

Interactive comment on “Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene” by R. M. Healy et al.

Anonymous Referee #1

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General Comments

This manuscript demonstrates the utility of a recently developed denuder-filter sampling technique to the study of the gas/particle partitioning of carbonyl products produced from the photooxidation of isoprene and 1,3,5-trimethylbenzene (1,3,5-TMB) under high-NO_x conditions. To the knowledge of this reviewer, this is the first time that such measurements have been conducted for these two systems. Isoprene and 1,3,5-TMB photooxidation experiments were conducted in collaboration at the Paul Scherrer Institut (PSI) and University of College Cork (UCC) using the denuder-filter sampling technique for intercomparison of the results. The authors carefully conducted well-designed experiments/tests for determining the collection efficiency of the PFBHA-coated denuder. A major strength of these tests involved the use of a PTR-MS, which

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allowed the authors to measure in real-time the breakthrough of carbonyl products of interest. The use of the PTR-MS after the denuder clearly showed that the setup of the denuder-filter sampling technique efficiently collects the carbonyl products from the chamber air mixture. The determination of the denuder collection efficiency allowed the authors to establish a very reasonable sampling time (i.e. 50 min for the PSI chamber and 20 min for the UCC chamber), which allowed for enough sample to be collected on both the denuders and the filters for offline chemical analysis by GC/MS. The main result of this study was the authors found that the $K_{p,i}$ (experimental) values were much larger than the $K_{p,i}$ (theoretical) values for many of the carbonyl products identified; this was especially true for dicarbonyl products like that of methylglyoxal and glyoxal. In addition to previously published mass spectra, this main result provides further evidence for heterogeneous reaction pathways contributing to SOA formation. The main weakness of this study lies in the fact that many experimental details were left out (see comments below). In addition, the discussion of the results in Section 3.3.1 failed to include some recent work that elucidated other potential heterogeneous pathways (besides hydration followed by oligomerization) that may lead to significant amounts of SOA (see comments below). This paper is well written, concise, and is scientifically sound; therefore, it is recommended that this paper be accepted for publication in ACP once the authors clearly address the specific comments/questions outlined below.

Specific Comments/Questions

1.) Experimental Section, Page 4732, Line 11: Although the authors refer the readers to Temime et al. (2007) for the details of how the denuder tubes and filters were coated, the extraction protocols for the denuders and filters should be more completely described here.

a.) How were the carbonyl products extracted from the filters/denuders (e.g. sonication)? If sonication was used, how long did you sonicate for?

b.) What type of filter media (e.g. quartz, glass fiber, or Teflon) was used? What is the

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diameter and pore size of the filter media?

c.) What gas was used to blow down the 1 mL of filter extracts to near dryness? Was heat employed when drying down these filter extracts to near dryness?

d.) How long did you allow the filter extracts to derivatize with PFBHA and was this at room temperature?

2.) Experimental Section: Since the authors extract the denuders/filters using different solvents/solvent mixtures, how do you expect this to affect the results? Are the extraction efficiencies different? If so, were these considered in your calculations? Also, it appears from your experimental description that you have different final volumes for your filters collected from each chamber. Do you also expect this to affect your calculations? Was this taken into consideration? These questions should be addressed either in the experimental or results/discussion section.

3.) What potential artifacts need to be considered with the employed denuder-filter-denuder sampling device? For example, does the removal of gas-phase carbonyl products from the chamber air mixture sampled by the first denuder affect the properties of the aerosol (e.g. chemistry and loading) collected on the filter? Some discussion of this issue should be included in either the experimental or results/discussion section.

4.) Page 4742, Lines 14-15: Why was 120 used for the MW_{om} parameter in the K_{p,i} (theoretical) calculations for both the isoprene and 1,3,5-TMB systems? Recent mass spectra published for isoprene (Dommen et al. 2006; Surratt et al, 2006) and 1,3,5-TMB (Kalberer et al., 2004) SOA suggest that this number is not the same for both systems and is actually higher (i.e. average MW of ~ 300 and 500 for isoprene and 1,3,5-TMB, respectively).

