

We thank the Referees for their constructive comments on our manuscript. Below are our point-to-point replies to the different questions raised by the Referees. For clarity, the Referees' comments are reproduced in blue color text and modified/inserted text in the revised manuscript are in red color text.

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 copy-editing 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.

Authors' reply

We sincerely thank the Referee for this reminder. The multiphase oxidation of SO₂ is an important path for sulfuric acid formation in the atmosphere and thus, this has been updated in the revised manuscript

The sentence at Page 2, Lines 3-5 has been modified as:

“Sulfur dioxide (SO₂), the most abundant sulfur-containing molecule in the atmosphere, is known to react both in the gas-phase and in multiphase oxidation processes following different mechanisms to form sulfate as the final oxidation species.”

The following sentence has been inserted at Page 2, Lines 8-10:

“The main routes for SO₂ heterogeneous/multiphase oxidation include reactions with mineral dust (Harris et al., 2013), O₃ and H₂O₂ in cloud droplets (Caffrey et al., 2001; Hoyle et al., 2016; Harris et al., 2012; Hegg et al., 1996), NO₂ and O₂ in aerosol water and on CaCO₃ particles (Cheng et al., 2016; Wang et al., 2016; Zhang et al., 2018; Yu et al., 2018; Zhao et al., 2018).”

Referee's comment:

-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.

Authors' reply

It has been indeed demonstrated by previous studies that the contribution of ions in atmospheric particle formation is relatively small. To update this information in the revised manuscript, the text at Page 2, Lines 13-18 has been modified as follows:

“Sulfate is known to be the main driving species in atmospheric aerosols formation and its formation is critical in the determination of aerosol formation rates (Nieminen et al., 2009; Sipila et al., 2010; Kuang et al., 2008; Kulmala et al., 2000). The role of ions in this formation has been well established (Yu, 2006; Yu and Turco, 2000, 2001; Enghoff and Svensmark, 2008; Kirkby et al., 2011; Wagner et al., 2017; Yan et al., 2018), although relatively minor compared to the mechanism involving neutral particles, exclusively (Eisele et al., 2006; Manninen et al., 2010; Kirkby et al., 2011; Hirsikko et al., 2011; Wagner et al., 2017)”

Referee's comment:

-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).

Authors' reply

The treatment of the extra charge in anionic species is a known challenge to density functional theory in general. Extra electrons of anions are known to occupy diffuse, long ranging orbitals and, therefore, require special density functionals and basis sets for their accurate treatment. While for sulfur-containing species it is recommended when using the Dunning type basis sets to include extra *d* functions for the sulfur atom, Bork et al. recently showed that this is not desirable, for example, in predicting electron affinities, and they used the aug-cc-pVTZ basis set to study a reaction involving an electron transfer process (Bork et al., 2013). Using the CAM-B3LYP functional, they found that the aug-cc-pVTZ basis set gives a much better agreement with experiment than aug-cc-pV(T+d)Z, when calculating the difference between the electron affinities of O₃ and SO₃ (Bork et al., 2013). It should, however, be noted that the type of density functional used might also play a non-negligible role. Since our calculations involve similar species than in the above-mentioned study and also induce electron transfer, we used the aug-cc-pVTZ in our study.

Referee's comment:

-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.

Authors' reply

We used a spin multiplicity of 2 and hence the UM06-2X variant of the M06-2X density

functional and the UCCSD(T) variant of CCSD(T) were used in our calculations. This has been updated in the revised manuscript.

It is well-known that the use of UM06-2X as other unrestricted density functionals gives rise to spin contamination in the studied system. The spin contamination of all states was evaluated and found to be negligible for the electronic states in reaction (R2) while being important for the states in reaction (R3). The latter is likely due to O₂ formation in the pre-reactive complexes, transition states and products. In reaction (R3), the spin contamination is lowest in the pre-reactive complexes and highest in the products, as a result of O₂ formation with different multiplicities. We added the following in the revised manuscript to account for spin contamination.

Page 3, Lines 27-32

“The use of UM06-2X implies using unrestricted wavefunctions to describe the quantum state of the system. Spin contamination often arises from unrestricted density functional theory (DFT) calculations and it is not guaranteed that the electronic states from these calculations are eigenstates of the \hat{S}^2 operator. The spin contamination was then evaluated for all electronic states as $\Delta S = \langle \hat{S}^2 \rangle - \langle \hat{S}^2 \rangle_{\text{ideal}}$, where $\langle \hat{S}^2 \rangle$ is the actual value of the expectation value of the \hat{S}^2 operator from DFT calculations and $\langle \hat{S}^2 \rangle_{\text{ideal}}$ is the ideal expectation value. For systems explored in this study, $\langle \hat{S}^2 \rangle_{\text{ideal}} = 0.75$.”

Page 6, Line 30

“The spin contaminations for RC1 and RCW1 are negligible, being 0.0086 and 0.0081, respectively.”

Page 9, Lines 27-32

“The spin contamination for electronic states in reaction (R3) is quite significant, being 1.0122, 1.4666, and 2.0374 for the pre-reactive complex, transition state and product, respectively, and is almost insensitive to the presence of water. The actual values of the expectation values of the \hat{S}^2 operator for all electronic states obtained from our calculations are given in the Supplement, along with their cartesian coordinates. The high values of spin contamination likely reflect the formation of O₂ with different multiplicities within the system. As the charge analysis indicates, starting with singlet O₂ in the pre-reactive complexes of reaction (R3), both singlet and triplet O₂ are formed in the final products.”

Referee's comment:

-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.

Authors' reply

The word “barrierless” at Page 4 and Page 6 has been changed to “submerged barrier” and “low-lying” and the new sentences in the revised manuscript now read as:

Page 5, Line 17

“This consideration is, however, not valid for reactions with submerged barrier, since the pre-

reactive intermediate seldom thermally equilibrates.”

Page 6, Line 22

“The second process is the low-lying formation of a molecular complex in which the SO₂ entity of O₂SOO⁻⋯(H₂O)₀₋₁ is oxidized to SO₃⁻.”

Referee's comment:

-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 O₂ molecules are expected to be in the singlet state.

Authors' reply

The electronic charge analysis, according to the Bader charge partitioning, is an intuitive way of dividing molecules into atoms, which are purely defined based on electronic charge density (Bader, 1998). This approach assumes that the charge density in molecular systems reaches a minimum between atoms, and this minimum density is a natural place to separate atoms from each other (Bader, 1998; Henkelman et al., 2006). The calculations performed by this method produce different output files among which, a file that can be visualized and a file containing the electronic charge associated to each atom according to the Bader partitioning. In our calculations, these files allow to see how the extra electron (charge) is distributed over the atoms of the system. Due to the possibility of the O₂ molecule to form both in its singlet and triplet states, the Bader charge partitioning can equally indicate the presence of free electrons, especially in the case of the triplet.

For Reaction (R3), the files that can be visualized were plotted for the unhydrated system and given in **Fig. 3** in the main manuscript, wherefrom the electron cloud on atoms can be seen. Examining the files containing the electronic charge associated to each atom, it is seen that the electronic charge on the pre-reactive complex is essentially on two oxygen atoms of the O₃ moiety that is coordinated to SO₂. The net charge on these atoms is 1.04e, whereas the net charge on the free O₂ molecule is 0.01e. The latter value shows that the O₂ molecule released in the optimization of the pre-reactive complex (**Fig. 3(a)**) has no unpaired electrons, indicating that this O₂ molecule is in its singlet state.

In the transition state structure (**Fig. 3(b)**), the charge is still on the O₃ moiety, although mostly located on the oxygen atom bound to sulfur. The net charge on the two outer oxygen atoms of O₃ that will form the O₂ molecule in the product state has substantially decreased to 0.30e while the charge on the free O₂ molecule has slightly increased to 0.04e. The free O₂ molecule can

still be considered to be in the singlet state. The strong decrease in the charge of the two outer oxygen atoms of O₃ from the pre-reactive complex to the transition state suggests that the O₂ molecule to form in the product will likely be a singlet.

