Atmos. Chem. Phys. Discuss., 14, C10902–C10905, 2015
www.atmos-chem-phys-discuss.net/14/C10902/2015/

Atmospheric Chemistry and Physics
Discussions
Open Access

Interactive comment on “Elemental composition and clustering of α-pinene oxidation products for different oxidation conditions” *by* A. P. Praplan et al.

Anonymous Referee #2

Received and published: 6 January 2015

General Comments:

Praplan et al describe a series of measurements of a-pinene oxidation products made in the CLOUD chamber at CERN. The measurements described are primarily from three API-ToFs (+ mode, - mode, nitrate chemical ionization). Oxidation of a-pinene was studied under two different conditions: 1) dark, in the presence of O3, and 2) light, in the presence of UV light, OH, NO, and trace O3. As has been well established over the past decade, the oxidation mechanism is a strong function of oxidizing conditions and it is not unexpected that the resulting oxidation products from these two scenarios would differ in their oxidation state (among other metrics of their volatility). The

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

manuscript provides helpful mass spectral tools for understanding these mechanisms and contributes to the growing number of publications from this group on the topic. However, the manuscript is very observation based for the two select conditions studied here. A case has been made that these two oxidation scenarios correspond to O3 vs OH oxidation. This may very well be the case, however the difference in other experimental factors between the two experiments (UV, NOx) make this direct comparison quite challenging. More detail on the experimental conditions and a discussion of how they may impact the results would be very helpful.

Specific Comments:

Page 30799: I am surprised to see an author list of 33 for a manuscript that appears to be reliant on three instruments. Perhaps the authors can briefly elaborate on the contributions on the groups to the data and analysis?

Page 30801: The manuscript discusses in general terms the difference between oxidation products for a-pinene oxidation under to different scenarios. In the abstract these two scenarios are painted as OH and O3. However, the scenarios differ in many other (potentially even more important) way (e.g., NOx, hv). This should be mentioned in the abstract. It would also be of help to the reader to understand what the broader implications of these observations are. For example, is the point of this manuscript to provide molecular markers for oxidation pathways that could then be looked for in field observations? Is the primary point that the oxidation state of the resulting oxidation products between the two scenarios is different?

Page 30803: Were any of the unique features of the synchrotron utilized in this study? Or was the CERN chamber primarily utilized because of its low background?

Page 30804: What does “decrease contaminant levels to a minimum” mean? What contaminants are of importance to this study, and what defines a minimum? These details should be added here.

Page 30804: What does “trace gases are carefully adjusted and monitored” mean? Which ones, what is the control on those of importance? For example what is the confidence in the initial HONO concentration and the time decay in OH?

Page 30804: Please add more details on the light source and intensity and how this translates into OH concentrations. Does using the “UV sabre” mean that 1.9 ppbv OH is generated at t=0? Again, what does “increase OH levels” mean quantitatively? Was O3 or NO measured in time? Was OH calculated from hydrocarbon concentrations?

Page 30806: How confident are the author that these C20, C30, and C40 compounds are actually gas phase molecules and not formed in the expansion in the API-ToF? I am sure that this has been asked in the review of other nitrate ion CIMS. As such, perhaps a reference will suffice.

Page 30807: What is the source of sulfuric acid, NH3, and amines in this experiment? Are these contaminants? Were they added intentionally?

Page 30808: Given that each ion detected (at least via nitrate CIMS) has a different calibration factor, what do these average oxidation state values mean? I would almost guess that the calibration factor for each molecule would be a function of its oxidation state. Also, what is the uncertainty in the -0.7 and -0.3 values that are reported?

Page 30812: I would encourage the authors to think about how wall loss may be impacting the time series of the neutral compounds in the chamber. Specifically, isn’t this a key to telling whether the C20 compound is actually covalently bound molecule with extremely low volatility (it would condense on the wall promptly), as compared with a C10 molecule. It would be interesting to quench oxidation and watch the decay of these compounds in the chamber to assess their volatility as compared to their measured oxidation state.

Page 30831: Figure 6A, following peak concentration, there appears to be a 15min oscillation in the signal intensity. What is this caused by?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30799, 2014.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper