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Atmospheric
Chemistry
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Discussions

Interactive comment on "Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol" *by* C. D. Cappa and K. R. Wilson

Anonymous Referee #2

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The paper by Cappa and Wilson presents a new 'statistical oxidation model' (extending previous work from the authors) and applies it to prediction of SOA formation from OH from multiple precursors, with a special focus on alkanes. Six tunable parameters are used, namely the decrease in volatility per unit oxygen added, the probability of fragmentation upon reaction, and four parameters that represent the probabilities of adding 1-4 oxygens upon a reaction step. Results from a number of simulations and sensitivity studies are presented, as are comparisons to two chamber studies, after tuning the mechanism specifically for each experiment.

This paper represents an important original contribution to the literature and fits well

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in ACP. The new model will be very useful for interpretation of the basic trends behind SOA formation in chambers and maybe also in ambient studies. I recommend the paper for publication in ACP, but only after the following major issues are addressed.

Major issues

The main problem with the manuscript in its present form is that it dramatically overreaches in some of its conclusions. Strong conclusions are made about the importance of some species on SOA formation in the real world based on a very simplified model that has undergone very little experimental verification, and likely also due to some confusion about the results of field studies.

It is true that SOA is observed to form quickly in field studies, especially in urban areas. It is also true that SOA of high O:C is observed in field studies. However these are not typically observed together. O/C of bulk OA peaks at ~0.4 in the afternoon in Riverside, CA (when SOA represents ~90% of the OA and some very aged background OA is present, Docherty et al. ACP 11:12387-12240, 2011) and at 0.55 in Mexico City on on a typical day (Aiken et al. 2008). However SOA formed over a few hours of oxidation in Mexico City has an O/C~0.37 (Dzepina et al. ACP 9:5681, 2009, their Fig 11). Similarly the SV-OOA factors that are associated with fresh SOA have O/C~0.35 across many locations (Jimenez et al., Science 326: 1525-1529, 2009). Precursors with many carbon numbers can contribute with SOA with those ranges of O/C according to the results of the SOM model, especially if it is taken into account that a mixture of precursors is always present. With a mixture of precusors, some will lead to SOA of lower O/C (such as IVOCs) and others of higher O/C (such as toluene, or glyoxal via accretion reactions that are ignored here), so that intermediate O/Cs result for the total SOA. This was clearly illustrated by e.g. Chhabra et al (ACP 11: 8827-8845, 2011, their Fig. 9) who showed that no individual precursor produces SOA that matches the chemical properties of total ambient SOA, and that a mixture of precursors is essential. The fact that an individual precursor produces SOA with O/C~0.2 does not mean that it cannot substantially contribute to fresh ambient SOA with O/C~0.35 if e.g. some

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smaller precursors and glyoxal are also present. Thus the very strongly stated conclusions about IVOCs not being important contributors to ambient SOA are unwarranted and should be removed from the paper.

The very high O:C observed in some field studies and OOA factors (such as the LV-OOA with O:C∼0.75 reported by Jimenez et al. 2009) is more frequently observed in rural and remote areas. It appears to be the result of multi-day oxidation and perhaps aqueous chemistry, but to my knowledge it has not been observed for fresh SOA in ambient air. The authors somehow appear to be assuming that it has, and this potential confusion may lead to the overstated conclusions about IVOCs. Although higher values of O:C approaching 1 have been reported for very aged OOA, they are less frequently observed. But the authors seem to assume (for ex. P3311 line 22) that for an SOA precursor to be relevant, it needs to reach O:C > 0.8 in 1 day.

Another reason why the conclusions about ambient SOA should be stated much less strongly is that the structural and parametric uncertainties in the SOM are very large at this point. As in other models, in the SOM there are multiple tunable parameters. These parameters are fitted to a-pinene and pentadecane experiments presented in the paper, with very different results, adding an important caveat about the generality of the numerical values of the parameters. It is also a strong assumption that parameters such as DIVP and cfrag are constants and not distributions, and are the same for all precursors, molecular sizes and structures, degrees of unsaturation and oxidation, presence or absence of aromatic structures, functional groups, high vs low NOx chemistry, etc. Although the model focuses mostly on alkanes, important chemistry about the formation of hemiacetals and dihydrofurans which is important for SOA formation from these species (Lim and Ziemann, PCCP 11: 8029-8039, 2009) is ignored. While simple assumptions are necessary to construct the model and start exploring its behavior, the authors should not forget that those strong assumptions have been made when comparing the results with observations. In addition the model is based on partitioning theory, which has recently been suggested by several groups (including the authors themselves in Cappa and Wilson ACP 11:1895-1911, 2011) to be insufficient to capture SOA formation processes due to potentially large mass transfer kinetic limitations. Accretion reactions are also ignored, when there is evidence (e.g. Hall and Murray, 'Oligomer content of alpha-pinene secondary organic aerosol', Aerosol Sci. Tech. 45: 37-45, 2011) that oligomers often represent over 50% of the SOA mass, at least for some precursors. Heterogeneous oxidation is also ignored, even though the authors have also done significant work on this topic and it starts to be important for timescales of several days which are considered in some parts of the manuscript. Given the extremely limited experimental verification of the model structure and parameters and the important processes that have been omitted, strong conclusions about ambient SOA are simply not warranted and should be removed from the manuscript before it can be accepted into ACP.

