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Atmospheric
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Interactive comment on "The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of NO_x" *by* T. E. Kleindienst et al.

Anonymous Referee #1

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This manuscript describes the characterization of laboratory-generated secondary organic aerosol from the OH-initiated oxidation of isoprene. Gas phase and aerosol phase (in some cases) products were identified and many bulk aerosols parameters were determined, including the aerosol yield, the organic mass to organic carbon ratio, the organic peroxide yield, and the effective enthalpy of vaporization. The work has been carefully executed and the analysis of the results is appropriate and clearly described. The results provide new insights into mechanism of SOA formation resulting from isoprene oxidation.

The most intriguing finding is that 2-methyl tetrols are observed in the absence of acidic

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sulfate aerosol. Other workers have invoked acid-catalyzed aqueous aerosol phase chemistry to rationalize the presence of 2-methyl tetrols in isoprene-derived SOA. The authors have obviously gone to some lengths to ensure that aqueous phase aerosols are not apparently present in the reactor. However, I do worry that the extensive aerosol collection, derivatization and workup schemes might actually be causing the hydrolysis of more unstable aerosol phase species and that this is why polyols are apparently observed even under dry aerosol conditions.

In any case, because of this new finding, the authors propose an entirely gas phase mechanism for the production of 2-methyl tetrols in their experiments. The authors propose a mechanistically logical (if kinetically highly uncertain) series of gas phase reactions to ultimately produce polyols such as 2-methyl tetrols. Since the relevant RO2 + RO2 rate constants have not been measured for the peroxy radicals produced in the OH-initiated oxidation of isoprene, the authors cite the Jenkin and Hayman paper as evidence that the rate constants for self reactions of beta-hydroxy peroxy radicals could be large. While it is true that such rate constants were larger for beta-hydroxy peroxy radicals generated from ethene than for peroxy radicals generated from ethane, the Jenkin and Hayman work also showed that there is a very large substituent effect on the self reaction rate constants. In particular, Jenkin and Hayman found that the secondary beta-hydroxy peroxy radical self reaction rate constant is an order of magnitude slower than for the primary substituted ethane case, and that the tertiary case is three orders of magnitude slower than for the primary case. In the case of isoprene, the majority of peroxy radicals are predicted to be secondary or tertiary (Lei et al. J. Phys. Chem. A. 2001, 105, 471). Therefore, it seems unlikely that the “average” RO2 + RO2 rate constant for the isoprene system is larger than the secondary beta-hydroxy peroxy radical self reaction rate constant measured by Jenkin and Hayman: 8.4 x 10-13 cm3 molecule-1 s-1. In addition, Jenkin and Hayman also found that the similar RO2 + HO2 rate constants were largely invariant at a value of about 2 x 10-11 cm3 molecule-1 s-1. Therefore, under NOx-free conditions in these experiments, it seems that the major fate for peroxy radicals should be reaction with HO2 to form peroxides. Indeed, the authors do find that the organic peroxide yield is substantial. For this reason, the authors should mention the work of Claeys and coworkers in which aerosol phase peroxides are proposed as possible key oxidants in the production of polyols derived from isoprene.

The authors also surmise that there still must be substantial RO2 + RO2 chemistry occurring in the presence of NOx. However, if one uses the NOY concentration given in Table 2 as an upper limit for NO, and the delta isoprene concentration given in Table 2 as an upper limit for RO2 and kRO2 + RO2 = 8.4 x 10-13 cm3 molecule-1 s-1 and kRO2 + NO = 8.8 x 10-12 cm3 molecule-1 s-1 (Miller et al., Phys. Chem. Chem. Phys. 2004, 6, 3402), the RO2 lifetimes are about 50 and 100 s-1, respectively. Since the RO2 concentration is probably grossly overestimated within this approximation (5 x 1013 molecule cm-3), it seems likely that RO2 + NO reactions are dominant in the NOx-present experiments. It would have been interesting if the authors had tried experiments with very high NOx levels to see if the aerosol properties were changed in such a situation where RO2 + NO chemistry is clearly dominant. In any case, this is also an important point, since one would expect different aerosol products if RO2 + NO reactions are dominant.

In summary, I think that the authors should point out that their proposed mechanism is contingent on the RO2 + RO2 rate constants being much larger than one would expect by extrapolating the Jenkin and Hayman results. With the more conservative estimates outlined above, it seems more likely that RO2 + HO2 or RO2 + NO reaction pathways are more important under the experimental conditions.

The authors should also consider the following technical comments (in manuscript order).

1) Typo: p. 10016 line 23: “that previous” should be “that used previously”

2) Typo: p. 10016 line 25: “masses” should be “mass loadings”

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3) Typo: p. 10018 lines 4-5: “contributions isoprene oxidation” should be “the contributions that isoprene oxidation”

4) Typo: p.10019 line 6: “2-vinyloxirine” should be “2-vinyloxirane”

5) Clarification: p. 10026 lines 18-23: The statistical uncertainty in the enthalpy of vaporization values should be reported so that the reader can assess whether the NOx-free and NOx-present values are significantly different.

6) Figures 2, 3, and 4 would be much more readable if the structures of the key species were overlaid on the plots.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10015, 2009.

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