**Atmospheric
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Comment

Interactive comment on "Heterogeneous oxidation of saturated organic aerosols by hydroxyl radicals:Uptake kinetics and condensed-phase products" *by* I. J. George et al.

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Background

The purpose of the above manuscript is to examine the potential for the OH heterogeneous reaction to initiate oxidation of liquid alkane-like aerosols as well as to probe the reaction mechanism. The kinetics experiments confirmed the high efficiency of OH radicals to initiate oxidation of liquid organic aerosols, whereas the product studies showed for the first time formation of non-radical products such as alcohols and ketones in the condensed phase. Based on these studies the authors concluded that oxidation preferentially leads to long-chain hydroxyl- and carbonyl-containing products

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accumulated in the liquid phase rather than to volatilization of small oxygenated organics into the gas phase, as was observed in our own studies for solid organics.

The results presented in the manuscript are undoubtedly an important contribution to our understanding of the atmospheric chemistry of organic aerosols. On the other hand, we believe that not all the conclusions reported by the authors are completely supported by their experimental data. Based on results of the condensed-phase product study described in the manuscript in question and of the separate gas-phase product studies of the OH-initiated oxidation of Bis(2-ethylhexyl) sebacate (BES) films (to be presented in a forthcoming paper), the authors conclude that the VOC to OH product yield is 10% and that formation of RO is minor in the RO_2 self-reaction compared to the alcohol+ketone reaction pathway. In the following paragraphs we question these conclusions.

Product studies
Table 1 of the manuscript shows the results of the product studies. The stoichiometry of the RO_2 self-reaction (Figure 10 of the manuscript) suggests that alcohols and ketones should form in equal amounts. However, the data in Table 1 indicates a formation ratio of alcohols to ketones of 1:4. If this imbalance is indeed real, it can be taken as evidence that only a fraction of the ketones (1/4) are formed directly via the RO_2 self- reaction while the remaining (3/4) are formed via the heterogeneous reaction between RO and O_2 (Figure 10). Accounting for the stoichiometry of ketone formation in the latter case, the branching ratio between non-radical (f_{NP}) and radical product (f_{RP}) formation in the RO_2 self-reaction, f_{NP}:f_{RP} is 0.4:0.6, i.e., only 40% yield of non-radical products such as alcohols and ketones should be expected. On the other hand, the reaction pathway leading to ketone formation via $RO+O_2$ is one of three other channels in which RO is consumed. The branching ratio in the RO reactions (isomerization, scission, and HO_2 elimination) depends on the O_2 concentrations, which are not reported by the authors. This means that the above estimate can be considered as the lower limit for the alkoxy radical branching ratio, f_{RP}, which in the gas phase

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typically ranges from 0.3 to 0.8 depending RO_2 structure (Atkinson et al, 1997). Based on this analysis of the condensed-phase product distribution, the reaction pathway of alkoxy radical production is *not* minor, as is concluded in the manuscript.

In our OH+organic film study we found that 3 OH radicals are needed to volatilize one RH molecule (Fig. 3a, Molina et al, 2004). This suggests that 2 of 3 OH radicals are additionally required to activate the non-radical products, i.e. the branching ratio in the RO_2 self-reaction is expected to be f_{NP}:f_{RP} = 0.67:0.33. The difference in the branching ratio in the two studies could be due to the different reactivities of the alkanes used or possibly to the formation of RO via RO_2 + OH (with a rate constant of 10^{-10} cm^3/molec s, see NIST chemical kinetic database), which would matter if the OH concentration is sufficiently high, as is the case in the experiments reported in the manuscript. The RO_2 + OH reaction is not likely to be important under atmospheric conditions.

Volatilization rate
The volatilization of BES aerosols described in the manuscript is shown in Fig. 7. Changes in aerosol volume with the OH flux clearly show non-monotonic behavior, indicating that at the very beginning O_2 attachment (RO_2 formation) via R + O_2 precedes the RO_2 self-reaction until RO_2 reaches such a concentration level that the self-reaction rate becomes equal to the rate of RO_2 production (the plateau at 2×10^{-8} atm s in Fig. 7). The characteristic time of reaching the maximum RO_2 (the plateau) is about 15-17 s at the initial OH concentration of $\sim 3 \times 10^{10}$ molec/cm^3 and the residence time of 75 s (OH exposure of 9×10^{-8} atm s). Comparable times were determined for NO_x-free oxidation of solid organic films in our own studies (to be published). In the current study it appears that at times greater than 20 sec the RO_2 self-reaction efficiently generates RO at concentrations large enough for scission to become dominant, eventually leading to an overall volume loss rate of about 17% per minute. The observed linear volume loss with time suggests that BES particles will be nearly completely volatilized after 6 min with an OH exposure of 9×10^{-8} atm s. Assuming the same concentrations of

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C-H bonds in solid and liquid organics, a comparison of volatilization rates per carbon atom (volatilization rate = thickness of organic layer/(time$\times[OH]_0$) shows similar values of 8.3×10^{-10} and 5.4×10^{-10} in nm/(min molec/cm^3) for OTS (C$_{18}$ monolayer studied in our earlier work) and BES, respectively. Accounting for the different chain lengths (BES has 44 % more carbon atoms than OTS), the difference in the volatilization rates becomes a factor of 2.2. As a result, compared to OTS, a BES molecule is expected to be about 2 times less efficient in terms of its volatilization due to the longer chain length and the lower RO reactivity (the lower C-C bond scission rate). This analysis indicates that volatilization is indeed an effective reaction pathway that ultimately leads to chemical decomposition of both solid and liquid alkane-like aerosols. Therefore the data as reported by the authors is not necessarily in disagreement with our previous results or on-going work.

Comments by Andrey V. Ivanov and Mario J. Molina

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