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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.

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Thank you very much for your valuable comments. We reply your comments as follows:

"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."

This was typical in experiments in which the NO2 photolysis rate was 0.12 min-1. Reported SOA yields in these experiments are probably underestimated. These are described in section 3.1 in the new manuscript.

"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."

Thank you for the comment. We plotted "yield curves" of the present and previous results for our reference (it is not shown here).

Discussion of the difference in SOA yields among different studies is added. The present yield results are compared with results of Kroll et al. (2006); the difference in the aerosol loading is discussed. Further we add a new paragraph in section 3.2 to discuss the effects of NOx level and reaction rate on the SOA yield. We remove the description of the differences in reactor characteristics.

"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."

In this study, AMS was basically operated in V mode in order to detect oligomers with high sensitivities. Table R3-1 shows AMS-measured m/z of oligoesters. Values of m/z were determined by single-Gaussian fits to raw AMS spectra. Measured m/z values were compared with those calculated assuming chemical formulae shown in Table 2. An each measured m/z value agreed with a calculated value within m/z of 0.04. We briefly explain these results in section 4.4.

“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.”

Thank you for the comment. We measured the time profiles of m/z 71 and 72 by PTR-MS in an experiment with isoprene-13C. However, we cannot find new valuable information.

In the experiment with isoprene-13C, the signals of m/z 71 and 72 increased after lights on and then decreased; we found no great difference between the profiles of m/z 71 and 72.

The ratio of m/z 71 to m/z 72 was about 2.4, which was higher than a literature value of MVK/MACR branching ratio (= 1.5) (Miyoshi et al., 1994). Note that the PTR-MS sensitivities are depending on compounds and detection conditions (Warneke et al., 2003). Further, the signals of m/z 71 and 72 will be significantly affected by the secondary reactions with OH and O3. We could not obtain information of the yields of MVK and MACR.

“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).”

This is mentioned in the same place of the new manuscript.

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

Cocker et al. (2001) estimated a typical condensation time scale to 2 min (please see Fig. 2 of their paper). This time scale is much shorter than the time resolution of the

analysis (30 min). We can rule out condensation of semi-volatile compounds that are already present.

“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?”

Yes, the O3 level is high enough to account for loss of MVK + MACR. The O3 level when lights were turned off was about 300 ppb. The loss rates of MVK and MACR due to the reaction with OH, O3, and NO3 were calculated (Table R3-2). The loss of m/z 71 after the lights are turned off will mainly be explained by the reactions of MVK and MACR with O3. For example, the loss rate of MVK by O3 reaction ([O3] = 300 ppb) is 3.2 x 10-5 s-1; this corresponds to 11% decrease per hr. The reaction of MACR with NO3 radical also occurs in the dark, but contributions will be lower than those of the reactions with O3. These results are briefly described in section 6.3 in the new manuscript.

“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?”

In the new manuscript, “clearly different” is substituted by “slightly different”. Further, we tone down a conclusion of this section and descriptions in the conclusion section. The pentamer was not detected in the lights-off experiment. This is also explained in the same place.

“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.”

We fix it.

“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)?”

Thank you for the comment. This place is rewritten following comments by referees 4 and 6 (please see also replies to these referees). By these revisions, the sentence describing the SOA volatility becomes unnecessary. This sentence was removed in the new manuscript.

“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.”

The following explanations are added in sections 2.3 and 7 of the new manuscript: If the temperature dependence of SOA yield is purely determined by the gas/particle partitioning of semi-volatile compounds, the total volume concentration remaining of the particles at 373 K (which could be measured by a thermodenuder-SMPS system) is independent of the temperature of chamber experiment. On the other hand, the particles with a specific diameter are measured by VTDMA (DMA-thermodenuder-SMPS system). We monitored the VFRs of 75, 100, and 125 nm particles in both the experiments at 300 and 278 K, and confirmed that the VFR was independent of the diameter within an experimental uncertainty.

