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Atmospheric
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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.

Z. M. Chen et al.

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We appreciate the constructive comments of Prof. Claeys and are grateful for his time and effort. Here are our responses to the comments:

(1) Limit the discussion to aqueous-phase oxidation of MAC and MVK.

This is a good suggestion. The conjecture extend of the present results to the aqueous-phase ozonolysis of isoprene, up to date, is short of enough experimental evidence. The related content in the text will be corrected.

(2) The amount of isoprene SOA from aqueous-phase reactions.

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First, the aqueous-phase reaction mentioned in our manuscript includes not only the reaction in the bulk of liquid but also the reaction on the surface of liquid (Herrmann, Chem. Rev. 103, 4691-4716, 2003). Moreover, water clusters, $(H_2O)_n$, which are ubiquitous in the atmosphere, are considered to potentially participate in the atmospheric chemistry (Ryzhkov et al., Chem. Phys. Lett. 419, 479-485, 2006; Sennikov et al., ChemPhysChem 6, 392-412, 2005). We think the reaction in regard to water clusters can also be categorized into the aqueous reaction. We propose three scenarios for the aqueous-phase reaction in the atmosphere, as shown in Fig. 6 in page 17623. These scenarios may enlarge the aqueous-phase reaction scope than that considered usually in previous multi-phase chemical models. Although only the reactions in the bulk of liquid were investigated in the present study, we think all the three scenarios for aqueous-phase reactions described in Fig. 6 are present simultaneously in the atmosphere, especially for the rapid reactions, such as the aqueous-phase ozonolysis of MAC or MVK. However, what is the percentage for each of the three reaction scenarios? This needs further laboratory and modeling studies.

Secondly, Henze et al. estimated that the amount of SOA produced directly from isoprene is 6.2 Tg yr^{-1}, only considering the contribution from OH oxidation (Geophys. Res. Lett. 33, L09812, 2006). Hoyle et al. estimated that the amount of SOA from the oxidation products of isoprene is 15 Tg yr^{-1} (Atmos. Chem. Phys., 7, 5675-5694, 2007). Matsunaga et al. estimated a source of SOA from isoprene in the range of 10-120 Tg yr^{-1} (Atmos. Chem. Phys. Discus., 1, 11143-11156, 2005). Obviously, the amount of isoprene SOA may be larger as more and more laboratory and field evidences are found. These estimations about the amount of isoprene SOA include the amount from both the gas-phase reaction and aqueous-phase reaction. The part of isoprene SOA from the aqueous-phase reaction can be produced through the reaction in solution (Claeys et al., Atmos. Environ. 38, 4093-4098, 2004; Quivet et al., 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), the reaction in the presence of droplets with a yield of SOA from iso-

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prene about 0.22% (Böge, et al., Atmos. Environ. 40, 2501-2509, 2006), the process of cloud processing with a amount about 1.6 Tg yr^{-1} (Lim et al., Environ. Sci. Technol. 39, 4441-4446, 2005), and the reaction on acidic humid particles (Surratt et al., J. Phys. Chem. A 110, 9665-9690, 2006). All these reactions belong to the categories of aqueous-phase reactions mentioned in the text.

In summary, the amount of SOA from isoprene and its oxidation products through the aqueous-phase reactions should be substantial, and the amount may be larger if all the three aqueous-phase reaction scenarios proposed by us were considered in the aqueous-phase models.

(3) The amount of SOA from the aqueous-phase oxidation of isoprene is estimated at 0.00025 Tg yr^{-1}, which is much lower than the value derived from field and laboratory studies.

0.00025 Tg yr^{-1} is the value calculated from the aqueous-phase reaction only occurring in the bulk of liquid on the basis of the Henry constant of isoprene. Obviously, this part cannot involve total amount of isoprene SOA from the aqueous-phase reaction in which the other two aqueous-phase reaction scenarios may provide more important contribution to isoprene SOA. Thus, 0.00025 Tg yr^{-1} should be smaller than the total amount of isoprene SOA from the whole aqueous-phase reaction.

(4) Relevant content of the production of a high yield of 2-methylglyceric acid and oligoesters thereof through particle-phase reactions of MAC, under high-NOx conditions (Surratt et al. J. Phys. Chem. A 2006).

A sentence of this effect will be added to the text.

(5) Estimate of the amount of MAC and MVK participating in aqueous-phase reactions, based on the yield of SOA from isoprene through aqueous-phase reactions.

Based on the yield of ∼0.2% obtained for the 2-methyltetrols, it cannot estimate the amount of MAC and MVK participating in aqueous-phase reactions, because a part of

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2-methyltetrols is from gas-phase reactions. However, according to the recent studies (Henze et al., 2006; Hoyle et al., 2007; Matsunaga et al., 2005; Koll et al., Geophys. Res. Lett. 32, L18808, 2005; Koll et al., Environ. Sci. Technol. 40, 1869-1877, 2006), the yield of SOA from isoprene is about 1-3%.

According to the estimation of Böge, et al. (2006) and Lim et al., (2006), the yield of SOA from isoprene through aqueous-phase is ~0.22%. On the basis of this yield, it can be estimated that there are a great amount of MAC and MVK participating in the aqueous-phase reaction, as mentioned in page 17610/17611 in the text.

(6) Other specific suggestions will be accepted.

(7) Technical points will be corrected.

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