Atmos. Chem. Phys. Discuss., 11, C735–C739, 2011
www.atmos-chem-phys-discuss.net/11/C735/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on “Secondary organic aerosol formation from the photooxidation of isoprene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene under high NO_x conditions” *by* K. Sato et al.

Anonymous Referee #3

Received and published: 10 March 2011

This paper describes chamber studies of the formation of SOA from the photooxidation of isoprene, as well as of other conjugated dienes. A range of analytical techniques is used to characterize the yields, composition, and volatility of the aerosol, and experiments carried out under various conditions help constrain the reaction mechanism. This work certainly contributes to our understanding of SOA chemistry, and will be of interest to the community, so is worthy of publication of ACP. However, there are several areas in which the analysis and/or text could be improved; the points below need to be addressed prior to publication.

Fig. 2 (and Figs 11-12): the SOA volume had not leveled off by the end of the experiment. Is this typical for all experiments? If so, reported yields are probably underestimates, and this needs to be stated explicitly.

P. 4321, paragraph starting on line 22: more discussion of the differences in SOA yields among different studies is necessary. One major difference that deserves some attention is the aerosol loadings, which are well-known to affect SOA yields (Odum et al. 1996). In general, the loadings in this study are higher than in Kroll et al 2006. It would be worthwhile to plot these on a “yield curve” (yield vs. loading). NOx level and reaction rate may also play an important role, as discussed by Carlton et al (2009); these should be discussed as well. I suspect that these differences (rather than other differences in reactor characteristics) can explain most differences in measured yields.

Section 4.4: The high resolution of the AMS should be taken advantage of here. The m/z values of the oligomer peaks are high, but not so high that they can’t be identified in W mode. Even without exact identification of each ion (which requires a good absolute m/z calibration), the mass differences between peaks (delta m/z =102) can be determined with high accuracy, allowing for the determination of the exact formula of the monomeric subunit.

P. 4327, lines 21+: the use of the isotopically-labeled isoprene provides some nice checks on the SOA-formation mechanisms. It might also provide insight into the gas-phase chemistry – for example the differences in m/z 71 and 72 in the PTRMS might provide new information a about different MVK-MACR chemistry and yields.

P. 4328, lines 5-13: this is a really nice demonstration of the importance of aldehydes in the formation of low-volatility species. It might be worth mentioning that this is consistent with the prior observation that MACR gas-phase oxidation makes SOA but MVK oxidation does not (Kroll et al 2005, Surratt et al 2006).

Section 6.3: Can the authors rule out slow condensation of semivolatiles that are already present? (Some sort of mass-transfer limitation?)

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Figure 11: the loss of m/z 71 (MVK+MACR) doesn't change when the lights are turned off – given their fast reaction with OH, this seems very unusual to me. Are the levels of O3 and NO3 high enough to account for this rapid loss of these carbonyls?

P. 4330, lines 24-27 & Figure 11: This conclusion is strongly dependent on just two data points- LC measurements of the trimer and tetramer at ∼260 min (no data are shown for 330 min, as in Figure 10). Given this limited amount of data, I think the term "clearly different" is far too strong. Also, for comparison with Figure 10, how did the pentamer (m/z 527) change?

P. 4331, line 17: This sentence needs to be clarified. The text "volume fraction remaining (VFR) measured at 300 K. . ." reads as if it's a VFR at 300K, as opposed to a 373 K VFR for the 300K experiment. Instead, the reader should be reminded that this is from the VTDMA, run at 373K.

P. 4331, lines 19-20: I think of "volatility" as depending not just on the molecular structure but also temperature. I understand what the authors are trying to say, that "less condensable" (smaller or less polar) molecules condense out at the lower temperatures, but right now that's not how it reads. Perhaps it could be rewritten in terms of c*(298K)?

P. 4331, lines 21-24: I don't understand this argument. It seems to be implying that VFR and SOA yield are expected to be linearly related. However, because of nonlinearities arising from the volatility distribution of semivolatiles, this doesn't have to be the case.

P. 4331, lines 26-28. I think this is a false distinction –the differences in chemical composition of the SOA at different temperatures could be a direct result of the partitioning differences! In other words, the two effects could be one and the same.

Minor points:

P. 4315, line 22: Kroll (2005) examined SOA formation from 1,3-butadiene as well.

Table 1: SOA densities can be measured using the AMS. Is there a reason the density

was assumed to be 1 g/mL?

P. 4327 lines 1-7: what is the relevance of the general discussion of the RO2+NO mechanism? The formation of a ROONO* intermediate is generally accepted, but its intermediacy plays little direct role in SOA formation, so this discussion seems rather out of place.

P. 4328, line 22: the first AMS identification of oligomers in isoprene+OH SOA was carried out by Kroll et al (2006); these experiments were in fact carried out under low loadings (2-10 ug/m3, according to Tables 1-2 of that paper).

Section 5: This section is titled “Proposed reaction mechanism”, but the mechanism seems to me to be largely in line with previous proposals (Surratt et al 2006, etc.). Differences should be highlighted here; if there are no major differences, I would suggest changing the title of the section simply to “Reaction mechanism”.

References: A. G. Carlton, C. Wiedinmyer, and J. H. Kroll (2009); A review of Secondary Organic Aerosol (SOA) formation from isoprene; Atmospheric Chemistry and Physics; 9(14); 4987-5005.

J. H. Kroll, N. L. Ng, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2006); Secondary organic aerosol formation from isoprene photooxidation; Environmental Science and Technology; 40(6); 1869-1877.

J. H. Kroll, N. L. Ng, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2005b); Secondary organic aerosol formation from isoprene photooxidation under high-NOx conditions; Geophysical Research Letters; 32(18); L18808, doi:18810.11029/12005GL023637.

Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/particle partitioning and secondary organic aerosol yields. Environ. Sci. Technol. 1996, 30, 2580-2585.

J. D. Surratt, S. M. Murphy, J. H. Kroll, N. L. Ng, L. Hildebrandt, A. Sorooshian, R. Szmigielski, R. Vermeylen, W. Maenhaut, M. Claeys, R. C. Flagan, and J. H. Seinfeld

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

(2006); Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene; J. Phys. Chem. A; 110(31); 9665-9690.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4313, 2011.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper