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

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Abstract: Extensive chemical characterization of ozone (O₃) depletion events in the Arctic boundary layer during the TOPSE aircraft mission in March–May 2000 enables analysis of the coupled evolution of bromine (BrO₅), chlorine (ClO₅), hydrogen oxide (HO₅), and nitrogen oxide (NO₅) radicals during these events. We project the TOPSE observations onto an O₃ chemical coordinate to construct a chronology of radical chemistry during O₃ depletion events, and we compare this chronology to results from a photochemical model simulation. Comparison of observed trends in ethyne (oxidized by Br) and ethene (oxidized by Cl) indicates that ClO₅ chemistry is only active during the early stage of O₃ depletion (O₃ > 10 ppbv). We attribute this result to the suppression of BrCl regeneration as O₃ decreases. Formaldehyde and peroxy radical concentrations decline by factors of 4 and 2 respectively during O₃ depletion and we explain both trends on the basis of the reaction of CH₂O with Br. Observed NO₅ concentrations decline abruptly in the early stages of O₃ depletion and recover as O₃ drops below 10 ppbv. We attribute the initial decline to BrNO₅ hydrolysis in aerosol, and the subsequent recovery to suppression of BrNO₅ formation as O₃ drops. Under halogen-free conditions we find that HNO₅ heterogeneous chemistry could provide a major NO₅ 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, NO₅, HO₅

1. Introduction

Events of near-total ozone (O₃) 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 (BrO₅ ≡ Br + BrO) [Barrie et al., 1988; Hausmann and Platt, 1994]. These events are also associated with high concentrations of chlorine oxide radicals (ClO₅ ≡ 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 (NO₅ ≡ NO + NO₂) and of precursors of hydrogen oxide radicals (HO₅ ≡ OH + peroxy radicals) during spring [Sumner and Shepson, 1999; Honrath 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 BrO₅–ClO₅–HO₅–NO₅ radical chemistry during O₃ 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 O₃ depletion is relatively well understood [Barrie et al., 1988; Fan and
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

\[
\begin{align*}
\text{(R1)} & \quad 2 \times (\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2) \\
\text{(R2)} & \quad \text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2 \\
\text{(R3)} & \quad \text{Net} \frac{\text{Br}_2 + \text{h}v}{2\text{O}_3} \rightarrow 2\text{Br} + \text{O}_3 \rightarrow 3\text{O}_2 \\
\end{align*}
\]

[1] 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 lived with respect to both photolysis and reaction with OH. We include the snow emissions of NOₓ and CH₂O in our analysis and propose by oxidation in standard models. We will present an evaluation here and examine the chemical coupling of BrOₓ with other radical families. Although physical adsorption and desorption may also take place.[Jacob et al., 1992; Hausmann and Platt, 1994; Michalowski et al., 2000].

[4] 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].

[5] The HBr is readily soluble and dissolves in aerosols to release bromide (Br⁻) in solution. Similarly, the other non-radical bromine reservoirs BrNO₃ (produced from NO₂ + BrO) and HOBr (produced from HO₂ + BrO) are taken up by aerosol, where BrNO₃ hydrolyzes to HOBr [Hanson et al., 1996]. In acidic aerosols, as are observed in the Arctic spring [Sirois and Barrie, 1999], HOBr reacts with Br⁻ to produce Br₂, which escapes into the gas phase and is photolysed:

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

[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] 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].

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[12] 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].
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 NOₓ appear to increase slightly as the O₃ concentrations decreases and PAN concentrations shows a more substantial increase. These intriguing trends in the NOₓ 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 depletion.

![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.](image1)

![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.](image2)
The chemistry scheme used in the model has been described before [e.g., Jaegle et al., 2000] and has been extended here to include halogen and aerosol chemistry following Michalowski et al. [2000]. It includes a detailed description of the oxidation of C1-C6 hydrocarbons updated with recent developments [Sander et al., 2000].

The rate constants for the reactions of Br with aldehydes [Ramacher et al., 2000] and ethylene [Ramacher et al., 2001] have been updated. Reactions of BrO with CH2O and HBr are not included, based on evidence that they are negligibly 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 (J(O1D)) and the J(NO2) scaling factor to higher wavelengths. 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 HNO3 chemistry.

