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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.

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Reviewer# 1. We wish to extend our sincere appreciation to the reviewer for the time and effort spent in evaluating this manuscript. The comments have been very helpful in improving the manuscript. We have carefully considered the comments from the reviewer, and our revisions have been made to reflect these comments. We have addressed each point separately below. The comments are delineated as Comments and this is followed by a Response which note changes made to the manuscript.

We thank him for his suggestions and comments. Below, are our response to issues and comments raised by this reviewer?

Major Comments:

Comment # 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 became 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. Should provide the GCMS detection limit for the compounds studied."

Response. To reflect the reviewer concern, the following sentences were added on page 14 (original manuscript) just before "Characterization of SOA Products section" and read:

"The yield results obtained in this study are different than those reported by Chan et al. (2009). While it is not expected that different experimental chambers provide identical results. Under high NOx conditions, the yield data reported here agree with Chan et al. (2009) and show that aerosol formation is negligible. However, yields under low NOx vary by an order of magnitude, even under similar seed conditions. The one difference between the two studies under low NOx conditions is the relative MBO concentrations. The MBO concentrations in this study are a factor of 100 higher, while the H2O2 concentrations are about the same. This suggests that the branching between RO2+RO2 and RO2+HO2 is different between the two studies (Kleindienst et al., 2009). Since DHIP is a product of RO2+RO2 reactions, this may explain why DHIP, and the overall aerosol formation is higher in this study. Another possible explanation is the organic loading. Semi-volatile 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 to overcome saturation, and hence the organic loading became high enough for semi-volatiles to condense. In this case, the results from the present work are more relevant to the ambient atmosphere, in which an organic phase is always present for sub-saturated semi-volatile to condense."

In our previous analytical paper (Jaoui et al., 2004), the detection limit of a series of organic compounds (as BSTFA derivatives) was evaluated including ketopinic acid (KPA). Since standards of the compounds reported in this study are not available, all concentrations are estimated using the response factor of ketopinic acid (KPA). To reflect the reviewer concern about the GCMS detection limit, the following sentence (page 18, original manuscript) was changed from

"SOA products from the BSTFA derivatization have been quantified in the MBO system using the ketopinic acid (KPA) calibration method (Jaoui et al., 2004, 2005), since

authentic standards are not available for these compounds."

To

"SOA products from the BSTFA derivatization have been quantified in the MBO system using the ketopinic acid (KPA) calibration method (Jaoui et al., 2004, 2005), since authentic standards are not available for these compounds. The detection limit of a series of organic compounds including ketopinic acid was determined previously by Jaoui et al., 2004."

Comment # 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."

Response. It's unclear what the reviewer wants to say. DHIP concentrations were measured in experiments ER-462, ER-464, and ER465b as shown in Figure 6. DHIP concentration (53 μgm-3) has been determined in ER462. This concentration does not represents the average in all chamber experiments conducted in this study as can be seen in Figure 6. In experiment ER462, H2O2 at high initial concentration was used (see table 1: 19 ppm) compared for example to experiment ER464a (low NOx system without SO2 present), in which DHIP concentration was measured and was found to be ∼5 ug m-3, a value much lower that the 52 ugm-3 (see Figure 6).

To reflect the reviewer concern and to eliminate any confusion, DHIP data for experiment ER-462 (in which a high initial concentration of H2O2 was used) in Figure 6 was deleted. In addition, the following sentence "Concentrations of 52 ug m-3 have been determined for DHIP." was deleted from the original manuscript.

In our experiments, the contribution of MBO to ambient aerosol was estimated using the average of the mass fraction as described by Kleindienst et al. (2007) and not the average of the DHIP concentration. This method was used previously by our group as well others to estimate the contribution of isoprene, monoterpenes, and sesquiterpenes etc to ambient aerosol. The presence of DHIP in both MBO SOA and ambient PM2.5 strongly suggests that MBO in fact contributes to ambient organic aerosol in places with high MBO emissions. We added the following sentence to the revised manuscript at the end of section 3.4 and reads:

“At 1 ng m-3, the contribution of MBO SOA is estimated to be no more than 0.02 ug m-3 of organic mass.”

Comment # 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?.”

