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Reactive uptake of NO_3 on pure water and ionic solutions

Yinon Rudich, Ranajit K. Talukdar[1] and A. R. Ravishankara[1,2]

Acronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado

R. W. Fox

Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado

Abstract. The reactive uptake coefficients (γ) of NO_3 onto pure water and dilute solutions of NaCl, NaBr, and $NaNO_2$ were measured using a wetted-wall flow-tube setup combined with a long-path absorption cell for the detection of NO_3. The measured γ values were in the range 1.5×10^{-4} - 6×10^{-3}, depending on the salt concentration in the water. By measuring γ as a function of salt concentration, $HD_\ell^{0.5}$ for NO_3 in water was determined to be $(1.9\pm0.4)\times10^{-3}$ M atm^{-1} cm s$^{-0.5}$ at 273 K, assuming that the rate coefficient for the reaction of NO_3 with Cl^- is 2.76×10^6 M^{-1} s^{-1} at 273 K. The Henry's law coefficient for NO_3 in water is estimated to be 0.6 ± 0.3 M atm^{-1}, assuming that the diffusion coefficient of NO_3 in water is $D_\ell = (1.0\pm0.5)\times10^{-5}$ cm^2 s^{-1}. Uptake of NO_3 on pure water is interpreted as due to reaction of $NO_{3(aq)}$ with $H_2O_{(\ell)}$ to produce HNO_3 and OH in the liquid phase. Implications of these findings to the chemistry of NO_3 in the troposphere are also discussed.

Introduction

The NO_3 radical is a major tropospheric nighttime oxidant and its gas phase reactions are important loss pathways for many compounds during the night [*Atkinson*, 1991; *Wayne et al.*, 1991]. NO_3 can also be important in initiating radical reactions within cloud droplets [*Chameides*, 1986a,b; *Lelieveld and Crutzen*, 1991; *Mozurkewich*, 1986] and in aerosols [*Pederson*, 1995]. NO_3 scavenging by wet aerosols may explain the short lifetime of NO_3 that was observed in the troposphere [*Heikes and Thompson*, 1983; *Mihelcic et al.*, 1993; *Noxon*, 1983], especially during episodes of high humidity and fog [*Platt et al.*, 1981,1984].

Odd nitrogen species such as NO and NO_2 have limited solubility in liquid water [*DeMore et al.*, 1994]. Thus the main removal pathways of NO_x species from the atmosphere are believed to be via the formation of HNO_3, which is removed by both dry and wet deposition. HNO_3 is formed in the atmosphere either by the gas phase reaction of OH with NO_2 or heterogeneous hydrolysis of N_2O_5. Since the NO_x family plays very important roles in various reaction cycles in the atmosphere, the removal pathways for the members of this family from the atmosphere needs to be well known. The NO_3 radical, which is formed by reaction of NO_2 and ozone, may also provide a removal pathway of NO_x from the atmosphere through its gas phase and heterogeneous loss processes.

The uptake of a compound into a liquid is determined by diffusion, its solubility and its liquid phase reactions [*Danckwerts*, 1951; *Hanson et al.*, 1994; *Schwartz*, 1986]. To model the heterogeneous chemistry of NO_3 accurately, properties such as Henry's law coefficient (H) and the reactive uptake coefficients (γ) must be known accurately. In previous studies, H for NO_3 was estimated to be between 3×10^{-2} and 2×10^5 M atm^{-1} [*Chameides*, 1986a,b; *Jacob*, 1986; *Lelieveld and Crutzen*, 1991; *Mozurkewich*, 1986]. To our knowledge, the only experimentally determined value of H, the Henry's law coefficient for NO_3, H= 1.8 ± 1.5 M atm^{-1} is that reported in the thesis of *Thomas* [1992].

To understand the nighttime processing of NO_3 in the troposphere and its impact on cloud and fog chemistry, we have undertaken the studies of its uptake on pure water and on some representative ionic solutions relevant to the marine troposphere and to cloud droplets. In this paper we report measurements of the uptake coefficients of NO_3 by water and by aqueous solutions of NaCl, NaBr, and $NaNO_2$. From these measurements we also determine $HD_\ell^{0.5}$ for NO_3 in water and discuss the atmospheric implications of these results.

Experimental and Data Analysis

Setup

Uptake of NO_3 by distilled water (pH~7) and by NaCl (0.01-0.5 M), $NaNO_2$ (0.0005-0.0038 M), and NaBr (0.001-0.01 M) solutions was measured. The experimental setup was an adaptation of the one described by *Utter et al.* [1992], and only details specific to the current experiment are described here. It consisted of a vertical wetted-wall flow tube, a movable injector through which NO_3 is introduced, a long path absorption cell, and a stabilized diode laser system. A schematic diagram of the apparatus is shown in Figure 1. The reactor was 85 cm long with an internal diameter of 1.9 cm. The first 60-cm section enabled thermal and water vapor equilibration between the gas flow and the liquid film. The uptake coefficients were measured in the lowest 25-cm section of the flow tube, where the injector could move up to 18 cm. About 5 L of liquid were stored in a 12-L bulb above the system and the rate of flow through the reactor was controlled using a Teflon needle valve. The liquid was continuously pumped back to the reservoir by a Teflon gear pump.

[1]Also at the Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder.

[2]Also at the Department of Chemistry and Biochemistry, University of Colorado, Boulder.

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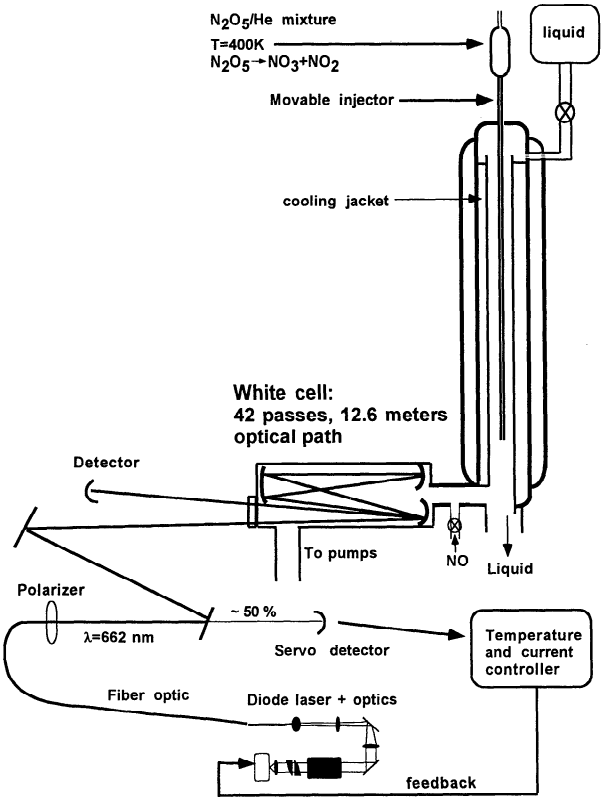

Figure 1. A schematic diagram of the experimental apparatus.

The NO_3 radical was generated by thermal dissociation of N_2O_5 in an oven mounted on top of the injector and maintained at a constant temperature of 400 K. High purity He was passed through an N_2O_5 trap, which was kept at ~220 K, to generate a mixture of N_2O_5 in He. This mixture was flowed to the oven via Teflon tubing. NO_3 concentrations of 2×10^{-11} - 1×10^{12} cm^{-3} were used.

The concentration of NO_3 coming out of the wetted-wall reactor was determined as a function of exposure time to the liquid surface by measuring the attenuation of light at 662 nm, from a diode laser, in a long-path absorption cell [*White*, 1942; 1976]. The cell was covered with a glass jacket with an inner diameter of 2.3 cm and a total volume of about 130 cm^3. The dielectric coated mirrors had a reflectance of >99% between 450 and 700 nm. The distance between the mirrors of the cell was 30 cm. The beam was multipassed, 42 times, to get a total path length of 12.6 m.

The temperature and current of the diode laser were adjusted to give single-mode operation near 662 nm, the peak of the NO_3 absorption [*Wayne et al.*, 1991]. An optical fiber was used to spatially filter and relay the beam to the White cell. To minimize optical feedback-induced amplitude noise, the fiber ends were polished at an 8° angle, and an optical isolator was used. Approximately 60% of the laser power (~4 mW total power) was coupled into the fiber by using a spherical lens, an anamorphic prism pair, and a telescope (×3), in addition to the collimating and focusing objectives.

At the fiber output, approximately 50% of the power was directed to a photodiode for an amplitude stabilization servo. A stable offset current was subtracted from the photocurrent to provide an error signal, and then fed back to the laser's injection current with a bandwidth of 100 kHz. The offset current was derived from a stable, well-filtered voltage reference and a precision low temperature-coefficient resistor. The remaining laser power was mode-matched to the waist of the White cell, and the cell output directed to a photodiode.

The fiber caused the beam polarization to vary slightly with temperature and acoustic noise, which resulted in amplitude noise on the signal photocurrent due to the polarization sensitivity of the optics. This noise was minimized by using a polarizer immediately after the collimated fiber output but before sampling the beam for the servo.

The laser's wavelength was tuned to the NO_3 absorption line using a diode array spectrometer and a Neon lamp as a wavelength reference. The correction current for the amplitude stabilization (<0.1 mA) did not significantly change the wavelength. The laser's mode structure and wavelength were periodically checked with an optical multichannel analyzer.

The output of the detector was averaged for 3 s and read by a digital voltmeter; the voltmeter signal was monitored by a computer for further analysis. The stability of the detection system was about 8×10^{-5}, limited by vibrations of the multipass cell or optical feedback to the laser. This corresponds to a sensitivity of $\sim5\times10^9$ molecules cm^{-3}, using $\sigma(662\text{ nm}) = 2\times10^{-17}$ cm^2 [*Wayne et al.*, 1991].

Water vapor (~4.5 torr in these experiments) absorbs 662 nm light. Therefore to obtain I_0, the light level in the absence of NO_3, NO was added to the gas flow at the entrance to the cell to completely convert NO_3 to NO_2. Such I_0 values were measured for each injector position before and after taking a reading with NO_3.

All experiments were performed at 273±1 K and at a total pressure of 9 - 14 torr. Typical liquid flow rates were 2-3 cm^3 s^{-1}, implying a Reynold's number of ~80 and liquid flow velocities of ~10-15 cm s^{-1}. Typical liquid film thickness was calculated to be about 0.025 cm. Care was taken to minimize ripples on the water film by controlling the liquid flow rate, and maintaining constant wetting of the wall. Flow velocities of the gas were typically ~1000 cm s^{-1} but were varied from 650 to 1600 cm s^{-1}. A flow velocity of ~1000 cm s^{-1} corresponds to a Reynold's number of ~100. The liquid solutions were bubbled with He for at least 15 hours to remove dissolved N_2 and O_2. Removal of these dissolved gases helped maintain constant unperturbed liquid flow and minimize possible reactive uptake of NO_3 by O_2^- . To maintain a well-defined temperature in the flowing liquid and to avoid rapid evaporation of the film, we added water vapor from a saturator to the main He flow. The temperature of the gas, as well of as the liquid film, were measured in several of the runs and found to be 273±1 K.

Ozone was prepared by a commercial ozone generator using high purity (>99.995%) oxygen, which was passed through a molecular sieve trap at 195 K to remove water. N_2O_5 was synthesized by the reaction of ozone with NO_2. The ozone/O_2 mixture from the ozone generator was mixed with NO_2 which was formed in situ by the reaction of O_2 with pure NO. The gases were mixed in a 50 cm long, 3.8 cm inner-diameter reactor at a pressure of 800 torr and the resulting gas mixture was passed through a trap at dry ice temperature to collect N_2O_5. High purity He (>99.9995%) and chemically pure (ASC reagent grade, >99%) salts were used throughout the experiments.

