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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.

Anonymous Referee #1

Received and published: 8 July 2008

General comments

This paper contributes an excellent gas-phase organic dataset to the aerosol community s efforts to better understand the composition of organic aerosol and species responsible for nucleation. The comparison of experiments under varying NOx/VOC concentration ratios and with/without inorganic seed provides insight into the relevant radical chemistry and importance of acid-catalyzed heterogeneous reactions, which have been discussed lately in the literature. While the data presented are clearly significant and will be of great interest to the aerosol community, I recommend changes to improve the impact and clarity of this paper. For example, in my opinion, the richness

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of the dataset here presented is worthy of more lengthy discussion, and I suggest the authors add further discussion on the interpretation of these observations.

Specific comments

Specifically, I recommend expanding the discussion on:

(1) How the different SOA formation kinetics in various runs could affect yields (esp. since wall losses are not accounted for)

(2) How the use of HONO vs. NO+NO2 NOx sources could affect the peroxy radical mixture and influence chemistry

(3) Is an explicit correlation of phi with yield possible? What can be concluded?

(4) Do the results of phi as a function of (NOx) imply that organic peroxides only dominate SOA formation in chambers, and could be less important in the real atmosphere?

(5) How to reconcile the observations that low-NOx experiments gave lower-MW products, but nevertheless more SOA?

(6) Do the time traces of lower-MW features (continually increasing until the end of the experiment) suggest re-volatilization of the organic aerosol? How do you interpret their high yields?

(7) How to interpret the enhancement of bicyclic nitrate formation under low-NOx conditions?

(8) More generally, how to interpret the observations that nitrates are clearly important to SOA formation, but the low-NOx experiments exhibited higher SOA yields

Other specific scientific comments:

(1) I find the experiment number confusing. Could you instead refer to experiments by their panel labels (i.e., a,b,c,d) throughout? The same letters would not show up in all figures, but this would aid in the ease of comparison of data from the same run.

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(2) Recommend putting all masses cited in Da also in g/mole units.

(3) In experimental section: was a fan used in your chamber? Can you comment on likely magnitude of error due to wall losses? (here or on pg. 14 line 4)

(4) pg. 8 line 1: mention what ug/m3 sulfate aerosol was produced from the addition of 7400 pptV SO2

(5) pg. 8, bottom: in the absence of the filter, how does the CIR-TOF-MS reject particles?

(6) pg. 11 1st full paragraph: What about O3 oxidation of TMB? Doesn t it build up before TMB is fully removed?

(7) ibid: I recommend mentioning the dark phase in expts 1a and 1d here where you first introduce the figure, and in the figure caption.

(8) pg. 14 around equation E1: estimate error due to wall loss here, or earlier

(9) pg. 14 bottom: I disagree with labeling the SOA mass at the conclusion of an experiment where particles appear to still be growing a Yield . I think you can compare the kinetics but not the mass yield in this case. This slower SOA production would also be disproportionately affected by wall loss of aerosols, so this SOA yield of 0.3

(10) pg. 15 R1-R4: Should formation of (peroxy)nitrates ROONO / RONO2 be included here?

(11) pg. 17 2nd paragraph in 3.4: Again, I disagree with the use of quantitative yields from the experiments that did not run to completion.

(12) p. 18 just before 3.5: These experimental findings ... crucial role played by organic peroxides during SOA formation : in chambers only? Or relevant to atmospheric conditions?

(13) p. 32 bottom: you interpret the relative yields of acetic/formic acid, but earlier you

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noted a potentially large wall source of these species! How can you draw quantitative conclusions despite this wall source, which may be different under differing chamber [Ox]?

(14) pg. 33 line 7: similarly, I disagree with this supplying confirmation to recent reports ... importance of organic acids

(15) Figure 12 is really compelling. Can you do the same plot for a O2-bridged ketone or hydroperoxide?

FIGURES:

1: mention dark phase in caption

2: make caption consistent with Fig. 1. As mentioned above, if possible, remove experiments numbers in favor of consistent letter labels.

3: in caption: peroxides -> hydroperoxides

5: colorbar in panel a is not elucidating - changes to dark blue long before change. this doesn t show the NOx control that you intend to show. rescale color bar? or is the interpretation wrong?

8: y label typo: Minutes . This figure is not useful as plotted. Maybe show discrete spectra at several time slices? or a wire mesh? It s illegible in its current form.

9 and 10: y-axes are very confusing. Label somehow, or color code list in caption? Spurious comma in caption to Fig. 9.

12 and 13: as mentioned above, it would be great to have this figure for the bridged ketone/peroxide, since those are your focus in the discussion, more than the nitrate.

TABLES:

2: caption: aerosol phase parameter -> aerosol-phase parameters

4: Mass is not in Da, right? looks like g/mole. Also add a header indicating what the

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data is: Appearance time (minutes) above Experiment Number

Technical corrections/comments:

(1) pg. 11 line 8: add comma after Consequently

(2) pg. 12 line 5: remove was after VOC/NOx ratio

(3) pg. 13 just below 3.3: FigureS 2a - 2d

(4) pg. 13 10 lines from bottom: for some 100 minutes -> for 100 minutes

(5) pg. 13 8 lines from bottom: During this time -> After this time ?

(6) pg. 14 13 lines from bottom: particles grew to possess larger -> particles grew to larger

(7) pg. 16 line 3: R1 - R4 -> R2 - R4

(8) pg. 16 l6 lines below E2: i.e. hence peroxide -> i.e. peroxide

(9) pg. 16 5 lines from bottom: The hypothesis suggesting that -> The hypothesis that

(10) pg. 16 2 lines from bottom: remove a nominal value of

(11) pg. 20 line 1: expenditure -> consumption

(12) pg. 21 last line: sufficiently non-volatile enough to -> sufficiently non-volatile to

(13) pg. 22 line 3: recommend starting a new Paragraph at Further oxidation and ring opening ...

(14) section 3.7.2: font format on H3O+.H2O looks funny - should . be elevated?

(15) pg. 23 2 lines from bottom: Both of which were -> Both were (16) pg. 24 line 3 and elsewhere in the manuscript: mass transit -> mass transfer

(17) pg. 25 line 1: liable -> likely

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(18) pg. 25 6 lines from bottom: a variety of functional groups -> multiple functional groups - is this what you mean? Multiple on a single molecule?

(19) pg. 27 last sentence above 3.7.5: the oxidation products of the reverse system -> the oxidation products of this system

(20) pg. 28 4 lines from bottom: provides key insight -> provides insight

(21) pg. 29 3.8: is there a citation for Martens Naes?

(22) pg. 28 4 lines from bottom: Consequently, it may therefore be : remove either Consequently or therefore

(23) pg. 30 line 2: aren t you showing that the vast majority of the temporal variability is captured by two principal components, since the third is 0.6-1.5

(24) pg. 32 line 2: remove comma after include

(25) pg. 32 first P: why are there 2 separate lists of early appearance masses?

(26) pg. 33 line 2: yield concentration artefacts -> concentration-dependent yield artefacts

(27) pg. 36 line 4: portioning -> partitioning

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

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