Atmos. Chem. Phys. Discuss., 7, S2146–S2149, 2007
www.atmos-chem-phys-discuss.net/7/S2146/2007/

Atmospheric
Chemistry
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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 #3

Received and published: 29 May 2007

Overview

This paper describes laboratory experiments examining the oxidation of single-component Bis(2-ethylhexyl) sebacate (BES) aerosol particles by the hydroxyl radical. An Aerodyne Aerosol-TOF-MS was used to monitor the decay of a signal representative of BES upon exposure to OH. The latter was generated using UV radiation, O3, and H2O. A thorough analysis of the kinetics, products, and aerosol particle size/density changes is presented. The topic is highly relevant to ACP, and the manuscript contains significant new contributions and is very well written. I highly recommend publication and I have only a few minor comments that the authors might wish to address.

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Comments

1. An overall uncertainty of +/- 30% error is quoted at the end of section 3.1, and I suggest this value should be listed in the abstract, not the error derived from standard deviation, because potential systematic errors likely dominate the uncertainty. Is it fair to assume the uncertainty in the OH concentrations in the reaction vessel alone is ˜ 30% given that those inferred from SO2 oxidation were within +/-30% of the model predicted values? In addition I would think that undetected fluctuations in lamp output could also affect inferred OH concentrations given that the SO2 oxidation was done separately. Can the authors briefly expand on their reasoning for the ultimate experimental uncertainty given?

2. The kinetics were determined by monitoring m/z 297 in the TOF-MS spectra. Given the nature of the ionization used, how likely is it that products resulting from OH oxidation gave rise to some signal at this m/z? The authors state that this signal showed the steepest drop upon oxidation compared to all other signals identified in unreacted particle spectra, but interferences could arise during reaction, correct (Of course, this would imply a higher gamma and thus secondary chemistry)? On a related issue, is it possible to derive BES oxidation kinetics from the ESI-MS analysis of filter-collected particles? Perhaps this was discussed and I missed it, but it would provide some validation of the kinetics obtained with the A-TOF-MS.

3. Can the authors comment on the possibility of particle size changes due to increased water uptake after oxidation? It appears from the experimental and figure 1 that the RH in the aerosol flow tube was $>$30% such that without subsequent drying, the second SMPS (after oxidation) would provide a measurement at RH$>$30%. The first size measurement however was always RH ˜ 0. Does the ozone denuder also scrub water vapor such that only dry mass is being obtained with the second SMPS or were experiments conducted where a drier was put in place before the second SMPS?

4. I think RO radicals are referred to as “alkoxy” radicals, not “alkyl” radicals as used in

the manuscript.

5. In regards to section 3.4 and the discussion of the reaction mechanism, I suggest the authors label each pathway in figure 10 with a number instead of using only descriptions like “carbonyl + alcohol” given that more than one of the pathways yield either one or both.

6. The authors state that the high OH, NOx-free conditions used may lead to an enhancement of the RO2-self reaction channel that produces carbonyls and alcohols over the self reaction that leads to the RO radical. I don’t see the reasoning here aside from the possibility that with high OH and no NOx the steady-state RO2 concentration will be higher. Would the product yields from this reaction depend on the reactant concentration?

7. It is my recollection that the Kwan 2006 paper assumed the Molina, et al yields of VOC from heterogeneous OH oxidation and from these determined particle volatilization was a potentially important source in the upper troposphere. The authors could note here that their measurements suggest aerosol oxidation is a less important source than Kwan et al calculate. As it is now, the readers of this manuscript would need to have read Kwan 2006 to reflect on what the present manuscript implies.

8. Along the lines of comment 7, should a phrase "implications for volatilization of aerosol mass" be added to the title?

9. It might be worth referencing a few other papers in this area. Field observations have shown significant levels of peroxide moeities in aerosols (above Henry’s law partitioning of H_2O_2). I’m thinking of papers by Hasson and Paulson Journal of Aerosol Science 2003. It is possible that this pathway is important although SOA formation may be the source of such peroxides. Lambe, et al ES&T 2007 41(7) report an OH reaction probability for hexacosane particles in a smog chamber using a different OH source but a similar detection method.

10. A few of us still print out manuscripts in black and white. Can the format of the colored lines be changed to appear differently when printed out in black and white?

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

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