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The effect of the novel $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ reaction channel at South Pole, Antarctica

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Abstract: It is well established that the reaction of HO$_2$ with NO plays a central role in atmospheric chemistry, by way of OH/HO$_2$ recycling and reduction of ozone depletion by HO$_x$ cycles in the stratosphere and through ozone production in the troposphere. Utilizing a photochemical box model, we investigate the impact of the recently observed HNO$_3$ production channel ($\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$) on NO$_x$ (NO + NO$_2$), HO$_x$ (OH + HO$_2$), HNO$_3$, and O$_3$ concentrations in the boundary layer at the South Pole, Antarctica. Our simulations exemplify decreases in peak O$_3$, NO, NO$_2$, and OH and an increase in HNO$_3$. Also, mean OH is in better agreement with observations, while worsening the agreement with O$_3$, HO$_2$, and HNO$_3$ concentrations observed at the South Pole. The reduced concentrations of NO$_x$ are consistent with expected decreases in atmospheric NO$_x$ lifetime as a result of increased sequestration of NO$_x$ into HNO$_3$. Although we show that the inclusion of the novel HNO$_3$ production channel brings better agreement of OH with field measurements, the modelled ozone and HNO$_3$ are worsened, and the changes in NO$_x$ lifetime imply that snowpack NO$_x$ emissions and snowpack nitrate recycling must be re-evaluated.

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Key words: boundary layer, ice photochemistry, nitric acid, NO$_x$, ozone, polar chemistry

Introduction

The South Pole station is located on the central high latitude (~3000 m) polar plateau, which is sufficiently inland to avoid the influence of short-lived chemical species that originate from the marine environment. Given Antarctica's huge separation from pollution sources, it was expected to be pristine with very low photochemical activity - an example for clean air conditions (Crawford et al. 2001). Given this expectation, it was assumed that concentrations of trace gases (e.g. NO$_x$ (NO + NO$_2$), hydrocarbons, HO$_x$, O$_3$, HNO$_3$ etc.) were low. On the contrary, a series of field campaigns have revealed intense chemical activity as implied by unexpectedly high concentrations of trace gases (e.g. Davis et al. 2001), occurring within the Antarctic Boundary Layer (ABL), most notably at the South Pole. The geographical position and meteorology of the South Pole also contributes to this unique chemistry, rather than direct anthropogenic pollution. The low average temperatures during springtime and summertime, ~223 and ~243 K, respectively, frequently cause temperature inversions at the surface, thus limiting the depth of mixed air and greatly impacting boundary layer chemistry. Compounding this issue, the prevailing wind upon the plateau, down-slope off the continent towards the sea, results in longer plateau residence times for air masses. Thus far, the following chemistry has been discovered: 1) NO$_x$ associated with high ozone (O$_3$) and NO$_x$ (Crawford et al. 2001, Davis et al. 2001, 2004, 2008, Dibb et al. 2004, Huey et al. 2004), 2) higher than expected HO$_x$ (Chen et al. 2004, Mauldin et al. 2004), and 3) emissions of formaldehyde (HCHO) and hydrogen peroxide (H$_2$O$_2$) from the South Pole snowpack (Hutterli et al. 2004). These measurements have shown that the South Pole boundary layer can be a highly oxidizing environment. The ABL depth has a strong influence on the photochemical activity present as this governs the mixing volume and, therefore, the impact emissions will have on overlying boundary layer chemistry (Davis et al. 2008).

