Uptake coefficient of HO$_2$ onto deliquesced inorganic aerosols with and without transition metal ions

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The uptake of hydroperoxyl radicals onto aerosols potentially affect VOC oxidation, ozone formation, and SOA generation considering HO$_2$ as major OH reservoirs under atmospherically relevant conditions. Also, the uptake process changes the properties of aerosols such as size, oxidative capacity, and nucleation which will further impacts the climate. However, the uptake process is poorly understood since the detection of multiphase reactions remains challenging and most previous studies using aerosol flow tube combined with a radical detector and such approaches require manual controlling of the interaction time of radicals with aerosols and thereby is in low time resolution. This work combines a chemical conversion (CC) method with laser-pump and laser-induced fluorescence (LP-LIF) technique to detect the loss rate of HO$_2$ radicals onto deliquesced inorganic aerosols as OH reactivity (the inverse of OH lifetime). The detection process is shortened because we can detect the total aerosol surface area for uptake coefficient promptly, which also make it possible to test with various aerosols efficiently.

We jointly applied the CC/LP-LIF technique with an atomizer to detect the loss rate of HO$_2$ radicals due to aerosol uptake under high RH conditions. Polydisperse salt aerosols were produced from (1) NaCl, (2) (NH$_4$)$_2$SO$_4$, (3) Na$_2$SO$_4$, and (4) Seawater using a commercial constant output atomizer (TSI, model 3076). The 0.03% w/v reagent alone or contained with 0.0015% w/v additions (Cu(II), Fe(II) or L-ascorbate) were dissolved in ultrapure water to produce target aerosols. RH of the system is controlled by the dilution rate of wet zero-air, passing by a bubbler. The effective uptake coefficient can be calculated from the radical loss rate measured by LP-LIF, the mean molar velocity, and the total surface area of aerosols measured by scanning mobility particle sensor (TSI, model 3938). HO$_2$ was detected by converting into OH after reacting with NO. The detected loss rate of radicals can be explored by a single exponential fitting equation assuming pseudo-first order reactions. Gas phase diffusion effect was removed to estimate the real uptake coefficient. The determined gamma of reactive oxygen species onto aqueous aerosols made from different components were generally consistent with respective reported values. For the first time, gamma measured from Na$_2$SO$_4$ and two seawater samples have been reported in this study. The limit of detection (LOD) of this CC/LP-LIF method is decided by the uncertainty of HO$_2$ reactivity from zero-air measurement, which is around 0.1 s^{-1}. Considering the maximal total surface concentration of aerosols generated from atomizer is 7.5x10^{10} nm^{2}cm^{-3}, accordingly the detectable smallest gamma should be ~0.01. Note that the total surface concentration of aerosols depends on the RH and water content of aerosols, and lower RH enlarges LOD.

This study provides uptake coefficients onto NaCl/(NH$_4$)$_2$SO$_4$/Na$_2$SO$_4$/seawater sample detected with respect to 9 to 10 orders of magnitude of HO$_2$ concentration. For the first time, the established method reported gamma from seawater spray and enhancement effect was confirmed from ion-doping aerosols regardless of the inorganic aerosol type, with Cu(II) faster than Fe(II) in all cases. L-ascorbate is additionally dissolved in the deliquesced NaCl aerosols, from which gamma is smaller than Cu(II) but larger than Fe(II). Seawater samples showed quite big variations from two sites, and this may indicate the pH dependence considering one sample was buffered as pH=8.3. The enhancement effect of dissolved ions and discrepancy between seawater samples emphasizes the heterogeneous loss pathway of HO$_2$ in

the real atmosphere like marine areas. The result of this study can be embedded in model simulations for further oxidation evaluation.

Keywords: Heterogeneous loss, Multiphase reaction, LP-LIF

Fig. 1 Result of the uptake coefficient reported by this study.

solutions	RH	γ_{eff}	γ	reference
NaCl	82.1%	0.03 ± 0.01	0.03 ± 0.01	0.01 ± 0.02 (George et al., 2013); 0.10 ± 0.02 (Taketani et al., 2008)
NaCl + Cu(II)	74.4%	0.65 ± 0.17	0.72 ± 0.17	0.65 ± 0.17 (Taketani et al., 2008)
NaCl + Fe(II)	83.5%	0.27 ± 0.06	0.28 ± 0.06	
NaCl + L-ascorbic acid	82.4%	0.40 ± 0.15	0.46 ± 0.15	
$(NH_4)_2SO_4$	83.7%	~0.01	~0.01	0.004 ± 0.002 (Lakey et al., 2016); 0.01 ± 0.01 (George et al., 2013); 0.19 ± 0.04 (Taketani et al., 2008); ~0.1 (Thornton and Abbatt, 2005)
$(NH_4)_2SO_4$ + Cu(II)	85.6%	0.60 ± 0.19	0.67 ± 0.19	0.23 ± 0.07 (Lakey et al., 2015); 0.4 ± 0.3 (George et al., 2013); 0.53 ± 0.13 (Taketani et al., 2008); 0.5 ± 0.1 (Thornton and Abbatt, 2005)
$(NH_4)_2SO_4$ + Fe(II)	83.3%	0.25 ± 0.05	0.26 ± 0.05	
Na_2SO_4	83.6%	0.04 ± 0.00	0.04 ± 0.00	
Na_2SO_4 + Cu(II)	82.1%	0.49 ± 0.21	0.56 ± 0.21	
Na_2SO_4 + Fe(II)	83.3%	0.16 ± 0.02	0.17 ± 0.02	
Seawater (Izu)	82.2%	0.11 ± 0.01	0.12 ± 0.01	
Seawater (Hachijojima)	78.9%	0.22 ± 0.04	0.24 ± 0.04	

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