Coupled evolution of BrOx-ClOx-HOx-NOx chemistry during bromine-catalyzed ozone depletion events in the arctic boundary layer

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Citation

Published Version
doi:10.1029/2002JD002732

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Coupled evolution of BrO$_x$-ClO$_x$-HO$_x$-NO$_x$ chemistry during bromine-catalyzed ozone depletion events in the arctic boundary layer


Received 8 July 2002; revised 8 October 2002; accepted 10 October 2002; published 28 February 2003.

[1] Extensive chemical characterization of ozone (O$_3$) depletion events in the Arctic boundary layer during the TOPSE aircraft mission in March–May 2000 enables analysis of the coupled chemical evolution of bromine (BrO$_x$), chlorine (ClO$_x$), hydrogen oxide (HO$_x$) and nitrogen oxide (NO$_x$) radicals during these events. We project the TOPSE observations onto an O$_3$ chemical coordinate to construct a chronology of radical chemistry during O$_3$ depletion events, and we compare this chronology to results from a photochemical model simulation. Comparison of observed trends in ethyne (oxidized by Br) and ethane (oxidized by Cl) indicates that ClO$_x$ chemistry is only active during the early stage of O$_3$ depletion (O$_3$ > 10 ppbv). We attribute this result to the suppression of BrCl regeneration as O$_3$ decreases. Formaldehyde and peroxy radical concentrations decline by factors of 4 and 2 respectively during O$_3$ depletion and we explain both trends on the basis of the reaction of CH$_2$O with Br. Observed NO$_x$ concentrations decline abruptly in the early stages of O$_3$ depletion and recover as O$_3$ drops below 10 ppbv. We attribute the initial decline to BrNO$_3$ hydrolysis in aerosol, and the subsequent recovery to suppression of BrNO$_3$ formation as O$_3$ drops. Under halogen-free conditions we find that HNO$_4$ heterogeneous chemistry could provide a major NO$_x$ sink not included in standard models. Halogen radical chemistry in the model can produce under realistic conditions an oscillatory system with a period of 3 days, which we believe is the fastest oscillation ever reported for a chemical system in the atmosphere. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; KEYWORDS: Polar, ozone, boundary layer, bromine, NO$_x$, HO$_x$

1. Introduction
[2] Events of near-total ozone (O$_3$) depletion in Arctic spring surface air have been observed since the 1980s [Oltmans, 1981; Oltmans and Komhyr, 1986] and are known to be due to fast catalytic loss driven by unusually high concentrations of bromine oxide radicals (BrO$_x$ ≡ Br + BrO) [Barrie et al., 1988; Hausmann and Platt, 1994]. These events are also associated with high concentrations of chlorine oxide radicals (ClO$_x$ ≡ Cl + ClO) as demonstrated by observations of differential hydrocarbon depletion [Yokouchi et al., 1994; Jobson et al., 1994]. More recently, several studies have pointed out the importance of polar snow as a source of nitrogen oxide radicals (NO$_x$ ≡ NO + NO$_2$) and of precursors of hydrogen oxide radicals (HO$_x$ ≡ OH + peroxy radicals) during spring [Sumner and Shepson, 1999; Horrath et al., 2000; Jones et al., 2001]. Extensive chemical observations during the Tropospheric Ozone Production around the Spring Equinox (TOPSE) aircraft campaign [Atlas et al., 2003] offer the first opportunity to analyze the coupled evolution of BrO$_x$-ClO$_x$-NO$_x$-HO$_x$ radical chemistry during O$_3$ depletion events in the Arctic spring. We present such an analysis here and use photochemical model calculations to place the TOPSE observations in the context of current understanding.

[3] The bromine chemistry leading to O$_3$ depletion is relatively well understood [Barrie et al., 1988; Fan and
Jacob, 1992; Hausmann and Platt, 1994; Michalowski et al., 2000]. It involves the catalytic O₃ destruction by BrOₓ radicals and it requires the recycling of BrOₓ from its non-radical reservoirs. The main catalytic mechanism for O₃ depletion is

\[
\begin{align*}
\text{(R1)} & \quad 2 \times (\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2) \\
\text{(R2)} & \quad \text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2 \\
\text{(R3)} & \quad \text{Net} \frac{\text{Br}_2 + \text{hv}}{2\text{O}_3} \rightarrow 2\text{Br} + \text{O}_3
\end{align*}
\]

[5] The efficiency of this cycle is limited by conversion of BrOₓ to the non-radical reservoir HBr, which is long-lived with respect to both photolysis and reaction with OH. Production of HBr is mostly by the reaction between Br and CH₂O, although reactions with other carbonyls can also be significant [Shepson et al., 1996].

\[
\begin{align*}
\text{(R4)} & \quad \text{Br} + \text{CH}_2\text{O} \rightarrow \text{HBr} + \text{CO} + \text{H}_2\text{O} \\
\text{(R5)} & \quad \text{Br}^- + \text{HOBr} + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O} \\
\text{(R3)} & \quad \text{Br}_2 + \text{hv} \rightarrow 2\text{Br}
\end{align*}
\]

[6] In this manner the radical bromine is regenerated, sustaining the O₃ loss cycle (R1–R3). Although there is now substantial evidence from field and laboratory studies to support the above mechanism, model calculations of the O₃ loss rate in relation to the BrOₓ radical supply have never been evaluated with observations. We will present such an evaluation here and examine the chemical coupling of BrOₓ with other radical families.

[7] A complicating factor for the NOₓ and HOₓ radical budgets in the Arctic boundary layer is the emission of NOₓ and CH₂O from the snow surface. These emissions appear to be driven by sunlight [Sumner and Shepson, 1999; Ridley et al., 2000; Honrath et al., 1999; Jones et al., 2001] although physical adsorption and desorption may also take place [Hutterli et al., 1999, 2001]. Surface measurements at Alert in the Canadian Arctic show a pronounced diurnal cycle of NOₓ concentrations [Ridley et al., 2000] with a noon maximum, suggesting a shorter lifetime for NOₓ (less than 4 hours) than would be expected from atmospheric loss by oxidation in standard models. We include the snow emissions of NOₓ and CH₂O in our analysis and propose that heterogeneous oxidation of HNO₄ in aerosols provides a major sink of NOₓ in the Arctic boundary layer.

[8] Section 2 describes the O₃ depletion events observed during TOPSE with focus on the evolution of radical chemistry. We apply a photochemical model (section 3) to simulate the chemical development of these events and interpret the TOPSE observations (section 4). An intriguing chemical oscillation taking place in the model under certain conditions is presented in section 5. Conclusions are in section 6.

2. Ozone Depletion Events Observed During TOPSE

[5] The TOPSE aircraft program took place between February and May 2000 [Atlas et al., 2003]. Its goal was to investigate the origin of the springtime O₃ maximum observed at northern extra-tropical latitudes [Monks, 2000]. The NSF C-130 aircraft flew between Boulder (Colorado), Churchill (Manitoba), and Thule (Greenland), with some flights north to 85°N over the Arctic Ocean. A total of 37 flights were carried out (see Figure 1). The aircraft carried a wide range of chemical instrumentation including measurements of O₃, NOₓ, and total reactive nitrogen oxides (NOₓ) [Ridley et al., 2003], speciated hydrocarbons [Blake et al., 2003], OH [Mauldin et al., 2003], total peroxy radicals (RO₂) (C. A. Cantrell et al., Peroxy radical observations using CIMS during TOPSE, manuscript submitted to J. Geophys. Res., 2002), H₂O₂ and CH₃OOH [Snow et al., 2003], CH₂O [Fried et al., 2003], peroxyacetyl nitrate (PAN) and soluble bromide [Scheuer et al., 2003]. Photolysis frequencies [Shetter and Mueller, 1999] and aerosol size distributions were also measured. Individual cases of O₃ depletion events observed during TOPSE are discussed by Ridley et al. [2003].

[10] Figure 2 shows the cumulative probability distribution of O₃ concentrations observed in the Arctic boundary layer (below 500 m altitude and north of 50°N) during spring (March 23 to May 22) and around local noon (1100 to 1300). Most TOPSE data were collected around midday; introducing the 1100 to 1300 restriction filters out 50% of the data and makes little change to the distribution. The O₃ concentrations range from 0.2 to 50 ppbv; 50% of the measurements are below 23 ppbv. The accuracy of the O₃ measurements was 0.06 ppbv at 1 ppbv of O₃ [Ridley et al., 2003]. For further analysis we partitioned the data into four O₃ bins (0 to 1 ppbv, 1 to 10 ppbv, 10 to 30 ppbv and above 30 ppbv). Table 1 gives the means and standard deviations of the ensemble of TOPSE observations in these four bins. Selection of data below 100 m rather than 500 m leads to an increased probability of low O₃ concentrations but little change to the concentration of species within each O₃ bin. We will assume in what follows that differences in composition between the four categories of air masses in Table 1 reflect different degrees of processing by halogen radical chemistry. In support of this assumption, we see in Table 1 that CO (unaffected by halogen chemistry) is uniform across all four categories.

[11] Soluble bromide concentrations observed during TOPSE are highest in the O₃ depleted air masses. Ethyne and ethane show differing trends as O₃ decreases. Whereas the ethyne concentration drops continuously with O₃, the ethane concentration changes little below 10 ppbv of O₃. We propose in section 4.2 that this reflects different temporal evolutions of bromine and chlorine radicals during O₃ depletion events. Concentrations of HOₓ radicals and reservoir species (OH, RO₂, CH₂O, H₂O₂ and CH₃OOH) all
decrease with decreasing O3 concentration. A previous study of CH2O evolution during O3 depletion events observed at Alert [Rudolph et al., 1999] showed a gradual increase in CH2O concentrations from 40 to 15 ppbv of O3 followed by a decline similar to that observed during TOPSE. The budgets of these species are discussed in section 4.3.

Concentrations of NOx observed in TOPSE decrease as O3 drops below 30 ppbv but then recover as O3 drops below 10 ppbv, so that concentration under conditions of strong O3 depletion (O3 < 1 ppbv) are similar to those with little or no depletion (O3 > 30 ppbv). The initial reduction in NOx at the onset of O3 depletion events has been seen before [Beine et al., 1997]. Concentrations of NOy appear to increase slightly as the O3 concentration decreases and PAN concentrations shows a more substantial increase. These intriguing trends in the NOy species are examined further in section 4.4.

3. Photochemical Model

We apply a 0-D (box) photochemical model of the Arctic boundary layer to interpret the relationships described above and examine the coupled evolution of BrOx-ClOx-HOx-NOx radical chemistry during O3 deple-

Figure 1. Flight tracks during TOPSE (February–May 2000). Symbols show location of boundary layer tracks (below 500 m altitude) with O3 concentrations less than 15 ppbv. The dates during which these air masses were encountered are given.

Figure 2. Cumulative probability distribution of midday (1100 to 1300 local time) O3 concentrations measured north of 50°N and below 500 m altitude between March 23 and May 22 during TOPSE. 252 1-minute measurements are included in the distribution. The dashed lines define the O3 bins used for analysis.
The oxidation of C₁-C₆ hydrocarbons following extended here to include halogen and aerosol chemistry. That the sole source and reservoir of bromine is the Martinez et al. 1997; (in general agreement with surface and thus assumes that the bromine cycling within the deposition or emission of halogens to or from the snow deposition events. We do not consider IO₅ chemistry as there is IO₅ chemistry as there is negligible slow; even at the upper limits reported by Orlando et al. 2000 we find that they have little effect on the evolution of O₃ depletion. Photolysis frequencies are calculated with a clear-sky radiative transfer model and are scaled to the mean midday photolysis frequencies of NO₂ (J(NO₂)) and O₃ → O(¹D) (J(O¹D))). The J(O¹D) scaling factor is applied to wavelengths less than 330 nm and the J(NO₂) scaling factor to higher wavelengths. Aerosol processes in the chemical mechanism are listed in Tables 2a and 2b and include halogen radical as well as aerosol size distribution.

