

Introduction

- The hydroxyl (OH) and hydroperoxyl (HO₂) radicals, together known as HO_x, play a vital role in atmospheric chemistry by controlling the oxidative capacity of the troposphere.
- HO₂ radicals determine the atmospheric lifetime and concentrations of many trace reactive species, such as NO_x, O₃ and volatile organic compounds (VOCs).
- Several recent field studies have observed significantly lower steady-state concentrations of HO₂ radicals than predicted using box models with heterogeneous loss onto aerosols being suggested as a loss mechanism (Sommariva, 2006; Kanaya, 2007).
- Yet relatively few laboratory studies have been performed to determine the kinetic parameters for HO₂ loss onto aerosols.

In this work, laboratory experiments were conducted to measure the heterogeneous HO₂ uptake kinetics onto submicron aerosol particles that are representative of tropospheric aerosols.

Experimental Methods

Particle Generation/Measurement:

- Salt particles were produced by atomizing dilute aqueous salt solutions.
- Stearic acid, oleic acid and squalane particles were produced by homogeneous nucleation.
- Particle size distributions were measured using a Scanning Mobility Particle Sizer (SMPS, TSI 3936).
- Mean number diameters ranged from approximately D = 70-100 nm and total number concentrations ranged from approximately N = 10⁴ – 10⁶ cm⁻³.

HO₂ Production/Detection:

- HO₂ radicals were produced from the photolysis of H₂O in presence of O₂ inside the injector.
- HO₂ radicals were chemically converted to OH in the detection cell using NO.
- OH radicals were detected using the FAGE technique by measuring their laser induced fluorescence at λ = 308 nm under low pressure (~0.7 torr).
- HO₂ concentrations were near atmospheric levels ([HO₂]~10⁸ – 2x10⁹ cm⁻³).

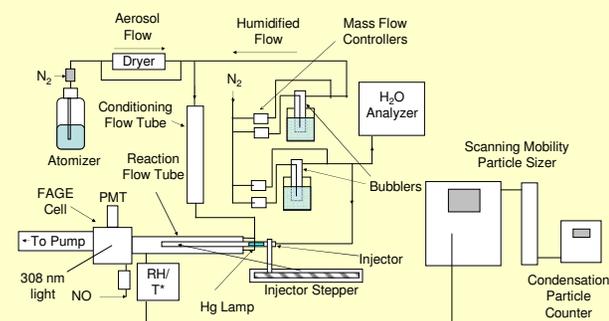


Figure 1. Experimental setup *RH = relative humidity; T = temperature

Kinetic Experiments:

- HO₂ uptake kinetics were observed by measuring the decay of the HO₂ LIF signal as a function of injector position.
- HO₂ uptake coefficients (γ^{HO₂}) were calculated from rate coefficients (k') using the equation above where v is HO₂ mean molecular speed (cm s⁻¹).
- For temperature experiments, jacketed flow tube was cooled with recirculating chiller.

$$k' = \frac{\gamma^{HO_2} v S}{4}$$

Results

Inorganic Salts:

- HO₂ uptake coefficients onto inorganic salt aerosols at room temperature (Table 1) were below the lower limit for dry salt particles (γ ≤ 0.002) and above detection yet quite slow for wet particles (γ = 0.002 – 0.006).
- Observed γ values in this study are much lower than previous studies, particularly for wet particles.
- Solution pH (pH 3.5-9.5) and flow tube relative humidity did not significantly impact γ^{HO₂} values of wet salt aerosols.

Table 1. Summary of γ^{HO₂} values for inorganic salts at room temperature.

Aerosol Composition	γ ^{HO₂}	
	Dry Aerosol	Wet Aerosol
Cu(II)-doped (NH₄)₂SO₄		
This work	-	0.28 (0.03)
Taketani et al., 2008	-	0.53 (0.13)
Thornton et al., 2005	-	0.5 (0.1)
(NH₄)₂SO₄		
This work	<0.002	0.003 (0.004)
Taketani et al., 2008	0.05 (0.02)	0.11-0.15 (0.03)
NH₄NO₃		
This work	-	0.005 (0.001)
NaCl		
This work	<0.001	0.016 (0.008)
Taketani et al., 2008	0.02 (0.01)	0.11 (0.03)
Remorov et al., 2002	0.012 (0.002)	-
Loukhovitskaya et al., 2009	0.0018 (0.0004)	-
Artificial Seawater		
This work	<0.001	0.006 (0.003)
Taketani et al., 2009	-	0.07-0.13 (0.04)
Loukhovitskaya et al., 2009	0.0023 (0.0005)	-
Natural Seawater		
This work	0.002 (0.001)	0.006 (0.003)

