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Interactive comment on "A Functional Group Oxidation Model (FGOM) for SOA formation and aging" *by* X. Zhang and J. H. Seinfeld

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First I must apologize and accept public shaming for the amount of time it took to complete this review. Also, while I am editorializing I will take this opportunity to point out that I have not read my much more prompt colleague's review, and as a general rule I favor this and suggest that *ACPD* develop some mechanism to keep initial reviewers blind from each other's comments (though as a several month tardy reviewer this seems a poor time to bring that up).

1 General Review

This paper describes a much needed and carefully conceived model framework for evolving organic aerosol chemistry. The Functional Group Oxidation Model is a semi-empirical model of organic-aerosol evolution where the kinetics of functional-group addition to carbon backbones are constrained by a detailed chemical mechanism (the Master Chemical Mechanism in this case) but key uncertain parameters such as the fragmentation probability (the probability that a given reaction step involves C-C bond cleavage) and aspects of condensed-phase association reactions are left as fitting parameters for a least-squares optimization to chamber data.

The fitting is split into two cases. The first case allows for only gas-phase and heterogeneous oxidation, with a fragmentation probability and a condensed-phase "slow down" factor left as the two fitting parameters. The second case adds to this first case a phenomenological condensed-phase (oligomerization) process with four new free parameters – a second-order rate constant and the n_C, n_H, and n_O of the quasi non-volatile product.

In general, the FGOM even with only 2 oxidative parameters can do a very good job reproducing chamber data for Secondary Organic Aerosol formation from alkane oxidation, but it has trouble with the composition data, overestimating both O:C and H:C. Consequently, adding the oligomerization parameterization allows the model to (eventually) match those observables fairly well. Because both O:C and H:C are lowered via this parameterized reaction, the authors focus on the plausible possibility that condensation (dehydration) reactions are responsible and important for organic aerosol development.

Here is my one serious concern with this work. While the hypothesis that condensation reactions may be important for SOA evolution is certainly plausible – indeed backed up by theoretical and experimental evidence – I am not at all convinced that the FGOM results make that case persuasively. There is an old saying in Chemical Engineering

(I am told by old chemical engineers...) that runs roughly “give me enough free parameters and I can fit an elephant.” Here, the elephant in the room is that the oxidative portion of the FGOM overpredicts both O:C and H:C, so a mechanism with C:H:O as free parameters will with certainty be able to fit that elephant, to a point. However, the authors have been intellectually honest and also included a rate constant for this process. Even with that rate constant as a free parameter, the FGOM fails miserably with the timing of the O:C and H:C data. As shown in Figures 6 and 7, it takes many hours – almost a day – for the mechanism to draw the purely oxidative results down to the data. For much of this period, the optimized mechanism gets the sign of the trends wrong – while the observed O:C is rising, for example, the model O:C is falling (because it started out far too high). Because of this, I would much rather conclude that the hypothesized condensation reactions can *not* explain the observations.

Finally, this comparison between oxidative and non-oxidative processes emerges slowly in the paper, culminating in a very strong conclusion that dehydration / oligomerization reactions are very important in SOA chemistry. While this figures prominently in the conclusion, it is almost hidden in the abstract “The sensitivity of the model prediction to variation of the adjustable parameters allows one to assess the relative importance of various pathways involved in SOA formation.” Given my reservations about the stronger conclusion, I am OK with what is written in the abstract, but I feel the authors should soften the conclusion about condensation reactions substantially

2 Representation of the 2D-VBS

The 2D-VBS descriptions are mostly accurate in this paper, but not universally so. That is almost entirely because we have yet to publish a single, coherent description of the 2D-VBS. There are a few points however where I disagree with the authors’ description.

