PHOTOENHANCEMENT... OR PHOTODEPRESSION?... OF THE HYDROLYSIS OF NO₂: IMPLICATIONS FOR THE CHEMISTRY OF POLLUTED ATMOSPHERES

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1. INTRODUCTION

Nitrous acid (HONO) was first identified in ambient urban air in 1979 [Perner and Platt, 1979]. Since then, a number of atmospheric measurements have been made showing that HONO accumulates during the night, and undergoes photolysis in the early morning to produce a pulse of hydroxyl radicals (OH) [Platt et al., 1980; Winer and Biermann, 1994; Harrison et al., 1996; Lammel and Cape, 1996; Lammel, 1999; Schiller et al., 2001; Alicke et al., 2002; Stutz et al., 2002]. HONO photolysis is believed to be a major source of OH in the early morning. [Winer and Biermann, 1994; Harrison et al., 1996; Alicke et al., 2002; Stutz et al., 2002]. Both the OH and nitric oxide (NO) formed participate in reactions with volatile organic compounds (VOC) which lead to tropospheric O₃ formation, the principal component of photochemical smog [Finlayson-Pitts and Pitts, 2000]. Therefore, it is important to understand the sources and sinks of HONO, and the mechanism of its formation.

The major atmospheric source of HONO is believed to be the heterogeneous reaction of NO₂ with water. This hydrolysis of NO₂ is generally represented by (1):

\[
2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3(\text{surface}) \tag{1}
\]

It involves gas phase NO₂ reacting with water on surfaces, such as the walls of laboratory reactors, glass, concrete or foliage [Wingen et al., 2002 (Paper No. P1.8)]. Reaction (1) has been studied extensively by reacting gas phase NO₂ in reaction chambers in the presence of water vapor [Wayne and Yost, 1952; Caudle and Denbigh, 1953; Peters and Holman, 1955; Graham and Tyler, 1972; England and Corcoran, 1974; Sakamaki et al., 1983; Pitts et al., 1984; Akimoto et al., 1987; Svensson et al., 1987; Jenkin and Cox, 1988; Febo and Perrino, 1995; Kieffmann et al., 1998; Goodman et al., 1999; Cheung et al., 2000; Finlayson-Pitts et al., 2002]. The mechanism of reaction (1) is currently poorly understood. In these NO₂ hydrolysis experiments, the HONO produced was measured in the gas phase, but gas phase HONO was not detected [England and Corcoran, 1974; Sakamaki et al., 1983; Pitts, 1984]. The HNO₃ is now known to remain adsorbed on the walls of the reaction chamber, and has been directly observed using transmission FTIR spectroscopy [Barney and Finlayson-Pitts, 2000; Goodman et al., 2001]. One mechanism for (1), suggested many years ago, includes dinitrogen tetroxide (N₂O₄) as an intermediate [Caudle and Denbigh, 1953; England and Corcoran, 1974]. More recently this species has been observed on silica surfaces [Goodman et al., 1999; Barney and Finlayson-Pitts, 2000]. This, and the additional detection of other species such as NO₃⁻, has led Finlayson-Pitts and coworkers to propose a new mechanism [Finlayson-Pitts et al., 2002]. A schematic diagram of the main points of this proposed mechanism is shown in Figure 1:

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products. The HNO₃ stays adsorbed to the surface also leading to the production of various side products.

Akimoto and coworkers (1987), using a 6065 L smog chamber, showed that the HONO production by NO₂ hydrolysis in air is significantly enhanced in the presence of light (λ > 290 nm) [Akimoto et al., 1987]. Nitrous acid formation was determined to be photoenhanced by the comparison of HONO concentration time-profiles measured using long path Fourier transform infrared spectroscopy (LP-FTIR) to model-predicted results. However, the mechanism of such a photoenhancement is not clear.

