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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modelling the formation and composition of secondary organic aerosol from α- and β-pinene ozonolysis using MCM v3" *by* M. E. Jenkin

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I am grateful to all the referees for their generally supportive comments on this paper. Each referee raises a number of discussion points, which are dealt with in detail below. A revised manuscript reflecting some (but not all) of the referees' suggestions will be submitted, based on the responses given below.

Referee 1, comment 1: Product vapour pressures

The referee notes the requirement to reduce substantially the vapour pressures of the product species in order to simulate the observed SOA mass concentrations, and suggests that the use of vapour pressures with respect the solid phase (rather than sub-cooled liquid vapour pressures) might be more appropriate for the temperatures of the experiments considered. A supplementary comment queries the assumption of the

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SOA being an ideal mixture.

It is noted in the manuscript that the species would generally be expected to be solid in their pure states, and certainly the use of estimated solid vapour pressures would increase the simulated quantity of SOA formed. However, the absorptive partitioning theory of Pankow (1994) (the initial basis for the procedure adopted) makes the assumption that the depression of melting points in a complex mixture is sufficient for the aerosol to act as an amorphous liquid, and that the sub-cooled liquid vapour pressure is therefore the appropriate quantity. This assumption has been made previously by numerous authors (cited in the manuscript), and is also pointed out in the comments made by referee 2. Although the present methodology ultimately requires modifications to the treatment, it is necessary to use the sub-cooled liquid vapour pressures as the starting point, consistent with the theory of Pankow (1994). Similarly, the assumption of an ideal mixture has been made in most (if not all) previous appraisals using that theory, and therefore has to be the initial assumption in the present work even if some of the subsequent modifications applied to improve the simulations of observed SOA are indicative of a degree of non-ideality.

Referee 1, comment 2: Acid dimer formation

The referee questions the use of the supplementary mechanism, based on acid dimer formation, suggesting that it is not supported by reported observations. The referee points out that aerosol nucleation has been shown to depend on water vapour concentration, and that this is inconsistent with a mechanism involving acid dimers.

It is acknowledged that reported results at low water vapour concentrations are indicative of the participation of secondary ozonides or acyloxy-hydroperoxides formed from the secondary reactions of Criegee biradicals with carbonyls and carboxylic acids (as already stated in the manuscript). However, as also discussed in the manuscript, the mechanism applied in the present manuscript successfully recreates the observed initial accumulation of SOA mass concentration in numerous experiments at various relative humidities. In particular, initial accumulation of SOA mass observed in the OSOA alpha-pinene experiments at 45% relative humidity (when secondary ozonide and acyloxy-hydroperoxide formation is precluded) and with 60 ppm water was indistinguishable, indicating that an alternative mechanism is generally required for the conditions of the experiments being considered. Although this is not in itself proof for a mechanism involving acid dimers, independent support is provide by the studies of Hoffmann and co-workers (cited), who observed prompt formation of a number of such species during alpha-pinene ozonolysis. The present simulations therefore serve to illustrate the possible impact of gas-phase dimer formation on SOA formation, using a simplified mechanism. It is recognised that acid dimer formation may not be solely responsible for the initial accumulation of SOA, and no such claim is made: it is simply pointed out that supplementary use of this simplified mechanism results in a substantial improvements to the simulations.

Referee 2, comment 1: 2-butanol oxidation

The referee queries the basis for assigning a branching ratio 64% to the major oxidation route for 2-butanol (reactions R3 and R4).

This figure is based on that used in the MCM (since v2), which was calculated using the group reactivity method of Porter et al. (1997). This is also consistent with the reported determinations of the yield of 2-butanone by Chew and Atkinson (1996), 69.5% and Baxley and Wells (1998), 60%. This will be clarified in the revised manuscript, and the typographical correction identified for R4 will be applied.

Referee 2, comment 2: Reference molecular weight

The referee seeks clarification on the molecular weight value used to calculate the partitioning coefficients presented in Table 1.

The reference value of 130 g/mol, given in the text, is applied. Although this value appears arbitrary, preliminary work (not presented in the manuscript) was carried

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out to compare the partitioning coefficients calculated by the method described with estimated octanol-air partitioning coefficients, based on Henry's Law constants and octanol-water partitioning coefficients. The octanol-air partitioning coefficient has been suggested as a suitable surrogate for organic partitioning to ambient aerosols (Finizio et al., 1997). To assist comparison, a reference molecular weight equivalent to that for octanol (130 g/mol) was therefore used. In the revised manuscript, a brief footnote will be added to Table 1 to clarify this point.

Referee 2, comment 3: Solid vapour pressures

The referee suggests that the brief discussion of solid vapour pressures in section 2.2 and the inclusion of examples in Table 1 is unwarranted.

The purpose of these calculations was to facilitate comparison of the estimated vapour pressures with those reported in the literature for the pure compounds which, as the referee points out, are solids.