That is to say, if the temperature dependence of the SOA yield (Y) is purely determined by the gas/particle partitioning of semi-volatile compounds, the VFR(300 K)/VFR(278 K) ratio would be the same as the Y(278 K)/Y(300 K) ratio. In the present study, the VFR(300 K) was 0.45–0.56, whereas the VFR(278 K) was 0.26–0.43 (Fig. 12c). The

change in SOA yield cannot be solely explained by changes in the VFR (SOA yield increased 2–3 times while the VFR changes by less than a factor of 2). Although the temperature dependence of SOA yield is largely explained by gas/particle partitioning of semi-volatile compounds, present results of the VFR measurements suggest that reactions of aerosol compositions occur in the particle phase.

“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.”

This paragraph is removed in the new manuscript.

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

We describe this in the same place of the new manuscript.

“Table 1: SOA densities can be measured using the AMS. Is there a reason the density was assumed to be 1 g/mL?”

We did not conduct PTOF measurements using AMS. We employed a density value of 1.0 g cm-3 because resultant yield values can easily be converted by another density value.

“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.”

We checked the GC peak of methacrolein at 278 and 300 K; the methacrolein yield was basically constant between 278 and 300 K (see also reply to referee 2). The comment is correct. We remove this discussion from the new manuscript.

“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)."

We describe this in the same place of the new manuscript.

"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"."

The title of the section is substituted to "Reaction mechanism".

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Table R3-1. AMS-measured and calculated *m/z* of oligoesters observed.

	1A (ISO)	3A (ISO)	4A (ISO)	1A (ISO-13C)	3A (ISO-13C)	4A (ISO-13C)	1B (BD)
Monomer							
AMS-measured *m/z* [b]	103.040	a	145.050	104.043	132.039	146.053	89.025
Calculated *m/z*	103.039	131.034	145.050	104.042	132.037	146.053	89.023
m/z Error	-0.01	-	0.00	-0.01	-0.02	0.00	-0.02
Dimer							
AMS-measured *m/z* [b]	205.069	233.062	247.081	a	a	249.089	177.040
Calculated *m/z*	205.071	233.066	247.081	207.077	235.072	249.088	177.039
m/z Error	0.02	0.04	0.00	-	-	-0.01	-0.01

[a] No value of *m/z* was determined since a doubly peaked spectrum was observed.

[b] ToF-AMS was operated in V-mode.

Fig. 1.

Table R3-2. Loss rates of methyl vinyl ketone ($k_{\mathrm{MVK}}[\mathrm{O_x}]$) and those of methacrolein ($k_{\mathrm{MACR}}[\mathrm{O_x}]$).

	Conc. （molecule $\mathrm{cm^{-3}}$）	$k_{\mathrm{MVK}}[\mathrm{O_x}]$ ($\mathrm{s^{-1}}$)	$k_{\mathrm{MACR}}[\mathrm{O_x}]$ ($\mathrm{s^{-1}}$)
OH (lights on)	2×10^{6}	3.7×10^{-5}	6.1×10^{-5}
$\mathrm{O_3}$ (lights on/off)	7.5×10^{12}	3.2×10^{-5}	8.2×10^{-6}
$\mathrm{NO_3}$ (lights off)	5×10^{8}	$<6.0\times10^{-8}$	1.7×10^{-6}

The rate constants used are 3.1×10^{-11} (OH + MACR (Atkinson, 1986)), 1.9×10^{-11} (OH + MVK (Atkinson, 1986)), 1.1×10^{-18} ($\mathrm{O_3}$ + MACR (Treacy et al., 1992)), 4.2×10^{-18} ($\mathrm{O_3}$ + MVK (Treacy et al., 1992)), 33×10^{-15} ($\mathrm{NO_3}$ + MACR (Chew et al., 1998)), and $<1.2\times10^{-16}$ ($\mathrm{NO_3}$ + MVK (Rudich et al., 1996)); the unit of rate constants is $\mathrm{cm^{3}}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$.

Fig. 2.