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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Amine exchange into ammonium bisulfate and ammonium nitrate nuclei" *by* B. R. Bzdek et al.

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The authors thank Dr. Petrucci for several helpful comments. Our responses are given below:

1. The equation the reviewer refers to in the Su and Chesnovich paper is similar to Eq. 15 in the Ridge reference, which contains a 2π term in the expression for the Langevin rate constant. (Ridge, D. P. In The Encyclopedia of Mass Spectrometry; Armentrout, P. B., Ed.; Elsevier: San Diego, CA, 2003; Vol. Volume I: Theory and Ion Chemistry, pp 1-8.) The form of the equation for the Langevin rate constant that we use in this manuscript is given by Eq. 26 in the Ridge reference. The two forms are equivalent, but the form we use is a simplified form where all constants (i.e. charge of an electron, vacuum permittivity) are combined, α is replaced by the volume polarizability (α'), μ' is

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the reduced mass of the colliding pair in Daltons, and units are adjusted to a convenient form.

2. We will adjust Eq. 11 and Eq. 12 in our manuscript accordingly. The collision rate, kcollision, is equivalent to kSC. We will adjust the manuscript by replacing kcollision with kSC in Eq. 14.

3. The first and third entries for the substitution of NH3 were inverted – we thank the reviewer for pointing this out. These values have been corrected appropriately and the remaining entries in all tables have been checked. We did make a few other minor corrections, none of which impact the conclusions of the manuscript. The corrected tables will be uploaded as a separate author comment and will be incorporated into the revised manuscript. As to error propagation: we performed error propagation for a significant number of reactions and found the uncertainties to be between 20 and 30%. However, error propagation does not account for all uncertainties in the experiment, for example possible systematic error associated with literature constants (polarizability for second order rate constant determination, dipole moment for uptake coefficient determination). Therefore, we decided to be conservative in our analysis and report a uniform uncertainty of 30% for all values of the second order rate constants.

4. We will include values for the volume polarizability and the dipole moment of ammonia and the amines in the revised manuscript text for clarification.

5. The reason for the discrepancy is that the two tables are reporting different entries. The Supplemental Information gives values for the pseudo-first order rate constants for partially substituted bisulfate clusters. For a given substitution, the rate constant was measured both directly (i.e. the precursor to the substitution of interest was generated by electrospray and its rate determined directly as the first step in the reaction) and indirectly (i.e. the substitution of interest was observed as a later step in the reaction). What we present in Table 1 is the average of the individual values in the Supplemental Information for a given exchange step. Since there was only one measure of the first

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substitution, its rate is the same in Table 1 and the Supplemental Information. All other substitutions have multiple measurements, so the two entries are different.

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