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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In-cloud processes of methacrolein under simulated conditions – Part 3: Hygroscopic and volatility properties of the formed Secondary Organic Aerosol" *by* V. Michaud et al.

Anonymous Referee #1

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The authors couple volatility and hygroscopicity measurements to characterise SOA formed from the aqueous phase photo-oxidation of methacrolein. The authors find the SOA formed via aqueous photo-oxidation to be more hygroscopic than previously reported SOA values formed via gas-phase reactions with terpenes. As the SOA ages, the products become less volatile and hygroscopicity decreases. These results contribute to the growing evidence between the correlation of SOA volatility and hygroscopicity. The implications of this work are of use and importance to the larger scientific community.

This paper is part 3 of a larger body of work, however if treated as a solo entity not enough information is provided as to why methacrolein SOA is important; a few sentences are placed in the summary but more should be written in the introduction. This work is unique in that it studies specifically methacrolein aqueous photo-oxidation SOA formation but the results are similar to and can be correlated with other SOA ageing studies. For instance, Perri et al, 2009 observe the production of low volatility organic acids and oligmers via aqueous photo-oxidation. Meyer et al, 2009 and Asa-Awuku et al, 2009 also observed that more volatile compounds appear to be more hygroscopic. Meyer et al, 2009 found VH-TDMA measurements of unseeded SOA show a decrease in the hygroscopic growth (HGF) factor for increased volatilisation temperatures. Asa-Awuku et al, 2009 quantified the effect of changes in volatility and hygroscopicity for the CCN behaviour of beta-caryophyllene SOA. Incorporating these and other findings (see specific comments) will strengthen this works importance and implications. Once these and subsequent minor comments are addressed, the reviewer recommends this paper for publication.

COMMENTS

1.What is the temperature of the water in the nebulizer? Is it the same as the aqueous solution used to generate the SOA? If not what kind of an effect will it have on the volatility of the atomized systems?

2.What is the ambient temperature? And how does it range within the experiments? How can we compare values in Table 2 if T_ambient is significantly different?

3.How does adding salt to the aqueous solution after the reaction validate that the SOA is not influenced by the presence of inorganic salt? If the SOA contain polar compounds, interactions with the positive and negative ions could be of importance once salt is added to the solution (e.g. ion-dipole interactions, salting out effects).

4. The work of Warren et al, 2009 found SOA (from gaseous-phase oxidation) was altered in the presence of gaseous water during their hygroscopicity measurements. In

addition, Volkamer et al also found SOA formation in the aqueous phase was not limited to cloud droplets, but proceeded in the absence of clouds. How much would additional ageing during H-TDMA and V-HTDMA effect the composition of methacrolein SOA material in this study? The authors refer to properties characterized in Part 1 (Liu et al) and Part 2 (El Haddad et al), Can it be assumed that we are characterizing the same material? Any assumptions should be clearly stated in the text.

5.P6454. The authors state, " the aerosol physical properties change due to aqueous-phase photooxidation has never, to our knowledge, directly been quantified with identified compounds". The measurements of Sorooshian et al, should be quoted. For example, Sorooshian et al, 2007a found "aqueous phase reactions to produce organic acids, mainly oxalic acid, followed by droplet evaporation is a source of elevated organic acid aerosol levels above cloud. Oxalic acid is observed to be produced more efficiently relative to sulfate as the cloud liquid water content increases, corresponding to larger and less acidic droplets." Sorooshian et al, 2007b also found similar results.

SPECIFIC COMMENTS:

Please be consistent with the word aging and ageing.

P6453 L7: The direct and indirect effects are both dependant on.... The statement reads as though size distribution and hygroscopic properties are the only properties. Include some of the factors mentioned in following sentences (e..g composition, optical properties)

P6453 L14: Are the authors referring to only known mixtures of organics? It is unclear. If not there are several SOA ageing experiments that belong here and that are mentioned later on (e.g Varutbangkul, 2006)

P6453 L22: Replace "the resulting ambient" with "the resulting aged ambient"

P6453 L28: Previous VHTDMA technique and measurement papers should be cited as well (e.g. Johnson et al, 2005).

P6454 L8: Along the same lines as Kalberer et al, 2004, Perri et al, 2009 can be cited here.

P6454 L17 and L21: "However the aerosol physical properties ..... " Include the works of Sorooshian et al.

P6454 L19. Chen et al have also shown that methacrolein is an important precursor for SOA and Fu et al, 2009 have demonstrated the importance of the aqueous phase reactive uptake for SOA formation. This is related to the statement that methacrolein can form SOA and will reinforce its significance for this study.

P6460 L5: replace "Jin" with "In"

P6460 L8: replace "equivalent" with "similar". 1.8 seconds and 2 seconds

P6460 L10. Replace " we evidence" with "we see evidence"

P6463 L2: Methacrolein is misspelled.

P6467 L5: Include chen et al reference

P6467 L5: Replace "which seem to be different" with differ

Table 5: Please add a Table annotation for the abbreviation ND.

Figure 1: Text in figures is very small , blurry, and difficult to read.

Additional References

1. Meyer, NK; Duplissy, J; Gysel, M; et al. Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles ATMOSPHERIC CHEMISTRY AND PHYSICS, 9 (2): 721-732 2009

2. Asa-Awuku A; Engelhart GJ , Lee BH; Pandis SN; Nenes A; Relating CCN activity, volatility, and droplet growth kinetics of beta-caryophyllene secondary organic aerosol ATMOSPHERIC CHEMISTRY AND PHYSICS , 9 , (3): 795-812, 2009

3. Volkamer, R; Ziemann, PJ; Molina, MJ: Secondary Organic Aerosol Formation from Acetylene (C2H2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase ATMOSPHERIC CHEMISTRY AND PHYSICS, 9 (6): 1907-1928 2009

4. Warren, B; Malloy, QGJ; Yee, LD; et al. Secondary organic aerosol formation from cyclohexene ozonolysis in the presence of water vapor and dissolved salts ATMOSPHERIC ENVIRONMENT, 43 (10): 1789-1795 MAR 2009

5. Fu, TM; Jacob, DJ; Heald, CL Aqueous-phase reactive uptake of dicarbonyls as a source of organic aerosol over eastern North America ATMOSPHERIC ENVIRONMENT, 43 (10): 1814-1822 MAR 2009

6. Perri, MJ; Seitzinger, S; Turpin, BJ Secondary organic aerosol production from aqueous photooxidation of glycolaldehyde: Laboratory experiments ATMOSPHERIC ENVIRONMENT, 43 (8): 1487-1497 MAR 2009

7. Chen, ZM; Wang, HL; Zhu, LH; et al. Aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone: a potentially important source of atmospheric aqueous oxidants ATMOSPHERIC CHEMISTRY AND PHYSICS, 8 (8): 2255-2265 2008

8. Johnson GR, Ristovski ZD, D'Anna B, et al. Hygroscopic behavior of partially volatilized coastal marine aerosols using the volatilization and humidification tandem differential mobility analyzer technique : JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES Volume: 110 Issue: D20 Article Number: D20203 Published: OCT 25 2005

9. Sorooshian A, Lu ML, Brechtel FJ, et al. On the source of organic acid aerosol layers above clouds Source: ENVIRONMENTAL SCIENCE & TECHNOLOGY 41, 13 , 4647-4654, 2007a

10. Sorooshian A, Ng NL, Chan AWH, et al. Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmo-

spheric Composition and Climate Study (GoMACCS) JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES Volume: 112 Issue: D13 Article Number: D13201 Published: JUL 3 2007b

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