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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* "The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of $NO_x$" *by* T. E. Kleindienst et al.

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We wish to express our appreciation to the reviewers for the comments and helpful suggestions. We particularly appreciate the insight they have provided on the mechanistic issue of forming the diols and tetrols which we expected to be the major issue of the reviews. We have made changes to the manuscript in the spirit of what the reviewers have requested. The interpretative arguments have been adapted to these comments. Other changes are minor and a substantial portion of the manuscript remains the unchanged. Our responses to the specific comments are given below. In some case where the two reviewers have made essentially the same point, we have

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combined the response into a single statement. (These points have been noted by specifically referencing the appropriate reviewer for each comment.)

REVIEWER 1: This manuscript describes the characterization of laboratory-generated secondary organic aerosol from the OH-initiated oxidation of isoprene. Gas phase and aerosol phase (in some cases) products were identified and many bulk aerosols parameters were determined, including the aerosol yield, the organic mass to organic carbon ratio, the organic peroxide yield, and the effective enthalpy of vaporization. The work has been carefully executed and the analysis of the results is appropriate and clearly described. The results provide new insights into mechanism of SOA formation resulting from isoprene oxidation.

The most intriguing finding is that 2-methyl tetrols are observed in the absence of acidicsulfate aerosol. Other workers have invoked acid-catalyzed aqueous aerosol phase chemistry to rationalize the presence of 2-methyl tetrols in isoprene-derived SOA. The authors have obviously gone to some lengths to ensure that aqueous phase aerosols are not apparently present in the reactor. However, I do worry that the extensive aerosol collection, derivatization and workup schemes might actually be causing the hydrolysis of more unstable aerosol phase species and that this is why polyols are apparently observed even under dry aerosol conditions.

RESPONSE: For any collection technique, gas- or aerosol-phase, the possibility always exists that collection process itself, the subsequent analytical methods, and the analysis itself could generate unforeseen processes that may convert the analytes to other compounds. This is particularly true for oxygenated species. We have emphasized this point in the summary of the revised draft to ensure that the reader understands the possibility of confounding sampling artifacts.

REVIEWER 1. In any case, because of this new finding, the authors propose an entirely gas phase mechanism for the production of 2-methyl tetrols in their experiments. The authors propose a mechanistically logical (if kinetically highly uncertain) series

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of gas phase reactions to ultimately produce polyols such as 2-methyl tetrols. Since the relevant RO2 + RO2 rate constants have not been measured for the peroxy radicals produced in the OH-initiated oxidation of isoprene, the authors cite the Jenkin and Hayman paper as evidence that the rate constants for self reactions of beta-hydroxy peroxy radicals could be large. While it is true that such rate constants were larger for beta-hydroxy peroxy radicals generated from ethene than for peroxy radicals generated from ethane, the Jenkin and Hayman work also showed that there is a very large substituent effect on the self reaction rate constants. In particular, Jenkin and Hayman found that the secondary beta-hydroxy peroxy radical self reaction rate constant is an order of magnitude slower than for the primary substituted ethane case, and that the tertiary case is three orders of magnitude slower than for the primary case. In the case of isoprene, the majority of peroxy radicals are predicted to be secondary or tertiary (Lei et al. J. Phys. Chem. A. 2001, 105, 471). Therefore, it seems unlikely that the "average" RO2 + RO2 rate constant for the isoprene system is larger than the secondary beta-hydroxy peroxy radical self reaction rate constant measured by Jenkin and Hayman: 8.4 x 10-13 cm3 molecule-1 s-1. In addition, Jenkin and Hayman also found that the similar RO2 + HO2 rate constants were largely invariant at a value of about 2 x 10-11 cm3 molecule- 1 s-1. Therefore, under NOx-free conditions in these experiments, it seems that the major fate for peroxy radicals should be reaction with HO2 to form peroxides. Indeed, the authors do find that the organic peroxide yield is substantial. For this reason, the authors should mention the work of Claeys and coworkers in which aerosol phase peroxides are proposed as possible key oxidants in the production of polyols derived from isoprene.

REVIEWER 2. Radical chemistry: it is mentioned that either RO2+RO2 or RO2+HO2 reactions may account for some of the products formed; the paper mostly focuses on RO2+RO2 reactions (forming tetrols, etc.) but it is not clear this is the dominant channel. It would be useful if the relative contributions of these pathways were estimated. A simple box model using measured isoprene and H2O2 concentrations, inferred OH levels (from isoprene loss), and estimated peroxy-peroxy rate constants would allow for

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the estimates of [RO2] and [HO2], and therefore a reasonable estimate of the important RO2 chemistry in these experiments.