Referee 2, comment 4: Temperature dependence of partitioning

The referee questions the representation of the temperature dependence of the partitioning coefficients, through use of the kinetics expression for desorption (equation 5), suggesting that application of equations (1) and (2) to derive the temperature dependence would be more consistent. A supplementary comment queries the necessity to present the results of simulations without the acid dimer mechanism operating.

The application of equations (1) and (2) would allow the calculation of temperature dependent partitioning coefficients which are consistent with the absorptive partitioning theory of Pankow (1994), such that the temperature dependences would be constrained accordingly. One of the major conclusions of the present analysis is that the observed formation of SOA cannot be fully accounted for by the absorptive partitioning theory, and it would not be possible to fit the experimental data without flexibility in both the absolute magnitudes of the partitioning coefficients and in their temperature dependences. For that reason, the representation of the temperature dependence was decoupled, using a method which is very similar to that adopted by Kamens and co-workers (cited), as indicated in the manuscript.

The presentation of the results without the acid dimer mechanism operating is considered necessary, as it emphasises that it is required to account for the initial accumulation of SOA. Given that no figures would actually be removed by eliminating the results of these simulations from Figures 3 and 4, it seems that little benefit would be achieved by omitting them.

Referee 2, comment 5: Relative humidity of Yu et al. experiments

The comment of the referee regarding the ca. 5% relative humidity in the Yu et al. experiments is noted, and Table 2 will be amended accordingly. Use of this value is consistent with that applied in the original simulations.

Referee 2, comment 6: Observed product yields

The referee suggests that the reported product yields for pinene ozonolysis should be included in Table 3.

A comprehensive summary of product yields is available in Atkinson and Arey (2003), Tables 3 and 4. Inspection of these tables quickly reveals that there is far too much data to present in Table 3 of the present manuscript, and indeed that reported yields for some species cover considerable ranges. Any inclusion of experimental yield data would therefore need to be selective. The statement in section 4.1 that the simulated yields are generally consistent with "reported ranges" in the product yields (with reference to a number of studies and the Atkinson and Arey review) is therefore considered adequate.

Referee 2, comment 7: Temperature dependence of acid chaperone mechanism

The referee queries the large temperature dependence of the acid chaperone mechanism, and the necessity to present the temperature dependence of the SOA yields.

The temperature dependences derived for both the acid chaperone and partitioning mechanisms are based on fitting to the experimental data in Table 2, and reflect that the initial stages of SOA accumulation appear to be more dependent on temperature than the final yields. The comparatively low temperature dependence of partitioning mechanism is, perhaps, a little surprising, but is a consequence of the results of the series of experiments considered (Table 2). The large temperature dependence of the dimer mechanism (influenced by the initial rate of SOA formation) is not unreasonable, because it is representative of the temperature dependences of monomer-dimer equilibria involving particularly strongly-bound acid dimers (i.e. such as those involving acids from alpha-pinene ozonolysis, reported by Kuckelmann et al., 2000).

As indicated by the referee, the calculated temperature dependence of SOA yields (based on the Pankow absorptive partitioning mechanism) has been reported previously by Sheehan and Bowman (2001). A statement will be added to the revised manuscript to indicate that the present results may be compared and contrasted with those of Sheehan and Bowman.

Referee 3, comment 1: Recent cyclohexene ozonolysis paper

The referee summarises the findings of a recent interesting paper considering the formation of SOA from the ozonolysis of cyclohexene, and the dependence of SOA yields on added OH radical scavengers (Keywood et al., 2004). A main conclusion is that larger [HO2]/RO2] ratios increase SOA formation from endocyclic alkenes, and decrease it from exocyclic alkenes. Some discussion of the results of that paper are sought.

The Keywood et al. (2004) paper is clearly relevant to the present study, and it will be cited and discussed in the revised manuscript. The general observations of increased SOA yield when 2-butanol is used as an OH scavenger indicate an opposite-sense dependence from that reported for beta-pinene (Docherty and Ziemann, 2003), which is the main basis for the general conclusion regarding endocyclic and exocyclic alkenes.

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The comparison of yields calculated for alpha- and beta-pinene with the present mechanism predicts a decrease for beta-pinene when 2-butanol is used instead of cyclohexane, but predicts very little yield dependence for alpha-pinene (cyclohexane slightly favoured at low SOA mass concentration; 2-butanol slightly favoured at higher SOA mass concentration, > ca. 150 microg/m3). Cyclohexene and alpha-pinene are both endocyclic alkenes: however, it is not clear in advance whether a mechanism constructed using the same MCM methodology as that used for alpha-pinene would yield similar results for cyclohexene. Key differences are that alpha-pinene is bicyclic and contains an alkyl substitution on the double bond: this does influence the degradation mechanism and, possibly, the response to using different OH scavengers:

(i) The organic radical likely to be formed in conjunction with OH following the ozonolysis of cyclohexene can yield HO2, CO and pentandial via a single RO2 radical. Such a prompt source of HO2 is unavailable for alpha-pinene (as a direct consequence of the structural features indicated above), such that the yield of HO2 purely from alpha-pinene ozonolysis is very small. Consequently, the [HO2]/[RO2] ratio during cyclohexene ozonolysis is naturally much higher than during alpha-pinene ozonolysis, such that the system is in a regime where it is sensitive to further change resulting from using 2-butanol to scavenge OH (in preference to cyclohexane)

