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Atmospheric
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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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On the OH uptake coefficient. In the work described in the manuscript, the MS signal from mass 297, a proxy for a BES molecule, was used to determine the initial OH uptake coefficient on a liquid aerosol surface (Fig. 4 of the manuscript). The reported value of 1.26 ± 0.04 is corrected for OH diffusion and is not associated with OH-initiated secondary chemistry. The authors ‘see no strong indication of such secondary chemistry’ within the experimental uncertainties. Note, however, that the uptake coefficient (gamma) is a probability, so by definition it can be at most unity.

On the other hand, uptake of a gas phase species on a liquid aerosol surface is de-

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scribed in the framework of a resistance model (Kolb et al, 1995) that accounts for mass transport, mass accommodation, and uptake in the gas phase as well as diffusion, solubility, and reaction in the condensed phase. Additionally, fast gas uptake, which is the case for OH uptake on an alkane-like droplet, causes distortion of the Boltzmann velocity distribution for gas molecules above the surface, and a general correction for this effect (Motz and Wise, 1960) has to be applied.

Based on results of our studies (Bertram et al, 2001), gamma for OH on organic surfaces ranges from 0.1 to 1, and therefore, alpha as the upper limit of gamma is expected to be near unity. According to the resistance model approximation, in the limit of fast OH uptake and α=1, the diffusionally corrected value of 1.26 reported in the present work has to be related to 2γ/(2 - γ) instead of γ (as assigned by the authors). Accounting for this effect, for uncertainty in the OH diffusion coefficient (0.21 $\pm$ 0.04 atm cm^2 s^{-1}, Ivanov et al, 2007), and for the overall experimental $\pm$30% uncertainties, the gamma value is found to be 0.7 $\pm$ 0.2. For the reported value of 2 (Hearn and Smith, 2006), the gamma value is in the range of 0.7 to 1. These values are consistent with our early measurements. More accurate estimates for the OH uptake coefficient require knowledge of an aerosol surface area or volume (not reported in the manuscript). The reported aerosol parameters are not related to the aerosol size distribution and so cannot be used to estimate an aerosol surface area or volume.

On the equation 1 used in the work. This equation was originally derived for determination of the ozone uptake coefficient on alkene liquid aerosols (Katrib et al, 2005) and with some restrictions describes the reaction in the bulk since the ozone uptake is relatively slow. Compared to ozone, OH uptake is 3-4 orders of magnitude faster and the OH heterogeneous reactions take place on the surface rather than in the bulk. Almost every collision of OH with a BES droplet (see the first comment) leads to production of a surface alkyl radical that reacts at the surface because of the faster reaction with O_2 as compared to diffusion into the bulk. To make this point clear let us calculate the depth within which the R+O_2 reaction occurs. According to a resistance model, the reaction will occur in a depth $\sim$ D$_l$/k$_r$)$^{1/2}$, i.e., using D$_{BES}$ = 1.5$\times$10^{-7} cm^2 s^{-1} (for triacontane D$_{C30H62}$ = 7.5$\times$10^{-7} cm^2 s^{-1} (Vardag et al, 1991) whereas for a polar BES molecule the diffusion coefficient is expected to be slower by a factor of 4-5) and k$_{R+O2}$ = 1$\times$10^6 s^{-1} at few Torr of O_2 (O_2 concentrations are not reported in the work) and room temperature, the estimated value of a reaction depth is about 3.7 nm which is comparable with the size of a BES molecule. It means that 2/3 of alkyl radicals will be transformed to alkyl peroxy radicals within the interfacial layer of thickness comparable with the size of a BES molecule. Therefore, to describe fast OH uptake accurately the equation 1 should be modified by including interfacial reactions. Under atmospherically relevant conditions the heterogeneous R + O_2 reaction occurs within an interfacial layer only.

On a mass 297 signal as a proxy for BES. Based on the dependence of a MS signal from mass 297 on OH exposure (Fig. 4 of the manuscript), one may conclude that the OH uptake coefficient is time dependent because ‘the reactive uptake coefficient ... is expected to decrease with increasing OH exposure due to the reduction of condensed-phase BES concentration with increasing OH exposure’; this assumption does not explain why the uptake coefficient (a probability) should depend on concentrations or time. The above conclusion is inconsistent with predictions of a resistance model that, in the limiting case of relatively long liquid exposure time and fast uptake, gives a time-independent uptake coefficient. This conclusion is also not in agreement with results of our direct CIMS measurements for OH uptake on organic films that indicate the uptake rate independent of time (Molina et al, 2004). One of the possible explanations for such unexpected behavior of a mass 297 signal is that other products of oxidation, such as alcohols and ketones, can contribute to the mass 297 signal that will eventually result in its non-linear decrease with time. This contribution can be important at small OH exposures, even at 2.5$\times$10^{-9} atm s used to calculate the initial OH uptake coefficient. It appears that the ability of a fragment at mass 297 to represent OH uptake seems uncertain.

On a liquid organic aerosol as a proxy. Compared to studies of solid organic films, studies used liquid organic aerosols as proxies are more complicated because they also require accurate knowledge of other key parameters, such as a mass accommodation coefficient, a self-diffusion coefficient of long-chain alkanes, and aerosol surface area and volume.

The cited references (that are not in the reference list of the manuscript):

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Comments by Sofia Trakhtenberg and Andrey V. Ivanov

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