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LETTERS

Enhancement of N_2O_4 on Porous Glass at Room Temperature: A Key Intermediate in the Heterogeneous Hydrolysis of NO_2?

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The heterogeneous hydrolysis of NO_2 at surfaces in the atmosphere is believed to be a significant source of HONO, a key OH precursor in urban areas. However, the mechanism of this reaction is not known. The uptake of 2.9 Torr of NO_2 in N_2 at a total pressure of 508 Torr on a porous glass surface with varying amounts of surface-adsorbed water was studied using FTIR at 294 K. The ratio of N_2O_4 to NO_2 was enhanced on the glass surface relative to the gas phase. On a relatively dry surface, the formation of surface-adsorbed HNO_3 was observed over a period of ∼20 h, likely due to the reaction with small amounts of water on the surface. Gas-phase NO and N_2O were also generated. When larger amounts of water were initially present on the surface, surface-adsorbed HNO_3 was formed immediately, as well as gas-phase NO, N_2O, and HONO. Although the NO_2 concentrations used in the present studies are much larger than those found in the atmosphere, this work suggests that N_2O_4 should be considered as a key intermediate in the heterogeneous hydrolysis of NO_2 to form HONO.

Introduction

Oxides of nitrogen play key roles in the chemistry of the troposphere and stratosphere.[1] While the gas-phase chemistry of species such as NO and NO_2 is reasonably well-known, heterogeneous reactions occurring on surfaces are not well understood. For example, the hydrolysis of NO_2 on surfaces

$$2NO_2 + H_2O \xrightarrow{\text{surface}} HONO + HNO_3 \qquad (1)$$

was proposed some 16 years ago to explain the formation of HONO observed when NO_2 was injected into large environmental chambers in the presence of water vapor,[2,3] which was confirmed in a number of subsequent studies.[4−9] This is important because HONO is believed to be the major source of OH in many urban areas at dawn.[10,11] However, despite almost two decades of work in this area, its formation by reaction 1 is not included in airshed models because the mechanisms and kinetics are not sufficiently well understood. For example, while HONO has been observed in the gas phase, the corresponding amount of HNO_3 shown in reaction 1 has not. The reason has been proposed to be that HNO_3, which is notoriously “sticky”, remains adsorbed on the surface. This is consistent with the observations of nitrate in washings of the surface postreaction,[4] and with a very recent observation[12] of the formation of adsorbed HNO_3 on the surface of hydrated silica particles.

Silica surfaces such as powders or porous glass are known to hold adsorbed water readily because of their polar surface −Si−OH groups.[13] While this adsorbed water can be removed by heating under vacuum, and indeed the surface can be dehyroxylated at sufficiently high temperatures, heating at lower temperatures leaves adsorbed water on the surface. As a result, such surfaces can be used as supports for water to study surface reactions involving water. For example, Grassian and coworkers[12] recently reported studies of reaction 1 using silica powders.

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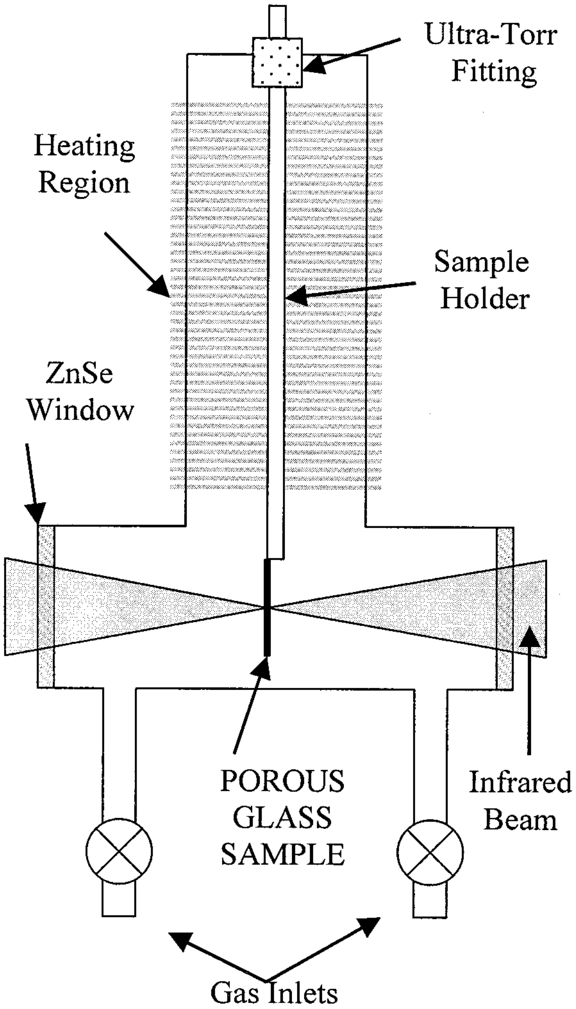