The model is initialized on April 15 at 73°N, at local noon at 100 m altitude, with TOPSE measurements representative of Arctic conditions unaffected by halogen chemistry (Table 1: Background). The composition of the boundary layer aerosol is derived from previous studies. We assume that the dominant bromine activation mechanism is the bromine cycling within the aerosol and that the sole source and reservoir of bromine is the aerosol.
HNO$_2$ are kept constant in the simulation but the Cl$^-$ concentration is allowed to evolve. I$^-$ and HNO$_2$ are included in the model as aerosol-phase sinks of HNO$_4$ (see later) and play no further chemical role. Concentrations of CH$_3$CHO (18 pptv) and (CH$_3$)$_2$CO (300 pptv) are assumed from reasonable assumptions for O$_3$ depletion events in general (Boundary conditions at boundary layer top). This is a chemical steady state with the background hydrocarbon concentrations given in Table 1.

The boundary layer in our model is taken to be 200m deep. We assume NO$\times$ and CH$_2$O during the summer of 2000 [Wolff et al., 1997] and 200 m in this work. Our implied NO$_x$ 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 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 H$_2$O$_2$ (0.004 cm s$^{-1}$, 0.008 cm s$^{-1}$, and 0.09 cm s$^{-1}$ respectively). Emission of NO$_x$ and CH$_2$O 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 NO$_2$. The resulting 24-hour average emissions of CH$_2$O and NO$_x$ are $1.2 \times 10^{9}$ cm$^{-2}$ s$^{-1}$ and $3.6 \times 10^{8}$ cm$^{2}$ s$^{-1}$ respectively. Our implied CH$_2$O 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 NO$_x$ 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

### 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>HNO$_4$ + HSO$_3$ $\rightarrow$ SO$_4^{2-}$ + NO$_3^-$ + 2 H$^+$</td>
<td>$1.1 \times 10^7$ [H$^+$]$+ 3.3 \times 10^8$</td>
<td>Amel et al. [1994]</td>
</tr>
<tr>
<td>HNO$_4$ + HNO$_2$ $\rightarrow$ 2 NO$_3^-$ + 2 H$^+$</td>
<td>12</td>
<td>Lagerger and Sehested [1993]</td>
</tr>
<tr>
<td>HNO$_4$ + Cl$^-$ $\rightarrow$ HOCl + NO$_3^-$</td>
<td>0.014</td>
<td>Regimbhal and Mozurkewich [1997]</td>
</tr>
<tr>
<td>HNO$_4$ + Br$^-$ $\rightarrow$ HOBr + NO$_3^-$</td>
<td>0.54</td>
<td>Regimin and Mozarkewich [1997]</td>
</tr>
<tr>
<td>HNO$_4$ + Cl$^-$ $\rightarrow$ HOI + NO$_3^-$</td>
<td>890</td>
<td>Regimin and Mozarkewich [1997]</td>
</tr>
<tr>
<td>Br$^+$ + O$_3$ + H$^+$ $\rightarrow$ HOBr + O$_2$</td>
<td>11.7</td>
<td>Haag and Hoigné [1983]</td>
</tr>
<tr>
<td>HOBr + Cl$^-$ + H$^+$ $\rightarrow$ BrCl + H$_2$O</td>
<td>$5.6 \times 10^9$</td>
<td>Wang et al. [1994]</td>
</tr>
<tr>
<td>HOBr + Br$^-$ + H$^+$ $\rightarrow$ Br$_2$ + H$_2$O</td>
<td>$1.6 \times 10^{10}$</td>
<td>Beckwith et al. [1996]</td>
</tr>
<tr>
<td>HOCl + Cl$^-$ + H$^+$ $\rightarrow$ Cl$_2$ + H$_2$O</td>
<td>$2.2 \times 10^9$</td>
<td>Wang and Margerum [1994]</td>
</tr>
<tr>
<td>BrCl + H$_2$O $\rightarrow$ HOBr + Cl$^-$ + H$^+$</td>
<td>$1.0 \times 10^5$</td>
<td>Wang et al. [1994]</td>
</tr>
<tr>
<td>Br$_2$ + H$_2$O $\rightarrow$ HOBr + Br$^-$ + H$^+$</td>
<td>$9.7 \times 10^1$</td>
<td>Beckwith et al. [1996]</td>
</tr>
<tr>
<td>Cl$_2$ + H$_2$O $\rightarrow$ HOCI + Br$^-$ + H$^+$</td>
<td>$2.2 \times 10^1$</td>
<td>Wang and Margerum [1994]</td>
</tr>
<tr>
<td>BrCl + Br$^-$ $\rightarrow$ Br$_2$Cl$^-$</td>
<td>$5 \times 10^5$</td>
<td>Note a</td>
</tr>
<tr>
<td>Br$_2$ + Cl$^-$ $\rightarrow$ BrCl$^-$</td>
<td>$5 \times 10^9$</td>
<td>Note a</td>
</tr>
<tr>
<td>BrCl + Cl$^-$ $\rightarrow$ BrCl$_2^-$</td>
<td>$5 \times 10^9$</td>
<td>Note a</td>
</tr>
<tr>
<td>Br$_2$Cl$^-$ $\rightarrow$ Br$_2$ + Cl$^-$</td>
<td>$3.9 \times 10^9$</td>
<td>Note b</td>
</tr>
<tr>
<td>Br$_2$Cl + Br$^-$</td>
<td>$2.8 \times 10^9$</td>
<td>Note b</td>
</tr>
<tr>
<td>BrCl$_2^-$ $\rightarrow$ Cl$_2$ + Cl$^-$</td>
<td>$6.9 \times 10^9$</td>
<td>Note b</td>
</tr>
<tr>
<td>Br + Br$^-$ $\rightarrow$ Br$^+$ + H$^+$</td>
<td>$0.3 \times 10^9$</td>
<td>Schweitzer et al. [2000]</td>
</tr>
<tr>
<td>HCl + Cl$^-$ + H$^+$</td>
<td>$0.3 \times 10^9$</td>
<td>Schweitzer et al. [2000]</td>
</tr>
<tr>
<td>BrNO$_3$ + H$_2$O $\rightarrow$ NO$_3^-$ + NO$_2$ + H$^+$</td>
<td>$0.3 \times 10^9$</td>
<td>Hansson et al. [1996]</td>
</tr>
<tr>
<td>CINO$_2$ + H$_2$O $\rightarrow$ HOCI + NO$_2$ + H$^+$</td>
<td>$0.002 \times 10^9$</td>
<td>Robinson et al. [1997]</td>
</tr>
<tr>
<td>SO$_4^{2-}$ + H$_2$O $\rightarrow$ 2 NO$_3^-$ + 2 H$^+$</td>
<td>$0.1 \times 10^9$</td>
<td>Jacob [2000]</td>
</tr>
</tbody>
</table>

