Efficient Conversion of Nitrogen Dioxide into Nitrous Acid on Ice Surfaces
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ABSTRACT The hydrolysis of nitrogen dioxide (NO₂) on ice surfaces is studied by measuring the reaction products on the surface with the reactive ion scattering (RIS) technique, and the desorbing species is studied with temperature-programmed desorption (TPD) mass spectrometry. NO₂ adsorbs molecularly on an ice film surface at a temperature of 90 K. Upon heating the film to 140 K, NO₂ adsorbates are readily converted into nitrous acid (HONO), and nitrous acid products desorb intact from the surface at higher temperatures. The result indicates the efficient formation of nitrous acid gas on the ice surface with only a small activation energy. It is shown that the hydrolysis occurs from isolated NO₂ adsorbates rather than through NO₂–NO₂ interactions. The implications of these findings for the atmospheric heterogeneous reaction of NO₂ are mentioned.

SECTION Surfaces, Interfaces, Catalysis

It is well-known that nitrogen dioxide (NO₂) hydrolyzes in aqueous solution to form nitrous acid (HONO) and nitric acid (reaction 1).¹

$$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$$ (1)

Reaction 1 is important in a number of technologies and in atmospheric chemistry. For example, the heterogeneous hydrolysis of NO₂ on wet surfaces is potentially important as a source of atmospheric nitrous acid (HONO) gas,²,³ which is recognized as a precursor for hydroxyl radicals. The mechanism of this reaction has been the subject of many studies.⁴–⁹ These studies show that the reaction of NO₂ with water is more complex than its simple stoichiometry suggests. The rate of nitrous acid formation has been observed to be first-order with respect to the concentrations of both NO₂ and water vapor.⁴–⁹ This suggests that reaction 1 does not occur in a single step as a termolecular process. Several proposals have been made for the heterogeneous hydrolysis mechanism of NO₂, which include the formation of a NO₂–water complex at the air–water interface⁶–⁹ as well as reaction pathways involving N₂O₄ intermediates.¹⁰,¹¹ In general, it is difficult to unambiguously identify the mechanism of atmospheric heterogeneous reactions owing to the complexity of the reactions involving surfaces and adsorbed species.⁴ In the case of NO₂ hydrolysis, even the solution-phase mechanism is not completely understood at the molecular level,¹ and this poses additional difficulties for studying the reaction mechanism at the gas–solution interface. Moreover, only limited information is available at present about the chemical properties of NO₂ residing at the surface of condensed water or ice.¹²–¹⁶

Ice surfaces offer an interesting model for the investigation of NO₂–water interactions in a two-dimensional water environment. On a cold ice surface, the speed of a reaction is greatly reduced compared to that on a liquid water surface at room temperature, and sometimes, the reaction intermediates can be isolated on the ice surface as a result of kinetic trapping, as demonstrated for several reactions in recent investigations.¹⁷–²⁰ Spectroscopic identification of reaction intermediates trapped on the ice surface is important for the study of reaction mechanisms, and it may also provide valuable information about the corresponding reaction on liquid water surfaces. The interactions of NO₂ with ice surfaces have been studied in previous works with infrared reflection–absorption spectroscopy (IRAS), temperature-programmed desorption (TPD) mass spectrometry, and photoelectron spectroscopy.¹²–¹⁶ and these studies reveal the adsorption states of NO₂ on ice and its thermal desorption behavior. In the present work, we study the reaction of NO₂ on ice films by examining the surface species with reactive ion scattering (RIS) and the desorbing species with TPD. Efficient conversion of NO₂ into nitrous acid is observed on the ice surface at a temperature of 140 K, which is below the surface premelting regime. We also provide evidence that the reaction occurs through the interactions of isolated NO₂ adsorbates with water, which opposes a reaction mechanism involving NO₂–NO₂ intermediates.

