

Introduction

The OH and HO₂ radicals, together known as HO_x radicals, play a vital role in determining the oxidizing capacity of the lower atmosphere. A detailed understanding of sources and sinks controlling HO_x levels is needed to accurately predict regional air quality and tropospheric O₃ production.

Modeling studies have shown that HO₂ uptake onto aerosols may be an important HO_x sink (Figure 1).^{1,2} Furthermore, field measurements of HO_x levels have suggested heterogeneous uptake onto aerosols with a reactive uptake coefficient of $\gamma = 0.1-1.0$ to explain the lower observed HO₂ levels than predicted steady-state concentrations with photochemical models.³⁻⁵

Despite the potential importance of HO₂ uptake onto aerosols on the tropospheric HO_x budget, the kinetics of this reaction and its dependence on atmospheric conditions and aerosol composition is not well understood. The objective of this laboratory study is to measure the reactive uptake coefficients of heterogeneous HO₂ uptake onto (NH₄)₂SO₄ and NaCl aerosol particles as proxies for atmospheric aerosols using Fluorescence Assay by Gas Expansion (FAGE) technique to quantify HO₂ concentrations.

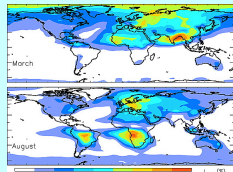
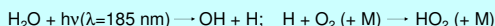


Figure 1. Modelled fractional HO₂ loss in lower troposphere due to HO₂ uptake onto aerosols ($\gamma = 0.2$).¹

Experimental

A schematic of the laboratory setup used to study HO₂ uptake kinetics onto aerosol particles is shown in Figure 2.

- Particle Generation/Measurement:** Wet salt particles were produced by atomizing aqueous solutions of 0.05 – 1% by mass (NH₄)₂SO₄ and NaCl, and 0.025% by mass CuSO₄·5H₂O for Cu(II)-doped aerosols. Aerosol flow was passed through a diffusion dryer (TSI 3062) to produce dry salt particles. Particle size distributions were measured using a Scanning Mobility Particle Sizer (SMPS: TSI 3080, 3081, 3775). 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 are produced from the photolysis of H₂O by passing a humidified flow over a mercury penray lamp located inside the stainless steel injector as follows:



HO₂ radicals were chemically converted to OH in the detection cell by reaction with NO (i.e. HO₂ + NO = OH + NO₂) and OH radicals were detected using the FAGE technique by measuring their laser induced fluorescence at $\lambda = 308 \text{ nm}$ under low pressure (~0.7 torr). HO₂ concentrations were near atmospheric levels and in the range of 10⁸ – 2x10⁹ cm⁻³.

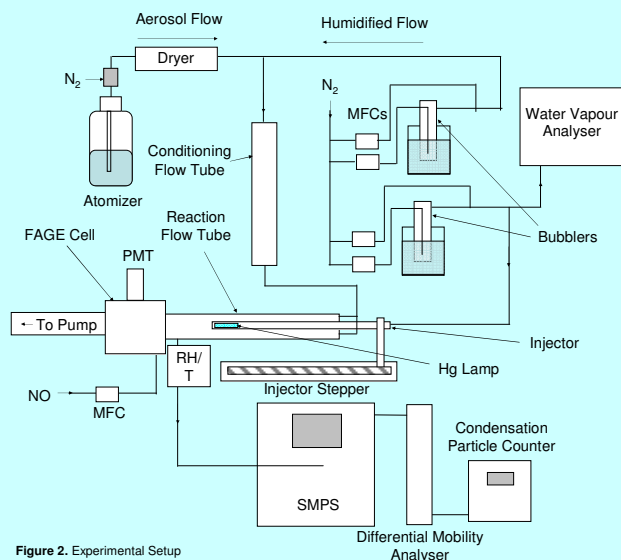


Figure 2. Experimental Setup

- Aerosol Reaction Flow Tube:** Aerosol flow and HO₂ flow from injector tip were introduced into the glass aerosol flow tube (100 cm length, 5.9 mm ID). The injector was moved back to increase reaction time between HO₂ and aerosol particles, and HO₂ uptake kinetics were observed by measuring the decay of the HO₂ LIF signal as a function of injector position. Experiments were conducted at room temperature and atmospheric pressure.

Results

The mass accommodation (α), or 'sticking coefficient', was determined by measuring HO₂ uptake onto Cu(II)-doped aqueous (NH₄)₂SO₄ particles as the Cu(II) quickly scavenges HO₂ in the aqueous phase with $\alpha^{\text{HO}_2} = 0.75 \pm 0.15$ calculated for the data shown in Figure 3.

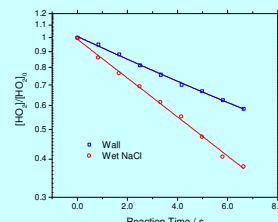


Figure 3. Flow corrected rate coefficients as a function of aerosol surface area for Cu(II)-doped AS particles (RH=43%)

Rate coefficients (k_{obs}) for HO₂ decay in the absence and presence of aerosol particles (Cu(II)-doped (NH₄)₂SO₄, wet and dry (NH₄)₂SO₄ and NaCl) were measured as a function of aerosol surface area. The k_{obs} for aerosol uptake were corrected for non-plug flow conditions (k'). HO₂ decay curves (Figure 4) display pseudo-first order kinetics.

$$k' = \frac{\gamma^{\text{HO}_2} v S}{4}$$

Reactive uptake coefficients for HO₂ onto aerosols (γ^{HO_2}) was calculated from the equation above, where v is HO₂ mean molecular speed (cm s⁻¹) and S is the aerosol surface area (cm² cm⁻³). γ^{HO_2} values obtained from this work are summarized in Table 1.

Table 1. Reactive uptake coefficient for HO₂ onto (NH₄)₂SO₄ and NaCl Salts at room temperature. Values in parentheses are error values.

Aerosol Composition	RH (%)	Aerosol Phase	HO ₂ HO ₂	Reference
Cu(II)-doped (NH ₄) ₂ SO ₄	43	wet	0.75 (0.15)	this work
	42	wet	0.5 (0.1)	[7]
	45	wet	0.53 (0.13)	[8]
(NH ₄) ₂ SO ₄	49	wet	0.08 (0.03)	this work
	42	wet	~0.1	[7]
	45	wet	0.11 (0.03)	[8]
	49	dry	<0.01	this work
NaCl	45	dry	0.05 (0.02)	[9]
	52	wet	0.15 (0.03)	this work
	53	wet	0.11 (0.03)	[9]
	50	dry	0.012 (0.003)	this work
	0	dry	0.012 (0.001)	[9]
	53	dry	0.02 (0.01)	[8]
	0	dry	1.8(0.36)x10 ⁻³	[10]

Conclusions

- Reactive uptake and mass accommodation (for Cu(II)-doped aerosol) coefficients for HO₂ uptake onto inorganic aerosol particles have been measured under HO₂ concentrations that are close to atmospheric levels, which are mostly consistent with literature values
- Significantly enhanced uptake onto aqueous aerosols compared to dry aerosols for (NH₄)₂SO₄ and NaCl particles was observed
- Therefore, the importance of heterogeneous HO₂ loss onto aerosols on tropospheric HO_x budget will strongly depend on factors that control aerosol phase, such as RH and aerosol composition

Acknowledgements:

Funding for this work was provided by NERC (#NE/F020651/1).

References

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