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Atmospheric
Chemistry
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Discussions

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

R. M. Healy et al.

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We would like to thank the reviewers for their comments and helpful suggestions. We have made changes to the manuscript in order to address these issues. Most of these changes are minor and the overall conclusions of the work remain the same. Nevertheless, the comments of the reviewers have helped us to improve the quality of the manuscript and are very much appreciated. Our responses to the specific comments of each reviewer are given below.

Responses to comments from Reviewer 1:

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

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described here.

This section has now been expanded to include the required details.

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

Full details of the extraction procedure are now provided in the manuscript. Sonication was not used.

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

The filters used were Pallflex Fiberfilm fluorocarbon-covered glass fibre filters, 47 mm. This information has been included in the manuscript.

(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?

Nitrogen was used to blow down the samples at room temperature; no heating was used. This information has been included in the manuscript (5 to 6 lines from the end of section 2.2).

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

Prior to GC-MS analysis, the denuder and filter extracts were left in the dark at room temperature for at least 72 h to ensure complete derivatization. These details have been added to the manuscript (start of section 2.3).

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 calcula-

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tions? Was this taken into consideration? These questions should be addressed either in the experimental or results/discussion section.

This section (final paragraph in section 2.2) has now been expanded to include the required details. Although the volumes of the filter extracts obtained in the UCC and PSI experiments are different, these factors have been incorporated into the calculations of the concentrations of the derivatives.

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.

The final paragraph in section 3.2 has been expanded to address this point. The potential artifacts arising from use of the D-F-D sampling configuration are (i) deposition of gas-phase species on the filter, leading to an overestimate of the particle-phase concentrations, and (ii) volatilisation of species from the filter, leading to an underestimate of the particle-phase concentrations. Deposition of gas-phase compounds to the filter can occur if the denuder collection efficiency is poor. The collection efficiency of the denuder tube was determined during each experiment at PSI using the F-D-D configuration, shown in Figure 1. GC-MS data obtained for glyoxal and methylglyoxal in experiment ISO_PSI_1 are shown in Figure 6. The results show that significant amounts of these dicarbonyls were collected on the filter and first denuder tube (Tube 1), while the amounts collected on Tube 2 were negligible. This confirms that gas-phase breakthrough of these compounds did not occur to any noticeable extent over a sampling period of 50 min and that the collection efficiency of the PFBHA-coated denuder tube was virtually 100% under the sampling conditions employed. Thus, potential artifacts due to deposition of gas-phase species on the filter were negligible. Volatilisation of species from the filter could occur as a result of a shift in the gas/particle partitioning equilibrium of the mixture following removal of the gas-phase species by the denuder.

The D-F-D configuration was employed to investigate this possibility by using the second denuder to collect any volatilised particle phase species. However, no significant amount of any carbonyl was observed on the second denuder tube, indicating that volatilisation is not an issue.

4. Page 4742, Lines 14-15: Why was 120 used for the MWom parameter in the Kp,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 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.

This is a good point, which is also raised by reviewer 3. The reviewer is correct in stating that recent mass spectra indicate that MWom values could be up to a factor of 4 higher because of the presence of oligomers in the SOA. However, these simulation chamber experiments also showed that the average molecular weight of the SOA increased considerably with the age of the aerosol. Unfortunately the average molecular weight was not determined in the experiments reported here due to the lack of available instrumentation. In addition, the denuder-filter samples were collected at different stages during the experiments, and the average molecular weight was therefore expected to vary between samples. As a result, an arbitrary value had to be selected for MWom. In the study of the gas/particle partitioning of the photooxidation products of toluene (Jang and Kamens, 2001) a value of MWom = 120 was assumed to be representative of the average molecular weight of the toluene oxidation products present in the particle phase. For similar reasons, a value of 130 was selected by Johnson et al, 2005, for determining Kp values for a range of aromatic oxidation products in a large number of SOA formation experiments. In line with these previous studies, a value of MWom = 120 was selected for the calculations performed in this work. Although it is accepted that this value may be an underestimate, it does enable a direct comparison of our results with previous studies to be made. As pointed out in the discussion, the observed difference between the theoretical and experimental gas/particle partitioning coefficient values for glyoxal, for example, is about four orders of magnitude, and it is this significant difference we aimed to highlight in this study. Increasing the average molecular weight even to 500 would only reduce the theoretical partitioning coefficient by a factor of 4 and would not change the interpretation and conclusions of this work. These salient details have been added to the relevant part of the manuscript (following equation 2 in section 3.3.1).

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. ˜5-10 ug/m3), 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.

This is another good point. The amounts of SOA generated in the experiments reported in this work are significantly higher then the typical atmospheric organic aerosol loading. Although the particle mass concentrations are taken into account when calculating the experimental Kp values it is difficult to predict whether the yields of carbonyls found in the particle phase would be similar under typical atmospheric organic aerosol

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loadings since it is likely that these elevated particle concentrations favour the reactive uptake of carbonyls simply by providing a much larger surface area for reaction. Barsanti and Pankow have performed some theoretical calculations on the potential of carbonyls to add mass to ambient particulate matter through accretion reactions, using an initial background organic particulate matter concentration of 15 μgm-3 (Barsanti and Pankow, 2004; Barsanti and Pankow, 2005). The results indicate that accretion reactions of straight-chain aldehydes up to C10 are thermodynamically unfavourable under atmospheric conditions, whilst those of the dicarbonyls, and in particular, glyoxal and methylglyoxal, were expected to have an effect on particulate matter mass loading through hydration/oligomerization and aldol condensation reactions respectively. This indicates that reactive uptake of the dicarbonyls is possible under typical atmospheric organic aerosol loadings. However, it is uncertain how the particle-phase yields of these compounds would differ from those obtained in the presence of elevated particle concentrations. The details outlined above have been incorporated into the relevant part of the manuscript (second last paragraph in section 3.3.1).

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 ˜50%. Surprisingly, even at high mixing ratios (˜960 ppb), Kroll et al. showed that methylglyxoal does not reactively uptake under dark conditions on inorganic seed aerosol at a RH of ˜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 Kp,i (experimental) and Kp,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 Kp,i (experimental) and Kp,i (theoretical) for methylglyoxal and possibly for glyoxal, especially considering that

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the experiments conducted in the present study were done in the presence of light. Can the authors provide any additional alternative explanation for the above differences observed between the Kp,i (experimental) and Kp,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 a., 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-NOx 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.

We very much appreciate this series of helpful comments. This section has been expanded to include discussion of these studies and their relevance to the interpretation of the results obtained in this work. Unfortunately it is not possible to perform more advanced GC-MS analysis of the filter samples because they have been used up. However, the analysis proposed by the reviewer could form the basis of an interesting follow-up study.

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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-NOx SOA.

This sentence has been changed to "GC-MS analysis did not reveal the presence of oligomers in extracts of the filter samples."

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-NOx and hemiacetals and peroxides under low-NOx conditions) observed.

Both studies have been cited at this point in the manuscript. The work of Szmigielski et al. has been added to the list of references.

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

This was an oversight. The full reference details have been added.

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.

This has been done.

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.

The experiments were performed in the absence of seed aerosol and this detail has been added to the manuscript (second paragraph in section 2.1 and second paragraph in section 2.2).

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?"

This sentence has been amended to read as follows: "The filter is also doped with PFBHA to enable detection of particle-phase carbonyls 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.

The chamber at UCC does not have any cooling system and the temperature gradually increased during the experiments from 293 to 305 K. Temperatures were in the range 303-305 K during denuder-filter sampling. The exact temperature at the time of sampling was used for calculations of Kp,i (theoretical). The following sentence has been added to section 2.2 (start of second paragraph); "The chamber does not have any cooling system and the temperature gradually increased during the experiments from 293 to 305 K". The following sentence has been added to section 2.2 (start of third paragraph); "Temperatures were in the range 303-305 K during sampling".

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

An ion trap mass spectrometer was employed. This detail has been added to the manuscript (start of section 2.4)

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

This has been done.

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

The additional reference has been added here and the text altered accordingly to encompass oligoesters.

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

This reference has been added.