### Table 1. Arctic Boundary Layer Observations During TOPSE

<table>
<thead>
<tr>
<th>Ozone Range (ppbv)</th>
<th>Bin 1</th>
<th>Bin 2</th>
<th>Bin 3</th>
<th>Bin 4</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Note b</td>
</tr>
<tr>
<td>Day of year</td>
<td>107 ± 26</td>
<td>108 ± 23</td>
<td>107 ± 13</td>
<td>105 ± 9</td>
<td>106.7</td>
</tr>
<tr>
<td>Latitude (°N)</td>
<td>72 ± 9</td>
<td>77 ± 8</td>
<td>74 ± 10</td>
<td>67 ± 11</td>
<td>73</td>
</tr>
<tr>
<td>Longitude (°E)</td>
<td>-77 ± 11</td>
<td>-70 ± 11</td>
<td>-75 ± 10</td>
<td>-78 ± 12</td>
<td>-75</td>
</tr>
<tr>
<td>Altitude (m)</td>
<td>144 ± 140</td>
<td>96 ± 107</td>
<td>97 ± 104</td>
<td>52 ± 57</td>
<td>100</td>
</tr>
<tr>
<td>O₃ column (DU)</td>
<td>370 ± 42</td>
<td>371 ± 55</td>
<td>428 ± 67</td>
<td>470 ± 59</td>
<td>398</td>
</tr>
<tr>
<td>Aerosol area (10⁻⁷ cm²/cm³)</td>
<td>4.7 ± 2.5</td>
<td>3.8 ± 2.0</td>
<td>5.3 ± 1.0</td>
<td>4.7 ± 1.2</td>
<td>4.9</td>
</tr>
<tr>
<td>Aerosol volume (10⁻¹² cm³)</td>
<td>4.2 ± 3.0</td>
<td>3.7 ± 3.4</td>
<td>4.5 ± 0.95</td>
<td>4.1 ± 1.3</td>
<td>4.4</td>
</tr>
<tr>
<td>H₂O (kg/kg)</td>
<td>0.88 ± 0.54</td>
<td>0.76 ± 0.35</td>
<td>0.71 ± 0.35</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>CH₄ (ppmv)</td>
<td>7.8 ± 5</td>
<td>12.9 ± 9.4</td>
<td>23.0 ± 8.5</td>
<td>23.6 ± 2.8</td>
<td>48</td>
</tr>
<tr>
<td>CO (ppmv)</td>
<td>153 ± 10</td>
<td>151 ± 10</td>
<td>156 ± 4</td>
<td>157 ± 3</td>
<td>153</td>
</tr>
<tr>
<td>CH₄₃ (ppmv)</td>
<td>1.84 ± 0.01</td>
<td>1.85 ± 0.01</td>
<td>1.85 ± 0.01</td>
<td>1.85 ± 0.01</td>
<td>1.84</td>
</tr>
<tr>
<td>Propane (ppmv)</td>
<td>423 ± 250</td>
<td>352 ± 198</td>
<td>234 ± 85</td>
<td>179 ± 62</td>
<td>484</td>
</tr>
<tr>
<td>n-Butane (ppmv)</td>
<td>109 ± 90</td>
<td>87 ± 61</td>
<td>40 ± 23</td>
<td>26 ± 13</td>
<td>136</td>
</tr>
<tr>
<td>i-Butane (ppmv)</td>
<td>64 ± 52</td>
<td>63 ± 36</td>
<td>34 ± 18</td>
<td>25 ± 12</td>
<td>73</td>
</tr>
<tr>
<td>n-Pentane (ppmv)</td>
<td>32 ± 15</td>
<td>19 ± 9.3</td>
<td>7.2 ± 3.6</td>
<td>4.3 ± 1.3</td>
<td>48</td>
</tr>
<tr>
<td>i-Pentane (ppmv)</td>
<td>41 ± 20</td>
<td>31 ± 12</td>
<td>11 ± 6.3</td>
<td>6.5 ± 2.7</td>
<td>62</td>
</tr>
<tr>
<td>Hexane (ppmv)</td>
<td>10 ± 4</td>
<td>6.8 ± 1.6</td>
<td>3.8 ± 0.5</td>
<td>&lt;3²</td>
<td>15</td>
</tr>
<tr>
<td>OH (x 10⁻³ cm⁻³)</td>
<td>11. ± 9</td>
<td>5.0 ± 3.6</td>
<td>2.7 ± 2.1</td>
<td>1.7 ± 1.4</td>
<td>N/A</td>
</tr>
<tr>
<td>RO₂ (x 10⁶ cm⁻³)²</td>
<td>2.2 ± 1.2</td>
<td>1.9 ± 1.2</td>
<td>1.3 ± 0.6</td>
<td>1.6 ± 0.4</td>
<td>N/A</td>
</tr>
<tr>
<td>CH₃O (ppmv)</td>
<td>143 ± 104</td>
<td>137 ± 93</td>
<td>94 ± 89</td>
<td>35 ± 110</td>
<td>143</td>
</tr>
<tr>
<td>H₂O₂ (ppmv)</td>
<td>264 ± 128</td>
<td>183 ± 113</td>
<td>92 ± 41</td>
<td>92 ± 74</td>
<td>254</td>
</tr>
<tr>
<td>CH₃OOH (ppmv)</td>
<td>240 ± 123</td>
<td>230 ± 99</td>
<td>151 ± 43</td>
<td>131 ± 40</td>
<td>206</td>
</tr>
<tr>
<td>NO₂ (ppmv)</td>
<td>13 ± 8</td>
<td>4.6 ± 7.3</td>
<td>5.2 ± 4.7</td>
<td>15.0 ± 4.8</td>
<td>16</td>
</tr>
<tr>
<td>NO (ppmv)</td>
<td>5.0 ± 5.0</td>
<td>1.1 ± 4.6</td>
<td>2.9 ± 3.2</td>
<td>11.7 ± 4.2</td>
<td>7.0</td>
</tr>
<tr>
<td>NO₃ (ppmv)</td>
<td>7.5 ± 4</td>
<td>3.4 ± 3.7</td>
<td>2.4 ± 2.4</td>
<td>3.2 ± 2.1</td>
<td>9.9</td>
</tr>
<tr>
<td>PAN (ppmv)</td>
<td>225 ± 39</td>
<td>200 ± 38</td>
<td>258 ± 16</td>
<td>253 ± 13</td>
<td>N/A</td>
</tr>
</tbody>
</table>

