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Measurement of overall uptake coefficients for HO₂ radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang, China

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Abstract

HO₂ uptake coefficients for ambient aerosol particles, collected on quartz 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 HO₂ 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 the minor components such as metal ions and organics in the particle could contribute to the HO₂ uptake. A box model calculation suggested that the heterogeneous loss of HO₂ by ambient particles could significantly affect the 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 + HO₂) radicals are recently made, due to their importance in atmospheric chemistry. The HO₂ concentrations determined from these measurements were 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 presence of missing loss processes of HO₂. Heterogeneous reactions of HO₂ on the surface of aerosol particles may in part account for these missing processes. Atmospheric modelling calculations

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(Thornton et al., 2008; Martin et al., 2002; Macintyre and Evans, 2011) have suggested the potential importance of the heterogeneous reactions of HO₂ radicals with aerosol particles in the areas with high aerosol loading.

Using various techniques, kinetic studies for the heterogeneous reactions of HO₂ radicals with aerosol particles have been investigated by several groups (Hanson, 1992; Bedjanian et al., 2005; Remorov et al., 2002; Gershenzon et al., 1995; Mozurkewich et al., 1987; Thornton and Abbatt, 2005; Taketani et al., 2008, 2009, 2010). The HO₂ 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, 2010). These results indicate that particles in different phases have different HO₂ uptake coefficients, and the uptake coefficients change with the RH throughout the phase transformation. However, there are very few studies on HO₂ uptake coefficients by multiple-component particles. The heterogeneous loss of HO₂ on aqueous inorganic particles doped with CuSO₄ has been investigated previously (Thornton and Abbatt, 2005; Mozurkewich et al., 1987; Taketani et al., 2008). These studies revealed that the uptake coefficients of HO₂ by particles containing CuSO₄ were higher than those not containing CuSO₄. Some ions (e.g., Cu⁺ and Fe²⁺) can act as scavengers for the catalytic reaction of HO₂ (Jacob, 2000). In our previous study (Taketani et al., 2009), the HO₂ 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 implied that MgCl₂, 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 HO₂ radical uptake coefficients. Although the heterogeneous reactions of HO₂ radicals in field measurements are important, it is difficult to assess their actual contribution from directly observed parameters, as the uptake coefficient of the HO₂

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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 the particle composition (George et al., 2007; 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 demonstrated 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 HO₂ by the particles. However, it was difficult to assess this contribution because HO₂ 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 the laboratory experiments measuring the uptake coefficients of HO₂. We determined the overall HO₂ 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 the tropospheric chemistry.

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 an 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

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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 daytime. Between September 8 and October 5, 2007, we carried out sampling of particles with diameters of less than 2.5 μm (PM_{2.5}). 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 PM_{2.5} was performed during the daytime (9 h) or night-time (14 h). All PM_{2.5} samples were collected onto pre-baked (900 °C for 3 h) quartz filters (ϕ 110 mm) with a flow rate of 0.5 m³ min⁻¹, using a high-volume air sampler (SHIBATA HV-700F). To collect PM_{2.5}, 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.

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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 experiment.

5 2.2 Composition analysis for $\text{PM}_{2.5}$ 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 (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) 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 cm^2 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% O_2 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 cm^2 for filters from Mt. Tai, and 39 cm^2 from Mt. Mang) was cut into pieces and loaded particles were extracted with Milli Q water ($\sim 30\text{ ml}$) under ultra-sonication for 30 min. The extracts, including the water-soluble compounds, were passed through a membrane filter (pore diameter, $0.22\text{ }\mu\text{m}$) to remove any large particles and filter debris. Blank filters from each site were employed for background measurements.

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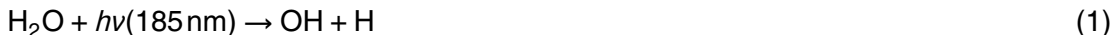
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3.2 Measurement of kinetic data

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 ($\phi = 12$ mm).



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 ($\phi = 60$ mm). The RH in the AFT was kept at 75 % by mixing the dry airflow with a flow of air, which 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 × 10⁵ to 5.7 × 10⁵ 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.

