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1. INTRODUCTION

Heterogeneous production of gaseous nitrous acid (HONO) has been observed for decades in a variety of laboratory systems containing NO₂ and water. Although the stoichiometry of the hydrolysis reaction is generally represented by reaction (1), the mechanism is not well understood.



Hydrolysis of NO₂ is believed to be a significant source of HONO, especially at night (e.g. *Calvert et al.*, 1994; *Harrison et al.*, 1996; *Lammel and Cape*, 1996; *Lammel*, 1999). Several studies have shown that HONO is a major source of OH in urban areas not only at sunrise, but even when averaged over the full day (*Winer and Biermann*, 1994; *Harrison et al.*, 1996; *Alicke et al.*, 2002; *Stutz et al.*, 2002). Since oxidation of organics by OH leads to formation of ozone and other pollutants, an accurate understanding of reaction (1) is essential to determine its effects on air pollution and to develop effective control strategies. In addition to its atmospheric impacts, HONO has direct and indirect adverse health effects (*Pitts et al.*, 1978; *Rasmussen et al.*, 1995).

There are recent intriguing reports of photochemical HONO production from Arctic snow exposed to sunlight or artificial light ($\lambda > 280$ nm) (*Zhou et al.*, 2001; *Dibb et al.*, 2002) and from a sunlight-exposed glass sampling tube used to sample rural ambient air (*Zhou et al.*, 2002). *Zhou et al.* (2002) proposed that a layer of hydrated nitric acid present on the sampling tube walls photolyzes primarily to OH and NO₂, which undergoes hydrolysis via reaction (1). While the mechanisms of these reactions are not yet clear, they do appear to require sunlight. The rates of HONO production observed may have the potential to impact OH and HO₂ levels.

We present laboratory studies of NO₂ hydrolysis which have led us to propose a mechanism for the reaction of NO₂ with water films. The experiments described here were performed on borosilicate glass surfaces as (i) it provides an important first step in understanding the mechanism as studied in previous

laboratory systems and (ii) silicates are an important atmospheric component in the urban boundary layer such as building materials, soils, and dust particles (*Gillette*, 1997; *BNZ Materials*, 1999a,b; *USGS*, 1999). The mechanism proposed to occur on silica surfaces is consistent with many of the common observations from previous laboratory studies of gaseous NO₂ and water vapor in the presence of solid surfaces such as glass, quartz, Teflon, and Teflon-coated chambers. Some of the common observations are as follows:

- (a) While the major gas phase product is HONO, significant amounts of NO have also been observed (*England and Corcoran*, 1974; *TenBrink et al.*, 1978; *Sakamaki et al.*, 1983; *Pitts et al.*, 1984; *Svensson et al.*, 1987; *Wainman et al.*, 2001) and smaller amounts of N₂O have been reported (*Wiesen et al.*, 1995; *Kleffmann et al.*, 1998a,b). The yield of HONO is usually less than the 50% expected from the stoichiometry of reaction (1) (*England and Corcoran*, 1974; *TenBrink et al.*, 1978; *Sakamaki et al.*, 1983; *Pitts et al.*, 1984, 1985; *Svensson et al.*, 1987; *Jenkin et al.*, 1988; *Perrino et al.*, 1988; *Wiesen et al.*, 1995; *Kleffmann et al.*, 1998a,b; *Wainman et al.*, 2001).
- (b) In most studies, the rate of HONO formation is reported to be first order in NO₂ (*Sakamaki et al.*, 1983; *Pitts et al.*, 1984; *Svensson et al.*, 1987; *Jenkin et al.*, 1988; *Perrino et al.*, 1988; *Febo and Perrino*, 1991; *Wiesen et al.*, 1995; *Harrison and Collins*, 1998; *Kleffmann et al.*, 1998a,b) and first order in water vapor (*England and Corcoran*, 1974; *Sakamaki et al.*, 1983; *Pitts et al.*, 1984; *Svensson et al.*, 1987; *Jenkin et al.*, 1988; *Perrino et al.*, 1988; *Febo and Perrino*, 1991; *Bambauer et al.*, 1994; *Mertes and Wahner*, 1995; *Wiesen et al.*, 1995; *Harrison and Collins*, 1998; *Kleffmann et al.*, 1998a,b).
- (c) Nitric acid is not observed in the gas phase, but nitrate ion has been measured after rinsing the reaction chamber surface (*Svensson et al.*, 1987; *Febo and Perrino*, 1991), and undissociated nitric acid has been observed on silica surfaces exposed to NO₂ and water (*Goodman et al.*, 1999; *Barney and Finlayson-Pitts*, 2000).
- (d) The reaction rates in clean chambers are higher than in chambers contaminated by previous experiments ("conditioned" chambers) (*Pitts et al.*, 1984; *Svensson et al.*, 1987).

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- (e) The reaction rates in conditioned chambers do not depend heavily on the nature of the underlying surfaces.
- (f) The use of isotopically labeled water, H_2^{18}O , leads to formation of H^{18}ONO at relative humidities of ~15 – 40% (Sakamaki *et al.*, 1983; Svensson *et al.*, 1987).

The major features of the proposed mechanism are first outlined briefly below, followed by a description of the experimental results which support this mechanism.

2. FEATURES OF THE PROPOSED MECHANISM OF HONO PRODUCTION

The major steps of the proposed mechanism are described briefly here and are shown in Figure 1.

- N_2O_4 is an important surface species in the reaction.
- The symmetric form of N_2O_4 isomerizes on the surface to asymmetric ONONO_2 . A fast back reaction occurs between ONONO_2 and gaseous NO_2 to reform the symmetric N_2O_4 .
- Asymmetric ONONO_2 autoionizes to form nitronium nitrate, NO^+NO_3^- , which reacts with water to form HONO and HNO_3 .
- The HNO_3 remains on the surface and generates NO_2^+ , which is known to exist in concentrated solutions of HNO_3 .
- The reaction of HONO with NO_2^+ is proposed to yield nitric oxide.

We describe in the next section our experimental evidence for the proposed mechanism and support from previous studies.

3. PRESENT AND PAST EXPERIMENTAL EVIDENCE

3.1 Products, Intermediates, and Mass Balance

3.1.1 Gas Phase Products. Gaseous product formation from heterogeneous NO_2 hydrolysis experiments was studied in this laboratory using long path FTIR with two borosilicate glass long path cells with White optics (White, 1942). Experiments were carried out by adding a few Torr of a dilute NO_2/N_2 mixture to the cell and bringing the cell to atmospheric pressure using an appropriate combination of flows of dry and humid N_2 to reach the desired relative humidity (RH). Experiments were performed using initial NO_2 levels of 10 – 100 ppm at 20%, 50%, and 80% RH. The first cell has a volume of 7.4 L and a surface-to-volume ratio of $\text{S/V}=70 \text{ m}^{-1}$ including optics and mounts. Its base path is 0.8 m with a total path length of 32 m used here. The second cell is 19.4 L with $\text{S/V}=46 \text{ m}^{-1}$ including optics and mounts. Its base path is 1.0 m with

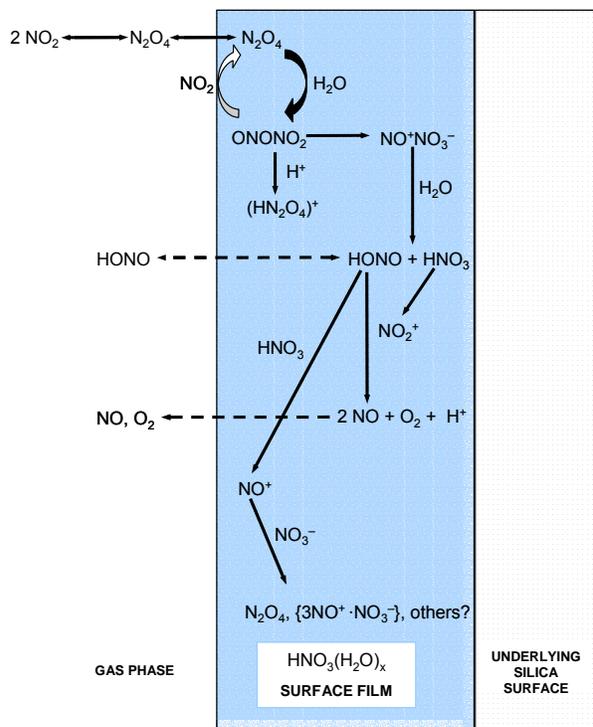


Figure 1. Major steps in the proposed mechanism of heterogeneous NO_2 hydrolysis.

a total path length of 84 m or 112 m. The metal mounts were coated with halocarbon wax (Halocarbon Products, Inc., Series 1500) to prevent reactions on the metal surfaces. All experiments were carried out at $296 \pm 2 \text{ K}$.

Gaseous reactants and products were measured by FTIR in the dark for up to 15 hours. Typical plots of concentration versus time for three different relative humidities are shown in Figure 2a-c. The yields of each gaseous product were measured as a function of time and are shown in Fig. 2d-f. The yield of HONO is much less than 50% of the NO_2 loss, especially at longer times where secondary chemistry is significant. While HONO is indeed a major product initially, NO becomes the major product at longer reaction times, and N_2O is a minor product at higher RH and longer reaction times. The yields of all gas phase species (Fig. 2d-f) total ~50% of the NO_2 loss, consistent with the overall reaction (1) stoichiometry. This suggests that NO and N_2O are formed from secondary reactions of HONO. Scatter in the yield plots at early reaction times is due to the low concentrations of products and the small changes in NO_2 concentration at these early times (Finlayson-Pitts *et al.*, 2002).

3.1.2 Surface Species. Exposure of silica surfaces to gaseous NO_2 at room temperature is known to result in the immediate formation of surface N_2O_4 , as observed by infrared spectroscopy (Goodman *et al.*, 1999; Barney and Finlayson-Pitts, 2000). However,

