

# ***Interactive comment on “Modelling the formation and composition of secondary organic aerosol from $\alpha$ - and $\beta$ -pinene ozonolysis using MCM v3” by M. E. Jenkin***

**Anonymous Referee #1**

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## **1. General comments**

This paper is focussing on the details of secondary organic aerosol formation and its complexity in a quite novel approach. By using the highly detailed Master Chemical Mechanism (MCM) version 3 of the Leeds university, it is tried to use as much information as possible about the chemical nature and the formation of the SOA mass production observed in smog chamber studies such as performed e.g. in the EU-project OSOA or by the group of Richard Kamens [[Kamens \*et al.\* \(1999\)](#)] in the United States. Previously, modelling studies have only treated a selected group of organic compounds detected in laboratory studies usually with a lumped chemistry mechanism or even not.

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These studies are most probably affected by the overestimated partitioning coefficients used for the conversion of the gas phase species to the aerosol phase especially with respect to carbonyl compounds such as pinonaldehyde ( $\alpha$ -pinene) and nopinone primary volatile products of both monoterpene oxidation reactions. The current study by Jenkin is calculating the partitioning coefficients for at least 200 organic compound candidates for SOA formation with the group contribution methods from Joback and Reid cited by Joback and Reid and Stein and Brown. The dynamical process of Kamens is then used to describe the adsorption and desorption process of gas phase molecules at the aerosol surface and the sticking probability.

Because of the fact that partitioning requires organic aerosol mass previously produced the author sets up not only a small amount of organic 'seed particles' but also his 'acid chaperone' mechanism associated with dimer formation of acids in the gas phase and its subsequent aerosol formation by achieving an extremely low saturation vapour pressure. Therefore, Jenkin directly forms SOA by a chemical reaction without a limitation by a saturation vapour pressure assuming a sufficiently low volatility. This procedure is comparable to the approach of Kamens assuming secondary ozonides with an assumed vapour pressure of  $1.0 \times 10^{-12}$  Pa. With this, the author states that only negligible amounts of SOA were calculated reflecting the current mismatch of understanding and reality of the process of aerosol production in its entirety. There was a need to increase the partitioning coefficients and therefore the saturation vapour pressures by a species independent scaling factor of 120 in order to simulate the observed SOA mass time evolution. By doing so, the final aerosol mass yield could be achieved, with the acid chaperone mechanism needed to simulate the initial SOA mass increase observed.

One highlight of this study is the calculation of hydroperoxy- and hydroxy-compounds contribution to the SOA mass not experimentally investigated, which is in a good agreement to our findings on a global scale [Bonn *et al.* (2004)]. Although, in our study the chemical mechanism was highly lumped compared to the MCM the general outcome

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was similar for the laboratory studies been considered.

## 2. Specific comments

There are two points tackled in this paper, for whom additional comments have to be made. The first one is the reduction of the saturation vapour pressures by a factor of 120 in order to meet the observed SOA mass concentration. Because of the fact that all investigated compounds are solid in the aerosol phase for the usual meteorological conditions chosen, the partitioning coefficient might be used with the solid vapour pressure instead of the liquid vapour pressure as formulated by Pankow Pankow. This would explain some of the mismatch. Moreover, the organic mixture inside the aerosol phase is most probably non-ideal. By taking this into account, the match of simulations and observations might improve as well. Of course affected by the high complexity of SOA composition this is no easy task to perform and needs probably to be reduced on groups such as acids, alcohols and hydroperoxides. This is linked to the second point to be made. The acid chaperone mechanism as described in the paper is used for acid dimerization but without any saturation vapour pressure limitation. This criterion might be fulfilled by a different specification of the participating species and processes. Some of them might be currently not known. E.g. a shutdown of the desorption by e.g. a polymerisation reaction [Jang *et al.* (2002), Kalberer *et al.* (2004)] or a rapid aerosol phase processing of the condensed compounds would prevent any equilibrium between adsorption and desorption causing a rapid condensation process. Unfortunately, this is a current topic of intensive discussions and might be investigated with the tools presented by the author best in the near future. Therefore, the presented acid dimers might be one explanation out of a bunch of possibilities and should be discussed in more detail in this paper. The assumption of acids (and their dimers) for the initial particle formation step contradicts the experimental observations with nucleation affected by water vapour,

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but not the yield of acids [Bonn *et al.* (2002), Bonn and Moortgat (2002), Bonn (2002)]. Especially, the very first steps of particle formation from organic gas phase precursors and the subsequent processing until the analytical detection remain unresolved although needed in order to understand the occurring processes in detail. But with the set-up described in this paper and heterogeneous extensions, it is most likely that the current knowledge will improve significantly.

### 3. Technical comments

Finally, the arrows shown in Figure 3 have not been explained in the text as well as in the figure caption. What is expressed by these, a different shift in time ?

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