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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).

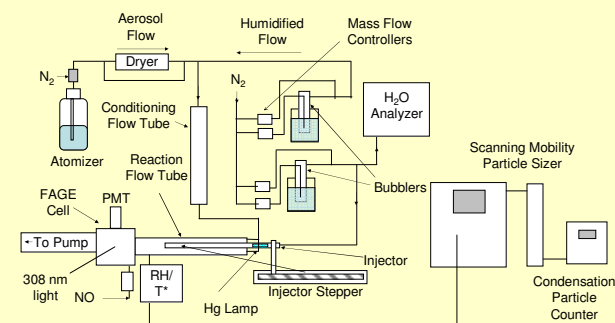


Figure 1. Experimental setup *RH = relative humidity; T = temperature

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

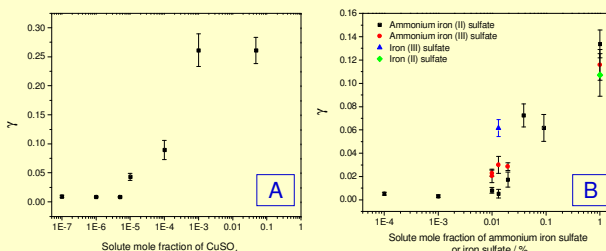


Figure 2. HO₂ uptake coefficients for A) Cu(II)-doped and B) Fe(II)- and Fe(III)-doped (NH₄)₂SO₄ aerosols at RH=60% and room temperature.

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.

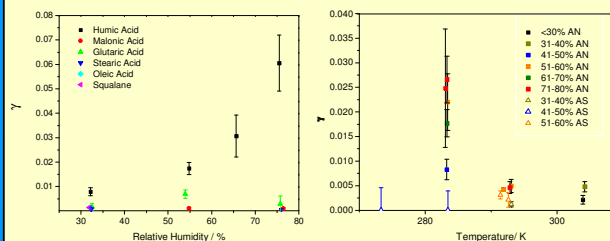


Figure 3. HO₂ uptake coefficients for organic aerosols as function of relative humidity.

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

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