To determine the degree of photoenhancement, Akimoto et al. (1987), used a gas phase kinetics model that specified all the gas phase reactions occurring in the chamber. In order for the model to accurately predict the results in the cell, gas phase modeling data first had to be formulated for the heterogeneous NO₂ hydrolysis reaction in the dark. Akimoto et al. accomplished this by adding the following heterogeneous reactions to the gas phase model:

\[
\begin{align*}
\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HONO} \\
\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HNO}_3(\text{wall}) \\
\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{NO} \\
\text{NO}_2 & \rightarrow \text{NO}_2(\text{wall})
\end{align*}
\]

By fitting these reactions to the experimental data, in both the dark and light experiments, Akimoto et al. determined the photoenhancement factor to be \((k'_2/k_2)-1\) = \((6.8 \pm 2.5)k_p\) where \(k'_2\) is the rate constant of (2) in the presence of light and \(k_p\) is the photolysis rate constant of NO₂, which is included as a measure of light intensity.

In the present study, the rate of HONO formation is determined from NO₂ hydrolysis with varying concentrations of initial NO₂ (20 – 100 ppm) and relative humidities (20 – 80% RH) in the presence and absence of light (300 – 400 nm). Kinetics modeling is used to elucidate differences between experimental data and results expected based on the newly proposed mechanism of NO₂ hydrolysis.

2. EXPERIMENTAL METHODS

A cylindrical borosilicate glass long path cell (LPC) (150 mm i.d., 1 m base path, and 19.4 L volume) equipped with White optics [White, 1942] aligned and calibrated to a path length of 84 meters was used as a reaction vessel (Figure 2). The flanges and inner supports consist of anodized aluminum which is covered in a thin coating of halocarbon wax to minimize reactions with metal surfaces.

Concentrations of NO₂, HONO, and NO in the LPC were measured using FTIR (Mattson, Research Series) at 1 cm⁻¹ resolution. Spectra were typically averaged over 64 scans, but when a faster sampling rate was required, they were averaged over 16 scans. NO₂, HONO, and NO were measured by the net absorbance of their peaks at 2917 cm⁻¹, 1263 cm⁻¹, and 1875 cm⁻¹, respectively. NO₂ and NO were calibrated in the LPC, while the HONO concentrations were calculated from an effective cross section of \((3.7 \pm 0.4) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1} \text{ base 10}) \,[Barney et al., 2001].

In each hydrolysis experiment, NO₂ was injected into the LPC in diluent nitrogen (N₂) (Oxygen Service Co., 99.9999%) gas. NO₂ was synthesized by mixing NO (Matheson, 99%) with excess oxygen (O₂) (Oxygen Service Co., 99.993%) for ~ 2 hr. The NO₂ was then purified by condensing at 195 K and then pumping away the excess O₂. The LPC was filled to atmospheric pressure with the appropriate amount of humidified air from a collapsible Teflon chamber. Humidified air was added to a Teflon chamber by flowing N₂ gas through a bubbler filled with Nanopure® water (Barnstead, 18.2 MΩ cm) and mixing with dry N₂ to give the relative humidity desired. The use of a Teflon chamber provides a method of quickly bringing the cell to 1 atm. The HONO was allowed to build up in the dark for ~2 hr and then the photolysis lamps were switched on while continuously monitoring by FTIR. Irradiation (300-400 nm) entered the LPC through the borosilicate walls and was provided a Sylvania 350 black light (30 W, F30T8 / 350BL). All experiments were performed at room temperature.
To determine the extent to which NO₂ hydrolysis was affected by irradiation, the time dependencies of NO₂, NO, and HONO formation were compared to model-predicted concentration time-profiles for these species. These model predictions are generated from a kinetics model created by specifying all the reactions (with their rate constants) known to be occurring in the LPC (Table 1) with the inclusion of several reactions used to simulate the heterogeneous reactions in the NO₂ hydrolysis as per the mechanism suggested by Finlayson-Pitts et al. (2002). The gas phase rate constants are from known sources [Tsang and Herron, 1991; DeMore et al., 1997; DeMore et al., 2000; Atkinson et al., 2001]. Heterogeneous reactions are not explicitly represented by the model; instead they are represented in terms of a gas phase analog. The heterogeneous reactions were fit in the model to match experimental data over a range of concentrations (20 – 100 ppm NO₂) and relative humidities (20 – 80%). The chemical model software used was REACT v1.2 [Braun et al., 1988; Bozzelli, 2000; Manka, 2001]; it is a zero-dimensional gas phase model that numerically integrates rate equations for all species over specified time intervals.

