**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO$_3$)" *by* N. L. Ng et al.

Anonymous Referee #2

Received and published: 7 May 2008

This is an extremely interesting paper showing large SOA production from NO3 + isoprene as well as evidence that some fraction of the SOA products are organic peroxides (ROOR), which have twice the carbon number of their parent peroxides and thus very low volatility. The 'standard' SOA formation data are supported by extensive measurements of both gas-phase (via CIMS) and condensed phase (via high mass resolution MS on filter extracts) products.

The work should obviously be published, but I have one major concern and a whole host of comments and thoughts described line by line below.

My major concern is that the 2-product fit the authors present is completely at odds with their conclusion that a significant fraction of the SOA is made up of C10 peroxides with

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

additional functional groups such as nitrates (and even sulfates). These products would be effectively non volatile, and yet their SOA formation data display the now standard 'Odum-like' increase in aerosol mass yield with increasing organic aerosol loading. This is typically interpreted via Pankow partitioning theory to mean that the products are semi volatile, with vapor pressures (saturation concentrations) roughly in the range of the aerosol loadings. If the products really were non volatile, one would see a flat line on an Odum plot. Everything we and others have done to test the central assumption of the Odum-Pankow formalism supports its basic veracity for many systems – thermal denuders easily evaporate SOA (for example An et al AS 2006), isothermal dilution also causes SOA to evaporate (Grieshop et al, GRL, 2006), so I se very little reason to suddenly doubt the standard interpretation here. Finally, the products one would expect from NO3 attack on 2 double bonds of isoprene, which are in fact observed here, should have vapor pressures in the right range to generate the observed partitioning behavior.

Another issue is very important here. When experiments produce a little SOA from a lot of precursor (10% mass yield is about 5-7% carbon yield, here), we should be really worried about strange side reactions. Minor pathways could in fact be responsible for SOA formation in the atmosphere as well as in chambers – the ROOR formation proposed here could be one such pathway. In fact, a 2% ROOR formation would not be outside the limits suggested by earlier experiments for even light hydrocarbons, and it would help reconcile the product identification with the observed semi-volatile behavior (if ROOR were responsible for 1/4 or 1/3 of the total SOA mass. Of course, the danger is that the pathway observed in the lab does not occur with the same branching ratio in the atmosphere (it could easily be orders of magnitude lower or even possibly higher). This is not a criticism specific to this study, and I don't think it should in any way block publication of this work. Rather, these data give the authors a unique opportunity to issue a well-framed warning about how we interpret these low-yield experiments.

Another are of interest would the the daytime NO3 chemistry that Jose Fuentes has been proposing for the sub-canopy of many forests. It seems to me that this could

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

be extremely important because, of course, some of those forests are swimming in isoprene.

Also, did the authors consider HO2 at night from ozone + alkenes in their model?

Line-by-line comments:

Fig 2: Can you provide the isoprene mass too? Given the mass yield

Fig 6: I don't think that 'evolutions' should be plural. It would be nice to have some information about the likely identity of these masses, either directly on the figure or in the figure caption. That way the casual reader will pick up on what's going on.

Fig 7: How much processing has gone on developing this AMS spectrum? For example the m/z 18 and 44 peaks appear to be the same height, which is typical of the organic signal after the fragment table has been used, and after the contribution from water has been removed. If water has not been subtracted, this is of some interest to AMS experts because the appropriate ratio of 18 to 44 is currently under debate in the AMS community [see for example Aiken et al 2008].

Fig 11: Is it possible to put some rough yields on the arrows in this mechanism figure? It is nice to know what is thought be be important and by what margin.

p 3171 l 12 The C* (1/K) for product 1 is about 5.5 ug/m3, with a 9% yield, while the C* for the 2nd species is 22 ug/m3 with a yield 20%. For these particular parameters the SOA formation at lower organic aerosol loadings typically found in remote areas. Thus the global projections are very sensitive to the assumed total organic aerosol loading. Now, the lowest mass actually constraining these parameters is 2.2 ug/m3, with another at 4.8. Is it really plausible that the experiments just happened to hit on the concentration where the organic aerosol started to saturate? I think not. A difficulty with the 2-product empirical model is that the C* values adjust to help the function fit the data, and with only two lumped products a lot of that fitting work has to be done by the K values. It is very common for the lower C* to come out near the lower C_OA

of the data, and the higher C* to come out near the higher C_OA of the data. That is exactly what is going on here. Let's consider the observed products. There are a lot of C10 multifunctional nitrates in Table 2. Those are going to have very, very low saturation concentrations – 1 ng/m3 or less.

p3173 line 10 There is certainly further chemistry going on in the slow isoprene injection case too! It is just rate-limited by the actual injection, not by the chemistry. This statement is misleading in this case .

