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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photodegradation of secondary organic aerosol generated from limonene oxidation by ozone studied with chemical ionization mass spectrometry" *by* X. Pan et al.

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In this manuscript the authors describe experiments in which volatile products from the irradiation of model SOA (secondary organic aerosol), generated from the ozonolysis of D-limonene, are observed using chemical ionization mass spectrometry. The wavelength dependence of the yields of these products tracks the absorption spectrum of the SOA material closely. The dominant observed photodegradation products are small (three carbons or fewer) oxygenated molecules such as acetaldehyde and acetic acid. The primary precursors responsible for these degradation products are proposed to be carbonyl- or carboxyl-containing species. Similar photodegradation products may

also be generated from SOA produced from OH reactions, as well, since these will also lead to the formation of similar precursors.

The authors do a very good job of explaining the experiments and their analysis of the data. They do not overreach in their conclusions and explicitly state assumptions made, such as assuming that each product is ionized at the same rate. This manuscript should be published after the following points are considered.

1. The particles are stated to be $\sim$ 100 nm at a concentration of 8 x 10ˆ5 cmˆ-3 after 10 minutes of reaction and then $\sim$ 220 nm at a concentration of 3 x 10ˆ5 cmˆ-3 after an hour. This represents a four-fold increase in particulate mass over this timespan (not accounting for particle loss on the walls of the bag). How is the overall mass increasing by this much? It seems unlikely that it can be explained by additional ozone reactions since half of the ozone is already reacted after the first 10 minutes.

2. What was the timescale for the drop in total PIC (product ion current) after the light was turned off? Comparing this timescale to the 5-20 minutes required for the PIC signal to reach steady-state values when the light was turned on could indicate whether the photodegradation occurred in a single step (in which case the PIC signal drop should be prompt) or through multiple steps (in which case these photo-initiated reactions could persist for some time after the light was turned off).

3. To determine the potential atmospheric significance of such photodegradation, the rate for volatile product formation should be estimated for typical actinic fluxes. Will such a process be competitive with reactions of the SOA with OH, O3 or NO3?

4. Is it possible that the findings from this study could explain some of the volatilization measured from OH-initiated reactions of organic aerosols and films by other researchers? More specifically, in those studies 254 nm light from mercury lamps is used to initiate ozone photolysis to create O(1D) which then reacts with H2O to make OH radicals. The resulting products include carbonyl and carboxyl groups which may absorb the 254 nm light and lead to photodegradation just as observed in the present

work.

5. In Figure 7, why is the product ion signal so high ($\sim$ 0.7 x 10ˆ6 cps) before the UV lamp is turned on? This signal doesn't even double (at 290 nm) when the light is turned on which indicates that there is a significant dark source of these peaks (50-400 m/z). Hence, the photodegradation seems to be relatively minor compared to this dark source.

6. In Figure 10, is the normalized relative yield plotted the same normalized yield defined by equation 5? Or are these yields just normalized so that the results from the CRDS and CIMS experiments overlay one another?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4727, 2009.