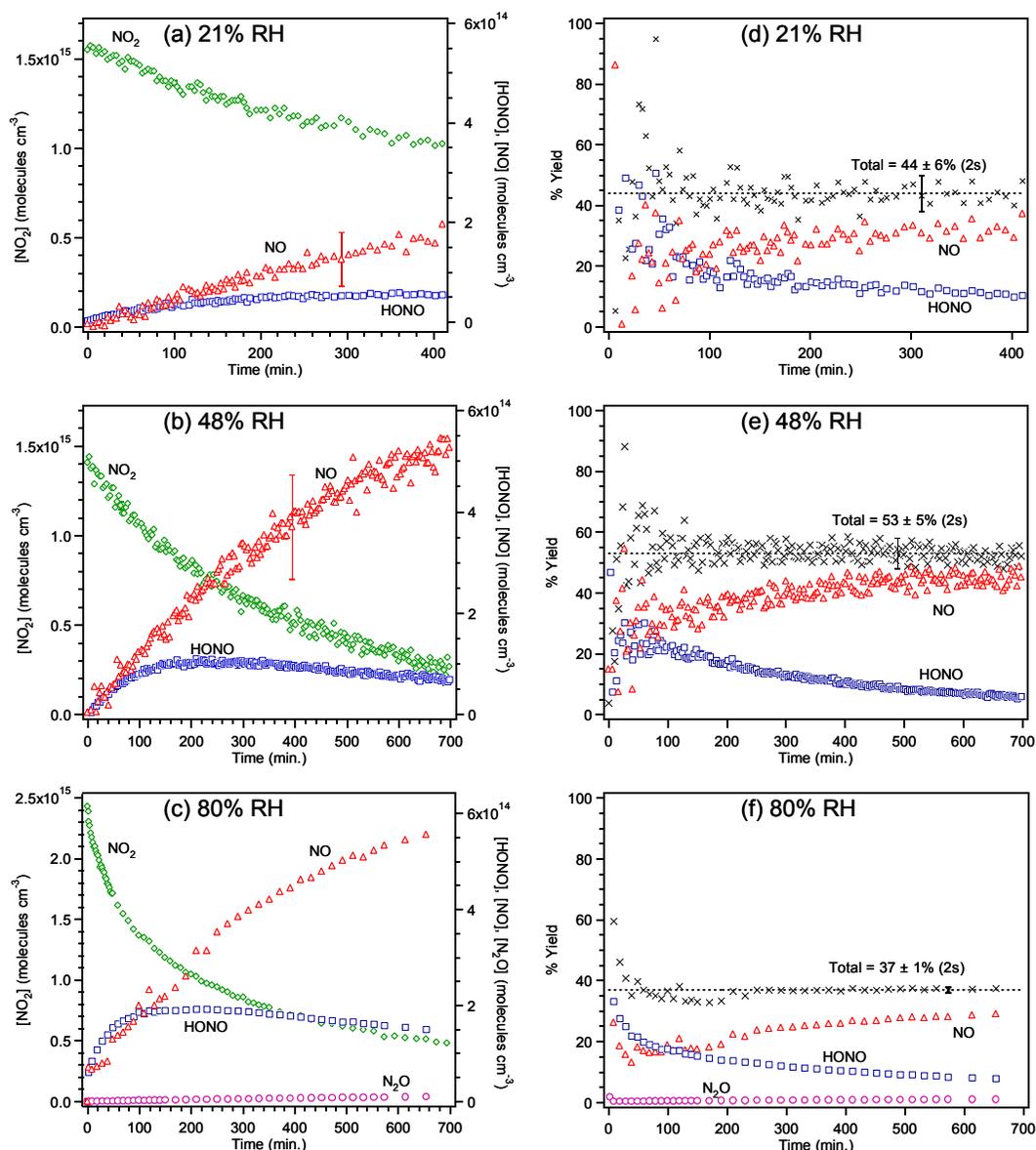


Figure 2. Concentration-time profiles for NO_2 hydrolysis experiments in long path cells in this laboratory at (a) 21% RH, $[\text{NO}_2]_0 = 1.5 \times 10^{15}$ molecules cm^{-3} , 7.4 L cell (b) 48% RH, $[\text{NO}_2]_0 = 1.4 \times 10^{14}$ molecules cm^{-3} , 7.4 L cell (c) 80% RH, $[\text{NO}_2]_0 = 2.5 \times 10^{15}$ molecules cm^{-3} , 19.4 L cell. The corresponding yields of gas phase HONO, NO, and N_2O relative to the loss of NO_2 are shown in (d) – (f).

how the N_2O_4 interacts with the surface film, for example by hydrogen-bonding with water (Chou *et al.*, 1999) or with nitric acid present on the surface, is unknown. To investigate the effect of surface HNO_3 on N_2O_4 , transmission FTIR spectroscopy was performed using a small, borosilicate glass cell (~100 mL) containing a porous glass plate (Vycor 7930) with and without surface HNO_3 . The glass plate had been exposed to room air and hence held adsorbed water prior to placing it in the cell. The plate was treated three times with dry HNO_3 vapor followed by pumping to remove HNO_3 vapor, leaving surface HNO_3 on the

glass. The “conditioned” porous glass was then exposed to 1.2 Torr gaseous NO_2 . Figure 3a shows the spectrum taken after adding N_2 to 1 atm. The peak at 1680 cm^{-1} is due to undissociated HNO_3 and that at 1740 cm^{-1} is surface N_2O_4 . For comparison, a clean porous glass plate was exposed to approximately the same amount of NO_2 without prior conditioning of the glass with HNO_3 . Figure 3b shows the resulting spectrum (the HNO_3 present at 1680 cm^{-1} was formed from reaction of $\text{NO}_2/\text{N}_2\text{O}_4$ with the water on the glass). Fig. 3c is the difference spectrum (a-0.92b) with the slight difference in NO_2 pressure taken into account.

These experiments show that the amount of N_2O_4 formed on the porous glass surface increases with the presence of surface HNO_3 . This suggests that N_2O_4 interacts with HNO_3 on the surface.

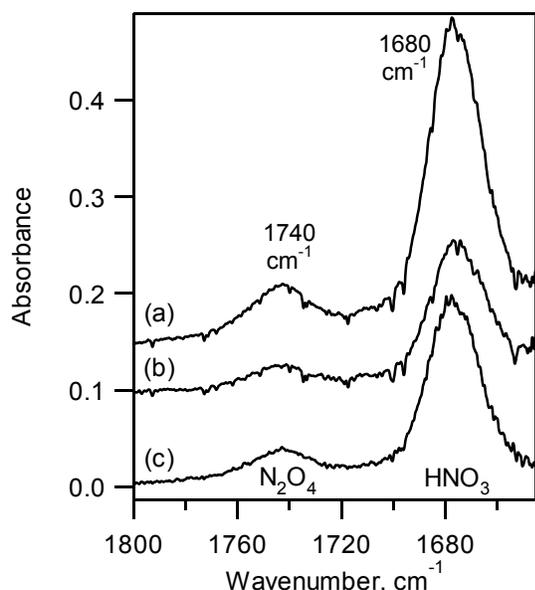


Figure 3. Transmission FTIR spectra of porous glass plate (a) in the presence of surface HNO_3 with 1.2 Torr NO_2 added, (b) in the absence of surface HNO_3 with 1.3 Torr NO_2 added, and (c) difference: (a) - 0.92(b). All spectra were taken at 1 atm in N_2 at 296 ± 1 K.

