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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates" *by* K. S. Hu et al.

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We thank the reviewer for the encouragement to clarify the thermodynamics discussion and to elaborate on other potential atmospheric implications. We include below our reply to the specific issues:

1. I suggest making it clear that by "acid catalyzed" the authors mean catalyzed by H+ (specific acid catalysis) not by the acids themselves (general acid catalysis).

We agree that this more specific definition should be made explicit and plan to include it in the revised manuscript.

2. I suggest providing some explanation as to why the discussion of thermodynamics is based on standard state values (activities = 1) whereas the lifetimes are based on compositions typical of the atmosphere (H2SO4 and H2O activities = 67.7 and 0.591). It would also be useful to make it clear that these are very different conditions, so that, for example, under atmospheric conditions the [alcohol]/[organosulfate] ratio at equilibrium is lower by a factor of _100 compared to the standard state. The authors comment on this at the end of the first paragraph of “Atmospheric Implications”, but it would help to clarify this issue earlier.

This is a good point. Because we used several experimental sources (with different activities for various species) for the organosulfate systems, we had to actually calculate equilibrium constants (which, of course are referenced to the standard state of unity activity) in order to compare the various values. However, because we carried out all of the kinetics measurements (at 55 wt% H2SO4 for the primary and secondary systems and in H2O for the tertiary systems) ourselves, we chose to report the kinetics information at these specific, non-standard state conditions, which also brackets the range of acidities found at atmospheric conditions. We intend to add a more detailed explanation of these choices in Section 3.1 of the revised manuscript.

3. Page 14391, line 11: I suggest being more precise about what is meant by “these systems”. Although it looks like it means the standard state, readers not up on their thermodynamics may think that conclusions based on standard state conditions apply to all conditions. This again relates to my concern that not all readers will easily translate the discussion of standard state behavior to atmospheric behavior.

Here, “these systems” refers to the different organonitrate and organosulfate species. In other words, we are claiming that all organonitrates and organosulfates that we have studied show the same thermodynamic behavior. Hopefully, the manuscript revision planned in response to the comment above will clarify both the connection between thermodynamic standard state and atmospheric conditions and the issue of the similar thermodynamic properties for the systems under study.

4. I suggest being more precise about what is meant by “neighboring OH groups” and their effects. I believe it means an OH group anywhere else on the molecule, but is that all that is necessary for an effect? I believe that all the molecules studied have betahydroxy groups (and sometimes also others), which I suspect have the largest effect. Is there reason to believe that hydrolysis of a hydroxynitrate with only a distant OH group would be much different from an alkylnitrate? This issue is relevant to questions about oxidative aging, during which the density of functional groups increases.

This is a very good point. We are actually referring to directly adjacent OH groups in our discussion and will replace “neighboring” with “adjacent” everywhere in the revised manuscript.

5. Page 14402, first paragraph: Can any comments be made about the effect of temperature on the kinetics? Would nitrates be significantly more stable in the colder and drier upper troposphere so that they might be transported long distances?

We did not carry out any temperature dependent kinetics measurements for the hydrolysis of the organonitrates. However, if a typical activation energy is assumed for the hydrolysis reaction (the rule of thumb is that the rate constant doubles for every 10 K temperature change), the lifetime at 226 K for the tertiary isoprene-derived organonitrate could be several days. On the other hand, these aerosols would also be highly acidic and the tertiary organonitrates might undergo similar nitronium- or nitrosyl-assisted reactions, such as those we observed for the primary and secondary organonitrates. We intend to include a discussion of these issues in the revised manuscript.

6. Atmospheric Implications or Conclusions: Although these results indicate that most organonitrates will have relatively long lifetimes with respect to H+ catalyzed hydrolysis in the atmosphere, what effect might metals have on this conclusion? I suspect they would be present and quite soluble in fine acidic aerosol. Since the thermodynamics seems to favor hydrolysis, might metal catalysis be important in allowing this to happen?

This is also a good point. Since the present work establishes the thermodynamic instability of organonitrates with respect to alcohols, it is reasonable to speculate whether there might be more efficient catalysts (such as metals) present in ambient aerosols. We intend to include this point in the revised manuscript.

7. The authors may want to mention the observations of Matsunaga and Ziemann [PNAS, 107, 6664–6669 (2010)], who note in their study on hydroxynitrate formation that tertiary beta-hydroxynitrates in SOA filter samples collected under very dry conditions were stable for at least 1 week when stored at -20C, but that samples extracted and analyzed after 1 month of storage showed decomposition. This was in contrast to the other beta-hydroxynitrates and also dihydroxynitrates and trihydroxynitrates they had studied, which were stable for at least 1 month.

This is obviously quite relevant to the present study and will be included in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14383, 2011.