**Note a**: Assumed [Michalowski et al., 2000].
**Note b**: Derived from the equilibrium constant [Wang et al., 1994] and the assumed forward rate constant (see footnote a).
**Reaction probabilities (γ)**, dimensionless.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>H (M/atm) 250K</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOB(r) → HOBr (aer)</td>
<td>$3.0 \times 10^4$</td>
<td>0.3</td>
</tr>
<tr>
<td>HOCI(g) → HOCl(aer)</td>
<td>$1.8 \times 10^4$</td>
<td>0.3</td>
</tr>
<tr>
<td>Br$_2$ (g) → Br$_2$ (aer)</td>
<td>$1.0 \times 10^4$</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl$_2$ (g) → Cl$_2$ (aer)</td>
<td>$3.7 \times 10^4$</td>
<td>0.01</td>
</tr>
<tr>
<td>BrCl (g) → BrCl (aer)</td>
<td>$5.6 \times 10^4$</td>
<td>0.01</td>
</tr>
<tr>
<td>O$_3$ (g) → O$_3$ (aer)</td>
<td>$3.5 \times 10^4$</td>
<td>0.002</td>
</tr>
<tr>
<td>HNO$_4$ (g) → HNO$_4$ (aer)</td>
<td>$1.2 \times 10^4$</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**References**
- H: Waschewsky and Abbatt [1999]
- H: Atlantic et al. [1997]
- H: Huthwelker et al. [1995]
- H: Abbat and Molina [1992]
- H: Kelley and Tartar [1956]
- H: (estimated) Sander and Crutzen [1996]
- H: Wilhelm et al. [1977]
- H: (estimated) Sander and Crutzen [1996]
- H: Bartlett and Mergerum [1999]
- H: (estimated) Sander and Crutzen [1996]
- H: Kosak-Channing and Helz [1983]
- H: Magi et al. [1997]
- H: Regimbhal and Mozarkewich [1997]
- H: Li et al. [1996]
amplification of the diurnal cycle of NOx concentrations observed (1200) suggesting that the lifetime of NOx in the model maximum (1400 local time) is still later than 2000; Dentener et al. of HNO4 in the oxidation of S(IV) in clouds. Our understanding of the role of HNO4 in the atmospheric chemistry 10\[\text{thermal dissociation constant is uncertain by a factor of uncertainties in its chemistry (for example at 250K its system is limited by both a lack of field observations and of reactants ]}\]

