Measurement of overall uptake coefficients for HO$_2$ radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang (China)

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Abstract. HO$_2$ uptake coefficients for ambient aerosol particles, collected on quartz fiber filter using a high-volume air sampler in China, were measured using an aerosol flow tube coupled with a chemical conversion/laser-induced fluorescence technique at 760 Torr and 298 K, with a relative humidity of 75 %. Aerosol particles were regenerated with an atomizer using the water extracts from the aerosol particles. Over 10 samples, the measured HO$_2$ uptake coefficients for the aerosol particles at the Mt. Tai site were ranged from 0.13 to 0.34, while those at the Mt. Mang site were in the range of 0.09–0.40. These values are generally larger than those previously reported for single-component particles, suggesting that reactions with the minor components such as metal ions and organics in the particle could contribute to the HO$_2$ uptake. A box model calculation suggested that the heterogeneous loss of HO$_2$ by ambient particles could significantly affect atmospheric HO$_x$ concentrations and chemistry.

1 Introduction

Aerosol particles are ubiquitous in the atmosphere and play a significant role in physical and chemical phenomena in the troposphere, where they scatter solar radiation and undergo chemical reactions. Heterogeneous reactions between atmospheric gases and particles represent a significant portion of tropospheric chemistry (Jacob, 2000; Finlayson-Pitts and Pitts Jr., 2000). An increasing number of field measurements of HO$_x$ (= OH + HO$_2$) radicals have been made recently, due to their importance in atmospheric chemistry. The HO$_2$ concentrations determined from these measurements are lower than those expected from the rates of known source and sink reactions in the gas phase under a steady-state approximation (Carslaw et al., 2002; Sommariva et al., 2004; Smith et al., 2006; Kanaya et al., 2007). This indicates the possible presence of missing loss processes for HO$_2$. Heterogeneous reactions of HO$_2$ on the surface of aerosol particles may in part account for these missing processes. Atmospheric modelling calculations (Thornton et al., 2008; Martin et al., 2002; Macintyre and Evans, 2011) have suggested the potential importance of the heterogeneous reactions of HO$_2$ radicals with aerosol particles in the areas with high aerosol loading.

Using various techniques, kinetic studies for the heterogeneous reactions of HO$_2$ radicals with aerosol particles have been investigated by several groups (Hanson, 1992; Bedjanian et al., 2005; Remorov et al., 2002; Gershenzon et al., 1995; Mozkurkewich et al., 1987; Thornton and Abbatt, 2005; Taketani et al., 2008, 2009, 2010). The HO$_2$ uptake coefficients for single-component particles containing water were reported to be 0.1–0.2 at 45–75 % relative humidity (RH), whereas those for dry particles were < 0.01–0.05 at 20–53 % RH (Thornton and Abbatt, 2005; Taketani et al., 2008, 2009,
These results indicate that particles in different phases have different HO$_2$ uptake coefficients, and the uptake coefficients change with the RH throughout the phase transformation. However, there are very few studies on HO$_2$ uptake coefficients by multiple-component particles. The heterogeneous loss of HO$_2$ on aqueous inorganic particles doped with CuSO$_4$ has been investigated previously (Thornton and Abbatt, 2005; Mozurkewich et al., 1987; Taketani et al., 2008). These studies revealed that the uptake coefficients of HO$_2$ by particles containing CuSO$_4$ were higher than those not containing CuSO$_4$. Some metal ions (e.g. Cu and Fe) can act as catalysts for the catalytic reaction of HO$_2$ (Jacob, 2000). In our previous study (Taketani et al., 2009), the HO$_2$ uptake coefficients in the presence of sea-salt particles, which are multi-component, were higher than those for single-component NaCl particles at low RH, below the efflorescence point of NaCl (Martin, 2000). This result implies that MgCl$_2$, which is a minor component in sea salt and seawater, could play a significant role in retaining water within the particles, even if the RH is below the efflorescence point of the major component (NaCl) of the particle. These results suggest that minor compounds in the particles can control the overall properties of the particles, and affect the HO$_2$ radical uptake coefficients. Although the heterogeneous reactions of HO$_2$ radicals in field measurements are important, it is difficult to assess their actual contribution from directly observed parameters, as the uptake coefficient of the HO$_2$ radical can depend on minor components in ambient aerosol particles, which consist of various compounds.

The heterogeneous reactions of the HO$_x$ radicals can also be important for the chemical evolution of particle composition (George et al., 2008; George and Abbatt, 2010). In an aircraft study of aerosol properties over Mexico, using a high-resolution time-of-flight aerosol mass spectrometer, DeCarlo et al. (2008) observed that the organic O/C ratio in the particles doubled as the particles travelled from the source to the downwind areas, experiencing photochemical aging. To achieve a high O/C ratio through photochemical aging, they hypothesized the importance of the heterogeneous oxidation of organic particles by OH. From their results, however, the heterogeneous oxidation by OH was too slow to explain the observed increases in O/C. Alternatively, the high O/C ratio could be explained by the uptake of HO$_2$ by the particles. However, it was difficult to assess this contribution because HO$_2$ uptake coefficients for ambient aerosol particles were not easily estimated.