One of the most intriguing aspects of these field campaigns is the high NO (e.g. maximum emission rates of 600 pptv s$^{-1}$ ~ 1.70 x 10$^{10}$ molecules cm$^{-3}$ s$^{-1}$) found in the summer at the South Pole (Davis et al. 2001), which would normally be associated with suburban pollution. Field studies have shown that nitrate photochemistry at the Arctic and coastal Antarctic snowpack predominantly governs the release of NO$_x$ to the overlying boundary layer, reaching levels up to ~200 pptv s$^{-1}$ ~ 5.70 x 10$^9$ molecules cm$^{-3}$ s$^{-1}$ (Grannas et al. 2007). In addition, laboratory studies have shown that the photolysis of µM NO$_3^-$ (2 and 30 µM NO$_3^-$-doped ice films) on ice produces at most 100 pptv s$^{-1}$ ~ 2.80 x 10$^9$ molecules cm$^{-3}$ s$^{-1}$ and ~240 pptv s$^{-1}$ ~ 6.80 x 10$^9$ molecules cm$^{-3}$ s$^{-1}$ of NO$_2$, respectively (Cotter et al. 2003, Boxe et al. 2003, 2005).

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Nitric oxide (NO) production solely from nitrate photochemistry at the South Pole on snow/ice does not account for 600 pptv s⁻¹ ~ 1.70 x 10¹⁰ molecules cm⁻³ s⁻¹ of NO (Davis et al. 2001). It appears that photochemistry and the changing boundary layer height (BLH) contribute to trace gas emissions at the South Pole. Two campaigns have shown that the photochemistry at the South Pole is being driven by the emission of NOₓ from the snowpack and the changing BLH (Crawford et al. 2001, Davis et al. 2004), which in turn determines the concentration of NOₓ by altering the mixing volume. A shallower ABL means a smaller mixing volume, therefore, NOₓ emissions will produce higher resultant NOₓ concentrations (Davis et al. 2004). In addition, the 24 hour sunlight exposure of the plateau in conjunction with the enhanced photon flux, due to the high surface albedo, plays an important role in determining the photochemical activity (Lefer et al. 2001, Jones & Wolff 2003). The concentration of trace gases in the ABL is also affected by the emissions of HCHO, H₂O₂, oxygenated volatile organic compounds (OVOCs) from the snowpack (Hutterli et al. 2004, Frey et al. 2005), which have been shown through modelling studies to enhance the HOₓ budget (Chen et al. 2004) and impact ozone production and OH sequestration. Simultaneously, OVOCs can be HOₓ sinks, depending upon environmental conditions. For instance, Hamer et al. (2007) showed that up to 3-4 pptv of the observed ozone results from the oxidation of OVOCs by OH. In addition, the low average temperatures lead to temperature inversions at the surface, thus limiting the depth of mixed air and greatly impacting overlying boundary layer chemistry. Air masses tend to have long plateau residence times, which are due to the prevailing wind upon the plateau, down-slope off the continent towards the sea.

It is well known that HO₂ + NO → OH + NO₂ (R1a) (Table I) plays a major role in atmospheric chemistry. Recently, HO₂ + NO → HNO₃ (R1b) (Table I) was discovered in the laboratory (Butkovskaya et al. 2005, 2007) and subsequently investigated using the GEOS-CHEM 3-D tropospheric chemical transport model (CTM) (Carlile et al. 2008). The Carlile et al. (2008) study was performed at a global scale with a representation of the atmospheric chemistry mostly for the free troposphere. Therefore, the impact could be different for specific regions, where background species concentrations vary from the mean values produced by GEOS-CHEM. This could be the case in boundary layers, over continents or polluted areas. One specific example is in Antarctica, where GEOS-CHEM specifically lacks any parameterization for the modelling of snowpack NOₓ emissions. Hence, given the need for additional snowpack-polar boundary layer chemical modelling (Jacobi & Hilker 2007, Boxe & Saiz-Lopez 2008, 2009, Bock & Jacobi 2010) and given the potentially significant impact on regional-scale boundary layer chemistry, we investigate, via a photochemical box model, the impact of (R1b) on NOₓ, HOₓ, HNO₃, and O₃ concentrations just above the South Pole snowpack.

