Shouldn’t snowpacks be sources of monocarboxylic acids?

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Measurements of pernitric acid at the South Pole during ISCAT 2000

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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 NOx and HOx. Another is that the photochemistry of HO2NO2 in the Antarctic snowpack may be a NOx 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 NO2 with HO2 [Niki et al., 1977]. Loss pathways include thermal decomposition, photolysis, reaction with OH, and dry deposition.

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

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

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

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

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 (0–120º 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.

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NO2 mixing ratios were derived from steady-state calculations utilizing measurements of NO, O3, photolysis frequencies, and a combination of measured and estimated HO2 and CH3O2. We assumed CH3O2 was the only RO2 species of significant concentration. The (HO2 + RO2) data is limited because it and OH could not be measured simultaneously. Therefore, a method for estimating HO2 and CH3O2 during OH measurements was devised. The fractional CH3O2 contribution to (HO2 + RO2) calculated by a full photochemical box model [Chen et al., 2001] was used to extract standalone experimental CH3O2 and HO2 mixing ratios from the (HO2 + RO2) measurements. The average CH3O2/(HO2 + RO2) was 0.22 with a range of 0.18 to 0.28. The ratios of HO2/OH and CH3O2/OH were fit as functions of NO to generate predicted HO2 and CH3O2 values during OH measurement periods. The median predicted HO2 and CH3O2 matched experimental values within 8%. Of 159 data pairs, 156 predicted HO2 values and 157 predicted CH3O2 values were within 50% of the corresponding experimental values. Consequently, the overall uncertainty of the model predicted concentrations is essentially the same as the (HO2 + RO2) measurement error of ±60%. The mean [NO2]/[NO] was 0.44. Reaction of NO with O3, HO2, and CH3O2 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 HO2NO2 and ±30% for HNO3. NO and O3 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, HO2NO2 concentrations were predicted from reactions (1)–(3) assuming that steady state was achieved. The HO2NO2 model was constrained by measured NO, OH, O3, pressure, and temperature; experimental and estimated HO2; and calculated NO2. 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 HO2NO2 lifetime of 1.7 hr obtained by dividing the measured concentrations by the instantaneous production rate ($P_{HO2NO2} = k_{13}[HO2][NO2]$).

Figure 2 compares the pernitric acid measurements and the calculated production rate. The HO2NO2 production rate is also presented versus temperature for reference. The fact that [HNO3] 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, $P_{HO2NO2}$ tends to increase because [NO3] also increases (Figure 2 bottom panel); however, the NOx flux measured from the snow appears

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.

Figure 2. Measured pernitric acid concentration, pernitric acid production rate, temperature measured at 1.6 m, and NOx. NOx = measured NO + modeled NO2.
Keq is a factor of 10.3 \[ \text{primarily due to the uncertainty in } k(-1) \text{ we assumed the HO2NO2 deposition loss frequency to be constant } \pm 30\% \text{ [Davis et al., in preparation]. This indicates that the mixing depth decreases with decreasing temperature, allowing for the buildup of NOx 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.}

Changing \[ k(-1) \text{ so that predicted HO2NO2 levels agree well with measurements at a particular temperature without dry deposition results in overprediction at lower temperatures and underprediction at higher temperatures (e.g., SS no dd (3.3) in Figure 3). A similar result is obtained when a constant loss due to dry deposition is used with no modification to } k(-1). \text{ 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) \text{ 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; 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_{ss} = -2 \times 10^{-5} (27 + T) + 7 \times 10^{-5} \text{ s}^{-1} \text{ where } T \text{ 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.}

[13] Setting the HO2NO2 deposition lifetime equal to that of HNO3 allows us to put an upper limit on \[ k(-1). \text{ As shown in Figure 3, found that multiplying } k(-1) \text{ by 1.5, equivalent to dividing } K_{eq} \text{ 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) \text{ by 1.5 is equivalent, within 1\% across our temperature range, to increasing the activation energy } (E_a) \text{ in the Arrhenius equation from 20134 cal/mol to 20332 cal/mol.}

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} \text{ 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 NOx source via reaction (-1) is amplified. Steady-state calculations using } k(-1) \times 3.3 \text{ show that thermal decomposition of the observed HO2NO2 can account for all of the observed NOx at } -26^\circ \text{C, and even more than the observed NOx would be produced at warmer temperatures. Changing } E_a \text{ for } k(-1) \text{ from 20134 cal/mol to 20717 cal/mol is equal to multiplying } k(-1) \text{ by } 3.3 \pm 2\% \text{ between } -23.5^\circ \text{C and } -31.5^\circ \text{C.}

[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} \text{ 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 NOx source via reaction (-1) is amplified. Steady-state calculations using } k(-1) \times 3.3 \text{ show that thermal decomposition of the observed HO2NO2 can account for all of the observed NOx at } -26^\circ \text{C, and even more than the observed NOx would be produced at warmer temperatures. Changing } E_a \text{ for } k(-1) \text{ from 20134 cal/mol to 20717 cal/mol is equal to multiplying } k(-1) \text{ by } 3.3 \pm 2\% \text{ between } -23.5^\circ \text{C and } -31.5^\circ \text{C.}}
A thermal decomposition rate constant that fast would require a transition from net deposition of HO2NO2 to temperatures \(-28^\circ\)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 NOx 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 NOx [Honrath et al., 1999], and a large, relatively constant NOx flux was measured during ISCAT 2000 [Davis et al., in preparation], we do not think this is a realistic scenario.

4. Discussion and Conclusions

We believe that our data are only consistent with efficient deposition of HO2NO2 to the snow and that k_{(-1)} = 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 \(-23^\circ\)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.

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 in thermodynamic equilibrium. However, pernitric acid dominates the HOx loss under these conditions due to its faster reaction with OH [DeMore et al., 1997]. The fact that a large fraction of the NOx released from 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 NOx. 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 HNO2 [DeMore et al., 1997] for wavelengths \(>205\) nm. However, to our knowledge, the photochemistry of HO2NO2 and pernitric acid, NOx, has not been determined on an ice surface or in aqueous solution.

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 NOx source. If pernitric acid photochemistry on and in snow does enhance NOx 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 NOx levels.

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