The present experiments were conducted in an ultrahigh vacuum (UHV) surface analysis chamber equipped with instrumentation for RIS, TPD, and Auger electron spectroscopy.²¹ A D₂O-ice film was grown on a Ru(0001) substrate at a growth rate of 0.01 BL s⁻¹ (bilayer; 1 BL = 1.1 × 10¹⁵ water molecules cm⁻²) by backfilling the chamber with D₂O vapor. The ice film thickness was typically 4 BL, as deduced from the TPD experiments. For this thickness, the reaction of...
NO\textsubscript{2} on the ice film surface was not affected by the catalytic effect of the Ru substrate. The ice films were prepared in a polycrystalline phase by controlling the water deposition temperature at 135 K and by postannealing the ice film at 140 K for 5 min. The results presented in this paper were obtained with these polycrystalline ice films, but we should mention that qualitatively similar results were observed with amorphous ice films grown at 90 K. NO\textsubscript{2} gas (99.99+\% purity) was introduced into the chamber and guided close to the sample surface through a separate dosing line. NO\textsubscript{2} was adsorbed on the ice films at the temperature of 90 K and a NO\textsubscript{2} partial pressure of 1.0 × 10^{-7} Torr as read by an ionization gauge located ∼20 cm away from the sample. The actual NO\textsubscript{2} pressure near the sample surface was about 10 times higher. At this pressure, the equilibrium population ratio of N\textsubscript{2}O\textsubscript{4} in NO\textsubscript{2} gas was negligible (∼10^{-10}). The surface coverage of NO\textsubscript{2} on the ice films was measured from TPD experiments.

Chemical species present on the ice films were identified by RIS.\textsuperscript{17} In this technique, a low-energy (30 eV) Cs\textsuperscript{+} ion beam was directed onto a sample surface, and the scattered ions were analyzed for their mass. The scattered ions were composed of reflected Cs\textsuperscript{+} primaries and RIS products (CsX\textsuperscript{+}), which were formed by an ultrafast (<1 ps) association reaction between scattering Cs\textsuperscript{+} projectiles and neutral species (X) on the surface.\textsuperscript{21} The RIS products were detected by a quadrupole mass spectrometer with its ionizer filament switched off, thereby obtaining the ion mass spectrum with almost zero background noise. It has been shown\textsuperscript{22} that RIS measurement at this low energy has a probing depth of 1 BL on ice films, and the measured signals have a negligible contribution from the secondary surface reactions induced by the Cs\textsuperscript{+} beams.

Figure 1 shows the result of RIS measurements on a polycrystalline D\textsubscript{2}O-ice film adsorbed with NO\textsubscript{2} for the coverage (θ) of 0.8 monolayer (ML). The RIS spectrum in Figure 1a was obtained at the sample temperature of 90 K, and it shows RIS peaks of Cs\textsubscript{2}D\textsubscript{2}O\textsubscript{n}\textsuperscript{+} (n = 1, 2) at m/z = 153 and 173 amu/charge and CsNO\textsubscript{2}\textsuperscript{+} at m/z = 179 amu/charge. A reflected Cs\textsuperscript{+} peak appeared at m/z = 133 amu/charge. The Cs\textsubscript{2}D\textsubscript{2}O\textsubscript{n}\textsuperscript{+} signals were due to the pickup of surface water molecules by the scattering Cs\textsuperscript{+} projectiles, and the CsNO\textsubscript{2}\textsuperscript{+} signal was due to NO\textsubscript{2} adsorbates. These signals indicate that NO\textsubscript{2} adsorbs onto the surface in molecular states without undergoing dissociation or hydrolysis reactions at 90 K.

Figure 1b shows the result obtained after the sample temperature was increased to 140 K. A new RIS peak appeared at m/z = 181 amu/charge, which corresponded to CsDNO\textsubscript{2}\textsuperscript{+}. Also, a smaller peak appeared at m/z = 201 amu/charge, which was assigned as Cs(DNO\textsubscript{2})(D\textsubscript{2}O)\textsuperscript{+} produced by the pickup of independent D\textsubscript{2}O and DNO\textsubscript{2} species on the surface. This interpretation is supported by the fact that the CsDNO\textsubscript{2}\textsuperscript{+} and Cs(DNO\textsubscript{2})(D\textsubscript{2}O)\textsuperscript{+} signals have an intensity ratio of about 6:1, similar to the ratio of Cs(D\textsubscript{2}O)\textsuperscript{+} and Cs(D\textsubscript{2}O)\textsubscript{2}\textsuperscript{+}. The CsDNO\textsubscript{2}\textsuperscript{+} and Cs(DNO\textsubscript{2})(D\textsubscript{2}O)\textsuperscript{+} signals indicate the formation of DNO\textsubscript{2} through the reaction of NO\textsubscript{2} and D\textsubscript{2}O. We believe that the DNO\textsubscript{2} species is nitrous acid (DONO), which is a well-known product of NO\textsubscript{2} hydrolysis. Its structural isomer DONO(O), which is energetically less stable, has not been observed in NO\textsubscript{2} hydrolysis studies. In the remaining text, describing our experimental results, however, we will denote nitrous acid by its molecular formula (DNO\textsubscript{2}) to be consistent with the mass spectrometric information. In spectrum (b), the CsNO\textsubscript{2}\textsuperscript{+} signal disappeared from the surface, and this was attributed to the desorption of NO\textsubscript{2}, which occurred at temperatures above 130 K.\textsuperscript{14,16} Also, N\textsubscript{2}O\textsubscript{4} species were not detected on the surface.

Figure 2a shows a RIS spectrum obtained after NO\textsubscript{2} adsorption for a multilayer coverage (6 ML) on a D\textsubscript{2}O-ice film at a temperature of 90 K. The RIS signals include CsNO\textsubscript{2}\textsuperscript{+} (m/z = 163), CsNO\textsubscript{2}\textsuperscript{+} (m/z = 179), CsN\textsubscript{2}O\textsubscript{3}\textsuperscript{+} (m/z = 209), and CsN\textsubscript{2}O\textsubscript{4}\textsuperscript{+} (m/z = 225). CsNO\textsubscript{2}\textsuperscript{+} is the strongest among these peaks. The Cs(D\textsubscript{2}O)\textsuperscript{+} intensity is greatly reduced due to the presence of a NO\textsubscript{2} overlayer. The CsN\textsubscript{2}O\textsubscript{3}\textsuperscript{+} and CsN\textsubscript{2}O\textsubscript{4}\textsuperscript{+} peaks indicate that N\textsubscript{2}O\textsubscript{3} and N\textsubscript{2}O\textsubscript{4} molecules are present on the NO\textsubscript{2} multilayer surface. One might consider that these peaks are produced by the pickup of independent NO\textsubscript{2} and/or NO species on the surface, but their intensity being stronger than CsNO\textsubscript{2}\textsuperscript{+} refutes this possibility. A small CsNO\textsuperscript{+} signal may indicate NO on the surface; however, this interpretation is only tentative because the CsNO\textsuperscript{+} signal can also be produced by the fragmentation of N\textsubscript{2}O\textsubscript{2} due to collision during the RIS process. The detection of N\textsubscript{2}O\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} species confirms the observation of IRAS studies\textsuperscript{12–14,16} that a mixed adsorbate layer of N\textsubscript{2}O\textsubscript{2} (ON−NO\textsubscript{2}) and N\textsubscript{2}O\textsubscript{4} (O\textsubscript{2}N−NO\textsubscript{2}) is formed upon the multilayer adsorption of NO\textsubscript{2} on ice films at temperatures below 100 K.
When this ice film was warmed to 140 K, shown in Figure 2b, CsNO\(^+\), CsNO\(_2\)\(^+\), CsN\(_2\)O\(_4\)\(^+\), and CsN\(_2\)O\(_4\)\(^+\) signals disappeared from the surface. Instead, a CsDNO\(_2\)\(^+\) peak appeared along with a Cs(DNO\(_2\))(D\(_2\)O)\(^+\) peak, which indicated the formation of a DNO\(_2\) species. A CsDNO\(_3\)\(^+\) peak (m/z = 197) of small intensity also appeared, indicating that DNO\(_3\) (nitric acid) was also formed. The CsDNO\(_3\)\(^+\) peak was not seen in the spectrum of Figure 1b obtained at \(\theta(\text{NO}_2)\) = 0.8 ML, but this signal appeared at small levels of intensity for ice samples with submonolayer NO\(_2\) coverages as well when the sample temperature was higher than 140 K. The observations indicate that NO\(_2\) hydrolysis produces DNO\(_2\) as a major product at 140 K. A small amount of DNO\(_3\) is also formed at higher levels of NO\(_2\) coverage. The CsDNO\(_2\)\(^+\) signal is undetectably small for \(\theta(\text{NO}_2)\) < 1.0 ML and its intensity increases with NO\(_2\) coverage for \(\theta(\text{NO}_2)\) > 1.0 ML. The inverse correlation between the population changes of DNO\(_2\) and N\(_2\)O\(_4\) suggests that N\(_2\)O\(_4\) is not a precursor to DNO\(_2\) in the reaction, and vice versa.

