

Comments for Carlton et al. (2009, ACPD)

1.) Introduction. Page 8264. Lines 4 – 5.

For both citations provided here, I would suggest adding in “eg.,” or include ALL other relevant field and laboratory studies (since this is a review article) that have also shown that isoprene oxidation does contribute to SOA formation. If the authors choose the latter, then to make it easier for the authors I suggest that the authors add the following reference, which recently summarized all the relevant lab and field studies related to isoprene SOA in Table 4 of this other recent review article:

Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, Th. F.; Monod, A.; Prévôt, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys. Discuss.*, 9, 3555–3762, 2009.

2.) Section 2.1. Page 8265. Lines 16 – 19.

I should point out that Hallquist et al. (2009) provided a table (i.e., Table 4) summarizing all the field studies in which the 2-methyltetrols have been measured, as well as the locations of these measurements. In addition, it is noted that the highest concentrations of the 2-methyltetrols observed thus far was in the Research Triangle Park, NC (~365 ng/m³). Maybe citing this other review article as something like “(Hallquist et al., 2009, and references therein)” might help to include all other field studies that have observed 2-methyltetrols in ambient aerosol? This is only a suggestion.

3.) Section 2.1. Page 8265. Line 18.

Please add “Wang et al., 2004” to the citation on this line. Wang et al. (2004) was a complimentary manuscript to Claeys et al. (2004a) that provided the detailed mass spectral interpretations of the trimethylsilyl derivatives of the 2-methyltetrols detected by GC/MS, which makes this study extremely important to include in the reference section of this present manuscript.

The reference details of Wang et al. (2004) are:

Wang, W.; Vas, G.; Dommisse, R.; Loones, K.; Claeys, M. Fragmentation study of diastereoisomeric 2-methyltetrols, oxidation products of isoprene, as their trimethylsilyl ethers, using gas chromatography/ion trap mass spectrometry. *Rapid Commun. Mass Spectrom.*, 18, 1787–1797, 2004.

4.) Section 2.1. Page 8265. Line 26.

The word “adduct” currently used to describe heterogeneous particle-phase reaction products is not appropriate. The word “adduct” could give the wrong impression to readers who are not as familiar with this topic; more specifically, it gives the impression that these could be artifacts. I suggest that the authors change the word “adduct” to something like “heterogeneous particle-phase reaction products” or “accretion products.”

5.) Section 2.1. Page 8264. Lines 26–28.

For the hemiacetal dimer the authors need to remove the Szmigielski et al. (2007) reference from the citation. Szmigielski et al. (2007) was a complimentary paper to Surratt et al. (2006) that focused on characterizing only oligoester products produced from the photooxidation of isoprene under high-NO_x conditions.

The authors should also add here that diesters formed by the esterification of two 2-methylglyceric acid residues, previously characterized by Surratt et al. (2006) and Szmigielski et al. (2007) in laboratory-generated high-NO_x isoprene SOA, was detected in ambient aerosol for the first time by Jaoui et al. (2008). The reference information for Jaoui et al. (2008) is:

Jaoui, M.; Edney, E. O.; Kleindienst, T. E.; Lewandowski, M.; Offenberg, J. H.; Surratt, J. D.; Seinfeld, J. H. Formation of secondary organic aerosol from irradiated α-pinene/toluene/NO_x mixtures and the effect of isoprene and sulfur dioxide. *J. Geophys. Res.*, 113, D09303, doi:10.1029/2007JD009426, 2008.

It is suggested that the authors change “organosulfates” to “organosulfates (including nitrated derivatives).” Both nitrooxy-organosulfates and organosulfates of isoprene have been detected in ambient aerosol collected from the U.S. (Surratt et al. 2007a, b, 2008) and Europe (Gómez-González et al., 2008). Additionally, the authors should add two additional relevant references in the citation provided here for the detection of organosulfates of isoprene in ambient aerosol. These include Surratt et al. (2008) and Gómez-González et al. (2008). The following is the detailed reference information that should be added to the reference section:

Gómez-González, Y., Surratt, J. D.; Cuyckens, F.; Szmigielski, R.; Vermeylen, R.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Kleindienst, T. E.; Edney, E. O.; Blockhuys, F.; Van Alsenoy, C.; Maenhaut, W.; Claeys, M. Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-)electrospray ionization mass spectrometry. *J. Mass Spectrom.*, 43, 371–382, 2008.

Surratt, J. D.; Gómez-González, Y.; Chan, A. W. H.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.;

Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H. Organosulfate formation in biogenic secondary organic aerosol. *J. Phys. Chem. A*, 112, 8345–8378, 2008.

6.) Figure 2. Chemical structures of isoprene SOA constituents and referencing.

This figure does not include all of the known isoprene SOA tracers (see Hallquist et al., 2009, Table 4). For example, the diester formed from the esterification of two 2-methylglyceric acid residues (as detected in the lab by Surratt et al. (2006)) was recently reported for the first time in ambient aerosol collected from RTP, NC (Jaoui et al., 2008, see above for reference details).

