

Interactive comment on “Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs low-yield pathways” by D. K. Henze et al.

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Reviewer comments are italicized. References to specific text of the revised manuscript are given as sYpZ for section Y, paragraph Z.

1) The SOA yield from aromatic hydrocarbons may also depend on the RO₂/HO₂ concentration ratio and on the identity of the individual RO₂ species present. The authors of the present article and Ng et al. (2007) appear to only consider the HOArO₂ peroxy radical. However, in both chamber experiments and the ambient atmosphere other organic peroxy radicals are present (for example, in chamber photooxidations of toluene and m-xylene there must at a minimum be CH₃C(O)OO and CH₃O₂ radicals aris-

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ing from reactions of methylglyoxal). These RO₂ + HOArO₂ reactions may not be as slow as assumed for the HOArO₂ + HOArO₂ reactions. While this comment may have little effect on the overall conclusions, it may be worthwhile to note that the results of chamber experiments carried out under low-NO conditions or in the absence of added NO_x may not be totally applicable to the ambient atmosphere because of the different HO₂/RO₂ concentration ratios and the different mix of RO₂ radicals present.

The concentrations of HO₂ are so high in the low-NO_x chamber studies of Ng et al. (2007) that other sinks of the bicyclic peroxy radicals in these runs is unlikely. Further discussion of possible self reaction, or reaction with other peroxy radicals, in the atmosphere is now included in the revised manuscript. Both seem less likely than reaction with HO₂ or NO given the available surface observations of RO₂/HO₂, the relative reactivity of these species, and the fact that more than half of the SOA from aromatics is formed above the boundary layer (1.5 km), where RO₂/HO₂ ratios are likely lower. With respect to the other significant sources of uncertainty listed in Section 5, uncertainty associated with such additional peroxy radical chemistry seems small.

2) This may be a rather trivial comment, but a real upper limit to the SOA formation from aromatic hydrocarbon atmospheric degradation can be obtained assuming a 100% SOA yield, and with a SOA density approximately 1.5 times that of the precursor aromatic hydrocarbon, then an upper limit to SOA formation rate from aromatic hydrocarbons (assuming of course that the emissions inventory is correct) is about 25 Tg yr⁻¹, which would then be approximately 50% of the estimated SOA production rate.

Indeed, such an estimate constitutes an important maximum theoretical limit of SOA production from aromatic compounds. This is now included in s5p6.

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3) Page 14577, line 11. I suggest replacing “hydrocarbon” with “hydrocarbon peroxy radical”.

Done.

4) No mention is made about the effect of temperature on SOA formation. With atmospheric lifetimes of benzene and toluene of approximately 10 days and 2.5 days, respectively, these two aromatic hydrocarbons (and especially benzene) will be distributed regionally or globally. Hence benzene and, to a lesser extent, toluene will be reasonably well-mixed vertically in the atmosphere and hence SOA formation will occur at temperatures well below 298 K. It is surely expected that SOA formation will be increased at lower temperatures. Is this taken into account in the global chemical model, and if not, why not?

Yes, the temperature dependence of the equilibrium partitioning constants is taken into account using the Clausius-Clapeyron equation and an assumed effective ΔH_v for the SOA of 42 kJ mol⁻¹. This was mentioned in the original manuscript, though only in two sentences beginning at lines 14577, line 27. Uncertainty in ascribing a single, highly approximate, value of ΔH_v for the SOA is quite large; this fact is pointed out more clearly in the revised manuscript, see the end of s5p2.

5) Table 2. The authors use a rather unconventional version of the Arrhenius expression in that the temperature dependence is expressed as $\exp(B/T)$ and not by the more usual $\exp(-B/T)$, thereby resulting in values of B of opposite sign to “normal”. Maybe the authors should use the more conventional expression.

While it is not the conventional version of the Arrhenius expression, the form $\exp(B/T)$

is consistent with the GEOS-Chem documentation,* so it is probably best left in the current form.

*http://www.as.harvard.edu/chemistry/trop/geos/geos_mech.html

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14569, 2007.

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