

Concerning the research article:

Exploring the chemical fate of the sulfate radical anion by reaction with sulfur dioxide in the gas phase

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Atmos. Chem. Phys. Discuss., 14, 12863–12886, 2014

We thank the referee for the many constructive comments. Here, we present a point-to-point response to all comments. For clarity, the referee comments are reproduced in blue colored text.

On behalf of all authors,



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Replies to Anonymous Referee #1

The paper calculates bond strengths of SO₂ and H₂O to SO₄⁻ species. The calculations seem fine. However, the kinetics discussion is simplistic, outdated, and sometimes conflicting. Some of the more obvious points are

1) R1 is an association reaction. They assume it goes at the collision rate. Most association reactions do not. There are detailed kinetics approaches to that type of reaction. That could only happen if the reaction is in the high pressure limit. No estimate of why they think it is in the high pressure limit is given. Even if in the high pressure limit, sometimes the reaction saturates at the collision rate and sometimes it doesn't. See the work of Troe on how anisotropy affects the limiting behavior.

It is correct that we have made an implicit assumption that reaction R1 is in the high pressure limit since we treat all species as thermally equilibrated. Considering that evaporation rates of the SO₂SO₄⁻(H₂O)_n cluster ion are 2.3×10^6 , 6.1×10^7 and 4.1×10^8 s⁻¹ for n=0,1 and 2, respectively, it is clear that reaction R1 is in the high pressure limit, since typical collision rates in the atmosphere are on the order of one per 100 ps.

We also acknowledge that anisotropy may be an important issue to address when treating sterically hindered collisions/reactions. Related to this matter, in an earlier molecular dynamics simulation of collisions of SO₂ and the O₃⁻(H₂O)₅ ionic cluster, we found an overall sticking probability of ca. 75 % (Bork et al, 2013). For the SO₂ + SO₄⁻(H₂O)_n system, the sticking probability is likely to be even higher (due to the lower number of water molecules). Hence, although the effective collision rate could be slightly overestimated in the original manuscript, considering also the uncertainties on the evaporation rates and reaction rates from the ab initio based thermodynamics, anisotropy seems of minor importance.

These considerations will be clarified in the revised manuscript.

2) No mention of other chemistry is discussed. Whether the steady state of equation 2 holds will depend greatly on that.

Similar to the above considerations, the effect of "other chemistry" depends on the lifetimes of the considered reactions relative to collision rates of the most abundant atmospheric oxidants, e.g. O₃ with a typical concentration of at least 10¹² molecules/cm³ corresponding to a collision rate of ca. 10³ per second.

The slowest evaporation reaction, i.e. unhydrated reaction R2b, has a half-life of just ca. 300 ns, much faster than collisions with typical atmospheric oxidants. The oxygen transfer reactions (R2a) are slower, but still, half-lives of ca. 2500, 315 and 9000 ns are found, much faster than collisions with typical atmospheric oxidants besides O₂.

Also these considerations will be presented in the revised manuscript.

3) All hydrates are sometime lumped into one species and other times they are not.

We agree that all thermal and structural data could be presented for each hydrate separately. However, we argue that such a format does not convey the data in the smoothest and most easy-to-follow way. Lumping hydrates together, whenever logical and appropriate, makes the paper shorter and lighter without omitting information and we therefore choose to retain this format.

4) Reaction 3 is not included in the steady state calculations.

Reaction 3 assesses the stability of $\text{SO}_3\text{SO}_3^-(\text{H}_2\text{O})_n$ towards decomposition to $\text{SO}_3 + \text{SO}_3^-(\text{H}_2\text{O})_n$ and back-reaction to $\text{SO}_2\text{SO}_4^-(\text{H}_2\text{O})_n$ (Reactions R3a and R3b, respectively). Reaction R3a is highly endothermic (with Gibbs free energies 21.4, 17.6, and 15.0 kcal/mol at 298.15 K for $n = 0, 1,$ and $2,$ respectively) and SO_3 dissociation would therefore be negligible.

Reaction R3b has relatively higher energy barriers than the energy barriers in $\text{SO}_2\text{SO}_4^-(\text{H}_2\text{O})_n \rightarrow \text{SO}_3\text{SO}_3^-(\text{H}_2\text{O})_n$, with rate constants of orders of magnitude lower at 298.15 K. The fate of the $\text{SO}_3\text{SO}_3^-(\text{H}_2\text{O})_n$ cluster ion can thus not safely be assumed to be independent of other oxidants and we therefore choose not to include this back-reaction in the steady state calculations. Instead, the fate of the SO_3SO_3^- cluster ion will be targeted in a separate study.

This will be further clarified in the revised manuscript.

5) Barriers of ~10 kcal/mol for isomerization are ok, but prevent SO_3 from dissociating. This is inconsistent.

We thank the reviewer for this comment, since there was an error in reporting the Gibbs free energies of SO_3 evaporation from $\text{SO}_3\text{SO}_3^-(\text{H}_2\text{O})_n$ at 298.15 K. By accident, we reported the energies relative to the separated $\text{SO}_4^-(\text{H}_2\text{O})_n + \text{SO}_2$ and the true values are 21.4, 17.6, and 15.0 kcal/mol for $n = 0, 1,$ and $2,$ respectively. These energies will certainly prevent SO_3 from dissociating. These values will be updated in the revised manuscript.

Reference in this reply

Bork, N., Loukonen, V., and Vehkamäki, H.: Reactions and reaction rate of atmospheric SO_2 and $\text{O}_3^-(\text{H}_2\text{O})_n$ collisions via molecular dynamics simulations, *J. Phys. Chem. A*, 117, 3143 – 3148, [dx.doi.org/10.1021/jp3111103z](https://doi.org/10.1021/jp3111103z), 2013.