Heterogeneous Uptake of HO\textsubscript{2} Radicals onto Submicron Atmospheric Aerosols

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Field measurement studies have reported significantly lower HO\textsubscript{2} radical concentrations than calculated by constrained box models using detailed chemical mechanisms. Although in some cases for the marine boundary layer (MBL) part of the discrepancy has now been attributed to the influence of halogen chemistry (1,2), uptake of HO\textsubscript{2} by aerosols is postulated as a loss mechanism, for example in the MBL (2) the Arctic troposphere (3) and the upper troposphere (4). However, there have been very few laboratory studies on HO\textsubscript{2} uptake by aerosols and the rates and mechanism of the HO\textsubscript{2} loss by aerosols are still uncertain.

The HO\textsubscript{2} uptake coefficients for a range of inorganic and organic aerosols have been measured at room temperature and atmospheric pressure using an aerosol flow tube combined to a Fluorescence Assay by Gas Expansion (FAGE) detector. The sensitive FAGE method enables low concentrations ($10^8-10^9$ molecule cm\textsuperscript{-3}) of HO\textsubscript{2} to be injected into the aerosol flow tube using a moveable injector, and position dependent decay profiles of HO\textsubscript{2} are recorded as a function of aerosol surface area. The aerosols were generated using an atomiser or by using homogeneous nucleation, and the particle size and number distributions were measured with a Scanning Mobility Particle Sizer.

The HO\textsubscript{2} uptake coefficient ($\gamma$) was measured for dry inorganic aerosols ($\gamma=0.000-0.001$), wet inorganic aerosols ($\gamma=0.002-0.005$), wet copper doped ammonium sulfate aerosols ($\gamma=0.28$, Figure 1) and ammonium sulfate aerosols doped with different molar amounts of iron ($\gamma=0.003-0.06$). The pH dependence of the HO\textsubscript{2} uptake coefficient was also investigated, however, no dependence was observed. The HO\textsubscript{2} uptake coefficients onto a range of both wet and dry organic aerosols were found to be small ($\gamma<0.008$) with the exception of humic acid aerosols which had a larger uptake coefficient that was also dependent on relative humidity ($\gamma=0.008-0.13$). However, humic acid was found to contain metals, which may explain the higher uptake coefficient. HO\textsubscript{2} uptake coefficients are currently being measured at low temperature for a range of aerosols.

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References


Figure 1. HO\textsubscript{2} uptake onto Cu doped (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} aerosols at RH = 53%, giving $\gamma = 0.28 \pm 0.05$. 