

Interactive comment on “Effect of humidity on the composition and yield of isoprene photooxidation secondary organic aerosol” by T. B. Nguyen et al.

Anonymous Referee #2

Received and published: 14 May 2011

Overall Comments:

This paper examines the effect of RH on SOA formed from the photooxidation of isoprene under high-NO_x conditions; specifically, this study employed H₂O₂ photolysis to generate sufficient OH radicals to drive the chemistry forward as was done in Kroll et al. (2006, ES&T) and Surratt et al. (2006, JPCA). This is a well-presented and concise study that will certainly be of high interest to the atmospheric aerosol research community, especially since the effect of RH on isoprene SOA formation has not yet been extensively examined. Most of the prior work has examined the effects of NO_x (Dommen et al., 2006, GRL; Kroll et al., 2005, GRL; Kroll et al., 2006, ES&T; Surratt et al., 2006, JPCA; Surratt et al., 2010, PNAS) and aerosol acidity (Edney et al., 2005, Atmos. Environ; Surratt et al., 2007, ES&T; Surratt et al., 2010, PNAS) on iso-

C3325

prene SOA formation under dry conditions only. Importantly, the present manuscript's chemical composition results are quite consistent with the recent findings of the Surratt research group at UNC (i.e., Zhang et al., 2011, ACPD); specifically, oligoesters of 2-methylglyceric acid (2-MG) are enhanced under dry conditions. The Zhang et al. (2011, ACPD) study was published about 1 month before this study appeared in the online discussion of ACP, and thus, the authors were probably unaware of the Zhang et al. (2011) study. With that said, the authors should include this new study in their discussion, as there are some important differences that need to be compared and discussed thoroughly. For example, there were several differences in how the experiments were designed in these studies. These experimental differences might explain why the SOA yield results differ between these two studies. As will be mentioned below in my specific comments, these experimental differences include the different oxidative conditions employed (i.e., an OH precursors versus no OH precursor) and also nucleation versus condensation of semivolatiles onto preexisting seed aerosols. This study should be published in ACP only when the authors fully address the detailed and technical comments outlined below in this review.

Detailed/Specific Comments:

1.) SOA Yields – Use of H₂O₂ as an OH precursor:

The biggest issue that needs to be resolved by the authors is related to the SOA mass measurements (or yields). The reason for this concern is it is unclear how the authors of this study deal with H₂O₂ partitioning into wet aerosols in their humid experiments, and thus, further reacting with semivolatiles or nonvolatiles in the aerosol phase. The latter could cause undesired chemistry to occur. More importantly, how can the authors correct their SOA mass measurements due to absorption of H₂O₂ in wet aerosols? This absorption could cause an overestimate of the true SOA mass yield under humid conditions. As Kroll et al. (2006) pointed out, the use of H₂O₂ as an OH precursor required that isoprene SOA generation be done under dry conditions due to its relatively high Henry's law constant. H₂O₂ is known to be miscible in water. In addition to

C3326

this concern, the observation of similar amounts of 2-MG monomer under both humid and dry conditions is at odds with the Zhang et al. (2011, ACPD) study. In Zhang et al. (2011) they observed enhanced concentrations of both 2-MG and its corresponding oligoesters under dry conditions. This raises the concern now that H₂O₂ is not only affecting the SOA mass measurements, but it is also absorbed in the wet aerosol (or humid) experiments of the present manuscript causing formation of 2-MG from H₂O₂ + methacrylic acid or H₂O₂ + methacrolein pathways, which these pathways were demonstrated by Claeys et al. (2004, Atmos. Environ). I caution the authors to tone down their conclusion that RH does not seem to affect the SOA yields from isoprene photooxidation under high-NO_x conditions. Have the authors considered examining this system again but without the use of H₂O₂ as an OH radical precursor? For example, rely on the “classical photooxidation” experimental approach where one only injects NO and VOC into chamber and then irradiate the mixture. I wonder what the authors will find with their SOA mass measurements in that case. It should be noted here that 2-MG and its corresponding oligoesters have now been demonstrated to form from the further oxidation of methylacryloylperoxynitrate (MPAN), especially under increasing NO₂/NO ratios (Surratt et al., 2010, PNAS; Chan et al., 2010, ACP).

2.) SOA Yields – Nucleation versus Seed Aerosol Experiments:

Both the present study and the Dommen et al. (2006, GRL) study did not use seed aerosol. That is probably why they also both did not observe SOA yield changes between the dry and humid experiments. This is at odds with the recent study by Zhang et al. (2011, ACPD). However, in the ambient atmosphere, there is background aerosol. How does seed aerosol affect SOA yield? Kroll et al. (2007, ES&T) pointed out that SOA yield may vary with or without seed aerosol (higher SOA yield with seed aerosol). It is very likely that the isoprene SOA yield under different RH could be different in the presence of seed aerosol, such as demonstrated by Zhang et al. (2011, ACPD). Thus, the yield result in this study is not sufficient to conclude that RH does not significantly affect isoprene SOA yield in the atmosphere.

