Atmos. Chem. Phys. Discuss., 10, C5286–C5292, 2010
www.atmos-chem-phys-discuss.net/10/C5286/2010/
© Author(s) 2010. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Role of aldehyde chemistry and NO$_x$ concentrations in secondary organic aerosol formation" *by* A. W. H. Chan et al.

A. W. H. Chan et al.

achan@caltech.edu

Received and published: 13 July 2010

We thank the review for the helpful comments. Please see responses below:

- *10220; 16: Is there any reference that suggests that 2-hydroxy-2-methylpropanal forms PAN-type compounds? Why does the statement warrant being in the abstract?*

  Both this study and Carrasco et al. (2006) show that 2-HMPR does not form PAN-type compounds. This is a result of the neighboring OH group leading to decomposition of the acyl radical, as explained in Section 6.2. Aerosol formation is not favored, and is consistent with PAN-type compounds being important SOA intermediates. This is an important point, as it suggests that the PAN chemistry shown in this work can be applied to other compounds. It also provides an explanation for why MBO232 is not a significant SOA precursor.

- *10220; 18: Specify the atmospherically relevant NO_2/NO ratios. As given, the sentence connects an imprecise statement of the ratios with a precise statement of the increase in yields.*

  The atmospheric NO_2/NO ratios are often between 1 and 10. In our "high NO_2" experiments, the NO_2/NO ratios were between 3 and 8. This information has been added to the abstract and Section 5.

- *10225; 5: Since HONO concentrations are being used in the model, were HONO line losses to the monitors or other measuring devices evaluated. They can often be significant.*

  Line losses of HONO were not systematically evaluated. With the measured HONO concentrations, the photochemical model is able to reproduce the decay of the hydrocarbon. As a result, we do not expect HONO line losses to be greater than 20%. The insignificant line losses could be a result of the dry conditions employed in these experiments.

- *10225; 7: The temperature at which the experiments are conducted at should be given. Since PAN-type compounds (which are highly temperature sensitive) are being studied, this listing should include both the initial and maximum temperature during the irradiation. Table 2 would be a reasonable location to place the data.*

  We agree that PAN compounds are highly temperature sensitive. The temperatures in all experiments did not vary by more than 2 degrees Celsius. In the footnote of Table 2, we report 293–295K as the range of temperatures in all experiments.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

- *10227; 28: What is criteria for a high NO_2 experiment; they all look like high NO_2 experiments to me. In general, the use of descriptive terms such as high-NO_2 and low-NO_2 represents a weakness in the paper. Substantially more precision is need in this regard.*

  We agree with the reviewer that the absolute concentrations of NO_2 are high in all of the experiments. The following has been added in the Experimental Section to clarify this point:

  ‘ For “high NO” experiments, OH radicals were generated from photolysis of HONO. We refer to these experiments as “high NO” experiments because NO concentrations are sufficiently high that RO_2+NO $\gg$ RO_2+NO_2, most notably for acyl peroxy radicals, even though NO_2 concentrations are high (e.g. greater than 100 ppb). ’

  ‘ To achieve high NO_2 concentrations, CH_3ONO was employed as the OH precursor. These are referred to as “high NO_2” experiments, as NO_2 concentrations are sufficiently higher than NO concentrations such that PAN formation is favored over reaction of acyl peroxy radicals with NO.’

- *10229; 5: Some consistency should be used for the yields. On the previous page, the yields are presented as percentages and in this instance they are given as fractional values.*

  To be consistent, all percentage yields have been changed to fractional yields.

- *10229; 23: The paragraph starting at this line should be rewritten. Many of the statements in the paragraph are imprecise and should have values associated with them (e.g., ...consistent with yields published in previous studies). Simply give the yields. What does the phase (“To first order...”) mean in this context? Does it refer to some sort of reaction rate?*

  Values of glycolaldehyde and HMPR yields, and an upper limit of SOA yields from previous studies have been added to make the statements more precise. The phrase “to first order” has been removed.

- *10231; 28: Subscript 2 in* O_2 *is probably correct.*

  We apologize for the confusing statement about “loss of O_2^- group”. In the negative mode of ESI, depronated acidic anions $[M\text{-}H]^-$ are detected. In the positive mode of the AMS, a hydroxyl group can be lost to form a cation $[M\text{-}OH]^+$. Instead of a loss of O_2^- group, it should be a difference of O_2^- group between ions detected by the two techniques. The paragraph has been rewritten to be clearer about the mass spectrometry results. See also response to comment below (10232; 1).

