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Atmospheric Chemistry and Physics Discussions

Interactive comment on "SOA formation from the atmospheric oxidation of 2-methyl-3-buten-2-ol and its implications for $PM_{2.5}$" *by* M. Jaoui et al.

Anonymous Referee #1

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Review of "SOA formation from the atmospheric oxidation of 2-methyl-3-buten-2-ol and its implications for PM2.5" by Jaoui et al.

2-methyl-3-buten-2-ol (MBO) is a major, if not the most dominant, hydrocarbon emitted from forests. Here the authors investigate the SOA formation from MBO oxidation in the presence of UV lights under high- and low-NOx conditions. Although measured mass yields of aerosol formation was low, they were significantly higher than in previous studies. The authors also studied the aerosol composition in detail, and determined that dihydroxyisopentanol (DHIP) is a unique particle-phase tracer of SOA generated from MBO and can be found at detectable levels in field samples. This manuscript examines an important question in atmospheric chemistry, using results from well-designed experiments. The authors should place this work in better context of the body of published literature, and I strongly believe that addressing these concerns will make the results from this work more convincing. This work is within the scope of ACP, and should be considered for publication after addressing these concerns.

Major comments:

1. The major finding from this study is that the measured aerosol yields are high enough that MBO could be a significant source of SOA in high MBO emission areas. However, these results are in direct contradiction with previous study by Chan et al. (2009). While it is not expected that different experimental chambers provide identical results, there is insufficient effort in this manuscript to reconcile the differences. Most importantly, the authors should compare the atmospheric relevance of these two bodies of work. As recent work suggests, peroxy radical chemistry is one of the most important factors in determining SOA formation potential. While the experiments here agree with Chan et al. (2009) that under high NOx (RO2+NO-dominated) conditions aerosol formation is negligible, the low NOx yields vary by an order of magnitude, even for the same seed conditions.

The one difference I notice between the two studies is the relative MBO magnitudes. The MBO concentrations here are a factor of 100 higher, while the H2O2 concentrations are the same. This suggests that the branching between RO2+RO2 and RO2+HO2 are vastly different between the two studies. Since DHIP is a product of RO2+RO2 reactions, that may explain why DHIP (and hence overall aerosol formation) is higher in this study. At the very least, the authors should provide a disclaimer about the different RO2/HO2 ratios. A more detailed set of experiments examining this effect (by increasing H2O2 relative to MBO) can be very informative.

Another possible explanation is the organic loading. Semivolatile partitioning is nonlinear, and once saturation is reached, partitioned organics can induce more condensation into the organic phase. Here it is plausible that MBO was present in high enough concentrations (>10 ppmv) to overcome saturation, and hence the organic loading be-came high enough for semivolatiles to condense. In this case, it can be argued that these results from the present work are more relevant to the ambient atmosphere, in which an organic phase is always present for sub-saturated semivolatile to condense.

2. If the average concentration of DHIP for the 3 experiments is in fact 53 ug/m3, it will suggest that DHIP is accounting for almost all of the aerosol formed in the experiments. At the very least (for ER465b), 53 ug/m3 of DHIP would account for 35% of the aerosol. This would imply that in the field samples with 1 ng/m3 DHIP, 3 ng/m3 is derived from MBO, which is very minor compared to other sources. Therefore I disagree with the authors that MBO could be an important source of SOA.

3. While DHIP could be a good marker for MBO oxidation, one needs to be careful about its use as a tracer for MBO-SOA. DHIP is primarily in the gas phase (SIMPOL gives a saturation concentration of 723 ug/m3; it has also been measured in the gas phase by Chan et al. (2009)) and thus could be misleading as an aerosol-phase tracer. A semivolatile tracer can lead to miscalculations during source apportionment (e.g. loss of tracer by dilution and subsequent evaporation). Also, is it possible that there is oligomerization of DHIP and the observed DHIP is a breakdown product?