First, when the authors are discussing vapor-pressure estimation, they assert “The

molecular vapor pressure prediction method used also plays an important role in the overall SOA yield predicted (Valorso et al., 2011), although this is the case for any SOA model.” I disagree with this statement. Fully empirical models, including the Odum 2-product model and the original VBS, have no intrinsic sensitivity to estimated vapor pressures. They rely on empirical fitting of chamber data to deduce the volatility distribution of SOA formed in a chamber, but not on vapor pressure estimation; there are no molecules in those models, just material of some volatility. Even the 2D-VBS is not overly sensitive to vapor pressure estimation uncertainty – it enters only in the average change in volatility caused by addition of a functional group (taken to be 1.7 decades per O on average, but as much as 2.5 decades per O, as in an -OH group, or as little as 1 decade per), as in an =O group). The uncertainty in the 2D-VBS arises when we attempt to figure out the typical composition of molecules in a given C^*,O:C bin.

Second, I don’t understand the statement “The 2D-VBS and SOM do not require an explicit VOC oxidation mechanism, although [sic] the chemical intuition is required in the choice of the adjustable parameters.” The actual process of parameter estimation in the 2D-VBS goes beyond chemical intuition – the oxidation kernel described in Donahue *et al., PNAS,* 2012 is based on an assessment of typical functional groups added during oxidation reactions adding 1-6 oxygen atoms to a carbon backbone (really a distribution of -OH and =O groups taken to be on average about evenly distributed because of the Van Krevelen constraints presented by Heald *et al*). That is not so very far from the FGOM.

The discussion of fragmentation in the 2D-VBS in Section 2.2, line 22ff is incomplete. The authors correctly describe the first step in the fragmentation process, where randomly fragmented compounds are distributed in a “dog leg” extending from the reactant toward higher volatility (and ultimately higher oxidation state), but half of these products are assumed to be radicals that can further functionalized. This is shown for an example cell in the supplementary material for Donahue *et al., PNAS,* 2012. As an example, the triacid MBTCA shown in Figure 4 of Jimenez *et al., Science*, 2009 is technically a fragmentation product of cis-pinonic acid (also shown in the figure), though it is orders of magnitude less volatile.

While the 2D-VBS *doesn't* describe condensed-phase association reactions, there is no reason it *can't*. However, nobody to my knowledge has implemented oligomerization in the 2D-VBS.

Finally, I don't at all understand the statement in the second paragraph of Section 4 "As a result, a number of free parameters representing the stoichiometric amount of product bins need to be assigned manually after each generation of oxidation." (it is also not clear to me why a paragraph about the 2D-VBS is in a section entitled "Comparison of FGOM with SOM". Whatever this is intending to say, there is no manual adjustment after any generations in the 2D-VBS. It is fully recursive and conserves carbon while allowing H and O to evolve based on inference of the average composition in each bin. I believe the authors are referring to the distribution of functionalization products in various C^*,O:C bins whose average composition (carbon number) differs from the carbon number of the reactant bin. However, while the 2D-VBS mechanism is informed by the average composition, it does not require any information about it – the chemistry moves carbon about in the 2D space. No renormalization is required.

Finally, finally, the retardation factor or effective OH rate constant for heterogeneous uptake is described in Lambe *et al., ES&T* 2009, 3, 8794–8800.

3 Walls

The model is being employed to simulate a chamber experiment, and yet there almost no discussion of the chamber walls. The sole mention in the first sentence of section 3.1 is that the simulations consider wall-corrected data; to me this is a curious choice. Wall loss corrections are themselves a model, and there are numerous assumptions

about mass transfer behavior either implicitly or explicitly included in the correction. The wall loss correction should be discussed here (or at least the method should be cited), but it would be far better in my opinion to actually include mass transfer to (and possibly from) the walls in the simulation. This way, all or most of the current hypotheses about wall behavior could be included in the chamber model and the sensitivity to these assumptions could be explored.

4 $\overline{\mathrm{OS}}_C$ vs O:C

One of the less appreciated advantages of $\overline{\mathrm{OS}}_C$ is that it is insensitive to dehydration (δ(2O - H)/C = 0 when H_2O is eliminated). This is potentially very important here, because $\overline{\mathrm{OS}}_C$ is also insensitive to assumptions about production of the *m/z* = 18,17,16 fragments in the AMS. Actual dehydration of organics in the instrument is incredibly uncertain, and strange things have happened to the AMS "fragmentation tables" over the past few years as estimates of *m/z* = 28 (CO^+) have evolved. Thus, depending on both the treatment of the air beam in the AMS (which influences how accurately 28 can be recovered from the interfering N_2 signal) and assumptions about 18, the O:C and H:C can vary systematically. Furthermore, the standard fragmentation tables are thought to be reasonable for ambient sampling, but there is no reason to believe that they will apply for any given single precursor chamber experiment. Because of the prominent role that O:C and H:C from the AMS play in this paper, this should be discussed.