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HO₂ 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 HO₂ by chemical conversion via the reaction of HO₂ and NO to form OH radicals and NO₂. 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 HO₂ 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 HO₂ 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 [SO₄²⁻], [NO₃⁻], and [NH₄⁺] 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 [SO₄²⁻], [NO₃⁻], and [NH₄⁺] 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 HO₂ 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 HO₂ signal intensity is normalized against that at the initial injection position. In this study, HO₂ decays were found to be exponential and are consistent with first-order kinetics,

$$\frac{[\text{HO}_2]_t}{[\text{HO}_2]_0} = \exp(-k_{\text{obs}}t), \quad (3)$$

where [HO₂]₀ is the initial concentration of HO₂ radicals at the injector position, *t* is the reaction time that is estimated based on the injection position of HO₂ and flow velocity in the AFT, and *k*_{obs} is the effective first-order rate constant (s⁻¹) for the heterogeneous reaction of HO₂ with the aerosol particles. To estimate the background losses of HO₂, 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 HO₂ are plotted against the total surface concentrations of the regenerated particles from sample T1. The first-order rate constants (*k*_{obs}) were used to derive the uptake coefficients (*γ*_{obs}) after correcting for the wall losses and diffusion under non-plug conditions using the techniques of Brown (1978). *k*_{obs} is related to *γ*_{obs} by the following equation:

$$k_{\text{obs}} = \frac{\gamma_{\text{obs}} \varpi_{\text{HO}_2}}{4} S, \quad (4)$$

where *ϖ*_{HO₂} is the molecular thermal speed of HO₂ (cm s⁻¹), and *S* is the total surface concentration of aerosol (cm² cm⁻³). The *γ*_{obs} values were estimated from the observed first-order rate constants for HO₂ and are plotted against the total surface concentrations of aerosol. However, in deriving *γ*_{obs} from Eq. (4), the gas-phase diffusion has not been taken into account, but, using established methods (Fuchs and

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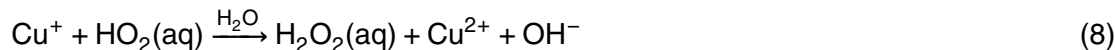
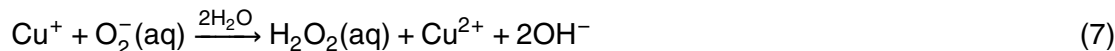
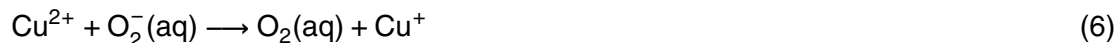
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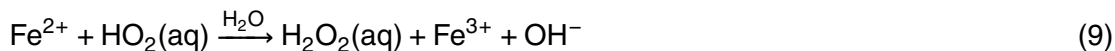


Sutugin, 1970; Fried et al. 1994), γ_{obs} can be modified to a corrected uptake coefficient γ . In this study, the correction was within 3% of the observed value. Values of γ are listed in Tables 2 and 3. Quoted errors are single standard deviations from a least-square fit, combined with the estimated 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 γ 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 HO_2 losses are attributed to the self-reaction of HO_2 in the aqueous phase, the uptake coefficient could be < 0.01 , under tropospheric conditions ($[\text{HO}_2] \sim 1 \times 10^8 \text{ molecules cm}^{-3}$), 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 HO_2 losses in the sampled particles.

It has been reported that some ions (e.g., Cu^+ and Fe^{2+}) can act as scavengers for the reaction of HO_2 (Jacob, 2000). Since the HO_2 radical can undergo acid dissociation in the aqueous phase ($\text{HO}_2(\text{aq}) \leftrightarrow \text{H}^+ + \text{O}_2^-$, $pK_{\text{eq}} \sim 4.7$), the following reaction processes can contribute to HO_2 loss:





The rate constants for Eqs. (5)–(10) are 1.0×10^8 , 8.0×10^9 , 1.5×10^9 , 9.4×10^9 , 1.2×10^6 , and $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Cabelli et al., 1987; von Piechowski et al., 1993; Jacob, 2000). 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 γ for the reaction on the aerosol particle is given by Hanson et al. (1992),