Data Analysis

The uptake coefficients of NO_3 were calculated from the measured first-order rate coefficients for the loss of NO_3 from the gas phase, k_w. The loss of NO_3 from the gas phase is described by

$$[NO_3]_{z_1} = [NO_3]_{z_2} exp(-k_w z / c) \quad (1)$$

where $[NO_3]_{z1}$ and $[NO_3]_{z2}$ are the NO_3 concentrations at injector positions z_1 and z_2, with $z=z_2-z_1$ and c is the gas flow velocity. A plot of $\ln[NO_3]$ versus relative injector position (z) yielded a straight line with a slope of $-k_w/c$. Then k_w was corrected for the radial concentration gradient generated by the uptake of NO_3 into the liquid, using the method developed by Brown [*Brown*, 1978; *Hanson et al.*, 1992].

To determine the true wall loss rate coefficient, k_w^{corr}, the gas phase diffusion coefficients of NO_3 in He and H_2O are needed. Since these diffusion coefficients were not measured before, they were calculated [*Mason and Monchick*, 1962; *Monchick and Mason*, 1961] using estimated Lennard-Jones parameters for NO_3 (σ=3.77 Å, ε/K=395 K [*Patrick and Golden*, 1983]) to be 100 and 370 torr cm^2 s^{-1}, respectively. Variation of ε/K, the well depth, by a factor of 2 changed the diffusion coefficients by only 10%. The calculated diffusion coefficient of NO_3 was between 13 and 17 cm^2 s^{-1} under our experimental conditions (4.5 torr H_2O, 5-10 torr He). In addition to calculating them, we measured the pressure-independent diffusion coefficients of NO_3 in He and water vapor under our experimental conditions (*Y. Rudich et al.*, Uptake of NO_3 on KI Solutions: Rate Coefficient for the NO_3 + I^- Reaction and Gas-Phase Diffusion Coefficients for NO_3, Submitted to Chemical Physics Letters, 1996). The calculated values agreed very well with the measurements.

The reactive uptake coefficient γ was calculated from the corrected first-order rate coefficient, k_w^{corr}, using the relation for a cylindrical reactor [*Howard*, 1979]

$$\gamma = 2\, r\, k_w^{corr} / \omega \quad (2)$$

where ω is the average molecular speed of NO_3 and r is the flow tube radius. Here, k_w was measured 10-25 times for each salt concentration, while varying pressure and liquid flow velocities. Such measurements were repeated at various salt concentrations. The relationship between γ and reactive loss in the aqueous phase is given by (e.g., *Hanson et al.* 1992)

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4RT\mathrm{H}\sqrt{D_\ell}\sqrt{k_\ell}} \quad (3)$$

where α is the mass accommodation coefficient, H is Henry's law coefficient (M atm^{-1}), T is the temperature (K), R is the gas constant (L atm mol^{-1} K^{-1}), and k_ℓ is the first-order loss rate coefficient of NO_3 due to reaction in the aqueous phase (ℓ), that is, $k_\ell = k^{II} \times$ [salt]$\times f$ (k^{II} is the second-order rate coefficient for reaction of NO_3 with the salt in the aqueous phase, and f is the activity coefficient of the reactive ion in the salt solution). D_ℓ is the diffusion coefficient of NO_3 in liquid water (cm^2 s^{-1}).

In cases where multiple reactions can simultaneously take place in the aqueous phase, equation (3) should be modified to include all reactive channels:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4RT\mathrm{H}\sqrt{D_\ell}\sqrt{\sum_i k_{\ell i}}} \quad (4)$$

In equation (4) $k_{\ell i}$ is the first-order loss rate coefficient for reaction of NO_3 with species R_i in the aqueous phase (ℓ), i.e., $k_{\ell i} = k_i^{II}[R_i] \times f_i$ (k_i^{II} is the second-order rate coefficient for reaction of NO_3 with species i in the aqueous phase). The summation is over all the reactants. In cases where the uptake is not limited by mass accommodation, i.e., $\gamma \ll \alpha$, equation (4) reduces to

$$\gamma = \frac{4RT}{\omega}\mathrm{H}\sqrt{D_\ell}\sqrt{\sum_i k_{\ell i}} \quad (5)$$

When NO_3 was lost by more than one reaction, γ was measured as a function of the concentration of one reactant i, while the concentrations of the other j reactants were held constant. Under these conditions,

$$\gamma^2 = \mathrm{H}^2 D_\ell \left[\frac{4RT}{\omega}\right]^2 \sum_j k_{\ell j} + \mathrm{H}^2 D_\ell \left[\frac{4RT}{\omega}\right]^2 k_{\ell i} \quad (6)$$

a plot of measured $\gamma 2$ versus $\left[(4RT)/\omega\right]^2 k_{\ell i} = \left[(4RT)/\omega\right]^2 k_i^{II}[X_i]$ yields $\mathrm{H}^2 D_\ell$ as the slope and $\mathrm{H}^2 D_\ell \left[(4RT)/\omega\right]^2 \sum_j k_{\ell j}$ as the intercept. For this analysis, k_i^{II} must be known.

Results and Discussion

First-order decay plots of NO_3 for a few NaCl concentrations and pure water are shown in Figure 2. From such plots, γ for that set of conditions was calculated. The measured uptake coefficients of NO_3 on water and NaCl, NaBr, and $NaNO_2$ solutions are given in Table 1. The error bars in Figure 2 are the standard deviation of the mean of 10 - 25 measurements of γ for each salt concentration.

Determination of $\mathrm{H}D_\ell^{0.5}$ and Measurements of Liquid Phase Rate Coefficients

To extract $\mathrm{H}D_\ell^{0.5}$ for NO_3 in water from reactive uptake coefficients measurements, at least one aqueous phase rate constant (k^{II}) has to be known. The reaction of NO_3 with Cl^-

(R1) $\quad NO_3(aq) + Cl^-(aq) \xrightarrow{k_1} NO_3^-(aq) + Cl(aq)$

has been previously studied by *Exner et al.* [1992] as a function of temperature and by *Neta and Huie* [1986] and *Kim and Hamill* [1976] at 298 K. The values of k_1 at 298 K reported by Neta and Huie and by Kim and Hamill are 7-10 times higher than the value reported by Exner et al. This difference was attributed to the effect of high ionic strength of the $NaNO_3$ solutions used in the pulsed radiolysis studies [*Exner et al.*, 1992]. Therefore, we used the rate coefficient, $k_1(T) = (1.9\pm0.2)\times10^{13}$ exp[-(4300±500)/T] M^{-1} s^{-1}, measured by Exner et al. at low ionic strength for the analysis of our results.