| aMeans and standard deviations of aircraft observations made north of 50°N below 500 m altitude, from March 23 to May 22, 2000 and around local noon (1100–1300). The data are partitioned by O₃ concentration range (see text) to determine the chemical characteristics of O₃ depletion events.  

bMean concentrations of species in air masses with O₃ > 45 pptv and no detected soluble bromide. These concentrations are used as initial condition for the model simulation (Section 3). Initial condition for species not measured during TOPSE are given in section 3. 

cIntegrated over the 0.1–3 μm aerosol size distribution. 

dSoluble bromide in gas (HBr) and aerosol phase (Br²⁻). 

eModel simulations are conducted with initial bromide concentrations in the range 0–43 pptv [Sirois and Barrie, 1999]. 

²Below level of detection (~<3 pptv). 

²RO₂ is the sum of all peroxy radicals (HO₂ + organic peroxy radicals). 

²NO₂ is the sum of all gas phase nitrogen oxide species (NO, NO₂, NO₃, 2 × N₂O₅, HNO₂, HNO₃, HNO₄, organic nitrates).
**Table 2a. Aerosol Chemistry: Aqueous-Phase Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant (M⁻¹ s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₄ + HSO₃ → SO₄²⁻ + NO₃⁻ + 2 H⁺</td>
<td>1.1 × 10⁷ [H⁺] + 3.3 × 10⁴</td>
<td>Amel et al. [1996]</td>
</tr>
<tr>
<td>HNO₂ + HNO₂ → 2 NO₃⁻ + 2 H⁺</td>
<td>12</td>
<td>Laguer and Sehested [1993]</td>
</tr>
<tr>
<td>HNO₂ + Cl⁻ → HOCl + NO₃⁻</td>
<td>0.014</td>
<td>Régimbal and Mozurkewich [1997]</td>
</tr>
<tr>
<td>HNO₂ + Br⁻ → HOBr + NO₃⁻</td>
<td>0.54</td>
<td>Régimbal and Mozurkewich [1997]</td>
</tr>
<tr>
<td>HNO₂ + I⁻ → HOI + NO₃⁻</td>
<td>890</td>
<td>Régimbal and Mozurkewich [1997]</td>
</tr>
<tr>
<td>Br₂ + O₃ + H⁺ → HOBr + O₂</td>
<td>11.7</td>
<td>Haag and Hoigné [1983]</td>
</tr>
<tr>
<td>HOBr + Cl⁺ + H⁺ → BrCl + H₂O</td>
<td>5.6 × 10⁹</td>
<td>Wang et al. [1994]</td>
</tr>
<tr>
<td>HOBr + Br⁻ + H⁺ → Br₂ + H₂O</td>
<td>1.6 × 10¹⁰</td>
<td>Beckwith et al. [1996]</td>
</tr>
<tr>
<td>HOCl + Cl⁺ + H⁺ → Cl₂ + H₂O</td>
<td>2.2 × 10⁹</td>
<td>Wang and Margerum [1994]</td>
</tr>
<tr>
<td>HOCl + Br⁻ + H⁺ → BrCl + H₂O</td>
<td>1.3 × 10⁶</td>
<td>Kumar and Margerum [1987]</td>
</tr>
<tr>
<td>BrCl + H₂O → HOBr + Cl⁺ + H⁺</td>
<td>1.0 × 10⁵</td>
<td>Wang et al. [1994]</td>
</tr>
<tr>
<td>Br₂ + H₂O → HOBr + Br⁻ + H⁺</td>
<td>9.7 × 10⁴</td>
<td>Beckwith et al. [1996]</td>
</tr>
<tr>
<td>Cl₂ + H₂O → HOCl + Br⁻ + H⁺</td>
<td>2.2 × 10⁴</td>
<td>Wang and Margerum [1994]</td>
</tr>
<tr>
<td>BrCl + Br⁻ → Br₂Cl⁻</td>
<td>5 × 10⁹</td>
<td>Note a</td>
</tr>
<tr>
<td>Br₂Cl⁻ → BrCl + Cl⁻</td>
<td>5 × 10⁸</td>
<td>Note a</td>
</tr>
<tr>
<td>BrCl + Cl⁻ → BrCl₂⁻</td>
<td>5 × 10⁸</td>
<td>Note a</td>
</tr>
<tr>
<td>Br⁻ → Br⁻ + H⁺</td>
<td>0.3³</td>
<td>Schweitzer et al. [2000]</td>
</tr>
<tr>
<td>HCl → Cl⁻ + H⁺</td>
<td>0.3³</td>
<td>Schweitzer et al. [2000]</td>
</tr>
<tr>
<td>BrNO₃ + H₂O → NO₃⁻ + Br⁻ + H⁺</td>
<td>0.002²</td>
<td>Robinson et al. [1997]</td>
</tr>
<tr>
<td>N₂O₅ + H₂O → 2 NO₃⁻ + 2 H⁺</td>
<td>0.1³</td>
<td>Jacob [2000]</td>
</tr>
</tbody>
</table>

*Assumed [Michalowski et al., 2000].

