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Received 19 June 2002; revised 13 September 2002; accepted 13 September 2002; published 2 November 2002.

[1] The first measurements of pernitric acid at the South Pole were performed during the second Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT 2000). Observed HO$_2$NO$_2$ concentrations averaged 25 pptv. Simple steady-state calculations constrained by measurements show that the lifetime of pernitric acid was largely controlled by dry deposition, with thermal decomposition becoming increasingly important at warmer temperatures. We determined that the pernitric acid equilibrium constant is less uncertain than indicated in the literature. One consequence of pernitric acid deposition to the snow surface is that it is an important sink for both NO$_x$ and HO$_x$. Another is that the photochemistry of HO$_2$NO$_2$ in the Antarctic snowpack may be a NO$_x$ source in addition to nitrate photolysis. This might be one of the important differences in snow photochemistry between the South Pole and warmer polar sites.


1. Introduction

[2] Atmospheric pernitric acid is formed via the association reaction of NO$_x$ with HO$_2$ [Niki et al., 1977]. Loss pathways include thermal decomposition, photolysis, reaction with OH, and dry deposition.

$$\text{HO}_2 + \text{NO}_x + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M} \quad (1, -1)$$

$$\text{HO}_2\text{NO}_2 + \text{hv} \rightarrow \text{products} \quad (2)$$

$$\text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_x + \text{O}_2 \quad (3)$$

$$\text{HO}_2\text{NO}_2 \rightarrow \text{deposition} \quad (4)$$

2. Methods

[4] HO$_2$NO$_2$ and HNO$_3$ were detected using the SF$_6$ chemical ionization mass spectrometry (CIMS) technique described in detail by Slusher et al. [2001]. The instrument is essentially identical to the one described by Leibrock and Huey [2000]. Measurements were made from the second floor of the Atmospheric Research Observatory (ARO). The CIMS inlet was located 10 m above the snow extending 0.25 m beyond the outer wall of the ARO facing prevailing winds from the clean air sector (0–120° longitude).

[5] The HO$_2$NO$_2$ sensitivity was typically 2.0 Hz/pptv at 2 MHz of reagent ion signal, and the detection limit was 5 pptv for data averaged over 1 min. The detection limit is based on a signal-to-noise ratio of 3:1 where the noise is the standard deviation of the background counts. Pernitric acid was measured between 12/18/00 and 12/28/00. Simultaneous measurements of NO, OH, O$_3$, actinic fluxes, and meteorological parameters were performed as in the ISCAT 1998 campaign [Davis et al., 2001; Mauldin et al., 2001; Lefer et al., 2001]. The OH instrument was switched to (HO$_2$ + RO$_2$) measurement mode on several occasions employing the CIMS procedure described by Cantrell et al. [1997]. This method converts HO$_2$ and RO$_2$ to OH via addition of NO.
NO\textsubscript{2} mixing ratios were derived from steady-state calculations utilizing measurements of NO, O\textsubscript{3}, photolysis frequencies, and a combination of measured and estimated HO\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2}. We assumed CH\textsubscript{3}O\textsubscript{2} was the only RO\textsubscript{2} species of significant concentration. The (HO\textsubscript{2} + RO\textsubscript{2}) data is limited because it and OH could not be measured simultaneously. Therefore, a method for estimating HO\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2} during OH measurements was devised. The fractional CH\textsubscript{3}O\textsubscript{2} contribution to (HO\textsubscript{2} + RO\textsubscript{2}) calculated by a full photochemical box model \[Chen et al., 2001\] was used to extract standalone experimental CH\textsubscript{3}O\textsubscript{2} and HO\textsubscript{2} mixing ratios from the (HO\textsubscript{2} + RO\textsubscript{2}) measurements. The average CH\textsubscript{3}O\textsubscript{2}/(HO\textsubscript{2} + RO\textsubscript{2}) was 0.22 with a range of 0.18 to 0.28. The ratios of HO\textsubscript{2}/OH and CH\textsubscript{3}O\textsubscript{2}/OH were fit as functions of NO to generate predicted HO\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2} values during OH measurement periods. The median predicted HO\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2} matched experimental values within 8%. Of 159 data pairs, 156 predicted HO\textsubscript{2} values and 157 predicted CH\textsubscript{3}O\textsubscript{2} values were within 50% of the corresponding experimental values. Consequently, the overall uncertainty of the model predicted concentrations is essentially the same as the (HO\textsubscript{2} + RO\textsubscript{2}) measurement error of ±60%. The mean [NO\textsubscript{2}]/[NO] was 0.44. Reaction of NO with O\textsubscript{3}, HO\textsubscript{2}, and CH\textsubscript{3}O\textsubscript{2} contributed 86%, 11%, and 3% respectively to the total ratio.