Response. We understand and agree with the reviewer concern when using organic tracers. In this study, DHIP was measured mainly in the particle phase and at relatively low concentration in the gas phase (see figure 2). As indicated by the reviewer in his comment #1, DHIP may partition preferably to the aerosol phase due to the high organic loading used in this study or found in the real atmosphere (see response to comment #1). DHIP was detected in this study in both field and chamber SOA, suggesting that MBO contribute to ambient organic aerosol. In addition, tracers used for alpha-pinene for example (pinic acid ..) were also detected in the gas phase and previous works show that the tracer method developed in our lab as reported by Kleindienst et al. (2007) give reasonable estimate for ambient secondary organic aerosol estimates (e.g. Kleindienst et al., 2007).

Comment # 4. A: “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.

B: 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.”

Response. A: All yields in this study were calculated based on SOA mass or SOC mass, specifically to avoid having to estimate aerosol densities. It doesn’t matter if the density is 1.0 or 1.1 or 1.4, it never enters into the calculation. In addition, we feel that a density of 1.4 g/cm3 is not justified in this study based on our survey of a series on more than 30 SOA types witch shows an average density of (1.10 +0.04) (Docherty et al., 2012: in preparation). To eliminate any confusion, the following sentence was changed from:

“SOA was obtained from gravimetric measurement of the filter when there is a reasonable degree of consistency with the particle mass obtained from the SMPS volume assuming a density of unity.”

To

“SOA was obtained from gravimetric measurement of the filter when the total aerosol mass was predominantly SOA (i.e., non-SO2 experiments).”

B: As we stated in our original manuscript on page 13 (section 3.3, 1st paragraph), MBO/NOx system produced only very low levels of aerosol, which was typically insufficient for determining aerosol parameters including aerosol yield. In fact, aerosol yields were not reported for experiments involving NOx system due to the high uncertainties associated with them. Section 3.3, 1st paragraph reads:

“Aerosol Parameters. The production of aerosol was found to be highly dependent on the exact conditions under which the experiments were carried out, in particular the presence of NOX in the system. This system produced only very low levels of aerosol, which was typically insufficient (using standard procedures for aerosol quantification) for determining aerosol parameters and detailed organic analysis. Except for a minor organic nitrate channel, the photooxidation system in the presence of NOX converts virtually all RO2 formed into RO radicals, which then decompose or isomerizes to produce carbonyl or hydroxycarbonyl compounds (Atkinson, 2000). Without NOX in the system, RO2 radical typically react with HO2 or self react to produce a product molecule with five carbons while adding functional groups to the product. These products are sufficiently nonvolatile to condense into the particle phase and the system without NOX was the only one where aerosol parameters and composition were measured.”

In addition, paragraph 3 (section 3.3) states that gravimetric mass from static experiments were overestimated because of the extended sampling time and low levels of aerosol mass of SOA in the chamber at the end of sampling period (due to dilution). Then as stated in the original manuscript no aerosol yields were reported for static experiments. To reflect the reviewer concern, this paragraph was rewritten from:

“Yields for some experiments conducted in this study are found in Table 3. The gravimetric yield values originated from the static experiments were considerably higher

than those measured using the SMPS system. The SOA gravimetric mass was found to be overestimated during these static experiments because of the extended sampling time and low SOA mass in the chamber at the end of the sampling period (due to dilution). For example, ER-463 was conducted in the presence of NOx, and while a measurable SOA yield (0.2%) was obtained from the gravimetric analysis, this value was considerably higher than that measured using the SMPS values. However, some experiments conducted in the presence of H2O2 with and without acidic sulfate aerosol (ER-464a,b and ER-465b), organic aerosol was formed and measured using the carbon analyzer with carbon yields (YSOC) ranging from 0.2% to 0.9%. The SOA yield was also found to be 0.7% for the system in the absence of NOX (ER464a). For all experiments with MBO, the yield tended to be systematically higher for experiments conducted under acidic conditions, particularly under high NOx conditions. The implications of these findings are discussed below.”

To

“Yields were not calculated for the static experiments because the long sampling times produced very high dilution correction. Yields for dynamic experiments conducted in this study are found in Table 3. Note no measurable yield for experiments ER-465a was obtained. The SOA yield was also found to be 0.7% for the system in the absence of NOX (ER-464a). However, some experiments conducted in the presence of H2O2 with and without acidic sulfate aerosol (ER-464a,b and ER-465b), organic aerosol was formed and measured using the carbon analyzer with carbon yields (YSOC) ranging from 0.2% to 0.9%. For all experiments with MBO, the yield tended to be systematically higher for experiments conducted under acidic conditions, particularly under high NOx conditions. The implications of these findings are discussed below.”