In this study, we tested ambient aerosol particles sampled on filters at two mountain sites in China, in laboratory experiments measuring the uptake coefficients of HO$_2$. We determined the overall HO$_2$ uptake coefficients for the realistic particles with multiple chemical components using an aerosol flow tube (AFT) and chemical conversion/laser-induced fluorescence (CC/LIF). The measured uptake coefficients were used for the assessment of the impact of the heterogeneous processes on tropospheric chemistry.

### Table 1. Information of aerosol particle sampling sites.

<table>
<thead>
<tr>
<th>Location</th>
<th>Height</th>
<th>Date</th>
<th>Size of Collected Particles</th>
<th>Number of experimental samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Tai</td>
<td>36°26′N, 117°11′E</td>
<td>1530m</td>
<td>TSP</td>
<td>10</td>
</tr>
<tr>
<td>Mt. Mang</td>
<td>40°15′N, 116°17′E</td>
<td>170m</td>
<td>PM$_2.5$</td>
<td>12</td>
</tr>
</tbody>
</table>

2 Aerosol sampling and analysis

2.1 Sampling sites and protocol

The ambient particles employed in this study were collected at two sites in China as part of intensive field campaigns (Kanaya et al., 2008, 2009; He and Kawamura, 2010). Figure 1 and Table 1 show the locations and other information about the aerosol particle collection. More information on each sampling site and the aerosol collection procedure is given below.

Mt. Tai aerosol particles: Mt. Tai (36°26′N, 117°11′E, 1534 m a.s.l., China) is located at the centre of the Northern China Plain. In June 2006, we performed an intensive field campaign at the top of the mountain focusing on aerosol and ozone chemistry. The site is isolated from local pollution sources and thus we expected to observe regional-scale air pollution. In this field campaign, the total suspended particles
(TSP) were sampled between 28 May and 28 June 2006. The sampling technique has been described in detail in the literature (Fu et al., 2008) and will be reviewed briefly here. Essentially, daytime/nighttime TSP sampling was performed. All samples were collected onto pre-baked (450 °C for 6 h) quartz filters (8 × 10 inch) with a flow rate of 1.0 m³ min⁻¹, using a high-volume air sampler. Eighty-one samples were collected during this campaign, of which 10 samples were used in the present kinetics experiment.

Mt. Mang aerosol particles: Mt. Mang is located 40 km north of the city of Beijing. Our observation site (40°15′ N, 116°17′ E, 170 m.a.s.l.) was in a forest park on the southern slope of the mountain. The dominant wind direction was southerly during the day and northerly at night during the observation period in September 2007. It was expected that at the Mt. Mang site we could catch the air mass, which had travelled over Beijing and been strongly affected by photochemical processes in the daytime. Between 8 September and 5 October 2007, we carried out sampling of particles with diameters of less than 2.5 µm (PM₂.₅). Details of the analysis and compositions of the aerosol particles at Mt. Mang will be reported in the future (Taketani et al., 2012a). Briefly, the sampling of PM₂.₅ was performed during the daytime (9 h) or night-time (14 h). All PM₂.₅ samples were collected onto pre-baked (900 °C for 3 h) quartz filters (ϕ110 mm) with a flow rate of 0.5 m³ min⁻¹, using a high-volume air sampler (SHIBATA HV-700F). To collect PM₂.₅, a custom-made particle-size separator was installed on the high-volume air sampler. Seventy-four samples were collected during this period, of which 12 samples were used for the kinetics experiment.

Before sampling, each filter was placed in a clean glass jar and sealed with a Teflon-lined screw cap during transport and storage. After sampling, the filter was placed back in the glass jar, transported to the laboratory and stored at −20 or 5 °C prior to the experiment.

2.2 Composition analysis for PM₂.₅ samples

Ion chromatography (DX-AQ, Dionex) and inductively coupled plasma-atomic emission spectrometry (IRIS/AP model, Nippon Jarrell-Ash) were employed to determine the concentrations of water-soluble inorganic ions (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺) and metals (Zn, Pb, Mn, Fe, Cu, and Al) on the filters, respectively. The concentrations of organic carbon (OC) and elemental carbon (EC) were determined using an EC/OC analyzer (Sunset Lab.). The 2.0 cm² filter punches were individually placed in the EC/OC analyzer oven. To determine the OC level, the sample was heated in three temperature steps to 550 °C under a stream of ultrahigh-purity He (99.999 %). Then, the sample was heated under a mixture of 2 % O₂ and 98 % He to 900 °C, to determine the amounts of EC and pyrolyzed OC. To correct for the pyrolyzed OC, laser transmission was utilized.