In the products (**Fig. 3(c)**), the old free O₂ molecule has a net charge of 1.99e, whereas the charge on the newly formed O₂ is 0.06e. The 1.99e charge on the old free O₂ molecule indicates the presence of two unpaired electrons in its configuration, meaning that the singlet O₂ has been transformed into triplet. This clearly shows that a spin flip has occurred in O₂ during further optimization of the products. The newly formed O₂ with 0.06e charge is obviously a singlet.

This analysis shows for the unhydrated system that the singlet O₂ initially formed in the pre-reactive complex transforms into triplet in the products state, while a new singlet O₂ is also formed. In the monohydrated system, the singlet O₂ initially formed in the pre-reactive complex remains as singlet and a triplet O₂ is also released in the products state.

Overall, the two forms of O₂ (singlet and triplet) are formed in the studied reaction, despite following different mechanisms. Although the water molecule in the monohydrated system does not retain any electric charge, it is most likely that it stabilizes the initially formed singlet O₂ and prevents the spin flip.

In addition to updating the energy values of the product of reaction (R3) in the text, in **Fig.2** and in **Table 1**, the following texts were inserted in the revised manuscript for clarification:

Page 4, Lines 24-27

“This is an intuitive way of dividing the molecules of a system into atoms, which are purely defined in terms of electronic charge density. The Bader charge partitioning assumes that the charge density between atoms of a molecular system reaches a minimum, which is an ideal place to separate atoms from each other.”

Page 8, Lines 4-21

“The charge analysis on this system indicates that the electronic charge on the pre-reactive complex is essentially on two oxygen atoms of the O₃ moiety that is coordinated to SO₂ as can be seen in Fig. 3(a). The net charge on these two oxygen atoms is 1.04e, whereas the net charge on the free O₂ molecule is 0.01e. The latter value shows that the O₂ molecule formed in the pre-reactive complex has no unpaired electrons, and hence is a singlet. Although the charge is still on the O₃ moiety in the transition state configuration, it is mostly located on the oxygen atom bound to sulfur (**Fig. 3(b)**). The net charge on the two outer oxygen atoms of the O₃ moiety in the transition state has substantially decreased to 0.30e while the charge on the free O₂ molecule has slightly increased to 0.04e. The strong decrease in the charge of the two outer oxygen atoms of O₃ from the pre-reactive complex to the transition state suggests that the O₂ molecule to form in the product will likely be a singlet. In the products (**Fig. 3(c)**), the old free O₂ molecule has a net charge of 1.99e, whereas the charge on the newly formed O₂ is 0.06e. The 1.99e charge on the old free O₂ molecule indicates the presence of unpaired electrons in

its configuration, meaning that the singlet O₂ has been transformed into triplet. This clearly shows that a spin flip has occurred in O₂ during further optimization of the products. The newly formed O₂ with 0.06e charge is obviously a singlet. This analysis shows for the unhydrated system that the singlet O₂ initially formed in the pre-reactive complex transforms into triplet in the products state, while a new singlet O₂ is also formed. In the monohydrated system, the singlet O₂ initially formed in the pre-reactive complex remains as singlet in the products state and a triplet O₂ is also released. Overall, the two forms of O₂ (singlet and triplet) are formed in the studied reaction, despite following different mechanisms. Although the water molecule in the monohydrated system does not retain any electric charge, it most likely stabilizes the initially formed singlet O₂ and prevents the spin flip.”

Referee's comment:

-Page 7, line 23: It could be mentioned earlier on in the manuscript that the bonds between the SO₂ and O₂ moieties in “O₂SOO-“ are also co-ordination bonds, not proper covalent bonds. This makes it easier to understand how the conversion of O₃...O₂SOO- to O₂...O₂S-O₃- can be barrierless (breaking a covalent bond would usually be associated with a barrier).

