

Interactive comment on “Modeling SOA formation from the oxidation of intermediate volatility *n*-alkanes” by B. Aumont et al.

Anonymous Referee #1

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The paper provides a detailed and systematic examination of the formation of secondary organic aerosol (SOA) from the oxidation of a series of C8–C24 *n*-alkanes, using chemical mechanisms generated by the well-documented GECKO-A generator in conjunction with estimated vapour pressures for the very large numbers of oxygenated products formed over successive generations. The *n*-alkanes are likely to contribute to intermediate volatility organic compounds (IVOCs) that are components of primary (emitted) organic aerosol, and which evaporate upon dilution. This investigation is therefore of relevance to understanding the processes which contribute to the formation and ageing of organic aerosol in the atmosphere.

The authors are careful to highlight and discuss the shortcomings and approximations in the work they have been able carry out. These approximations are primarily

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necessary because of computational limitations, and in one case an approximation is classed as “severe” by the authors (on page 14453). Although some additional assessment of the likely impact of that simplification might be desirable (see below), the work nonetheless presents an interesting and informative examination and discussion of the complexity of the system. It provides a clear illustration of a number features which are instinctively expected (as stated by the authors), but which have not previously been demonstrated in a formal way. The paper is well written and should be published. The authors may wish to consider the following comments in producing a revised version of the manuscript.

Specific comments

p 14451: It is stated that GECKO-A was updated to include the latest alkoxy radical SAR of Atkinson (2007). Although this provides an excellent basis for estimating many alkoxy radical reaction rates, it is noted that there are other reported methods for selected aspects of alkoxy radical chemistry with broader coverage. For example, Vereecken and Peeters (PCCP, 11, 9062, 2009) reported a method for estimating decomposition rates for alkoxy radicals containing a much wider set of relevant substituents. This included –ONO₂ groups, which must be prevalent in the schemes for the long-chain alkanes considered in the present work. Given the stated importance of representing competitive fragmentation processes on the end result, can the authors comment on how their applied methodology for the wider set of functional groups compares with more recently reported methods such as that of Vereecken and Peeters (2009)?

p14453: The assumption of restricting the study to high NO_x conditions is clearly a major simplification, and is acknowledged as a “severe approximation” by the authors. The necessity for applying such an approximation is largely justified, but there is no discussion of what its impacts might be. Given the known NO_x-dependence of chamber SOA yields from a number of precursors, it would be useful to have some assessment. Accepting that the authors probably cannot answer this question without running the

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more complex simulations, would this have been possible for the simplest (C8) alkane – or a simpler one (e.g. C5 or C6) – just to allow an illustration of the likely impact?

p14457: A representative OH rate coefficient of $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ is used for the illustrative calculation. Is it not possible to use an actual average value from the mechanism?

p14461, line 7: It is stated that fragmentation expectedly decreases with for parent hydrocarbons with shorter chains. Given that fragmentation (of alkoxy radicals) presumably occurs in competition with isomerisation, is such a decrease expected?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 14447, 2012.

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