This figure is missing several other isoprene SOA constituents that have been previously characterized in lab-generated aerosol that have now been detected in ambient aerosol. These include:

- (a) Sulfated and nitrated derivatives of C5-alkane triols, and isomers (MW 245) (yes, alkane not alkene!). (Surratt et al., 2008)
- (b) Sulfated derivatives of C5-dihydroxydinitrates of isoprene, and isomers (MW 306) (Surratt et al., 2008; and also seen in isoprene SOA generated by NO₃ oxidation – Ng et al., 2008).
- (c) Sulfated derivatives of hemiacetal dimers with a C5-dihydroxycarbonyl part, and isomers (MW 334) (Surratt et al., 2008)

For the citation provided in the last sentence of the Figure Caption, I suggest the authors include the study of Surratt et al. (2008) since this study recently characterized additional nitrated and sulfated isoprene SOA constituents in both lab-generated and ambient organic aerosol.

Other minor corrections for this Figure:

- (a) Change reference for the C5 trihydroxy nitrate sulfate ester to Gómez-González et al. (2008). Surratt et al. (2007a) only mentioned unpublished results for this compound. This was the first time MS data was published for this compound.
- (b) Change reference for the 2-methylglyceric acid sulfate ester to Gómez-González et al. (2008). Again, Surratt et al. (2007a) only mentioned the unpublished result but was published for the first time here.
- (c) Add “(and isomers)” to the “C5-trihydroxy nitrate sulfate ester,” to the “2-methyltetrol sulfate ester,” and to the “C10 hemiacetal dimer” in the figure.

7.) Section 2.1. Page 8265. Line 28.

The authors mention here that the isoprene SOA tracers shown in Figure 2 only add up to about 100 ng/m³, resulting in isoprene SOA having low contributions to the overall organic mass fraction found in ambient aerosol. First, as mentioned earlier in my review, the 2-methyltetrols have actually been observed alone to be as high as 365 ng/m³ in ambient aerosol. Additionally, I think some caution is warranted here, especially since recent work has estimated the contribution of organosulfates to the total organic mass

fraction observed in ambient aerosol (using bulk chemical methods, i.e., the subtraction of total S [measured by PIXE or XRF] and inorganic S [measured by IC methods]). Surratt et al. (2008) recently estimated that upwards of ~30% of the TOM could be due to organosulfates. Most (if not all) of the organosulfates characterized in ambient aerosol thus far form from isoprene and monoterpene oxidation products. Unfortunately, we do not have suitable surrogate or authentic standards to estimate the individual mass fractions of the organosulfates of isoprene. However, based on recent work by Surratt et al. (2008) and Lukács et al. (2008, see reference info below), it is possible that the sulfated and nitrated (i.e., nitrooxy organosulfates) derivatives of isoprene contribute a substantially higher fraction of isoprene SOA to the organic mass observed in ambient aerosol than currently estimated.

Lukács, H.; Gelencsér, A.; Hoffer, A.; Kiss, G.; Horváth, K.; Hartyáni, Z. Quantitative assessment of organosulfates in size-segregated rural fine aerosol. *Atmos. Chem. Phys.*, 9, 231–238, 2009.

8.) Section 2.1. Page 8266. Lines 10 – 16.

What is interesting about Matsunaga and coworkers observations is how this likely relates to recent work done by Surratt and coworkers (Surratt et al. 2008; Gómez-González et al., 2008). Surratt et al. (2008) recently observed and characterized organosulfates of glyoxal, methylglyoxal, and hydroxyacetone in both laboratory-generated isoprene high-NO_x SOA and ambient aerosol collected from the S.E. USA. These sulfated derivatives of these very volatile oxidation products of isoprene could explain why they have been observed previously in ambient aerosol collected by Matsunaga et al. (2003, 2004, 2005). The sulfated derivatives likely decrease the volatility enough to keep these oxidation products in the particle phase. It should be pointed out that Matsunaga and coworkers derivatized the SOA constituents and then analyzed them by GC methods. It has been discussed recently that this approach could degrade particle-phase reaction products or cause for the mis-interpretation SOA constituents (like that of the organosulfates) (Surratt et al., 2008). There do remain many open questions on how these oxidation products, like glyoxal, become sulfated, especially due to recent results provided by Galloway et al. (2008). Galloway et al. (2008, reference information below) demonstrated that glyoxal uptake in the dark in the presence of wet highly acidified sulfate seed does not produce the sulfated derivative of glyoxal; however, this study did demonstrate that it forms when glyoxal is reactively taken up onto wet ammonium sulfate seed aerosol in the presence of light. This latter finding is significant because it does suggest that there is likely some aqueous-phase photochemical reaction leading to the formation of the glyoxal sulfate (which was formed near neutral pH due to the use of only ammonium sulfate seed aerosol). Additionally, it shows that unrealistically high aerosol acidities (typically used in chamber studies) are not necessary to form some types of organosulfates (like that of the glyoxal sulfate – now characterized as glycolic acid sulfate). Maybe something should be noted here along these lines?

Galloway, M. M.; Chhabra, P. S.; Chan, A. W. H.; Surratt, J. D.; Flagan, R. C.; Seinfeld, J. H.; Keutsch, F. N. Glyoxal uptake on ammonium sulphate seed aerosol: reaction

products and reversibility of uptake under dark and irradiated conditions. *Atmos. Chem. Phys. Discuss.*, 8, 20799–20838, 2008.

9.) Page 8279, Lines 15-17

Semivolatile loss does not necessarily mean running experiments under atmospherically relevant oxidation rates. In addition to photolysis or chemical loss, vapors can be lost to the walls, which does not occur in the atmosphere. In that case, running at high OH levels is more relevant because semivolatile vapor wall loss is minimized. Until the exact nature of this loss is known, one cannot conclude at what OH levels experiments should be conducted.