Figure 1. Schematic diagram of the cell. The path length for the infrared beam through the cell is 6.7 cm.

We report here FTIR studies of the uptake of NO_2 on porous glass at room temperature and show that adsorbed NO_2 exists preferentially in the form of the dimer, N_2O_4. In the presence of water on the surface, surface-adsorbed HNO_3 is formed and detected directly by FTIR. Possible atmospheric implications are discussed.

Experimental Section

Figure 1 is a schematic diagram of the reaction cell. It is made of borosilicate glass and has ZnSe windows at each end, providing a 6.7 cm path length for the infrared beam. The porous glass is held at the end of a positioning rod and can be withdrawn into the sidearm for heating and for obtaining the infrared spectrum of the gases alone. With the porous glass sample in the infrared beam, the spectrum of both the surface species and the gases is recorded. Spectra of the surface species are obtained by ratioing the single-beam spectra of the porous glass before and after addition of the NO_2 and subtracting a gas-phase spectrum recorded with the glass raised. Gas-phase spectra are recorded approximately 2 min before and after the glass spectrum, and the amount subtracted is determined by interpolation. Even during the fastest part of the NO_2 decay, the absorbance difference between the two gas-phase spectra was never more than 5%. Spectra were recorded as 64 co-added scans at 0.5 cm^{-1} resolution at pressures between 500 and 700 Torr of N_2.

Porous glass transmits infrared radiation well above ~2000 cm^{-1}; however, it drops off rapidly at lower wavenumbers.[13] Commercially available porous glass plates are too thick (~1 mm) to transmit in the region of interest from 1800 to 1500 cm^{-1}. To obtain sufficiently thin plates for these experiments, a plate of porous glass (Corning) approximately 1 mm thick was further etched by immersion in a 7.7% (v:v) HF solution for 21 min to a thickness of ~0.3 mm. This was found to be the maximum thickness at which usable spectra in the 1800–1500 cm^{-1} region could be obtained. The plate was then rinsed in Nanopure water and dried in an oven for 1 h at 120 °C. The plate was then mounted on the holder and inserted into the cell. For those experiments in which the porous glass was heated prior to exposure to NO_2, the cell was evacuated and heated from the outside for 35 min at 280 °C and then cooled to room temperature before gases were added. When the plates are left in air over a period of time, they adsorb gaseous organics, which were removed by heating in air at 800 °C for 1 h.

NO_2 was synthesized by mixing in a 5 L bulb excess O_2 (Oxygen Service Company, 99.993%) with NO (Matheson, 99%) which had been passed through a trap at 196 K to remove impurities such as HNO_3. The N_2 was Ultrahigh Purity Grade (>99.999%, Oxygen Service Company). Gaseous HNO_3 used for reference spectra was obtained using the vapor above a 1:2 (v:v) mixture of HNO_3 (Fisher, 70%, 15.8 M) and H_2SO_4 (Fisher, 95.7%, 18 M).