We performed TPD measurements on NO\(_2\)-adsorbed ice films. The TPD signals of NO (30 amu) and NO\(_2\) (46 amu) appeared in the temperature region of 120–150 K, in agreement with the report of previous TPD studies.\(^{12-14}\) In addition, a small TPD signal appeared at the mass of 48 amu, which corresponded to the desorption of DNO\(_2\) and/or \(^{14}\)N\(^{15}\)O\(^{18}\)O. The isotopomeric abundance of \(^{14}\)N\(^{15}\)O\(^{18}\)O is very small (4 x 10\(^{-3}\)) relative to \(^{14}\)N\(^{16}\)O\(^{18}\)O, yet it can make a substantial contribution to the small-intensity 48 amu signal. The TPD spectrum of DNO\(_2\) was extracted from the 48 amu spectrum after quantitative subtraction of the \(^{14}\)N\(^{15}\)O\(^{18}\)O desorption signal, which was proportional to the \(^{14}\)N\(^{16}\)O\(^{18}\)O desorption signal (46 amu), in accordance with its isotopomeric abundance. The inset of Figure 4 shows the TPD spectrum of DNO\(_2\) thus obtained, along with a NO\(_2\) spectrum recorded at 46 amu. They show that the desorption temperature of DNO\(_2\) (130–160 K) is somewhat higher than the NO\(_2\) desorption of NO\(_2\) on a D\(_2\)O-ice film. The intensity ratio of CsDNO\(_3\)\(^+\) to Cs(NO\(_2\))\(^+\) is also plotted (•). CsNO\(_2\)\(^+\) and CsN\(_2\)O\(_4\)\(^+\) signals were measured at the sample temperature 90 K, and the CsDNO\(_3\)\(^+\) signal was measured at 140 K. The lines are for an eye guide only.

\(\theta(\text{NO}_2)\), which illustrates the semiquantitative nature of NO\(_2\) adsorbate detections by RIS and TPD methods. The CsDNO\(_2\)\(^+\) intensity increased with \(\theta(\text{NO}_2)\) up to 1.0 ML but then decreased at higher levels of \(\theta(\text{NO}_2)\). Also shown in the figure is the ratio of the CsDNO\(_2\)\(^+\) and CsNO\(_2\)\(^+\) signal intensities. This ratio continuously decreased with increasing \(\theta(\text{NO}_2)\) over the entire range of the investigation (the bend at \(\theta = 1.0\) ML is due to the fluctuation in this particular data set, not a general trend). The DNO\(_2\)/NO\(_2\) ratio indicates the conversion efficiency of NO\(_2\) adsorbates into DNO\(_2\). Therefore, it reveals that NO\(_2\) hydrolysis occurs more efficiently at a lower NO\(_2\) coverage. The CsN\(_2\)O\(_4\)\(^+\) signal is undetectably small for \(\theta(\text{NO}_2)\) < 1.0 ML, and its intensity increases with NO\(_2\) coverage for \(\theta(\text{NO}_2)\) > 1.0 ML. The inverse correlation between the population changes of DNO\(_2\) and N\(_2\)O\(_4\) suggests that N\(_2\)O\(_4\) is not a precursor to DNO\(_2\) in the reaction, and vice versa.
The amount of DNO$_2$ desorption rapidly increased with \(\theta\) (NO$_2$) from 0 to 1.2 ML, but the increase slowed down at higher NO$_2$ coverage. These estimates indicate that a large portion of surface DNO$_2$ species is desorbed as DNO$_2$ gas upon the heating of the sample, without undergoing further surface reactions.