Authors' reply

Indeed, the O₂S-OO⁻ bond is a coordination bond rather than covalent and this has been clarified in the revised manuscript by re-writing the sentence at Page 2, Lines 30-32 as:

“A previous study demonstrated that two forms of SO₄⁻ separated by a high energy barrier may exist in the atmosphere (Tsona et al., 2014): the sulfate radical ion henceforth indicated as SO₄⁻, and the peroxy form, O₂SOO⁻, in which the O₂S-OO⁻ bond nature is more dative than covalent.”

Referee's comment:

-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.

Authors' reply

According to our calculations, the density functional theory (DFT) calculations based on the UM062X/aug-cc-pVTZ method predict the TSW2 configuration to be located ~9 kcal mol⁻¹ electronic energy above RCW2. However, upon correction by the UCCSD(T)/aug-cc-pVTZ method the energy of the transition state considerably drops to 3 kcal mol⁻¹ below that of the RCW2. As an uncommon fact for atmospheric reactions and since this could not be assigned to entropic effects, we first speculated that wrong structures for RCW2 and TSW2 would have been optimized. We then repeated the calculations twice and found that the results were similar to the previous case. For each trial, although the UM062X/aug-cc-pVTZ calculations gave TSW2 located above RCW2, the UCCSD(T)/aug-cc-pVTZ correction reversed the situation. Most likely, the low-lying TSW2 is due the correlation effect on the electronic energy since without UCCSD(T) correction, TSW2 lies above RCW2. This can further be explained by the difference in the electronic configurations of the two outer oxygen atoms of the O₃ moiety in the TS2 and TSW2 transition states, as clarified in our reply to a comment above. Further clarification is given in the manuscript at Page 9, Line 16-18 as:

“Another reason for this substantial drop in energy barrier is the difference in the electronic

configurations of the two outer oxygen atoms of the O₃ moiety in the two transition states that form O₂ with different multiplicities in the products.”

Referee's comment:

-Page 8, line 9. A unimolecular rate of $6.5 \times 10^{15} \text{ s}^{-1}$ 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 N₂ is valid, it's just the numerical value that doesn't make sense.

Authors' reply

With the negative energy barrier of reaction (R3) in the presence of water, the overall rate constant is essentially collision limited as indicated by the reported value of $8.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As explained in the manuscript, the outer transition state provides the dominant bottleneck to the rate constant of reaction (R3) in the presence of water, which can then be calculated directly by eq. (4). To avoid using unphysical number, the unimolecular rate constant value of $6.5 \times 10^{15} \text{ s}^{-1}$ is deleted in the revised manuscript and the sentence at page 9, Lines 20-23 is revised as:

“Based on the TS2 energy, the unimolecular decomposition of O₂···O₂S–O₃⁻ at 298 K in the absence of water was found to occur at a rate constant of $3.1 \times 10^5 \text{ s}^{-1}$, corresponding to an atmospheric lifetime of 3.3 μs. Both this short lifetime and the negative energy barrier of the monohydrated reaction indicate that O₂···O₂S–O₃⁻ would not live long enough to experience collisions with other atmospheric oxidants.”

Referee's comment:

-Page 11 line 1: Why do the authors assume that OH and NO_x 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.

Authors' reply

Though we initially focused on OH and NO_x as scavengers that may form well-known stable HSO₄⁻ and NO₃⁻ species, it is reasonable that other species like HO₂ and organic acids which have relatively high concentrations may be good scavengers as well. They may form HSO₄⁻ and CO₃⁻ to scavenge the free electron. Noting that organic acids are mainly dominated by formic and acetic acid in the atmosphere, their concentrations are considered in Eq. (9) as representative examples of organic acids. Taking into account $10^8 \text{ molecule cm}^{-3}$ concentration for HO₂ (Holland et al., 2003; Dusanter et al., 2009) and $110 \text{ ppt} = 2.4 \times 10^9 \text{ molecule cm}^{-3}$ for organic acids (formic acid and acetic acid) (Le Breton et al., 2012; Baasandorj et al., 2015) in Eq. (9), the contribution of ion-induced SO₂ oxidation to H₂SO₄ formation is in the 0.1-2.0% range depending on the altitude. This has been updated in the revised manuscript.

The sentence at Page 12, Line 14 was modified as:

“The main ones are likely NO_x, OH, HO₂ and organic acids, which lead to the formation of the stable NO₃⁻, HSO₄⁻, and CO₃⁻ species.”

The text at Page 12, Line 33 to Page 13, Lines 1-5 was modified as:

“We assume nearly pristine conditions with $[\text{SO}_2] = 5 \text{ ppb} = 1.2 \times 10^{11} \text{ molecule cm}^{-3}$, $[\text{NO}_x] = 200 \text{ ppt} = 4.9 \times 10^9 \text{ molecule cm}^{-3}$, $[\text{OH}] = 5.0 \times 10^5 \text{ molecule cm}^{-3}$ (day and night average), and $[\text{HO}_2] = 10^8 \text{ molecule cm}^{-3}$ (Dusanter et al., 2009; Holland et al., 2003). Noting that formic acid and acetic acid are the most abundant organic acids in the atmosphere, their concentrations are considered in Eq. (9) as representative examples for organic acids, $[\text{organic acids}] = 110 \text{ ppt} = 2.7 \times 10^9 \text{ molecule cm}^{-3}$ (Le Breton et al., 2012; Baasandorj et al., 2015). We then determine J_{ion} in the range $3.2 \times 10^1 - 1.6 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$.”

The sentence at Page 13, Line 14 was modified as:

“We find that the contribution of ion-induced SO_2 oxidation to H_2SO_4 formation can range from 0.1 to 2.0% of the total formation rate.”

Equation (9) has been modified to

$$\text{TON} \approx \frac{[\text{SO}_2]}{[\text{OH}] + [\text{HO}_2] + [\text{NO}_x] + [\text{organic acids}]} \quad (9)$$

Referee's comment:

-Page 11, line 9: Is it a good assumption that $[\text{O}_3] \gg [\text{SO}_2]$? The authors perform their calculations with $[\text{SO}_2]$ set to 5 ppb - $[\text{O}_3]$ certainly exceeds this in polluted areas, but not by many orders of magnitude, and in cleaner areas $[\text{O}_3]$ may not be much greater than this...

Authors' reply

Although the $[\text{O}_3] \gg [\text{SO}_2]$ assumption might be somewhat overestimated, the fact remains that $[\text{O}_3] > [\text{SO}_2]$ as indicated also by the referee. This condition reinforces the condition that SO_2 should be the limiting factor in the reaction process, which was our original idea. Hence, to remove the confusion concerning the O_3 concentration relative to that of SO_2 , we simply changed $[\text{O}_3] \gg [\text{SO}_2]$ to $[\text{O}_3] > [\text{SO}_2]$ in the revised manuscript and re-wrote the sentence at Page 12, Lines 22-23 as:

“The concentration of the catalyst can be approximated to the concentration of the scavengers and, considering that at most atmospheric conditions $[\text{O}_3] > [\text{SO}_2]$, SO_2 is the limiting species in reaction (R4).”

Referee's comment:

-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.

Authors' reply

Reaction (R2) involves a charge transfer, followed by cluster decomposition. The immediate outcome of $\text{O}_2\text{SOO}^- + \text{O}_3$ optimization is RC1, formed with -5.1 and 4.5 kcal mol⁻¹ electronic and Gibbs free energy, respectively. While the electronic energy, which defines the best

possible arrangement of the electrons in the system, shows that the formation of RC1 is possible at 0 K, the positive Gibbs free energy at 1 atm and 298 K indicates that this complex is not stable under these atmospheric conditions and will surely decompose or react further upon formation. The RC1 formation represents the lowest state at which O_2SOO^- can interact with O_3 to allow electron transfer and O_2S-OO decomposition. The energy of this state then corresponds to the energy barrier to form the $O_2 + SO_2 + O_3^-$. For more clarification, the following texts were added in the revised manuscript

The sentence at Page 6, Line 31 to Page 7, Lines 1-3 was modified as:

“The electronic energies of formation of RC1 and RCW1 are -5.1 and -4.6 kcal mol⁻¹, respectively. Despite these complexes may form at 0 K, the Gibbs free energies of their formation under atmospheric pressure and 298 K (4.5 and 4.7 kcal mol⁻¹, respectively) indicate that their formation is endergonic under atmospherically relevant conditions.”