A loss of NO_3 on water was observed even in the absence of NaCl. This observation points to a possibility that NO_3 is lost due to reaction with the water. To account for this additional loss, we used equation (6) to extract $\mathrm{H}D_\ell^{0.5}$

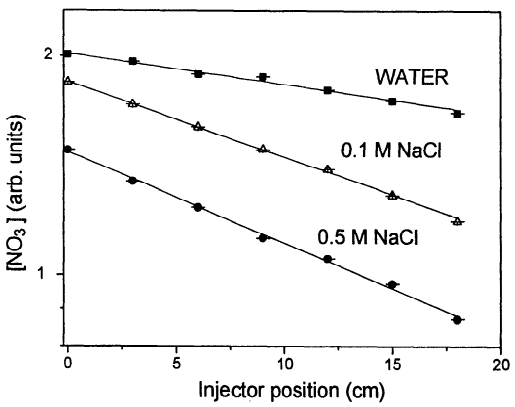

Figure 2. Plots of NO_3 concentrations as a function of exposure to pure water and solutions of NaCl: squares, pure water; triangles, 0.1 M NaCl; circles, 0.5 M NaCl.

Table 1. Measured Values of γ Over Various Ionic Solutions Along With Experimental Parameters

	[*salt*] *M*	Activity[a] (*f*×[salt])	Total pressure, torr	Flow Velocities, cm s^{-1}	$\gamma \times 10^3$ [b]
H_2O	0.000	0.0000	10.0-16.2	580-1000	0.20 ± 0.10
NaCl	0.0087	0.0079	11.8-14.0	640-1020	0.78 ± 0.12
	0.0096	0.0087	12.0-14.75	700-960	0.85 ± 0.12
	0.0101	0.0091	11.5-14.5	620-860	1.14 ± 0.12
	0.0123	0.0111	10.2-14.7	730-1500	0.67 ± 0.20
	0.0150	0.0136	8.1-10.3	860-1500	1.39 ± 0.25
	0.0506	0.0458	10.4-14.6	650-1000	1.98 ± 0.28
	0.0790	0.0717	12.2-13.0	920-1100	0.21 ± 0.06
	0.100	0.0904	7.2-12.8	500-1380	2.73 ± 0.40
	0.2090	0.1890	11.6-13.3	920-1180	3.01 ± 0.53
	0.2620	0.2370	9.2-13.8	730-1300	4.21 ± 0.53
	0.5000	0.4520	6.6-9.1	830-1870	4.70 ± 0.65
	0.5000	0.4520	11.5-13.0	910-1050	6.00 ± 1.50
$NaNO_2$	0.0005	0.0005	10.5-14.5	620-1000	1.74 ± 0.20
	0.0010	0.0010	11.3-13.5	660-950	2.75 ± 0.53
	0.0011	0.0010	11.0-13.5	690-960	2.61 ± 0.52
	0.0038	0.0037	10.1-12.5	730-1050	4.6 ± 1.2
NaBr	0.0010	0.0010	10.6-13.8	520-800	1.56 ± 0.26
	0.0040	0.0037	11.1-13.6	700-800	3.22 ± 0.22
	0.0083	0.0076	10.7-12.6	790-1330	5.32 ± 0.58
	0.0100	0.0090	11.7-13.1	660-780	5.5 ± 1.3

[a]Here *f* is the activity coefficient of ions in the solution.
[b]The quoted errors are 2σ in the standard deviation of the mean of many measurements and do not include any systematic error. Precision of each measurement is much smaller.

$$\gamma^2 = \left[\frac{4RT}{\omega}\right]^2 H^2 D_\ell \left[k_{f4}[H_2O] + k_1[NaCl] \times f\right] \qquad (7)$$

where $k_{f4}[H_2O]$ is the first-order loss rate coefficient of NO_3 in the liquid phase due to its reaction with water. Figure 3 shows a plot of γ^2 versus $[(4RT)/\omega]^2 H^2 D_\ell [k_{f4}[H_2O] + k_1[NaCl] \times f]$, where $k_1 = 2.76 \times 10^6$ $M^{-1}s^{-1}$ at 273 K [*Exner et al.*, 1992]. By fitting these data to a straight line, we obtain $HD_\ell^{0.5} = (1.9 \pm 0.4) \times 10^{-3}$ M atm^{-1} cm $s^{-0.5}$ for NO_3 in water. Taking the value of D_ℓ for NO_3 in water to be $D\ell = (1.0 \pm 0.5) \times 10^{-5}$ cm^2 s^{-1}, we obtain $H = 0.6 \pm 0.3$ M atm^{-1}.

Using our measured value of $HD_\ell^{0.5}$, we can extract the rate coefficients of other aqueous phase reactions, such as the reactions of NO_3 with NO_2^- and Br^- by measuring γ as a function of their concentration in water. The rate coefficients for the reactions

(R2) $NO_{3(aq)} + Br^-_{(aq)} \xrightarrow{k_2} NO_3^-{}_{(aq)} + Br_{(aq)}$

and

(R3) $NO_{3(aq)} + NO_2^-{}_{(aq)} \xrightarrow{k_3} NO_3^-{}_{(aq)} + NO_{2(aq)}$

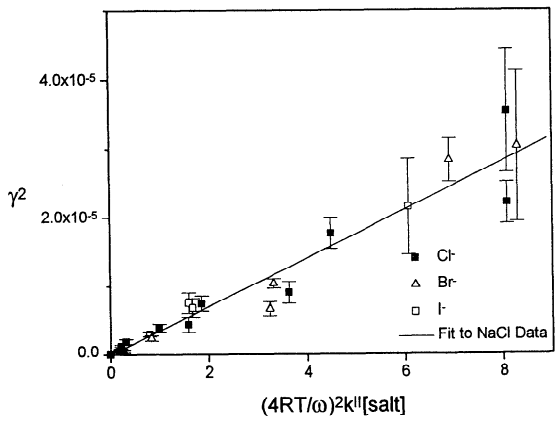

Figure 3. A plot of γ^2 versus $(4RT/\omega)^2(k_{salt}[salt] \times f)$ for water, NaCl, NaBr, and $NaNO_2$. The solid line is a weighted fit of the NaCl data, and from the slope we calculate $HD_\ell^{0.5} = (1.9 \pm 0.4) \times 10^{-3}$ M atm^{-1} cm $s^{-0.5}$.

