

Interactive comment on “Volatility and lifetime against OH heterogeneous reaction of ambient Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA)” by Weiwei Hu et al.

Anonymous Referee #2

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This paper describes detailed field measurements of “IEPOX-SOA”, secondary organic aerosol deriving the reactive uptake IEPOX, a major product of isoprene oxidation. Key results include evidence that IEPOX-SOA is quite low in volatility, suggesting the importance of accretion products (consistent with other recently-published work), and measurements of the rate of atmospheric degradation of IEPOX-SOA material (which is a fundamentally new result). These are important results, and overall this is a solid study of general interest to the atmospheric chemistry community. It is certainly publishable in ACP; first, I have a number of detailed comments, listed below, that should be addressed prior to publication.

246-263 (and elsewhere): The manuscript makes repeated reference to the IEPOX-

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SOA compounds being oligomers. However, it seems to me that other accretion products (namely organosulfates) could also explain much of the data (such as the low volatility of the compounds). The authors should either explain why organosulfate formation is unlikely, or change the language throughout the paper to reflect this possibility.

Figs 1-2: A comparison with the sulfate thermogram would be helpful here for context.

273-276: These two possibilities seem closely related to me. The “real” volatility distribution (from physical volatilization only) is irrelevant if the room temperature evaporation is governed by chemical decomposition to more volatile monomers. The TD is measuring “effective volatility”, which takes into account both physical evaporation and oligomer decomposition; this effective volatility (at atmospheric temperatures at least) is what matters for phase partitioning in the atmosphere. Therefore I’m not sure it’s correct to say this approach is overestimating the volatility distribution.

279-280: The Vaden reference may be describing a very different effect, namely slow evaporation of monomers out of low-viscosity (and very dry) particles.

314-316: Here it is argued that wall loss of IEPOX cannot happen because of the high saturation vapor pressure of the molecule. But this is the wrong quantity to use, since IEPOX condenses almost entirely via reactive uptake. (If saturation vapor pressure is what determined IEPOX condensation, there’d be no such thing as IEPOX-SOA!) It is highly likely that there is reactive uptake to the walls, since there’s probably a reasonable amount of sulfate (aqueous, likely quite acidic) from previous deposition. This effect needs to be included in these calculations.

351-354: This is an important definition, because it specifically excludes reactions that lead to the reaction of IEPOX-SOA components without major changes to the PMF factor (namely, with little change to m/z 82). This should be mentioned explicitly, as should the implication that these rates and uptake coefficients may be lower limit values.

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378: "IEPOX-SOA" should be in brackets to signify concentrations (as written, the left side of formula looks like IEPOX minus SOA/IEPOX minus SOAo).

379-384: "ith OH exposure step" is an unusual (and to me, confusing) way to describe chemical kinetics. A better way to word this is in terms of the integrated OH exposure, up to some reaction time t.

411-412: the paper cited here (Slade and Knopf 2014) did not attribute the RH effect to differences in surface area, as stated. The effect described really derives from the surface-area-to-volume ratio, which is well known to have an influence on the KOH value; Robinson 2006 may be the more appropriate reference here. (Though it may have been derived even before then?)

480-484: This is a long, wordy way to argue that the V/SA ratio is equal to D/6, and that the assumption that the reacted species is well-mixed (with the mass fraction the same at the surface and in the bulk) simplifies the calculations. These have been inherent to all heterogeneous oxidation studies going back to at least Robinson et al (2006), so probably does not need to be included here.

494-496: Based on the paper cited, and the text immediately following (lines 497-498), the authors appear to be arguing that this implies a role of oxidative processing of the IEPOX within the aqueous phase. But organosulfate formation (or even the catalytic promotion of IEPOX uptake by sulfate) would also seem to be a reasonable explanation for this effect, with no additional oxidation required.

514-517: Probably more important than changes to gamma at higher [OH] is changes at lower (atmospherically relevant) [OH]. This effect has been observed previously [Che, et al. 2009, PCCP 11, 7885–7895].

518: this statement appears to be directly contradicted in line 546.

Figure 3: An extra pathway should be included, since the SOA "yield" from Riedel et al was used (lines 319-325). This small yield implies that most (~90%) of the IEPOX

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reactive uptake leads to non-SOA (i.e., gas-phase) products, different from those generated by OH reaction; the formation of these should be therefore included in the figure as well.

Figure 7: The caption (or legend) should explain what the different symbols mean.

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