The following was inserted at Page 7, Lines 4-6:

“Hence, the Gibbs free energies of formation of RC1 and RCW1 define the lowest states at which O_2SOO^- can interact with O_3 to allow electron transfer and O_2S-OO decomposition, and thus represent the energy barrier towards $O_2 + SO_2 + O_3^-$ formation.”

References

Baasandorj, M., Millet, D. B., Hu, L., Mitroo, D., and Williams, B. J.: Measuring acetic and formic acid by proton-transfer-reaction mass spectrometry: sensitivity, humidity dependence, and quantifying interferences, *Atmos. Meas. Tech.*, 8, 1303-1321, doi:10.5194/amt-8-1303-2015, 2015.

Bader, R. F. W.: A Bond Path: A Universal Indicator of Bonded Interactions, *J. Phys. Chem. A*, 102, 7314-7323, doi:10.1021/jp981794v, 1998.

Bork, N., Kurtén, T., and Vehkamäki, H.: Exploring the atmospheric chemistry of $O_2SO_3^-$ and assessing the maximum turnover number of ion-catalysed H_2SO_4 formation, *Atmos. Chem. Phys.*, 13, 3695-3703, doi:10.5194/acp-13-3695-2013, 2013.

Dusanter, S., Vimal, D., Stevens, P. S., Volkamer, R., Molina, L. T., Baker, A., Meinardi, S., Blake, D., Sheehy, P., Merten, A., Zhang, R., Zheng, J., Fortner, E. C., Junkermann, W., Dubey, M., Rahn, T., Eichinger, B., Lewandowski, P., Prueger, J., and Holder, H.: Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign - Part 2: Model comparison and radical budget, *Atmos. Chem. Phys.*, 9, 6655-6675, doi:10.5194/acp-9-6655-2009, 2009.

Henkelman, G., Arnaldsson, A., and Jónsson, H.: A fast and robust algorithm for Bader decomposition of charge density, *Comput. Mater. Sci.*, 36, 354-360, doi:10.1016/j.commatsci.2005.04.010, 2006.

Holland, F., Hofzumahaus, A., Schafer, R., Kraus, A., and Patz, H. W.: Measurements of OH and HO₂ radical concentrations and photolysis frequencies during BERLIOZ, *J. Geophys.*

Res.-Atmos., 108, D4, 8246, doi:10.1029/2001jd001393, 2003.

Le Breton, M., McGillen, M. R., Muller, J. B. A., Bacak, A., Shallcross, D. E., Xiao, P., Huey, L. G., Tanner, D., Coe, H., and Percival, C. J.: Airborne observations of formic acid using a chemical ionization mass spectrometer, *Atmos. Meas. Tech.*, 5, 3029-3039, doi:10.5194/amt-5-3029-2012, 2012.

Anonymous Referee #2

Received and published: 28 November 2018

Authors are Narcisse Tchinda Tsona and Lin Du

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

Comments: The authors have theoretically studied the role of the superoxides such as O₂⁻ in SO₂ oxidation. The simulations were performed using a combination of DFT and CC levels of theory (CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ). Calculations were performed in the gas phase with and without one water molecule. Two possible mechanisms for the titled reaction were suggested and considered.

It is well known, that sulfur oxidation products play an important role in the atmosphere: formation of secondary aerosols, clouds and acid rains. Therefore, this theoretical work is an important contribution to a better understanding of the total mechanism of atmospheric sulfuric acid formation. I recommend publication this paper in the Atmospheric Chemistry and Physics Discussions after minor revisions.

Referee's comment:

Page 1, line 18. Misspelling the word "modelling". It does not need double LL.

Authors' reply

This has been corrected.

Referee's comment:

Page 3, line 9. Does not need a dot in the middle of sentences "with O₃. in"

Authors' reply

This has been corrected.