**Model description**

The same photochemical box model used in Hamer et al. (2007, 2008) was used in the present investigation. This photochemical box model was built using ASAD ('A Self-contained Atmospheric chemistry code', Carver et al. 1997) and was set up to describe the South Pole boundary layer conditions. The model consists of two vertically stacked boxes of air that mix at a rate such that 10% of the box volume is exchanged with a time step of 1/12 h. The upper layer of the model mixes with the free tropospheric background concentrations of long-lived species at a rate of 5% per model 1/12 h time step. The model mechanism has 472 gas phase reactions, representative of 163 species and is based on the Master Chemical Mechanism (Jenkin et al. 1997). The mechanism includes inorganic reactions, initial reactions of non-methane hydrocarbons (NMHCs) with OH, NO₃, and O₃, and detailed chemical mechanisms describing the degradation pathways of NMHCs containing up to five carbon atoms. The free tropospheric background concentrations of CO, CH₄, and NMHC were adjusted to be consistent with their respective measured background concentrations at Antarctica. The model achieves these

### Table I. List of all reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO₂ + NO → OH + NO₂ (R1a)</td>
<td></td>
</tr>
<tr>
<td>HO₂ + NO → HNO₃ (R1b)</td>
<td></td>
</tr>
<tr>
<td>OH + CO₂ → HO₂ + CO₂ (R2)</td>
<td></td>
</tr>
<tr>
<td>OH + VOC → HO₂ + products (R3)</td>
<td></td>
</tr>
<tr>
<td>OH + NOₓ → HNO₃ + M (R4)</td>
<td></td>
</tr>
<tr>
<td>OH + CO₂ → HO₂ + NO₂ (R5)</td>
<td></td>
</tr>
<tr>
<td>NO + M → O(P) + O₂ (R6)</td>
<td></td>
</tr>
<tr>
<td>O(P) + O₂ → O₃ (R7)</td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Background concentrations used in the model.

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>Background free tropospheric concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>25 pptv</td>
</tr>
<tr>
<td>CO</td>
<td>44 pptv</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.72 ppmv</td>
</tr>
<tr>
<td>Ethene</td>
<td>200 pptv</td>
</tr>
<tr>
<td>Propane</td>
<td>10 pptv</td>
</tr>
<tr>
<td>Ethene</td>
<td>8 pptv</td>
</tr>
<tr>
<td>Butane</td>
<td>5 pptv</td>
</tr>
<tr>
<td>Methyl hydroperoxide</td>
<td>140 pptv</td>
</tr>
<tr>
<td>Acetone</td>
<td>140 pptv</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75 pptv</td>
</tr>
</tbody>
</table>

Ppbv = parts per billion by volume, ppmv = parts per million by volume, pptv = parts per trillion by volume.

*Background concentrations of shorter-lived species are higher than reported for ambient South Pole boundary layer levels. The highly oxidizing nature of the South Pole boundary layer requires that free tropospheric concentrations must be elevated relative to the boundary layer concentrations to maintain the observed ambient boundary layer concentrations.
concentrations via free tropospheric mixing in the upper box. Non-methane hydrocarbon concentrations and other background species used in the model were obtained from the ISCAT 2000 (Investigation of Sulfur Chemistry in Antarctic Troposphere) campaign and the CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) project. CO and CH₄ concentrations were obtained from National Oceanic and Atmospheric Administration South Pole flask data. Given the recent identification of OVOCs (methyl hydroperoxide, acetaldehyde, and acetone) at the South Pole (Frey et al. 2005, Hamer et al. 2007), their corresponding background concentrations were also added, such that there is a flux of OVOCs into the upper box. All of the free tropospheric background concentrations are specified in Table II. The albedo of the snowpack surface in the model was set at 0.8 (Lefèvre et al. 2001). Nitrate photolysis and NOₓ emissions from the snowpack was described by using a prescribed emission ratio of 1:2 for NO with respect to NO₂ (Jones et al. 2000, 2001, Cotter et al. 2003). This reflects studies of snowpack concentrations of NOₓ observed during field campaigns at the South Pole and Neumayer (Crawford et al. 2001, Davis et al. 2004). The flux of NOₓ out of the snowpack is 2.4 x 10^{10} molecules cm^{-2} s^{-1}. In addition to the snowpack NOₓ emissions, fluxes of O(3P) atoms were included into the lower box in line with Hamer et al. (2008) and Yabushita et al. (2007). HCHO and H₂O fluxes were added to the model, which were equivalent to their respective fluxes observed at the South Pole (Hutterli et al. 2004). A wide range of chemical species are also deposited in the lower box onto the snow. A complete list of the deposited species and the deposition rates used is included in the supplemental material (M. King, personal communication 2004; http://dx.doi.org/10.1017/S0954102012000144).

Model simulations

In all of the simulations the model was run over a 15 day period using the same calendar day (30 December) in order to achieve steady state. All of the results presented represent model values from the 15th day though the model does achieve steady state by the 10th day of the simulation. Initial model concentrations of long-lived species are fixed at their background concentrations for the South Pole site and are maintained in part by the downward fluxes due to the free tropospheric background concentrations presented in Table II. These downward fluxes are sufficient to maintain these long-lived species at their observed concentrations. The spin-up period is sufficiently long to prevent model result sensitivity to short-lived species concentrations. A sensitivity analysis was carried out, where the model was setup to run under two scenarios, using the kinetic rate coefficient data for reaction (R1b). The model was run 15 times using a range of BLHs (500, 400, 350, 300, 250, 200, 150, 125, 100, 75, 60, 50, 40, 35 and 30 m) with a constant NOₓ emission of 2.4 x 10^{10} molecules cm^{-2} s^{-1}. The model produces a range of NOₓ concentrations that are consistent with observed ranges. Using this full range of tropospheric BLHs, the model was run using a branching ratio (β) of zero for the ‘Base Case’ and using β ≈ 0.78 equivalent to 243 K and surface pressure at the South Pole for the perturbed case, run ‘β-Rate 1’. To be consistent with the central Antarctic plateau region, the location of the box model was set to the surface at 88°S. This location has a weak diurnal cycle in actinic flux, which is not fully representative of the South Pole, but allows for more stable simulations. Further details of the ‘Base Case’ model run can be found in Hamer et al. (2007) under ‘run B’ and in Hamer et al. (2008) in relation to the ‘1 x O(3P) run’.

Reaction (R1a) plays a central role in atmospheric chemistry by way of OH/HO₂ recycling, reduction of ozone depletion by HOₓ cycles in the stratosphere, and in ozone production in the troposphere. In the stratosphere this reaction moderates the effectiveness of the cycle involving HOₓ radicals, which is an important removal mechanism of ozone (Wayne 2000). In the troposphere this reaction plays a key role in controlling the interconversion between HO₂ and OH radicals through cycles involving OH, CO, and volatile organic compounds (VOCs) (see (R2) and (R3) Table I). The VOCs include methane, NMHCs, and other volatile carbon-containing species. Reaction (R3) is a secondary source of OH radicals as well as the major source of tropospheric ozone, through the conversion of NO and NO₂, followed by the photolysis of NO₂ to NO and O(3P) atoms. The O(3P) atoms produced combine with O₂ to produce ozone. The OH and O₃ production rates are, therefore, limited primarily by the chain termination reaction involving OH and NO₂ (see Table I for (R4)).