4. The calculation of mass yields described in the second and third paragraphs in Section 3.3.1 is very confusing. First of all, a density of unity is not a good approximation. Given the oxidized nature of the aerosol (and small carbon backbone), I would expect the O/C ratio to be quite high. OM/OC of 2.1 would imply O/C of 0.8 and the density would most likely be significantly higher than 1. A density of 1.4 g/cm3 might be more appropriate.

Second, there appears to be a large scatter and no apparent trend in measured values. It seems to me that the mass yields are below limit of quantification (still within the noise). Why are the yields from other experiments not quantified or shown here? They could help reduce the noise and establish a clearer trend (e.g. difference between acidified and non-acidified seed, high- and low-NOx).

This paragraph is just confusing in general, and could benefit from revision and clarification. For example, gravimetric determination of filter mass should be described in the Experimental Section. Also, it seems that the gravimetric measurements are verified against SMPS measurements, and are rejected when they do not agree with SMPS. Why not directly use SMPS measurements? Given the importance of the actual value of aerosol yield in determining whether or not MBO is a significant SOA precursor, how this number is calculated draws more attention.

5. Both isoprene and MBO irradiation with H2O2 (Kroll et al., 2006; Chan et al., 2009) showed a significant volatilization of aerosol over time. Did these experiments also exhibit the same trend? If so, at what extent of reaction were these yields measured? If they were measured after significant loss of SOA, the discrepancy between this study and Chan et al. (2009) could be even larger. Was there enough time resolution to determine if DHIP was also decreasing over time?

Minor comments:

Pg. 24050, line 5: The abbreviation BSTFA should be provided here.

Pg. 24053, lines 1–13: I do not understand how the authors came up with the estimate of less than 1% MBO-to-isoprene conversion, when the drying experiments showed 12% conversion. Did the authors repeat the drying experiments after reducing the pre-concentration temperatures? If so, what was the final result?

Pg. 24054, line 12: a reference should be provided here.

Pg. 24054, lines 14–22: while 2-HMP can be formed from OH addition to the most substituted position, it can also be formed from OH addition to the least substituted position. The carbon onto which O2 adds neighbors OH groups on both sides (one from MBO originally, and the other from OH addition). Scission of C-C bond with the former leads to glycolaldehyde and acetone (as suggested in the manuscript), but scission of C-C bond with the latter leads to 2-HMP and formaldehyde. In fact, this should be the major source of 2-HMP because OH addition to the most substituted carbon is highly unlikely, whereas scission of CH(O.)–CH2OH bond is almost as likely as scission of CH3C(CH3)OH–CH(O.) bond.

Pg. 24054, line 20: “substituent” should be “substituted”

Pg. 24054, line 29: Presumably the authors mean standards are NOT available?

Pg. 24055, lines 7–21: This paragraph seems unnecessary and confusing. I am not aware of any methylglyoxal formation from acetone photolysis or oxidation. As the author suggests, acetone is unreactive towards OH (lifetime of days with 2E6 OH), and even if it does react with OH, methylglyoxal formation is a very minor channel (fragmentation or PAN formation dominates). It is likely that methylglyoxal is formed from reactions of trace isoprene. Also, uptake of dicarbonyls is irrelevant here because the low-NOx experiments (in which SOA formation is noticeable) are run under dry conditions. This paragraph should be rewritten to be more concise and accurate.

Pg. 24056, lines 7–9: Which of these compounds can come from isoprene?

Pg. 24061, line 7: Typo in “2,3-tridroxy-3-methylbutanal”

Pg. 24061, lines 17–20: Can glycerol be used as a surrogate standard for DHIP?

Pg. 24062, lines 5–9: This will have no effect on SOA apportioned to MBO (as long as DHIP is used as the tracer), but will decrease the amount of SOA apportioned to isoprene.

Pg. 24064, line 15: The tracer should not be referred to as “Compound 20”, as this is just internal numbering. “DHIP” should be used instead.

Table 2: it could be helpful to label which ones of these peaks were also detected from isoprene oxidation

Figure 6: Typo in the legend “methyltetols”

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