Referee's comment:

Page 6, line 10. Delete the empty space between "4. 5"

Authors' reply

This has been corrected.

Referee's comment:

Page 12, line 16. Need to add a negative charge to the formula O₂SOO.

Authors' reply

This has been corrected.

Referee's comment:

1) In the Methods section, please, mention what multiplicity and charge did you use for the calculations of considered systems.

Authors' reply

The sentence at Page 3, Line 25-27 was re-written as:

“As the substrate in this study is a radical anion, all stationary points in the energy surface were optimized using density functional theory (DFT) based on the UM06-2X density functional (Zhao and Truhlar, 2008) and the aug-cc-pVTZ basis set (Dunning Jr et al., 2001), setting the charge to -1 and the spin multiplicity to 2.”

Referee's comment:

2) Did you perform IRC (intrinsic reaction coordinate) analysis, to prove that all your saddle points from the same PES (Pre-reactive complex – TS – Products)? If not, you should do it.

Authors' reply

The IRC analysis was performed as indicated at Page 3, Line 4, they indeed connected the transition states to the pre-reactive complexes and the products.

Referee's comment:

3) Do you think that just one water molecule is it a sufficient model to simulate liquid phase? Authors can additionally apply PCM models to the monohydrated system. Probably, in this case, the reaction will run spontaneously, without pre-reactive complex and TS (now, authors have a situation where in the case monohydrated system the energy of TSW2 is lower than the energy of the pre-reactive complex RCW2).

Authors' reply

The reaction was performed in the gas-phase, exclusively. In the gas-phase, it was shown that only one water molecule can attach to O₂SOO⁻ and we also verified from our calculations that the addition of a second water vapor molecule to RC2 is not favorable under atmospheric conditions. It is, however, possible that O₂SOO⁻ would bind several water molecules in the liquid phase and the reaction properties would then be greatly affected.

The energy of TSW2 being lower than the energy of RCW2 is likely the effect of correlation since without CCSD(T) correction, TSW2 lies above RCW2. This difference in energy can also be explained by the difference in the electronic configurations of the two outer oxygen atoms of the O₃ moiety in the two transition states.

This information has been updated in the revised manuscript at Page 9, Lines 16-18 as:

“Another reason for this substantial drop in energy barrier is the difference in the electronic configurations of the two outer oxygen atoms of the O₃ moiety in the two transition states that form O₂ with different multiplicities in the products.”

Referee's comment:

4) Please, add [Units] to the mentioned constants in Eq. 4 and 5 (for q, h, ε₀ etc.)

Authors' reply

The units used in Eq. (4) are CGS units, whereas SI units are used in Eq. (5).

Constants and variables	CGS units	SI units
T	K	K
k_B	1.38×10^{-16} erg K ⁻¹	1.38×10^{-23} J K ⁻¹
h	6.63×10^{-27} erg s	6.63×10^{-34} J s
q	4.80×10^{-10} statC	1.60×10^{-19} C
ϵ_0	$1/(4\pi)$	8.85×10^{-12} F m ⁻¹
μ	g	kg
α	cm ³	F m ²
α_D	StatC cm	C.m

The following related sentences were added in the manuscript.

Page 6, Lines 13-15:

“The constants and variables in Eq. (4) and Eq. (5) are given in centimetre-gram-second (CGS) system of units and International System (SI) units, respectively. Details on these units are given in the Supplement.”

A potential source of atmospheric sulfate from O_2^- -induced SO_2 oxidation by ozone

Narcisse Tchinda Tsona and Lin Du

Environment Research Institute, Shandong University, Binhai Road 72, 266237 Shandong, China

5 *Correspondence to:* Lin Du (lindu@sdu.edu.cn)

