears in the 1800$-$1850 cm^{-1} range in the spectra of all of the compounds. In the case of CF$_3$Cl, a relatively sharp peak appears at 1805 cm^{-1}. In the spectra of the other three compounds, the 1800$-$1850 cm^{-1} absorption feature is broad, but a separate feature at $\sim$1850 cm^{-1} can nonetheless be discerned. The 1800$-$1850 cm^{-1} absorption may be due to a CO stretching mode in chemisorbed carbon monoxide or a bridged carbonate ion (structure **III**) (again, with possible frequency shifts induced by halogen atoms adsorbed nearby or bonded to the carbon atom, e.g., a halocarbonyl).[10,40,42,43]

Some of the infrared absorption features observed in the 1300$-$1850 cm^{-1} region for halomethanes on γ-alumina may be due to formate ions.[30,37] For instance, Brown et al. have assigned peaks at $\sim$1440 and $\sim$1580 cm^{-1} in the inelastic tunneling spectra of alkanoic acids on Al$_2$O$_3$ to stretching modes of CO$_2^-$ groups.[30] In the case of CO$_2$ adsorbed on incompletely dehydroxylated γ-alumina, several groups have observed absorption peaks at 1450 and 1642 cm^{-1} that were attributed to bicarbonate ions (HOCO$_2^-$) arising from the reaction of OH with CO$_2$ on the surface.[36-40] As will be discussed further below, we have evidence that some OH groups remain on the surface after heating to 1000 K and that they are depleted as a result of reaction with CCl$_4$. In a separate study, we have also observed HCl desorption from halomethane-dosed γ-alumina at temperatures as low as 120 K.[17] HCl can only be formed if some OH groups are present on the surface. Thus, some of the infrared absorption features that we observe may in fact be due to bicarbonate ions.

D. Surface Reactive Sites. The infrared absorption spectra presented above implicate surface oxygen ions and, perhaps, OH in the low-temperature dissociative chemisorption of halomethanes on heat-treated γ-alumina. In this section, we will present additional evidence as to the nature of the reactive sites involved in this chemisorption process.

It was not possible for us to detect Al$-$X and O$-$X absorptions in our IR experiments, but our X-ray photoelectron spectroscopic studies clearly indicate that inorganic surface fluorides and chlorides are formed as a result of halomethane adsorption at 150 K.[17] Therefore, in order to assess the specific role of Al^{3+} sites in the reactions of halomethanes with γ-alumina, we performed studies of CF$_2$Cl$_2$ adsorption on γ-alumina powders that had been predosed with pyridine. Pyridine, which is a Lewis base, is commonly used to titrate Lewis acid, coordinatively unsaturated (cus) Al^{3+} sites.[6,45] In these experiments, the γ-alumina powder was heated to 1000 K and then cooled to 100 K and subsequently dosed with 6 $\times$ 10^{18} cm^{-2} of pyridine. The pyridine-dosed sample was then heated to 500 K to promote pyridine binding to Al^{3+} sites and to desorb excess molecules. Two sharp IR absorption features that are characteristic of pyridine adsorbed on alumina powder are observed at 1628 and 1457 cm^{-1} (Figure 6).[45] No evidence of physisorbed pyridine was observed after heating. (Some gas phase water lines are visible as a result of a humidity change in the IR path during the course of the day.)

After the spectrum of the pyridine-dosed and heated sample was recorded, the sample was cooled to 100 K and exposed to a dose of CF$_2$Cl$_2$. IR spectra taken with the sample held at 103 K and after heating to 223 K are also shown in Figure 6.
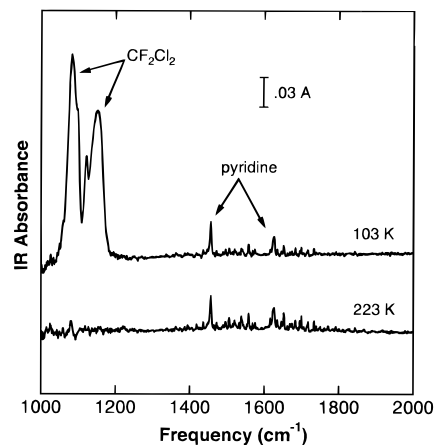

Figure 6. IR absorption spectra of γ-alumina predosed with pyridine and subsequently exposed to CF$_2$Cl$_2$.
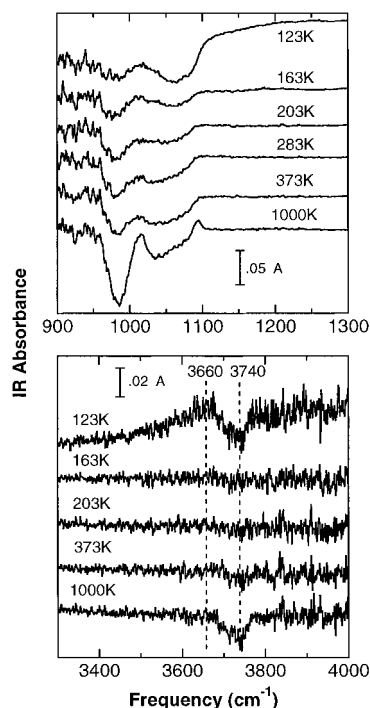

Figure 7. IR absorption spectra of γ-alumina dosed with CCl$_4$ at 100 K and then heated to a series of higher temperatures. Spectra are referenced to a spectrum of the heat-treated powder prior to dosing.