¹Reaction probabilities (γ), dimensionless.

HNO₂ are kept constant in the simulation but the Cl⁻ concentration is allow to evolve. I⁻ and HNO₂ are included in the model as aerosol-phase sinks of HNO₄ (see later) and play no further chemical role. Concentrations of CH₃CHO (18 pptv) and (CH₃)₂CO (300 pptv) are assumed from chemical steady state with the background hydrocarbon concentrations given in Table 1.

[16] The boundary layer in our model is taken to be dynamically isolated from the free troposphere (zero flux boundary conditions at boundary layer top). This is a reasonable assumption for O₃ depletion events in general [Wessel et al., 1998] and TOPSE in particular [Ridley et al., 2003]. The surface is assumed to be snow and to provide a source or sink of nitrogen oxides, H₂O₂, and CH₂O. The surface flux boundary conditions for these and other non-radical secondary species are chosen to reproduce observed concentrations in background air (Background: Table 1) in a steady state calculation; for that purpose the boundary layer represented by the model is assumed to be 200m deep. We thus specify small deposition velocities for PAN, PPN and H₂O₂ (0.004 cm s⁻¹, 0.008 cm s⁻¹, and 0.09 cm s⁻¹ respectively). Emission of NOₓ and CH₂O from the snow surface is necessary to reproduce the observed concentrations with the model. We assume that these emissions vary diurnally following the photolysis of NO₂. The resulting 24-hour average emissions of CH₂O and NOₓ are 1.2 × 10⁹ cm⁻² s⁻¹ and 3.6 × 10⁸ cm³ s⁻¹ respectively. Our implied CH₂O emission is a factor of 4 less than that found by Sumner and Shepson [1999]. This is mainly due to differing assumptions for the boundary layer height in the calculation (600m in Sumner and Shepson [1999] and 200 m in this work). Our implied NOₓ emission is roughly 4 times higher than that observed by Jones et al. [2001] in Antarctica; such a difference could be rationalized as reflecting higher nitrate concentrations in the Arctic snow compared to the Antarctic [Wolff et al., 1995]. It is in reasonable agreement (40% higher) with measurements made at Summit, Greenland during the summer of 2000 [Honrath et al., 2002].

**Table 2b. Aerosol Chemistry: Henry’s Law Equilibria (H) and Mass Accomodation Coefficients (α)**

<table>
<thead>
<tr>
<th>Species</th>
<th>H (M/atm) 250K</th>
<th>α</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOBr(g) → HOBr (aer)</td>
<td>3.0 × 10⁴</td>
<td>0.3</td>
<td>H: Waschewsky and Abbatt [1999]</td>
</tr>
<tr>
<td>HOCI(g) → HOCl(aer)</td>
<td>1.8 × 10⁴</td>
<td>0.3</td>
<td>H: Huthwelker et al. [1995]</td>
</tr>
<tr>
<td>Br₂ (g) → Br₂ (aer)</td>
<td>1.0 × 10¹</td>
<td>0.01</td>
<td>α: Abbat and Molina [1992]</td>
</tr>
<tr>
<td>Cl₂ (g) → Cl₂ (aer)</td>
<td>3.7 × 10¹</td>
<td>0.01</td>
<td>α: (estimated) Sander and Crutzen [1996]</td>
</tr>
<tr>
<td>BrCl (g) → BrCl (aer)</td>
<td>5.6 × 10¹</td>
<td>0.01</td>
<td>α: (estimated) Sander and Crutzen [1996]</td>
</tr>
<tr>
<td>O₃ (g) → O₃ (aer)</td>
<td>3.5 × 10¹</td>
<td>0.002</td>
<td>α: (estimated) Sander and Crutzen [1996]</td>
</tr>
<tr>
<td>HNO₄ (g) → HNO₄ (aer)</td>
<td>1.2 × 10⁴</td>
<td>0.05</td>
<td>α: H: Régimbal and Mozurkewich [1997]</td>
</tr>
</tbody>
</table>

α: Allanic et al. [1997]
amplification of the diurnal cycle of NO\textsubscript{x} concentrations observed (1200) suggesting that the lifetime of NO\textsubscript{x} in the model maximum (1400 local time) is still later than that calculated here. Previous studies \cite{Warneck, Leriche, Dentener} have shown the importance of HNO\textsubscript{4} in the oxidation of S(IV) in clouds. Our understanding of the role of HNO\textsubscript{4} in the atmospheric chemistry system is limited by both a lack of field observations and uncertainties in its chemistry (for example at 250K its thermal dissociation constant is uncertain by a factor of 10 \cite{DeMore}).

4. Radical Chemistry During Ozone Depletion Events

4.1. Temporal Evolution and O\textsubscript{3} Chemical Coordinate

We find that the uptake of HNO\textsubscript{4} by aerosols and its subsequent reaction in the aerosol phase (mostly with HNO\textsubscript{2} and I\textsuperscript{−}) provides a significant NO\textsubscript{x} sink in the Arctic boundary layer outside of O\textsubscript{3} depletion episodes. It accounts in the model for 40\% of the NO\textsubscript{x} loss on a 24-hour average basis and 50\% at noon. This heterogeneous HNO\textsubscript{4} chemistry increases the amplitude of the diurnal cycle of NO\textsubscript{x} concentrations and shifts the diurnal maximum to mid afternoon, as compared to a sensitivity simulation with no HNO\textsubscript{4} uptake by aerosols (Figure 3). The rate of the aerosol HNO\textsubscript{4} sink is limited by the rate of reaction in the aerosol phase, which in turn depends on the assumed concentration of reactants \cite{Sirois, Li}. The amplification of the diurnal cycle of NO\textsubscript{x} concentrations due to HNO\textsubscript{4} chemistry in our model is consistent with the Alert observations of Ridley et al. \cite{Ridley}, but the timing of the model maximum (1400 local time) is still later than observed (1200) suggesting that the lifetime of NO\textsubscript{x} in the measurements of Ridley et al. \cite{Ridley} may be even shorter than that calculated here.