p3174 line 3. As the authors point out here, the SOA can always be from later generation products even under circumstances where the later generations are suppressed. A theme that will pervade this review is that the low-yield SOA experiments we are all now striving for have an intrinsic trap: the SOA we sample is by definition a minor product, and minor product channels are the most prone to experimental artifacts as they can arise from conditions that don't occur in the atmosphere. Thus, simply stating that there is a lot of NO3 and not much isoprene is not really enough. Please make some effort to estimate the relative production of first and later generation products with reasonable estimates of the kinetics for NO3 addition to the residual double bond.

p3174 line 21. The 393 ion only appears slowly during the first injection. This is presumably because its precursor has reached some sort of steady state before the second injection?

p 3180 ROOR. This is a pretty big deal. the RO2+RO2 reaction is presumed to proceed via a common tetroxide intermediate, ROOOOR. Even for the RO + RO + O2 radical pathway, this intermediate must decompose via a concerted transition state (much like the primary ozonide cycloreverts to a carbonyl and carbonyl oxide. The reason is that the overall reaction is nearly thermoneutral and the peroxide well is quite deep. Even for a small ROOR, the RRKM-type rate constant $[(E-Eo)/E]\hat{}s$ * Prod(nu ROOR)/Prod(nu TS) will be very low because the fractional excess energy $[(E-Eo)/E]$ in the fresh ROOR will be very small. Consequently, we can be pretty sure that any vibrationally excited

ROOR generated will be collisionally stabilized. So, this evidence for ROOR formation seems to me to suggest a direct pathway out of a 4-member transition state RO[OO]OR -> ROOR + O2.

p 3185. Excess isoprene. We return to the point that a relatively minor amount of 2nd generation chemistry can have a big effect on a 10% yield (5% by carbon, or so). Are the authors certain that HETEROGENEOUS NO3 uptake is not significant here?? This of course requires some seed aerosol to start the process off, which might just not work here. However, if unsaturated products are formed with a low enough C* to get into the condensed phase, it is likely that NO3 will be taken up with near unit efficiency. Rudich and also Smith et al. have shown the NO3 uptake can be quite rapid even to saturated organic surfaces. What role does that play here??

p 3186 line 27. Can the authors give some bounds for 'significantly'? There is a basic inconsistency here. The 2-product fit discussed above has 2 surrogate products with C* values of 6 and 22 ug/m3. Using the SAR relationships recently published in ACP by Pankow, one can estimate that doubly oxidized C5 di-hydroxy di-nitrate compounds like those seen here would have C* values in that general range. However, the ROOR products, as I mention above, will have C* more like 0.001 ug/m3. If these are a major portion of the overall product mass: a. It is inconsistent with the 2-product model, and b. Why does the observed aerosol mass fraction increase so significantly in the range 2-70 ug/m3, as it does??? The standard interpretation of the 'Odum Plot' in Fig3 is that the rise in 'yield' reflects semi-volatile products with C* values in the range of the aerosol mass (Mo) present. Now, Kroll and others have proposed other models that could explain this apparent contradiction, but given that the 'expected' products have about the 'right' vapor pressure, and given that the Odum Plot is 'doing what it should', is not the simpler interpretation that the bulk of the SOA products have approximately this volatility?? It is one thing to say that the 2-product model is empirical, but the parameters from the 2-product fit are going to be put into models and they are going to behave like they 'should' – in other words for C_OA < 5 ug/m3 most of the products

are going to evaporate (and then hover in a mysterious, non-reactive state in the gas phase in the model, but that is another discussion for another day). So, if the authors are arguing that the SOA products from this reaction are really so non-volatile, they really should propose parameters that reflect this. Now, if the ROOR have a mass yield of 0.02, then all is well – that can easily be accommodated by another product with very low volatility (or, of course, a basis set...). This brings me to an analytical question. Is there any way that 2 ROOH could react in the MS to give ROOR??

p 3188 line 26. Woooooa. I don't want to insult Davin, but please don't quote the SOA production from his model as if it were a fact. It is a model result. You should also quote Goldstein et al, who suggest that SOA production is somewhere between 150 and 400 Tg/yr. I believe that the strongest of the many constraints in the Goldstein mass balance is the org:sulfate. Observations suggest that this is around 1:1 throughout most of the atmosphere (ie, Qi Zhang et al, Dan Murphy et al). Given a global sulfate flux of about 80 TgS/yr this suggests a global carbon flux of about 80 TgC/yr. If that is only 50Tg/yr SOA, and if the SOA has an OM:OC of 2:1, that gives 100 Tg/y. That seems close to a lower limit. Still, 3 Tg/yr would be worth noticing.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3163, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper