

Pascale Matthews¹ Ingrid George² Lisa Whalley^{1,3} Barbara Brooks^{3,4} Maria T. Baeza Romero⁵ Dwayne Heard^{1,3}

(1) School of Chemistry, University of Leeds, UK. (2) National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Durham, USA. (3) National Centre for Atmospheric Science, University of Leeds, UK. (4) School of Earth and Environment, University of Leeds, UK. (5) Escuela de Ingenieria Industrial de Toledo, Universidad de Castilla la Mancha, Spain.

Introduction

- It is important to be able to accurately predict HO_x (OH + HO₂) concentrations as HO₂ is responsible for the majority of the oxidation in the troposphere and can control the concentrations of many trace species in the atmosphere.
- Comparisons between field measurements and model calculations of radical concentrations are a measure of how well we understand the chemistry occurring in the atmosphere. In many previous studies models have overpredicted the concentration of HO₂ compared to the observed concentrations^{1,2}.
- HO₂ uptake onto aerosols has been suggested as a possible sink. However, halogen chemistry can explain the differences in some of the marine boundary layer studies¹.
- An uptake coefficient (γ) is defined as the probability that a molecule impacting the surface of an aerosol undergoes irreversible reaction and is the quantity measured in this work.
- There have been a few laboratory studies of HO₂ uptake by aerosols, however, the reported values have varied from γ = 0.005 to γ = 0.9³. Both first and second order uptakes have been reported in the literature. Therefore, it is unknown whether one or two molecules are involved in the rate determining step of the uptake process.

Experimental

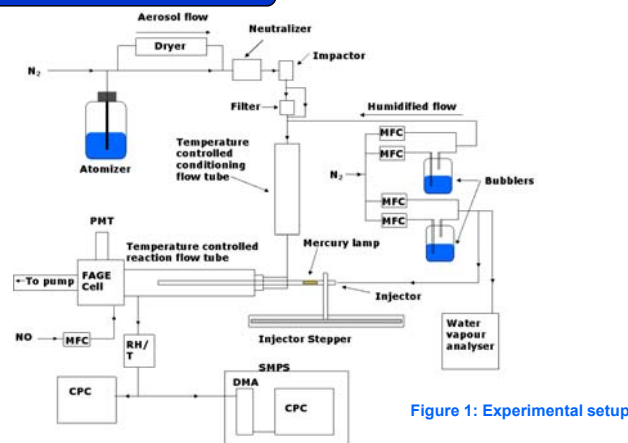


Figure 1: Experimental setup

- Checks using ozone profiles were carried out to ensure that the flows were well mixed. It was also determined that two neutralisers were required and that the impactor had to be placed before the flow tube in order to measure the correct aerosol surface areas.
- Experiments were performed using HO₂ at an initial concentration of 5 × 10⁸ – 1.5 × 10⁹ cm⁻³.
- Kinetics of the HO₂ heterogeneous loss were measured by moving the injector (which introduced the HO₂ into the flow tube) along the flow tube with and without aerosols. The kinetics were observed to be first order:

$$\ln[\text{HO}_2]_t = -k_{\text{obs}}t + c \text{ (Figure 2a)}$$
- By moving the injector backwards and forwards the contact time between the HO₂ radicals and the wall and / or aerosols could be changed.
- Aerosols were produced by an atomiser and their total surface area was measured using a Scanning Mobility Particle Sizer. (Figure 2b)
- The HO₂ concentration was measured by a Fluorescence Assay by Gas Expansion (FAGE)⁴ detection cell at the end of the flow tube.

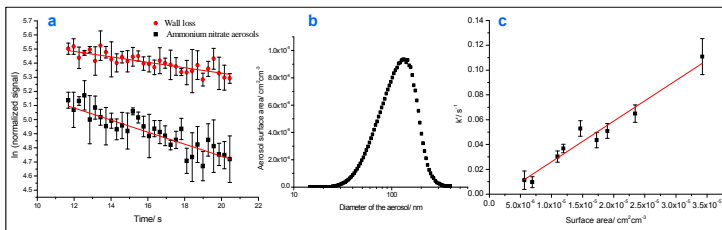


Figure 2: (a) Decay of HO₂ radicals in the absence and presence of aerosols. (b) Surface area distribution. (c) First order loss rate of HO₂ as a function of aerosol surface area for copper doped ammonium sulfate aerosols at 50% RH.

- The first order rate constant (k') is related to the uptake coefficient (γ_{obs}) by the equation:

$$k' = (\gamma_{\text{obs}} \omega_{\text{HO}_2} S) / 4$$
 where ω_{HO₂} is the molecular thermal speed of HO₂ and S is the total surface area of the aerosols. (Figure 2c)
- The uptake coefficient is then corrected for gas phase diffusion but changes the uptake coefficient by less than 1%.