3 Experiments

3.1 Preparation of particle source

To obtain a solution of source particles, part of each filter (approximately 10 cm² for filters from Mt. Tai, and 39 cm² from Mt. Mang) was cut into pieces and the loaded particles were extracted with Milli Q water (∼30 mL) under ultrasound for 30 min. The extracts, including the water-soluble compounds, were passed through a membrane filter (pore diameter, 0.22 µm) to remove any large particles and filter debris. Blank filters from each site were employed for background measurements.

3.2 Measurement of kinetic data

Kinetic measurements for the heterogeneous reaction of HO₂ with aerosol particles were performed in our laboratory. Experiments were conducted using an AFT coupled with a CC/LIF apparatus, which we have developed and employed in previous studies (Taketani et al., 2008, 2009; Kanaya and Akimoto, 2006). The HO₂ degradation kinetics in the AFT was measured by changing the position of the HO₂ radical injector to vary the contact time between the HO₂ radicals and the aerosol.

All experiments were performed at atmospheric pressure and 296 ± 2 K in the AFT. A zero air generator supplied purified carrier gas in the experiments and flow rates were regulated using eight mass flow controllers (models 3660 and 3650, Kofloc). The HO₂ radicals were generated by photolysis of H₂O using a mercury lamp via the following reactions in air at 760 Torr, and then they were injected into the AFT through a Pyrex tube (ϕ = 12 mm).

\[
\text{H}_2\text{O} + h\nu (185 \text{ nm}) \rightarrow \text{OH} + \text{H}
\]

\[
\text{H} + \text{O}_2 + \text{M} (\text{N}_2 \text{or O}_2) \rightarrow \text{HO}_2 + \text{M}
\]

Poly-dispersed submicron aerosol particles, generated with an atomizer (model 3076, TSI) using the extract from the filter, as described in Sect. 3.1, were introduced into the top of the AFT (ϕ = 60 mm). The RH in the AFT was kept at 75 % by mixing the dry airflow with a flow of air that had been passed through a water bubbler. The total volumetric flow rate in the AFT was kept at 9.4 L min⁻¹. A scanning mobility particle-sizing instrument (DMA3080 and CPC3010, TSI) was used to measure the aerosol distributions and concentrations. The regenerated aerosol concentrations in this study ranged from 1.9 × 10⁷ to 5.7 × 10⁹ particles cm⁻³. Since the aerosol distribution is well characterized by a log-normal radius distribution, the mean surface-area-weighted radius \( r_s \) (Hanson et al., 2003; Lovejoy et al., 1995) can be determined, and was found to be 50–75 nm in this study. The geometric standard deviation of the log-normal size distribution was 1.8 ± 0.1.
HO$_2$ was detected using a CC/LIF-FAGE (fluorescence assay by gas expansion) technique. The LIF instruments for measuring OH radicals can be applied for the measurement of HO$_2$ by chemical conversion via the reaction of HO$_2$ and NO to form OH radicals and NO$_2$. The total pressure in the LIF cell was about 2.2 Torr and was measured with a capacitance manometer (Baratron 127, MKS). The LIF signals were detected using a channel photomultiplier (C1982P, Perkin-Elmer Optoelectronics) coupled with the photon-counting method. The concentration of HO$_2$ radicals in this study was estimated to be $\sim 1 \times 10^8$ molecules cm$^{-3}$ at an injector position of 30 cm and in the absence of aerosol particles, and this is similar to ambient concentration levels. In addition, the effect of the self-reaction of HO$_2$ in the gas phase is negligible in this system.

### 4 Results and Discussion

#### 4.1 Components of ambient aerosol

Tables 2 and 3 summarize the chemical compositions of the collected ambient aerosols. POM denotes the particulate organic matter whose mass concentration was estimated by multiplying the OC concentration by a factor 1.4 (Turpin et al., 2000; Russell et al., 2003). The fraction of the metals was minor, but largely variable. For the aerosol particles collected at Mt. Mang, concentrations of [SO$_4^{2-}$], [NO$_3^-$], and [NH$_4^+$] were usually very high, suggesting that ammonium sulphate and nitrate are the major components in the particles. Details of the aerosol composition analysis, along with other samples from Mt. Mang will be reported elsewhere (Taketani et al., 2012a). The dominant components at the Mt. Tai site were more diverse, while [SO$_4^{2-}$], [NO$_3^-$], and [NH$_4^+$] generally made large contributions to the total, [K$^+$] and POM were high in samples T2, T3, and T10. Over the sampling period, the ambient aerosol should be strongly affected by biomass burning.

