Kinetic Isolation of Reaction Intermediates on Ice Surfaces. Precursor States of SO₂ Hydrolysis

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We studied the interaction of SO₂ with ice films at temperatures above 80 K, with emphasis on the examination of the precursor states of SO₂ hydrolysis, or SO₂ surface complexes. Cs⁺ reactive ion scattering (RIS) and low energy sputtering (LES) techniques were used to examine the surface reaction products, in conjunction with temperature-programmed desorption (TPD) to monitor the desorbing species. The study indicated that the reaction of SO₂ with the ice surface occurred through several distinct intermediate states, including a solvated SO₂ species, a DSO₂ species, and a strongly ionic molecular species, and these intermediates could be isolated on the ice surface due to kinetic trapping.

Reactions on the surfaces of water droplets and ice particles are important for the chemical transformation of atmospheric trace gases. For example, the uptake of SO₂ gas into water or ice in clouds and fog produces sulfurous acid, which becomes sulfuric acid through oxidation. In an aqueous solution at room temperature, SO₂ undergoes a hydrolysis reaction

$$\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- (\text{aq}) + \text{H}_2\text{O}^+ (\text{aq})$$

corresponding to pKₐ = 1.89. The mechanism of SO₂ hydrolysis is still unclear at the molecular level. Interestingly, recent studies suggest that an "SO₂ surface complex" forms as a precursor to SO₂ hydrolysis during the interaction of SO₂ with water surfaces.¹⁻⁷ Davidovits and co-workers¹⁴ reported that the uptake of SO₂ gas by water surfaces was very efficient compared with other gases such as CO₂ and H₂S, and this observation could be explained by chemical reactions between SO₂ and the surface water molecules, rather than by Henry’s law of solubility which accounts for simple solvation processes. Supporting the formation of SO₂ surface complexes, vibrational sum-frequency spectroscopic studies⁶⁻⁷ have shown that the hydrogen bonding structure of surface water molecules changes when exposed to SO₂ gas. However, the structure of the surface complex could not be identified in these studies. Investigations⁸ using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and ab initio calculations indicated that neutral SO₂ complexes either did not exist on the surfaces or had a concentration below the detection limit.

Devlin and co-workers⁸⁻¹⁰ studied the interactions of SO₂ with the surfaces of ice nanoparticles at low temperatures (120⁻¹⁴₀ K) by using FTIR spectroscopy. Their results indicated the presence of molecular SO₂ species in the ice particles⁹ and an absorption band that could be assigned to anionic products of SO₂ ionization.¹⁰ Photoelectron spectroscopic studies¹¹ of SO₂ adsorption on ice films at 100 K revealed the presence of molecular SO₂ adsorbates as well as sulfuric acid-like species with distinguished S(2p) electron binding energies. In this Letter, we study the interactions of SO₂ with ice films by using the techniques of reactive ion scattering (RIS), low-energy sputtering (LES), and temperature-programmed desorption (TPD). It is demonstrated that the ice surfaces can isolate the precursor states of SO₂ hydrolysis, though they may have only a fleeting existence on the liquid water surfaces interacting with SO₂ gas.

We conducted experiments in an ultrahigh vacuum analysis chamber equipped with instrumentation for RIS, LES, TPD, and Auger electron spectroscopy.¹⁵ A crystalline ice film was grown on a Ru(0001) surface at 140 K by backfilling the chamber with D₂O vapor for a deposition rate of 0.005 BL s⁻¹ (bilayer; 1 BL = 1.1 × 10¹⁵ water molecules cm⁻²). The ice film thickness was typically 4 BL, as deduced from the TPD experiments. For this thickness, the Ru substrate did not affect the reaction occurring on the ice surface.¹³ SO₂ (99.99+-% purity) gas was introduced into the chamber through a separate leak valve and was adsorbed on the ice film at 80 K by the backfilling method. The ice film surface was analyzed by the RIS and LES methods.¹³ In these experiments, a Cs⁺ beam from a low-energy ion gun (Kimball Physics) collided with the sample surface at an incident energy of 25 eV, and the positive and negative ions emitted from the surface were detected by a quadrupole mass spectrometer (ABB Extrel) with its ionizer filament switched off. In RIS, neutral species (X) on the surface were picked up by the scattering Cs⁺ projectiles to form Cs⁺-neutral clusters (CsX⁺). In LES, ionic species (Y⁺ and Z⁻) on the surface were ejected by the Cs⁺ impact. Thus, the RIS and LES signals revealed the identities of neutrals (X) and ionic species (Y⁺ and Z⁻) on the ice film surface. It has been shown¹³ that RIS and LES measurements have a probing depth of 1 BL on ice films under these conditions, and the measured signals represent the preexisting species on the surface, with a negligible contribution from the secondary surface reactions induced by the Cs⁺ beams.
The results of the RIS and LES measurements on the ice film with SO2 adsorbates are shown in Figure 1. The samples were prepared by adsorbing SO2 on a crystalline D2O-ice film at 80 K, and the sample temperature was raised to 140 K to desorb physisorbed SO2 molecules before the measurements. Spectrum a shows RIS signals from this surface, and these include the reflected Cs+ primaries at m/z = 133 amu/charge and Cs(D2O)+ (n = 1–3) peaks at m/z = 133 + 20n, due to the pickup of water molecules by Cs+ projectiles. The signals related to SO2 adsorbates include CsSO2+ (m/z = 197), CsDSO2+ (m/z = 199), and Cs(D2O)(SO2)+ (m/z = 217). The CsSO2+ peak indicates the presence of molecular SO2 adsorbates, and the CsDSO2+ peak indicates that the DSO2 species is formed on the surface. The Cs(D2O)(SO2)+ peak is due to the pickup of independent D2O and SO2 species. The m/z = 199 peak can also be produced from SO2 isotopomers (34S16O2, 32S16O18O), but this contribution is 14% of the observed total intensity, as estimated from the elemental isotopic abundances and the Cs16O32+ intensity at m/z = 197.