Starting from the steady state background conditions described in the previous section and summarized in Table 1, the model atmosphere was perturbed instantaneously with varying levels of bromide (Br\textsuperscript{−}) from 0.2 to 43 pptv (range observed by Sirois and Barrie \cite{Sirois}) and then allowed to evolve chemically for 10 days. The initial activation of the halogen radicals is through the reactions of Br\textsuperscript{−} and O\textsubscript{3} \cite{Haag} and HNO\textsubscript{4} \cite{Régimbald} to release HOBr. After this initial activation, the recycling of bromine radicals from non-radical reservoirs is controlled by Cl\textsuperscript{−} + HOBr + \text{H}^\text{+} \rightarrow BrCl + H\text{O}_2 \cite{Wang} and Br\textsuperscript{−} + HOBr + \text{H}^\text{+} \rightarrow Br_2 + \text{H}_2\text{O} \cite{Beckwith}, with the recycling of Br\textsuperscript{−} being dominated by the latter.

Figure 3 shows the temporal evolution of O\textsubscript{3}, ethyne, NO\textsubscript{i} (NO + NO\textsubscript{2}) and BrO concentrations over 10 days for 3 of the cases (0, 13 and 43 pptv initial bromide). Without any bromine the model is at steady state for the radicals and their reservoirs; ethyne concentration decreases very slowly due to reaction with OH. With 13 pptv of initial bromide the O\textsubscript{3} concentration drops slowly from 45 to 30 ppbv over the 10 days of the simulation. This is accompanied by a slow linear loss of ethyne. The NO\textsubscript{x} concentration drops precipitously due to BrNO\textsubscript{3} hydrolysis. The formation of BrNO\textsubscript{3} is favored toward dawn and dusk when Br/BrO and NO/NO\textsubscript{2} ratios are low, leading to a large diurnal cycle in the NO\textsubscript{x} concentration. The small increases in NO\textsubscript{x} concentrations simulated during night are due to the slow thermal decay of PAN and HNO\textsubscript{4}. The daytime BrO concentrations remain steady at 9 pptv. If the concentration of initial bromide is increased to 43 pptv, the impact is much greater. O\textsubscript{3} concentrations drop down to a steady state of 1 – 2 ppbv after 6 days. As the O\textsubscript{3} concentration drops below 3 ppbv the bromine radical chemistry essentially shuts down, as seen in the disappearance of BrO and the leveling off of ethyne. This suppression of bromine radical chemistry is due to a change in the balance between gas-phase and aerosol-phase bromine. As the O\textsubscript{3} concentration drops, the NO/NO\textsubscript{2} and Br/BrO concentration ratios increase. Eventually, HOBr production by BrO + HO\textsubscript{2} is suppressed, preventing the recycling of bromine radicals by R5. The suppression of bromine radical chemistry and the increase in the NO/NO\textsubscript{2} ratio suppress in turn the formation of BrNO\textsubscript{3}. The longer NO\textsubscript{x} lifetime, together with the surface source, allows the NO\textsubscript{x} concentration to recover.

Simulations of the temporal evolution of O\textsubscript{3} and halogen radical concentrations in the Arctic boundary layer during O\textsubscript{3} depletion events have been reported in previous model studies \cite{Sander, Michalowski}. Important new aspects here include the depletion and recovery of NO\textsubscript{x} driven by BrNO\textsubscript{3} hydrolysis, and the coupling of Br and Cl chemistry which affects the evolution of ethyne and alkanes differently, as discussed below. As in previous modeling studies \cite{Sander}, we find that the BrO self reaction is the dominant mechanism for halogen-catalyzed O\textsubscript{3} loss (~70\%), with BrO + HO\textsubscript{2} playing a subsidiary role (~25\%). Other mechanisms (BrO + CH\textsubscript{3}O\textsubscript{2}, BrNO\textsubscript{3} + aerosol, and ClO + BrO) play minor roles (~1\%).

It is difficult to compare this temporal evolution in the model directly with the TOPSE observations, which were not collected in a Lagrangian framework, and this has been a general problem in the evaluation of models of Arctic O\textsubscript{3} depletion. In order to enable such a comparison, we use the O\textsubscript{3} concentration as a proxy for chemical history and make the comparison along this chemical coordinate.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Normalized diurnal profile of NO\textsubscript{x} (NO + NO\textsubscript{2}) concentration simulated in the model with heterogeneous HNO\textsubscript{4} chemistry (solid line) and without (dashed line). Concentrations are normalized to the maximum concentration calculated over the diurnal cycle. Results are from a steady state Arctic boundary layer simulation for background conditions (Table 1) and no Br\textsuperscript{−}-Cl\textsuperscript{−} chemistry.}
\end{figure}
Figure 5. Simulated evolution of $O_3$, ethyne, NOx ($NO + NO_2$) and BrO concentrations over 10 days with 3 different initial aerosol phase bromide concentrations (zero (continuous line), 13 pptv (dashed line) and 43 pptv (dotted line)). Initialization is at local noon.

