

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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We are grateful for S. Trakhtenberg’s helpful comments regarding heterogeneous kinetics.

Trakhtenberg’s comments on the reported uptake coefficient imply that we need to clarify the nature of the uptake coefficient value we reported. We will discuss the differences between the reported reactive loss of BES particles and the OH uptake coefficient that has been measured by flow tube studies such as Bertram et al. (2001), i.e. that the flow tube studies measure this quantity more directly by observing gas-phase loss of OH, whereas the aerosol studies calculate this quantity from the loss rate of aerosol reactants. Note that our reported value of 1.3(+0.4), which includes

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systematic uncertainties, is consistent with a unity loss of OH.

Trakhtenberg suggests that our initial uptake coefficient value may be biased high because of the distortion in the Maxwell-Boltzmann velocity distribution of OH molecules. The processes involving mass transport near the particle interface are complex and not completely understood, especially in the transition regime (intermediate Kn values). Because our experimental conditions are in the transition regime, we believe that the Fuchs and Sutugin (1970) formulation is the most appropriate approach, and thus have used it to correct our initial uptake coefficient value for mass transfer effects. We believe that the Fuchs-Sutugin formula also takes into account the velocity distortion. We note that most studies in the area of heterogeneous kinetics with aerosols have also used the same Fuchs and Sutugin formula to correct for mass transfer (e.g., Lovejoy et al., 1995; Hanson and Kosciuch, 2003; Hanson, 2005). A number of these studies have reported unity uptake coefficients (when a value of unity is likely) without making an additional correction beyond the Fuchs Sutugin approach. In particular, the Motz and Wise (1960) correction was formulated for conditions of the Knudsen number approaching zero, adding complications to its use for the transition regime. For these reasons, we do not feel it necessary to use the Motz and Wise (1960) correction when using the Fuchs-Sutugin formula, but we thank Trakhtenberg for raising this issue given that the chapter may not be closed on how to deal with these corrections.

We agree with Trakhtenberg that the OH reaction with BES particles is likely a fast surface reaction. We would expect particle-phase BES to decay in an exponential-like manner as a function of OH exposure according to Case 4 in Worsnop et al. (2002), where the uptake coefficient is controlled by a fast surface reaction. We were unable to successfully fit the data over all OH exposures to an exponential fit due to somewhat slower kinetics at higher OH exposures. It is not unexpected that non-exponential behavior will prevail when the reactants are highly depleted because the nature of the particle will have changed substantially from its original condition (and so, in Equation (16) of Worsnop et al., many of the constants relating the change in concentration to expo-

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sure may have changed as well). Thus, we focused on the data at low OH exposures to extrapolate an initial uptake coefficient using equation (1) in our manuscript. This equation assumes that the Case 4 equation in Worsnop et al. (2002) can be approximated with a Taylor expansion of the exponential function for very low OH exposures. The initial uptake coefficient values calculated from the expression from Worsnop et al. (2002) and the equation (1) in our text differs only by 13% (18% for diffusion corrected values), which is within our overall experimental error.

The reactive loss rate of particle-phase species from a surface reaction is linearly correlated to the surface concentration of the particle-phase species (Worsnop et al., 2002). Because we calculate the uptake coefficient by observing BES loss and by referencing to the OH collision rate with the particle, the inferred uptake coefficient will indeed appear to decrease at high OH exposure. The reason for this is that products are building up in the particle and the BES concentration is decreasing, so that not all OH collisions with the aerosol will result with OH seeing a BES molecule. This is another reason that uptake coefficients are calculated in the limit of low exposure in aerosol experiments of this type. Of course, if we had referenced instead to the collision rate of OH with BES molecules in the interfacial layer (which is much harder to do), then the uptake coefficient would not be expected to decline as a function of exposure. This issue will be clarified in the discussion of kinetics.

As stated in the original manuscript, a comparison of the kinetics of m/z 297 loss and the formation kinetics of several major reaction product fragments (m/z 127, 153, 181) suggest that 297 does not contain significant intensity from products, i.e. the rate constants for m/z 297 loss and product formation agree to within 20%. Although, it is possible that m/z 297 is a minor product peak, the data suggest that if this is the case the effects on the reported kinetics are within this uncertainty range. See reply to Anonymous Referee #3 for more detail regarding the choice of m/z 297 as a tracer for BES.

References:

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