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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.

Anonymous Referee #3

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Overview: The paper describes experiments to determine changes in aerosol yield from a selected group of unsaturated aldehydes (methacrolein, acrolein, cis/trans-crotonaldehyde), isoprene, and two C5 unsaturated alcohols. Aerosol yields are studied as a function of the NO2/NO ratio. The authors put forth the argument that at increased NO2/NO ratios, secondary organic aerosol (SOA) yields also increase. This is of potential importance in atmospheres where isoprene emissions lead to SOA formation. Most of the recent interest in aerosol production from isoprene has been focused under conditions where NOx levels were found to be low, in which cases RO2 + RO2 reactions have been thought to be important (e.g., Paulot et al. 2009 Science; see authors' reference list). The authors make the argument at even under more urbanized conditions where NO and NO2 levels are relatively high, isoprene SOA yields are considerably higher than those estimated in models such as Henze and Seinfeld,

2006 GRL. Previous measurements of the yield (Kroll et al. 2005; 2006) did not consider the influence of the NO2/NO ratio and under most atmospheric conditions the yields used were probably systematically low. The authors also argue for the importance of peroxyacyl nitrates (or more properly termed peroxyacyl nitric anhydrides) as closer generational precursors to aerosol formation than the parent hydrocarbons or aldehydes. Finally, the authors try to argue that the findings from this work help to explain recent noted discrepancies between the importance of biogenic or anthropogenic sources for controlling SOA formation.

General comments. The paper deals with an important topic that has generated a fair amount of controversy as to the importance of isoprene as both a regional and global source of SOA. At the present time aerosol yields are thought to range between 1 – 3% depending on the NOx level and the organic aerosol loading present. The present paper suggest that under NO2/NO ratios typical of the atmosphere, aerosol yields could be as high as 8%. Certainly, this could make a large difference in air quality model predictions of SOA from isoprene. The body of experiments resembles more of a survey study than a comprehensive study designed to obtain a parameterization of the effect. Some of the difficulties in the study include (1) the inability to state very precisely the initial conditions of the system, (2) very high total NOx levels used in the study, and (3) the limited number of experiments for any single hydrocarbon precursor. Thus, a follow on study examining in more detail the change in yields with NO2/NO ratios for isoprene would be valuable as a means to parameterize the effect being reported for this compound. Nonetheless, as a survey study, I believe it should be published after considering the following minor revisions, arranged in order of appearance in the manuscript rather than in order of importance. (Each comment is prefaced by the page and line numbers.)

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?

10220; 18: Specify the atmospherically relevant NO2/NO ratios. As given, the sen-

tence connects an imprecise statement of the ratios with a precise statement of the increase in yields.

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.

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.

10227; 28: What is criteria for a high NO2 experiment; they all look like high NO2 experiments to me. In general, the use of descriptive terms such as high-NO2 and low-NO2 represents a weakness in the paper. Substantially more precision is need in this regard.

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.

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?

10231; 28: Subscript 2 in O2 is probably correct.

10232: Section 5: This is a general comment probably best inserted here. While there is considerable discussion of the NO2/NO ratio, there is no discussion of the influence of the NO2/O2 ratio. This is especially notable since the NO2 concentrations during SOA processing periods is probably between 500 and 1000 ppb. This begs the ques-

tion as to the importance of the report effect (NO2/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.

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

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

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.

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.

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

10237; 12: Is it dioxketone or dioxoketone?

10237; 18: The sentence beginning on this line needs a reference.

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.

10242; Appendix A: The mechanism does not show the loss of NO2 by reaction with OH. Given the high OH and NO2 levels in the system throughout the reactive process, this sink reaction is essential for adequately predicting NO2 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.

10242; 13: Figures 3-5 shows considerable SOA formation at times longer than 200 min. It is not clear why the NO2/NO ratio averages were only taken over the first 200 min of the HONO irradiations. Similarly, is the 100 min average appropriate for the CH3ONO irradiations?

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