Our mechanism proposes that asymmetric ONONO_2 autoionizes and is the reactive species in HONO formation. Isomerization of N_2O_4 to asymmetric ONONO_2 is known to occur in solid matrices, on ice, and in solution (Addison, 1980; Bolduan and Jodl, 1982; Agnew et al., 1983; Bolduan et al., 1984; Jones et al., 1985; Givan and Loewenschuss, 1989a,b, 1990a,b, 1991a,b; Wang et al., 1998; Wang and Koel, 1998, 1999). This asymmetric form is known to autoionize to nitrosonium nitrate, NO^+NO_3^- . Although asymmetric ONONO_2 has not been observed on surfaces at room temperature, its autoionization and reaction with water to form HONO and HNO_3 are consistent with previous isotope studies of NO_2 hydrolysis. For example, Sakamaki et al. (1983) used H_2^{18}O at ~15 – 40% RH and reported formation of H^{18}ONO only. Reaction of asymmetric ONONO_2 would result in the experimentally observed product, while reaction of symmetric N_2O_4 would not, as shown in Figure 4.

Several studies have reported that the HNO_3 formed from NO_2 hydrolysis remains on the surface (Sakamaki et al., 1983; Pitts et al., 1984; Svensson et al., 1987; Febo and Perrino, 1991) and exists, in part, in the undissociated form (Goodman et al., 1999; Barney and Finlayson-Pitts, 2000) in agreement with observations in Figure 3. It has also been shown in this laboratory that thin films of water present on silica

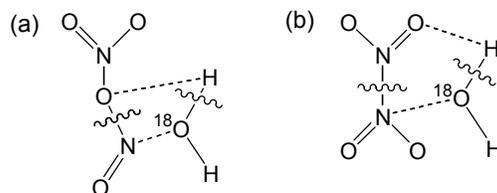


Figure 4. Formation of HONO from reaction of (a) the asymmetric form of ONONO_2 with H_2^{18}O showing the formation of the experimentally observed H^{18}ONO (Sakamaki et al., 1983; Svensson et al., 1987) (b) symmetric N_2O_4 with H_2^{18}O showing formation of unlabeled HONO.

surfaces do not behave as bulk water (Sumner and Finlayson-Pitts, 2002 (Paper No. 1.4); Saliba et al., 2001), thus the undissociated form of HNO_3 is reasonable in such an environment. It is well known that HNO_3 forms hydrates in aqueous solutions (Chédin, 1952; Högfeldt, 1963; Addison, 1980) and on ice (Tolbert and Middlebrook, 1990; Ritzhaupt and Devlin, 1991; Koch et al., 1996; Tisdale et al., 1999; Pursell et al., 2002). Studies of aqueous HNO_3 have shown that as the concentration increases, the form of HNO_3 changes from dissociated ions to nitric acid trihydrate to nitric acid monohydrate, and finally to pure HNO_3 (Chédin, 1952; Högfeldt, 1963; Addison, 1980). In addition, the dihydrate is observed on ice (Tolbert and Middlebrook, 1990; Ritzhaupt and Devlin, 1991; Koch et al., 1996; Tisdale et al., 1999). It has been shown that the trihydrate exhibits a higher degree of dissociation than the monohydrate (Ritzhaupt and Devlin, 1991; Pursell et al., 2002). This is in agreement with theoretical studies which show that four water molecules are required for dissociation of HNO_3 (Kay et al., 1981; Zhang et al., 1994; Gilligan and Castleman, 2001).

Nitric acid hydrates are likely to be present on the reaction chamber walls during NO_2 hydrolysis experiments as well as after evacuating the chamber. In most NO_2 hydrolysis studies, including our own, chambers were not cleaned between each experiment, but rather were evacuated with little or no heating that may remove surface HNO_3 . The presence of a surface film of HNO_3 hydrates may explain the observation that hydrolysis rates do not depend heavily on the underlying surface of the reaction chamber (Finlayson-Pitts et al., 2002).

The effect of pumping on the surface film of HNO_3 hydrates was investigated in additional experiments using porous glass. The porous glass was first heated to 400 K to reduce adsorbed water, then cooled to room temperature and exposed to 10 Torr water vapor in 723 Torr N_2 . A transmission spectrum was obtained and the peaks due to water vapor subtracted, shown in Figure 5a. Adsorbed water appears at 1620 cm^{-1} (bend), 3400 cm^{-1} (stretches), and 5272 cm^{-1} (combination), with a negative peak at 3750 cm^{-1} due to free Si-O-H stretching. The first (top) spectrum in Figure 5b was taken after

