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Measurements of pernitric acid at the South Pole during ISCAT 2000

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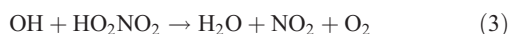
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[1] The first measurements of pernitric acid at the South Pole were performed during the second Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT 2000). Observed HO₂NO₂ concentrations averaged 25 pptv. Simple steady-state calculations 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 HO₂NO₂ 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.

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1. Introduction

[2] Atmospheric pernitric acid is formed via the association reaction of NO₂ with HO₂ [Niki *et al.*, 1977]. Loss pathways include thermal decomposition, photolysis, reaction with OH, and dry deposition.



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Uncertainties in the HO₂NO₂ equilibrium constant ($K_{\text{eq}} = k_{(1)}/k_{(-1)}$) and absorption cross-section at long wavelengths have fueled recent speculation, often conflicting, in the literature about pernitric acid's roles as a radical source and sink in the upper atmosphere [Wennberg *et al.*, 1999; Brune *et al.*, 1999; Jaeglé *et al.*, 2001]. The discovery of elevated NO_x levels at Summit, Greenland; Alert, Canada; Neumayer Station in Antarctica; and the South Pole [Honrath *et al.*, 1999; Ridley *et al.*, 2000; Jones *et al.*, 2000; Davis *et al.*, 2001] indicates that HO₂NO₂ may also play an important role in the low altitude photochemistry of polar regions.

[3] One interesting feature of the South Pole is that the average NO level (based on 1998 and 2000 ISCAT observations) is nearly ten times larger than that observed at any of the other polar stations. These high NO_x levels along with very cold temperatures make the South Pole an ideal place to study pernitric acid. Modeling results from the 1998 ISCAT study predicted that pernitric acid is the second most important HO_x sink at the South Pole, behind HNO₃, by way of dry deposition and reaction with OH [Chen *et al.*, 2001]. It follows that dry deposition of pernitric acid should also be an important NO_x sink in this environment. Presented here is an analysis of pernitric acid measurements made at the South Pole during ISCAT 2000.

2. Methods

[4] HO₂NO₂ and HNO₃ were detected using the SF₆⁻ 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 HO₂NO₂ 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, O₃, 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 (HO₂ + RO₂) measurement mode on several occasions employing the CIMS procedure described by Cantrell *et al.* [1997]. This method converts HO₂ and RO₂ to OH via addition of NO.

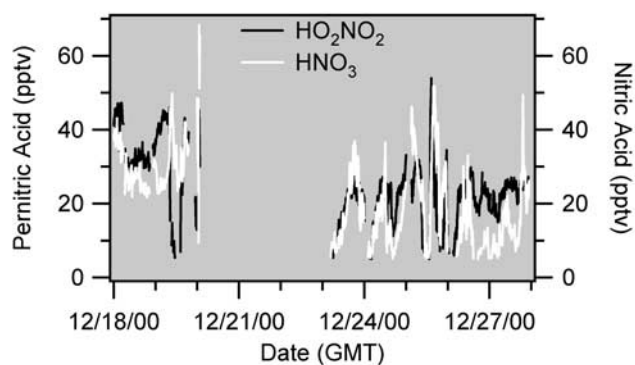


Figure 1. Measured pernitric acid and nitric acid. All data has been averaged for 10 min. No data is available for 12/20/00 – 12/22/00 due to snow sampling experiments.