Spectrum b shows LES anion signals from the surface, which include OD− (m/z = 18), SO2− (m/z = 64), DSO2− (m/z = 66), and D3O− (m/z = 82). The various molecular ion signals indicate that SO2− is transformed into different molecular species by reacting with water molecules. These signals appear at Cs+ impact energy above 20–25 eV. Such low threshold energies indicate that these signals are produced from preexisting surface species, either via direct desorption of the molecular species or via collisional fragmentation, rather than from secondary surface reactions induced by Cs+ impact which occur at substantially higher energies. In contrast with the appearance of various molecular anions, the positive-ion LES spectrum (spectrum c) does not show any cation related to SO2 adsorbates, including D3O+ which is expected from reaction 1. The small Na+, K+, and Rb+ peaks in the spectrum are due to the scattering of alkali ion impurities in the Cs+ beam.

We examined how the molecular signals (CsSO2+, CsDSO2+, OD−, SO2−, DSO2−, and DSO3−) changed as a function of the temperature by performing temperature-programmed RIS and LES (TP-RIS and TP-LES) experiments. TPD experiments were also performed to monitor the desorbing species, which provided complementary information to the TP-RIS and TP-LES measurements of the surface species. Figure 2a shows the TP-RIS and TP-LES measurements for the signals of interest appearing from a D2O-ice film with adsorbed SO2. Figure 2b shows the TPD measurements for the desorption of SO2 and D2O. The changes in these signals during a temperature increase from 100 K to the point of ice sublimation can be described as follows.

During the temperature increase of 110–140 K, the CsSO2+ intensity sharply decreases (Figure 2a), and this indicates a decrease in the population of physisorbed SO2 species. This species can either desorb from the surface or be converted to different surface species by reactions. The desorption of physisorbed SO2 is observed in the TPD spectrum (b) as an α desorption peak that starts from ∼110 K and reaches a maximum at ∼130 K. The reaction of physisorbed SO2 with the ice surface is indicated by the increase in the signal intensities of CsDSO2+, OD−, SO2−, DSO2−, and DSO3− in this region.

Among these signals, the SO2− intensity increases strongly up to 130 K but then decreases above this temperature. In contrast, the other signals continuously increase until ∼150 K. These behaviors suggest that at least two different surface species are produced from the reaction of physisorbed SO2: one producing the SO2− signal and the others responsible for the OD−, DSO2−, DSO3−, and CsDSO2+ signals. The early decrease of the SO2− signal suggests that this signal comes from solvated SO2 molecules with a partial negative charge, whereas the other signals may originate from reaction products with strong chemical bonding to the surface. We designated the former species as intermediate I. This species is distinguished from the weakly physisorbed SO2 states that are unstable at 130...
K. In the narrow temperature range of 130–150 K, the OD\(^-\), DSO\(_2\)^- and CsDSO\(_2\)^- intensities grow at the expense of the decreasing SO\(_2\)^- intensity. This observation indicates the conversion of intermediate I into the other species. This process most likely involves chemical reactions between SO\(_2\) and water, as judged from the appearance of the various molecular signals. The chemical transformation is accompanied by SO\(_2\) desorption at ~130 K (q. peak).

