Atmos. Chem. Phys. Discuss., 8, S7867–S7874, 2008
www.atmos-chem-phys-discuss.net/8/S7867/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation" *by* K. P. Wyche et al.

K. P. Wyche et al.

Received and published: 2 October 2008

The authors are grateful to both referee's for their excellent, thoughtful and insightful reviews, their comments were most welcome and indeed were very useful for manuscript improvements to be implemented. A series of corrections have been made in accordance with both the referee's suggestions; the following document lists these changes and the author's response to all comments.

Authors Response to Anonymous Referee 1

Specific Comments

(1) It is not clear what the referee is asking for in this point. It is clear that if the wall

loss is not characterised the longer the time to reach an endpoint to calculate a yield the higher the uncertainty.

(2) The authors believe that the use of HONO vs. NO+NO_2 and the resultant effect on the chamber peroxy radicals has been thoroughly discussed throughout the manuscript and indeed this issue will be discussed further in our companion paper (Rickard et al.), in which compelling evidence from modelling studies will be presented (in comparison with measurements) to provide support to the theory that organic hydroperoxides play an important role in SOA formation. As the manuscript is quite lengthy as it stands, the authors are somewhat reticent to add further discussion regarding this issue.

(3) ϕ is a time-dependent factor within the experiment and the ultimate aerosol yield obtained occurs at a fixed time, hence the best possible correlation to draw between ϕ and YSOA would be ϕ at nucleation with YSOA achieved. This has now been performed and Section 3.4 has been modified to state this, which usefully further highlights the role of organic hydroperoxides; i.e. the low NOx experiments gave the largest ϕ value at nucleation and the largest ultimate SOA yields: *"From the results obtained within this work it would appear that ϕ at the point of nucleation exhibits positive correlation with the ultimate SOA yield achieved, i.e. both low NOx experiments exhibit the largest ϕ values as well as presenting the largest SOA yields. These experimental findings further strengthen theories which propose a crucial role for organic hydroperoxides in the SOA formation process, both under chamber conditions and potentially under NOx limited ambient conditions."*

(4) In the real atmosphere which in general is low NOx it is more likely that the hydroperoxide route will predominate. The major difference is in the relative concentrations between the "real" atmosphere and a chamber. A chamber experiment indentifies and quantifies processes that then can be mapped (even parameterized) for "real" conditions.

(5) The low NOx experiments appear to have an ultimately higher proportion of lower

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

molecular weight products; however, this is only due to the higher oxidant levels employed within those specific experiments and the subsequent decay along the oxidation chain. However, yields for certain high molecular weight products which are liable to partition to the condensed phase (e.g. the bicyclic compounds) were also larger during the low NOx experiments. Furthermore, as we state, under the low NOx conditions employed, the formation of low volatility organic hydroperoxides is favoured, which are believed to be significant contributors to SOA mass. These points, highlighted throughout the manuscript, can be employed to explain the enhanced SOA yield observed under low NOx conditions.

(6) It is possible that some small fraction of the lower molecular weight compounds observed were present within the gas phase due to re-volatilization from the aerosol, however, the amount of aerosol mass formed was quite small compared to the gas phase concentration of these species, and furthermore in all experiments there still remained heavier precursor VOCs/OVOCs which would have been able to undergo oxidation to yield such lower MW compounds. Without further strong evidence to state otherwise, it is difficult to confirm the presence of any gas phase compounds due to re-volatilization from the aerosol.

(7) There is indeed an enhancement in the yield of the bicyclic nitrate under low NOx conditions; however, as highlighted in Section 3.9 this enhancement is not as great as for certain other compounds, e.g. the bicyclic ketone and diol. It should be noted here that a similar result has been obtained using MCM model simulations of our high and low NOx conditions (which will be presented within our companion paper). The authors believe that this yield enhancement is most likely due to the higher oxidant levels within the chamber when HONO was employed as the NOx source. The manuscript has been modified accordingly.

