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

Anonymous Referee #2

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General Comments

The authors describe the results of laboratory experiments and computations related to the kinetics and thermodynamics of the hydrolysis of organonitrates and organosulfates. These classes of compounds are important products of atmospheric oxidation reactions and may be significant components of secondary organic aerosol. Their stability in particles is not well established, however, and previous work by this group has indicated that some classes of these compounds are quite stable with respect to acid-catalyzed hydrolysis, a potential loss process, while others are not. This study extends the previous one by investigating both reaction kinetics and thermodynamics

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for a wider range of product structures and also adds quantum chemical computations. The experiments employ NMR to monitor the kinetics and products of the hydrolysis of a variety of synthesized compounds in sulfuric acid/water, and provide both rate and equilibrium constants for reactions. The results indicate that hydrolysis of organonitrates and organosulfates to alcohols is thermodynamically favored under atmospheric conditions, but that the rates of acid catalyzed hydrolysis are too slow for this to occur on significant timescales, except for tertiary organonitrates. The experiments are well done and when combined with the computations provide a clear picture of the relative importance of kinetics and thermodynamics, and the effects of molecular structure, on the atmospheric stability of these compounds. I think this is an excellent study and that there should be many more of this type, which provide valuable understanding of atmospheric physical-chemical processes and also quantitative kinetic and thermodynamic data that are useful for modeling purposes. The manuscript is well written and should be published in ACP. I have only a few specific comments for the authors to consider.

Specific Comments

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).
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.
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

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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.

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 beta-hydroxy 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 alkyl nitrate? This issue is relevant to questions about oxidative aging, during which the density of functional groups increases.

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?

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?

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.

Technical Comments

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None.

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