4.1. Temporal Evolution and O3 Chemical Coordinate

4. Radical Chemistry During Ozone Depletion Events

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\(^-\)) from 0.2 to 43 pptv (range observed by Sirois and Barrie [1999]) and then allowed to evolve chemically for 10 days. The initial activation of the halogen radicals is through the reactions of Br\(^-\) and O\(_3\) [Haag and Hoigne, 1983] and HNO4 [Regimbal and Mozurkewich, 1997] to release HOBr. After this initial activation, the recycling of bromine radicals from non-radical reservoirs is controlled by Cl\(^-\) + HOBBr + H\(^+\) \rightarrow BrCl + H\(_2\)O [Wang et al., 1994] and Br\(^-\) + HOBBr + H\(^+\) \rightarrow Br\(_2\) + H\(_2\)O [Beckwith et al., 1996], with the recycling of Br\(^-\) being dominated by the latter.

Figure 3 shows the temporal evolution of O3, ethyne, NO\(_x\) (NO + NO\(_2\)) 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 O3 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\(_x\) concentration drops precipitously due to BrNO\(_3\) hydrolysis. The formation of BrNO\(_3\) is favored toward dawn and dusk when Br/BrO and NO/NO\(_2\) ratios are low, leading to a large diurnal cycle in the NO\(_x\) concentration. The small increases in NO\(_x\) concentrations simulated during night are due to the slow thermal decay of PAN and HNO\(_4\). 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. O3 concentrations drop down to a steady state of 1–2 ppbv after 6 days. As the O3 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 O3 concentration drops, the NO/NO\(_2\) and Br/BrO concentration ratios increase. Eventually, HObBr production by BrO + HO2 is suppressed, preventing the recycling of bromine radicals by R5. The suppression of bromine radical chemistry and the increase in the NO/NO\(_2\) ratio suppress in turn the formation of BrNO\(_3\). The longer NO\(_x\) lifetime, together with the surface source, allows the NO\(_x\) concentration to recover.

Simulations of the temporal evolution of O3 and halogen radical concentrations in the Arctic boundary layer during O3 depletion events have been reported in previous model studies [Sander et al., 1997; Michalowski et al., 2000]. Important new aspects here include the depletion and recovery of NO\(_x\) driven by BrNO\(_3\) 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 [e.g., Sander et al., 1997], we find that the BrO self reaction is the dominant mechanism for halogen-catalyzed O3 loss (~70%), with BrO + HO2 playing a subsidiary role (~25%). Other mechanisms (BrO + CH\(_3\)O\(_2\), BrNO\(_3\) + 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 O3 depletion. In order to enable such a comparison, we use the O3 concentration as a proxy for chemical history and make the comparison along this chemical coordinate
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 \(Br_2Cl^-\), 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 \(CH_2O\) (~40%) with the photolysis of \(O_3\) providing a smaller contribution (~20%). Most of the \(CH_2O\) (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 \(H_2O_2\). With the inclusion of halogens this balance changes substantially. The primary source of \(HO_x\) becomes the reaction between Br and \(CH_2O\). HOBr
acts as a temporary reservoir for HOx, producing OH when photolysed and consuming HO2 when produced. The uptake and subsequent destruction of HOB 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
CH$_3$O$_2$ + NO). As O$_3$ concentrations drop below 10 ppbv, the recovery of NO$_x$ as well as the decline in total RO$_2$ act to decrease CH$_3$OOH.

4.4. Nitrogen Oxide Radicals

As O$_3$ concentrations decrease from 40 to 10 ppbv, the measured NO$_x$ exhibits a rapid decline from about 20 pptv to 3 pptv. As O$_3$ is further depleted the NO$_x$ concentration recovers, eventually reaching similar concentrations to those observed in air masses with O$_3$ concentrations above 40 ppbv. The model reproduces this evolution as shown in Figure 5. In the model the decline and subsequent recovery in the NO$_x$ concentration is due to a combination of BrNO$_3$ hydrolysis and NO$_x$ emission from the snow. When BrO$_x$ chemistry is active and O$_3$ concentrations are still high, formation and hydrolysis of BrNO$_3$ ($\nu = 0.3$) leads to loss of NO$_x$. At lower O$_3$ concentrations, BrNO$_3$ formation is suppressed due to increases in both the NO/NO$_2$ and Br/BrO ratios.