#### 4.2 Measurement of uptake coefficient

Figure 2 shows typical profiles observed for the HO$_2$ signal decay in the presence of regenerated aerosol particles, using sample T1 and a blank filter. The vertical axis in Fig. 2 is on a logarithmic scale and the HO$_2$ signal intensity is normalized against that at the initial injection position. In this study, HO$_2$ decays were found to be exponential and are consistent with first-order kinetics,

$$
[\text{HO}_2]_t = \exp \left( -k_{\text{obs}}t \right),
$$

where $k_{\text{obs}}$ is the observed uptake coefficient.
where \([\text{HO}_2]_0\) is the initial concentration of \(\text{HO}_2\) radicals at the injector position, \(t\) is the reaction time that is estimated based on the injection position of \(\text{HO}_2\) and flow velocity in the AFT, and \(k_{\text{obs}}\) is the effective first-order rate constant (s\(^{-1}\)) for the heterogeneous reaction of \(\text{HO}_2\) with the aerosol particles. To estimate the background losses of \(\text{HO}_2\), the decay rates were measured at the same RH for the particles generated from the blank filter in each experiment. The decay rates ranged from 0.02 to 0.05 s\(^{-1}\). In Fig. 3, the observed first-order rate constants for \(\text{HO}_2\) are plotted against the total surface concentrations of the regenerated particles from sample T1. The first-order rate constants \((k_{\text{obs}})\) were used to derive the uptake coefficients \((\gamma_{\text{obs}})\) after correcting for the wall losses and diffusion under non-plug conditions using the techniques of Brown (1978). \(k_{\text{obs}}\) is related to \(\gamma_{\text{obs}}\) by the following equation:

\[
k_{\text{obs}} = \frac{\gamma_{\text{obs}} [\text{HO}_2]}{4 \times \text{S}},
\]

where \(\sigma_{\text{HO}_2}\) is the molecular thermal speed of \(\text{HO}_2\) (cm s\(^{-1}\)), and \(\text{S}\) is the total surface concentration of aerosol (cm\(^2\) cm\(^{-3}\)). The \(\gamma_{\text{obs}}\) values were estimated from the observed first-order rate constants for \(\text{HO}_2\) and are plotted against the total surface concentrations of aerosol. However, in deriving \(\gamma_{\text{obs}}\) from Eq. (2), gas-phase diffusion has not been taken into account, but, using established methods (Fuchs and Sutugin, 1970; Fried et al., 1994), \(\gamma_{\text{obs}}\) can be modified to a corrected uptake coefficient \(\gamma\). In this study, the correction was within 3% of the observed value. Values of \(\gamma\) are listed in Tables 2 and 3. Quoted errors are single standard deviations from a least-squares fit, combined with the estimated systematic uncertainties for the measurements of the aerosol surface concentration (5%) and flow speed (2%).

The uptake coefficients from the Mt. Mang site ranged from 0.13 to 0.34, while those at Mt. Tai were in the range 0.09–0.40. In our previous studies, the \(\gamma\) values for single-component particles of \((\text{NH}_4)_2\text{SO}_4\), NaCl, and levoglucosan with a RH of 75% were 0.19 ± 0.04, 0.10 ± 0.02, and 0.09 ± 0.02, respectively (Taketani et al., 2008, 2009, 2010). NASA-JPL recommends that values for aqueous ammonium sulphate and sodium chloride are < 0.1 (Sander et al., 2011). The uptake coefficients for sampled ambient aerosol particles in this study were sometimes higher than those reported in the previous studies. If the \(\text{HO}_2\) losses are attributed to the self-reaction of \(\text{HO}_2\) in the aqueous phase, the uptake coefficient should be < 0.01, under tropospheric conditions \(([\text{HO}_2] \sim 1 \times 10^8\) molecules cm\(^{-3}\)), which are similar to our experimental conditions. These results suggest that minor components, such as reactions with metal ions and/or organics, may make a significant contribution to the observed \(\text{HO}_2\) losses in the sampled particles.

### Table 3. Concentrations (µg m\(^{-3}\)) of the measured components in sampled particles (TSP) at Mt. Tai, together with measured uptake coefficients (\(\gamma\)) in this study.