- *10232: Section 5: This is a general comment probably best inserted here. While there is considerable discussion of the* NO_2/NO *ratio, there is no discussion of the influence of the* NO_2/O_2 *ratio. This is especially notable since the* NO_2 *concentrations during SOA processing periods is probably between 500 and 1000 ppb. This begs the question as to the importance of the report effect (*NO_2/NO *ratio) at total NOx concentrations more relevant to ambient atmospheres, for example an order of magnitude lower in concentration. I recommend a paragraph or at least 3-4 sentences considering this issue probably included in this section.*

  We agree with the reviewer that the NO_2 concentrations in these experiments are higher than ambient levels. Competition between NO_2 and O_2 exists in aromatic systems, as the cyclohexadienyl radical (following OH addition) can react with NO_2 to form nitroaromatic compounds, or with O_2 to form a bicyclic intermediate. For aromatic compounds, such as benzene, toluene, and naphthalene, these processes are shown to be competitive at NO_2 levels of 10–100 ppb. However, for alkenes and aldehydes studied here, the reaction of alkene-OH adduct or acyl radical with NO_2 is likely to be slow compared to addition of O_2 to form peroxy radicals. We do not observe any compounds with nitro ($R\text{-}NO_2$) functional groups, with the exception of methyl nitrite. The above has been added to Section 5 to address this issue.

- *10232; 7: It is not clear why the web address is being repeated.*

  This has been corrected.

- *10232; 1: The sentence beginning on this line should be expanded. As it stands, the agreement being referred to is inadequately addressed.*

  The following has been added to explain the agreement between offline LC/MS and online AMS results:

  “The ions suggested by these elemental formulas differ from many of the ions detected by UPLC/(–)ESI-TOFMS by an O_2^- group. The observed AMS ions are consistent with loss of a hydroxyl group from the molecular ion (i.e. α-cleavage of a hydroxyl group under electron impact ionization). In UPLC/(–)ESI-TOFMS, these compounds are detected in their deprotonated form (loss of H^+). As shown in Table 3, the oligoesters are detected by both online and offline mass spectrometry, and the agreement between the two techniques confirms that the oligoesters identified are indeed present in the SOA, and that the observations by offline aerosol analysis are not the result of filter sampling artifacts. ”

- *10232; 10: The introductory material here is somewhat arbitrary and represents too much of a generalization which is not needed. Either remove the paragraph or at least rewrite it in a more limited context (e.g., There is no need for the sesquiterpene discussion; it has already been mentioned in the Introduction and in any case is irrelevant to the present work.) Examine the rest of the paragraph for similar extraneous material.*

  This paragraph has been shortened to limit the repetition from the introduction.

- *10235; Section 6: The transport of PAN-type compounds in the free troposphere* *serve as important means of redistributing NOx. Are there any implications to SOA formation from this redistribution in the atmosphere.*

The thermal decomposition of MPAN is strongly temperature dependent, and the lifetime of MPAN against thermal decomposition (followed by fragmentation through reaction with NO) increases signficantly at lower temperatures. This allows for enhancement of SOA formation through reaction of MPAN with OH. As a result, if methacrolein or MPAN is advected to higher altitudes, the potential for SOA formation becomes greater than near the surface. This is not simply a result of temperature-dependent gas-particle partitioning, but rather of lower temperatures favoring SOA-forming chemistry. This aspect is yet to be accounted for in global models. As the reviewer noted, the distribution of SOA could be changed, as SOA can be formed further away from emission sources of isoprene. The inclusion of this chemistry in regional and global modeling could therefore affect not only the amount of SOA, but also the temporal and spatial distribution isoprene-SOA.

- *10234; 6: Some insight as to the conditions where such a transition occurs would be helpful.*

  Since the reaction rate constants of acyl peroxy radicals+NO and acyl peroxy radicals + NO_2 are similar, the transition would likely occur at NO_2/NO ratio of approximately 1.

- *10237; 12: Is it dioxketone or dioxoketone? 10237; 18: The sentence beginning on this line needs a reference.*

  To the authors' knowledge, the only known dioxoketone compound is 1,2-dioxethanedione (a CO_2 dimer). The compound name has been changed to "dioxoketone". No reference has been added as there is no direct relevance of 1,2-dioxethanedione to the proposed dioxoketone compound proposed here.

- *10241; 3: The recent paper by Carlton et al. (Environ. Sci. Technol. 2010, 44, 3376–3380) should also be referenced in addition to the Goldstein et al.*

  The reference has been added.

- *10242; Appendix A: The mechanism does not show the loss of NO_2 by reaction with OH. Given the high OH and NO_2 levels in the system throughout the reactive process, this sink reaction is essential for adequately predicting NO_2 and NO levels. I assume the reaction was included in the model, but it should also be written in the mechanism presented in the appendix.*

  This reaction is included in the photochemical model. It is mentioned in the text as part of the $O_3/HO_X/NO_X$ reactions. It is not explicitly mentioned in the list of reactions as they are other reactions in the photochemical model (e.g. $NO_2/NO/O_3$ cycle, HO_2+NO_2, OH+NO) that are also important.

- *10242; 13: Figures 3–5 shows considerable SOA formation at times longer than 200 min. It is not clear why the NO_2/NO ratio averages were only taken over the first 200 min of the HONO irradiations. Similarly, is the 100 min average appropriate for the CH_3ONO irradiations?*

  In Figs. 3–5, the x-axes denote the concentration of hydrocarbon reacted, not time. Figures 1 and 2 show that most of the SOA growth occur in the first 200 and 100 minutes for HONO and CH_3ONO irradiations, respectively. As a result, NO_2/NO ratios are averaged over those time periods. References to Figs. 1 and 2 have been added to clarify the averaging time period used.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 10219, 2010.