Other topics

3298\23, Kroll et al proposed a framework for representing organic species but not a model per se

3300\10, it is not the 'structure' but the elemental composition of the molecules that is specified by the SOM. This should be reworded for clarity.

3305\23, here the authors say that DIVP is 0.74 for nitrates, however in most of the rest of the manuscript they ignore this value and emphasize that 1 is the lowest reasonable value. This needs more explanation as nitrates are thought to be important components in fresh SOA in urban areas where alkanes are important (see for example Lim and Ziemann, AST 43: 604-619, 2009).

3308\4, my understanding is that oxygen may be added more rapidly upon fragmentation than if no fragmentation occurs, however the model does not appear to consider this.

3308\14, I would call that a 2d space, as in a 2d data structure with a value (abundance) at each point in the structure, and not a 3d space.

3310\20, although here the model has been run for low Coa, there is no reason for not simulating the results of the experiments that have been reported at higher concentrations to verify that the experimental trends are captured by the model. Although this may be left for a latter paper, an extended exercise along those lines is needed to build confidence that the model represents reality with a reasonable degree of approximation.

3311\12, the results presented here contrast with the experimental results of Shilling et al. (ACP: 9, 771-782, 2009) who measured a much larger change on O/C over this range of Coa.

3313\9-10 and again 3314\22-24 and other places, this is true if accretion reactions are ignored as they are in the current version of the SOM. This needs to be explained here and throughout the paper. It could be that other formulations of Pfrag may work better once accretion is represented in a realistic manner in the model.

3313\24, shouldn't this probability be the product of Pfrag and not of (1-Pfrag)?

3315\6 and other places, although the model uses the word 'statistical' in its name, there is nothing new from an statistical point of view compared with the mechanism of Robinson et al. (2007) and several other VBS implementations, where individual precursors also underwent a variety of reaction generations. What is newest here is the implementation of a simplified SOA model on a Nc-No grid as opposed to the variety of other representations proposed in the literature. Although the statistical aspect not being novel for SOA models is mentioned (somewhat unclearly) towards the end of the paper, I suggest that this is clarified early in the paper.

3319\20, again this is only true if accretion with some of the small molecules resulting from fragmentation is ignored.

3320\25, dilution does not always proceed at a constant rate in the real world, so that

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less time always means less dilution. When the boundary layer rises in the morning very rapid dilution can be achieved in very little time, of the order of 100% per hour, compared with a few percent per hour during horizontal transport in the free troposphere. Once this is taken into account, some of the conclusions in this paragraph do not hold.

3322\11-13, I think their Fig 9 contradicts the conclusions that the authors make here. A mixture of different precursors can easily produce material in the SV-OOA range in the figure after ONLY ONE oxidation generation. With additional oxidation generations, accretion, aqueous processing, it does not seem too difficult to reach LV-OOA over realistic timescales of a few days.

3323\11, unless the measurement is proven wrong, this type of disagreement should give the authors pause about the completeness of their model and the generality of the conclusions that can be extracted from it at this level of development.

3323\ section 3.4, I find this section confusing and unclear. I suggest that it is removed from the manuscript to allow a tighter focus on the more fundamental topics being explored.

3331\21, I strongly disagree with the statement that ‘gas-phase mechanisms have been shown unable to form OOA’. With a mixture of compounds such as in Figure 9, they seem perfectly capable of forming fresh SOA with the O:C of SV-OOA ($\sim$0.35) observed in the atmosphere.

3333\19, if SOA is converted to a non-absorbing phase upon condensation then O:C would be lower than in the current implementation of the model. So while that may be the case, it does not seem like a suggestion to produce SOA of higher O:C in the model.

Typos

3301\5, precursor

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3326\27, overpredicted

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 3295, 2012.