We can summarize the key observations of the RIS and TPD experiments as follows. (i) The hydrolysis of NO$_2$ on an ice surface produces nitrous acid as a major product at 140 K. A nitrous acid product is formed regardless of whether NO$_2$ coverage is small or multilayer, yet the conversion efficiency of NO$_2$ into nitrous acid is higher at lower NO$_2$ coverage. (ii) A large portion of surface nitrous acids desorb intact at a high temperature. (iii) At high temperatures, nitric acid is produced in small amounts. (iv) NO$_2$ and N$_2$O$_4$ species are formed only when a NO$_2$ multilayer exists on the ice film at 90 K. Nitrous acid is not formed under these conditions, and the surface populations of nitrous acid and N$_2$O$_4$ exhibit inverse correlation as a function of NO$_2$ coverage. Combined together, these observations provide clear evidence that NO$_2$ hydrolysis occurs through the interaction between isolated NO$_2$ adsorbates and water molecules on the ice surface, rather than through the formation of N$_2$O$_3$ or N$_2$O$_4$ intermediates. The efficiency of nitrous acid formation is not enhanced but decreased by the presence of additional NO$_2$ molecules near the reaction sites.

An important feature of NO$_2$ hydrolysis on the ice surface is that it requires only a small activation energy, which is evidenced by the efficient nitrous acid formation at a low temperature (140 K). Apparently, the ice surface provides an efficient reaction pathway for nitrous acid formation. On the other hand, NO$_2$ hydrolysis is difficult to occur in the gas phase and requires a substantially high activation energy (\(\sim 120\) kJ mol$^{-1}$).

Figure 4 shows the TPD peak areas of DNO$_2$ as a function of NO$_2$ coverage for 0.15–6.5 ML on a D$_2$O-ice film. The inset displays the TPD spectra of NO$_2$ (dashed line) and DNO$_2$ (solid line) measured on the ice film at \(\theta\) (NO$_2$) = 0.8 ML. The temperature ramping rate in TPD was 0.5 K s$^{-1}$.

The observation is informative for understanding the NO$_2$ hydrolysis mechanism in its early stage, where the reaction occurs only to the formation of nitrous acid and nitric acid is not yet formed. A plausible reaction mechanism in this stage may be

$$\text{NO}_2 + \text{D}_2\text{O-ice} \rightarrow \text{NO}_2 - (\text{D}_2\text{O})_n\text{complex} \rightarrow \text{DONO}(\text{D}_2\text{O})_n - 1\text{OD}$$

(2)

NO$_2$ adsorption on the ice surface forms a NO$_2$–water complex first, and then it is converted into a “nitrous acid” structure at 140 K. In molecular details, however, the reaction mechanism is expected to be more complex than expressed by these simple chemical formulas. For instance, nitrous acid and hydroxyl radical may not form as isolated molecular species as written in this equation, but actually, they may be a part of a larger molecular structure connected through hydrogen bonds on the ice surface. The reaction is driven in such an extended molecular system by hydrogen-bonding interactions and proton (or H atom) transfers between NO$_2$ and water molecules.

The present study may have the following implications for the atmospheric chemistry of NO$_2$. Considering that NO$_2$ hydrolysis is efficient on cold ice surfaces, it is expected that the corresponding reaction will readily occur under atmospheric conditions at the surfaces of water films, aerosols, and icy particles. There seems to be no critical factor that will, in principle, prevent the occurrence of the reaction on these surfaces at ambient temperatures, which offer higher molecular mobility, solvation efficiency, and thermal energy than the cold ice surface environment of the present experiment. Since the reaction has a very small activation energy, it can easily occur with thermal energy in the absence of any extra energy input, such as the absorption of sunlight. Therefore, nitrous acid gas is expected to be produced efficiently during the night time by the heterogeneous hydrolysis of NO$_2$ on the surfaces of condensed atmospheric moisture, in accordance with measurements taken during field observations. The early stage hydrolysis mechanism of NO$_2$ suggested here, the reaction between an isolated NO$_2$ molecule and water, agrees with the kinetic observations of laboratory studies.
that nitrous acid formation is first-order in both NO₂ and water vapor concentrations. If this mechanism is efficient in the atmosphere, it will not be necessary to consider alternative complex mechanisms such as those involving N₂O₄ intermediates. It is very difficult to build up a significant amount of N₂O₄ population at the gas–water interface or in its interior due to low concentrations of NO₂ in the atmospheric conditions. Finally, the facile, intact desorption of nitrous acid from ice surfaces strengthens the possibility that the heterogeneous hydrolysis of NO₂ is an important source of nitrous acid gas in the atmosphere.

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