have not been measured under experimental conditions that are applicable to ours [*Daniels*, 1969; *Neta and Huie*, 1986]. The measured γ of NO_3 on Br^- and NO_2^- solutions were fitted to equation (6) using the $HD_\ell^{0.5}$ value obtained above to extract k_2 and k_3. The derived values for k_2 and k_3 are used in Figure 3, where γ^2 values for NaBr and $NaNO_2$ solutions are plotted against $[4RT/\omega]^2 k_{\ell i}$ (where i can be either 2 or 3). Since we have measured k_2 and k_3 relative to k_1, the ratios k_2/k_1 and k_3/k_1 are more accurate than the absolute values. We report k_2/k_1=37±4 and k_3/k_1=67±7, for dilute NaBr and $NaNO_2$ solutions, at *p*H~6 and 273±1 K.

The majority of the experiments discussed here were obtained by using solutions which were bubbled with He to remove dissolved oxygen. To simulate conditions relevant to the atmosphere, some experiments were carried out with water saturated with O_2. No differences in the measured uptake coefficients were observed in these experiments. The effect of ionic strength and dissolved oxygen on these measurements will be discussed in a separate publication (T. Imamura et al., manuscript in preparation, 1996).

Uptake of NO_3 on Pure Water

A value of $\gamma = (2.0^{+1.0}_{-0.5})\times10^{-4}$ was measured for the uptake of NO_3 by pure water. The first-order decays for NO_3 on pure water were exponential (see Figure 2) and did not show effects of saturation. Using $HD_\ell^{0.5}$ that was obtained from the measured uptake coefficients, saturation is expected to occur within [*Hanson et al.*, 1992] less than 100 ps, given by

$$\tau_{sat} = \left[\frac{4HRT}{\omega}\right]^2 D_\ell < 100\ ps \qquad (8)$$

(assuming α=1). This time is much smaller than the contact time between NO_3 and the water-film in our experiments (18-26 ms). Hence the observed uptake of NO_3 on pure water implies that a reactive loss is taking place. The reaction of NO_3 with OH^- (k(273 K) = 4×10^7 $M^{-1}s^{-1}$ [*Exner et al.*, 1992]) cannot account for the observed uptake of NO_3 in pure water at *p*H of ~7. Further, the measured uptake coefficient onto water did not change when the *p*H was ~6 or even ~5. In addition, we have used ion-chromatography to analyze the water sample for possible presence of other reactive ions prior to the uptake measurements. The analysis revealed that none of the ions present in the water were in concentrations that could lead to the measured loss rate of NO_3. After exposure to NO_3, NO_3^- ions were detected in the water. However, since N_2O_5 is also present in our gas flow and is efficiently taken up by water, we cannot attribute the presence of the nitrate ion as solely due to uptake of NO_3.

The gas phase loss of NO_3 due to the reaction

$$NO_3 + NO_2 + M \xrightarrow{k_{rec}} N_2O_5 + M,$$

followed by rapid uptake of N_2O_5 into the liquid can potentially contribute to the measured loss rate coefficient of NO_3 in the absence of reactants in the water. We measured k_{rec} under our experimental conditions by adding known amounts of NO_2 ($[NO_2]$=2.5-27$\times10^{12}$ cm^{-3}) to the gas flow and by measuring the enhancement in the rate constant for the loss of NO_3 (see Figure 4). The slope of a plot of the measured loss rate constant as a function of $[NO_2]$ resulted in k_{rec} = (3.0±0.2)$\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (where the error is 1σ due to precision of the measurements), corresponding to a loss rate constant of less than 0.5 s^{-1} under most of our experimental conditions. The loss of NO_3 due to recombination with NO_2 is negligible compared to the measured loss of NO_3. The intercept of the plot did not change when the gas phase concentration of NO_3 was 2 times higher. This further indicates that there were no major loss processes other than the reactive loss on the water film and that NO_2 concentrations in the gas flow were comparable to that of NO_3. Finally, a plot of the measured loss rate constants versus $[NO_3]$ resulted in a similar values of k_{rec}.

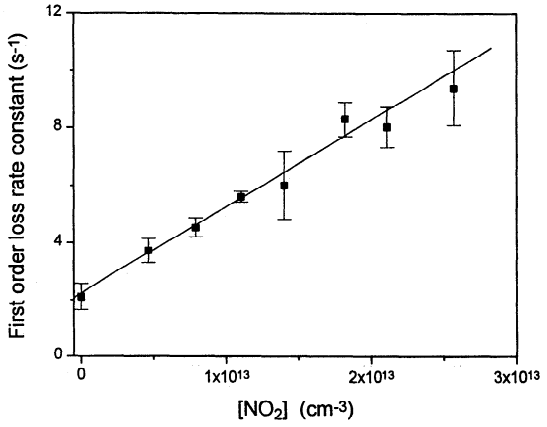

Figure 4. First-order rate coefficients of NO_3 in the presence of excess NO_2. The initial concentration of NO_3 in this experiment were 1.3×10^{12} cm^{-3}, while $[NO_2]$ ranged between 4.6×10^{12} and 2.6×10^{13} cm^{-3}. The slope of this line is the second-order rate coefficient for the recombination of NO_3 with NO_2, k_{rec}=(3.0±0.2)$\times10^{-13}$ cm^{-3} $molecule^{-1}$ s^{-1}, where the error bars denote only precision. The intercept corresponds to uptake of NO_3 on pure water, $\gamma=1.2\times10^{-4}$. This intercept did not change upon changing $[NO_3]$ by a factor of 2.