Additional change was made in Table 3 caption. The caption changed from :

“Table 3. OM/OC ratio and SOA and SOC yields. Note in experiment ER-464a, the aerosol mass concentration is SOA mass concentration, and in Experiments ER-464b and ER-465b the aerosol mass concentration is a mixture of SOA and inorganic sulfate compounds originated from SO2 reaction."

To

"Table 3. OM/OC ratio and SOA and SOC yields. SOA yields could not be calculated for runs involving SO2 because the filter masses consisted of both SOA and inorganic sulfate, and inorganic sulfate mass concentrations were not independently measured."

Comment # 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?"

Response. (see also our response to comment # 4) As reported in sections 3.3 aerosol yields were reported only for dynamic experiments (see Table 3) for which volatilization of aerosol over time is negligible.

Minor comments:

Comment # 6. "Pg. 24050, line 5: The abbreviation BSTFA should be provided here."

Response. The BSTFA is defined now on page 7 in the revised manuscript, the first time that was introduced in the text. Thanks to the reviewer.

Comment # 7. "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?

Response. The estimation was based on dry experiments using the reduced pre-concentration temperature.

Comment # 8. "Pg. 24054, line 12: a reference should be provided here."

Response. We added the following reference "Jaoui and Kamens, 2001" to the revised manuscript.

Comment # 9. 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."

Response. The reviewer is correct; we changed the following paragraph on page 24054, original manuscript from:

"Of greater interest are the carbonyl compounds formed during the irradiation shown in Fig. 1b. It is clear that the carbonyl products from the OH+MBO reaction are detected from the first DNPH sample taken at (0.7 h) with NO is still present in the system at relatively high concentrations. According to conventional reaction kinetics, OH adds to the double bond in MBO to form an RO2 radical which oxidizes NO to NO2 with the resultant alkoxy radical producing a carbonyl product. If OH adds to the least substituted position of MBO, glycolaldehyde and acetone result as the major carbonyl products. If 20 OH is added to the most substituent position, scission of the alkoxy radical produces formaldehyde and 2-hydroxy-2-methylpropanal (2-HMP) as the predominant carbonyl products."

To

"Of greater interest are the carbonyl compounds formed during the irradiation shown in Fig. 1b. It is clear that the carbonyl products from the OH + MBO reaction are detected from the first DNPH sample taken at (0.7 h) with NO is still present in the system at relatively high concentrations. According to conventional reaction kinetics, OH adds to the double bond in MBO to form an RO2 radical which oxidizes NO to NO2 with the resultant alkoxy radical producing a carbonyl product. If OH is added to the most substituent position, scission of the alkoxy radical produces formaldehyde and 2-hydroxy-2-methylpropanal (2-HMP). 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, 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."

Comment # 10. "Pg. 24054, line 20: "substituent" should be "substituted"

Response. The reviewer is correct and this was corrected.

Comment # 11. Pg. 24054, line 29: Presumably the authors mean standards are NOT available?

Response. The reviewer is correct and this was corrected.

Comment # 12. 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.

Response. As suggested by the reviewer this paragraph was deleted in the revised manuscript. The reference in this section was also deleted from the reference section.

Comment # 13. Pg. 24056, lines 7–9: Which of these compounds can come from isoprene?

Response. No attempt was made to measure gas phase from isoprene and compares them to MBO gas phase products. We expect based on literature data that some of these compounds could also be in the isoprene gas phase.

Comment # 14. Pg. 24061, line 7: Typo in "2,3-tridroxy-3-methylbutanal"

Response. This was corrected.

Comment # 15. Pg. 24061, lines 17–20: Can glycerol be used as a surrogate standard for DHIP?

Response. Glycerol can be a good surrogate compound for DHIP. However, since all of our mass fractions for monoterpene, isoprene and sesquiterpenes etc... were measured relative to ketopinic acid, this study uses ketopinic acid as surrogate for DHIP (See also our response to comment 1 at the end).

Comment # 16. 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.

Response. It shows that isoprene tracers "methyl tetrols" may also be originated from MBO.

Comment # 17. 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. Response. This was corrected.

Comment # 18. Table 2: it could be helpful to label which ones of these peaks were also detected from isoprene oxidation

Response. We added to Table 2 caption, the following sentence to reflect the reviewer concern: “Methyltetrols were also detected in isoprene SOA.”

Comment # 19. Figure 6: Typo in the legend “methyltetols”

Response. This was corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24043, 2011.