(ii) The organic radical likely to be formed in conjunction with OH is also partially broken down into smaller products (C4 and C5) via propagating channels of peroxy radical permutation reactions, followed by fragmentation routes. It is therefore possible that a greater proportion of the product mass is directed into multifunctional C5 and C6 products at higher [HO2]/[RO2]. In the cases of alpha- and beta-pinene, fragmentation processes do not have such a dramatic effect because the change from C10 to C8 products is not as significant as the change from C6 to C4: furthermore, their bicyclic character can result in the occurrence of supplementary ring-opening processes (which do not decrease carbon number), instead of fragmentation pathways.

Referee 3, comment 2: Influence of dimer mechanism

The referee queries whether the purpose of the dimer mechanism is to produce lower vapour pressure species, or species of higher molecular weight. In the former case, a supplementary point queries whether the same effect would result from assuming a zero desportion rate for the component acids in question.

The simplified dimer mechanism was considered mainly as a method of producing low volatility species for which there is reported evidence (Kuckelmann et al., 2000). Its effect it notably different from assuming that the component acids are irreversibly adsorbed, in two ways. First, it displays a second order dependence on the concentration of multifunctional acids, such that it is most important in the early stages of the experiment when their gas-phase concentration is highest. Secondly, the process is reversible, because it notionally incorporates the dimer-monomer equilibration in the condensed phase.

Referee 3, comment 3: SOA formation in atmospheric models

The referee seeks some discussion of the relation between chamber SOA data, associated formation mechanisms, and the representation of SOA formation in atmospheric models.

There are many issues which could be covered in such a discussion, which could form a paper on its own. In my opinion, a detailed discussion of this type is outside the scope of the present paper, which is one contribution amongst many seeking to advance general understanding in this field. However, some comments in this discussion response are warranted. These will not appear in the revised manuscript.

It is clear that SOA formation mechanisms in atmospheric models require some basis for their formulation, which ideally should incorporate contributions from theory and experiment. It is not generally feasible to construct an atmospheric model code without some validation of the code through experimentation, and there is no doubt that chamber experiments have a role to play in this process. However, it is important that the formation mechanisms are understood, and that yields are not simply taken from

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chamber experiments and applied in models. There are two important points here:

(i) Chamber experiments are often performed with conditions which are unrealistic for atmospheric purposes. An important example relates to the oxidation of aromatic hydrocarbons, where the mechanism is believed to be substantially different at NOx concentrations of a few ppm, compared with that which actually occurs under most atmospheric conditions. Despite this, many studies of SOA formation from photo-oxidation of aromatics employ such elevated levels of NOx.

The referee specifically highlights the situation for alkenes, and the impact of [HO2]/[RO2]: however, there are clearly many other atmospheric conditions which also have an important impact on SOA formation, most notably the effect of multicomponent inorganic and organic aerosol constituents, and processes such as acid-catalysed polymerisation. It is important, therefore, that experiments are carried out for ranges of conditions and that, where possible, the results are interpreted in terms chemical processes and the actual products formed.

(ii) A further problem with SOA mechanisms based on chamber yields is that such mechanisms commonly assume the oxidation to a limited number of (usually unspecified) oxygenated products which partition into the aerosol phase. This seriously misrepresents the complexity of atmospheric organic chemistry, because it assumes that SOA formation can be described in a similar fashion to the formation secondary inorganic aerosol components, such as sulphate and nitrate. Whereas these ultimate oxidation products of SO2 and NOx are the forms which are most associated with the particulate phase, SOA is formed from the gas-to-particle transfer of partially oxidized organic material, which occurs in competition with further oxidation in the gas phase. The further oxidation may produce species with a greater or smaller propensity to form SOA: however, it eventually generates CO2 as the ultimate oxidation product.

There is also a more general problem which results from the necessity for substantial simplification of organic chemistry in atmospheric models, through lumped speciation

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of emissions and reduced chemical schemes. It is known that at least several hundred different organic species are emitted into the atmosphere, and each of these inevitably has a different impact on SOA formation. The initial assignment of lumped representatives for the emitted species is a difficult task, even from the point of view of the gas phase chemistry. The inevitable simplification of the gas phase chemistry of the lumped representatives has traditionally sought to preserve the impacts on the oxidising capacity of the atmosphere, and it is probable that the simplifications do not easily lend themselves to the representation of SOA formation.

The treatment of SOA in atmospheric models therefore apparently requires a combination of activities to ensure that confidence can be placed in their output, many of which are already occurring. This includes a key role for chamber data on single VOC and VOC mixtures under a variety of conditions, and the development and validation of explicit physico-chemical mechanisms to interpret those data. In turn, such mechanisms provide benchmarks for developing and validating reduced mechanisms.

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