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

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I am writing because I believe that our recent work on the reaction of bis-(2-ethylhexyl) sebacate, BES (also called dioctyl sebacate, DOS) with Cl radicals in the presence of O_2 (Hearn et al., Physical Chemistry Chemical Physics, in press, DOI: 10.1039/b707523e) has some bearing on the discussion of this paper. In particular, the reactions occurring after the initial H-abstraction by either OH or Cl are expected to be the same; namely, peroxy radicals (RO_2) will be formed quickly in the presence of a large concentration of O_2. Thus, much of what we and George et al. observe is the result of RO_2 reactions. One considerable difference between our two studies is

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that we used Aerosol CIMS (chemical ionization mass spectrometry) to characterize the composition of the particles whereas George et al. have used an AMS (aerosol mass spectrometer).

Much of what we observe is in agreement with the work of George et al. Namely, we find: 1) no decrease in particle volume until 60% of the DOS has reacted, 2) the primary identified products are the ketone and alcohol, 3) a DOS-based uptake coefficient, γ_{DOS}, larger than unity.

Below, I mention some of our other findings, how they relate to the work of George et al. and what they indicate about the mechanism of radical-initiated oxidation of DOS.

1. Product yields.

We find that the ketone yield varies with O_2 concentration (from 21% at 0.1% O_2 to 38% at 20% O_2) while the alcohol yield does not (constant at 14%). The O_2 dependence provides evidence that the RO + O_2 -> ketone + HO_2 reaction is important and is responsible for almost half of the ketone generation (at 20% O_2). While common in the gas phase, this reaction has not generally been indicated to be important in condensed phases.

The O_2 dependence is fit well with a Langmuir-Hinshelwood type of expression indicating a surface reaction to create the ketone. Furthermore, this reaction demonstrates that RO radicals must be created with relatively high yields, as was pointed out by Ivanov in his comment to this paper. This is in contrast to the claim of George et al. "that the RO_2 self-reaction leads predominately to the carbonyl + alcohol channel." (page 6820).

All of our observed product peaks account for 86% of the DOS that reacts. Each one of these peaks is only detected in the particles and not in the gas phase.

I would like to point out that our ESI (electrospray ionization) mass spectra appear to be very similar to those of George et al. In particular, we find that the ketone product peak is approximately 4x larger than the alcohol product peak, just as they report. However, the relative yields of these products cannot be inferred from the relative peak intensities because the ionization efficiencies for the products may not be identical. Thus, George et al. should be careful in interpreting the intensity of the m/z = 463.3387 peak as representing "the most abundant peak" (page 6821). Nonetheless, it is the most abundant peak/product (38% yield) in our Aerosol CIMS spectra.

2. Volatile products

We do not detect any aldehydes (< 0.3% yield) in the gas phase or in the particles. Such aldehydes would be expected if the β-scission of the RO radicals was a significant fate.

We do, however, detect gas-phase H_2O_2 from the reaction of a DOS film which indicates that the RO_2 + RO_2 -> ketone + ketone + H_2O_2 reaction (the so-called Bennett & Summers mechanism) is active. The H_2O_2 was not detected from the reaction of the particles, so we could not measure its branching ratio.

3. Kinetics

We measure an uptake coefficient from the rate of loss of DOS of γ_{DOS} = 1.7. George et al. measure a value of 1.26. Both they and we have interpreted these values, which are greater than unity, to mean that there may be other reactions (other than with OH/Cl) which remove DOS.

There has been some discussion of how the rate of loss of the particle species should be interpreted since the effective speed of OH/Cl at the surface of the particle may be faster due to the OH/Cl gradient there (see comments of Trakhtenberg on this paper). In essence the value could be overestimated by as much as a factor of 2. Consequently, our value of γ_{DOS} and that of George et al. may not truly indicate that there are other reactions removing DOS.

However, we have found that the rate of loss of DOS is faster in the presence of 20%

O_2 than in its absence. We conclude that reactions involving the RO and/or RO_2 radicals contribute to the rate of DOS loss meaning that secondary chemistry is, in fact, important in determining the kinetics. Thus, the rate of loss of a particle species could be larger than the rate of OH/Cl uptake which could be of importance for determining lifetimes of tracer/marker species in the atmosphere.

Reference:

Bennett, J. E.; Summers, R., Product Studies of Mutual Termination Reactions of Sec-Alkylperoxy Radicals - Evidence for Non-Cyclic Termination. Canadian Journal of Chemistry-Revue Canadienne De Chimie 1974, 52, (8), 1377-1379.

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