similar heating of the porous glass, then exposure to 1.5 Torr HNO₃, and finally addition of 10 Torr water vapor. As seen in Figure 5b, the presence of HNO₃ resulted in a red-shift of the peak at 3400 cm⁻¹ by ~70 cm⁻¹ and the appearance of undissociated HNO₃ at 1680 cm⁻¹. Ab initio calculations have shown that the OH stretch of the HNO₃-H₂O complex is predicted to appear at ~3200 – 3300 cm⁻¹, a red-shift of ~300 – 500 cm⁻¹ relative to HNO₃ alone (Tao *et al.*, 1996; Staikova and Donaldson, 2001; McCurdy *et al.*, 2002). The peak at 3300 cm⁻¹ is therefore believed to be due in part to a complex of nitric acid and water. As pumping was initiated, the peaks at 1620 cm⁻¹, 1680 cm⁻¹, 3300 cm⁻¹ and 5275 cm⁻¹ decreased (Fig. 5b-d), indicating that water, HNO₃, and the HNO₃-H₂O complexes were removed. Figure 5d, however, shows that the peak at 1620 cm⁻¹ decreased faster than that at 1680 cm⁻¹, indicating that water was removed faster while HNO₃ remained. Thus, the composition of the surface film changes upon pumping as water is removed, leaving HNO₃ on the surface.

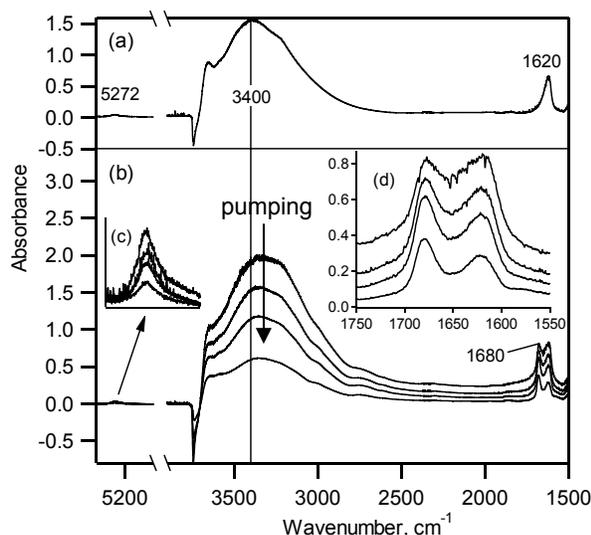


Figure 5. Spectra of porous glass (a) with surface water only, (b) both surface water and HNO₃, and insets showing effect of pumping on (c) surface water and (d) HNO₃, water, and HNO₃-water complexes. Pumping times in (b) – (d) are 0, 5, 10, and 35 s.

The presence of nitronium ion, NO₂⁺, was also identified on the surface of porous glass at room temperature. Figure 6a shows a spectrum of the porous glass, which contained a significant amount of adsorbed water, that was exposed to gaseous NO₂. Comparison of this spectrum to that of porous glass exposed to HNO₃ vapor alone (Fig. 6b) reveals a peak at 2297 cm⁻¹ in both spectra, in agreement with previous reports of NO₂⁺ (Forney *et al.*, 1993; Koch *et al.*, 1995; Agreiter *et al.*, 2001). To verify this assignment, a clean piece of porous glass was treated with H¹⁵NO₃ vapor resulting in a red-shift by 33 cm⁻¹ (Fig. 6c) as expected for N-15 labeled NO₂⁺.

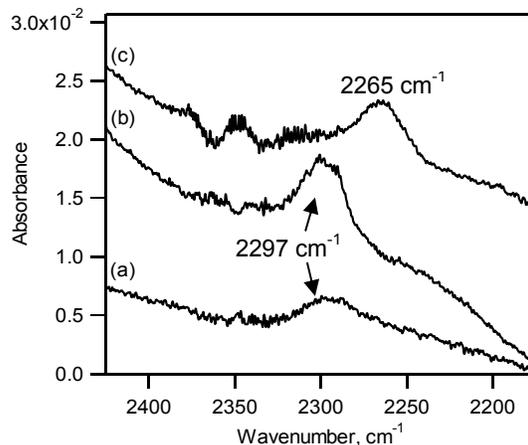
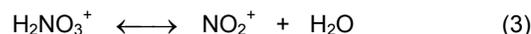
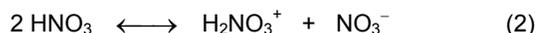


Figure 6. Spectra of NO₂⁺ on porous glass (a) after exposure to NO₂ for an NO₂ hydrolysis experiment, (b) after exposure to HNO₃ vapor alone and (c) after exposure to H¹⁵NO₃ vapor.

Concentrated solutions of HNO₃ are known to undergo self-reaction to form NO₂⁺ via the equilibrium reactions, (2) and (3) (Addison, 1980).



In addition, gas phase clusters of NO₂⁺ and water are known to form HNO₃ when at least four water molecules are present, indicating that the reactions are reversible in the presence of water (Fehsenfeld *et al.*, 1975; Sunderlin and Squires, 1993; Cao *et al.*, 1993, 1994).

In summary, thin water films present on silica surfaces of chambers during NO₂ hydrolysis studies are known to contain nitric acid, its hydrates, and other intermediates that are sensitive to the amount of nitric acid and water present in the film.

3.2 Kinetics

There have been many previous studies of the kinetics of NO₂ loss and product formation (England and Corcoran, 1974; Sakamaki *et al.*, 1983; Pitts *et al.*, 1984; Svensson *et al.*, 1987; Harrison and Collins, 1998; Jenkin *et al.*, 1988; Kleffmann *et al.*, 1998a,b; Perrino *et al.*, 1988; Febo and Perrino, 1991). The overall rate law for reaction (1) as written is given by equation (I):

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{HONO}]}{dt} = k [\text{NO}_2]^a [\text{H}_2\text{O}]^b \quad (I)$$

Previous studies have been in general agreement that NO₂ hydrolysis is first order with respect to both NO₂ and water vapor. Kinetics studies were performed in this laboratory and are presented below.

