**Atmospheric
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Comment

Interactive comment on "Evaluation of the atmospheric significance of multiphase reactions in atmospheric secondary organic aerosol formation" *by* A. Gelencsér and Z. Varga

A. Gelencsér and Z. Varga

Received and published: 12 September 2005

We fully agree with the referees that the conceptual model is a gross simplification with respect to the complexities of atmospheric systems. The Achilles' heel of the approach is that it assumes consecutive reactions in the aqueous phase with prescribed rate constants leading to prescribed reductions in vapor pressure and increases in solubility. If for any given precursor these reaction steps did not take place, or their rates were much lower, or the intermediate and particularly the reaction product were more volatile than assumed, it would fail to lead to significant SOA formation via this route despite its potential based on its Henry constant alone. However, the few recent studies on multiphase photooxidation of specific precursors have shown that in such reactions

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the carbon skeleton tends to be retained as against gas-phase photooxidation which leads to shorter (and thus possibly more volatile) carbon chain products (Warneck, 2003; Ervens et al., 2004a). Nevertheless, a rough sensitivity test regarding the equilibrium vapor pressures of the intermediate and the product is indeed necessary just as already done for the reaction rates in Figure 1 and 2. This will be provided in the revised version to be submitted to ACP. Reading the referees' comments we also feel necessary to add a schematic diagram reflecting the concept and the basic processes considered, including fundamental equations used in the model. The model itself is a simple numerical model calculating incremental mass changes in both the gas and aqueous phase then reestablishing equilibrium between the phases after each elementary time-step. Some set parameters used for the calculations are indeed missing from the paper: the average molecular weight and aerosol mass fraction of the absorbing organic phase are assumed to be 300 g/mol and 0.3, respectively.

The thermodynamic equilibrium between the phases is another critical issue as pointed out by Referee #2. Again, assuming instantaneous equilibrium between the gas and droplet phase is a simplification which could lead to overestimation of SOA production with respect to reality when establishment of equilibrium is delayed by transport processes. Part of these effects are accounted for by the use of the global reaction rate as described below. While this point will be mentioned in the revised manuscript, it should be noted that its effect may be compensated for by our initial assumption that the air parcel is sealed off from its environment during the entire duration of the cloud cycles, i.e. no replenishment of the precursor is allowed from outside. In any case, there is a clear need for incorporating such processes into realistic cloud models, but it is not worth the effort until exact reaction mechanisms, rates and physical properties of the products are established. There have been examples for more developed models for specific and better understood reaction systems in the studies by Warneck (2003) and Ervens et al. (2004a).

Indeed it is possible that under certain conditions low solubility species might contribute

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to aerosol mass formation. The role of ozone in S(IV) formation at high pH is mainly due to its very high abundance (in the order of few pbb) relative to H2O2 which can offset its very low solubility. On the other hand, it is indeed possible for a low solubility organic species to contribute, if, for example, its solubility in greatly enhanced by interactions with dissolved species in the cloud droplets. Examples are hydration of aldehydes (leading to a much higher effective Henry constant), or the well-established adduct formation between formaldehyde and S(IV)-species in cloud droplets.

Absorptive partitioning theory indeed predicts complete partitioning of oxalic acid into the aerosol phase. Recent studies quoted by Referee #2 have challenged this prediction. However, there are biases between theory and observations the other way, too: for examples, much more pinonaldehyde was found in the aerosol phase than would be predicted by this theory (see compilation by Anderson-Sköld and Simpson, 1999). In general, there have been more and more indications that the classic absorptive partitioning theory may not be adequate to describe gas-particle equilibria in the atmosphere–however, to date no better approach has been developed. In any case, this issue is beyond the scope of our work, though a paragraph will be added to the revised manuscript to show the uncertainties associated with the use of the theory in the calculations.

Regarding the difference between our model and that of Ervens et al. (2004) the most important difference is that our model is a conceptual one not specific to any known photooxidation mechanism but sweeping through a range of Henry-constant to establish its role in the process and identify potential precursors for further (experimental) research; on the other hand, the model by Ervens et al. (2004), being much more developed than ours, is a case study using chemically established reaction pathways for selected precursors with an experimentally determined set of parameters. Another less important difference is that our model assumes aerosol state and uses the absorptive partitioning theory for the calculation of equilibrium partitioning after the cloud cycle, whereas Ervens et al. admittedly retains organics in the aqueous particle phase.

Nevertheless, the results of the models agree well as far as our model suggests potentially significant SOA formation from glyoxal and glycolaldehyde based on their Henry-constants alone, in harmony with the more elaborated case study using experimental data and mechanisms.

In our model, the dynamics of cloud formation is not considered, thus LWC remains constant for the entire cloud period, for which thermodynamic equilibrium is also assumed. In our model no 100 % yield is assumed for any of the aqueous phase oxidation steps, but the incremental mass increase is calculated based on the assumed reaction rates in each time step then equilibrium is reestablished between the phases. 'Global reaction rate expression' is taken from Ravishankara (1997), defined as the overall first-order rate coefficient for the loss of reactant in the liquid phase, which combines the resistances of elementary steps such as gas-phase diffusion, mass accommodation, diffusion in the droplet, and the rates of chemical reactions. This explanation will be added to the revised manuscript for clarification. We fully agree with the referee that a comparison of the yields of gas and aqueous phase processes is very useful as it is readily available from the model, and should be presented in the revised manuscript. Given that consecutive reactions are considered, the sum of the masses formed in aqueous and gas-phase reactions is higher than the mass loss of the precursor. Of course, overall mass balance is not violated at any time. The study on the oxidation mechanism of hydroxyacetone kindly brought forward by Referee #2 will be referenced in the revised manuscript. The Henry's Law constant of methacrolein reported by Iraci et al. (1999) is the effective one as stated in their paper. Potentially, organic compounds may yield gas-phase species such as HCHO or CO_2 upon photooxidation, which leads to reduced SOA formation efficiency compared to S(IV) oxidation. This possibility, however, is not exploited in our model in which we assume a single less volatile product for each aqueous-phase oxidation step. The calculation of the aerosol yield does not require assumption for the molecular weight of the product, since it relates the mass of aerosol formed to the mass of the precursor lost on a carbon basis. It is exactly the same definition as commonly used in smog-chamber experiments (Hoffmann et

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al., 1997). The rate constants shown in Figure 1 and 2 are of second-order, but can also be expressed as (pseudo) first-order constants by multiplying with the assumed constant OH concentrations in both the gas and the aqueous phase. Page 4409, line 12: "Polluted boundary layer" may indeed be a better term instead of "source areas" in the context used.

The size-distribution of dicarboxylic acids observed by Chan et al. may indeed lend support to cloud processes as a potential source. However, in urban areas, the precursors of dicarboxylic acid could be totally different from those established for marine or remote environment (e.g. toluene instead of ethene or acetylene for oxalic acid), and direct emission of dicarboxylic acid and subsequent repartitioning into preexisting particles can also be taken into account in interpreting size-distribution measurements.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 4407, 2005.

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