RESPONSE: The issue raised by the reviewers reduces to the relative competition between the RO2 + RO2 and RO2 + HO2 channels in Reactions (2) and (3), respectively, in Scheme 1. (In this response, all numbered reactions refer to Scheme 1 in the APCD paper.) We concur with the analysis of Reviewer 1 regarding the rate constants for these processes. We should have stated in the text that secondary and tertiary peroxy radicals have self and cross reactions that are substantially lower than primary alkoxy radicals. As noted by Reviewer 1, for isoprene this is a more substantial issue (than perhaps for other compounds) because the branching ratios for the initial formation of the C5(OH)OO radicals tend to favor the secondary and tertiary radicals. However, there are more ways to form the primary radicals. Thus, when summing each of the pathways by peroxy radical type, the branching ratios for the primary: secondary: tertiary radicals are 0.32: 0.23: 0.45, respectively, using the data of Jenkin and Hayman, 1995. (These are essentially the same values one would obtain from Lei et al., 2001.) Thus, one-third of the peroxy radicals are primary and it is possible that these contribute most to the observed RO2 + RO2 chemistry. These points are now incorporated in the revised text.

However, the RO2 + RO2 vs. RO2 + HO2 rate constants are not the entire story for the laboratory experiments in the absence of NOX. Under conditions where NOX is not present, the main sources of HO2 are through the alkoxy radicals following the RO2 + RO2 reaction given by RO2 + R'O2 → RO + R'O + O2. (Under our reaction conditions, HO2 formed from OH + H2O2 is negligible; the rate of isoprene loss due to OH reaction is about a factor of 35 higher than the rate of H2O2 loss.) Thus, HO2 radicals result from either H-atom abstraction of RO by O2 or by an RO decomposition/isomerization. Furthermore, without NO, the rate constants for the processes forming RO are relatively slow. Since the HO2 formation pathways are considerably slower than its reactive pathways, the system would be considered HO2 limited. This succession of reactions is what allows the RO2 + RO2 reaction to form the multi-OH and aldehyde products, such as those given in Scheme (1). However, the atmosphere is typically not HO2-limited and thus,the atmospheric implications need careful consideration. The simplified version of these points have been included in the revised text.

With respect to Reviewer 2 comments regarding our emphasis on the RO2 + RO2 chemistry, we do not feel it has been undue emphasis given that diols and tetrols have been detected in the systems. Nonetheless, we have added more emphasis to the discussion of the RO2 + HO2 reactions to address these comments. However, the slow formation of HO2 radicals compared to their rapid removal by reaction with RO2 makes the modeling of the experimental system without NOX prone to instabilities. We prefer an alternative approach for understanding the branching ratio of RO2 + RO2 and RO2 + HO2 that has been given by Ruppert and Becker (2000). The determination is based on their measured yield of the methylbutenediols of 0.071. The analysis assumes that all the HO2 formed reacts very rapidly with RO2. Since the only source of HO2 is from reactions of the alkoxy radicals (again ignoring OH + H2O2), the formation of ROOH is necessarily equivalent to the removal of RO (0.429). From the calculation, they find that 75% of the RO2 + RO2 reaction forms alkoxy radicals (which subsequently generate HO2) and 25% of the RO2 + RO2 reaction forms stable products, that is the methyl butenediols and the carbonyl co-product. The ratio of the hydroperoxides to the methylbutenediol [ROOH / R(OH)(OH)] is 6:1 (i.e., 0.429/0.071). Since the isoprene to H2O2 ratio is only modestly lower in our experiments, we also use this value as an estimate for the formation of the hydroperoxides and diols in our experiments. Thus, while the RO2 + RO2 channel probably dominates in this system due to dearth of HO2 sources, in fact the hydroperoxides formed dominate the diols by nearly an order of magnitude and tetrols by considerably more. We believe this is an equally feasible approach to understanding the issue as modeling the system. It is clear, however, that these results cannot be applied directly to the ambient conditions, because under most conditions HO2 is probably not limited as it is in the experimental system.

