

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

B. Aumont et al.

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We thank the reviewers for their comments on the manuscript. We outline below responses to the points raised by each referee and summarize the changes made to the revised manuscript.

Reponses to Referee 1

> 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

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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)?

The SARs originally implemented in GECKOA for the chemistry of alkoxy radical was taken in the SAPRC-99 mechanism (Carter, 2000), as described by Aumont et al. (2005). The SARs provided by Atkinson (2007) use a conceptual framework similar to those already implemented in GECKO-A. Updating the alkoxy chemistry based on Atkinson's 2007 SAR was therefore straightforward in GECKO-A. As pointed out by the reviewer, the method reported by Vereecken and Peeters (PCCP, 2009) allows an estimation of alkoxy decomposition rates for a larger subset of leaving groups (in particular R.(ONO₂) radical). This later SAR will be considered in future versions of GECKO-A. Note that a rudimentary test was performed to evaluate the sensitivity of SOA yields to the decomposition rates of alkoxy radicals (Aumont et al., 2010). Results for n-alkanes oxidation showed only a weak sensitivity to the alkoxy decomposition rates. For example, SOA yields from the n-pentadecane was found to be decreased by a few percent only when the decomposition rate of all alkoxy radical was increased by one order of magnitude.

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

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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 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?

As stated in the manuscript, the study performed here is “exploratory and intended to examine some, though not all, aspect of SOA formation during the multigenerational oxidation”. Exploring SOA production and ageing from high NO_x to low NO_x conditions is clearly a key issue. This NO_x effect to SOA production was already examined with the GECKO-A tool in the past for a C8 hydrocarbon (1-octene, Camredon et al., 2007). However, we think that inferring the NO_x effect for long carbon chain hydrocarbons from shorter ones might be misleading. SOA production for hydrocarbons with large carbon backbone will be examined for various NO_x regimes in future studies.

>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?

For the hexadecane oxidation case with C_{OA} set to $10 \mu\text{g m}^{-3}$, the mean (concentration weighted) OH rate constant of the species in the aerosol phase decreases from 3.4×10^{-11} (begin of the simulation) to 2.8×10^{-11} (end of the simulation). The sentence (p14457, line 10) is changed to: After 5 days of atmospheric processing, the mean (concentration weighted) OH rate constant of the aerosol contributors is $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. For a typical OH concentration of $10^6 \text{ molecule cm}^{-3}$, a chemical lifetime of about one year may be estimated for $\xi = 0.999$ (i.e. $C^* = 10^{-3} C_{OA}$).

We thank the reviewer for providing us the opportunity to correct an error that was in the original sentence.

> 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?

Yes. The sentence was not correct. Fragmentation is expected to increase (not decrease) with shorter parent compound chain length (as also seen in the Fig. 6). The typo is corrected in the revised manuscript.

Reponses to Referee 2

> My primary concern is that the simulations are conducted only under high NOx conditions. Reactions of RO₂+HO₂ and RO₂+RO₂ have been neglected. In the real atmosphere, however, RO₂+NO, RO₂+HO₂ and RO₂+RO₂ will occur to some extent simultaneously, depending on the abundance of OH radicals, VOC, and NOx. Is it possible to simulate a scenario in which these three sets of reactions are retained in the mechanism? This will provide some indication of the validity of neglecting the radical-radical reactions under high NOx conditions.

See reply to reviewer 1 on the same topic.

*P14452, L5: Instantaneously partitioning theory is employed in this model. The fraction of species *i* in the aerosol phase is a function of *C** and total organic mass. Could the authors give an example to incorporate this equation into the 2-step solver for species *i*? I assume the authors use ODE equations in their codes.*

Thermodynamic equilibrium is enforced at each time step (typically set to $\Delta t = 5$ min or less). The 2-step solver is used to solve the set of ODE linked to the gas phase kinetic only. In concrete terms, (i) the time evolution of the gas phase species is computed from t to $t + \Delta t$ using the 2-step solver (note that the “internal” time step used by 2-step might be much smaller than Δt) (ii) based on the total concentration (gas+aerosols) of the species, a new thermodynamic equilibrium is computed using

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a simple iterative method (similar to Pankow, 1994) at time $t + \Delta t$ (iii) the gas phase concentration obtained at equilibrium are then used as the starting point to reach the next time step according to (i).

P14452, L15: Could the authors give any references for using 250 g/mol as the average MOA?

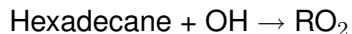
This value is a crude guess of the mean molecular weight of organic aerosols. A reasonable range might be around 100 and 300 g/mol, according to Pankow (1994). Similar values might be found in the literature, e.g. 200 g/mol in Donahue et al. (2011) or 250 g/mol in the 3D model Chimere (Hodzic et al., 2010). Explicit modeling of the Mexico city plume with GECKO-A (Lee-Taylor et al., 2011) leads to values ranging from 250 to 290 g/mol (unpublished results, private communication from A. Hodzic). Note that according to equation (2) in the manuscript, M_{OA} and C_{OA} have similar contributions to species partitioning, although in the opposite direction. Decreasing M_{OA} by a factor of 2 has therefore the same effect as increasing C_{OA} by a factor of 2. In this study, C_{OA} was changed within 4 orders of magnitude (from 0.1 to 1000 $\mu\text{g m}^{-3}$). Therefore, changes in the prescribed M_{OA} in the range of likely values should not affect the general conclusion of the study.