Results and Discussion

Figure 2a shows the gas-phase spectrum when 2.9 Torr of NO_2 is added to the cell, along with N_2, to a total pressure of 508 Torr at room temperature. Strong peaks in the 1600–1650 cm^{-1} region are due to NO_2. The smaller peak at ~1750 cm^{-1} is due to the dimer, N_2O_4, which is in equilibrium with NO_2. Using the equilibrium constant[14] $K_p = 2.5 \times 10^{-19}$ cm^3 $molecule^{-1}$ for the reaction

$$2NO_2 \leftrightarrow N_2O_4 \qquad (2,-2)$$

the concentrations of N_2O_4 and NO_2 under these conditions are 2×10^{15} and 9×10^{16} molecules cm^{-3}, respectively.

Figure 2b shows the spectrum of the surface-adsorbed plus the gas-phase species. Figure 2c shows the difference between Figure 2b and 2a, i.e., the spectrum of the adsorbed species present at approximately the same time that the gas-phase spectrum in Figure 2a was obtained. The band due to adsorbed N_2O_4 at 1740 cm^{-1} is clearly seen, while that due to NO_2 is not evident. (Porous glass absorbs particularly strongly between 1610 and 1660 cm^{-1}; imperfect subtractions in such regions are common when such strong bands are ratioed or subtracted.)[15]

Figure 2d shows the spectrum of the adsorbed species 20 h later. There is a new absorption centered at ~1680 cm^{-1}. The assignment of this band to HNO_3 is confirmed by a reference spectrum (Figure 2e) in which a clean plate of porous glass was exposed to 0.57 Torr of gaseous HNO_3 for 5 min. The gaseous HNO_3 was pumped away before the reference spectrum was taken. The relatively small change in the surface-adsorbed N_2O_4 peak while that due to HNO_3 is increasing is likely due to replenishment of the N_2O_4 from the gas phase during the run.

Figure 3 shows the results of a similar experiment but where the porous glass plate had been left exposed to room air overnight and was then was used without prior heating. In room air, the porous glass takes up large amounts of water. For example, a peak at 5260 cm^{-1} was observed due to surface-adsorbed water[13] for this sample, but not for that used for the experiments in Figure 2. Figure 3a shows the spectrum of the