<table>
<thead>
<tr>
<th>Component</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
<th>T5</th>
<th>T6</th>
<th>T7</th>
<th>T8</th>
<th>T9</th>
<th>T10</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_4^{2-})</td>
<td>68.0</td>
<td>50.0</td>
<td>76.1</td>
<td>37.3</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>26.5</td>
<td>35.6</td>
<td>48.1</td>
<td>19.4</td>
<td>4.8</td>
<td>8.8</td>
<td>5.6</td>
<td>3.8</td>
<td>8.1</td>
<td>23.6</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>1.5</td>
<td>19.2</td>
<td>14.3</td>
<td>2.0</td>
<td>0.6</td>
<td>2.5</td>
<td>1.0</td>
<td>0.7</td>
<td>0.9</td>
<td>20.9</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>23.6</td>
<td>22.5</td>
<td>31.1</td>
<td>15.6</td>
<td>3.2</td>
<td>5.2</td>
<td>3.2</td>
<td>2.3</td>
<td>4.9</td>
<td>14.6</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.28</td>
<td>0.35</td>
<td>0.17</td>
<td>0.20</td>
<td>0.23</td>
<td>0.47</td>
<td>0.42</td>
<td>0.21</td>
<td>0.20</td>
<td>0.26</td>
</tr>
<tr>
<td>K(^+)</td>
<td>7.0</td>
<td>15.7</td>
<td>18.2</td>
<td>5.3</td>
<td>0.7</td>
<td>2.5</td>
<td>1.5</td>
<td>0.9</td>
<td>2.5</td>
<td>13.9</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>8.1</td>
<td>9.1</td>
<td>4.8</td>
<td>4.0</td>
<td>4.9</td>
<td>9.4</td>
<td>11.0</td>
<td>6.2</td>
<td>6.7</td>
<td>13.2</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.7</td>
<td>0.9</td>
<td>0.7</td>
<td>0.4</td>
<td>0.5</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Al</td>
<td>–</td>
<td>27.8</td>
<td>–</td>
<td>29.2</td>
<td>–</td>
<td>5.7</td>
<td>19.6</td>
<td>4.8</td>
<td>11.9</td>
<td>9.1</td>
</tr>
<tr>
<td>Cu</td>
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<td>0.08</td>
<td>0.06</td>
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<td>0.04</td>
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</tr>
<tr>
<td>Fe</td>
<td>3.0</td>
<td>4.0</td>
<td>1.7</td>
<td>3.5</td>
<td>5.9</td>
<td>11.6</td>
<td>11.5</td>
<td>5.7</td>
<td>3.2</td>
<td>5.9</td>
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<tr>
<td>Mn</td>
<td>0.09</td>
<td>0.12</td>
<td>0.06</td>
<td>0.07</td>
<td>0.17</td>
<td>0.31</td>
<td>0.30</td>
<td>0.14</td>
<td>0.08</td>
<td>0.13</td>
</tr>
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<td>0.22</td>
<td>0.22</td>
<td>0.12</td>
<td>0.09</td>
<td>0.04</td>
<td>0.12</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>Zn</td>
<td>0.22</td>
<td>–</td>
<td>0.07</td>
<td>0.05</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.03</td>
<td>–</td>
</tr>
<tr>
<td>POM</td>
<td>32.8</td>
<td>73.6</td>
<td>66.5</td>
<td>25.2</td>
<td>17.3</td>
<td>29.7</td>
<td>29.7</td>
<td>16.9</td>
<td>22.3</td>
<td>51.7</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>0.31 ± 0.20</td>
<td>0.37 ± 0.20</td>
<td>0.25 ± 0.24</td>
<td>0.40 ± 0.09</td>
<td>0.19 ± 0.19</td>
<td>0.27 ± 0.27</td>
<td>0.10</td>
<td>0.04</td>
<td>0.09</td>
<td>0.04</td>
</tr>
</tbody>
</table>

POM: particulate organic matter.
It has been reported that some metal ions (e.g. Cu and Fe) can act as catalysts for the reaction of HO$_2$ (Jacob, 2000) in the aqueous phase. Since the HO$_2$ radical can undergo acid dissociation in the aqueous phase ($\text{HO}_2(\text{aq}) \leftrightarrow \text{H}^+ + \text{O}_2^-$, $pK_{\text{aq}} \approx 4.7$), the following reaction processes can contribute to HO$_2$ loss:

\[
\text{Cu}^{2+} + \text{HO}_2(\text{aq}) \rightarrow \text{O}_2(\text{aq}) + \text{Cu}^+ + \text{H}^+, \tag{5}
\]

\[
\text{Cu}^{2+} + \text{O}_2^-(\text{aq}) \rightarrow \text{O}_2(\text{aq}) + \text{Cu}^+, \tag{6}
\]

\[
\text{Cu}^+ + \text{O}_2^-(\text{aq}) \xrightarrow{2\text{H}_2\text{O}} \text{H}_2\text{O}_2(\text{aq}) + \text{Cu}^{2+} + 2\text{OH}^-, \tag{7}
\]

\[
\text{Cu}^+ + \text{HO}_2(\text{aq}) \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O}_2(\text{aq}) + \text{Cu}^{2+} + \text{OH}^-, \tag{8}
\]

\[
\text{Fe}^{2+} + \text{HO}_2(\text{aq}) \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O}_2(\text{aq}) + \text{Fe}^{3+} + \text{OH}^-, \tag{9}
\]

\[
\text{Fe}^{2+} + \text{O}_2^-(\text{aq}) \xrightarrow{2\text{H}_2\text{O}} \text{H}_2\text{O}_2(\text{aq}) + \text{Fe}^{3+} + 2\text{OH}^-, \tag{10}
\]

\[
\text{Fe}^{3+} + \text{O}_2^-(\text{aq}) \rightarrow \text{Fe}^{2+} + \text{O}_2(\text{aq}), \tag{11}
\]

\[
\text{Fe}^{3+} + \text{HO}_2(\text{aq}) \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2(\text{aq}). \tag{12}
\]

