

Interactive comment on “Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics” by E. L. Shapiro et al.

Anonymous Referee #2

Received and published: 16 February 2009

Review on the manuscript "Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics" by Shapiro et al.

This manuscript reports experimental studies of the reactions of glyoxal in aqueous solution of ammonium sulfate and sodium chloride and, in particular, the formation of large molecular weight products absorbing in the near UV and visible (300 - 600 nm). Unfortunately, this manuscript is not publishable for several serious reasons:

First, it fails to quote and discuss many previous articles of essential relevance to this study. Two recent studies of the same reaction of glyoxal in ammonium sulfate are not mentioned (Noziere et al., JPC A, 113, 231, 2009 and Galloway et al., ACPD, 8, 20799, 2008). This is perhaps understandable because of the short delay between

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



these papers and the present one, but would not be acceptable in a final version. But, much more disturbing, there is not a single word on any of the previous studies of these light-absorbing products in the same reactions (aldol condensation, as claimed in this manuscript), such as

- "Organic reactions increasing the absorption index of atmospheric sulfuric acid aerosols", Nozière, B., W. Esteve, Geophys. Res. Lett., 32, doi:10.1029/2004GL021942, 2005, - "Light-absorbing aldol condensation products in acidic aerosols: spectra, kinetics, and contribution to the absorption index", Nozière, B., W. Esteve, Atmos. Environ., 41, 1150, 2007, - "Kinetics of acid-catalyzed aldol condensation reactions of aliphatic aldehydes", Casale et al., Atmos. environ. 41, 6212, 2007, - "The Formation of Secondary Light-Absorbing fulvic-like Oligomers: A Common Process in Aqueous and Ionic Atmospheric Particles ?" Nozière et al., Geophys. Res. Lett., 34, L21812, doi:10.1029/2007GL031300, 2007,

and there might even be more. Not only these articles discuss in detail the importance of these light-absorbing products on the optical properties of aerosols but the latest (Noziere et al., GRL, 2007) demonstrates their molecular similarities with fulvic compounds. This is probably the reason for the comparison between these products and HULIS in the introduction of the present manuscript (otherwise there is no reason to suspect any similarities with HULIS in general).

Quoting all relevant previous works is not optional, it is mandatory (especially when these works establish the basis of the subject studied). But completely omitting all the previous works on a given topic is simply unacceptable.

Second, there seems to be some serious flaws in the experiments: It is very puzzling that these (strongly) light-absorbing compounds are observed while glyoxal is precisely the one carbonyl compounds that does NOT undergo aldol condensation. And neither Noziere et al., 2009 or Galloway et al., 2009 report such light-absorbing compounds. The imidazole products reported by Galloway et al. do absorb slightly near 230 nm,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



but not nearly as much as the pi-conjugated products proposed in this manuscript.

There is no mechanistic explanation for the formation of the pi-conjugated products proposed in this manuscript from glyoxal. The only possible explanations for the observations could either be a serious contamination of the reaction mixture (for instance with acetaldehyde), or cross-reactions between second-generation products if very large concentrations of glyoxal were used, but this did not seem to be the case (0 - 2.2 M of glyoxal).

Not only the results presented are in contradiction with all previous knowledge of the reactivity of glyoxal but the authors do not even seem to be aware of it. If they had, they should have at least offered some explanation or performed further investigations to justify these very surprising results. At the very least, they should discuss the atmospheric relevance of these results, as the above-mentioned previous works did (discussing absorption cross-sections, concentrations, and the general relevance of the results for aerosols).

Addressing all these issues would require a substantial amount of additional work, and can not be done only by major revisions to the manuscript. Therefore, unfortunately, this work would have to be re-submitted once all these issues have been solved.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 59, 2009.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)