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While similar arguments apply for the formation of the methyl tetrols, several additional uncertainties come into play. First, the rate constant for Reaction (4) (OH + methyl-butenediol) has never been measured but is probably an order of magnitude slower than OH + isoprene. The influence of multiple OH groups on the RO2 + RO2 rate constant as in Reaction (5) is unknown and difficult to estimate, although it is probably certain that secondary or tertiary peroxy radicals will have a lower rate constant than that of the primary peroxy radicals. RO2 + RO2 cross reactions are an additional complication. Admittedly, we have only shown the self reaction of RO2 + RO2 in Scheme 1 for tetrol formation. RO2 cross reactions are now mentioned in the caption of the Scheme 1. Finally, while limitations in the formation of HO2 in the system will mitigate the importance of Reaction (6) in the scheme, the production of hydroperoxides still dominates the production of tetrols in the aerosol as the experimental data suggests. We have now included a form of these arguments in the Atmospheric Implications section.

REVIEWER 1: The authors also surmise that there still must be substantial RO2 + RO2 chemistry occurring in the presence of NOx. However, if one uses the NOY concentration given in Table 2 as an upper limit for NO, and the delta isoprene concentration given in Table 2 as an upper limit for RO2 and kRO2 + RO2 = 8.4 x 10-13 cm3 molecule-1 s-1 and kRO2 + NO = 8.8 x 10-12 cm3 molecule-1 s-1 (Miller et al., Phys. Chem. Chem. Phys. 2004, 6, 3402), the RO2 lifetimes are about 50 and 100 s-1, respectively. Since the RO2 concentration is probably grossly overestimated within this approximation (5 x 1013 molecule cm-3), it seems likely that RO2 + NO reactions are dominant in the NOx-present experiments. It would have been interesting if the authors had tried experiments with very high NOx levels to see if the aerosol properties were changed in such a situation where RO2 + NO chemistry is clearly dominant. In any case, this is also an important point, since one would expect different aerosol products if RO2 + NO reactions are dominant.

RESPONSE: If we gave the impression that RO2 + RO2 chemistry was important

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under conditions of even modest NO concentrations, we certainly did not intend to. (We cannot find any statement in the text to support the conjecture of the reviewer.) We are more than aware of the competitive chemistry (RO2 + NO vs RO2 + RO2/HO2) described in the comment and obviously have no issue with it. In an experimental hydrocarbon/NOX system, the only possibility for HO2/RO2 cross- and self-reactions to be important would be during periods in the reaction profiles where ozone is sufficiently large to reduced the NO concentration to extremely low levels, experimentally that would mean to levels below the limit of detection on the NOX analyzer.

With respect to the suggestion of Reviewer 1 regarding conducting additional NOX experiments, we have already conducted and reported such experiments (Surratt et al., Environ. Sci. Technol. 41:5363, 2007). In that work, we found that the formation of organic aerosol occurred only when the NO was below the detection limit of the NOX monitor. At low NO levels, both the organic aerosol and the methyl tetrols were detected in the system albeit at very low levels for the methyl tetrols. As another indicator of isoprene aerosol formation, 2-methylglyceric acid was also detected in the system (through secondary reaction of the methacrolein system) and noted in the discussion section. The nature of the products formed and changes which occurred upon adding acidic aerosol were also described in the Surratt et al paper. What is clear in these experiments and from Surratt et al. is that NO levels must be very low for organic aerosol to form in the isoprene system in the absence of acidic aerosol.

REVIEWER 1: In summary, I think that the authors should point out that their proposed mechanism is contingent on the RO2 + RO2 rate constants being much larger than one would expect by extrapolating the Jenkin and Hayman results. With the more conservative estimates outlined above, it seems more likely that RO2 + HO2 or RO2 + NO reaction pathways are more important under the experimental conditions.

RESPONSE: We have implement the intent of this comment and that of Reviewer 2 into the revised version of the manuscript. We have now provided a more complete description of the limitations of the gas-phase chemistry including the following: (1)

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Inclusion of the possibility that other RO2 + RO2 and RO2 + HO2 reactions may be occurring. (2) Limitations of the present results on the Jenkin and Hayman (1995) results, in particular, by noting that the RO2 + RO2 rate constants would have to be considerably higher than what one would get by extrapolating Jenkin and Hayman (1995) to the peroxy radicals likely to be formed here. (3) Noted limitations in the possible sources of HO2 in these experiments as given above. Even under these circumstances, the ratio of ROOH to R(OH)2 is at least 6:1. (4) Explained that such limitations of HO2 are probably not found in real atmospheres even under low NOX conditions, given other sources of RO2 and HO2 radicals being present. (5) Included in Appendix A the possibility that the methyl butenediol-TMS compounds detected in ambient samples may have been produced from precursors other than the methyl butenediols themselves.

REVIEWER 1: The authors should also consider the following technical comments (in manuscript order).

1) Typo: p. 10016 line 23: “that previous” should be “that used previously”

RESPONSE: This has been corrected in the revision of the manuscript.

2) Typo: p. 10016 line 25: “masses” should be “mass loadings” C1310

RESPONSE: This has been corrected in the revision

3) Typo: p. 10018 lines 4-5: “contributions isoprene oxidation” should be “the contributions that isoprene oxidation”

RESPONSE: This has been corrected in the revision.

4) Typo: p.10019 line 6: “2-vinyloxirine” should be “2-vinyloxirane”

RESPONSE: This has has been corrected in the revision.

5) Clarification: p. 10026 lines 18-23: The statistical uncertainty in the enthalpy of vaporization values should be reported so that the reader can assess whether the NOx-free and NOx-present values are significantly different.

RESPONSE: We have now included an estimate of the uncertainty in the effective enthalpies of vaporization including random error and an estimate of the systematic error. At the 2-sigma level, the difference between NOX-free and NOX-present values are not statistically significant.

6) Figures 2, 3, and 4 would be much more readable if the structures of the key species were overlaid on the plots.

RESPONSE: We are currently working on doing this provided that the compound placement does not detract from the clarity of the chromatograms.

COMMENTS FROM REVIEWER 2. (Response to the comments not addressed earlier.)

REVIEWER 2: This work explores several aspects of secondary organic aerosol (SOA) formation by isoprene photooxidation. Studies are carried out in a steady-state chamber, and the focus of most experiments is on NOx-free conditions, which have received far less study than high-NOx photooxidation. The yields, composition, volatility, and formation mechanism of the SOA are all studied in some detail, significantly adding to our understanding of the overall reaction system. The results are important and interesting, the paper is well-written and easy to follow, and thus this work is certainly worthy of publication in ACP. However, a few major points, relating to the SOA formation mechanism and aerosol yields, need to be addressed prior to publication.

Issues from major point (1) are considered above together with Reviewer 1 comments.

REVIEWER 2:(2) Mechanism of tetrol formation: The lack of evidence of C5 hydroxycarbonyls in either the gas or particle phases seems significant. These species would be expected as co-products of diols (first-generation products) or tetrols (second-generation products), if such compounds are formed by RO2 + RO2 chemistry. The authors mention that these are not measured (p. 10032 line 8 and p. 10034 line 3) but do not comment on why this might be the case. Two possibilities include (1) the polyols are formed by mechanisms other than RO2+RO2 reactions (as shown in Scheme 1), or (2) hydroxycarbonyls are exceptionally reactive, possibly by oligomerization reactions. Either possibility would be an important result, and so should be mentioned at least briefly.

RESPONSE: This is an important comment from the reviewer and we may not have dealt with it in sufficient detail in the original manuscript draft. With the data obtained during the study, we cannot distinguish between the two possibilities raised by the reviewer. For point (1), another gas phase reaction involving RO2 + RO2 is certainly a possibility that cannot be ignored and the possibility is included in the text in the discussion of the absence of a hydroxycarbonyl co-product. Point (2) is a possibility for example if the hydroxycarbonyls have particularly large photolysis rates that would remove them rapidly. Oligomerization rates may also be a possibility but if the oligomeric SOA formation data from Kalberer et al. (2004, Science 303:1659; 2006, EST 40:5917) is any guide, the process may be too slow to account for their removal on the time scale of these experiments. In any case, we now consider in more detail the implication of not detecting the hydroxycarbonyls.

REVIEWER 2:(3) Comparison with previous results: the reported yields are significantly lower than the NOx-free yields measured by Kroll et al. 2006. This difference is reported but not explored in any detail. Possible reasons should be discussed, and atmospheric implications at least touched upon. I can think of at least three possibilities for such differences (others may be important also): (i) differences in radical chemistry (RO2 vs HO2, as described above) – based on the low isoprene concentrations, Kroll et al. 2006 estimated RO2+HO2 reactions would dominate over RO2+RO2 reactions in their experiments. (ii) differences in photolysis: the authors added UVB lights to their chamber to enhance the photolysis of H2O2. This would likely enhance organic peroxidephotolysis as well, and could lead to a reduction in SOA mass (greater than the reduction observed by Kroll et al. under UVA irradiation). Perhaps an average emission spectrum of the lights used would be useful here? (iii) differences in timescale:

significant amounts of butenediols are measured in the gas phase. If these are indeed intermediates to tetrol (and SOA) formation, then there exists a substantial amount of unreacted SOA precursors in the air removed from the steady-state chamber. This would have the effect of lowering yields below their atmospheric values. Of course, this is also a potentially important issue for static-chamber experiments (e.g. Kroll et al.), but the longer timescales of those experiments may lead to higher yields.