Reaction (R1b) could be another significant chain termination reaction. To assess the importance of reaction (R1b) in the troposphere, Bukovskaya et al. (2007) determined the branching ratio β(T, P) or rate constant ratio, β(T, P) = k_{1b}/k_{1a} = (530/7(T K)) + (6.4 x 10^{-12} x P(torr)) - 1.73, over the full range of tropospheric pressures and temperatures (i.e. 298 K and 760 torr (Earth’s surface)) to 220 K and 200 torr (Earth’s tropopause)). Consequently, at the Earth’s surface β(T, P) ≈ 0.5% and in the tropopause region β(T, P) ≈ 0.8%. Given the significant branching of (R1b) (i.e. β(T, P) ≈ 0.78%), for T = 243 K) at the surface in the central Antarctic plateau region, we conduct photochemical box model simulations with and without the inclusion of (R1b) and assess its impact on NOₓ, HOₓ, HNO₃, and O₃ concentrations just above the South Pole snowpack. The rate constant k₁b was derived from β(T, P) by considering the recommended value k₁b = 3.5 x 10^{-12} exp(250/T) cm³ molecule⁻¹ s⁻¹ (Sander et al. 2006). This NASA Jet Propulsion Laboratory evaluation panel recommended value and the one recommended by the International Union of Pure and Applied Chemistry (IUPAC) panel (Atkinson et al. 2004, updated in 2006 at http://www.iupac-kinetic.ch.cam.ac.uk, accessed June 2006) are very similar, the IUPAC one being higher by only 14% at 200 K and 10% at 300 K.
Fig. 1. Diurnal photochemical box model simulations, representative of South Pole conditions of a. O$_3$, b. NO, c. NO$_2$, d. OH, e. HO$_2$, and f. HNO$_3$ with (red lines) and without (blue lines) HO$_2$ + NO → HNO$_3$ (R1b). All model simulations start at midday. Note: in this figure (k1b) refers to the reaction rate constant of (R1b), which in turn, refers to the same reaction.
Results and discussion

Figure 1a–f displays diurnal photochemical box model simulations at 243 K (representative of the South Pole summer conditions and a BLH of 35 m) of O₃, NO, NO₂, OH, H₂O₂, and HNO₃ with and without (R1b) starting at midday. The blue profiles denote model simulations without (R1b) included, while the red profiles denote model simulations with (R1b) included. Box model simulations show that O₃ concentration diurnal profiles follow a typical pattern of variability for a polluted environment at the surface, i.e. ozone production beginning in the morning, followed by a peak in ozone concentrations in mid-afternoon, concluding with a decrease in ozone concentrations during the evening. In this simulation this occurs primarily due to the variability in actinic flux and its direct effects upon the chemistry due to the induced changes in snowpack NOₓ emissions and photolysis rates of photochemical species. Specifically, increased levels of sunlight lead to enhancements in ozone via reactions (R1a), (R5), (R6) and (R7) (Table I). The decrease in ozone occurs in the evening as the ozone production rate decreases to a point where the combined loss rate for ozone due to deposition and the reaction of O₃ and NO are faster. Ozone production decreases as the levels of HOₓ and RO₂ radicals diminish. Including (R1b) causes the net sink of HO₂ and NO to increase and, consequently, the ozone production rate is decreased, leading to decreased ozone concentrations throughout the entire day. HNO₃ follows a similar profile to HOₓ species at high NOₓ values (i.e. [NOₓ] > ~ 300 pptv), reduced HOₓ and NO₂ concentrations, which results in a decrease in production rate of HNO₃.

The inclusion of (R1b) decreases O₃, NO, NO₂, and OH by 3 ppbv, 200 pptv, 125 pptv, and 0.3 pptv, respectively, from their simulated peak concentrations, while HNO₃ increases by 125 pptv from its peak simulated concentration. Although the peak concentration of HO₂ is unaffected by the