To experimentally determine the photolysis rate constants for NO₂ and HONO for use in our kinetics model, NO₂ or HONO was added to the LPC in concentrations similar to those in the NO₂ hydrolysis experiments, and the cell then filled to 1 atm with N₂. Irradiation (300 – 400 nm) began after the cell was filled to 1 atm of N₂ and an initial FTIR spectrum was taken. The concentrations of the gaseous species were then monitored with time by FTIR with the photolysis lamp on. The HONO was generated using a HONO generator, which is described by [Barney et al., 2000], so only a brief description is described herein. In the generator, HONO is produced by passing humid air (80-100% RH) over NaNO₂ powder (Aldrich, 99.5%) which was then reacted with gaseous HCl prepared from flowing dry N₂ over 1:10 mixture of HCl (Fisher, 12.1 M) and Nanopure® water:

\[
\text{NaNO}_2(s) + \text{HCl(g)} \rightarrow \text{HONO(g)} + \text{NaCl(s)}
\]

3. RESULTS AND DISCUSSION

Figure 3 shows an NO₂ hydrolysis experiment carried out in the dark for ~7 hr at a relative humidity of 80% and 50 ppm initial NO₂. The NO₂ slowly decays while HONO and NO increase. The experimental data are compared to a model calculation specified by Table 1. There is a relatively good match between the data and model calculation for NO₂ and HONO. In addition, the model data predict that HONO formation is first order with respect to NO₂, in agreement with previous studies [Sakamaki et al., 1983; Pitts, 1984; Svensson et al., 1987; Jenkin and Cox, 1988; Perrino et al., 1988; Febo and Perrino, 1991; Wiesen et al., 1995; Harrison and Collins, 1998; Kleffmann et al., 1998]. The model over-predicts NO formation; this is most likely due to...
difficulties in quantifying NO by FTIR in these experiments. Water absorbs in the region of 1300 cm$^{-1}$ to 2000 cm$^{-1}$ while NO has overlapping fine rotational lines in the region of 1780 cm$^{-1}$ to 1960 cm$^{-1}$. Subtraction of this large amount of water from a spectrum with a small amount of NO results in a large uncertainty associated with NO quantification.

In Figure 4, a 50 ppm NO$_2$ hydrolysis experiment at a relative humidity of 80% is shown. In this experiment for the first ~2 hr the HONO accumulates in the dark. The model specified in Table 1 is in excellent agreement with the experimental HONO and NO$_2$ data during the first ~2 hours. Irradiation begins at ~6000 s and continues for the remainder of the experiment. As expected, the NO$_2$ and HONO photolysis and form a large amount of NO. After 6000 s the model incorporates the HONO and NO$_2$ photolysis rate constants measured in our cell, $(3.5 \pm 0.4) \times 10^{-4}$ s$^{-1}$ (2s) and $(1.6 \pm 0.1) \times 10^{-5}$ s$^{-1}$ (2s) respectively. It can be seen in Figure 4 that, although photolysis of HONO is included in the model, the modeled HONO is predicted to increase after 6000 s, while during the experiment the measured HONO actually decays. This indicates that the HONO formation steps in the model are overestimated in the presence of light. In the experiments of Akimoto et al. (1987), when photolysis began, a photoenhancement of HONO formation was observed, i.e., the experimental HONO data were greater than the model prediction. In our studies, however, the experimental data are far below the model prediction, indicating a “photodepression” of HONO formation.

Using the first order integrated rate equation (I),

$$\ln \frac{[\text{HONO}]}{[\text{HONO}]_0} = -kt$$

the rate constant for experimental HONO decay can be determined and compared to that for photolysis. The initial photolytic decay of HONO in Figure 4 (~6000 – 8000 s) was thus examined more closely in Figure 5 by
plotting $\ln \frac{[\text{HONO}]}{[\text{HONO}]}_0$ versus irradiation time. The initial slope of this plot resulted in a value of $(3.9 \pm 0.4) \times 10^{-4}$ s$^{-1}$ (2s) for the first order loss of HONO decay during irradiation, which is equal, within experimental error, to the measured HONO photolysis rate constant of $(3.5 \pm 0.4) \times 10^{-4}$ s$^{-1}$ (2s). This suggests that HONO production from NO$_2$ hydrolysis ceases when irradiated by light in the region of $300 - 400$ nm. In Figure 6 this is tested by removing the NO$_2$ hydrolysis mechanism from the model when the lights are turned on. Excellent agreement is obtained between the experimental data and the model calculation that suggests the NO$_2$ hydrolysis mechanism proposed is actually deactivated in the presence of $300 - 400$ nm light.

Although we do not see the photoenhancement effect that Akimoto et al. (1987) observed, the conditions of their experiments differed from ours. First, they used filtered Xe arc lamps which produce a broad range of light from 290 nm through the infrared region while the blacklights used in this study only produce light in the range of 300 nm to 400 nm. Since Akimoto et al., used a broader wavelength region, it is possible that a complex photoenhancement mechanism is occurring outside of our wavelength region and a “photodepression” is occurring in our narrow wavelength region. The second possibility lies in the diluent gas. Akimoto et al. used air while we used nitrogen. It is possible that oxygen plays a critical role in the photoenhancement effect of Akimoto et al. Work is currently in progress to elucidate these possibilities.

### 4. ATMOSPHERIC IMPLICATIONS

NO$_2$ hydrolysis is currently believed to be a major source of HONO in the atmosphere, especially at night when HONO photolysis does not occur. Since HONO photolysis at dawn is a major source of OH radicals, which drive the chemistry of the troposphere, it is important that reaction (1) be accurately included in airshed models to determine its impacts. While current airshed models typically utilize rates of HONO production from previous laboratory studies to represent reaction (1), this may not be appropriate given the complexities of the reaction. As we have shown, the presence of radiation significantly impacts NO$_2$ hydrolysis possibly by deactivating the reactive species leading to HONO formation. In addition, there may be a multipath mechanism dependent on the wavelengths of radiation present.

However, photochemical HONO formation has been recently reported in field studies [Zhou et al., 2001; Dibb et al., 2002; Zhou et al. 2002]. Both Dibb et al and Zhou et al. (2001) measured photochemical HONO production in the Artic snow exposed to either sunlight or artificial light ($\lambda > 280$ nm). Zhou et al. (2002) measured a peculiar formation of HONO while sampling rural air in a glass sampling manifold upon exposure to sunlight. They proposed that HONO was formed by hydrolysis of NO$_2$, which was generated upon photolysis of nitric acid present on the glass. Currently, this mechanism is unclear, but light does seem to play an important role.

The experiments carried out here were performed in a borosilicate glass long path cell in which the glass walls acted as the support for a thin film of water and other surface species. Water uptake measurements suggest that water films are likely to be present on surfaces typically found in the lower part of the troposphere, such as building materials, soils, and vegetation [Lammel, 1999; Sumner and Finlayson-Pitts, 2002 (Paper No. 1.4)]. Therefore, there are likely to be similarities in this chemistry and that occurring on thin films in the lower troposphere. This area of SURFACE (Surfaces, Urban, and Remote: Films As a Chemical Environment) may impact the ozone and NO$_x$ chemistry in the troposphere.

### 5. ACKNOWLEDGEMENTS

We are thankful to the California Air Resources Board (Contract No. 00-323) and the National Science Foundation (Grant No. ATM-0097573) for the support of this work. We would also like to thank J. N. Pitts Jr. and L. M. Wingen for many useful discussions.

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