Atmospheric
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Discussions

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Interactive comment on "A potential source of atmospheric sulfate from O_2^--induced SO_2 oxidation by ozone" *by* Narcisse Tchinda Tsona and Lin Du

Anonymous Referee #1

Received and published: 28 November 2018

Tsona and Du have studied the reaction of O3 with O2SO2- using computational methods. This extends and complements a series of similar studies performed by the authors and their co-workers, aimed toward understanding the ionic contribution to sulfur chemistry in the atmosphere. The computational methods are broadly appropriate to the task (see below for two minor caveats on this), and the results are interesting for atmospheric chemists despite the studied SO2 oxidation pathway ultimately being rather minor compared to neutral channels. Overall, the text is understandable, though there are a large number of odd word choices and formulations - some proofreading or copyediting would improve the manuscript. I recommend the manuscript be published in ACP subject so some minor revisions.

Comments:

-Page 2, Line 5-7: The authors list different oxidation routes for SO2 in the atmosphere: OH, sCIs, ions and mineral dust. The first three are gas-phase processes, the latter I assume corresponds to heterogeneous SO2 oxidation. However, there are many more heterogeneous pathways for SO2 oxidation, many of which are likely even more important than mineral dust, such as aqueous-phase oxidation inside cloud droplets. These could thus be mentioned.

-Page 2, Line 11: The role of ions in aerosol formation has indeed been well established, and that role is in most conditions essentially "real but small". I.e. ionic pathways make a non-negligible contribution to aerosols, but in most atmospheric conditions the neutral pathways still dominate. This could be mentioned.

-Page 3, Line 19: for sulfur-containing compounds, would it not be better/safer to use the aug-cc-pV(T+d)Z basis set instead of aug-cc-pVTZ? This should provide additional accuracy (especially for bond formation and bond breaking involving sulfur) at relatively small computational cost. (I'm not suggesting the authors redo all their calculations, this is just a suggestion for future studies).

-Page 3, line 29: Most of the systems treated here were radicals, I assume with a spin multiplicity of 2. Did the authors use UM06-2X or ROM06-2X? (I assume the former, if so this could be stated, and also spin contamination values could be briefly discussed). Similarly, did the authors do UHF-UCCSD(T) or ROHF-ROCCSD(T)? Both can be done with Gaussian 09.

-Page 4, line 28 (also Page 6, line 1): the second reactions studied is not "barrierless" as such, there is a TS but it is far below the reactants. The proper term in this case would be a "submerged barrier". (The existence of a TS is also assumed by the use of equation 5). Note: the overall kinetic treatment seems fine, this is just an issue of terminology.

-Page 7, line 10: Please give some details about the "charge analysis" that was performed to determine that the oxygen molecules are formed in the singlet state. Also, could this not simply be an artefact of the computational method used? I assume the overall spin multiplicity is set to "2" - it would be very difficult to find structures corresponding to a radical plus a triplet oxygen (or two triplet oxygens!) in a DFT calculation on the doublet surface. . . Or in other words, the channels leading to the singlet oxygen molecules found by the authors are probably real, but there might also be channels (not discoverable with single-reference methods) leading to triplet oxygen. However as already the channels going to singlet oxygen are thermodynamically allowed, and kinetically fast, then this would not affect the conclusions. But the possibility could be stated. Also, please state clearly if BOTH of the formed O_2 molecules are expected to be in the singlet state.

-Page 7, line 23: It could be mentioned earlier on in the manuscript that the bonds between the SO_2 and O_2 moieties in "O_2SOO^-" are also co-ordination bonds, not proper covalent bonds. This makes it easier to understand how the conversion of $O_3...O_2SOO^-$ to $O_2...O_2S$-O_3^- can be barrierless (breaking a covalent bond would usually be associated with a barrier).

-Page 8, line 4: how can TSW2 be located below RCW2 that it connects to? Is this some entropy effect (i.e. the TS is higher in energy but lower in free energy)? Please explain.

-Page 8, line 9. A unimolecular rate of $6.5 \times 1E15$ 1/s is unphysical, as it is faster than the typical frequency of molecular vibrations. This indicates that the used form of TST is not really applicable to this reaction where the TS is below the reactant (see above for a question on that). The conclusion that the reaction is extremely fast and likely occurs before any collisions with N_2 is valid, it's just the numerical value that doesn't make sense.

-Page 11 line 1: Why do the authors assume that OH and NOx are the main terminating

scavengers? Some other radicals, not to mention atmospheric acids, can easily have larger concentrations, and could thus increase the denominator of Eq 10.

-Page 11, line 9: Is it a good assumption that $[O_3] \gg [SO_2]$? The authors perform their calculations with $[SO_2]$ set to 5 ppb - $[O_3]$ certainly exceeds this in polluted areas, but not by many orders of magnitude, and in cleaner areas $[O_3]$ may not be much greater than this. . .

-Figure 2: I don't understand how RC1 can exist as a distinct minimum (stationary point) if there is no TS between it and P1. Or is this an energy/free energy issue, with RC1 below P1 in energy but above it in free energy? This should be discussed/mentioned - perhaps the potential energy surface could be shown also in terms of electronic energy, not just Gibbs free energy.