[6] NO_2 mixing ratios were derived from steady-state calculations utilizing measurements of NO , O_3 , photolysis frequencies, and a combination of measured and estimated HO_2 and CH_3O_2 . We assumed CH_3O_2 was the only RO_2 species of significant concentration. The $(\text{HO}_2 + \text{RO}_2)$ data is limited because it and OH could not be measured simultaneously. Therefore, a method for estimating HO_2 and CH_3O_2 during OH measurements was devised. The fractional CH_3O_2 contribution to $(\text{HO}_2 + \text{RO}_2)$ calculated by a full photochemical box model [Chen *et al.*, 2001] was used to extract standalone experimental CH_3O_2 and HO_2 mixing ratios from the $(\text{HO}_2 + \text{RO}_2)$ measurements. The average $\text{CH}_3\text{O}_2/(\text{HO}_2 + \text{RO}_2)$ was 0.22 with a range of 0.18 to 0.28. The ratios of HO_2/OH and $\text{CH}_3\text{O}_2/\text{OH}$ were fit as functions of NO to generate predicted HO_2 and CH_3O_2 values during OH measurement periods. The median predicted HO_2 and CH_3O_2 matched experimental values within 8%. Of 159 data pairs, 156 predicted HO_2 values and 157 predicted CH_3O_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 $(\text{HO}_2 + \text{RO}_2)$ measurement error of $\pm 60\%$. The mean $[\text{NO}_2]/[\text{NO}]$ was 0.44. Reaction of NO with O_3 , HO_2 , and CH_3O_2 contributed 86%, 11%, and 3% respectively to the total ratio.

3. Results and Analysis

[7] 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 $\pm 50\%$ for HO_2NO_2 and $\pm 30\%$ for HNO_3 . NO and O_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 .

[8] In order to analyze the pernitric acid measurements, HO_2NO_2 concentrations were predicted from reactions (1)–(3) assuming that steady state was achieved. The HO_2NO_2 model was constrained by measured NO , OH , O_3 , pressure, and temperature; experimental and estimated HO_2 ; and

calculated NO_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 $1 \times 10^{-5} \text{ s}^{-1}$ [Roehl *et al.*, 2002]. The resulting average J-value was $1.6 \times 10^{-5} \text{ s}^{-1}$ (with a constant solar zenith angle of $\sim 67^\circ$). This corresponds to a photolysis lifetime of 17.4 hr, which contributes little to the average total HO_2NO_2 lifetime of 1.7 hr obtained by dividing the measured concentrations by the instantaneous production rate ($P_{\text{HO}_2\text{NO}_2} = k_{(1)}[\text{HO}_2][\text{NO}_2]$).

[9] Figure 2 compares the pernitric acid measurements and the calculated production rate. The HO_2NO_2 production rate is also presented versus temperature for reference. The fact that $[\text{HO}_2\text{NO}_2]$ 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, $P_{\text{HO}_2\text{NO}_2}$ tends to increase because $[\text{NO}_x]$ also increases (Figure 2 bottom panel); however, the NO_x flux measured from the snow appears

