

Interactive comment on “Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution” by K. E. Daumit et al.

Anonymous Referee #2

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This is an interesting paper in which high soluble organics (polyols) are oxidized in both bulk solutions and in aqueous particles, using photo Fenton chemistry. The topic of aqueous phase chemistry within clouds and particles is hot currently, as the community tries to establish whether this chemistry is important in the atmosphere. And so, the work is of relevance to ACP. The choice of polyols is good because these are only present in the aqueous phase, removing complications from gas phase chemistry. The experiments appear to have been well done.

One finding – not surprising – is that the alcohols disappear rapidly forming highly oxidized products, such as oxalate. The products appear to be the same, as far as an

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AMS can tell, between the two reaction conditions (bulk vs particles). One difference though is that the carbon species are lost more rapidly from particle oxidation than from bulk phase oxidation. While I fully agree with the point being made by the authors that LWC will affect the partitioning of partially soluble species, I do wonder why they don't address more the possibility that oxidant levels are different between the two conditions? i.e. Could it be that higher OH levels are present in the particles due to the very high dissolved H₂O₂, and different production conditions involving iron, and/or from different light levels? Why not estimate the OH concentrations in the particles from the polyol decay rate as they did in the bulk work? This would address my main criticism of this paper, i.e. that it is an interesting qualitative study but that it is really very difficult to get anything quantitative out of the work. It is not surprising that if you have an OH source in the particles that they will get oxidized. What is really needed is an estimate of how fast that chemistry occurs. When re-writing the paper for ACP, I suggest the authors be more clear about these issues, stressing the uncertainties associated with such statements as “substantially less carbon loss”. For example, in the Conclusions I do not think that the authors can claim that this “is an efficient pathway for the rapid formation of highly oxidized material”. My problem is with the word “efficient”. Without OH concentration measurements in the particles, this study remains qualitative.

Regardless of this issue, this is a very nice paper illustrating the possibility of aqueous phase oxidation in particles, and should be published,

Smaller points:

Is the AMS spectrum of oxalate sufficiently unique that it can be uniquely identified? Or, is the spectrum instead indicating small di-acids are present?

Why state that 3.7×10^{-12} M is an upper limit to the OH concentration in the bulk experiments? Is it not a good measure of the concentration itself?

I realize there are huge uncertainties, but even a conceptual mechanism showing how you can go from these polyols to oxalate might be valuable, with OH as the oxidant.

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