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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous oxidation of saturated organic aerosols by hydroxyl radicals:Uptake kinetics and condensed-phase products" *by* I. J. George et al.

Anonymous Referee #2

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General Comments:

This manuscript describes laboratory studies of the heterogeneous oxidation of saturated hydrocarbon particles by OH radicals in the absence of NOx. The experiments serve as models for the oxidative aging of primary organic aerosol particles. The reactions were performed in a flow-tube reactor and changes in aerosol composition were monitored in real time with an Aerodyne AMS and off-line using electrospray mass spectrometry, and an SMPS was used to monitor particle size.

The measured reactive uptake coefficient for OH radicals was close to unity, consistent with previous studies, and the major reaction products were multifunctional compounds

containing hydroxyl and carbonyl groups. Volatile products appeared to be relatively minor. It is expected that in the atmosphere primary organic aerosol particles will become more oxidized via these reactions, and that this will enhance their hygroscopicity.

The experiments were carefully performed, the kinetics and product analyses were straightforward and convincing, and the data interpretation seems reasonable. The study is an important one because in spite of the potential atmospheric importance of OH radical oxidation of organic aerosols, there are considerable disagreements in the literature regarding the products and mechanisms of these reactions. This study therefore adds valuable new results and insights regarding this chemistry. The paper is well written and the figures, tables, and references are appropriate. I think the paper is certainly suitable for publication in Atmospheric Chemistry and Physics. I have a few comments that should be addressed.

Specific Comments:

1. Page 6820, lines 14-16: Do the authors mean that hydroperoxides are unstable in the particles (probably not true) or during MS analysis?

2. Page 6825, line 4-: The lifetime calculation presented here indicates that in about 2.6 days each molecule in the particle will react with one OH radical. If one is interested in understanding the lifetimes of specific particulate organic compounds (e.g., molecular tracers) or particle toxicity (reaction products could be more toxic than the parent compound), this calculation shows that heterogeneous oxidation could be important. If one is interested in particle hygroscopicity, however, the calculation suggests that heterogeneous oxidation is probably not very important. In this calculation, molecules are assumed to have a molecular weight of 300, which corresponds to a C22 hydrocarbon. In 2.6 days, one functional group is added to each molecule. A molecule with 22 CH2 units and one hydroxyl or carbonyl group is probably still quite nonpolar and hydrophobic. The degree of oxidation of these particles even after a week or so in the atmosphere (O:C ratio = 3:22) is therefore much less than SOA, which from ambient

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AMS measurements typically has a O:C ratio of about 1:2.

The authors are referred to the recent paper by Petters et al. Geophys. Res. Lett. 33, L24806 (2006), which concludes that heterogeneous oxidation is unlikely to compete with other processes (such as addition of hydrophilic components by condensation and coagulation) for converting primary organic aerosol particles from hydrophobic to hydrophilic.

Technical Comments:

1. Page 6805, lines 23-25: The recent study by Lambe et al. Environ. Sci. Technol., 41, 2357-2363 (2007) could be added to the list of heterogeneous OH reaction references.

2. Page 6820, line 3: Sentence should read: The alkoxy radical (RO)

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6803, 2007.