RESPONSE: Again the reviewer makes an important point and has provided some logical explanations to explain the differences in yields. We have now discussed the differences in our results with those of Kroll et al (2006) in the discussion section. However, the reviewer's point raises the more basic question of what the best way is to conduct a NOX-free experiment for generating organic aerosol in a smog chamber. If one uses radiation to enhance the formation of OH radicals from the photolysis of H2O2, the possible photolysis of organic peroxides always represents a drawback. By contrast, if one relies on a much slower generation of OH by using radiation that only weakly photolyzes H2O2, wall reactions from adsorbed NOX can playing a confounding effect on the system and aerosol losses to the chamber walls become a more important problem. Perhaps one way around the problem of generating OH radicals in the absence of H2O2 and NOX might be to use nonphotolytic sources of OH, such as the O3 + 2,3-dimethylbut-2-ene reaction (Lambe et al. Environ. Sci. Technol. 41:2357; 2007) or the O3 + hydrazine reaction (Tuazon et al. Int. J. Chem. Kinet. 15:619; 1983). However, such experiments would have to be thought through very carefully. And as stated above, limitations in the HO2 radical concentrations in the chamber limit the applicability of the experiments to ambient conditions. Of course, HO2 radicals can be enhanced by using higher H2O2:isoprene ratios as used by Kroll et al (2006). Taken together, these issues makes it difficult to study chemical systems in the absence of NOX. Some of the shortcomings of the such studies using photolytic techniques to generate OH without NOX are now more fully described in the text in the summary.

With respect to specific differences with this work and Kroll et al. (2006), one major

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difference is in the H2O2:isoprene ratios. As noted, Kroll et al. (2006) used much high ratios than those used in this study or by Ruppert and Becker (2000). This is the main reason the Kroll et al. (2006) conditions favored RO2 + HO2 reactions over the RO2 + RO2 reactions. A second difference is a far higher seed aerosol concentrations used in that study compared to the present study. Differences in the radiation distribution are also likely to be a factor. (We do not have the chamber radiation profile requested by the reviewer.) Finally differences in time scale are always a potential problem in SOA yield measurements. For a chamber experiment, it become a trade-off between creating a large extent of reaction while coping with aerosol wall loss rates that plague any chamber yield measurement. These points are now all covered toward the end of the discussion section.

Minor comments:

SOA/SOC ratios: these should also be compared to those reported from AMS measurements of isoprene photooxidation SOA by Aiken et al. (2008).

RESPONSE: Aiken et al. (2008) addressed OM/OC for a number of HC/NOX chamber systems including isoprene/NOX who reported a value of 1.75 (interpolated from Figure 3b in that paper). This compares favorably to values 1.5 with NOX and 1.9 in the absence of NOX. This comparison has now been included in the discussion section of the text.

SMPS data is collected but is not used for the aerosol yield measurements. Are these results (assuming a density) in general agreement with the gravimetrically-determined yields?

RESPONSE: For dynamic mode experiments where gravimetric mass measurements are made, we generally choose to use the SMPS data for qualitative purposes only and not for determinating yields. This is due mainly to the lack of an external calibration and systematic errors that can arise in using the SMPS data for determining absolute masses. These systematic errors tend to be far more pronounced when using the

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chamber in a dynamic mode of operation, where the aerosol distributions produced from hydrocarbon oxidations are considerably broader than those found in a static mode experiments having essentially the same initial concentrations. (For example, the aerosol distributions can exceed the SMPS size detection window in some cases.) By contrast, for measurements using only relative values, such as the VDMA measurements, the integrated SMPS volumes have been found to be work well and gives linear regressions. Thus, whenever we have gravimetric measurements, we have used the data from the SMPS for diagnostic purposes and now state this in the revised text. Nonetheless, as requested by the reviewer to see if using the SMPS absolute masses (volume data with an assumed density) gives closer correspondence to the yields of Kroll et al. (2006), we have examined a subset of the SMPS data at face value. The SMPS data suggests that the SOA yields could be 25 – 30% higher than that determined gravimetrically. While this brings it somewhat closer to the Kroll et al. (2006) values, it still does not completely account for the differences found.