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4HRT\sqrt{D_l k_r}} \left(\coth q - \frac{1}{q} \right)^{-1}, \quad (11)$$

where α is the mass accommodation coefficient, H is the effective Henry's constant, R is the gas constant, T is temperature and D_l 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_r is the first-order rate constant for the reaction of HO_2 in the bulk aqueous phase, and q is the reacto-diffusive parameter, which is the ratio of particle radius r_s to the reacto-diffusive length l . This length (l) is a distance from the interface in which the reaction occurs, and is defined as $l = \sqrt{D_l/k_r}$ (Hanson et al., 1992). 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 $(\text{NH}_4)_2\text{SO}_4$ (Martin, 2000), which was the dominant species in the particles we sampled. Using $\alpha = 0.5$ and properties of $(\text{NH}_4)_2\text{SO}_4$ in Eq. (11), we

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estimated the uptake coefficients to be in the range of 0.495–0.497. These values are very close to the mass accommodation coefficient $\alpha = 0.5$, 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 HO_2 , it has been reported that dissolved Cu and/or Fe in particles actually exist as complexes with OH^- , SO_4^{2-} and other organic ions. These are less reactive compared to the free ions (Jacob, 2000; von Piechowski et al., 1993). 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. In the case where the free Fe ions act as scavengers for HO_2 , and Cu plays no role in HO_2 loss, a Fe level of 0.02–9% is sufficient to achieve the γ values we measured. On the other hand, if the free Cu ions can act as scavengers for HO_2 , but Fe plays no role, then a Cu level of 0.003–0.09% is sufficient. In rainwater, the fraction of free Cu^{2+} is reported to be similar, 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. 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 the each component to their relative abundance in each samples were low ($R < 0.3$). This may suggest that effective species for the HO_2 loss in the particles are varied in each sample.

For the losses of HO_2 by organics, Bedjanian (2005) reported the uptake coefficient of HO_2 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 HO_2 by soot was larger than those reported in the presence of dry inorganic compounds. The report suggests that the mechanism for heterogeneous HO_2

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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; and 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 $\gamma = 0.24$ 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 γ 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 HO₂ uptake, determined for the ambient aerosol particles with multiple components, on HO_x chemistry, ozone production, and particle aging

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is discussed in this subsection. In terms of the Mt. Tai results, Kanaya et al. (2009) used the averaged uptake coefficient of 0.25 ± 0.09 ($n = 10$), which we presented here, to evaluate the impact on HO_x concentrations and ozone production rates in a photochemical box model. 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 ppb to 39 ppb, with the inclusion of heterogeneous HO_2 losses. On average, the net ozone production rate over the 6-h 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 for 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 2.30×10^7 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:

$$c = a \frac{\gamma \omega}{4} \pi d^2 [\text{HO}_2] \Delta t, \quad (12)$$

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 (ω), and γ to be $1 \times 10^8 \text{ molecule cm}^{-3}$, 440 ms^{-1} , and 0.24,

respectively, and then Eq. (12) gives an uptake of 6.8×10^7 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, the overall number of oxygen atoms gained by the particles would be 6.8×10^6 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 $\sim 1 \times 10^8$ 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 $(\text{NH}_4)_2\text{SO}_4$, NaCl, and levoglucosan. This suggests that minor components such as metal ions and organics can play a role in HO_2 loss. 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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Table 1. Information of aerosol particle sampling sites.

	Location	Height	Date	Size of collected particles	Number of experimental samples
Mt. Tai	36° 26' N, 117° 11' E	1530 m	28 May to 28 Jun 2006	TSP	10
Mt. Mang	40° 15' N, 116° 17' E	170 m	8 Sep to 5 Oct 2007	PM _{2.5}	12

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Table 2. Concentrations ($\mu\text{g m}^{-3}$) of the measured components in sampled particles ($\text{PM}_{2.5}$) at Mt. Mang, together with measured uptake coefficients (γ) in this study.