Both PAN and NO$_x$ show a similar relationship with O$_3$, reflecting the dominant role of PAN in the composition of NO$_x$. The measurements show increases of PAN and NO$_y$ during O$_3$ 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 NO$_x$. The model study of Shepson et al. [1996] found much more rapid production of PAN during O$_3$ depletion events because they did not include BrNO$_3$ hydrolysis in their mechanism.

5. An Oscillatory System in Bromine-Catalyzed O$_3$ 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 O$_3$ conditions if the reactive uptake coefficients ($\gamma$) 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 O$_3$, CH$_3$O, and NO$_x$ 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 O$_3$, the Br/BrO ratio increasingly favors HBr production over HOBr. This leads to an accumulation of
Br\textsuperscript{−} in the aerosol. Eventually virtually all of the model bromine resides in the aerosol (see Figure 6), suppressing BrO\textsubscript{x} chemistry. Those species which are depleted by bromine radical chemistry, notably CH\textsubscript{2}O and NO\textsubscript{x}, increase in concentration, leading to O\textsubscript{3} production. The increase in O\textsubscript{3} concentration leads to increased HOBr concentration which in turn leads to an increased rate of recycling of bromine. This leads to net O\textsubscript{3} 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 O\textsubscript{3} 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 BrO\textsubscript{x}-ClO\textsubscript{x}-HO\textsubscript{x}-NO\textsubscript{x} radicals and their reservoirs.

[34] Ethane and ethyne observations during TOPSE indicate that Cl radical chemistry is important only during the early stages of O\textsubscript{3} depletion while Br radical chemistry remains active even as O\textsubscript{3} drops below 1 ppbv. We reproduce these results in our model. As the O\textsubscript{3} concentration decreases below 5 ppbv, accumulation of Br\textsuperscript{−} in the aerosol leads Br\textsubscript{2} 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\textsuperscript{−} to produce Br\textsubscript{2}Cl\textsuperscript{−} further inhibits the release of BrCl. These two processes lead to a marked reduction in Cl chemistry below 10 ppbv of O\textsubscript{3}.

[35] Measured total peroxy radical concentrations (RO\textsubscript{2}) drop by a factor of 2 during O\textsubscript{3} depletion events, a trend well reproduced by our model. During these events there are strong interchanges between HO\textsubscript{x} and BrO\textsubscript{x} radicals, and HOBr serves as a major reservoir for both. We define a generalized H/Cl/BrO\textsubscript{x} radical family to account for this coupling. Production of this family is mostly from the photolysis of CH\textsubscript{2}O emitted from the snow, and loss is mostly by the self reactions of peroxy radicals. Thus, at steady state the RO\textsubscript{2} concentration is proportional to the square root of the CH\textsubscript{2}O concentration. Measured and simulated CH\textsubscript{2}O concentrations drop by a factor of 4 during O\textsubscript{3} depletion events due to reaction with Br atoms, explaining the observed decrease in RO\textsubscript{2} concentrations.

[36] Observed NO\textsubscript{x} concentrations show a marked decline during the early stages of O\textsubscript{3} depletion with subsequent recovery as the O\textsubscript{3} concentration drops below 10 ppbv. We reproduce this feature and ascribe the initial NO\textsubscript{x} depletion to BrNO\textsubscript{3} hydrolysis. As the O\textsubscript{3} concentration continues to drop, both the Br/BrO and NO/NO\textsubscript{2} ratios increase which leads to a reduction in the BrNO\textsubscript{3} concentration and thus the magnitude of the NO\textsubscript{x} sink. The emission of NO\textsubscript{x} from the snow then leads to a recovery in the NO\textsubscript{x} 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 O\textsubscript{3} depletion episodes, our model calculations suggest that aerosol phase reactions of HNO\textsubscript{4} with

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**Figure 7.** Temporal evolution of O\textsubscript{3}, CH\textsubscript{2}O, NO\textsubscript{x} and BrO concentrations over a 30-day period for our standard simulation of O\textsubscript{3} depletion events in the Arctic boundary layer (c.f. Figure 4) but with enhanced aerosol uptake of HBr and HOBr (γ = 0.8, or equivalent increase in aerosol surface area). The initial bromide concentration is 43 pptv.
HONO and \( \Gamma \) could represent a substantial sink for NO\(_x\). There is an obvious need for HONO measurements in the Arctic boundary layer and for better characterization of HONO chemistry.

[38] Our photochemical model simulation for the Arctic boundary layer shows a large-amplitude oscillation for O\(_3\) 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 it, it may because of it short period afford an opportunity for observing an oscillation in the real atmosphere.

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References