Although C$-$F vibrational modes characteristic of physisorbed CF$_2$Cl$_2$ are observed at 103 K, no evidence of surface reaction is seen at 223 K, contrary to what is observed on clean, dehydroxylated powders. This result clearly indicates that surface cus-Al^{3+} sites are crucial for the dissociative chemisorption of CF$_2$Cl$_2$, and presumably other halomethanes, on γ-alumina. When these Al^{3+} sites are blocked by pyridine, CF$_2$Cl$_2$ adsorbs only reversibly.

Besides the appearance of absorption features associated with CO$_n$ species, the involvement of surface oxygen ions in the low-temperature decomposition of halomethanes is illustrated by changes in the 1000 cm^{-1} region of the alumina spectra during reaction. Figure 7 (top panel) shows the IR absorption spectra of a CCl$_4$-dosed γ-alumina sample heated to a succession of higher temperatures. (Each spectrum is recorded after the sample was cooled to 100 K.) The spectrum of the clean, dehydroxylated sample was used for background subtraction. Two negative absorption features are observed: a broad absorption at $\sim$1034 cm^{-1} and a sharper peak at 986 cm^{-1}. These features correspond in frequency to those associated with

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Al_xO_y clusters on the clean, dehydroxylated surface (Figure 1). Their appearance suggests that these clusters are depleted as a result of reaction with CCl_4. The loss appeared to be permanent since heating to 1000 K did not restore the spectrum to that of the original clean surface. Similar results were observed when dosing with CF_2Cl_2 although the signal levels were not as high.

In order to examine the influence of the extent of dehydroxylation on surface reactivity, we conducted CF_2Cl_2 exposure experiments on γ-alumina preheated to 623 K for a period of 6 h (as compared to the usual 1000 K heat treatment described above). When this powder was dosed with CF_2Cl_2 at 100 K, absorption features associated with C−F vibrational modes in physisorbed CF_2Cl_2 were observed (data not shown; data are similar to those in Figure 6). Upon heating to 150 K these absorption features decreased in intensity, and no new features were observed. Heating to 210 K produced a spectrum without any absorption features.

Clearly, CF_2Cl_2 does not dissociatively chemisorb on alumina powders that have been preheated to only 623 K. As noted above (Figure 1), our data indicate that a substantial amount of physisorbed water and adsorbed hydroxyl groups remain on the surface at this temperature. Complete removal of adsorbed water and substantial dehydroxylation of the alumina surface require heating to at least 900 K. Although we have not completely mapped out the dependence of reactivity on preheating temperature, we conclude from our experiments that, in order for halomethanes to dissociatively chemisorb on the alumina surface, the powder needs to be heated to temperatures sufficient to promote dehydroxylation, which in turn leads to formation of critical reactive sites such as cus-Al^{3+} ions and/or clusters of ions. It should be noted that powders that had been preheated to 1000 and 1200 K displayed similar reactivity toward CF_2Cl_2, indicating that a limiting OH coverage has been reached at 1000 K.

Evidence for the involvement of residual OH in the dissociative chemisorption reaction is seen in Figure 7 (bottom panel), which shows the IR absorption spectrum of a CCl_4-dosed surface at 100 K referenced to a spectrum of the clean, dehydroxylated surface prior to dosing. A weak positive feature is observed at 3660 cm^{-1} which can be attributed to OH ions that remained on the surface after dehydroxylation. The shift in peak frequency from $\sim$3740 cm^{-1} (shown as a negative feature) to $\sim$3660 cm^{-1} upon dosing is likely due to a change in the environment of the OH group as a result of formation of a multilayer ice.[21] This feature gradually disappears as the sample is heated, presumably as a result of reaction with the halomethane molecule. Above 373 K, a discernible loss of hydroxyl groups is observed which is probably due to further temperature-induced dehydroxylation. Comparable spectra for the other compounds have too low signal-to-noise levels to discern any loss of residual OH.