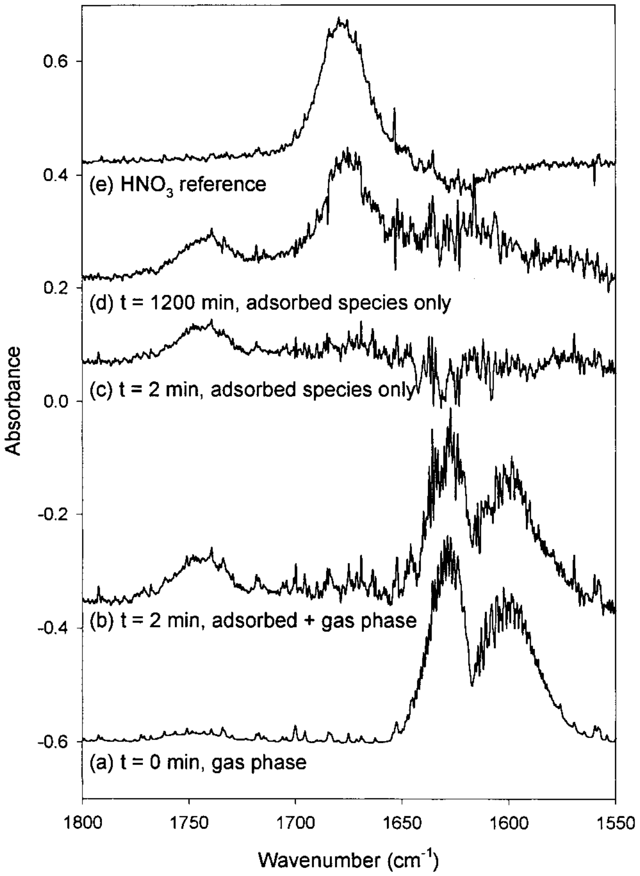

Figure 2. FTIR spectra of 2.9 Torr of NO_2 in N_2 (total pressure 508 Torr) (a) gas-phase only, (b) gas-phase plus surface-adsorbed species, (c) subtracted spectrum (b − a) showing the spectrum due to the adsorbed species, and (d) same as (c) but 20 h later; (e) reference spectrum of HNO_3 adsorbed on porous glass; 0.57 Torr of HNO_3 was added to the cell for 5 min and then pumped away before recording the spectrum. The porous glass had been heated under vacuum before the exposure to NO_2. All spectra are on the same scale.

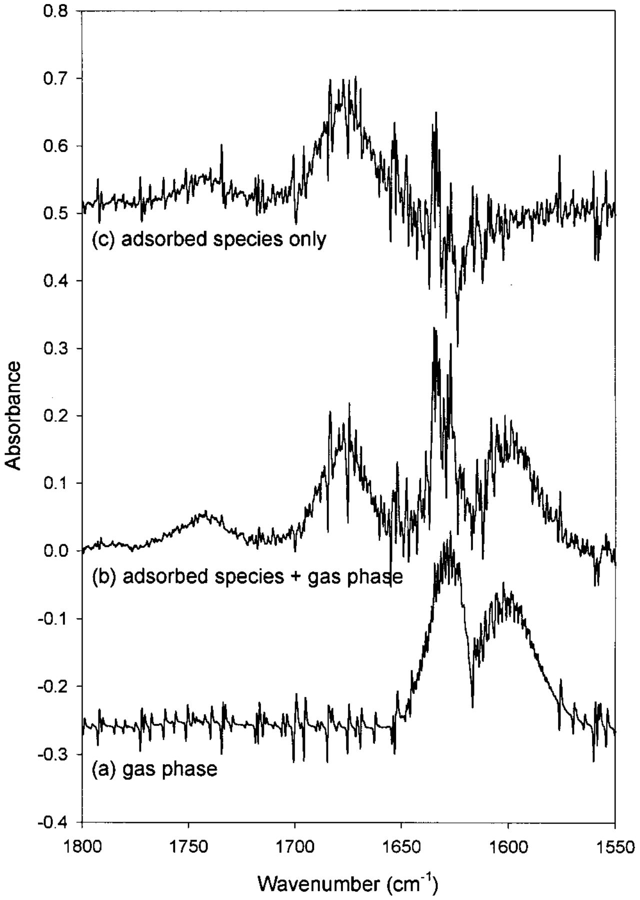

Figure 3. FTIR spectra of 3.3 Torr of NO_2 in N_2 (total pressure 573 Torr) (a) gas-phase only, (b) gas-phase plus surface-adsorbed species, (c) subtracted spectrum (b − a) showing the spectrum due to the adsorbed species. The porous glass was not heated to remove adsorbed water prior to exposure to NO_2.

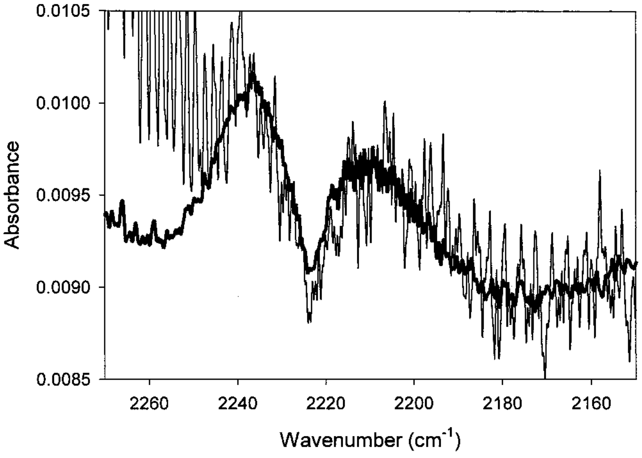

Figure 4. Gas-phase spectrum taken under the same experimental conditions as Figure 2d. The heavy line is a reference spectrum of gas-phase N_2O. Other absorptions are due to CO_2 outside the cell.

