Atmos. Chem. Phys. Discuss., 7, S7385–S7387, 2007
www.atmos-chem-phys-discuss.net/7/S7385/2007/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #5

Received and published: 29 November 2007

This article uses recent laboratory environmental chamber studies of secondary organic aerosol (SOA) formation from the OH radical-initiated reactions of benzene, toluene and m-xylene in a global chemical model to estimate the amount of SOA formed from aromatic atmospheric photooxidations on a regional and worldwide basis. The recent study of Ng et al. (2007), in which OH radicals were produced by the photolysis of HONO or H2O2 rather than by the photooxidation of VOC-NOx mixtures, found significantly higher SOA formation from toluene and m-xylene in the absence of NOx (i.e., when organic peroxy (RO2) radicals reacted dominantly with HO2 and/or organic peroxy radicals) than in the presence of NO, when the dominant reaction of RO2 radicals was with NO. The SOA yields from aromatic hydrocarbon degradations

are therefore treated as two separate pathways, with one SOA yield from the RO2 + NO reaction (applicable to "high-NO" conditions) and another SOA yield from what is presumed to be the RO2 + HO2 reaction (i.e., under low-NO conditions). The end result is that SOA formation from aromatic atmospheric degradations is higher than previously estimated because some of the aromatic degradations occur in low-NO conditions with higher SOA formation. The fraction of the aromatic degradation occurring under "low-NO" conditions depends on the reactivity, or lifetime, of the specific aromatic hydrocarbon and increases with increasing lifetime. The conclusion is that while SOA formation from aromatic hydrocarbons is higher than previously estimated, it is still minor (on a worldwide basis) compared to SOA from biogenic VOC degradations, although aromatic-derived SOA is important in certain locations. This is a useful and interesting article. Comments are as follows:

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 arising 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 NOx 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.

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

ACPD

7, S7385–S7387, 2007

Interactive Comment

EGU

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.

3) Page 14577, line 11. I suggest replacing "hydrocarbon" with "hydrocarbon peroxy radicals".

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?

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.

References Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909-3922, 2007.

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