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Atmospheric Chemistry and Physics 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 #1

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This study involves the description and implementation of a new scheme for SOA formation and aging – the "statistical oxidation model" (SOM) – based on the idea that different product generations can be co-present in a reaction mixture. This work builds directly on the work by Smith et al. [1] and Wilson et al. [2], which first examined this effect in the context of aerosol aging. (The effect itself arises directly from the series of sequential differential equations, and thus is implicit in any detailed chemistry model, but to my knowledge these were the first studies to examine it explicitly.) This new model focuses on secondary organic aerosol formation, and thus also includes a gas-particle partitioning component. Vapor pressures and key chemical properties are described in terms of changes to the number of carbon atoms and the number

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of oxygen atoms (Nc and No). After the model is described, a wide range of model runs are carried out, and several conclusions about the role of fragmentation and semivolatile/intermediate-volatility organic compounds (SVOCs and IVOCs) are made. The model itself is a nice development, since it allows for the direct investigation of the role of multiple generations on SOA loadings (C_oa), key chemical properties (O/C ratios), and volatility (C*). However, the study has a number of major weaknesses, including little discussion of the limitations of the chemical scheme employed, broad conclusions made about SOA chemistry based on an incomplete model, and insufficient discussion of the current state of the science; these are described below. Thus this paper needs to be reworked considerably before it can be published in ACP.

Major comments:

The many simplifications and assumptions in the modeled chemistry need to be discussed much more thoroughly. While these are certainly necessary for the construction of simple chemical schemes, it's important to note that they may have a major effect on the modeled results. However in the paper a large number of important simplifications/assumptions are never explored, and for the most part are not even identified, and yet some major conclusions about SOA chemistry are drawn and stated rather strongly. Several specific concerns are listed below.

- the SOM ignores the effects of carbon skeleton. The manuscript includes some discussion of the possible effect of double bonds, but all but ignores the effects of cyclic, aromatic, and branched carbon skeletons. These can have a governing effect on the oxidation of organic compounds, mostly via affecting alkoxy radical reactivity [3]. By not including these effects, the SOM in its current form essentially simulates the chemistry of only n-alkanes, species which are probably not a good surrogate for most atmospheric SOA precursors.

- An important reaction in the chemistry of n-alkanes is formation of dihydrofurans, whose subsequent chemistry has been shown to play a central role in SOA formation

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[4]. This leads to the formation of a ring and a C=C double bond; thus even n-alkane chemistry may not be well-simulated by the SOM.

- dIVP is treated as a single-valued parameter, but in reality it is a distribution, reflecting the effects of the various identities (and locations) of added functional groups. The paper makes a strong and convincing case that models should include a statistical mixture of generations; however by using a fixed value of dIVP, the paper risks neglecting the statistical mixture of products in a single generation, which is probably at least as important. (The use of an array for P_func offsets this somewhat, but not entirely). By contrast, the VBS explicitly includes this latter type of distribution. Accurate models need to include both distribution types, and it's not clear that including one at the expense of the other leads to a substantial improvement in accuracy.

- While the fragmentation probability (P_frag) is allowed to change over time (as the products become more oxidized), several key parameters (dIVP and P_func) are not. Yet we know these change with oxidation as well – for example the curvature in the van Krevelen plot with oxidation [5] strongly suggests that dIVP is an evolving parameter.

The point of the above list is not to point out the shortcomings of the model; the complexity of SOA chemistry requires that many simplifications be made. Instead the point is that it is very possible (even likely) that "real-world" SOA (from a range of precursors and conditions) may be substantially different from what is simulated by the SOM in its current form, even when only known gas-phase chemistry is involved. As a result, several strongly-worded conclusions (IVOCs and SVOCs cannot make OOA, the pumping mechanism is an inefficient oxidation channel, fragmentation reactions cannot increase O:C) are simply not well-supported by this work. A much wider range of compounds need to be examined, and much more chemical detail needs to be included in the model, before such broad conclusions can be made with any confidence. Thus these conclusions need to be removed, or at least softened considerably, with all the above caveats added.

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Other comments

Throughout: The paper would be improved if the ultimate aims of the SOM were made clearer. It's not clear whether it's intended to be a conceptual framework to think about SOA formation and aging, or a module for incorporation in 3D models, or an approach for fitting laboratory data (the focus seems to change throughout the paper). Much of the discussion focuses on the advantages of the SOM (over the 2-product model and VBS) for fitting chamber data. However, this fitting is done only at the very end of the paper, and the results of the fits are not used to inform the model itself. (This in my view is one of the strengths of the VBS, which is parameterized by chamber experiments)

Throughout: Much of the discussion is focused on contrasting the SOM with the VBS, with the VBS usually lumped together with the Odum two-product model as examples of "static" descriptions of SOA (e.g., P3302 L15, P3315 L11, P3334-35). While there are some references to kinetic parameterizations of the VBS, the casual reader would have no idea that an important aspect of the VBS is that it explicitly allows for aging (in contrast to the 2-product model). A more fair assessment of the literature and the current state of the science is thus necessary. It is true that the initial C* distribution in the VBS, taken from fitting chamber data, must assume an initially static population of SOA, but it is not at all clear what sort of error (in calculations of C_oa, O:C, etc.) this introduces, at least relative to the SOM (which is not constrained by chamber data, and, as stated above, does not fully consider distributions in volatilities for a single generation). After the initial SOA formation, the VBS then allows for aging of this SOA, using a general scheme that is quite similar to the new one adopted in the SOM. Of course, when implemented in a chemical transport model, this kinetic implementation of the VBS naturally includes the statistical distribution of generations. None of this is apparent from the text as currently written; thus these sections need to be made more balanced in content and tone.

3300, L17-21 and P3316 L28 – P 3317 L3: These discussions do not accurately reflect the Ng et al work [6]. That study involved compounds with one or more double bonds,

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allowing for good kinetic separation of generations: the first double bond reacts quickly (a large value of kOH), the next double bonds react quite a bit slower, and then after that the H-atom abstractions go slower still. This is in stark contrast with the n-alkane system modeled in the present paper, in which kOH's are all roughly the same, leading to generations mixing together as described by Wilson et al [2]. For the system studied by Ng et al, it is (to first order) correct to ascribe the different sections of the growth curve to different generations (in contrast to what is stated on P3300), just as it is correct (to first order) to interpret the data in terms of first- vs. second-generation products (in contrast to what is stated on P3316). Generalizing this result for non-alkenes does indeed require going beyond "second-generation products", but this has been recognized for some time (see discussions of "later-generation products" [7] or "subsequent-generation products" [8]).

P3302, L9-11: Similarly, the wording here makes it sound as if it is still generally believed that yields are a static quantity; but many papers over the last several years (going back at least to Donahue et al 2005 [9]) have discussed that this is not the case. I suggest changing "interpreted" to "fitted" to avoid implying this.

P3307: It is not clear from the text how the number of O atoms added to the fragmented products is determined; this needs to be clarified. From P3299 L9-10 ("the total number of carbon and oxygen atoms are conserved") it sounds as if some oxygen atoms are first added (via the P_func array) and then are divided up randomly into the two fragments. If this is the case, it can lead to the addition of only one oxygen total to both fragments, which is chemically nonsensical. Since each fragment must end up with at least one O atom, fragmentation necessarily leads to the net addition of more O atoms than does functionalization. (This difference can be quite large, given that acid groups may be introduced via fragmentation reactions.) If O atoms are indeed computed by the above method (application of P_func), it will lead to an underestimate of the O:C (and overestimate of volatility) of the fragments, and can give a misleading impression of the role of fragmentation in SOA chemistry. This would need to be corrected.

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Interactive Comment

P3324, L14: The relevance of examining SOA vs OPOA for a single pure compound is not clear to me. How is a comparison of the two meaningful when they are made up of the exact same species, formed by the same chemistry? A more useful test of the pumping mechanism would be to have some amount of a single SVOC present alongside an unreactive absorbing medium, and examine the evolution (partitioning and O:C ratio) of that SVOC. (Also, in this section the parameters of these simulations (dIVP, degree of fragmentation etc) need to be given.)

Section 4 (P3328-30): The agreement between the data and the fitted SOM is not surprising given that there are six fitted parameters. Since these are likely not unique solutions, it is risky to ascribe chemical meaning to the results. For example, for a-pinene the fitted parameters suggest 20% of the time only one oxygen is added per reaction (Pfunc(1)=0.20), which is not chemically realistic for the oxidation of a cyclic alkene. Similarly, growth data were reported without consideration of gas-phase SVOC loss to chamber walls, an effect which can be substantial [10] and should lead to a model-measurement discrepancy if the model accurately describes gas-phase chemistry and gas-particle partitioning of the system.

Minor points

P3300, L10: “Structure” should be replaced by “formula” (or some similar word). “Structure” refers to connectivity of atoms, something that is not simulated in the SOM.

P3301, L3: There seems to be an error in this expression; I think it should be tau=1/(k[OH]).

P3302, L18: The term “two constants and one array” is more precisely described as “six parameters”. But it is also worth mentioning that the strength here is that those six parameters include aging parameters, not just the initial distribution.

P3303: I don’t see how the SAR of Kwok and Atkinson leads to equations 1a-5b. This should be explained in greater detail (perhaps in a supplement). Also, it appears that

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these were computed for straight-chain organics only; this needs to be stated in the text.

P3303, L22-23: The units for these rate constants are in error or are missing.

P3310, L18: The expression for yield is incorrect: the denominator should be -delta[HC], not [HC]o. The two are the same only when all the hydrocarbon has reacted away, which is not the case here (since only one lifetime has elapsed).

P3313, L11: If the simulation in question involves the addition of only one O atom is added per reaction, the finding that O:C doesn't increase with fragmentation is not really that surprising.

P3316 L1, Fig 6: The simulation apparently includes fragmentation (since it is from case 2b, from section 3.1.2), but the figure shows no signs of fragmentation (i.e., compounds that are more volatile than the parent). Why is this?

P3321, S3.2, Fig 9: It's not clear to me how this section and figure contributes to the overall paper. The main results have either been shown already (O:C, shown in Fig. 2b) or, as mentioned in the text, are expected based on partitioning theory (volatility, with C*=C_oa). Related to this last point, the section/figure would be much more informative if [HC]o rather than C_oa were held constant. (Also, the circles at the bottom of the figure are confusing, since their size implies substantial aerosol formation.)

P3323 L26: This appears to be the incorrect reference for describing the pumping mechanism.

P3324 L18, P3327 L17: is the "x" in the [OH] expressions a typo?

P3333 L20: I'm unaware of any evidence (including in the papers cited) that OA can be truly "non-absorbing"; submicron particles made up of material in which diffusion is incredibly slow (D of ~1e-15 cm2/s) still allow for absorption over timescales of hours. "Viscous" might be a better word.

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