(Figure 5) for different initial bromide concentrations. The observed relationships apparent in Figure 5 between the different species and $O_3$ concentration were previously discussed in section 2. Many of these relationships are reproduced by the model and the mechanisms leading to them can therefore be elucidated.

4.2. Halogen Radicals and Hydrocarbons

[23] The TOPSE observations show a decrease of the hydrocarbon concentrations along with $O_3$ (Table 1) reflecting the presence of both Br and Cl radicals. The model reproduces the observed trends, as shown in Figure 5 for ethyne and ethane. The differing behavior of ethyne and ethane reflects different temporal evolution of Br atoms (ethyne oxidant) and Cl atoms (ethane oxidant) as the $O_3$ concentrations drop (see for example Ramacher et al. [1999]). Bromine chemistry continues to operate at low $O_3$ concentrations (the ethyne concentration declines at all $O_3$ concentrations) whereas chlorine chemistry is quenched below 10 ppbv of $O_3$ (ethane is not depleted further).

[24] Figure 6 describes the simulated evolution of the concentrations of halogen species as the $O_3$ concentration drops. Chlorine radical concentrations drop to near zero below 5 ppbv of $O_3$. A number of processes contribute to this decline. The only significant source of chlorine radicals in the model is the reaction of aerosol Cl$^-$ with HOBr to produce BrCl which volatilizes and photolyses. The Cl$^-$ concentration remains essentially constant during the simulation (Figure 6) so that the production of active chlorine is limited by the availability of HOBr. As the $O_3$ concentration drops, the production of HOBr decreases (as discussed previously), reducing the production of BrCl. The production of Br$^-$ increases, so that the reaction of Br$^-$ and HOBr competes with the reaction of Cl$^-$, further reducing the conversion of Cl$^-$ into BrCl. The increase in Br$^-$ also increases the rate of the reaction between Br$^-$ and BrCl to produce Br$_2$Cl$^-$, which predominantly decomposes to Br$_2$ and Cl$^-$. 

[25] In contrast to Cl, the concentration of Br atoms increases initially as $O_3$ declines, and remains relatively high even as $O_3$ drops down to 1 ppbv. The reduction in the HOBr concentration as the $O_3$ drops is to some extent compensated for by an increase in the Br$^-$ concentration, so that overall the rate of volatilization of Br$_2$ from the aerosol is maintained. Increasing Br/BrO ratio as the $O_3$ concentration declines further contributes to maintaining high Br atom concentrations.

4.3. Hydrogen Oxide Radicals

[26] We find that the RO$_2$ concentration drops by a factor of 2, both in the model and in the observations, as $O_3$ concentrations decrease from background values down to 1 ppbv (Figure 5). Measured OH declines by a factor of 5 while simulated OH declines by only a factor of 2. Problems with the OH instrumentation [Mauldin et al., 2003] make interpretation of the discrepancy difficult.

[27] Halogen radicals in the model drive profound changes in the HO$_x$ budget during $O_3$ depletion episodes. Without any halogens the production of HO$_x$ is mainly due to the photolysis of CH$_2$O (~40%) with the photolysis of $O_3$ providing a smaller contribution (~20%). Most of the CH$_2$O (60%) in the model originates from surface emission (as opposed to production from methane and higher VOC oxidation) and thus acts as a primary HO$_x$ source. The loss of HO$_x$ is mainly (~75%) through the HO$_2$ self reaction to produce H$_2$O$_2$. With the inclusion of halogens this balance changes substantially. The primary source of HO$_x$ becomes the reaction between Br and CH$_2$O. HOBr
acts as a temporary reservoir for HOx, producing OH when photolysed and consuming HO2 when produced. The uptake and subsequent destruction of HOBr in aerosols by R5 acts as a large HOx sink. The rapid oxidation of hydrocarbons and carbonyls by Br or Cl increases the importance of organic peroxy radicals (CH3O2 and above) in the HOx budget.

We see from the above discussion that there is strong coupling and interchange between the HOx and BrOx families, with major sinks of HOx serving as sources of BrOx and vice versa, and with HOBr serving as a reservoir for both radical families. One can consider these families together with ClOx (which plays little role and will not be discussed further) as components of a larger radical family H/Cl/BrOx. The primary production of H/Cl/BrOx is from the photolysis of CH2O and the primary sink is from peroxy–peroxy reactions. When H/Cl/BrOx is at steady state the photolysis of CH2O is approximately balanced by the self reaction between RO2 radicals. Reactions involving BrOx play little role in producing or destroying H/Cl/BrOx. Thus, the RO2 concentration should be proportional to the square root of the CH2O concentration regardless of the bromine chemistry. In both the model and the observations, CH2O concentrations decline by a factor 4 as O3 is depleted (Figure 5) and the RO2 concentration responds by dropping by a factor of 2, in line with this simple analysis. The decline in CH2O is driven by reaction with Br atoms. Thus the reaction between Br and CH2O, rather than acting to increase HOx concentrations, does in fact suppress them.

Concentrations of H2O2 decrease during O3 depletion events, while CH3OOH initially increases and then decreases, both in the model and in the observations. The decline of H2O2 is due both to the decline of total peroxy radicals (RO2) and to a shift in the partitioning of RO2 to favor organic peroxy radicals, as discussed above. The latter shift favors CH3OOH production, which is further favored by the drop in NOx concentration at the onset of O3 depletion events (the CH3O2 + H2O reaction proceeds faster under low NOx concentration due to less competition from...
As O₃ concentrations drop below 10 ppbv, the recovery of NOₓ as well as the decline in total RO₂ act to decrease CH₃OOH.