Responses to comments from Reviewer 3:

1. In the experimental section, the reviewer wondered if the authors used any internal standard to track the carbonyl loss during the preparation of the gas and particle samples. From the collection to the injection to the GC-MS, the samples went through several steps such as extraction and concentration etc.. The compounds of interest were volatile or semi-volatile, therefore the loss of these compounds is inevitable and need to be considered for the calculation of experimental partitioning coefficients. Please address this issue in the paper.

No internal standard was used for this procedure. Although several of the carbonyl products are volatile, they readily convert to their oxime derivatives on the denuder tube and filter. Since the oxime derivatives are considerably less volatile, sample loss is not a significant issue. The extraction efficiency and reproducibility of the method have been extensively tested for 22 carbonyls and full details are provided in a previous publication (Temime et al., 2007).

2. The compounds shown in Table 2-4 are multi functional. Some have two carbonyls and some have three carbonyls in their molecular structures. Thus derivatization of carbonyls is very complex resulting in various derivatives (e.g., mono, di, tri at different combinations). How do the authors quantify the carbonyls in the gas and the particle phase. How do the authors ensure that the gas phase carbonyls have the exactly

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same derivatization with the particle phase carbonyls. For example, is the gas phase tricarbonyls have the same fraction of di-derivatives or mono-derivatives with those in the particle phase?

This is a good question. Mono-derivatives were not observed for the dicarbonyl compounds identified in this study indicating that the derivatizing agent was present in sufficient amounts to completely convert the carbonyls to the di-derivative form in both denuder and filter extracts. Thus quantification of the dicarbonyls in the gas and particle phases was based on the signal responses observed for their di-derivatives. Oxopropanedial and 2,3-dioxobutanal were the only tricarbonyls identified as oxidation products of isoprene and 1,3,5-TMB. The molecular weights of the tri-derivatives (671 for oxopropanedial and 685 for 2,3-dioxobutanal) lie outside the mass range of the instrument (650 Da) employed in this work, and in the original manuscript, these products were identified and quantified by their di-derivatives. However, following closer inspection of the mass spectra in the literature (Yu et al., 1997; Edney et al., 2001), it seems that the peaks tentatively attributed to butenedial and methylbutenedial in the original manuscript, appear far more likely to be fragments of the tri-derivatives of oxopropanedial and 2,3-dioxobutanal respectively. Thus it appears that the tricarbonyls are present in both the di- and tri-derivatized forms (no mono-derivatives were detected for these compounds). The yields of the tricarbonyls have been recalculated, using the signal responses for both the di-and tri-derivatized forms. Although this has resulted in changes to the experimental partitioning values for oxopropanedial and 2,3-dioxobutanal, the interpretation of the results remains unchanged. However, the reviewer is correct in stating that the relative amounts of di- and tri-derivatives is not constant for these two compounds in every extract, undoubtedly introducing some error in the particle phase yields and experimental partitioning values for these compounds. As a result, the following changes have been made to the manuscript; (i) a number of sentences have been added (at the end of the second paragraph in section 3.3) to describe which derivatized forms were used for quantification of the dicarbonyls and tricarbonyls; (ii) the peaks tentatively attributed to butenedial and methylbutenedial in the original manuscript have been reassigned to the tri-derivatives of oxopropanedial and 2,3-dioxobutanal respectively. The particle phase yields and experimental partitioning coefficients of the tricarbonyls have been recalculated and Tables 2-5 have been changed to reflect this. The section explaining the possible formation of methylbutenedial and butenedial (lines 19-27 on page 4740 of the original manuscript) have been removed; (iii) the work of Edney et al., 2001 has been cited and included in the list of references.

3. Each sampling system (DFD and FDD) has different sampling artifacts. Explain why the DFD system was chosen for the partitioning study? Please explain the potential artifact from the sampling system used by the authors.

This point was also raised by reviewer 1 (point 3) and has been adressed above. The final paragraph in section 3.2 has been expanded to cover artifacts.

4. Page 4742, in the paragraph under the equation 2, the authors assumed the activity coefficients of compound i to be 1 and the MWom 120. How reasonable are these assumptions? Oligomers formed in the particle alter the physical properties and chemical compositions of SOA, which would influence the activity coefficients of semi-volatile products onto the particle. The reviewer looks forward to seeing authors effort on finding appropriate activity coefficients. Otherwise, the theoretical partitioning coefficients obtained in the paper are not much meaningful.