	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
Start time	11 Sep 09:00	13 Sep 09:00	22 Sep 13:30	25 Sep 18:30	3 Oct 09:00	4 Oct 18:30	11 Sep 18:30	12 Sep 18:30	23 Sep 18:30	2 Oct 18:30	2 Oct 09:00	17 Sep 18:30
Sampling time	9 h	9 h	6 h	14 h	9 h	14 h	14 h	14 h	14 h	14 h	9 h	14 h
SO_4^{2-}	62.8	21.9	40.1	28.4	17.5	16.3	62.9	47.4	42.8	7.2	9.5	51.9
NO_3^-	23.9	9.1	7.3	15.7	19.2	23.6	19.7	2.9	14.0	9.6	2.3	20.4
Cl^-	0.22	0.31	0.24	0.36	0.05	0.22	0.51	0.08	0.26	0.05	0.00	0.46
NH_4^+	33.2	8.0	22.5	18.1	18.1	17.9	35.0	23.4	26.2	7.1	4.5	31.0
Na^+	0.78	0.11	0.53	0.38	0.32	0.29	0.75	0.43	0.55	0.17	0.17	0.31
K^+	3.73	0.36	2.74	1.86	1.48	1.04	2.91	1.84	2.58	1.24	0.96	0.99
Ca^{2+}	0.54	–	0.26	0.19	0.17	0.11	0.42	0.23	0.22	0.07	0.13	0.19
Mg^{2+}	0.15	–	0.08	0.07	0.05	0.03	0.13	0.07	0.08	0.03	0.04	0.05
Al	0.60	0.05	3.17	0.48	0.27	0.21	1.00	0.46	0.27	0.07	0.10	1.70
Cu	0.08	0.02	0.12	0.04	0.03	0.04	0.07	0.03	0.04	0.01	0.01	0.04
Fe	0.95	0.18	0.90	1.00	0.59	0.41	1.00	0.51	1.40	0.21	0.29	0.56
Mn	0.10	0.02	0.09	0.07	0.04	0.04	0.11	0.07	0.09	0.03	0.03	0.05
Pb	0.35	0.05	0.24	0.20	0.13	0.15	0.47	0.21	0.25	0.05	0.05	0.15
Zn	0.88	0.11	0.68	0.36	0.34	0.34	0.83	0.51	0.50	0.08	0.11	0.36
POM	19.7	4.7	10.5	14.7	12.4	21.8	21.3	11.8	14.7	6.0	5.4	13.6
γ	0.22 ± 0.06	0.32 ± 0.10	0.32 ± 0.15	0.18 ± 0.10	0.26 ± 0.09	0.15 ± 0.06	0.13 ± 0.06	0.16 ± 0.10	0.19 ± 0.08	0.27 ± 0.10	0.34 ± 0.09	0.17 ± 0.07

POM: particulate organic matter.

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Table 3. Concentrations ($\mu\text{g m}^{-3}$) of the measured components in sampled particles (TSP) at Mt. Tai, together with measured uptake coefficients (γ) in this study.

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Start time	6 Jun 06:04–	6 Jun 18:05–	7 Jun 06:05–	7 Jun 17:57–	8 Jun 06:00–	8 Jun 18:02–	9 Jun 06:06–	9 Jun 18:00–	10 Jun 06:02–	11 Jun 17:56–
Sampling time	12.0 h	11.9 h	11.8 h	12.0 h	11.9 h	12.1 h	11.9 h	12.0 h	35.9 h	12.4 h
SO_4^{2-}	68.0	50.0	76.1	37.3	5.7	7.7	5.9	5.4	11.4	20.7
NO_3^-	26.5	35.6	48.1	19.4	4.8	8.8	5.6	3.8	8.1	23.6
Cl^-	1.5	19.2	14.3	2.0	0.6	2.5	1.0	0.7	0.9	20.9
NH_4^+	23.6	22.5	31.1	15.6	3.2	5.2	3.2	2.3	4.9	14.6
Na^+	0.28	0.35	0.17	0.20	0.23	0.47	0.42	0.21	0.20	0.26
K^+	7.0	15.7	18.2	5.3	0.7	2.5	1.5	0.9	2.5	13.9
Ca^{2+}	8.1	9.1	4.8	4.0	4.9	9.4	11.0	6.2	6.7	13.2
Mg^{2+}	0.7	0.9	0.7	0.4	0.5	0.7	0.7	0.5	0.2	0.7
Al	–	27.8	–	29.2	–	5.7	19.6	4.8	11.9	9.1
Cu	0.05	0.08	0.06	0.03	0.01	0.04	0.02	0.04	0.02	0.02
Fe	3.0	4.0	1.7	3.5	5.9	11.6	11.5	5.7	3.2	5.9
Mn	0.09	0.12	0.06	0.07	0.17	0.31	0.30	0.14	0.08	0.13
Pb	0.22	0.22	0.12	0.09	0.04	0.12	0.05	0.05	0.06	0.09
Zn	0.22	–	0.07	0.05	–	–	–	–	0.03	–
POM	32.8	73.6	66.5	25.2	17.3	29.7	29.7	16.9	22.3	51.7
γ	0.31 ± 0.10	0.20 ± 0.04	0.37 ± 0.09	0.20 ± 0.04	0.25 ± 0.18	0.24 ± 0.05	0.40 ± 0.16	0.09 ± 0.07	0.19 ± 0.06	0.27 ± 0.04

