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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.

I. J. George et al.

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We thank Referee #3 for helpful comments regarding the manuscript. We will reply to each point individually:

1. We reported an overall experimental error of 30%. This is an overall estimate including the deviations in modeled OH concentrations from measured values (average deviation 13%, maximum 24%) and the precision of the m/z 297 signal in the absence of OH (5%). We agree with the referee and will reflect this error in our reported error for the initial uptake coefficient. It is possible that the UV lamp may fluctuate from day to day. We have performed the OH calibration over several days and found that the data generally agree from day to day within 15% under similar experimental conditions, i.e.,

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O3 concentrations and relative humidity. The systematic variabilities in OH concentration, though not captured by the photochemical model, should be apparent in the spread of the kinetic data.

2. We monitored the m/z 297 fragment as a proxy for BES oxidation for the following reasons: 1) it is a characteristic fragment of BES, 2) it had the fastest decay kinetics of all characteristic fragments monitored, 3) the overall kinetic loss rate constant for m/z 297 was within 20% of the average rate constant for formation of the three intense product fragments. We mentioned in reply to a short comment from S. Trakhtenberg above that m/z 297 could be a minor product fragment. The BES oxidation kinetics could be monitored offline using electrospray ionization mass spectrometry. We have not developed an analytical methodology to measure BES quantitatively using ESI-MS, but it is possible. We will consider this option for future work.

3. We do not expect significant size changes due to hygroscopic growth for reacted or unreacted BES particles. For the volume change experiments, we compare size distributions of reacted BES particles under the same flow tube RH conditions as unreacted particles. We have measured particle size distributions before and after passing the unreacted BES particles through the humidified aerosol flow tube and found no significant change (<5%) in particle size. We have also measured the size distribution of oxidized particles at RH = 35 % and OH exposure of 3Œ10-8 atm-s and found less than 1% change in mean diameter as compared to size distribution of particles passed through a diffusion dryer. The ozone denuder does partially dry the flow, leaving the flow passing to the second DMA with an RH of 25% or less. Thus, for conditions of this experiment, the change in volume due to hygroscopic growth is considered to be negligible. According to Petters and Kreidenweis (2007) the measured growth factors for oxidized BES were below detection, thus confirming our assumption.

4. We will make necessary corrections.

5. We will change Figure 10 and text as suggested and refer to reaction pathways with

labeled numbers.

6. It is unclear how the branching ratios of the RO2 self-reactions leading either to carbonyl + alcohol or formation of RO depend on the steady-state RO2 concentration. However, our thinking was that the rate of this reaction may be quadratic in RO2 concentration, thus enhancing the probability that it will occur relative to the formation of RO. Of course, this also depends on the dependence on the RO2 concentration of the formation rate of RO as well. It is unlikely that the product yields will depend on concentration.

7. We will clarify this point in the text.

8. We will alter the title to include mention of "Particle Size Change".

9. We have added the Lambe et al. (2007) paper to the references, but not the Hasson and Paulson (2003) paper, given that it is not clear whether peroxides are formed in heterogeneous oxidation reactions or not.

10. We will alter the figures accordingly.

References:

Petters M. D. and Kreidenweis S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys. 7, 1961-1971, 2007.

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

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