Therefore we suggest that the observed value of γ measured with pure water is caused by reactive uptake of NO_3 due to the reaction of $NO_{3(aq)}$ with water:

$$\text{(R4)} \qquad NO_{3(aq)} + H_2O_{(\ell)} \underset{k_{r4}}{\overset{k_{f4}}{\rightleftarrows}} HNO_{3(aq)} + OH_{(aq)}$$

Based on kinetic and thermodynamic properties of the forward and reverse reactions (see the appendix), we estimate the rate coefficient k_{f4} to be about 6 $M^{-1}s^{-1}$ at 298 K and 1.5 $M^{-1}s^{-1}$ at 273 K. In principle, it should be possible to extract k_{f4} from the intercept of Figure 3. However, since $k_{f4}[H_2O]$ is very small compared to the uncertainties in some of the measured γ values, there is a very large error associated with the value of the intercept. For that reason, we use the values actually measured for γ to extract k_{f4}. The measured value of γ in our experiments corresponds to $k_{f4} \approx 23^{+30}_{-13}$ M^{-1} s^{-1} and is different from the value calculated from thermodynamic properties. This discrepancy may result either from errors associated with the thermodynamic parameters that we used or by another, unknown, loss process that occurs either in the gas phase or in the liquid. It should be noted that a change of ≈750 cal/mol in $\Delta G°$ for reaction (R4) can account for the observed difference.

Our interpretation that the γ measured on pure water is due to reaction (R4), critically depends on the rate coefficient for the reaction of NO_3 with liquid water. *Jiang et al.* [1992] reported the rate coefficients of k_{f4} and k_{r4} to be 5.3×10^5 and 5.3×10^7 M^{-1} s^{-1}, respectively, while our measured γ values on liquid H_2O suggest k_{f4} to be $k_{f4} \approx 23^{+30}_{-13}$ M^{-1} s^{-1} at 273 K. It appears that the value of k_{f4} quoted by Jiang et al. is too high. *Katsamura et al.* [1991] measured k_{r4}=(1.4±0.1)$\times10^8$ M^{-1} s^{-1}. Using this value of k_{r4} and the ΔG^0 for reaction (R4) calculated in the appendix, we

obtain a value of k_{f4} of 6 M^{-1} s^{-1} at 298 K. The redox potential for NO_3 calculated using our estimated ΔG_f^0 for $NO_{3(aq)}$ and ΔG_f^0 for $NO_3^-(aq)$ is 2.38 V, which is in excellent agreement with the value calculated by *Berdnikov and Bazhin* [1970] of 2.3±0.1 V. This value is lower than the value of 2.67 V, which was calculated by *Jiang et al.* [1992], based on what we believe is an erroneous value for k_{f4}. Finally, the value of $k_{r4}=(1.4\pm0.1)\times10^8$ M^{-1} s^{-1} reported by *Katsamura et al.* [1991] and used by us is consistent with the rate coefficient for the high pressure limit of the OH + HNO_3 reaction in the gas phase [*DeMore et al.*, 1994].

Possible Sources of Error

The major sources of uncertainty in these experiments are the fluctuations in the water vapor pressure in the flow tube and ripples on the liquid film. The water vapor pressure in the flow tube influences the NO_3 gas phase diffusion coefficient and the gas flow velocity [*Hanson et al.*, 1992; *Utter et al.*, 1992]. Ripples on the water film may also introduce an error in the measured γ due to enhanced transport of NO_3 caused by eddies near the wall. The effect of ripples is discussed by *Hanson et al.* [1992]. To minimize these uncertainties, slow liquid flows (Reynold's number of ~80) and almost laminar gas flows (Reynold's number ~100) were employed. We estimate that these phenomena can contribute 10% error to our measurements. To minimize fluctuations in the water vapor pressure, we added He saturated with water vapor to the flow tube. This procedure suppressed evaporation and cooling of the liquid film. In addition, we allowed a long time for the gas flow to equilibrate with the water film. Also, the experiments were carried out with slower liquid flows and at the highest possible pressures, so that fluctuations in water pressure had minimal effect. High uptake coefficients measured at high pressures are uncertain because k_w is close to the diffusion controlled loss rate coefficient, k_{diff} [*Hanson et al.*, 1992]. Under those conditions, the uncertainties in k_{diff} contribute to the error in the diffusion correction due to radial concentration gradient [*Brown*, 1978].

Finally, NO_2, which is also present in the NO_3 source, can enter the liquid water and form $NO_2^-(aq)$. Then NO_2^- can react with NO_3 and slightly enhance its uptake. Using the known low solubility constant of NO_2 [*Lee and Schwartz*, 1981; *Schwartz and White*, 1983], we calculate a $\gamma<1\times10^{-5}$ for this process.

Atmospheric Implications

Three results and conclusions from this study that are relevant to the atmosphere are (1) NO_3 is taken up by liquid water via a reactive process that produces OH radicals in solution, (2) the physicochemical parameters, such as $HD_\ell^{0.5}$ and k_l^{II}, which are necessary for deriving the reactive uptake of NO_3 into water containing various reactants are determined and (3) the solubility of NO_3 in water is small and the previous controversy about the magnitude of this quantity is settled. Of these, the production of OH oxidant from NO_3 uptake is probably the most important conclusion. Here, we discuss the implications of these findings to the chemistry of the lower atmosphere, including those of the marine boundary layer and polar troposphere.

The solubility of NO_3 in water has been a disputed issue, with the assumed values ranging from 3×10^{-2} to 2×10^5 M atm^{-1} [*Chameides*, 1986a,b; *Jacob*, 1986; *Lelieveld and Crutzen*, 1991; *Mozurkewich*, 1986]. Our value of $H=0.6\pm0.3$ M atm^{-1} is much lower than what has been assumed in many atmospheric calculations. This number is uncertain by ~50%, mostly because of the uncertainties in the rate coefficient for the reaction of NO_3 with Cl^- and the value of the diffusion coefficient of NO_3 in liquid water. Once these quantities are determined by some independent method, our measurement can be used to derive a more accurate value of H. To our knowledge, only *Thomas* [1992] has previously reported a value of H. Thomas could not derive a precise value of H because of experimental difficulties. However, her results greatly constrained the value of H and is in agreement with ours. Our measured value of H places a limit on the heterogeneous uptake coefficients that are possible.