gas, Figure 3b shows that of the gas plus adsorbed species, and Figure 3c shows the difference, all recorded immediately after introduction of NO_2 into the cell. In contrast to the relatively “dry” porous glass in Figure 2c, the HNO_3 absorption is much larger than that of N_2O_4 on the surface, suggesting that reaction with the water on the surface to form HNO_3 has occurred even at the shortest reaction times.

In the gas phase, N_2O and NO were observed as reaction products under all conditions and in the “wet” case, HONO was also observed. For example, Figure 4 shows the gas-phase spectrum in the 2200 cm^{-1} region taken at about the same time as that in Figure 2d. Superimposed on the narrow rotational bands of CO_2 (due to changes in purging of the air in the light beam) is a set of broad peaks, which can be seen by comparison to a reference spectrum (shown by the heavy line) to be due to gaseous N_2O, which increases linearly with time. The concentration after 1200 min is 2×10^{16} molecules cm^{-3}, compared to a loss of NO_2 of $\sim 7 \times 10^{16}$ molecules cm^{-3} during this period. NO first increases and then decreases, with a peak concentration of $\sim 2.5 \times 10^{16}$ molecules cm^{-3} after 200 min and 1×10^{16} molecules cm^{-3} at 1200 min.

Figure 5 shows the gas-phase spectrum in the 1250 cm^{-1} region during the experiment using “wet” glass in Figure 3. When the peak due to gaseous N_2O_4 is subtracted, a small band at 1263 cm^{-1} is detectable, which by comparison to a reference spectrum[16] (shown by the heavy line) is due to gaseous HONO at a concentration of $\sim 1 \times 10^{15}$ molecules cm^{-3}. In experiments where the porous glass had been heated under vacuum to remove surface water prior to introducing NO_2, gas-phase HONO was not observed, even at similar levels of NO_2 loss. HONO has been observed in other studies[17,18] to be a precursor to N_2O. However, the yield of N_2O we observed was not significantly affected by the amount of water on the porous glass, i.e., whether HONO was observed in the gas phase. This suggests that either HONO is not formed on the “dry” surface and there is more

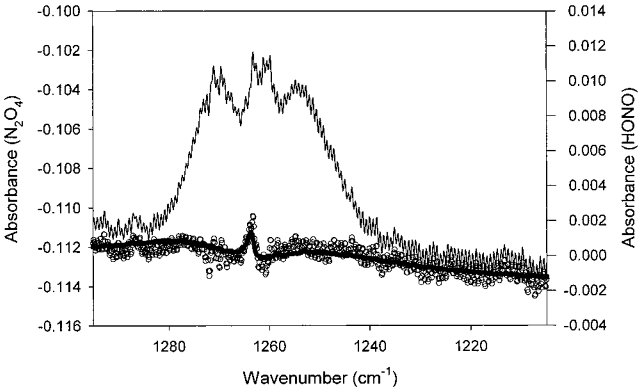

Figure 5. Gas-phase spectrum taken under the same experimental conditions as in Figure 3. The open circles show the spectrum remaining after the contribution of N_2O_4 has been subtracted out, and the heavy line is a reference spectrum of gaseous HONO.

than one path to N_2O formation, or that HONO remains adsorbed on the dry surface. The NO and N_2O concentrations measured at these short reaction times were $\sim 3 \times 10^{16}$ molecules cm^{-3} and 5×10^{15} molecules cm^{-3}, respectively, and hence were again the major gas-phase products.