3.2.1 Reaction Order with Respect to Water. To examine dependences on water vapor, initial rates of HONO and NO formation from the long path cell studies were plotted as a function of RH. In addition, separate experiments were carried out in this laboratory to determine the number of layers of water on smooth borosilicate glass as a function of RH (Sumner and Finlayson-Pitts, 2002 (Paper No. 1.4)). Figure 7 shows the initial HONO and NO rates plotted with the number of layers of water versus RH. The similarities in shapes of these data sets show that the rates of HONO and NO formation are dependent on the amount of water on the surface of the reaction chamber rather than on the water vapor concentration. However, the rates of HONO and NO formation are fairly linear below 65% RH where most previous studies were carried out. There are a few previous studies that report rates of HONO or NO formation above ~65% RH. For example, Svensson et al. (1987) reported a larger increase in the rate of NO formation than expected at $[H_2O] = 5 \times 10^{17}$ molecules cm^{-3} (77% RH under their conditions). Thus, while the overall NO_2 hydrolysis reaction is relatively linear in water vapor concentration below ~65% RH, the rate is more accurately expressed as a function of the amount of water present on the surface. Our proposed mechanism therefore shows surface water as the reactant rather than water vapor.

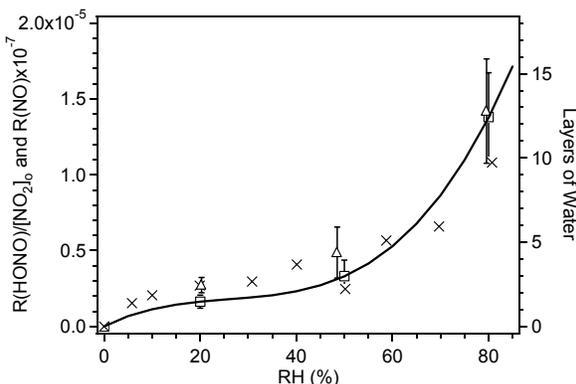


Figure 7. Left axis: initial rates of HONO (\square) formation (divided by $[NO_2]_0$) and of NO (Δ) formation versus RH. NO rates have been multiplied by 10^{-7} . All errors are 1s. The solid line is a fit through the combined rate data sets. Right axis: (x) Number of layers of water on smooth glass as a function of RH.

3.2.2 Reaction Order with Respect to NO_2 . The reaction order with respect to NO_2 was obtained using the logarithmic form of equation (I):

$$\log(R) = \log k + a \log[NO_2] + b \log[H_2O] \quad (II)$$

A log-log plot of the rate versus initial NO_2 concentration will have a slope of a , the reaction order with respect to NO_2 . Plots of this type were generated for experiments carried out in the 19.4 L long path cell at three different RH and a range of 10 – 100 ppm NO_2 using rates of

both HONO formation and NO_2 decay, shown in Figure 8. The use of HONO formation rates (Fig. 8a) yields an average slope of $a = 1.2 \pm 0.4$ (2s), in general agreement with previous reports that HONO formation is first order in NO_2 (Sakamaki et al., 1983; Pitts et al., 1984; Svensson et al., 1987; Jenkin et al., 1988; Febo and Perrino, 1991; Wiesen et al., 1995; Harrison and Collins, 1998; Kleffmann et al., 1998a). The data for NO_2 loss (Fig. 8b) result in a reaction order of 1.6 ± 0.2 (2s). To compare these results with previous studies, log-log plots were generated from the literature where appropriate data were available (Sakamaki et al., 1983; Pitts et al., 1984; Svensson et al., 1987; Jenkin et al., 1988; Febo and Perrino, 1991). The range of slopes from these literature studies was 1.0 to 1.2 for NO_2 loss. The discrepancy between our slope of $a = 1.6$ and previous slopes of $a \approx 1$ is not understood. The proposed mechanism, however, predicts that HONO formation is first order in gaseous NO_2 despite the key role of surface N_2O_4 in the formation of HONO.

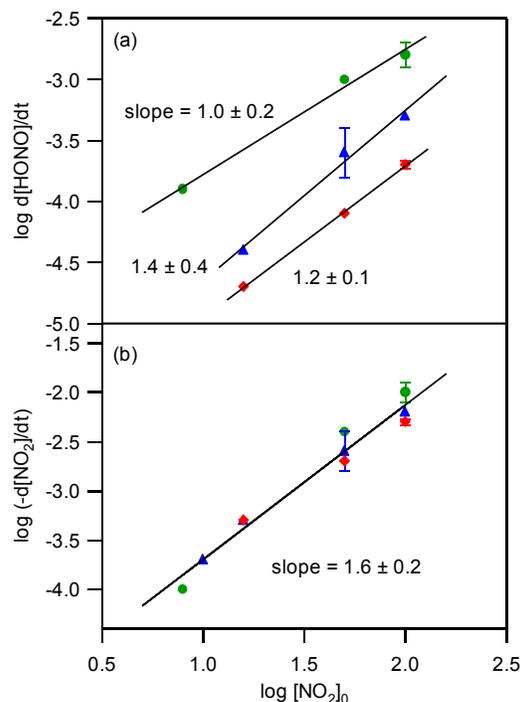
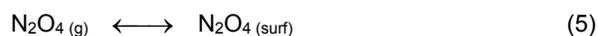


Figure 8. Log-log plots of the initial rates of (a) HONO formation and (b) NO_2 loss versus $\log [NO_2]_0$ for experiments carried out in the 19.4 L long path cell at 21% (\blacklozenge), 48% (\blacktriangle), and 80% (\bullet) RH. The slopes ($\pm 2s$) are equal to reaction order in NO_2 .