Results

Inorganic Salts

Aerosol type	Uptake coefficient (γ)		Reference
	Dry aerosols	Wet aerosols	
Sodium chloride	0.000-0.001 (0.001)	0.003 (0.002)	This work
Sodium chloride	0.02 (0.01)	0.09-0.11 (0.03)	Taketani et al. (2008) ⁵
Sodium chloride	0.012 (0.002)	-	Remorov et al. (2002) ⁶
Sodium chloride	0.0018 (0.0004)	-	Loukhovitskaya et al. (2009) ⁷
Ammonium sulfate	0.000 (0.001)	0.002-0.004 (0.002)	This work
Ammonium sulfate	0.04-0.05 (0.02)	0.11-0.15 (0.03)	Taketani et al. (2008) ⁵
Ammonium nitrate	-	0.005 (0.002)	This work

- The measured HO₂ uptake coefficients in this work are smaller than the uptake coefficients which have been measured in previous studies. We postulate that the differences are due to the HO₂ concentrations used and/ or a time dependence (as discussed below) or other experimental reasons.
- The uptake coefficient for dry aerosols is smaller than that for wet aerosols as the aqueous chemistry cannot happen.

Copper and iron doped aerosols

- The mass accommodation (the fraction of the HO₂ molecules which stick to the surface out of the total number of collisions) was measured to be 0.28 ± 0.05.
- The uptake of HO₂ onto ammonium sulfate doped with Cu(II), Fe(II) and Fe(III) showed a strong dependence on the transition metal concentrations. However, the uptake was faster for the copper doped aerosols (approximately a factor of 2). Metals act as a catalyst to convert HO₂ into H₂O₂ and O₂.

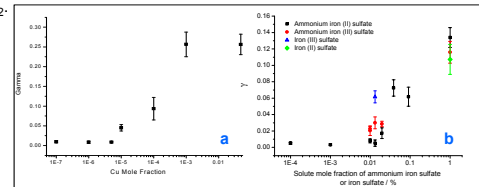


Figure 3: HO₂ uptake coefficients for (a) Cu(II)-doped and (b) Fe(II)- and Fe(III)-doped ammonium sulfate aerosols at RH=60% and room temperature.

The pH dependence

- The uptake coefficient was measured for sodium chloride and buffered ammonium sulfate (the atomiser solutions were pH 3.5 to pH 8.5).

- No pH dependence was observed. The uptake coefficients were γ = 0.005 ± 0.003.

Organics

- The uptake coefficient of humic acid, malonic acid, glutaric acid, stearic acid oleic acid and squalene were measured over a range of humidities (30% - 75%).
- For hydrophobic organic aerosols (stearic acid, oleic acid and squalene), the uptake coefficients were (≤ 0.002) and for wet aerosols (glutaric and malonic acid) the uptake coefficients were similar to inorganic salts (0.002 – 0.007).
- Humic acid (Aldrich) showed a humidity dependent uptake between 30% RH and 75% RH of 0.008 - 0.060. However, the humic acid was found to contain elevated concentrations of copper and iron. Further studies for organic aerosols are planned.

The time and HO₂ concentration dependence

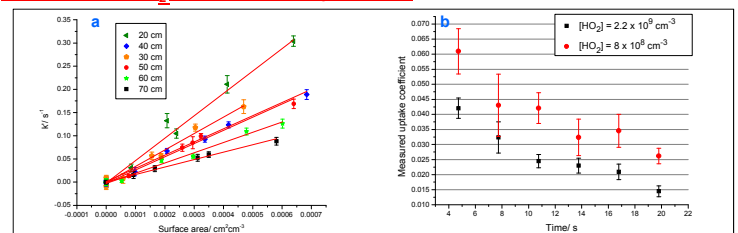


Figure 4: Fixed injector experiments. (a) Rate constants against surface area. (b) Measured uptake coefficients at different times.

- To check for a time dependence, fixed injector experiments were performed. The injector was placed in one position and the aerosol concentration was changed. The process was then repeated in a different position. The measured uptake is a cumulative uptake (it takes into account all of the uptake up to that point).

- There appears to be a fast initial uptake followed by a slower uptake representative of an equilibrated aerosol. There also seems to be a HO₂ concentration dependence. Aerosol modelling will be done to understand these dependencies.

The temperature dependence

- Initial experiments were done between 273 K and 313 K. A slight temperature dependence was measured (γ ≈ 0.01 at 273 K, γ ≈ 0.005 at 313 K).

Conclusions

- The uptake coefficient is small (< 0.01) for inorganic salts, organic aerosols and over a range of pHs except when doped with copper or iron. The uptake coefficient is smaller for dry aerosols than for wet aerosols as aqueous chemistry cannot occur. The small uptake coefficient values means that heterogeneous loss of HO₂ may be less important than previously thought for some environments.
- There is a time dependence, a HO₂ dependence and possibly a small temperature dependence.

Acknowledgements and References

We wish to thank the Natural Environment Research Council for funding this work (grant number NE/F020651/1).

References: 1. Sommariva et al. Atmos. Chem. Phys. 6, 1135-1153 (2006) 2. Kanaya et al. J. Geophys. Res.-Atmos. 105, 24205-24222 (2007) 3. Mao et al. Atmos. Chem. Phys. 10, 5823-5838 (2010) 4. Heard et al. Annual Rev. Of Phys. Chem. 57 191-216 (2006) 5. Taketani et al. J. Phys. Chem. 112, 2370-2377 (2008) 6. Remorov et al. J. Phys. Chem. 106, 4558-4565 (2002) 7. Loukhovitskaya et al. Phys. Chem. Chem. Phys. 11, 7896-7905 (2009)