5 FGOM SOM Comparison

This comparison is extremely interesting but yet extremely vexing. The mechanisms appear as two ships passing in the night. It should be pointed out that the Kroll et al.

paper in *Nature Chemistry* includes a fair amount of experimental data that appears qualitatively consistent with the SOM trajectory in this space, while the FGOM feels the pull of the oligomers in Figure 9. The performance of the FGOM in Figure 10 also deserves much more discussion. If the data evolve in the direction of the SOM (as they appear to do), this would seem to be *inconsistent* with significant dehydration chemistry, which will indeed tend to decrease both H:C and O::C as shown by the FGOM trajectory. However, I also don't understand how the FROM continues downward from the data between 20 and 30h (the red part of the trajectory in Figure 10), whereas in Figures 6 and 7 the FGOM appears to have locked onto the observed O:C and H:C (as it should, being empirical). I don't understand this deviation.

The location of the oligomers in the top panel of Figure 9 are fascinating. As discussed above, condensation (dehydration) is non-oxidative and thus conserves $\overline{\mathrm{OS}}_C$, and yet the oligomer is *more* oxidized than most of the condensed-phase products at higher C*. This would not be surprising if the oligomers derived from glyoxal or other highly oxidized monomers, but as far as I understand the chemistry presented here the oligomers are presumed to derive in some way from the existing condensed phase. The chemistry thus appears to be an oxidative process. This leaves me somewhat confused as I don't fully understand how it can lower both O:C and H:C while being oxidative...

6 Notational Consistency

I had a difficult time working out the details of the two simulation cases (oxidation only and oxidation plus oligomerization). They are described in perfect detail, but they are not named in the text. In the caption of Fig. 4 they are named sim.1 and sim.2, but here we find out "Note that "sim.1" represents the full fitting of the six empirical parameters in the FGOM to the chamber data and "sim.2" refers to fitting by only two

parameters, r_p and f_v, to the organic mass concentration." That's wonderful if the reader can immediately recall what r_p and f_v (or the other four parameters) are. This reader could not recall that at the time and had to go hunting. It would be far better to first describe sim.1 and sim.2 in the text and then add to the caption "Note that sim.1 refers to full fitting of both oxidation and oligomerization chemistry to the chamber data while sim.2 refers to fitting of only two oxidation parameters to the organic mass concentration." or something like that.

7 Conclusions

The conclusions section (paragraph) right now reads like something Molly Bloom in Ulysses might have said. Ideas just tumble out one after another almost without punctuation. The first half of the paragraph is quite coherent, but the final half to third is a succession of almost unrelated statements. The authors should take a little more time and space with the Conclusions section and put distinct concepts in separate paragraphs.

8 Minor editorial comments

Table 2: Please explain what the parameters are in the caption.

Figure 3: I was confused for a time by the gray rectangle cutting of an $n_C = 12$. I still don't fully understand why the authors do this, but the statement in the caption 'the shaded region ... is taken to represent the combination of carbon number and volatility for which a molecule can appreciably partition to the particle phase." is manifestly false, given that higher carbon number species with low C* can obviously also condense. It might be nice to put dodecane on this figure – it should sit just above $C^* = 10^6$.

Figures 4: Please explain at least briefly what the omitted parameters are (as discussed above).

Figure 8: Please make a more informative legend or caption. It is impossible to guess what the various cases are without reading the text; it will help the casual reader if the rp akd ka values are explained.

Figure 9: Please label the 2D spaces on the top panels – put a big FGOM to the left of the top row and a big SOM to the left of the middle row. Once I get used to it it is easy to pick out the oligomerization product and thus the FGOM graphs, but please save me the trouble!

Figure 10: Please describe the dashed black and cyan lines in the caption.

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