Heterogeneous HO2 Reaction with Inorganic Aerosol Particles

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Introduction

The OH and HO2 radicals, together known as HO radicals, play a vital role in determining the oxidizing capacity of the lower atmosphere. A detailed understanding of sources and sinks controlling HO levels is needed to accurately predict regional air quality and tropospheric O3 production.

Modeling studies have shown that HO2 uptake onto aerosols may be an important HO sink (Figure 1).1,2 Furthermore, field measurements of HO2 levels have suggested heterogeneous uptake onto aerosols with a reactive uptake coefficient of γ = 0.1–1.0 to explain the lower observed HO2 levels than predicted steady-state concentrations with photochemical models.3,4

Despite the potential importance of HO2 uptake onto aerosols on the tropospheric HO2 budget, the kinetics of this reaction and its dependence on atmospheric conditions and aerosol composition is not well understood. The objective of this laboratory study is to measure the reactive uptake coefficients of heterogeneous HO2 uptake onto (NH4)2SO4 and NaCl aerosol particles as proxies for atmospheric aerosols using Fluorescence ASSay by Gas Expansion (FAGE) technique to quantify HO2 concentrations.

Experimental

A schematic of the laboratory setup used to study HO2 uptake kinetics onto aerosol particles is shown in Figure 2.

- **Particle Generation/Measurement**: Wet salt particles were produced by atomizing aqueous solutions of 0.05 – 1% by mass (NH4)2SO4 and NaCl and 0.025% by mass CuSO4·5H2O for Cu(II)-doped aerosols. Aerosol flow was passed through a diffusion dryer (TSI 3062) to produce dry salt particles. Particle size distributions were measured using a Scanning Mobility Particle Sizer (SMPS; TSI 3081, 3081, 3775). Mean number diameters ranged from approximately D = 70-100 nm and total number concentrations ranged from approximately N = 1010 - 1012 cm-3.

- **HO2 Production/Detection**: HO2 radicals are produced from the photolysis of H2O2 by passing a humidified flow over a mercury penray lamp located inside the stainless steel injector as follows:

  \[
  \text{H}_2\text{O}_2 + \text{hv}(\lambda=185 \text{ nm}) \rightarrow \text{OH} + \text{H}_2. \]

  HO2 radicals were chemically converted to OH in the detection cell by reaction with NO (i.e. \(\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2\)) and OH radicals were detected using the FAGE technique by measuring their laser-induced fluorescence at \(\lambda = 308\text{ nm}\) under low pressure (~0.7 torr). HO2 concentrations were near atmospheric levels and in the range of \(10^{-5} - 10^{-3}\text{ cm}^{-3}\).

- **Aerosol Reaction Flow Tube**: Aerosol flow and HO2 flow from injector tip were introduced into the glass aerosol flow tube (100 cm length, 5.9 mm ID). The injector was moved back to increase reaction time between HO2 and aerosol particles, and HO2 uptake kinetics were observed by measuring the decay of the HO2 LIF signal as a function of injector position. Experiments were conducted at room temperature and atmospheric pressure.

Figure 1. Modelled fractional HO2 loss in lower troposphere due to HO2 uptake on aerosols (γ = 0.3).1

![Figure 1](image1.png)

Figure 2. Experimental Setup

Table 1. Reactive uptake coefficient for HO2 onto (NH4)2SO4 and NaCl Salts at room temperature. Values in parentheses are error values.

<table>
<thead>
<tr>
<th>Aerosol Composition</th>
<th>RH (%)</th>
<th>Aerosol Phase</th>
<th>HO2 uptake (10^-5 cm^3 cm^-2 s^-1)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH4)2SO4 dry</td>
<td>45</td>
<td>wet</td>
<td>0.25 (0.06)</td>
<td>[7]</td>
</tr>
<tr>
<td>(NH4)2SO4 dry</td>
<td>45</td>
<td>dry</td>
<td>0.05 (0.02)</td>
<td>[8]</td>
</tr>
<tr>
<td>NaCl dry</td>
<td>45</td>
<td>wet</td>
<td>0.10 (0.06)</td>
<td>[7]</td>
</tr>
<tr>
<td>NaCl dry</td>
<td>45</td>
<td>dry</td>
<td>0.05 (0.02)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) dry</td>
<td>45</td>
<td>wet</td>
<td>0.11 (0.06)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) dry</td>
<td>45</td>
<td>dry</td>
<td>0.05 (0.02)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) wet</td>
<td>45</td>
<td>wet</td>
<td>0.01 (0.005)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) wet</td>
<td>45</td>
<td>dry</td>
<td>0.001 (0.0002)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) wet</td>
<td>0</td>
<td>wet</td>
<td>0.012 (0.0061)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) wet</td>
<td>0</td>
<td>dry</td>
<td>0.006 (0.0003)</td>
<td>[8]</td>
</tr>
<tr>
<td>Cu(II) wet</td>
<td>0</td>
<td>dry</td>
<td>1.30x10^-6 (1x10^-7)</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Results

The mass accommodation (\(\alpha\)), or “sticking coefficient”, was determined by measuring HO2 uptake onto Cu(II)-doped aqueous (NH4)2SO4 particles as the Cu(II) quickly scavenges HO2 in the aqueous phase with \(\alpha\text{Cu(II)} = 0.76\pm0.15\) calculated for the data shown in Figure 3.

Figure 3. Modelled fractional HO2 loss as a function of aerosol surface area for Cu(II)-doped NaCl particles (RH=43%).

![Figure 3](image3.png)

Rate coefficients (\(k_{\alpha}\)) for HO2 decay in the absence and presence of aerosol particles (Cu(II)-doped (NH4)2SO4, wet and dry (NH4)2SO4 and NaCl) were measured as a function of aerosol surface area. The \(k_{\alpha}\) for aerosol uptake were corrected for non-plug flow conditions (\(k\)). HO2 decay curves (Figure 4) display pseudo-first order kinetics.

\[ k = \frac{\gamma \text{HO}_2 \cdot \nu \cdot S}{2} \]

\(\gamma\text{HO}_2\) and S is the aerosol surface area (cm2 cm-3), and \(\nu\) is the molecular speed (cm s-1). Aerosol surface area values from this work are summarized in Table 1.

Figure 4. HO2 signal decay curves in the absence (well) and presence of wet NaCl aerosol particles (5x7.5x105 cm3 cm-2, RH=52%)

![Figure 4](image4.png)

Conclusions

- Reactive uptake and mass accommodation (for Cu(II)-doped aerosol) coefficients for HO2 uptake into inorganic aerosol particles have been measured under HO2 concentrations that are close to atmospheric levels, which are mostly consistent with literature values.
- Significantly enhanced uptake into aqueous aerosols compared to dry aerosols for (NH4)2SO4 and NaCl particles was observed.
- Therefore, the importance of heterogeneous HO2 loss onto aerosols on tropospheric HO2 budget will strongly depend on factors that control aerosol phase, such as RH and aerosol composition.

Acknowledgements:

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References