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Atmospheric
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Discussions

Interactive comment on "Characterization of aerosol and cloud water at a mountain site during WACS 2010: secondary organic aerosol formation through oxidative cloud processing" *by* A. K. Y. Lee et al.

Anonymous Referee #3

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This study reports on aqueous phase processing in cloud water samples and filter samples from aerosols collected near clouds. It is complemented by laboratory studies that explore the oxidative processing of water-soluble cloud water constituents (aldehydes). The authors confirm prior studies that oxidative processing yields highly oxidized material that will remain in the particle phase after cloud evaporation but in addition, they show that continuous processing leads to the formation of volatile compounds that likely partition to the gas phase upon drop evaporation. This study is clearly highly interesting as it is the first one that indeed analyses AMS spectra of 'real' cloud water and cloud-processed aerosol and, thus, exceeds the numerous laboratory studies that were performed under controlled conditions with selected precursors.

I have several comments below that should be addressed prior to publication that focus on the atmospheric relevance of the experimental conditions.

Major comments

1) Possible salt formation: In ambient aerosol samples there are considerable concentrations of dicarboxylates that do not have gas phase sources. While the acids are indeed to volatile to remain in the particle phase, it has been shown that they likely form salts or metal complexes (e.g. ammonium oxalate, calcium oxalate, . . .[Yang et al., 2009; Furukawa and Takahashi, 2011]) and thus are not available anymore for any further processing upon drop evaporation. – Did the analysis of particles or cloud water give any evidence of such compounds? – Could they have been detected at all by the applied method? Smaller dicarboxylates tend to form more stable salts. It is known that oxidation of larger diacids yields smaller acids – thus, an apparent increase in volatility of the acid products might under atmospheric conditions actually help forming less volatile material. – Some discussion along these lines should be added.

2) OH(aq) concentrations: The initial concentration of H2O2 (70 mM) seems very high as compared to H2O2 in cloud water. Can you give an estimate of the resulting OH(aq) concentration? Are the oxidation rates k[OH][Org] comparable to those in cloud droplets? Given that a cloud droplet lives on the order of a few minutes, these rates should be discussed in the context of realistic time scales. It seems that the loss processes might have been overestimated

Aldehyde + OH -> SOA + OH -> volatile compounds

since at too high OH concentrations all aldehydes are likely very quickly consumed and thus OH might be available to further oxidize SOA (acids) to volatile compounds. In real clouds the turn-over rates of the individual steps might be much slower (due to lower OH) and thus less SOA will be oxidized before drops evaporate and possibly salt formation occurs.

Minor comments

p. 6021, l. 29: This sentence reads as if the oxalic acid formation rate (microg /m3/s) might exceed sulfate formation which was likely not the case since sulfate concentrations are always much greater than oxalate levels. I assume that the authors refer to the statement that relatively oxalate formation increases later (i.e. higher in the cloud where LWC is higher) due to the multistep formation as opposed to the one-step formation of sulfate.

p. 6029, l. 3f: A sentence could be added that compares the O/C ratios derived from typical aqueous phase oxidation experiments (e.g., Lee et al., 2011, Lambe et al., 2011).

p. 6029, l. 14: Have similar experiments been performed (in other studies) under dry conditions? How quickly does mz44 increases if it is only formed from processing on/in dry particles or in the gas phase? Acid functionalities are usually formed quicker in the aqueous phase because of different mechanisms (gem-diol oxidation in the aqueous phase versus slower aldehyde oxidation if no water is present). Such a comparison would be highly interesting in order to confirm this trend for atmospheric constituents.

p. 6030, l. 18: Can you do a rough estimate of sulfate production during oxidation based on measured S(IV) and used H2O2 concentrations?

p. 6032, l. 7: What is meant by ‘cloud activation’?

p. 6032, l. 25: I assume that you imply that low volatility acids (e.g. dicaboxylic) are oxidized to form more volatile compounds. Such compounds (as stated corrected earler) might include formic and acetic acid. In a recent study a potential role of SOA formation by acetic acid has been suggested and should be cited here [Tan et al., 2012]

Section 3.5: Even though the methodology is described in a previous study, the general

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conditions should be briefly noted (e.g., H2O2 and OH concentrations, duration of experiments)

p. 6034, l. 5: Bateman et al.[2011] have shown that aqueous phase processing of terpene-derived SOA actually acts as a sink due to photolysis. These findings mentioned should be mentioned here. p. 6036, l. 10: Using only the Henry's law constant (KH) as a measure for a potential role on SOA formation is somewhat too simplified. A KH of 9000 M/atm implies that a few % of the compounds are partitioned to the aqueous phase at typical cloud LWC. While this is a first requirement for the importance of aqueous phase processing, it is the further reactivity in the aqueous phase that determines whether this material is efficiently oxidized. A high KH does not necessarily imply a high reactivity.

Technical comments

p. 6024, l. 147: should that be 'column'?

p. 6026, l. 21: monoterpene oxidation (not monoterpeneS)

References

Bateman, A. P., S. A. Nizkorodov, J. Laskin, and A. Laskin (2011), Photolytic processing of secondary organic aerosols dissolved in cloud droplets, Phys. Chem. Chem. Phys., 13(26), 12199-12212.

Furukawa, T., and Y. Takahashi (2011), Oxalate metal complexes in aerosol particles: implications for the hygroscopicity of oxalate-containing particles, Atmos. Chem. Phys., 11(9), 4289-4301, 10.5194/acp-11-4289-2011.

Tan, Y., Y. B. Lim, K. E. Altieri, S. P. Seitzinger, and B. J. Turpin (2012), Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal, Atmos. Chem. Phys., 12, 801-813.

Yang, F., H. Chen, X. Wang, X. Yang, J. Du, and J. Chen (2009), Single particle mass spectrometry of oxalic acid in ambient aerosols in Shanghai: Mixing state and formation mechanism, Atmospheric Environment, 43(25), 3876-3882.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6019, 2012.

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