The rate constants for Eqs. (5) to (12) are $1.0 \times 10^8$, $8.0 \times 10^9$, $1.5 \times 10^9$, $9.4 \times 10^9$, $1.2 \times 10^6$, $1.0 \times 10^7$, $1.8 \times 10^8$, and $3.3 \times 10^5 \text{M}^{-1} \text{s}^{-1}$, respectively (Cabelli et al., 1987; von Piechowski et al., 1993; Jacob, 2000; Graedel et al., 1986). These reactive HO$_2$ losses may contribute to the relatively high uptake coefficients for ambient aerosol particles measured in this study.

In the steady-state concentration of the HO$_2$ between a particle surface and just inside the surface, the measured $\gamma$ for the reaction on the aerosol particle is given by Hanson et al. (1994):

\[
\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4\text{HRT} \sqrt{D_k k_t}}, \tag{13}
\]

where $\alpha$ is the mass accommodation coefficient, $H$ is the effective Henry’s constant, $R$ is the gas constant, $T$ is temperature and $D_k$ is the aqueous-phase diffusion coefficient, which is assumed to be $10^{-5} \text{cm}^2 \text{s}^{-1}$ for HO$_2$ (Jacob, 2000); $k_t$ is the first-order rate constant for the reaction of HO$_2$ in the bulk aqueous phase. Thus, the uptake coefficients for HO$_2$ by the liquid particles are dependent on particle composition and size. Thus, the uptake coefficients for HO$_2$ by the liquid particles are dependent on particle composition and size. First, when assuming that Cu and Fe are present only as free ions in the particles, the molarities of Cu and Fe were estimated to be 0.006–0.066 M and 0.081–19.3 M, respectively, in the wet particles at 75% RH. These values were estimated with the aerosol water content based on the hygroscopic growth of (NH$_4$)$_2$SO$_4$ (Martin, 2000), which was the dominant species in the particles we sampled. Using $\alpha = 0.5$
and properties of (NH₄)₂SO₄ in Eq. (3), we estimate the uptake coefficients to be in the range of 0.497–0.498. These values are very close to the mass accommodation coefficient α = 0.5, as used in the calculation. These are different than the measured γ values, which ranged between 0.09 and 0.40. Although we have assumed that the Cu and Fe are present in their free forms in the particles, and react with HO₂, it has been reported that dissolved Cu and/or Fe in particles actually exist as complexes with OH⁻, SO₄²⁻ and other organic ions. These are less reactive compared to the free ions (Jacob, 2000; von Ptechowski et al., 1993). Furthermore, the activity of Cu and Fe in the aqueous phase is important factor, because of the non-ideality of the concentrated solutions. The values of activity coefficient for Cu and Fe are roughly estimated to be less than 0.1, based on (NH₄)₂SO₄ particles at 68 % RH (Ross and Noone, 1991), suggesting the free form metal ions will be limited in the particles. In the following calculations, we assumed that the activity coefficients for Cu and Fe are 0.01–0.1. If the uptake coefficient, in the presence of organic and inorganic species, is 0.09, i.e. the lowest value in this study, the values subtracted by 0.09 from measured γ may be attributed to free metal ions, such as Cu and Fe. Here we simply consider two extreme cases where either of Cu or Fe ions act as catalysts: In the case where the free Fe ions act as catalysts for HO₂, and Cu plays no role in HO₂ loss, 0.0002–1.2 % of total activity of Fe in the aerosol particles is sufficient to explain the γ values we measured. On the other hand, if the free Cu ions can act as catalysts for HO₂, but Fe plays no role, then 0.0001–0.8 % of total activity of Cu is sufficient. Actually, Cu and Fe could act together for the HO₂ loss in the particles (e.g. Mao et al., 2012). In this case, the levels of Fe and Cu sufficient to explain the γ values should be lower than those we calculated above. In rainwater, the fraction of free Cu²⁺ is reported to be similar, that being 0.01–0.3 % of total Cu concentration (Spokes et al., 1996). This suggests that only small fractions of Cu and Fe are present in their free forms within the particles. Therefore, it is inferred that the high γ values in this study may be attributed, in part, to reactive losses via free metal ions. It should be noted that the following factors could influence the result or give uncertainties. First, it is suggested that the solubility for Cu and Fe decreases with pH (Deguil-laume et al., 2005). In this study, the pH values of extracts for Mts. Tai and Mang were measured in ranges of 6.4–7.1 and 5.6–6.7, respectively. From the viewpoint of chemical composition, ammonium is abundantly present in the studied particles, achieving almost full neutralization. Based on these facts, here we study uptake of HO₂ onto neutral particles, for which the pH could be reproduced at least roughly in the laboratory. However, the uptake of HO₂ onto acidic particles might give different results due to higher solubility for Cu. Second, the sampled particle size range might have affected the determined coefficient. Our regenerated particles have trace metal concentrations averaged over the sampled size range and they are not weighted by the aerosol surface area size distribution. Thus it is important to examine if Cu concentration is dominant in submicron size range (Lannefors et al., 1983) or not. At Mt. Tai, Xu et al. (2009) suggested a relatively flat size distribution of Cu. For Mt. Mang, we made no size-segregated observations of trace metals. Hence this effect could be variable on the situation. We also examined the relationship between the γ values and relative abundance of each metal element normalized by the total mass concentration. However, the correlation of the measured uptake coefficients for each component to their relative abundance in each samples were low (R < 0.3). This may suggest that effective species for the HO₂ loss in the particles are varied in each sample.