(8) The authors agree with the referee, nitrates do indeed appear to be important for SOA formation in this instance, as we state in the latter half of the discussion section. However, we also state that they are not necessarily the nucleating compounds and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

that some other species must also be important in this regard; we suggest organic hydroperoxides. We also state that organic hydroperoxides are likely to form early and to significant levels under the low NOx conditions of experiments 5 and 7 and we suggest that the presence of such compounds is the main reason for the enhanced SOA yield in this instance. Our companion modelling paper will present further compelling evidence to support this thesis, as stated in Section 3.9.

Other specific scientific comments (1) The authors thank the referee for highlighting this potential confusion, however they would prefer to isolate figure captions from experiment numbering, as various other figures with parts (a) and (b) refer to experiments 1 - 7, so we believe that referring a "letter to a letter" may introduce more confusion.

(2) Again the authors thank the referee for this comment, however as Table 4 is quite extensive in its present from they would prefer not to add further to it with information. Furthermore, the units employed are intended to be useful for other users of such instruments within the field.

(3) No fan was used to assist mixing within the chamber; the following statement has been inserted into the Experimental section (2.1) to clarify this: *The chamber does not employ fan assisted mixing.* See point (8) regarding wall losses.

(4) A limit as per full conversion of SO_2 into ${SO_4}^{2-}$ of 1.5 μg m^{-3} has been added to the text.

(5) The CIR-TOF-MS is an instrument designed to monitor the gas phase, in absence of the required aerodynamic lenses all particles would in all probability deposit to walls on route into ion source of the instrument. Moreover, it is not at all likely that PM could be directly ionised by PTR and the CIR-TOF-MS incorporates no means of dissociating the particle before entry to the ion source.

(6) 1,3,5-TMB is not known to react with O_3.

(7) As suggested by the referee, the "dark phase" section of the experiments has now

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

been introduced within the text during the discussion of Figure 1, as well as being noted within the caption of Figures 1 and 2. In this regard, the following paragraph has been added to page 10, Section 3.1: *In order to evaluate the chemical mechanisms underlying the TMB photooxidation system, at the conclusion of certain experiments the chamber lights were switched off and the total chamber ozone was titrated from the system with the addition of excess NO to the gas phase matrix. The effect of this "dark phase" on the VOC chemistry will be discussed below in Section 3.9, however, it should be noted at this point that the NO addition,* O_3 *titration and resultant* NO_2 *production can be seen in Figures 1(a) and (d) for experiments 6 and 7 (high and low NOx respectively).*

(8) A simple calculation suggest as uncertainty in the order of 20-30 percent would be a typical uncertainty in terms of wall loss. A comment has been added to the text.

(9) A statement has been added to Section 3.3 in order to highlight the fact that the yield used for experiment 3 is simply a guide. The authors recognise that it cannot be used in an absolute sense; it is simply used to show that under the experimental conditions discussed, very little SOA was formed. As stated within the manuscript, during experiment 3 most of the precursor had reacted by the conclusion of the experiment, most of the organic gas phase oxidation products were in decay or had reached a steady state and furthermore SOA number density had reached a peak. Consequently, it is expected that little further SOA growth would have occurred post 600 minutes. This is stated for the reader in the text. However, the authors agree with the referee and the following paragraph has been modified accordingly to state that the value used is simply a guide and caveats remain: *When the starting VOC/NOx ratio was reversed to 1:2 for experiment 3, SOA formation was significantly delayed, with nucleation occurring around 215 minutes later than in experiment 6. By the conclusion of experiment 3 (*$\sim$ *600 minutes) the chamber aerosol appeared to still be in a state of growth; no distinct peak in either size or mass had been reached, however, the SOA number density had reached its maximum (see Figure 2(d)). Consequently, a relative SOA yield*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

can only be approximated in this instance by taking the aerosol mass produced at the conclusion of the experiment. Although this yield value is not necessarily fully quantitative, it serves as a guide to indicate the level of SOA formed under the conditions of experiment 3. With a VOC/NOx ratio of 1:2, an approximate SOA yield of 0.3 percent was achieved, i.e. roughly an order of magnitude lower than for the larger VOC/NOx ratios. With more than 90 percent of the precursor VOC consumed by termination of the experiment and with primary and secondary oxidation products having reached their concentration peaks, it may be assumed that further aerosol growth after this point would be minimal.