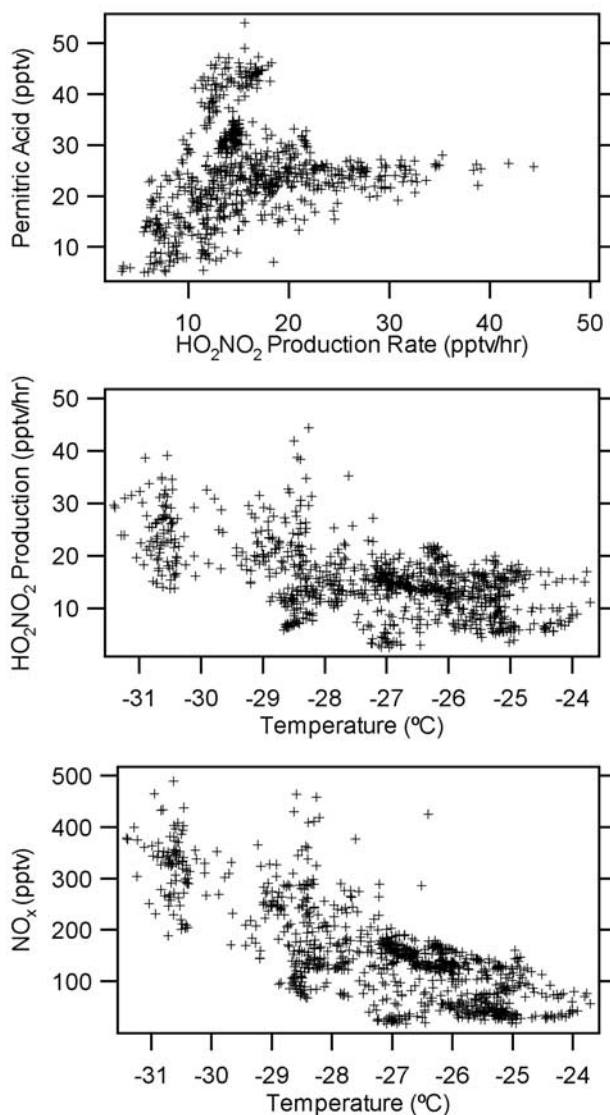


Figure 2. Measured pernitric acid concentration, pernitric acid production rate, temperature measured at 1.6 m, and NO_x . $\text{NO}_x = \text{measured NO} + \text{modeled NO}_2$.

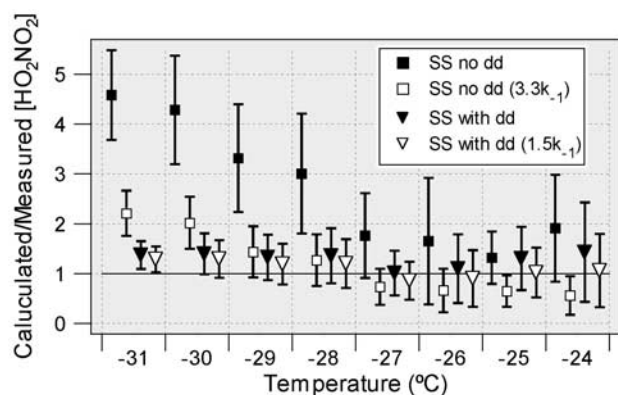


Figure 3. Comparison of pernitric acid measurements with calculations. SS indicates steady state and dd represents dry deposition. The various calculations were performed with $k_{(-1)}$ derived from *DeMore et al.* [1997], $k_{(-1)}$ multiplied by 3.3, and $k_{(-1)}$ multiplied by 1.5 as noted. Symbols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

to be constant $\pm 30\%$ [*Davis et al.*, in preparation]. This indicates that the mixing depth decreases with decreasing temperature, allowing for the buildup of NO_x released from the snowpack. It follows that the atmospheric pernitric acid concentration will decrease via deposition more rapidly at the colder temperatures associated with lower mixed layer heights.

[10] 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°C , the uncertainty in K_{eq} 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 HO_2NO_2 thermal decomposition rate coefficient used by *DeMore et al.* [1997] to calculate K_{eq} is based solely on an extrapolation of the results obtained by *Graham et al.* [1977] between -19°C and 10°C at 1 atm. The expression $k_{(-1)} = 4.13 \times 10^{-13} e^{(-20134/RT)}$ was derived for the thermal decomposition rate coefficient at 700 mb from the *DeMore et al.* [1997] recommended values for K_{eq} and $k_{(1)}$.

[11] Changing $k_{(-1)}$ so that predicted HO_2NO_2 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.

[12] In an effort to determine the thermal decomposition rate, we assumed the HO_2NO_2 deposition loss frequency was equal to that of HNO_3 . 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 HNO_3 lifetime of 3.5 hr (3.1 hr median) was calculated by dividing the measured concentrations by the instantaneous production rate when HNO_3 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 HNO_3 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: $k_{(4)} = -2 \times 10^{-5}(27 + T) + 7 \times 10^{-5} \text{ s}^{-1}$ where T is temperature in degrees Celsius. The resulting mean HNO_3 lifetime due to dry deposition using this equation is 3.9 hr (median 3.2 hr), which compares well with the calculation above.

[13] Setting the HO_2NO_2 deposition lifetime equal to that of HNO_3 allows us to put an upper limit on $k_{(-1)}$. As shown in Figure 3, we found that multiplying $k_{(-1)}$ by 1.5, equivalent to dividing K_{eq} by 1.5, reproduced the observed data best, with the median predicted value just 1% smaller than observed (average 5% larger). The 1st quartile was 30% smaller than the corresponding observations, and the 3rd quartile was 30% larger. Note that multiplying $k_{(-1)}$ by 1.5 is equivalent, within 1% across our temperature range, to increasing the activation energy (E_a) in the Arrhenius equation from 20134 cal/mol to 20332 cal/mol.

[14] The possibility that flux from the snow might be a source of pernitric acid under certain conditions is not supported by the measurements. Addition of a snow source term would require K_{eq} to be substantially smaller than the JPL recommendation, which is possible given the large uncertainty factor. However, as pernitric acid's thermal decomposition rate increases, its importance as a NO_x source via reaction (-1) is amplified. Steady-state calculations using $k_{(-1)} \times 3.3$ show that thermal decomposition of the observed HO_2NO_2 can account for all of the observed NO_x at -26°C , and even more than the observed NO_x would be produced at warmer temperatures. Changing E_a for $k_{(-1)}$ from 20134 cal/mol to 20717 cal/mol is equal to multiplying $k_{(-1)}$ by $3.3 \pm 2\%$ between -23.5°C and -31.5°C .

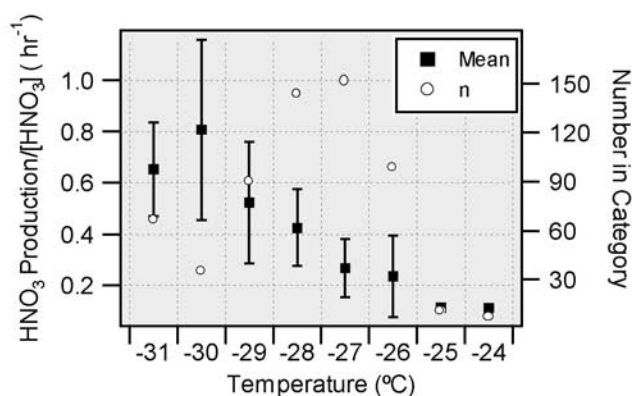


Figure 4. First order nitric acid loss as a function of temperature. Boxes represent the mean at each temperature and error bars span ± 1 standard deviation.

[15] A thermal decomposition rate this fast would require a transition from net deposition of HO_2NO_2 at temperatures $\leq -28^\circ\text{C}$ to net flux out of the snow above -28°C (see Figure 3) in order to maintain the observed HO_2NO_2 concentrations. Furthermore, the NO_x flux from the snow must also cease at the transition point because all of the gas phase NO_x would be produced by HO_2NO_2 decomposition alone. Since we know that sunlit snow emits NO_x [Honrath *et al.*, 1999], and a large, relatively constant NO_x 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 HO_2NO_2 to the snow and that $k_{(-1)} \times 3.3$ [DeMore *et al.*, 1997] is a firm upper limit to the thermal decomposition rate coefficient for pernitric acid between -31.5°C and -23.5°C based on our measurements and analysis. Consequently, it is likely that HO_2NO_2 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 HO_x and NO_x sinks due to dry deposition. However, pernitric acid dominates the HO_x loss under these conditions due to its faster reaction with OH [DeMore *et al.*, 1997]. The fact that a large fraction of the NO_x is returned to the snow in the form of pernitric acid warrants a closer examination of the source(s) of NO_x released from snow. Current understanding attributes the release of NO_x from snowpack to the photolysis of NO_3^- [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 NO_2 . This might produce more efficient cycling of NO_x between the snow and air than nitrate photolysis alone. HO_2NO_2 does have a larger gas phase absorption cross-section than HNO_3 [DeMore *et al.*, 1997] for wavelengths >205 nm. However, to our knowledge, the photochemistry of HO_2NO_2 and pernitrate, NO_4^- , 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 NO_x source. If pernitric acid photochemistry on and in snow does enhance NO_x 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 NO_x levels.

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