POM: particulate organic matter.

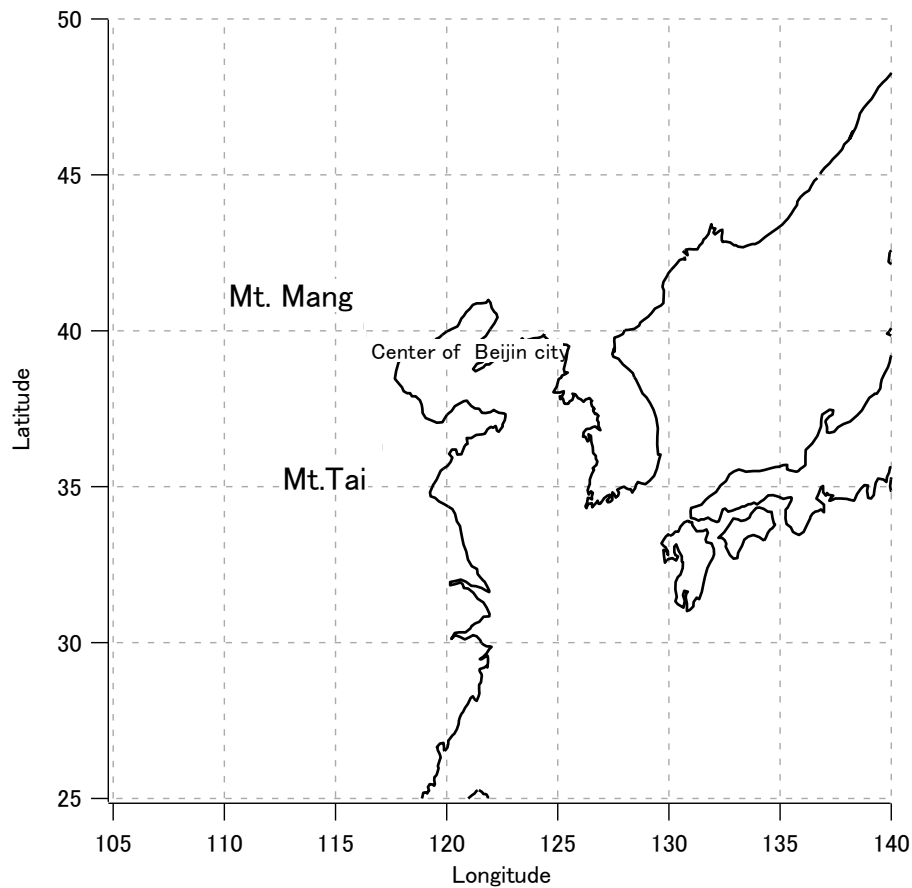


Fig. 1. Map of Eastern Asia with sampling sites of Mt. Tai and Mt. Mang in China.