The steps involving HONO formation (from Fig. 1) are reactions (4) – (8):





If the rate of the reaction (7) of ONONO₂ with gaseous NO₂ to reform symmetric N₂O₄ on the surface is much faster than the reaction of ONONO₂ with water (8), the steady-state concentration of ONONO₂ is given by (III):

$$[\text{ONONO}_2]_{\text{ss}} = \frac{k_6 K_4 K_5 [\text{NO}_2]^2}{k_7 [\text{NO}_2]} = k_{\text{eff}} [\text{NO}_2] \quad (\text{III})$$

where k_{eff} is the combination of rate constants and equilibrium constants, $k_{\text{eff}} = k_6 K_4 K_5 / k_7$. The rate of HONO formation is then given by (IV):

$$\frac{d[\text{HONO}]}{dt} = k_8 [\text{ONONO}_2] [\text{H}_2\text{O}(\text{surf})] = k_8 k_{\text{eff}} [\text{NO}_2] [\text{H}_2\text{O}(\text{surf})] \quad (\text{IV})$$

Equation (IV), derived from reactions (4) – (8), therefore shows the HONO formation rate as first order in gaseous NO₂ and first order in surface H₂O. As discussed above, the amount of surface water present on smooth silica surfaces is relatively linear below ~65% RH, thus it follows that previous studies in this range reported that HONO formation was first order in the water vapor concentration.

4. DISCUSSION: MODELS AND SUPPORT FOR THE MECHANISM

The following section discusses additional support for the proposed mechanism.

4.1 NO Production

Nitric oxide has been observed in this and other studies (England and Corcoran, 1974; TenBrink et al., 1978; Sakamaki et al., 1983; Pitts et al., 1984; Svensson et al., 1987; Wainman et al., 2001) and smaller amounts of N₂O have been reported (Wiesen et al., 1995; Kleffmann et al., 1998a,b). Although Pitts et al. (1984) reported NO at longer times, other studies report simultaneous HONO and NO production throughout the reaction. One reason for the apparent induction period in the studies of Pitts et al. (1984) is their use of much lower initial NO₂ concentrations (<1 ppm) relative to other studies (1 – 100 ppm). As discussed above, NO production is believed to result from secondary reactions of HONO on the surface. We propose that NO₂⁺ reacts with HONO to form NO which is then released to the gas phase, reaction (9).



At longer times, there may also be additional chemistry besides reaction (1) that forms HONO. For example, previous studies in this and other laboratories have shown that gaseous NO reacts with HNO₃ on silica surfaces to produce mostly NO₂ with HONO as an intermediate, reaction (10) (Smith, 1947; Jaffe and Ford, 1967; Kaiser and Wu, 1977; McKinnon et al., 1979; Streit et al., 1979; Besemer and Nieboer, 1985; Svensson et al., 1988; Fairbrother et al., 1997; Mochida and Finlayson-Pitts, 2000; Saliba et al., 2000, 2001; Rivera-Figueroa et al., 2002; Rivera-Figueroa and Finlayson-Pitts, 2002 (Paper No. 4.1)):



Because NO₂ and HONO are generated in reaction (10), this secondary chemistry makes the interpretation of kinetics data complex, especially at longer reaction times.

4.2 Testing with Kinetics Models

Kinetics models (REACT v. 1.2) were used to provide an initial test of the proposed steps of our mechanism (Braun et al., 1988; Bozzelli, 2000; Manka, 2001). The model does not explicitly represent heterogeneous chemistry, so surface reactions were represented in terms of gas phase analogs. The model included reactions (4) – (10), the net of (2)+(3), and a reaction that reversibly releases HONO from the surface into the gas phase (Ramazan et al., 2002 (Paper No. P1.5)), in addition to well-known gas phase chemistry (Tsang and Herron, 1991; DeMore et al., 1997; Sander et al., 2000; Atkinson et al., 2001). Rate constants were set to correspond to conditions described in the previous section (i.e. $k_8[\text{H}_2\text{O}] \ll k_7[\text{NO}_2]$) and it was assumed, based on observations above, that N₂O₄ and HNO₃ were present initially on the walls. A best fit was obtained to data for a typical 50% RH experiment with 60 ppm initial NO₂; the model was then applied to typical 20% and 80% RH experiments.

Figure 9 shows the results of the kinetics modeling. Included in the model is the reverse reaction of HONO with surface HNO₃ which was set to form an intermediate that slowly forms N₂O₄. Such a reaction has been proposed in a previous study of nitric acid decomposition (Johnston et al., 1955). While the model overpredicts NO at longer times, it provides a useful test of kinetics despite the unknown details of the mechanism. The kinetics modeling of the steps shown in Figure 1 predicted that the reaction order is 0.9 to 1.1 for initial HONO formation and 1.8 to 2.1 for initial NO₂ loss. These predictions are in good agreement with our experimentally observed values of 1.2 ± 0.4 for HONO and 1.6 ± 0.2 for NO₂.