![Fig. 2](image-url)  
Fig. 2. The mixing ratio dependence of a. O₃, b. OH, c. HO₂, and d. HNO₃ on the NO mixing ratio with (red profile) and without (blue profile) the new reaction HO₂ + NO → HNO₃ (R1b) included. Each data point represents midday concentrations for the individual model run, using different boundary layer heights.
new chemistry, a small decrease in the lower limit HO₂ is simulated, which is due to the increased efficiency of the HO₂ + NO → HNO₃ production channel at colder temperatures. Ozone concentrations have reached as high as ~ 45 ppbv during the summer at the South Pole (Crawford et al., 2001). The new reaction decreases peak ozone concentrations from ~ 37–34 ppbv, thus worsening the agreement with observations of maximum ozone concentrations at the South Pole. Reaction (R1b) brings better agreement with the peak NO amounts (600 pptv) measured (Davis et al., 2001, 2004) during summertime at the South Pole by decreasing peak NO concentrations from ~ 950 to ~ 750 pptv (Hamer et al., 2007, 2008). The new reaction reduces NO₂ concentrations from 525–400 pptv. Matsuki et al. (2002) provided the only ambient measurements of NO₂ at the South Pole and measure a peak NO₂ concentration of 2.8 ppbv. OH is brought into better agreement with observations (i.e. mean concentrations at the South Pole of 0.09 pptv (2.5 x 10^6 molecules cm⁻³)) (Mauldin et al., 2004). With (R1b) included the mean OH concentration is reduced from ~ 1.10–0.40 pptv (~ 3 x 10^7 molecules cm⁻³ to ~ 1 x 10^7 molecules cm⁻³), which brings our model simulations into better agreement with measured OH in the ABL. A substantial discrepancy remains, however, and this may be due in part to the absence modelled of loss of HO₂ due to reaction with NO₃ within the snowpack (Hamer et al., 2007). Given that the peak HNO₃ concentrations measured at the South Pole is ~ 70 pptv (Huey et al., 2004), our photochemical box model simulations still over predict the HNO₃ by an additional 125 pptv. Yet, modelled HNO₃ concentrations and observation agreement may not represent the best test of the new reaction channel since HNO₃ was substantially underestimated before the introduction of (R1b). This overestimation is probably due to the model over predicting HO₂ concentrations. HO₂ simulations are in congruent with maximum and mean concentrations of HO₂ measured at the South Pole, ~ 250 pptv to 0.04 pptv (~ 7 x 10^7 and ~ 1 x 10^6 molecules cm⁻³), respectively (Chen et al., 2001).

Figure 2 displays box model simulations of the mixing ratio dependence of O₃, OH, HO₂, and HNO₃ on the BLH (ranging from 30–500 m, where smaller BLHs lead to elevated NO). Table III displays modelled concentration ranges for select species with and without the new reaction channel compared to observed species concentration ranges. The NO mixing ratios are shown with (red profile) and without (blue profile) the inclusion of reaction (R1b) (Fig. 2). For low concentrations of NO (i.e. < 50 pptv) and high BLHs, ozone increases similarly with NO with and without (R1b) as NO concentrations are not large enough to significantly reduce HO₂, despite the extra loss pathway (Fig. 2a). As NO concentrations exceed 100 pptv, (R1b) starts to influence the loss of HO₂, which in turn leads to less ozone production. At NO > ~ 300 pptv, O₃ starts to decrease (without (R1b)), while at NO > ~ 250 pptv O₃ starts to decrease (with (R1b)). Both profiles exhibit this behaviour as OH start to decrease because of the decreased production of HO₂ and NO₂. OH follows a similar concentration dependence on NO as O₃ (Fig. 2b), which is linked to the decrease in OH at NO > ~ 100 pptv due to the increased destruction of HO₂, via (R1b), and decreasing solar radiation, which in turn, caused the production rate of HO₂ to decrease. OH concentrations (without (R1b)) start to decrease at NO > ~ 200 pptv, while it decreases (with(R1b)) at NO > ~ 150 pptv. Figure 2c shows less HO₂ with the inclusion of (R1b) as (R1b) represents an extra sink for HO₂. HO₂ decreases at lower NO concentrations (i.e. at NO > ~ 40 pptv without (R1b) and at NO > ~ 20 pptv with (R1b)), compared to O₃ (i.e. at NO > ~ 300 pptv without (R1b) and at NO > ~ 250 pptv with (R1b)) since the primary pathway leading to the formation of O₃ is preceded by the photolysis of NO₂, which itself is much larger in concentration than HO₂ (e.g. peak NO₂ ~ 500 pptv vs peak HO₂ ~ 5 pptv, see Fig. 1c & e) and is solely not produced from gas phase chemistry but is also emitted readily from the snowpack via nitrate photolysis and diffusion (Hamer et al., 2008). HNO₃ concentrations (without (R1b)) start to decrease at NO > ~ 500 pptv while it decreases (with (R1b)) at NO > ~ 250 pptv. HNO₃ production is a function of OH and NO₂ so (at NO > ~ 250 pptv) OH and NO₂ decrease due to (R1b).