This reviewer wanted to briefly mention that the assumption of 1 for the activity coefficients is likely the best these authors can do at this time. In order to know the exact activity coefficient, this would require complete knowledge of all organic constituents

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found in the aerosol collected. Currently, we are still limited in characterizing all of the organic products found in SOA due to the available analytical methods.

5.) Section 3.3, Page 4739, Lines 3-5: Even though it is required to use high mixing ratios of isoprene and 1,3,5-TMB to generate sufficient amounts of organic aerosol mass for the offline chemical measurements (i.e. GC/MS with prior derivatization), how does the high aerosol loadings affect the interpretation of the results? Specifically, at atmospherically relevant organic aerosol mass loadings (i.e. $\sim 5\text{-}10\text{ }\mu\text{g}/\text{m}^3$), would you expect to see the carbonyl products contributing 5 and 10 % to the total mass of SOA produced from the photooxidation of isoprene and 1,3,5-TMB, respectively? For example, the high organic aerosol loadings generated in these experiments likely favor the reactive uptake (and as a result oligomerization) of glyoxal and methylglyoxal. This reviewer believes that some discussion of this issue should be included somewhere in the text.

6.) Section 3.3.1: No mention or discussion of the results from Kroll et al. (2005, JGR) were included here. This study examined in detail the reactive uptake of many potential carbonyl products (e.g. glyoxal, methylglyoxal, formaldehyde) on inorganic seed aerosol under humid and dark conditions. Importantly, Kroll et al. found that only glyoxal reactively uptakes on ammonium sulfate seed aerosol under dark conditions and when the RH is $\sim 50\%$. Surprisingly, even at high mixing ratios ($\sim 960\text{ ppb}$), Kroll et al. showed that methylglyoxal does not reactively uptake under dark conditions on inorganic seed aerosol at a RH of $\sim 50\%$. From the discussion in Section 3.3.1, the authors seem to suggest that hydration reactions followed by oligomerization may explain the discrepancy between $K_{p,i}$ (experimental) and $K_{p,i}$ (theoretical) values for both glyoxal and methylglyoxal. This may be partially true for glyoxal, but based on previous results from Kroll et al., this would not hold true for methylglyoxal. Some other heterogeneous process must be occurring to explain the difference between $K_{p,i}$ (experimental) and $K_{p,i}$ (theoretical) for methylglyoxal and possibly for glyoxal, especially considering that the experiments conducted in the present study were done in the presence of light.

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Can the authors provide any additional alternative explanation for the above differences observed between the $K_{p,i}$ (experimental) and $K_{p,i}$ (theoretical) values for the detected carbonyls? It is highly recommended that recent work from Barbara Turpin's lab (i.e. Altieri et al., 2008 and Carlton et al., 2007) be cited and included in this discussion. Altieri et al. showed that OH oxidation of methylglyoxal in bulk water solutions yield acidic compounds (e.g. pyruvic acid) as well as oligoester products. Similarly, the work of Carlton et al. showed that the OH oxidation of glyoxal in bulk water solutions yields acidic compounds as well as oligomers. In addition to these studies, it might be helpful to the authors to include the discussion and citation of their own work done at PSI (i.e. Fisseha et al. 2004, Anal. Chem.), in which they identified organic acids in SOA generated from the photooxidation of 1,3,5-TMB under high-NO_x conditions using IC/API-MS. The organic acids they identified accounted for 20-45% of the SOA mass. Many of these acids previously identified are quite volatile and likely were detected as a decomposition product from an oligomer. The point the reviewer is trying to make here is that photolysis or particle-phase oxidation of methylglyoxal and glyoxal may be occurring and could play a role in forming these potential oligomers.

Considering the above, have the authors given any thought in trying to fully characterize the likely oligomers found in the aerosol phase? It could be worthwhile in extracting and analyzing the filter samples more closely using advanced MS techniques. For example, if the authors were able to identify oligoesters like that of Altieri et al. (2008), this could dramatically improve the quality of this already well-written publication.

The references for Altieri et al. and Carlton et al. are as follows:

Altieri, K. E., Seitzinger, S. P., Carlton, A. G., et al.: Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry, 42(7), 1476-1490, 2008.

Carlton, A. G., Turpin, B. J., Altieri, K. E., et al.: Atmospheric oxalic acid and SOA production from glyoxal: Results from aqueous photooxidation experiments, 41(35),

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7588-7602, 2007.

7.) Page 4743, Lines 23-24: The authors should either alter or delete this sentence, as recent work by Szmigielski et al. (2007, J. Mass. Spectrom.) has shown that trimethylsilylation in combination with GC/ion trap mass spectrometry can detect and elucidate oligoesters of 2-methylglyceric acid found in isoprene high-NO_x SOA. These authors showed that up to trimers could be elucidated by this very informative method. Naturally, the success of this technique in detecting oligomeric products in SOA likely depends upon the nature of the oligomers formed in the SOA. For oligomers of glyoxal and methylglyoxal, the analytical technique used by Szmigielski et al. may or may not be useful, as the oligomeric products could be degraded or altered by this method.

Technical Comments

1.) Page 4729, Lines 7-10: At the end of this sentence you should also cite the work by Surratt et al. (2006, J. Phys. Chem. A) and Szmigielski et al. (2007, J. Mass Spectrom.). These two studies have also confirmed the importance of isoprene as a biogenic SOA precursor and have fully characterized the oligomers (i.e. oligoesters under high-NO_x and hemiacetals and peroxides under low-NO_x conditions) observed.

The reference for Szmigielski et al. is as follows and should be added to the References section:

Szmigielski, R., Surratt, J. D., Vermeylen, R., et al.: Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry, J. Mass Spectrom., 42(1), 101-116, 2007.

2.) Page 4729, Lines 10: The authors cite Kroll et al. 2005 but do not provide the reference details in the References section. The details for this reference is as follows:

Kroll, J. H., Ng, N. L., Murphy, S. M., et al.: Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions, Geophys. Res. Lett., 32, L18808,

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doi: 10.1029/2005GL023637, 2005.

3.) Page 4729, Lines 26-27: I suggest you also include the work of Surratt et al. (2006) and Szmigielski et al. (2007) in this citation, especially since you reference work that studied isoprene SOA. These studies have fully characterized oligoesters formed from the photooxidation of isoprene in the presence of NO_x and found that these compounds accounted for a significant fraction of the total observed SOA mass (~22-34%).

4.) Experimental Section: Even though it is stated in the results section, I think it would be appropriate and useful to clearly state in the PSI and UCC experimental description sections that these experiments were conducted without the presence of inorganic seed aerosol.

5.) Experimental Section, Page 4731, Line 17-18: In this sentence, do the authors mean to say, "The filter is also doped with PFBHA to enable the detection of carbonyl products found in the collected SOA by GC/MS?"

6.) Experimental Section: It would be helpful to the readers to clearly state the temperature of the UCC experiments in the UCC experimental description section, especially since these were conducted at a different temperature from that of the PSI experiments.

7.) Page 4733, Experimental Section, Line 22: What type of mass spectrometer (i.e. ion trap or quadrupole) was used in this study? It would be more informative to list this here.

8.) Page 4740, Line 10: Add Surratt et al., 2006 to this citation.

9.) Page 4741, Lines 10 - 11: Change "oligomer" to "oligoesters" and add Szmigielski et al. (2007) to the citation.

10.) Page 4743, Line 9: Kroll et al. (2005, JGR) should also be included in the citation for reactive uptake studies of glyoxal. The details of this reference are as follows:

Kroll, J. H., Ng, N. L., Murphy, S. M., et al.: Chamber studies of secondary organic

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aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res.-Atmos., 110, D23207, doi: 10.1029/2005JD006004, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4727, 2008.

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