DSO\(_2\)^- and CsDSO\(_2\)^- signals start to decline at temperatures above ~150 K. However, the OD\(^-\) and DSO\(_2\)^- signals increase above ~160 K. This suggests that the species producing DSO\(_2\)^- and CsDSO\(_2\)^- signals, which we designate as intermediate II, transforms into another species (intermediate III), producing DSO\(_3\)^- and OD\(^-\) signals. The transformation is accompanied by SO\(_2\) desorption, which produces a \(\beta\) desorption peak around this transition temperature. The DSO\(_2\)^- and CsDSO\(_2\)^- signals decline as the water molecules in the multilayer of the ice film desorb at 150–180 K (spectrum b). This indicates that intermediate II is stable only under the appropriate solvation conditions afforded in the presence of the water multilayer. Because intermediate II is detected as DSO\(_2^-\) in LES and as DSO\(_3^-\) in RIS, its structure may be a partially charged form of DSO\(_3^-\) or a larger molecular unit containing such a moiety.

The OD\(^-\) and DSO\(_2^-\) signals increase at 160–200 K and show strong intensities as long as chemisorbed water molecules remain on the surface until ~300 K. These observations may reflect the change in the population of intermediate III. However, other factors may also affect the signal intensity from the thin ice film during water evaporation, such as the increased LES detection efficiency of the ions. Also, OD\(^-\) ions may be produced from the collisional ionization of water molecules chemisorbed on the metal surface at submonolayer coverage. Although OD\(^-\) and DSO\(_2^-\) signals are detected by LES, the corresponding neutral DSO\(_3^-\) and OD species are not observed by RIS at all temperatures of the investigation. This suggests that intermediate III has a strong ionic character with DSO\(_3^-\) (and OD\(^-\)) moieties. Besides OD\(^-\) and DSO\(_2^-\) signals, the SO\(_2^-\) signal appears at high temperatures even when the molecular SO\(_2\) adsorbates are desorbed, probably because the intermediates II and III produce a SO\(_2^-\) signal.

There are other noticeable features in our results. First, the signals corresponding to intermediates I–III have appeared at temperatures as low as 100 K (Figure 2a), though their intensities are small compared with that of physisorbed SO\(_2\) species. The occurrence of the reaction at low temperature may be attributable to the microscopic heterogeneity of the ice surface structure, which provides various adsorption geometries of SO\(_2\) and guides the reaction path to physisorption, solvation, and/or reaction.

Second, D\(_2\)O\(^+\) was not detected on the present surfaces (Figure 1c), though they were the final SO\(_2\) hydrolysis products in an aqueous solution. A D\(_2\)O\(^+\) signal appeared only at higher incident energies (>30 eV) of Cs\(^+\) at a temperature of 140 K. D\(_2\)O\(^+\) might have been formed underneath the ice film surfaces and thus were undetected at a low Cs\(^+\) energy, but this possibility opposes the behavior of the hydronium ion as it preferentially resides on the ice surface.\(^{15}\) An alternative possibility is that D\(_2\)O\(^+\) was emitted via collisional fragmentation of the reaction intermediates that were not fully dissociated to D\(_2\)O\(^-\) and DSO\(_2^-\). According to these considerations, the reaction of SO\(_2\) on the ice surface may not have reached the final stage of the hydrolysis. Instead, the reaction stopped at the intermediate stages due to the kinetic trapping of the reaction intermediates on the ice surface.\(^{16}\) Finally, the population of the intermediate species may be estimated from the observed RIS and LES signal intensities. The calculation procedure is described in the Supporting Information. This information shows that, when the sample in Figure 1 was heated from 100 to 140 K, about 10% of the SO\(_2\) adsorbates were converted to intermediate I, 20% were converted to intermediates II and III, and 70% were desorbed from the surface. These percentages may be accurate only in the order of magnitude, owing to the assumptions used in the estimations, but they show the efficient formation of the surface intermediates in the reaction of SO\(_2\) with the ice surface. The observation is in stark contrast with the nonreactivity of CO\(_2\) with ice surfaces.\(^{17}\)

In summary, the present work shows that the reaction of SO\(_2\) with ice surfaces occurs through various intermediate stages, which may include a solvated SO\(_2\) species with a partial negative charge (intermediate I), a partially charged DSO\(_2\) species (intermediate II), and a strongly ionic molecular species (intermediate III). The efficient formation of these intermediates at low temperatures indicates that the reaction occurs with very small or negligible energy barriers. Therefore, some of the intermediates identified in this work could form on liquid water surfaces as significant transient structures during the interaction with SO\(_2\) gas.

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Supporting Information Available: Estimation of the population of intermediate species from LES and RIS intensities. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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