4.3 Effect of “Conditioned” Chamber Walls.

There are reports in the literature that cleaning the reaction chamber surfaces results in higher initial rates

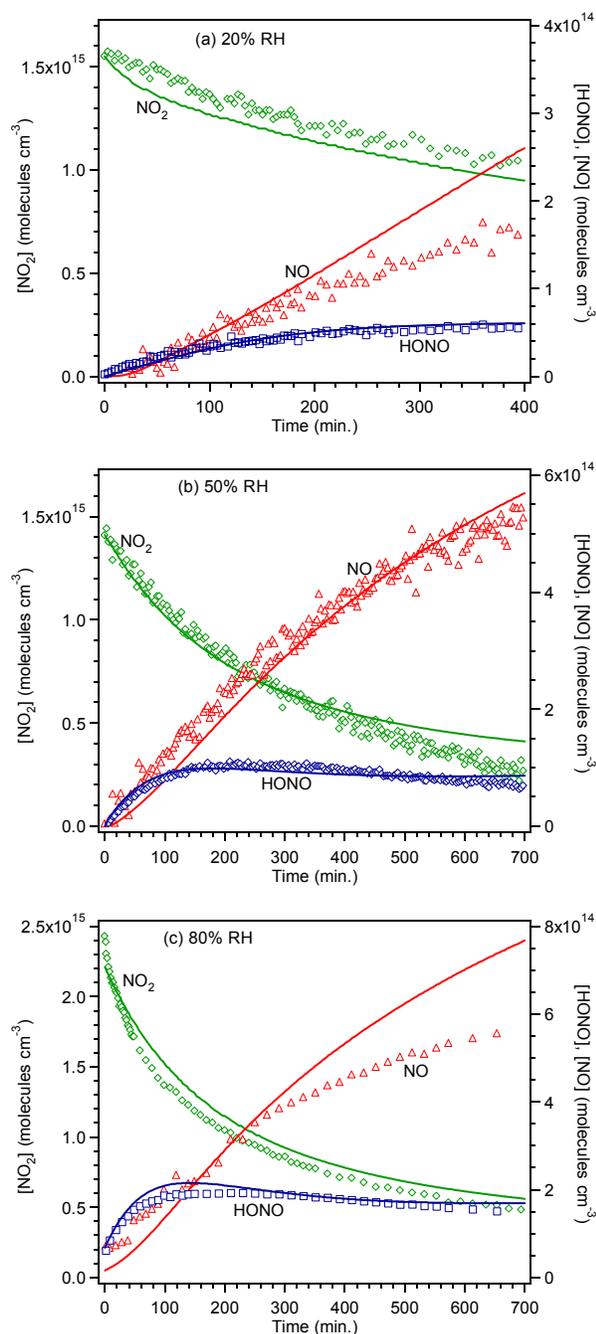


Figure 9. Comparison of kinetics modeling results (solid lines) to experimental data for (a) 21% RH, (b) 48% RH, and (c) 80% RH.

of NO_2 loss and HONO formation (Pitts *et al.*, 1984; Svensson *et al.*, 1987). In the studies of Pitts *et al.* (1984), cleaning the chamber by irradiation of Cl_2 and then heating and pumping for several hours resulted in a doubling of the HONO formation rate; the rate returned to normal after several more experiments were performed. Our studies have shown that N_2O_4 is enhanced on the surface when HNO_3 is present (Fig. 3),

indicating an interaction between N_2O_4 and HNO_3 . We propose that a surface contaminated with HNO_3 may tie up reactive N_2O_4 or ONONO_2 , for example by hydrogen bonding with or protonating one or both of these species. If N_2O_4 is unavailable due to interaction with HNO_3 , a decreased rate of hydrolysis would be observed.

5. ATMOSPHERIC IMPLICATIONS

The experiments carried out in this study were performed on borosilicate glass surfaces. An important conclusion of these studies, however, is that the composition of the *surface film* largely governs the species formed, their availability for further reaction, and hence the branching ratios of products observed. Many surfaces available in urban areas of the troposphere contain silicates which will support these thin films (e.g. building materials such as concrete and glass, soils, and mineral dust) (Gillette, 1997; BNZ Materials, 1999a,b; USGS, 1999).

The similarity in water uptake characteristics between borosilicate glass (Sumner and Finlayson-Pitts, 2002 (Paper No. 1.4)), stone, and soil is shown in Figure 10 as a function of relative humidity (Lammel, 1999). Hence, the mechanism proposed here is an important first step in understanding the mechanism by which HONO is formed in the boundary layer of urban areas, where most measurements are carried out. Figure 10 also shows a range of water uptake on vegetation.

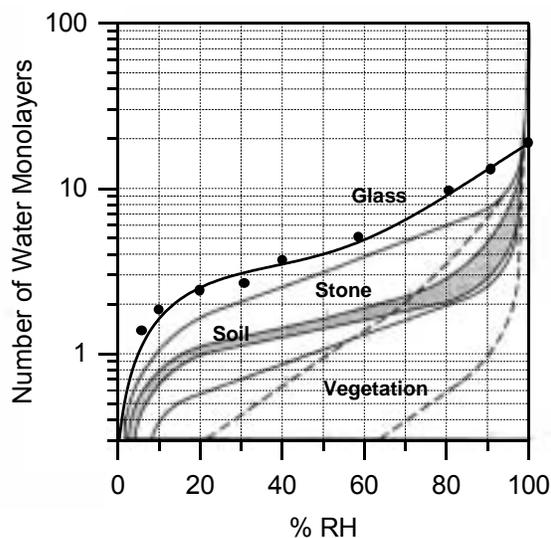


Figure 10. Water uptake on some materials found in the boundary layer as a function of RH. Adapted from Lammel (1999).

Although less water is present on vegetation surfaces than glass for a particular RH, about one monolayer is present above 50% RH, potentially allowing similar heterogeneous chemistry to occur. Given that water

films are present on a wide variety of surfaces, the topic of reactions in thin films (SURFACE = Surfaces, Urban and Remote: Films As a Chemical Environment) has the potential to strongly impact boundary layer chemistry.

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