

Interactive comment on “Parameterization of N₂O₅ reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate” by J. M. Davis et al.

Anonymous Referee #1

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This manuscript describes an effort to develop a parameterization of the N₂O₅ reaction probability that can be included in global and regional scale air quality models. The heterogeneous reaction of N₂O₅ is known to be an important factor in the lifetime of NO_x in the polluted boundary layer and thus more realistic parameterizations are needed and of interest to ACP readers. The advances made in this manuscript are the simultaneous inclusion of a nitrate effect, differentiation between solid, ice and aqueous phases, use of a larger (though not complete) data set and rigorous statistical models, and upper bounds on the gamma.

To be clear: I think the parameterization is an improvement over existing ones (e.g.

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EJ05). The authors are clear in their writing and in their reasoning. While I disagree with some of their approaches and reasoning, quite strongly in some cases, I do feel this paper is worthy of publication in ACP after the authors address several concerns.

Major Concerns (in no particular order)

1. The authors choose to focus on data obtained for ammonium nitrate, ammonium sulfate and ammonium bisulfate particles. The reasons given, that A N S systems are important contributors to total surface area in continental regions, and a large amount of data exists on these particle types (p. 16122, lines 9 -11) are not completely satisfactory.

Yes, A N S systems are substantial contributors to surface area, but so too is organic matter, and yet the authors do not discuss the role of organics. Organic films and total organic mass are not the same, though in either case (see later) there seems to be sufficient data on both at this point, at least compared to the amount of data used for ammonium nitrate (e.g. Folkers2001/2003, Thornton 2003). Additionally, while sea salt particles only affect polluted coastal regions, a good deal of data on these particle types exists. Dust and soot are not unimportant but are certainly substantially different from aqueous solution droplets.

This issue is important not only for rigor and completeness but also carries implications for the parameterization (see next).

2. I believe the authors focus exclusively on A N S systems has potentially affected the physical relevance of the parameterization itself. There is even mechanistic support for broadening the scope of data used. The mechanism provided in the manuscript (pg 1630) suggests that, with the exception of NO_3^- , particle composition should have little effect on the N_2O_5 reactivity so long as there is sufficient liquid water.

Most affected by this focus on A N S systems, in my opinion, is the parameterization's RH dependence, especially for aqueous particles.

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On page 16123, line 9-10, the authors state that the most prominent feature in the data is that gamma increases with RH. However, this conclusion seems questionable. Excluding the ammonium nitrate data due to the competing nitrate effect, the only data set I can see that increases uniformly with RH is that of Kane, et al. In fact, above 50% RH, the data of Hu and Abbatt decreases, while that of Folkers, et al, Halquist, et al, and Badger, et al are essentially flat, and that of Mozurkewich contains only on or two data points at a given temperature some of which go in opposite directions with RH.

If data sets from other particle compositions are included (e.g., Benkhe, et al JGR, 1997, Benhke et al, J. Aerosol Sci 1990, Stewart, et al ACP 2004, Thornton et al, PCCP 2003, Thornton and Abbatt, JPC 2005), I think the most reasonable conclusion is that there is not yet a discernable effect of RH above $\sim 50\%$ RH.

Indeed on pure water I believe the recommended value for gamma is ~ 0.02 (Sander, et al; JPL Handbook). In the presented mechanism, as RH increases, particle composition becomes more like pure water, so what is the physical basis for allowing gamma to increase to $\sim 3X$ this value (certainly outside of measurement uncertainties)?

3. In regards to figure 3, wouldnt it be a better comparison to show how the parameterization does when T is fixed and RH varies, and when T varies, but RH is fixed? That is is Figure 3 a true test of the validity of both the T and RH components of the parameterization?

Other comments

1. I think given the significant focus on A N S systems, the first line of the abstract should be altered to reflect this focus, unless the authors include other data sets. The word comprehensive seems inappropriate otherwise.

2. Pg. 16122, line 12, again organic coatings and organic mass are separate issues. A better justification for ignoring water-soluble organic material in the parameterization is needed.

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3. Pg. 16122, lines 24 to 26: I suggest altering the language here to start with the potential of an artifact in MOZ88. Does MOZ88 state the artifact might be present above 40% or is this speculation on the authors' part? As written the sentence raises the question: if four points from MOZ88 are removed because they greatly exceed those of Halquist et al, why not remove Kane, et al points which greatly exceed those of Folkers, et al and Halquist, et al at 80% RH?

4. Pg 1624 bottom, add where j is an integer between 275K and 296K.

5. Pg 16131, lines 25 to 29, Surface water has been observed to increase with RH on crystalline substrates as a possible explanation here [Sumner, et al., 2004].

6. Pg 16132, lines 21 to 22: As described in detail above, I think the FOL03 data is in agreement with the behavior of almost all the other data sets except Kane, et al. It would be interesting to know how different the parameterization becomes when equations 1 and 2 are solved without the Kane, et al data.

Some References:

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