

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 #2

Received and published: 2 June 2009

This work explores several aspects of secondary organic aerosol (SOA) formation by isoprene photooxidation. Studies are carried out in a steady-state chamber, and the focus of most experiments is on NO_x-free conditions, which have received far less study than high-NO_x photooxidation. The yields, composition, volatility, and formation mechanism of the SOA are all studied in some detail, significantly adding to our understanding of the overall reaction system. The results are important and interesting, the paper is well-written and easy to follow, and thus this work is certainly worthy of publication in ACP. However, a few major points, relating to the SOA formation mechanism and aerosol yields, need to be addressed prior to publication.

C1404

(1) Radical chemistry: it is mentioned that either RO₂+RO₂ or RO₂+HO₂ reactions may account for some of the products formed; the paper mostly focuses on RO₂+RO₂ reactions (forming tetrols, etc.) but it is not clear this is the dominant channel. It would be useful if the relative contributions of these pathways were estimated. A simple box model using measured isoprene and H₂O₂ concentrations, inferred OH levels (from isoprene loss), and estimated peroxy-peroxy rate constants would allow for the estimates of [RO₂] and [HO₂], and therefore a reasonable estimate of the important RO₂ chemistry in these experiments.

(2) Mechanism of tetrol formation: The lack of evidence of C₅ hydroxycarbonyls in either the gas or particle phases seems significant. These species would be expected as co-products of diols (first-generation products) or tetrols (second-generation products), if such compounds are formed by RO₂+RO₂ chemistry. The authors mention that these are not measured (p. 10032 line 8 and p. 10034 line 3) but do not comment on why this might be the case. Two possibilities include (1) the polyols are formed by mechanisms other than RO₂+RO₂ reactions (as shown in Scheme 1), or (2) hydroxycarbonyls are exceptionally reactive, possibly by oligomerization reactions. Either possibility would be an important result, and so should be mentioned at least briefly.

(3) Comparison with previous results: the reported yields are significantly lower than the NO_x-free yields measured by Kroll et al. 2006. This difference is reported but not explored in any detail. Possible reasons should be discussed, and atmospheric implications at least touched upon. I can think of at least three possibilities for such differences (others may be important also): (i) differences in radical chemistry (RO₂ vs HO₂, as described above) – based on the low isoprene concentrations, Kroll et al. 2006 estimated RO₂+HO₂ reactions would dominate over RO₂+RO₂ reactions in their experiments. (ii) differences in photolysis: the authors added UVB lights to their chamber to enhance the photolysis of H₂O₂. This would likely enhance organic peroxide photolysis as well, and could lead to a reduction in SOA mass (greater than the reduction observed by Kroll et al. under UVA irradiation). Perhaps an average emission

C1405

spectrum of the lights used would be useful here? (iii) differences in timescale: significant amounts of butenediols are measured in the gas phase. If these are indeed intermediates to tetrol (and SOA) formation, then there exists a substantial amount of unreacted SOA precursors in the air removed from the steady-state chamber. This would have the effect of lowering yields below their atmospheric values. Of course, this is also a potentially important issue for static-chamber experiments (e.g. Kroll et al.), but the longer timescales of those experiments may lead to higher yields.

Minor comments:

SOA/SOC ratios: these should also be compared to those reported from AMS measurements of isoprene photooxidation SOA by Aiken et al. (2008).

SMPS data is collected but is not used for the aerosol yield measurements. Are these results (assuming a density) in general agreement with the gravimetrically-determined yields?

10019, line 17: the observations by Kroll et al. 2006 and Dommen et al. 2006 were really that SOA appears when NO is low, not necessarily when RO₂+RO₂ reactions begin (RO₂ was not measured in either study). Kroll et al. attributed the SOA formation to the onset of RO₂ + HO₂ reactions.

10020, line 13: Below -> above?

10020, line 27: this effect (loss of H₂O₂ in the ozone scrubber) should be expanded upon. Have the measurements of H₂O₂ been validated in the laboratory using known concentrations of H₂O₂, or are they just rough estimates?

10022, lines 27-29: obtaining quantitative results from this technique requires assuming the SOA components have MWs similar to that of benzoyl peroxide; this needs to be stated explicitly here and in the results (p. 10034, line 9).

10029, line 2: C₅ tetrols are semivolatile and so likely have a significant gas-phase fraction. Based on the measured boiling point and dHvap (<http://webbook.nist.gov>), the

C1406

saturation vapor pressure of erythritol at 298K is ~25 ug/m³; adding an extra methyl group (making a C₅ tetrol) would lower this by a factor of ~3, for a tetrol vapor pressure of ~8 ug/m³. Thus the presence of C₅ tetrols in the gas phase should probably not be discounted.

10031, line 8: the Kornblum reference seems inappropriate, as that work focused on a closed-shell, base-catalyzed mechanism. Russell 1957 (JACS 79:3871) focuses on RO₂ self-reactions.

10034, line 22: according to Kroll et al. 2006, density was estimated using an AMS and SMPS rather than just assumed.

10035, line 25: it is unclear how oligomerization would increase oxygen content – most of the oligomers detected by Surratt et al 2006 have an equal or smaller number of Os.

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