> P14456, L5: The simulation results show that organic nitrates account for 49% of the first-generation products. However, previous chamber experiments found that molar yields of alkyl nitrates from C5-C8 alkanes range from 10.5 – 22.6 % (Atkinson et al., 1995; Arey et al., 2001). Could the authors give an explanation for the high yields of nitrates? What is the stoichiometric molar ratio of organonitrates from RO₂+NO reactions in the mechanism?

Branching ratios for organic nitrate and alkoxy radical formation are estimated using the SAR of Carter (2000), and depend on the RO₂ class, the presence of polar functional groups (e.g. hydroxyl, carbonyl, nitrate) and the length of the carbon chain.

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For a C16 secondary RO₂ radical, the SAR leads to a 28 % nitrate yield (as given in the text for the monofunctional nitrate). The first oxidation steps can thus be represented as:

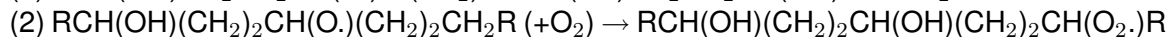
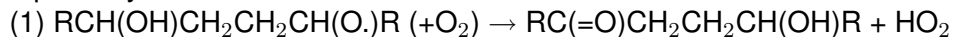


The RO radical next leads to 1-4 hydroxyperoxy (isomerisation pathway) with a yield close to 1, which in turn react with NO to produce a 1,4 hydroxy nitrate. The first generation 1,4 hydroxynitrate yield is then $0.72 \times 0.28 \approx 0.21$ (as given in the text). First generation nitrate yield is then $0.28 + 0.21 \approx 0.49$. Note that the presence of the hydroxyl group is expected to decrease the nitrate yield significantly (e.g. Jordan et al., 2008). For species with large carbon skeleton, this effect is currently not represented with the SAR implemented in GECKO-A and the 1,4 hydroxy nitrate yield is likely overestimated.

P14456, L7: There is a small amount of trifunctional species formed in the first generational products. How do the authors define “one generation”? It seems that there should be at most two functional groups produced upon the abstraction of one H atom from the parent hydrocarbon by an OH radical via the 1,5-H-atom shift isomerization. Could the authors give an example of trifunctional species and how they are formed?

A generation is defined as the first set of non radical species produced from a given parent compound. We included that definition in the revised version of the manuscript (section 3.2).

As seen from above, hexadecane oxidation will produce 1-4 hydroxyalkoxy radical with a yield of $0.72 \times 0.72 \approx 0.52$. The fate of this radical is mostly isomerization and follows 2 pathways:



Pathway (1) is the major transformation (with branching ratio estimated to 95%), lead-

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ing to the formation of 1-4 hydroxyketone with a yield of $0.72 \times 0.72 \times 0.95 \approx 0.49$ (as given in the text). The peroxy radical produced by the pathway (2) will mostly yield to trifunctional species (with a yield of about $0.72 \times 0.72 \times 0.05 \approx 0.02$, as given in the text), the dominant product being dihydroxy ketone (i.e. $\text{RCH}(\text{OH})\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}(\text{OH})\text{R}$ species). Dihydroxy ketone is included in the revised text as an example of first generation trifunctional species.

> P14457, L15: *I noticed from Figure 2 (k) that there are some 3rd-generation products with vapor pressure ranging from $10\text{E-}8$ to $10\text{E-}2$ atm. After 6 generation of oxidation, they are all gone. What is the fate of these products?*

As discussed in section 3.2 (page 14457, line 12), oxidation of these gas phase organic species will either lead to low volatility products that will be progressively transferred to the particle phase in a form that can be considered as permanent or finally lead to CO_2 . Figure 2 shows that about 6 generations must be taken into account to reach this state.

> P14459, L5: *The maximum yield was observed after the consumption of the parent hydrocarbon here. Chamber experiments, however, showed that for some VOCs like isoprene, secondary organic mass is still able to accumulate even after the parent hydrocarbon is completely consumed (Ng et al., 2006). The simulation here indicates that the further oxidation of semi-volatile products in the gas phase does not contribute to the SOA yield after the parent hydrocarbon is fully consumed. Given the constant OH radical supply, which is 2×10^7 moles $\text{cm}^{-3} \text{ s}^{-1}$, the remaining gas-phase products should still be able to react with OH radicals.*

We faithfully disagree. Our sentence indicates that “the maximum yield is observed after the consumption of the parent hydrocarbon”, and therefore clearly suggests that secondary organic mass is still able to accumulate even after the parent hydrocarbon is completely consumed. This is especially clear for octane oxidation, where SOA is

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still produced after the removal of the parent compounds (see figure 1b, 1c and 4d). Further oxidation of semi-volatile products in the gas phase therefore does contribute to the SOA yield after the parent hydrocarbon is fully consumed. For longer chain length, like hexadecane, further gas phase oxidation does not significantly change SOA mass (i.e. maximum yield is concomitant with parent compound removal) but still contributes to SOA ageing (see figure 3e and 3f) through the “gas phase chemical pump” process.

> P14461, L1: Figure 6 shows the distribution of parent compound vs. species with smaller carbon skeletons in the OSC/C space. Could the authors give an estimate in terms of the fraction of all the fragments in both gas and particle phase as a function of time?*

The paper already contains 50 figures and panels. We think that adding figures to give the time evolution of the fragments in the 2 phases will make the manuscript heavier and will in part be redundant with some information already given in paper (although in a scatter way). The major gas phase fragments are CO and CO₂ – their time evolutions are given in Figure 1. Particle phase fragments are negligible for the tetracosane and octane simulations, as can already be seen in Fig. 6. For hexadecane, the paper already states (page 14461, line 21) that “species with 16 carbons contribute to 92% of the SOA carbon budget”.

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