IV. Discussion

Summarizing our results, we have found that chlorofluoromethane compounds and CCl_4 dissociatively chemisorb on heat-treated γ-alumina at temperatures below 150 K. Powders of γ-alumina were heated to 1000 K to promote surface dehydroxylation and were then exposed to halomethane vapor (CF_3Cl, CF_2Cl_2, $CFCl_3$, or CCl_4) at 100 K. The powders were then gradually heated, and their surface chemical compositions were investigated as a function of temperature using *in situ* Fourier transform infrared absorption spectroscopy. IR absorption features characteristic of adsorbed CO_n intermediates (i.e., carbonate, bicarbonate, and/or formate) were observed for all of the compounds, indicating that the carbon atom in the

halomethane molecule bonds to surface oxygen ions and, by implication, carbon−halogen bonds dissociate. These CO_n species are apparently stable to temperatures in the range 250−400 K, depending on the halomethane compound. The stability of the surface CO_n species decreases as the degree of chlorination of the compound increases. A surface defect site identified as an Al_xO_y cluster is formed during the dehydroxylation process and is depleted as a result of halomethane exposure and subsequent heating. Pyridine exposure experiments demonstrated that cus-Al^{3+} sites are also central to the dissociative chemisorption process. OH groups, although present at very low coverages after heat treatment, may also participate in the surface chemistry as evidenced by spectral features associated with HCO_3^- as well as the observation of gas phase HCl in temperature-programmed reaction spectroscopic studies.[17]

Several groups have investigated the reactions of haloalkanes on γ-alumina under various gas exposure and surface preparation conditions. The most commonly studied compounds have been chloroalkanes (e.g., CCl_4). In general, our conclusions agree with those of these papers, namely, that C−X bonds dissociate on γ-alumina, Al−X and C−O bonds are formed, and, at sufficiently high temperatures, halide ions exchange with surface oxygen ions and CO_n species are released into the gas phase.[5−12] However, the temperatures at which these studies were performed were all higher than those used in our experiments, and dissociative chemisorption was not observed below $\sim$400 K. In addition, unlike our results, surface oxygen and aluminum ions were usually not both implicated in the dissociative chemisorption of the haloalkane. In the case of CH_3CCl_3 on γ-alumina, for instance, Yates and co-workers found that dehydroxylation of the surface promoted the dehydrochlorination reaction (i.e., elimination of HCl).[5] Little evidence was seen for C−O bonding on the surface. However, OH groups were found to be essential for the dissociative chemisorption of CH_3Cl which proceeds through formation of an adsorbed methoxy species.[7]

In order for adsorbed CO_n to form when halomethanes interact with dehydroxylated alumina at the low temperatures studied here, C−X (X = F, Cl) bonds must be broken or severely weakened. Thus, the dissociative chemisorption process is most likely initiated by the formation of Al−X bonds on the alumina surface. The resulting CX_{n-1} fragment, which is electropositive, can bind with surface oxygen that is in the form of cus-O^{2-} ions, O^{2-} clusters, and/or residual hydroxyl groups. Further C−X bond breakage leads to formation of adsorbed CO_n. Al−X and C−O bond formation in turn results in Al−O bond rupture. As the temperature of the powder is raised, CO_n species desorb, primarily as CO_2. It is probable, however, that some or most of the halomethanes desorb at lower temperatures (below the temperature at which CO_n is formed) in the form of CF_xCl_y radicals.[17] HCl formation,[17] made possible by the presence of residual OH, provides an additional thermochemical driving force for surface-mediated halomethane decomposition.

As noted in the previous section, the onset temperature and thermal stability of the CO_n species correlate with the degree of chlorination of the molecule. The more chlorinated the molecule, the lower the temperature at which CO_n features appear and disappear. We believe that this is due to systematic changes in the energetics of C−X (X = F, Cl) bond dissociation with degree of chlorination. Thus, the C−Cl bond dissociation energy (BDE) in CCl_4 is lower than that in CF_3Cl by 13 kcal/mol (73 kcal/mol in CCl_4 and 86 kcal/mol in CF_3Cl).[46] Likewise, the C−F BDE in CF_3Cl is higher than that in $CFCl_3$ by 21 kcal/mol (123 kcal/mol in CF_3Cl and 102 kcal/mol in $CFCl_3$).[46] Thus, we expect dissociative chemisorption to be

more facile for CCl_4 than for CF_3Cl. (Note that the Al—F and Al—Cl bond dissociation energies are 159 and 122 kcal/mol, respectively.[47])

The trend in the disappearance temperature of the CO_n IR features agrees with our finding that the more chlorinated the molecule, the lower the temperature at which CO_2 desorbs.[17] Differences in the energetics of the respective decomposition reactions may account for this trend, but it also may relate to differences in the energy of interaction of the adsorbed CO_n intermediate with the halogenated surface. Since the Lewis acidity of fluorinated alumina is higher than that of chlorinated alumina,[48,49] halogenated CO_n intermediates may interact more strongly with a fluorinated alumina 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 CCl_4-dosed surface.

V. Conclusions

The IR absorption studies reported here indicate that chlorofluoromethanes and CCl_4 dissociatively chemisorb on dehydroxylated γ-alumina surfaces at temperatures below those of the lower stratosphere. The decomposition reactions apparently proceed through C—X (X = F, Cl) bond rupture and Al—X and C—O bond formation and involve the participation of surface active sites such as cus-Al^{3+} ions and Al_xO_y clusters that are produced during dehydroxylation. In the accompanying paper,[17] we report on the species released into the gas phase during low-temperature halomethane—alumina reactions and on the relative efficiencies of these reactions. The potential impact of halomethane—SRM particle reactions on stratospheric chemistry will also be addressed.

VII. References

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