C3327

3.) In the manuscript, the authors mentioned “several types of processes may be induced by LWC, with conflicting effects”.

Based upon their results, apparently, the enhanced SOA from aqueous-phase uptake of glyoxal, methylglyoxal, and glycolaldehyde under higher RH and the enhanced SOA from oligomerization, such as esterification under lower RH conditions, are two major conflicting processes. The same SOA yields indicate that these conflicting processes offset each other. However, the experimental setting of this study only investigated one pair of high RH and one low RH (90% and <2%). Also, this study only investigated one isoprene/NO ratio (~1:3). As the RH changes from dry to humid and isoprene/NO ratio varies, the contribution to SOA formation and the extent of these process may alter as well. Therefore, the SOA yield could also be different under varying RH conditions and oxidative conditions (i.e., RO₂ + NO or RO₂ + RO₂ or RO₂ + HO₂ dominates the gas-phase chemistry).

4.) DMA Measurements: RH in the DMA was set to be <10%. When the particles in the humid experiment go through the SMPS, will this much lower RH change the chemistry before detection? For example, assuming glyoxal, methylglyoxal, and glycolaldehyde aqueous-phase uptake is not reversible, drying the aerosol will not change these SOA mass. But reactions like esterification will likely be driven towards more SOA formation by drying, which increases SOA yield. If this is the case, a higher SOA yield under dry conditions would be expected.

5.) ESI-MS and DESI-MS Analyses:

The analytical techniques employed are appropriate here; however, why was chromatographic separation not employed before ESI-MS detection? ESI is commonly known to easily form clusters or artifacts, and as a result, can cause for misinterpretation of mass spectral data. How do you know that what you observe in terms of oligomers is not simply a result of ions clustering together in the mass spectrometer? The use of chromatographic separation, like that done by Surratt et al. (2006, JPCA) and Zhang

C3328

et al. (2011, ACPD), clearly show that these oligoesters are real and resolvable on a chromatographic (in these prior cases a reverse-phase column) column. This further supports that these constituents are not artifacts in these prior studies.

6.) Comparison with other studies in Discussion Sections:

I suggest that the authors also compare their yields and chemical results with prior studies of Kroll et al. (2005, GRL), Kroll et al. (2006), Surratt et al. (2006, JPCA), Dommen et al. (2006, GRL) and Zhang et al. (2011, ACPD). It would be of use to include the discussion of how differences in seed aerosol conditions, oxidative conditions, etc., lead to differences in yields between the present study and these prior studies.

Technical Comments:

1.) Abstract:

The use of H₂O₂ as an OH radical precursor should be mentioned in the abstract to clearly designate to readers how aerosol from isoprene was generated under these varied conditions.

2.) Introduction:

The authors don't mention that 2-MG and its corresponding oligoesters have now been shown to form by the further oxidation of MPAN, especially under increasing NO₂/NO ratios. This was demonstrated recently by both Surratt et al. (2010, PNAS) and Chan et al. (2010, ACP). Since 2-MG and its corresponding oligoesters are of focus in this study, I suggest that the authors include these references here. I would also cite the work of Zhang et al. (2011, ACPD) here since they also recently examined the effect of RH on isoprene SOA formation; however, no OH radical precursor was used in that study.

3.) Introduction, Page 9219, Lines 1:

Citation needed for the sentence ending in "...of organic nitrogen (ON) compounds."

C3329

4) Introduction, Page 9219, Line 4:

Delete the word "organic"

4.) Introduction, Page 9219, Line 11-12:

Insert ", and references therein)" into the "Carlton et al, 2009)" citation, especially since this is a review article and not the actual studies that have studied isoprene SOA under variety of RH conditions.

5.) Introduction, Page 9220, Lines 11-12:

It turns out that hemiacetals observed in low-NO_x SOA by Surratt et al. (2006) have now been demonstrated to form from the acid-catalyzed reactive uptake of isoprene epoxydiols (IEPOX) (Surratt et al., 2010, PNAS).

6.) Experimental Section:

Just to be clear, what are the temperature ranges of these experiments? This should be clearly listed. Also, to be clear, were 6 total experiments conducted (i.e., 3 dry and 3 humid)? If so, please state that here.

7.) Mass Spectrometry Analysis of SOA Samples Section, Page 9226, Line 6:

Add ", consistent with the findings of Surratt et al. (2006)." to the sentence "Methyltetrols were not observed in the high-NO_x data."

8.) Figure 3:

Have these abundances been corrected for sampling volume differences?

9.) Figure 2:

The authors should add a detailed plot of NO, NO₂, and O₃ to this figure. From this figure, do you find that isoprene all primarily reacts away by the time NO reaches zero? This could explain why the 2-methyltetrols were not observed. Specifically, as Surratt et al. (2010, PNAS) study showed, the route to SOA formation under RO₂ +

C3330

NO dominate conditions is isoprene -> MACR -> MPAN -> SOA. The latter is a C4-preserving pathway.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 9217, 2011.

C3331