We have measured $HD_\ell^{0.5}$, the quantity that is most important for calculating the uptake of NO_3 by water. If $HD_\ell^{0.5}$ is known, the uptake coefficient can be calculated using equation (4) for a known composition of solution. We can calculate the rate of removal of NO_3 from the gas phase and the rate of product formation in the liquid phase using the $HD_\ell^{0.5}$ value determined here, if the concentrations of dissolved species in the liquid droplets and the rate coefficients for their reactions with NO_3 are known. Even in the absence of additional reactive species in the liquid water droplets, there will be loss of NO_3 due to its reaction with water. This loss alone leads to an uptake coefficient, γ, of $\sim2\times10^{-4}$. The presence of other reactive species in the water droplet will increase γ.

If the surface area of the water droplets in air is known, the loss rate of NO_3 can be calculated. For example, we calculate the NO_3 lifetime due to heterogeneous loss to be of the order of 5 min in clouds by assuming a surface area of $\sim3\times10^{-3}$ cm^2 per cm^3 of air (e.g., 40 particles cm^{-3} with 50 μm diameter [*Graedel and Crutzen*, 1993]). In fog, where the drop size is smaller than in a cloud, the diffuso-reactive length is close to the drop radius [*Hanson et al.*, 1994; *Ravishankara and Hanson*, 1994] and leads to effective uptake coefficients that are a factor of 2 - 3 smaller than in large droplets. The lifetime calculated here is in reasonable agreement with the short lifetime observed for NO_3 in the troposphere [*Mihelcic et al.*, 1993; *Platt et al.*, 1981]. Under certain conditions, NO_3 will be in equilibrium with N_2O_5. Then, removal of N_2O_5 by heterogeneous hydrolysis will affect gas phase NO_3 concentrations. As temperature increases to make $[NO_3]/[N_2O_5]>1$, the effect of heterogeneous N_2O_5 uptake on the NO_3 concentration becomes smaller. Such conditions are reached when $T\geq285$ K and for low NO_2 mixing ratios (<20 pptv).

In the marine boundary layer (MBL), sea-salt aerosols will be the medium for heterogeneous reactions. For sea-salt aerosols with $[Cl^-]\cong1$ M and $[Br^-]\cong5\times10^{-3}$ M, the uptake coefficient will be $\gamma\sim1\times10^{-2}$. Under these conditions, the uptake will be restricted by interfacial mass transport for particles of size up to about 15 μm [*Schwartz*, 1986]. For particles above this size, gas phase diffusion will be the rate limiting step. In the presence of sea-salt aerosols, the major loss process for NO_3 will be removal by the these particles. Its rapid heterogeneous removal in MBL may be responsible for the low concentrations of NO_3 in this region. Low concentrations of NO_3 in the MBL may also help explain the observed diurnal variation in the abundance of dimethyl sulfide (DMS) in spite of the large rate coefficient for the reaction of NO_3 with DMS [*Saltzman and Cooper*, 1988]. If the sea-salt aerosols are indeed suppressing NO_3 abundance in the MBL, NO_3 may not be a major oxidizer of DMS.

Outside of the MBL, based on the measured values of the rate constants and estimated concentrations of reactive species in tropospheric liquid droplets, loss of NO_3 via its direct reaction with water may be an important loss mechanism for NO_3. Liquid phase reactions of NO_3 with reactants other than water can also lead to the formation of very reactive oxidants within the

droplets. These oxidants can be Cl (reaction (R1)), Br (reaction (R2)), or OH (due to reaction (R4)). The radical products can initiate reactions of various organic and inorganic species dissolved in rain and fog drops or in sea-salt aerosols. Here we very briefly and qualitatively explore the consequences of such oxidant production.

Platt et al. [1984] hypothesized that there should be a mechanism for converting NO_3 to HNO_3 in the liquid phase. Our work very strongly suggests that the direct reaction of NO_3 with water is responsible for what was observed by Platt et al. The importance of this finding is that not only there is a reaction between liquid H_2O and NO_3, but also the product of this reaction is an oxidant in the liquid phase. This is in contrast to NO_3 removal via formation of N_2O_5 and its subsequent hydrolysis, which results in only formation of HNO_3.

Chameides [1986a,b] has shown that NO_3 can initiate an oxidation chain within cloud droplets that can convert S(IV) to S(VI) . However, Henry's law coefficient, H=12 M atm^{-1}, used in these calculations was larger than the one measured here and reaction (4) was not considered. Therefore the role of NO_3 in rain chemistry, sulfur chemistry, and chemical processes within sea-salt acrosols must be reevaluated using the lower solubility measured here and the reaction of NO_3 with liquid water to produce OH. Reevaporation of NO_3 from the droplets that was suggested by *Mozurkewich* [1986] will not be significant because the uptake of NO_3 even in pure water is reactive, i.e., not determined by physical solubility.

Uptake of NO_3 into sea-salt aerosols and cloud droplets can directly oxidize $SO_{2(aq)}$, HSO_3^-, and SO_3^{2-} dissolved in them and also indirectly via reactions of Cl_2^-, Br_2^-, and OH that are produced by the NO_3 reactions in the solution. These reactions produce SO_3^-, which is capable of further initiating catalytic oxidation reactions of S(IV). Production of SO_3^-, Cl_2^-, OH, and Br_2^- in the sea-salt aerosols can initiate a mechanism similar to that proposed by *Mozurkewich* [1995] for release of halogens (chlorine, bromine, and possibly iodine) by oxidation of halide ions via involvement of Caro's acid in the liquid phase. It will be interesting to investigate the role of such a mechanism in the Arctic springtime troposphere. Mozurkewich's mechanism is based on daytime radicals such as OH and HO_2 as initiators. However, NO_3 can be important during the dark.

The above discussion is very qualitative and highlights the many possible consequences of our laboratory findings. A quantitative assessment of the impact of the reaction of NO_3 with liquid water (oxidant production), the refined values of H, and the derived values of $HD_\ell^{0.5}$ require more sophisticated atmospheric modeling calculations.

Appendix: Estimation of Henry's Law Coefficient for NO_3 in Water, kf_4 and γ Due to Reaction of NO_3 with H_2O

In our experiments, we measured $HD_\ell^{0.5}$ for NO_3 in aqueous solutions. To estimate Henry's law coefficient for NO_3 in water from this value, the diffusion coefficient of NO_3 in water must be known or estimated. Crudely, the diffusion coefficient in the aqueous phase can be estimated by the equation [*Atkins*, 1990]

$$D_\ell = \frac{kT}{6\pi\eta R^*} \qquad \text{(A1)}$$

Where η is the viscosity of the liquid ($\eta(273\ K)$ = 1.787 cP), T is the temperature, k is Boltzmann constant and R^* is the effective radius of the solvated molecule. Since the exact value of R^* is unknown, we assume it to be 1.2±0.6 Å and obtain $D_\ell(NO_{3(aq)}) = (1.0\pm0.5)\times10^{-5}$ cm^2 s^{-1}. Such a diffusion coefficient yields H= 0.6±0.3 M atm^{-1}. A better knowledge of the diffusion coefficient of NO_3 in water will allow a better calculation of H and to reduce the uncertainties in the value determined here.

The reaction of $NO_{3(aq)}$ with H_2O can be considered to be a two-step process:

1. Solvation of NO_3 in water

$$NO_{3(g)} \overset{H}{\rightleftarrows} NO_{3(aq)}$$

2. Reaction of aqueous $NO_{3(aq)}$ with H_2O

$$\text{(R4)} \qquad NO_{3(aq)} + H_2O_{(aq)} \underset{k_{r4}}{\overset{k_{f4}}{\rightleftarrows}} HNO_{3(aq)} + OH_{(aq)}$$

Calculating the standard free energy change, ΔG^0, of step (R4) would allow us to evaluate k_{f4}. The ΔG^0 value for reaction (R4) can be estimated from the free energy change in the formation of individual species. The standard free energy change, ΔG^*_f, of compounds in the liquid phase are calculated by $\Delta G^*_f = \Delta G^0_f + \Delta G^\#_{sol}$, where $\Delta G^\#_{sol}$ is the ΔG due to solvation, which is calculated using Henry's law coefficient and ΔG^0_f is the standard energy of formation in the gas phase. Although the standard state for solutions is molality, we will use molarity throughout this calculation, since for dilute aqueous solutions, these quantities are essentially the same.

For NO_3, $\Delta G^\#_{sol} = -RT \ln(H) = 0.27^{-0.24}_{+0.40}$ kcal mol^{-1} using H = 0.6±0.3 M atm^{-1}. ΔG^0_f of $NO_{3(g)}$ is 27.75 kcal mol^{-1} [*Chase et al.*, 1985]. Hence ΔG^*_f of $NO_{3(aq)} = 27.75+0.27 = 28.0^{-0.24}_{+0.40}$ kcal mol^{-1}. For $HNO_{3(aq)}$ the physical Henry's law coefficient is needed. There are three equilibria processes that must be taken into account, i.e., Henry's law partition of the nonionized acid H_{HNO_3}

$$HNO_{3\,(g)} \rightleftarrows HNO_{3\,(aq)}$$

followed by the ionization equilibrium, K_{eq}

$$HNO_{3\,(aq)} \rightleftarrows H^+_{(aq)} + NO_3^-{}_{(aq)}$$

These can be combined to give the overall equilibrium for nitric acid K_H

$$HNO_{3\,(g)} \rightleftarrows H^+_{(aq)} + NO_3^-{}_{(aq)}$$

Several calculated values for K_H (M^2 atm^{-1}) at 298 K exist: 3.26×10^7 [*Schwartz and White*, 1981], 2.45×10^6 [*Brimblecombe and Clegg*, 1988], and 2.66×10^6 [*Tang et al.*, 1988]. For this calculation, we will use the most recent value of $K_H = 2.45\times10^6$. K_{eq} has been measured to be 20 M [*Redlich et al.*, 1968]. Henry's law constant for HNO_3 can be calculated by [*Schwartz and White*, 1981] to be

$$H_{HNO_3} = K_H / K_{eq} = 1.22\times10^5\ M\ \text{atm}^{-1}$$

Knowing H_{HNO_3} and ΔG°_f of $HNO_{3(g)}$ = -17.72 kcal mol^{-1}, we calculate ΔG^*_f of $HNO_{3(aq)}$ = -17.72 - $RT\ln(H_{HNO_3})$ = -24.66 kcal mol^{-1}. (Note that the ΔG°_f for $HNO_{3(aq)}$ in the CRC Handbook is actually that for $NO_3^-{}_{(aq)}$).

Using known ΔG^*_f for $OH_{(aq)}$, and $H_2O_{(aq)}$ (6.2 and -56.5 kcal mol^{-1}, respectively [*Golden et al.*, 1990]), ΔG^0 for reaction (R4) is calculated to be ΔG° = 10.0±0.3 kcal mol^{-1}. This standard free energy change yields an equilibrium constant $K_2 = k_{f4}/k_{r4} = exp(-\Delta G/RT) = 4.3\times10^{-8}$ at 298 K. Assuming $k_{r4} = (1.4\pm0.1)\times10^8$ M^{-1} s^{-1} [*Katsamura et al.*, 1991], $k_{f4} \cong 6^{+4}_{-2}$ M^{-1}s^{-1} is obtained at 298 K. With ΔG°= 10.0±0.3 kcal mol^{-1}, k_{f4} at 273 K is calculated to be k_{f4} = 1.3 M^{-1} s^{-1}, corresponding to $\gamma = 5\times10^{-5}$.

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A.R. Ravishankara, Y. Rudich and R.K Talukdar, Aeronomy Laboratory, NOAA, R/E/AL2, 325 Broadway, Boulder CO 80303. (e-mail: ravi@al.noaa.gov; yrudich@al.noaa.gov, talukdar@al.noaa.gov)

R.W. Fox, Time and Frequency Division, NIST, 325 Broadway, Boulder CO 80303. (e-mail: rich@nist.gov)

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