### 3. Results and Analysis

All statistics and analyses are based on 10 min data averages, and only data above established detection limits for each measurement are included. Pernitric acid mixing ratios ranged from <5 to 54 pptv (mean 25 pptv, median 24 pptv) during the measurement period compared with <5 to 68 pptv (22 pptv mean and median) of nitric acid. See Figure 1 for a time series of both species. The total estimated uncertainty is ±50% for HO\textsubscript{2}NO\textsubscript{2} and ±30% for HNO\textsubscript{3}. NO and O\textsubscript{3} mixing ratios averaged 115 pptv and 31 ppbv respectively. The mean dew point was −30.9°C with a range of −36.0°C to −26.5°C while temperatures ranged from −31.5°C to −23.6°C and averaged −27.7°C.

In order to analyze the pernitric acid measurements, HO\textsubscript{2}NO\textsubscript{2} concentrations were predicted from reactions (1)–(3) assuming that steady state was achieved. The HO\textsubscript{2}NO\textsubscript{2} model was constrained by measured NO, OH, O\textsubscript{3}, pressure, and temperature; experimental and estimated HO\textsubscript{2}; and calculated NO\textsubscript{2}. The J-value for pernitric acid was derived by combining the measured UV photolysis rate with an estimate of the near-IR photodissociation rate of \(1 \times 10^{-5}\) s\(^{-1}\) [Roehl et al., 2002]. The resulting average J-value was \(1.6 \times 10^{-5}\) s\(^{-1}\) (with a constant solar zenith angle of ~67°). This corresponds to a photolysis lifetime of 17.4 hr, which contributes little to the average total HO\textsubscript{2}NO\textsubscript{2} lifetime of 1.7 hr obtained by dividing the measured concentrations by the instantaneous production rate (\(P_{\text{HO2NO2}} = k_{\text{13}}[\text{HO2}][\text{NO2}]\)).

Figure 2 compares the pernitric acid measurements and the calculated production rate. The HO\textsubscript{2}NO\textsubscript{2} production rate is also presented versus temperature for reference. The fact that [HO\textsubscript{2}NO\textsubscript{2}] remains essentially flat at production rates above 20 pptv/hr, corresponding to colder temperatures, is contrary to loss controlled by thermal decomposition. As temperature decreases, \(P_{\text{HO2NO2}}\) tends to increase because [NO\textsubscript{x}] also increases (Figure 2 bottom panel); however, the NO\textsubscript{x} flux measured from the snow appears...
Keq is a factor of 10.3 \( k(1) \), primarily due to the uncertainty in \( k(1) \). The HO2NO2 deposition loss frequency can be obtained by reducing the equilibrium rate coefficient, adding dry deposition, or both. At colder temperatures and underprediction at higher temperatures, the atmospheric pernitric acid concentration will decrease via deposition more rapidly at the colder temperatures associated with lower mixed layer heights.

Figure 3 shows that measured pernitric acid levels were much lower than predicted by the simple steady-state model without dry deposition, suggesting that an important loss process is missing from the model. Better agreement can be obtained by reducing the equilibrium rate coefficient, adding dry deposition, or both. At \(-28^\circ C\), the uncertainty in Keq is a factor of 10.3 [DeMore et al., 1997]. This is primarily due to the uncertainty in k_{(-1)} because the forward rate coefficient is well characterized [DeMore et al., 1997]. The HO2NO2 thermal decomposition rate coefficient used by DeMore et al. [1997] to calculate Keq is based solely on an extrapolation of the results obtained by Graham et al. [1977] between \(-19^\circ C\) and \(10^\circ C\) at 1 atm. The expression \( k_{(-1)} = 4.13 \times 10^{-12} e^{\frac{-20134}{RT}} \) was derived for the thermal decomposition rate coefficient at 700 mb from the DeMore et al. [1997] recommended values for Keq and k_{(1)}.

Changing k_{(-1)} so that predicted HO2NO2 levels agree well with measurements at a particular temperature without any dry deposition results in overprediction at lower temperatures and underprediction at higher temperatures (e.g., SS no dd (3.3k_{(-1)}) in Figure 3). A similar result is obtained when a constant loss due to dry deposition is used with no modification to k_{(-1)}. Applying dry deposition as a function of temperature, however, produces much better results. Therefore, we hypothesized that both dry deposition and an adjustment to k_{(-1)} should be added to the steady-state model for pernitric acid.

