Atmos. Chem. Phys. Discuss., 7, S8040–S8043, 2007
www.atmos-chem-phys-discuss.net/7/S8040/2007/
© Author(s) 2007. This work is licensed
under a Creative Commons License.

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone: a potentially important source of atmospheric aqueous oxidants" *by* Z. M. Chen et al.

M. Claeys (Referee)

magda.claeys@ua.ac.be

Received and published: 29 December 2007

General comments:

This study provides experimental evidence for the formation of aqueous-phase oxidants including hydrogen peroxide through aqueous-phase ozonolysis of methacrolein (MAC) and methyl vinyl ketone (MVK), which can lead to substantial SOA formation in the aqueous aerosol phase and clouds. It remains questionable that the aqueous-phase ozonolysis of unreacted isoprene and other alkenes is relevant under atmo-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

spheric conditions; hence, I suggest to focus the discussion more on MAC and MVK. With respect to MAC, there is firm experimental evidence that it can indeed undergo further oxidation in the aerosol phase and clouds (see specific comments).

Specific comments:

Page 17600 - l. 18: I suggest to change this sentence as follows: "The formation of oxidants from the aqueous-phase ozonolysis of MAC and MVK supports the formation of aerosols from the aqueous-phase acid-catalyzed reaction of H2O2 with MAC." As stated by the authors (page 17601 - l. 3) the amount of SOA derived from the aqueous-phase oxidation of isoprene is estimated at 0.00025 Tg/yr, which is negligeable. With respect to MAC, it has been shown in the recent study by Surratt et al. (J. Phys. Chem A, 110, 9665-9690, 2006) that photooxidation of isoprene under high-NOx conditions results in the formation of 2-methylglyceric acid and oligoesters thereof through particle-phase reactions of MAC, a first-generation oxidation product of isoprene (see also below). I am also aware that MAC forms SOA through in-cloud aqueous-phase photooxidation (presentation by E. Quivet at the International Science Meeting of the ESF networks VOCBAS and INTROP "Biogenic Volatile Organic Compounds: Sources and fates in a changing world", Montpellier, France, 2-5 October, 2007).

Page 17601 - l. 5: it would also be appropriate to cite here the recent modeling study by Henze and Seinfeld (Geophys. Res. Lett. 33, L09812, 2006). It was indicated in this paper that inclusion of isoprene and its oxidation products as a source of SOA in a global model increases the global burden of SOA by more than a factor of two.

Page 17601 - l. 11: it cannot be claimed that all the SOA from the oxidation of isoprene is formed by aqueous-phase reactions; a major part of the isoprene SOA involves gas-phase photochemistry, especially at low-NOx conditions (see, for example, the article by Surratt et al. J. Phys. Chem A, 110, 9665-9690, 2006); therefore, I suggest to be more conservative here and to write: "in a SOA strength of 2-5 Tg/yr ...".

Page 17603 - l. 3: the amount of SOA derived from the aqueous-phase oxidation of isoprene is estimated at 0.00025 Tg/yr, which is much lower than the value derived from field and laboratory studies, suggesting that SOA formation from isoprene also occurs in the gas phase, as has originally been proposed by Claeys et al. (Science 303, 1173-1176, 2004). I suggest to omit l. 3-9 and to limit the discussion to SOA formation from the aqueous-phase reaction of MAC and MVK.

Page 17603 - l. 12: at this stage it would also be relevant to mention the following: "In this context, it has been demonstrated that photooxidation of isoprene under high-NOx conditions results in a high yield of 2-methylglyceric acid and oligoesters thereof through particle-phase reactions of MAC, a first-generation gas-phase oxidation product of isoprene (Surratt et al. J. Phys. Chem. A 2006)".

Page 17610 - l. 28: in my opinion, it is not possible to estimate the amount of MAC and MVK participating in aqueous-phase reactions, based on the yield of ˜0.2% obtained for the 2-methyltetrols, given that these products are mainly formed through gas-phase oxidation of isoprene.

Page 17611 - l. 9: again, I suggest to limit the discussion to aqueous-phase oxidation of the gas-phase oxidation products of isoprene, i.e., MAC and MVK.

Page 17611 - l. 16: replace the term "2,3-dihydroxymethacrylic acid" by "2-methylglyceric acid"; the term "2,3-dihydroxymethacrylic acid" has been introduced in the article by Claeys et al. (Atmos. Environ. 2004) but is incorrect.

Page 17612 - l. 3: in the light of the arguments made above, I suggest to omit l. 3- 7 (if this conjecture ... oxidants) and to rephrase the sentence starting on l. 7: "These aqueous oxidants, especially of peroxides, produced by the aqueous-phase reaction itself support the formation of SOA from MAC via the ...".

Page 17612 - l. 10: I suggest to slightly rephrase the sentences as follows: "Moreover, the present study also provides supporting laboratory evidence for field observations. In this respect, Valverde-Canossa et al. (2005) ...".

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Technical corrections:

Page 17600 - l. 10; ... methylglyoxal (MG), in both of these ...

Page 17601 - l. 18: ... has not been addressed: ...

Page 17602 - l. 5: ... emissions of biogenic alkanes, ...

Page 17604 - l. 25: ... dimer ...

Page 17605 - l. 4: ..., methylglyoxal (MG), ...

Page 17605 - l. 23: ... several tens of minutes but, ...

Page 17606 - l. 3: Thus, the H2O2 detected in the ... (omit "concentration")

Page 17606 - l. 7, 9 and 11: ... derivatization ...

Page 17606 - l. 11: ... derivatization conditions ...

Page 17608 - l. 9: ... is needed to support this assumption.

Page 17609 - l. 4: ... into other products.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 17599, 2007.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper