

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

I. J. George et al.

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We thank A. Ivanov for useful discussion of the manuscript.

With regard to the product studies, we did not quantify the relative ionization efficiencies of the condensed-phase products measured by electrospray ionization mass spectrometry (ESI-MS). Thus, we should refrain from making any definitive conclusions on the relative importance of reaction pathways based on the relative intensities of the products shown in Table 1. This point will be emphasized in the text. In addition, we now state clearly in the text that the relative yield into the alcohol + carbonyl channel (now labeled as channel (2)) can not be estimated relative to the yields of the pathways giving rise to carbonyls and alcohols via channels (5) (RO reaction with O₂) and (3) (RO

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isomerization), respectively. We agree with Ivanov that the RO + O₂ pathway may be a significant source of carbonyl containing products depending on the O₂ concentrations (which were taken as high as 20% oxygen, as now stated in the paper). Also, we refer readers to the recent paper by Hearn et al. (2007) for more information on the different reaction channels, where the condensed-phase product yields from the reaction of BES particles with Cl radicals were explicitly measured (see Short Comment by G. Smith).

With respect to the volatilization rate, it is clear from our work that a maximum of 17% of the particle volume volatilizes under the highest exposures. Similar results have been observed by Hearn et al. (2007) in their study of the reaction of BES with Cl radicals. We note that the highest OH exposure in our experiment corresponds to approximately 28 days of atmospheric OH exposure time, assuming a daily averaged OH concentration of $[OH] = 10^6$ molecules cm⁻³. Complete volatilization of the particle would occur with $(1/0.17) * 28 = 164$ days, i.e., a timescale not atmospherically significant. However, as noted in the original manuscript, we note that the volatilization rate may be higher if the exposures are conducted at lower OH concentrations than those used in our study, i.e. if the channel forming alcohol + carbonyl is diminished in importance at lower OH.

At the highest OH exposure in our work, we calculate a volatilization rate assuming linearity of volume loss for BES particles based on the equation stated by Ivanov of $2 \times 10^{(-10)} \text{ nm min}^{(-1)} \text{ molecules}^{(-1)} \text{ cm}^3$. This value is almost 4 times smaller than that for OTS. It is true as Ivanov states that BES has a longer carbon chain than OTS used in the Molina et al. (2004) study, and may require more OH molecules to completely volatilize. We note that we have also studied particle volume loss from stearic acid particles by reaction with OH using a similar approach to that described in this work. We find significantly faster volatilization rates compared to BES particles (unpublished). This work has been confirmed in our lab by coated-wall flow tube studies, where we measure higher VOC product yields from OH reaction with a stearic acid film compared to a BES film by a factor of 3 to 4 (Vlasenko and Abbatt, in preparation). The

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difference between the volatilization rates of BES and OTS (and stearic acid particles) may be due to several possibilities as discussed in detail in the Short Comment by P. Ziemann: 1) chemical structure, 2) particle phase, 3) O₂ concentration and 4) NO_x concentration. We will discuss these issues in the text more clearly.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6803, 2007.

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