In an effort to determine the thermal decomposition rate, we assumed the HO2NO2 deposition loss frequency was equal to that of HNO3. Pernitric acid has been observed to readily adsorb on ice [Li et al., 1996], and it seems reasonable to expect deposition behavior similar to that of nitric acid. Given their high sticking probabilities [Li et al., 1996; Diehl et al., 1995; Abbatt, 1997; Zondlo et al., 1997], uptake of both species is likely to be controlled by transport to the snow surface. An average HNO3 lifetime of 3.5 hr (3.1 hr median) was calculated by dividing the measured concentrations by the instantaneous production rate when HNO3 was thought to be in steady state. Loss due to reaction with OH and photolysis was found to be negligible. The required dry deposition rate for HNO3 was found to be temperature dependent, as apparent in Figure 4, due to changing mixing depths as discussed above. Therefore, the first order dry deposition loss coefficient was defined as: \( k_{dd} = -2 \times 10^{-5} (27 + T) + 7 \times 10^{-5} \text{s}^{-1} \), where T is temperature in degrees Celsius. The resulting mean HNO3 lifetime due to dry deposition using this equation is 3.9 hr (median 3.2 hr), which compares well with the calculation above.

Figure 4 shows that measured pernitric acid levels at the South Pole during ISCAT 2000 agree well with calculations. SS indicates steady state and dd represents dry deposition. The various calculations were performed with k_{(-1)} derived from DeMore et al. [1997], k_{(-1)} multiplied by 3.3, and k_{(-1)} multiplied by 1.5 as noted. Symbols represent the mean at each temperature and error bars span ±1 standard deviation.

Figure 3. Comparison of pernitric acid measurements with calculations. SS indicates steady state and dd represents dry deposition. The various calculations were performed with k_{(-1)} derived from DeMore et al. [1997], k_{(-1)} multiplied by 3.3, and k_{(-1)} multiplied by 1.5 as noted. Symbols represent the mean at each temperature and error bars span ±1 standard deviation.

Figure 4. First order nitric acid loss as a function of temperature. Boxes represent the mean at each temperature and error bars span ±1 standard deviation.
[15] A thermal decomposition rate this fast would require a transition from net deposition of HO₂NO₂ at temperatures \( \leq -28^\circ C \) to net flux out of the snow above \(-28^\circ C\) (see Figure 3) in order to maintain the observed HO₂NO₂ concentrations. Furthermore, the NO₂ flux from the snow must also cease at the transition point because all of the gas phase NO₂ would be produced by HO₂NO₂ decomposition alone. Since we know that sunlit snow emits NO₂ [Honrath et al., 1999], and a large, relatively constant NO₂ flux was measured during ISCAT 2000 [Davis et al., in preparation], we do not think this is a realistic scenario.

4. Discussion and Conclusions

[16] We believe that our data are only consistent with efficient deposition of HO₂NO₂ to the snow and that the \( k_{-1} \times 3.3 \) [DeMore et al., 1997] is a firm upper limit to the thermal decomposition rate coefficient for pernitric acid between \(-31.5^\circ C\) and \(-23.5^\circ C\) based on our measurements and analysis. Consequently, it is likely that HO₂NO₂ is stable in other cold regions of the atmosphere. In order to get a more accurate assessment of \( k_{-1} \), measurements are needed in the free troposphere where deposition is not a factor.

[17] When pernitric acid and nitric acid are present in similar amounts in the South Pole boundary layer, as observed during ISCAT 2000, the two species should be approximately equally important HO₃ and NO₃ sinks due to dry deposition. However, pernitric acid dominates the HO₃ loss under these conditions due to its faster reaction with OH [DeMore et al., 1997]. The fact that a large fraction of the NO₂ is returned to the snow in the form of pernitric acid warrants a closer examination of the source(s) of NOₓ released from snow. Current understanding attributes the release of NOₓ from snowpack to the photolysis of NO₃ [Honrath et al., 2000]. If pernitric acid remains intact on ice surfaces, as observed on pure water ice by Li et al. [1996], it has the potential to photodissociate, resulting in direct release of NO₂. This might produce more efficient cycling of NOₓ between the snow and air than nitrate photolysis alone. HO₂NO₂ does have a larger gas phase absorption cross-section than HNO₃ [DeMore et al., 1997] for wavelengths >205 nm. However, to our knowledge, the photochemistry of HO₂NO₂ and pernitrate, NO₄, has not been determined on an ice surface or in aqueous solution.

[18] Pernitric acid deposited to the snow might also undergo other chemical transformations analogous to its behavior in aqueous solution (e.g., Regimbal and Mozurkewich [1997], and references within). Studies of pernitric acid photochemistry on ice and snow surfaces are needed in order to determine its significance as a NO₄ source. If pernitric acid photochemistry on and in snow does enhance NO₃ release into the atmosphere, it might be one of the factors that makes South Pole snowpack chemistry unique. Pernitric acid mixing ratios are probably much lower at other polar sites because of warmer temperatures and much lower NO₃ levels.

Acknowledgments. We thank NOAA CMDL for O₃, CO, and meteorological data. We also appreciate the suggestions of two reviewers and Dr. Tom Ryerson. This work was funded by the NSF Office of Polar Programs and Division of Atmospheric Chemistry grant OPP-975465 and NASA Earth Systems Science fellowship grant NGT5-30384.

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