

Interactive comment on “Simulation of aromatic SOA formation using the lumping model integrated with explicit gas-phase kinetic mechanisms and aerosol-phase reactions” by Y. Im et al.

Anonymous Referee #1

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In this manuscript and modeling study is presented that predicts secondary organic aerosol (SOA) formation from toluene and 1,3,5 trimethylbenzene.

The SOA model applied here has been developed by the same group (Jang et al., 2005) and Cao and Jang (2010) is further developed in the current study by including organosulfate formation. The model is highly parameterized and for several processes and parameters empirical coefficients are introduced. The extent is not clear to which such a model can be extrapolated to any other conditions, such as ambient conditions. Several parts of the paper are obscure and require much more explanation why as-

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sumptions have been made. Only after these major comments are addressed, the manuscript might be publishable in ACP.

Major comments

1) The amount of organosulfates is calculated based on the difference of H⁺ concentration derived by two methods, namely PILS measurements in combination with E-AIM thermodynamic calculations and spectrometric data (C-RUV). It is well known that in aqueous aerosol phase, organic acids can be formed which would also change the pH value. Thus, the estimate of organosulfates is not a comprehensive method and might be heavily biased by organic acid formation.

2) Is assumed that all organics with aldehyde, epoxide and alcohol groups readily form organic sulfates? What is the basis for this assumption? It is known that such compounds undergo many more reactions in the aqueous phase than sulfate formation.

3) It is assumed that acid-catalyzed reactions do not occur if the relative humidity (RH) is below the efflorescence RH (ERH) of ammonium sulfate since then particles are dry and do not exhibit an aqueous phase. There are several studies that have shown that ERH of mixed organic/sulfate particles is much smaller than that of ammonium sulfate alone (e.g., (Marcolli et al., 2004; Bertram et al., 2011)). How does this effect affect the results?

4) Related to the previous comment, several studies (e.g., (Bertram et al., 2011)) have shown that the O/C ratio determines in which phase compounds will partition. What is the O/C ratio of the SOA constituents? Would a different phase partitioning impact the results?

5) Much progress in SOA modeling has been made since 2001. It is not clear why much more sophisticated SOA partitioning models that cover many more volatility bins (e.g. (Donahue et al., 2006; Donahue et al., 2011)) are ignored and instead the module by Schell et al. (2001) is used.

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6) I cannot believe that OM/OC has not been determined more accurately in studies more recent than 1990 (p. 5847, l. 27). I also expect that this ratio is a function of time, when products become more oxidized. What is the extent to uncertainty that is introduced by using this constant value?

7) The fact that an artificial OH source is needed and the great discrepancy between measured and predicted NO₂+HNO₂ for the 1,3,5-trimethylbenzene experiments (Fig S2c and d) suggest that something fundamentally is wrong in the model. Can you speculate on missing processes in the model or inappropriate reaction parameters?

Minor comments

Abstract: In the abstract, it should be mentioned specifically (i) which multiphase reactions are assumed and (ii) what the sulfur source is.

p. 5845, l. 9: Why is wide range of volatilities a limitation?

p. 5846, l. 14: In order to balance the discussion of acid-catalyzed reactions, it would be fair to add some references that state that acid-catalyzed reactions are likely not a major contributor to SOA (e.g., (Casale et al., 2007; Peltier et al., 2007; Minerath and Elrod, 2009))

p. 5846, l. 25: What is meant by 'gas phase ageing'? Oxidation processes in the gas phase often lead to fragmentation of the carbon backbone which results in more volatile products. Is this what is meant here?

p. 5852, l. 1: I think it should be either 'self-reaction' or 'dimerization'. Do you assume that the acid-catalyzed reaction in the inorganic phase is also a dimerization?

p. 5853, l. 1: Do you assume that the formed OM mass is equivalent to the consumed VOC mass? How about incorporation of oxygen or sulfate into the molecules? Shouldn't that change the product mass?

p. 5853, l. 8: How are the densities calculated? Do they change over time?

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p. 5856, l. 8: Sulfate is likely mostly formed in the aqueous phase either by S(IV) oxidation by O₃ or by H₂O₂. Even though you did not add H₂O₂ to the reaction mixture it is likely that it is formed in either the gas or aqueous phase by recombination of HO₂ that originates from OH + organic reactions.

p. 5856, l. 19: What are the yields in the other cited studies?

p. 5856, l. 23: What is meant by 'hypersensitivity'?

p. 5857, l. 7: Given that the prediction of organosulfate formation is an essential part of your study, more detailed discussion should be given on the predicted trends and apparent contradiction to previous results? Is the study by Wyche et al. (2008) the only one that compared SOA formation with/out SO₂?

p. 5858, l. 24: If the organosulfates are indeed hydrophobic, why aren't they predicted to go into the organic phase? Thus, they would not change the hygroscopicity of the aqueous phase.

Figure 1: More information is needed in the caption so the figure can be understood by itself. E.g., what does F, M, P, MA mean?

Technical comments

p. 5846, l. 11: 'aerosol chemistries' should be replaced by 'chemical reactions in the aerosol phase'

p. 5855, l. 1: This sentence is not clear.

p. 5857, l. 21: The figures should be discussed in numerical order. Fig. 5 is mentioned before Fig. 4.

p. 5858, l. 10: Do you mean SOA from 135-TMB?

Figure S2: The two different shades of blue (O₃ and NO₂+HONO) are hard to distinguish.

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