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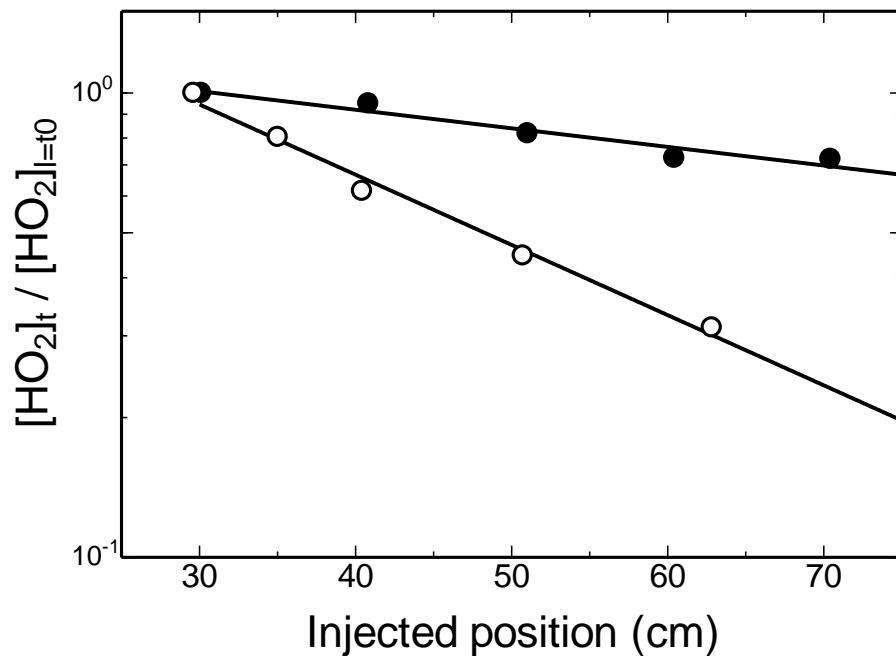


Fig. 2. Dependence of injector position (l) on HO_2 signals, at atmospheric pressure, using the T1 sample from Mt. Tai. Signal intensities are normalized against those at the initial injection position ($l_0 \sim 30$ cm). The filled circles indicate losses of HO_2 in the absence of aerosol particles. The open circles correspond to HO_2 profiles in the presence of aerosol particles, and the total surface concentration in this experiment was $0.49 \times 10^{-4} \text{ cm}^2 \text{ cm}^{-3}$ at 75 % RH. The fitting lines are exponential decay fits.

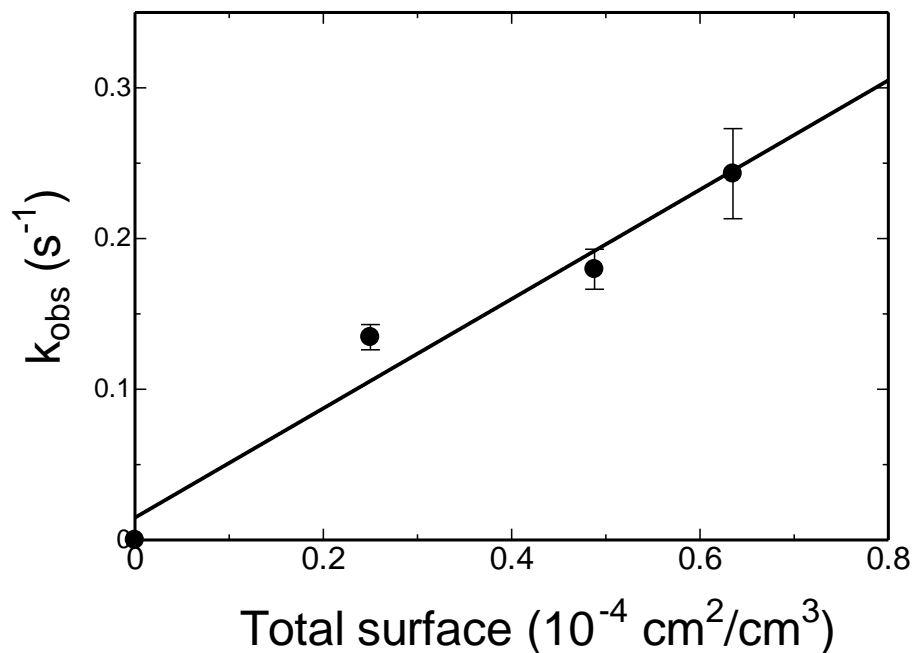


Fig. 3. Plots of first-order decay rates (k_{obs}) for HO_2 versus total surface concentrations of T1 particles at 75 % RH. The error bars are determined by combining the calculated uncertainties in the slopes from a least-square fit and the decay data, in both the absence and presence of aerosol particles.

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