This is a good point, which is also raised by reviewer 1 (point 4). Complete knowledge of all the organic constituents in the particle phase is required for determination of the exact value of the activity coefficient. Since the composition of the SOA produced from isoprene and 1,3,5-TMB photooxidation is largely unknown, the value of this parameter is assumed to be 1, as in previous studies (Johnson et al., 2006; Kamens et al., 1999, Jang and Kamens, 2001). As pointed out by reviewer 1, "the assumption of 1 for the activity coefficients is likely the best these authors can do at this time". The selection of a suitable value for MWom has been adressed above (point 4 in the response to

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comments from reviewer 1).

5. Page 4730 and Page 4742. On page 4730, the authors mentioned that temperature was 20oC (please use the same unit), while on page 4742 the experimental temperatures were 293 K (PSI) and 305 K (UCC). Please clarify the experimental temperature. The 12 K difference in temperature is significant enough to change chemical and physical property of aerosol. What is the potential impact of temperature and humidity on measured partitioning coefficient as well as heterogeneous reactions in aerosols?

The unit for temperature in the revised manuscript is Kelvin. Experiments at PSI were performed at 293 K in a temperature controlled chamber. The chamber at UCC does not have any cooling system and the temperature gradually increased during the experiments from 293 to 305 K. Temperatures were in the range 303-305 K during denuder-filter sampling. The exact temperature at the time of sampling was used for calculations of Kp,i (theoretical). The effect of temperature on the theoretical partitioning coefficient values can be seen in Tables 4 and 5. Temperature will, of course, have an effect on the measured partitioning coefficients and heterogeneous reactions in aerosols. However, this is difficult to decipher from our data since other parameters, such as the gas and particle concentrations, aerosol age and sampling times vary from experiment to experiment. Nevertheless, the fact that the same range of photooxidation products was detected in the particle phase in all experiments indicates that significant differences in chemistry were not occurring. The effect of humidity was not investigated in this study. The following sentence has been added to section 2.2 (start of second paragraph); "The chamber does not have any cooling system and the temperature gradually increased during the experiments from 293 to 305 K". The following sentence has been added to section 2.2 (start of third paragraph); "Temperatures were in the range 303-305 K during sampling". The relevant details on page 4742 have been changed to read as follows: "For experiments performed at PSI, the temperature was maintained at 293 K. At UCC temperatures were in the range 303-305 K during denuder-filter sampling and the exact temperature at the time of sampling was used for calculations of Kp,i

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(theoretical)".

6. Page 4743, Line 24-26, it stated that "the oligomers can revert to their monomeric form in the solution". How will this influence the quantification of the carbonyls in the filter samples as well as the experimental partitioning coefficients? Please discuss about it in the paper.

This should improve accurate quantification of dicarbonyls in the particle phase, but only in their monomeric form. In this way the reversion is seen as an advantage, allowing quantification of the mass of gas phase dicarbonyls that entered the particle phase through accretion reactions. Admittedly, complete reversion of oligomers to the monomeric form is not guaranteed and cannot be assumed, therefore the particle phase concentrations can be interpreted as a lower limit for the mass that has been taken up by accretion reactions. The following sentence has been added to the end of this paragraph in the manuscript; "However, it cannot be assumed that full reversion to the monomeric form is occurring and therefore the particle phase concentrations can be viewed as a lower limit for the mass that has been taken up through accretion reactions".

7. Figures 2-5, please move the legend to the bottom of the figures.

This has been done for most of the figures. However, in some cases this has not been done because moving the legend to the bottom would obscure more of the data shown in the plots.

8. Table 1. Please include the inforamtion of HC (e.g., isoprene or 135- trimethylbenzene). If the authors provide temp and RH information here, this will help the readers.

The caption for Table 1 has been amended as follows to include these details; "Starting concentrations and results for the isoprene (ISO) and 1,3,5-trimethylbenzene (TMB) photooxidation experiments performed at a relative humidity of approximately 50%". Temperature is not mentioned here as it is complicated and fully explained in the text.

Edney, E.O. et al., Formation of polyketones in irradiated toluene/propylene/NOx/air mixtures. Aerosol Science and Technology, 35(6): 998-1008, 2001.

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