10019, line 17: the observations by Kroll et al. 2006 and Dommen et al. 2006 were really that SOA appears when NO is low, not necessarily when RO2+RO2 reactions begin (RO2 was not measured in either study). Kroll et al. attributed the SOA formation to the onset of RO2 + HO2 reactions.

RESPONSE: We have corrected the text to more accurately reflect the terminology of Kroll et al. (2006) and Dommen et al. (2006). For experiments without NOX present, the RO2 + HO2 process clearly dominated. For the Kroll et al. (2006) measurements without NOX, the H2O2 concentrations were sufficiently high to generate HO2 by the reaction OH + H2O2 → HO2 + H2O.

10020, line 13: Below -> above?

RESPONSE: Clearly, it should have read above. However, we felt the parenthetical statement was superfluous and has been dropped.

10020, line 27: this effect (loss of H2O2 in the ozone scrubber) should be expanded

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upon. Have the measurements of H2O2 been validated in the laboratory using known concentrations of H2O2, or are they just rough estimates?

RESPONSE: They have not been independently validated for known H2O2 concentrations. The use has been based on previous work with compounds that are generally thought to be considerably more stable than H2O2, such as HCHO, which is completely destroyed in the MnO2 trap used to quantitatively remove ozone. Nonetheless, we now state in the text that H2O2 measurements are only estimates.

10022, lines 27-29: obtaining quantitative results from this technique requires assuming the SOA components have MWs similar to that of benzoyl peroxide; this needs to be stated explicitly here and in the results (p. 10034, line 9).

RESPONSE: For the organic peroxide determination, we have conducted all measurements and calibrations on a molar basis. We then assumed that the average molar extinction coefficient (at 470 nm) of the organic peroxide SOA components and that of benzoyl peroxide (MW 242 g mol-1) were the same. It is only in determining the organic peroxide SOA yields that the units are changed from molar concentrations to mass concentrations using an average molecular weight of 150 g mol-1. This is stated both in the text as well as in the caption of Table 4. We have rewritten these parts of the text to make them clearer.

10029, line 2: C5 tetrols are semivolatile and so likely have a significant gas-phase fraction. Based on the measured boiling point and dHvap (http://webbook.nist.gov), the saturation vapor pressure of erythritol at 298K is 25 ug/m3; adding an extra methyl group (making a C5 tetrol) would lower this by a factor of ∼3, for a tetrol vapor pressure of ∼8 ug/m3. Thus the presence of C5 tetrols in the gas phase should probably not be discounted.

RESPONSE: We have taken the reviewer's point and changed the text to acknowledge the possibility of the methyl tetrols being in the gas-phase. This is also suggested from the paper by Angove et al. (2006) for products from 1,3-butadiene.

10031, line 8: the Kornblum reference seems inappropriate, as that work focused on a closed-shell, base-catalyzed mechanism. Russell 1957 (JACS 79:3871) focuses on RO2 self-reactions.

RESPONSE: We have replaced the reference as suggested by the reviewer and adapted the text appropriately.

10034, line 22: according to Kroll et al. 2006, density was estimated using an AMS and SMPS rather than just assumed.

RESPONSE: The text has been changed to reflect the reviewer's comment. Assumed has been changed to measured.

10035, line 25: it is unclear how oligomerization would increase oxygen content – most of the oligomers detected by Surratt et al 2006 have an equal or smaller number of Os.

RESPONSE: We have changed the text to delete the reference to oligomers.

References mentioned not appearing in the APCD version of the paper:

Aiken, A.C. et al.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. Environ. Sci. Technol., 42, 4478-4485, 2008.

Kalberer et al.: Identification of polymers as major components of atmospheric organic aerosols. Science, 303, 1659-1662, 2004.

Lambe, A.T. et al.: Controlled OH radical production via ozone-alkene reactions for use in aerosol aging studies. Environ. Sci. Technol., 41, 2357-2363, 2007.

Lei, W. et al.: Theoretical study of OH – O2 – isoprene peroxy radicals. J. Phys. Chem. A, 105 471-477, 2001.

Russell, G.A.: Deuterium-isotope effects in the autooxidation of aralkyl hydrocarbons: Mechanism of the interaction of peroxy radicals, J. Amer. Chem. Soc., 79, 3871-3877,

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1957.

Tuazon et al.: The gas-phase reaction of hydrazine and ozone: A nonphotolytic source of OH radicals for measurement of relative OH radical rate constants, Int. J. Chem. Kinet., 15, 619-629, 1983.

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