

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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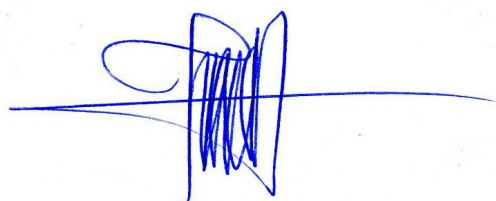
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We appreciate the positive comments and constructive suggestions by the referees. Here, we present a point-to-point response to all comments. For clarity, the referees' comments are reproduced in blue, replies to referees' comments are in black, and the changes made in the manuscript are in red colored text.

On behalf of all authors,



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Replies to A. Nadykto (Referee)

The manuscript is dedicated to the sulfur cycle relevant to the formation of H_2SO_4 , the key atmospheric nucleation precursor in the Earth's atmosphere. The topic is important and relevant directly to the atmospheric physics and chemistry. The paper is nicely written, easy to follow, interesting and probably deserves publication. However, there exist a few issues to be addressed prior to publication.

Specific comments:

1. The authors have mentioned that "PW91 and B3LYP are two of the most popular functionals, but for anionic systems the CAM-B3LYP functional is superior to B3LYP by the inclusion of long-range correction (Yanai et al., 2004)" and choose the CAM-B3LYP as the primary method for the geometry optimization and thermal correction. The authors provide a more detailed explanation of the importance of the "long-range correction" in the case, when strongly bonded ionic clusters are studied, and a clearer justification for the selection of the CAM-B3LYP as the primary computational method. In particular, additional tests/benchmarks of PW91, B3LYP and CAM-B3LYP methods on $\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^-(\text{H}_2\text{O})$ and $\text{SO}_4^- + \text{SO}_2 \rightarrow \text{SO}_4^-(\text{SO}_2)$ reactions (Table 1) should be included in the revised manuscript. Based on the results presented in Table 1 showing clearly that CAM-B3LYP significantly underestimates the reaction free energies, one could probably conclude that PW91, typically predicting stronger bonding, may be a better choice than both B3LYP and CAM-B3LYP.

The main difference between the B3LYP and CAM-B3LYP functionals is the amount of exact Hartree-Fock (HF) exchange included. The B3LYP functional includes a constant amount of 20 % HF exchange (and hence 80 % B88 exchange), whereas amount of HF exchange varies from 19 to 85 % in the CAM-B3LYP functional depending on distance (see e.g. Fig. 2 in Yanai et al. (2004)). In particular, the increased amount of exact HF exchange has been shown to be advantageous when treating anions and Rydberg states since the associated diffuse orbitals are ill described by the pure B88 exchange functional. We agree that further clarification will benefit a revised manuscript.

As suggested by the reviewer, we have conducted additional benchmarking of the PW91 and B3LYP functionals (see the revised Table 1, included in this document). As expected from the above considerations, we find that the B3LYP predictions are further from the experimental values than the CAM-B3LYP predictions and as expected by the reviewer, the performance of the PW91 functional on the $\text{SO}_2 + \text{H}_2\text{O}$ and $\text{SO}_4^- + \text{SO}_2$ binding energies is superior to the CAM-B3LYP functional. However, PW91 also predicts a very low energy barrier of the SO_2SO_4^- to SO_3SO_3^- conversion, just 2.8 kcal/mol above the SO_2SO_4^- ion complex, i.e. submerged by 3.8 kcal/mol compared to the $\text{SO}_2 + \text{SO}_4^-$ reactants. This is much lower than the predictions by CAM-B3LYP and B3LYP. If the PW91 prediction is correct, this suggests immediate conversion of the SO_2SO_4^- cluster ion into the SO_3SO_3^- ion and the experimental reference energy would, in fact, not be of the $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_2\text{SO}_4^-$ reaction, but of the $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^-$ reaction (unknowing to the experimentalists since the experiments are

conducted using mass spectrometry wherein the SO_2SO_4^- and SO_3SO_3^- cluster ions are indistinguishable). However, the latter reaction has a reaction free energy of -9.0 kcal/mol (PW91/aVDZ) clearly suggesting that the experimental value of -6.7 kcal/mol does correspond to $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_2\text{SO}_4^-$ (6.6 kcal/mol at PW91/aVDZ). This is a strong argument that a significant energy barrier does separate the conversion of SO_2SO_4^- to SO_3SO_3^- .

Hence, although the performance of the PW91 functional is superior when it comes to clustering reactions, PW91 seems to underestimate the energy barrier and we therefore choose the CAM-B3LYP functional to avoid overestimating the atmospheric importance of the $\text{SO}_2 + \text{SO}_4^-$ reaction. In the revised manuscript we will, however, stress that the true reaction rates could in fact be significantly higher than the reaction rates based on CAM-B3LYP which therefore are to be considered as lower limits to the true reaction rates.

These considerations and the revised Table 1 will be included in the revised manuscript.

Table 1. Comparison of Gibbs free energy changes at $T = 298.15$ K of the indicated reactions calculated by different DFT functionals, all using the aug-cc-pVDZ (aVDZ) basis set. Energy units are kcal mol⁻¹.

Method	$\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^-(\text{H}_2\text{O})$	$\text{SO}_4^- + \text{SO}_2 \rightarrow \text{SO}_4^-(\text{SO}_2)$	$\text{SO}_4^-(\text{SO}_2) \rightarrow \text{TS}$
PW91	-2.7	-6.6	2.8
B3LYP	-1.5	-4.4	7.8
CAM-B3LYP	-2.4	-5.0	9.3
CCSD(T)/aVDZ*	-3.3	-5.6	10.0
CCSD(T)/aVTZ*	-3.0	-4.2	9.8
VDZ-F12*	-2.8	-3.5	9.5
VTZ-F12*	-2.7	-3.6	-
Experiment**	-5.1	-6.7	-

*Electronic corrections on CAM-B3LYP/aVDZ structures calculated according to Eq. (1) using the indicated coupled cluster methods and basis sets, where VDZ-F12 and VTZ-F12 stand for CCSD(T)-F12/VDZ-F12 and CCSD(T)-F12/VTZ-F12, respectively.

**Fehsenfeld and Ferguson (1974).

This was inserted in line 26, page 12865

“Table 1 shows the changes in binding Gibbs free energy and Gibbs free energy barrier with the chosen methods for three representative reactions. It is seen that the performance of the PW91 functional is superior to that of B3LYP and CAM-B3LYP when it comes to clustering reactions. The low energy barrier (3.8 kcal/mol below the initial reactants) predicted by the PW91 functional implies that the formation of SO_3SO_3^- from $\text{SO}_2 + \text{SO}_4^-$ almost proceeds at collision rate. If this is the case, the experimental Gibbs free energy value -6.7 kcal/mol would correspond to the energy change of $\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^-$ reaction, for which PW91 predicts a Gibbs free energy change of -9.1 kcal/mol, thus overestimating the experiment by 2.4 kcal/mol. It is likely that PW91 is underestimating the energy barrier and to avoid

overestimating the atmospheric importance of the $\text{SO}_2 + \text{SO}_4^-$ reaction, we choose the CAM-B3LYP functional for our calculations.”

Page 12866, last paragraph: first two sentences were removed

This was appended to the second paragraph of the conclusion at page 12874

“Discrepancies within the available ab initio data (Table 1) suggest that the reaction rate constants could, in fact, be significantly higher.”

2. Based on the data shown in Table 1 one can conclude that in most cases the single point CCSD(T) and CCSD(T)-F12 energy corrections do not seem to systematically improve the quality of the DFT results. The authors should briefly comment on this issue.

We agree that this effect is striking and we suggest the following commenting:

“It is well known that entropy and zero point vibrational energy terms based on DFT may be several kcal/mol in error. Here, the sum of these terms by the CAM-B3LYP functional seems about 2.5 to 3 kcal/mol underestimated at $T = 298.15$ K since the most accurate electronic energy corrections leads to underestimating the binding energies by this amount.”

We agree that this effect is striking and we replaced the third sentence, last paragraph of page 12866 by the following:
“It is well known that entropy and zero point vibrational energy terms based on DFT may be several kcal/mol in error. Here, the sum of these terms by the CAM-B3LYP functional seems about 2.5 to 3 kcal/mol underestimated at $T = 298.15$ K since the most accurate of the four electronic energy corrections leads to underestimating the binding energies by this amount.”

3. The hydration range ($n = 0-2$) considered in the present paper does not seem to be wide enough to represent the real atmospheric conditions, at which higher hydrates may exist in significant concentrations. Please, explain your choice and comment on the impact of possible uncertainties related to hydration on conclusions made in the present paper.

It is correct that SO_4^- can bind up to five water molecules under typical atmospheric conditions, but after clustering with SO_2 several of these water molecules will evaporate and at $T = 298.15$ K and 50 % relative humidity, the SO_2SO_4^- cluster ion is most likely to be dehydrated. We therefore argue that the range of hydration is adequate for describing the reaction $\text{SO}_2 + \text{SO}_4^-(\text{H}_2\text{O})_n \rightarrow \text{SO}_3\text{SO}_3^-(\text{H}_2\text{O})_n$. This is discussed in section 3.3 of the article, but to avoid misunderstandings this will be further stressed in the revised manuscript.

This commenting should was inserted in line 22, page 12867 “In this work we limit the hydration range to two since several of the water molecules initially bound to SO_4^- will evaporate after collision with SO_2 , leaving the SO_2SO_4^- cluster ion mostly dehydrated as will be discussed in Section 3.3.”

Technical corrections.

Page 12864, last line, "," should be replaced with ".".

This line seems correct.

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.

Line 13 at page 12869 now reads “where the bimolecular rate constant $k_{\text{ox,bimol}}$ of the SO₂ + SO₄⁻(H₂O)_n reaction is obtained by combining Eqs. (2) and (3) as”.

New sentence was inserted before line 10 at page 12870:

“Finally we obtain evaporation rate constants of 2.3×10^6 , 6.1×10^7 and 4.1×10^8 s⁻¹ for n = 0, 1 and 2, respectively.”

New paragraph was inserted before last paragraph of Section 2 at page 12867:

“Often, anisotropy is an important issue to address when treating sterically hindered collisions. Related to this, our previous molecular dynamics simulation of SO₂ and the O₃⁻(H₂O)₅ ionic cluster showed an overall sticking probability of ca. 75 % (Bork et al, 2013). The sticking probability for the SO₂ + SO₄⁻(H₂O)_n system is likely to be even higher due to the lower number of water molecules. Considering also the uncertainties on the evaporation rates and reaction rates from the ab initio based thermodynamics, anisotropy seems of minor

importance.” In support of this, experimental studies on numerous ion-dipole reactions reported collision-limited reaction rate constants (see e.g., Fehsenfeld and Ferguson, 1974).

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. O_3 with a typical concentration of at least 10^{12} molecules/cm³ corresponding to a collision rate of ca. 10^3 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 O_2 .

Also these considerations will be presented in the revised manuscript.

The following was appended to line 14, page 12870:

“The obtained values of $k_{ox,(R2a)}$ are 2.8×10^5 , 2.2×10^6 , and 7.7×10^4 s⁻¹, corresponding to atmospheric half-lives of 3, 1, and 9 μ s for de-, mono- and di-hydrated systems respectively. These values, in addition to those obtained for reaction (R2b), indicate that $SO_2SO_4^-(H_2O)_n$ would react well before any collision with the most abundant atmospheric oxidants.”

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 $SO_3SO_3^-(H_2O)_n$ towards decomposition to $SO_3 + SO_3^-(H_2O)_n$ and back-reaction to $SO_2SO_4^-(H_2O)_n$ (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 $n = 0, 1, \text{ and } 2$, respectively) and SO_3 dissociation would therefore be negligible.

Reaction R3b has relatively higher energy barriers than the energy barriers in $SO_2SO_4^-(H_2O)_n \rightarrow SO_3SO_3^-(H_2O)_n$, with rate constants of orders of magnitude lower at 298.15 K. The fate of the $SO_3SO_3^-(H_2O)_n$ 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.

Section 3.2, last paragraph was replaced by the following:

Reaction (R3b) has energy barriers of 14.0, 12.4, and 13.4 kcal/mol for $n = 0, 1,$ and $2,$ respectively. The rate constants of this reaction at 298.15 K are $3.9 \times 10^2,$ $4.8 \times 10^3,$ and 8.9×10^2 $\text{s}^{-1},$ corresponding to halflives of 1760, 145, and 782 μs for $n = 0, 1,$ and $2,$ respectively. These lifetimes are comparable to collision rates between SO_3SO_3^- and $\text{O}_3.$ It is therefore likely that SO_3SO_3^- will react with $\text{O}_3,$ e.g. forming $\text{SO}_4^-,$ $\text{SO}_3,$ and $\text{O}_2,$ irreversibly preventing Reaction (R3). We therefore consider the SO_3SO_3^- cluster ion as a terminal sink for the $\text{SO}_2 + \text{SO}_4^-$ collision.

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.

The values 11.9, 10.4, and 9.8 kcal/mol at line 7, page 12871 were changed to 21.4, 17.6, and 15.0 kcal/mol

Reference in this reply

Yanai, T., Tew, D. P., and Handy, N. C.: A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP), Chem. Phys. Lett., 393, 51–57, 2004.

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/jp311103z, 2013.