(10) The referee is correct; the formation of peroxy nitrates should be, and indeed is included in equation (2). The rate constant k_2, is the overall rate constant for the reaction of NO + RO_2, which includes two fates: NO + RO_2 → alkoxy and NO_2 and NO + RO_2 → peroxy nitrates. Apologies, this was not made clear, reaction (R2) has now been amended to show that both pathways are indeed considered.

(11) Please see point 9 above.

(12) The final sentence of Section 3.4 has been modified in order to state the relevance of the discussed findings under chamber and ambient conditions: *These experimental findings further strengthen theories which propose a crucial role for organic hydroperoxides in the SOA formation process, both under chamber conditions and potentially under NOx limited ambient conditions.*

(13) During blank chamber experiments, ca. 10 ppbV of formic and acetic acid were measured within the chamber after seven hours, i.e. only by the very end of our experiments. The contribution made from the walls to the total formic and acetic acid levels within the chamber was also relatively small, at most being 10 percent. The authors are simply treating the data in all honesty and presenting it to the reader with the caveat that there may be some effect from the walls. This was stated clearly for the reader in paragraph of Section 3.7.3 of the original manuscript. However, in order

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

to allay the referees concerns a further statement has been added to Section 3.9 in order to further clarify this issue to the reader: *It should be noted at this stage that, as stated above, in the case of formic and acetic acid, some small contribution of that measured within the gas phase may have originated from the chamber walls (*$\sim$ *10 percent or less), hence care is required when assessing their potential contributions towards TMB-SOA formation.*

(14) The statement on line 7 of page 33 has now been amended as requested by the referee, the new paragraph now reads: *Considering that these organic acids were available in the gas phase matrix from early on in all experiments, it is possible that their enhanced gas phase yields were at least in some part responsible for the observed increase in aerosol yields which were obtained under low NOx conditions. Indeed, various recent reports have highlighted the importance of organic acids in the composition of SOA.*

(15) Unfortunately organic hydroperoxides, including the O_2-brigded peroxide are difficult to measure with PTR-MS and hence we were unable to measure it here. However compelling evidence from our companion article (Rickard et al. in preparation) will discuss the role of the O_2-bridged peroxide in SOA formation and growth. Also, as the profile of the O_2-bridged ketone had not reached a peak by the end of the focus experiments, similar figures cannot be drawn. However, the "ideal" gas phase behaviour of the O_2-bridged ketone and its potential loss from the gas phase will be discussed in our companion modelling paper.

Figures 1. As requested, the dark phase has been mentioned in the figure caption with following statement: *For (a) and (d) the chamber lights were switched off for the "dark phase" at 460 and 550 minutes, respectively, followed by NO injection (see text for details).*

2. Figure 2 caption has been amended.

3. Figure 3 caption has been amended to state *hydroperoxides*

5. Figure 5 has been redrawn in order to display the data in a clearer fashion.

8. Figure 8 has been amended and redrawn in order to display the data in a clearer fashion.

9. and 10. Figures 9 and 10 have been re-drawn, as suggested with colour coded labels.

12. and 13. Unfortunately organic hydroperoxides, including the O_2-brigded peroxide are difficult to measure with PTR-MS and hence we were unable to measure it here. However compelling evidence from our companion article (Rickard et al. in preparation) will discuss the role of the O_2-bridged peroxide in SOA formation and growth. Also, as the profile of the O_2-bridged ketone had not reached a peak by the end of the focus experiments, similar figures cannot be drawn. However, the "ideal" gas phase behaviour of the O_2-bridged ketone and its potential loss from the gas phase will be discussed in our companion modelling paper.

Tables 2. Legend to Table 2 has been corrected.

4. As uploaded, and as requested during initial review, Table 4 has Appearance Time (minutes) above the experiment number.

Technical Corrections/comments Minor technical corrections/comments (1 - 27) have been addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11685, 2008.