Cu(II)-, Fe(II)- and Fe(III)-doped aerosols

- Mass accommodation on Cu(II)-doped aerosol was α = 0.28(±0.03).
- HO₂ loss onto ammonium sulfate doped with Cu(II), Fe(II) and Fe(III) ions showed strong dependence on transition metal concentrations.
- HO₂ loss much faster for Cu(II)-doped than for Fe-doped aerosol, qualitatively consistent with condensed-phase kinetics

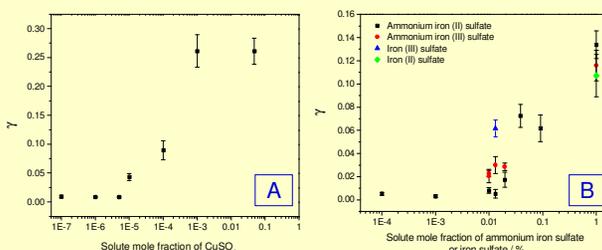


Figure 2. HO₂ uptake coefficients for A) Cu(II)-doped and B) Fe(II)- and Fe(III)-doped (NH₄)₂SO₄ aerosols at RH=60% and room temperature.

Organic Aerosols

- For hydrophobic organic particles (stearic acid, oleic acid and squalane), values were below detection (γ ≤ 0.002) and for wet particles (glutaric and malonic acids) were similar to inorganic salts (γ = 0.002 – 0.007).
- Aldrich humic acid was the major exception, exhibiting faster humidity dependent uptake kinetics, likely due to high concentrations of transition metal ions.

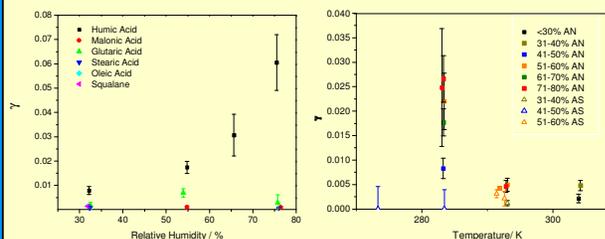


Figure 3. HO₂ uptake coefficients for organic aerosols as function of relative humidity.

Figure 4. HO₂ uptake coefficients for inorganic aerosols as function of temperature. AN=NH₄NO₃, AS=(NH₄)₂SO₄. Symbols are color-coded by relative humidity.

Temperature Dependence

- HO₂ uptake was enhanced at low temperatures (T = 10°C) for wet NH₄NO₃ aerosols, which may be humidity dependent.
- No uptake was observed on dry (NH₄)₂SO₄ aerosols for T = 0 – 20°C.

Conclusions

- Reactive uptake coefficients for HO₂ onto inorganic and organic aerosol particles have been measured under HO₂ concentrations that are close to atmospheric levels, which were significantly lower than literature values.
- Enhanced uptake onto aqueous aerosols compared to dry aerosols particles was observed for both inorganic and organic aerosols.
- Faster HO₂ uptake onto wet aerosols was observed at low temperature compared to room temperature values.
- Therefore, the importance of heterogeneous HO₂ loss onto aerosols on tropospheric HO_x budget will mostly depend on aerosol transition metal concentrations and aerosol phase.

Acknowledgements:

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References

- Kanaya et al., J. Geophys. Res., 112, D11308, 2007.
 Loukhovitskaya, E., Bedjanian, Y., Morozov, I., Le Bras, G., Phys. Chem. Chem. Phys., 11, 7896, 2009.
 Remorov, R.G., Gershenson, Y.M., Molina, L.T., Molina, M.J., J. Phys. Chem. A., 106, 4558, 2002.
 Sommariva et al., Atmos. Chem. Phys., 6, 1135, 2006.
 Taketani, F., Kanaya, Y., Akimoto, H., J. Phys. Chem. A., 112, 2370, 2008.
 Taketani, F., Kanaya, Y., Akimoto, H., Atmos. Env., 43, 1660, 2009.
 Thornton, J., Abbatt, J., J. Geophys. Res., 110, D08309, 2005.