For the losses of HO₂ by organics, Bedjianian (2005) reported the uptake coefficient of HO₂ for soot generated from a toluene/kerosene flame. The value was measured to be 0.081 ± 0.015 at room temperature, under low-pressure conditions, and using a discharge flow reactor coupled to a modulated molecular beam mass spectrometer. The uptake coefficient for HO₂ by soot was larger than those reported in the presence of dry inorganic compounds. The report suggests that the mechanism for heterogeneous HO₂ losses involves in either the reaction of a HO₂ radical with the H atom of a functional group, or the recombination of HO₂ radicals on the soot surface. Our previous study on the uptake coefficient of HO₂ with levoglucosan, which is recognized as a tracer of biomass burning (Schauer et al., 2001; Mochida and Kawamura, 2005), were < 0.01–0.13, depending largely on RH (Taketani et al., 2010). This suggests that the relative abundance of water in the particle is significant in controlling the rate of HO₂ loss. Furthermore, we measured the uptake coefficients of HO₂ with some dicarboxylic acid particles (succinic acid, glutaric acid, adipic acid and pimelic acid) at 30 % RH (dry particles) and 70 % RH (wet particles). These compounds are reported as important constituents of atmospheric organic aerosols (Kawamura and Yasui, 2005; Ho et al., 2011). Measured γ values ranged from 0.02–0.07 and 0.06–0.13 for 30 % and 70 % RH, respectively, suggesting potentially significant losses to carbonaceous compounds (Taketani et al., 2012b). These processes may also contribute to the observed HO₂ losses on the particles with ambient composition in this study.

Averaged γ values were estimated to be 0.23 ± 0.07 and 0.25 ± 0.09 for the aerosols collected at Mt. Mang and Mt. Tai sites, respectively, which are higher than that for (NH₄)₂SO₄. Therefore, it is recommended to employ an averaged value of γ = 0.24 for studying semi-urban/regional-scale air pollution, rather than the lower value found for a single composition (e.g. (NH₄)₂SO₄). The composition of the particles we employed in this study were only water-soluble ones; actual ambient particles also contain water-insoluble components. The effect of the water-insoluble compounds on the loss of HO₂ is currently unclear. However, the surface of ambient aerosol particles is likely wet at 75 % of RH (Pan et al., 2009; Martin, 2000) and therefore our approach to
determine overall $\gamma$ for the water-soluble species could give the current best estimate for the ambient aerosol particles.

### 4.3 Implications for atmospheric chemistry

The importance of the HO$_2$ uptake, determined for the ambient aerosol particles with multiple components, on HO$_2$ chemistry, ozone production, and particle aging is discussed in this subsection. In terms of the Mt. Tai results, Kanaya et al. (2009) used the averaged uptake coefficient of $0.25 \pm 0.09$ ($n = 10$), which we present here, to evaluate the impact on HO$_2$ concentrations and ozone production rates in a photochemical box model. Although the product suggested by Eqs. (7)–(10) included H$_2$O$_2$; Mao et al. (2012) proposed its consumption in the aqueous phase by a catalytic mechanism with Fe/Cu ions in the particles, recently. Therefore, we assumed that the reaction of HO$_2$ with aerosol does not have any gaseous products:

$$\text{HO}_2 + \text{aerosol} \rightarrow \text{no gas products.} \quad (14)$$

The first order decay rate $k_r$ of Eq. (14) is determined by the Fuchs-Sutugin equation (Fuchs and Sutugin, 1970):

$$k_r = \frac{4\pi D_r}{1 + K(r)} \left( \frac{1.333 + 0.71K(r)^{-1}}{1 + K(r)^{-1}} + \frac{4(1 - \gamma^2)}{3\gamma^2} \right) N(r) dr,$$

$$\quad (15)$$

where $r$ is the radius of the aerosol particle, $K(r)$ is the Knudsen number for the aerosol particle radius, $D$ is the gas-phase diffusion coefficient ($D$) of HO$_2$ as $\sim 0.25 \text{ cm}^2 \text{s}^{-1}$ and $N(r)$ is the number density distribution function of the aerosol. In that study, the maximum concentrations of OH, HO$_2$ and organic peroxy radicals (RO$_2$), with no heterogeneous losses of HO$_2$, were 0.20, 34 and 43 pptv, respectively, while those with heterogeneous HO$_2$ losses were 0.15, 20, and 39 pptv, respectively. Furthermore, the daily production of ozone decreased from 58 to 39 ppb, with the inclusion of heterogeneous HO$_2$ losses. On average, the net ozone production rate over the 6-hour daytime period decreased from 6.4 ppb h$^{-1}$ to 4.3 ppb h$^{-1}$. It is clear that heterogeneous HO$_2$ losses play a significant role.

As mentioned earlier, an airborne study of aerosol properties over Mexico, using a high-resolution time-of-flight aerosol mass spectrometer, revealed that the organic O/C ratio in the particles increased with increasing distance from the source area. This suggests that the particles have undergone photochemical aging. To achieve the high O/C ratio, addition of secondary organic aerosol (SOA) and/or the heterogeneous oxidation of aerosol particles would be required (DeCarlo et al., 2008). From their estimates, the number of oxygen atoms increases by $2.3 \times 10^7$ atoms per particle throughout the aging process over a 24 h period. However, heterogeneous uptake of OH was not fast enough to explain this increase. We propose that the heterogeneous uptake of HO$_2$ by aerosol particles may also help account for the high O/C ratios, if oxygen atoms from HO$_2$ are combined to the existing organic molecules, as suggested by Bedjanian (2005). The number of HO$_2$ molecules taken up by the particle surface, $c$, is estimated as:

$$c = a \frac{\gamma \omega}{4\pi d^2} \text{[HO}_2\text{]} \Delta t,$$

$$\quad (16)$$

where the correction factor for the diffusion limitation to mass transfer, $a = 0.9$; the particle diameter, $d = 230 \text{ nm}$; and the aging time, $\Delta t = 24 \text{ h}$. These parameters have been adapted from DeCarlo et al. (2008). Assuming the concentration of HO$_2$, the molecular speed of HO$_2$ ($\sigma$), and $\gamma$ to be $1 \times 10^8 \text{ molecule cm}^{-3}$, $440 \text{ m s}^{-1}$, and 0.24, respectively, and then Eq. (5) gives an uptake of $6.8 \times 10^7$ atoms of oxygen. Here we count two oxygen atoms per each HO$_2$ radical that undergo the heterogeneous reaction. If 10% of the oxygen atoms derived from the HO$_2$ radicals that are taken up by the particles remain in the particle phase and combine with the organics tentatively, the overall number of oxygen atoms gained by the particles would be $6.8 \times 10^6$ per particle. This number accounts for 30% of the required increase, suggesting that HO$_2$ uptake to the particles could potentially be contributing to the increase in the O/C ratio. Further experiments on the uptake of HO$_2$ by organics are needed to clarify the loss processes of HO$_2$ by the ambient aerosol particles.

### 5 Summary

We measured the overall uptake coefficients for HO$_2$ radicals with aerosol particles, which were regenerated from the water extracts of sampled particles collected at Mt. Tai and Mt. Mang, North China. The experiments, using an AFT coupled with a CC/LIF technique, were carried out at atmospheric pressure and, room temperature ($296 \pm 2 \text{ K}$), and at a RH of 75%. The initial HO$_2$ concentrations were $\sim 1 \times 10^8 \text{ molecules cm}^{-3}$, similar to ambient concentration levels. The measured uptake coefficients for Mt. Tai samples ranged between 0.09 and 0.40, while those at Mt. Mang were between 0.13 and 0.34. They were sometimes higher than those reported for single-component aerosol particles such as (NH$_4$)$_2$SO$_4$, NaCl, and levoglucosan. This suggests that minor components such as metal ions and organics can play a role in HO$_2$ loss. A few studies suggested that uptake coefficients of HO$_2$ radicals depend on temperature for aerosol particles with certain compositions (Thornton and Abbatt, 2005; Mao et al., 2010). Further experiments on the temperature dependence would be needed for better representation of this process in chemical transport models.

The averaged uptake coefficient was taken into account in a photochemical box model to assess the impact of the heterogeneous process. The results suggested that the uptake losses of HO$_2$ to aerosol particles can influence both HO$_x$ and ozone chemistry significantly. Furthermore, the HO$_2$...
uptake might contribute to the increase in the O/C ratios of the organic particles in the course of photochemical aging.

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