Table III. Modelled concentration ranges for select species with and without the new reaction channel compared to observed species concentration ranges. Note that the variability of these species in the model that leads to these ranges is due to the changes in boundary layer height.

<table>
<thead>
<tr>
<th>Model species</th>
<th>Range of modelled concentrations with (R1b)</th>
<th>Range of modelled concentrations without (R1b)</th>
<th>Observed concentration range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>23–34 ppbv</td>
<td>23–37 ppbv</td>
<td>20–45 ppbv</td>
</tr>
<tr>
<td>NO</td>
<td>0–1 ppbv</td>
<td>0–1.2 ppbv</td>
<td>1–600 pptv</td>
</tr>
<tr>
<td>OH</td>
<td>0.3–1 pptv</td>
<td>0.4–1.5 pptv</td>
<td>0.005–0.24 ppbv (0.04–0.24 pptv)*</td>
</tr>
<tr>
<td>HO₂</td>
<td>11–16 pptv</td>
<td>12.5–20 pptv</td>
<td>2.1–5.3 pptv</td>
</tr>
<tr>
<td>HNO₃</td>
<td>50–500 pptv</td>
<td>10–400 pptv</td>
<td>5–68 pptv</td>
</tr>
</tbody>
</table>

*Bracketed range excludes OH values affected by fog events as described by Chen et al. (2001).
location and for other cold regions of the atmosphere. Estimates of the photochemical lifetime of NOx with respect to (R4) are on the order of 3.5 hours, assuming summertime observed OH concentrations 0.09 ppbv (2.5 x 10^6 molecules cm^-3) (Mauldin et al. 2004) and that T = 243 K. The introduction of the new channel reduces the NOx lifetime with respect to oxidation to HNO3 to ~ 1 hour with the new channel now dominating the conversion of NO2 to HNO3 - again utilizing observations of summer H2O2 (Mauldin et al. 2004). Thus, existing estimates of snowpack NOx emissions relying on previous estimates of NOx lifetime, perhaps, need to be re-evaluated (Wang et al. 2008). Such a re-evaluation would need to be revised upwards, which presents a problem for NOx flux estimates based upon snow radiative transfer models that tend to underestimate snowpack NOx production rates (Wolf et al. 2002, Davis et al. 2008) when compared to current observationally derived flux estimates at the South Pole (Oncley et al. 2004). This further widens the apparent inconsistency between theoretically required emission burdens at the South Pole, conventional laboratory measurements, and eddy flux covariance estimates of snowpack NOx emissions (Davis et al. 2008). In addition, a significant revision of the photochemical lifetime of NOx due to the new channel would generally require other observationally constrained inverse estimates of NOx sources in other environmental regions to be revised. This wider re-evaluation of NOx lifetime due to the new channel would have particular significance for the emission inversion studies in the upper atmosphere, specifically, with regard to lightning and aircraft NOx inverse source estimation (Martin et al. 2007) since these studies rely on the forward model to accurately describe the NOx lifetime.

