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OH and HO_2 chemistry in clean marine air during SOAPEX-2

R. Sommariva[1], A.-L. Haggerstone[2], L. J. Carpenter[2], N. Carslaw[3], D. J. Creasey[1,*], D. E. Heard[1], J. D. Lee[1,**], A. C. Lewis[1,**], M. J. Pilling[1], and J. Zádor[4]

[1]Department of Chemistry, University of Leeds, Leeds, UK
[2]Department of Chemistry, University of York, York, UK
[3]Environment Department, University of York, York, UK
[4]Department of Physical Chemistry, Ëotvös University (ELTE), Budapest, Hungary
[*]Now at Photonic Solutions plc., Gracemount Business Pavilions Unit A2/A3, 40 Captains Rd., Edinburgh, UK
[**]Now at Department of Chemistry, University of York, York, UK

Abstract. Model-measurement comparisons of HO_x in extremely clean air ([NO]<3 ppt) are reported. Measurements were made during the second Southern Ocean Photochemistry Experiment (SOAPEX-2), held in austral summer 1999 at the Cape Grim Baseline Air Pollution Station in north-western Tasmania, Australia.

The free-radical chemistry was studied using a zero-dimensional box-model based upon the Master Chemical Mechanism (MCM). Two versions of the model were used, with different levels of chemical complexity, to explore the role of hydrocarbons upon free-radical budgets under very clean conditions. The "detailed" model was constrained to measurements of CO, CH_4 and 17 NMHCs, while the "simple" model contained only the CO and CH_4 oxidation mechanisms, together with inorganic chemistry. The OH and HO_2 (HO_x) concentrations predicted by the two models agreed to within 5–10%.

The model results were compared with the HO_x concentrations measured by the FAGE (Fluorescence Assay by Gas Expansion) technique during four days of clean Southern Ocean marine boundary layer (MBL) air. The models overestimated OH concentrations by about 10% on two days and about 20% on the other two days. HO_2 concentrations were measured during two of these days and the models overestimated the measured concentrations by about 40%. Better agreement with measured HO_2 was observed by using data from several MBL aerosol measurements to estimate the aerosol surface area and by increasing the HO_2 uptake coefficient to unity. This reduced the modelled HO_2 overestimate by ~40%, with little effect on OH, because of the poor HO_2 to OH conversion at the low ambient NO_x concentrations.

Local sensitivity analysis and Morris One-At-A-Time analysis were performed on the "simple" model, and showed the importance of reliable measurements of $j(O^1D)$ and [HCHO] and of the kinetic parameters that determine the efficiency of $O(^1D)$ to OH and HCHO to HO_2 conversion. A 2σ standard deviation of 30–40% for OH and 25–30% for HO_2 was estimated

for the model calculations using a Monte Carlo technique coupled with Latin Hypercube Sampling (LHS).

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