### 4.4. Nitrogen Oxide Radicals

As O₃ concentrations decrease from 40 to 10 ppbv, the measured NOₓ exhibits a rapid decline from about 20 pptv to 3 pptv. As O₃ is further depleted the NOₓ concentration recovers, eventually reaching similar concentrations to those observed in air masses with O₃ concentrations above 40 ppbv. The model reproduces this evolution as shown in Figure 5. In the model the decline and subsequent recovery in the NOₓ concentration is due to a combination of BrNO₃ hydrolysis and NOₓ emission from the snow. When BrO₃ chemistry is active and O₃ concentrations are still high, formation and hydrolysis of BrNO₃ (ν = 0.3) leads to loss of NOₓ. At lower O₃ concentrations, BrNO₃ formation is suppressed due to increases in both the NO/NO₂ and Br/BrO ratios.

Both PAN and NOₓ show a similar relationship with O₃, reflecting the dominant role of PAN in the composition of NOₓ. The measurements show increases of PAN and NOₓ during O₃ depletion events, and this is reproduced by the model (Figure 5). In the model, the rise in PAN is due to the oxidation of carbonyls and hydrocarbons by Cl and Br atoms, and is kept in check by the concurrent depletion of NOₓ. The model study of Shepson et al. [1996] found much more rapid production of PAN during O₃ depletion events because they did not include BrNO₃ hydrolysis in their mechanism.

### 5. An Oscillatory System in Bromine-Catalyzed O₃ Depletion

The search for oscillatory solutions in atmospheric chemistry models generates sporadic interest in the literature, both for theoretical curiosity and for possible implications for atmospheric stability [Madronich and Hess, 1994; Poppe and Lustfeld, 1996; Tinsley and Field, 2001]. We find in our photochemical simulation for the Arctic boundary layer described above that an oscillatory system with a period of 3 days develops under low O₃ conditions if the reactive uptake coefficients (γ) of HBr and HOBr are increased from 0.3 to 0.8 (alternatively this can be viewed as an increase in the aerosol surface area). Figure 7 shows the evolution of O₃, CH₃O₂, and NOₓ and BrO concentrations under these conditions over a 30 day model simulation period with 43 pptv of initial bromide. The strong 3 day oscillation is evident. As bromine destroys O₃, the Br/BrO ratio increasingly favors HBr production over HOBr. This leads to an accumulation of...
Eventually virtually all of the model bromine resides in the aerosol (see Figure 6), suppressing BrOx chemistry. Those species which are depleted by bromine radical chemistry, notably CH2O and NOx, increase in concentration, leading to O3 production. The increase in O3 concentration leads to increased HOBr concentration which in turn leads to an increased rate of recycling of bromine. This leads to net O3 destruction and thus an oscillation. This appears to be the fastest oscillation calculated by a numerical model of the troposphere. Previous studies reviewed by Tinsley and Field [2001] have investigated cycles which act on timescales of a few weeks or more. Measurements in the Arctic boundary layer may offer the best opportunity of observing a chemical oscillation in the real atmosphere.

6. Conclusions

[33] Observations from the TOPSE aircraft campaign over the Arctic in March–May 2000 provide extensive chemical characterization of O3 depletion events in the boundary layer. We used a combination of data analysis and photochemical modeling to investigate the processes controlling the coupled evolution of BrOx-ClOx-HOx-NOx radicals and their reservoirs.

[34] Ethane and ethyne observations during TOPSE indicate that Cl radical chemistry is important only during the early stages of O3 depletion while Br radical chemistry remains active even as O3 drops below 1 ppbv. We reproduce these results in our model. As the O3 concentration decreases below 5 ppbv, accumulation of Br− in the aerosol leads Br2 production to compete with BrCl production as a sink of HOBr leading to a reduction in the rate of Cl radical production. Also, the reaction between aerosol phase BrCl and Br− to produce Br2Cl− further inhibits the release of BrCl. These two processes lead to a marked reduction in Cl chemistry below 10 ppbv of O3.

[35] Measured total peroxy radical concentrations (RO2) drop by a factor of 2 during O3 depletion events, a trend well reproduced by our model. During these events there are strong interchanges between HOx and BrOx radicals, and HOBr serves as a major reservoir for both. We define a generalized H/Cl/BrOx radical family to account for this coupling. Production of this family is mostly from the photolysis of CH2O emitted from the snow, and loss is mostly by the self reactions of peroxy radicals. Thus, at steady state the RO2 concentration is proportional to the square root of the CH2O concentration. Measured and simulated CH2O concentrations drop by a factor of 4 during O3 depletion events due to reaction with Br atoms, explaining the observed decrease in RO2 concentrations.

[36] Observed NOx concentrations show a marked decline during the early stages of O3 depletion with subsequent recovery as the O3 concentration drops below 10 ppbv. We reproduce this feature and ascribe the initial NOx depletion to BrNO3 hydrolysis. As the O3 concentration continues to drop, both the Br/BrO and NO/NO2 ratios increase which leads to a reduction in the BrNO3 concentration and thus the magnitude of the NOx sink. The emission of NOx from the snow then leads to a recovery in the NOx concentration. The magnitude of this recovery is obviously dependent upon the strength of the surface source and thus may vary geographically and seasonally.

[37] Outside of O3 depletion episodes, our model calculations suggest that aerosol phase reactions of HNO4 with...
HNO₂ and Ι could represent a substantial sink for NO₃. There is an obvious need for HNO₄ measurements in the Arctic boundary layer and for better characterization of HNO₃ chemistry.

[38] Our photochemical model simulation for the Arctic boundary layer shows a large-amplitude oscillation for O₃ with a period of 3 days under certain realistic conditions with high bromine. The period of the oscillation is much shorter than previously reported oscillations in tropospheric chemistry mechanisms. Although it could be nothing more than a theoretical curiosity, since external forcing (such as from transport) is likely to disrupt its periodicity, it may be due to its short period afford an opportunity for observing an oscillation in the real atmosphere.

[39] Acknowledgments. This work was funded by the Atmospheric Chemistry Program of the U.S. National Science Foundation.

References