The model simulations including (R1b) result in a substantial increase in boundary layer HNO3(g), thus over predicting it by over 100 ppbv when compared to measurements. This effect would undoubtedly increase surface NOx concentrations via HNO3(g) deposition. Taking into account an increase in surface NOx concentrations, via an increase in HNO3(g), would have no effect on HOONO and HONO produced from nitrate photolysis. HOONO is produced from NO3- photodecomposition at λ < 280 nm, via NO3-*, still NO3-* quickly isomerizes back to NO3- (Boxe 2005). Concomitantly, as OH + NO3- → HOONO (within the solvent cage of ice), it also quickly isomerizes back to NO3- and H+.

HONO production was believed to have a substantial source from NO3- photolysis as NO3-, a primary product, at low pH readily protonates to form HONO (or nitrous acid in ice). Given that nitrate photochemistry proceeds via two primary photolytic channels (i.e. 10% branching to produce NO2 + O2(P) and 90% branching to produce NO2 + O1), NO2 concentrations will always be smaller than NO2. For example, snowpack kinetic modelling of nitrate photochemistry by Jacobi & Hilker (2007) revealed that NO2 concentrations are always lower than NO2 concentrations by a factor of approximately three. They also show that in addition to the difference in NO2 and NO2 concentrations, the transfer rate of HONO produced via NO2+ protonation at low pH would limit any release of HONO produced in the snowpack, whether it is sourced from nitrate photolysis or other chemical or photochemical reaction channels. In other words, Jacobi & Hilker (2007) showed that the high Henry's law constant for HONO at low temperatures (e.g. 930 M atm^-1 at -20°C, which is 3.6 x 10^5 higher than the solubility constant for NO2 at -20°C), dictates its slow transfer from the snowpack to the gas phase.

Conclusions

Here, we examined the effect of the new reaction channel, HO2 + NO → HNO3 (R1b) at the South Pole, Antarctica using a photochemical box model. The inclusion of this reaction decreases O3, NO, NO2, OH, and HO2 and increases HNO3. The decrease in O3 from 37-34 ppbv worsens the agreement between the model and the highest O3 concentrations observed at the South Pole (45 ppbv), which are associated with in situ photochemical production. As the mean concentration of OH at the South Pole is 2.5 x 10^6 molecules cm^-3, our box model simulations brings OH into better agreement with observations since OH is reduced from 1 x 10^6 to 8 x 10^5 molecules cm^-3. Box model simulations of HO2 are incongruent with maximum and mean concentrations of HO2 measured at the South Pole, ~ 7 x 10^6 and ~ 1 x 10^6 molecules cm^-3, respectively. Given that peak measured HNO3 concentration measured at the South Pole is 70 ppbv, our box model simulations still over predict it by an additional ~ 130 ppbv. The reduced concentrations of NOx, as a result of the application of the new channel, are consistent with expected decreases in atmospheric NOx lifetime as a result of increased sequestration of NOx into HNO3. We also show here that without (R1b) current models will overestimate NOx concentrations at the ABL, which has the following implications: 1) given that previous studies investigating snowpack emissions of NOx have relied upon accurate and comprehensive determinations of NOx losses in this environment, our result implies that NOx snowpack emissions are larger than currently reported, 2) current estimates of the nitrate recycling factor again rely upon accurate characterization of NOx, and therefore, current estimates are probably too low, and 3) the changes in NOx lifetime imply that snowpack NOx emissions and snowpack nitrate recycling must be re-evaluated. Further analysis is required to reduce the degree of incongruence. Our box model simulations of the concentration dependence of OH, O3, HO2, and HNO3 on NO with the new reaction included, overall, show a decrease in OH, O3, and HO2 and an increase in HNO3. Lastly, this new reaction should be further explored and validated experimentally for potential consideration and inclusion in the latest 'Chemical kinetics
and photochemical data for use in atmospheric studies evaluation handbook.

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Supplemental material

A Supplemental table will be found at http://dx.doi.org/10.1017/S0954102012000144.

References


