

Interactive comment on “Atmospheric organic-phase photo-sensitized epoxidation of alkenes by α -dicarbonyls” by G. Yu and F. N. Keutsch

Anonymous Referee #1

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The authors have studied the photochemical epoxidation of alkenes in the presence of alpha-dicarbonyls as photosensitizers. This is an interesting and potentially important study. Like much of the aerosol organic chemistry being studied these days, the chemistry described here has been known in the organic chemistry community for quite some time but its relevance to atmospheric aerosols was not previously recognized. Several recent studies have pointed to the potential importance of epoxide chemistry in the particle phase, but it was mostly discussed in the context of gas-phase epoxides partitioning to particles then reacting.

My main criticism of the paper is that the experiments were performed in a highly

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idealized laboratory system that does not have a direct resemblance to atmospheric aerosol. The paper is still a worthwhile contribution, but the limitations of the approach should be discussed more in the manuscript and also emphasized in the abstract. Recommendations for future work that could better test the atmospheric relevance of the mechanism should be made. The experiments took place in bulk solutions in NMR tubes, rather than in the aerosol phase. The reactants were at low concentrations in CDCl₃ as a solvent, which is very different from aerosol organic material phase (some experiments were performed with benzene solvent, but this also is not typical - see below). The authors correctly point out that in an aqueous/organic phase separated aerosol the alpha-dicarbonyl photosensitizer may not end up in the same phase as the alkenes, and they demonstrate this with their methylglyoxal experiments. Biacetyl to my knowledge has not been reported in atmospheric aerosols, although I guess it's being considered as representative of highly oxidized OA that would partition to the organic phase.

The authors perform an interesting calculation to try to estimate the prevalence of alpha-dicarbonyl species in typical atmospheric aerosol, in order to give some insight into the atmospheric relevance of this mechanism. Not enough information was given for me to assess whether the calculation is correct though. If LV-OOA has 8-12 carbon atoms and O:C = 0.8, that suggests that a typical molecule has 6-10 oxygen atoms. If 20% of those oxygens are carbonyl oxygens, that gives 1-2 carbonyls per molecule. Note that any molecule with < 2 carbonyls can't be an alpha-dicarbonyl. We then require that the carbonyls be adjacent to one another in order to be considered alpha-dicarbonyls, and neither of the carbonyls can be part of an organic acid group. After all this it seems that the percentage of molecules which qualify as alpha-dicarbonyls should be lower than 17% (same arguments hold for the SV-OOA calculation). Additionally, do we have a sense of how much unreacted alkenes are present in LV-OOA or SV-OOA? Finally, the “solvent” in these atmospherically relevant systems is clearly oxygenated organic material – why were no oxygenated organic solvents used in this study? How might this affect the results?

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