In short, when water is present on the porous glass surface, NO, N_2O, and HONO are formed at the same time that HNO_3 is generated on the surface. It should be noted that this chemistry is likely occurring on all of the surfaces of the reaction cell, not just the porous glass surface. However, "blank" runs in which NO_2 was followed with time in the cell in the absence of the porous glass showed that the loss of NO_2 was much smaller ($\sim$7% compared to 52% loss over 200 min), indicating that most of the chemistry observed was heterogeneous. In the "blank" runs, the only gas-phase product observed was NO.

Grassian and co-workers[12] recently reported studies of the interaction of NO_2 with dry and hydrated silica particles, respectively. Adsorbed HNO_3 was observed on the hydrated powders and N_2O_4 on both dry and hydrated powders, similar to the observations on porous glass reported here. Gaseous N_2O was not reported.

N_2O_4 has also been observed as an intermediate on the surface of ice at 86 K after exposure to NO_2,[19] and upon heating, generates HONO and HNO_3 among other products. The formation of N_2O_4 on the ice surface is not unexpected, given that the equilibrium (2, −2) will shift to the right at lower temperatures. However, the results presented here suggest that N_2O_4 is also an important intermediate at room temperature on other types of surfaces such as glass.

N_2O_4 in solution and at low temperatures is known[20−24] to isomerize and autoionize to $NO^+NO_3^-$. Reaction of this ionic form with water may then generate HONO + HNO_3, in a manner similar to that proposed for the N_2O_5 hydrolysis on ice surfaces.[25] For example, Choi et al.[26] have reported that NO^+ in clusters with gas-phase water containing more than four water molecules reacts to form HONO. HONO undergoes a self-reaction[27] to form N_2O_3:

$$2HONO \leftrightarrow N_2O_3 + H_2O \qquad (3,-3)$$

N_2O_3 is known to decompose to NO + NO_2. Hence, formation of HONO followed by reaction 3 on the porous glass surface and decomposition of the N_2O_3 may be at least partially responsible for the NO observed in our system. Consistent with this, HONO has been observed to decompose into NO + NO_2 in a glass smog chamber.[28] We propose that a minor reaction path in the N_2O_3 decomposition on the surface producing N_2O + O_2 may be responsible for the observed N_2O production. ΔH_{rxn} for the gaseous decomposition of N_2O_3 to NO + NO_2 is +9.7 kcal mol^{-1}, compared to −0.2 kcal mol^{-1} to produce N_2O + O_2; such reactions which are not highly exothermic are often found to be surface-catalyzed.

Whether this mechanism involving enhanced N_2O_4 concentrations on the surface and its isomerization and autoionization followed by reaction with water also applies in the atmosphere at the much smaller concentrations is not clear. Certainly the gas-phase N_2O_4 concentrations in equilibrium with atmospheric levels of NO_2 (<0.1 ppm generally) are much smaller than those in the present studies. Previous studies[2−8] of the formation of HONO in laboratory systems from the heterogeneous reaction of NO_2 at ppm concentrations have established that the reaction is first-order in NO_2. This is inconsistent with a direct reaction of gas-phase N_2O_4, which would be second-order. Various reaction schemes have been proposed. For example, a stepwise reaction involving a slow adsorption of NO_2 at the surface followed by a rapid reaction of two surface-adsorbed NO_2 with water has been proposed.[3] The uptake of NO_2 on liquid water[29] is known to be slow. Alternatively, a fast adsorption of NO_2 on the surface followed by slower reactions of intermediate species have been suggested.[3,9] Surface-adsorbed N_2O_4 may be a key short-lived intermediate in such mechanisms.

Summary

The ratio of N_2O_4 to NO_2 is enhanced on porous glass surfaces at room temperature, relative to that in the gas phase. Surface-adsorbed HNO_3 is also generated, at short reaction times on a "wet" surface and at longer reaction times on relatively dry surfaces. Production of HONO is observed simultaneously in the gas phase when there is water initially present on the surface, and NO and N_2O are also produced in both cases. These results suggest that N_2O_4 at the interface may be a key intermediate in the heterogeneous reaction 1 of NO_2 to form gaseous HONO and surface-adsorbed HNO_3.

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