Abstract. It was formerly demonstrated that O_2SOO^- forms at collisions rate in the gas-phase as a result of SO_2 reaction with O_2^- . Hereby, we present a theoretical investigation of the chemical fate of O_2SOO^- by reaction with O_3 in the gas-phase, based on *ab initio* calculations. Two main mechanisms were found for the title reaction, with fundamentally different products: (i) formation of a van der Waals complex followed by electron transfer and further decomposition to $O_2 + SO_2 + O_3^-$ and (ii) formation of a molecular complex from O_2 switching by O_3 , followed by SO_2 oxidation to SO_3^- within the complex. Both reactions are exergonic, but separated by relatively low energy barriers. The products in the former mechanism would likely initiate other SO_2 oxidations as shown in previous studies, whereas the latter mechanism closes a path wherein SO_2 is oxidized to SO_3^- . The latter reaction is atmospherically relevant since it forms the SO_3^- ion, hereby closing the SO_2 oxidation path initiated by O_2^- . The main atmospheric fate of SO_3^- is nothing but sulfate formation. Exploration of the reactions kinetics indicates that the path of reaction (ii) is highly facilitated by humidity. For this path, we found an overall rate constant of $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 50% relative humidity. The title reaction provides a new mechanism for sulfate formation from ion-induced SO_2 oxidation in the gas-phase and highlights the importance of including such mechanism in modeling sulfate-based aerosol formation rates.

1 Introduction

The chemistry of sulfur is highly important in the atmosphere. Through its oxidation products, sulfur participates in the formation of secondary atmospheric aerosols, clouds and acid rain. **Sulfur dioxide (SO₂), the most abundant sulfur-containing molecule in the atmosphere, is known to react both in the gas-phase and in multiphase oxidation processes following different mechanisms to form sulfate as the final oxidation species.** The main SO₂ oxidizers in the gas-phase include the hydroxyl radical (OH) (Seinfeld and Pandis, 2016), stabilized Criegee intermediates (Welz et al., 2012; Mauldin III et al., 2012; Vereecken et al., 2012) and atmospheric ions (Fehsenfeld and Ferguson, 1974; Enghoff et al., 2012; Tsona et al., 2015). **The main routes for SO₂ heterogeneous/multiphase oxidation include reactions with mineral dust (Harris et al., 2013), O₃ and H₂O₂ in cloud droplets (Caffrey et al., 2001; Hoyle et al., 2016; Harris et al., 2012; Hegg et al., 1996), NO₂ and O₂ in aerosol water and on CaCO₃ particles (Cheng et al., 2016; Wang et al., 2016; Zhang et al., 2018; Yu et al., 2018; Zhao et al., 2018).** In the gas-phase, the SO₂ oxidation by OH and Criegee intermediates leads to SO₃ that ultimately forms H₂SO₄ (Larson et al., 2000), whereas reactions with ions are generally more complex. In the aqueous phase, SO₄²⁻ is formed as the terminal oxidation species. Sulfate is known to be the main driving species in atmospheric aerosols formation and its formation is critical in the determination of aerosol formation rates (Nieminen et al., 2009; Sipilä et al., 2010; Kuang et al., 2008; Kulmala et al., 2000). The role of ions in this formation has been well established (Yu, 2006; Yu and Turco, 2000, 2001; Enghoff and Svensmark, 2008; Kirkby et al., 2011; Wagner et al., 2017; Yan et al., 2018), although relatively minor compared to the mechanism involving neutral particles, exclusively (Eisele et al., 2006; Manninen et al., 2010; Kirkby et al., 2011; Hirsikko et al., 2011; Wagner et al., 2017).

The immediate products of SO₂ oxidation by ions are mostly sulfur oxides ions intermediates (Fehsenfeld and Ferguson, 1974; Möhler et al., 1992; Bork et al., 2012; Tsona et al., 2014) that are susceptible of triggering new reactions or recombining with oppositely charged counterparts to form neutral species. Some of these ions, namely SO₃⁻, SO₄⁻, and SO₅⁻, were detected at relatively high concentrations in the ambient atmosphere (Ehn et al., 2010) and in chamber experiments of SO₂ ionic oxidation studies (Nagato et al., 2005; Hvelplund et al., 2013; Kirkby et al., 2011; Kirkby et al., 2016). The chemical fate of most sulfur oxides anions is relatively known. Bork et al. showed that SO₃⁻ can form SO₃, the precursor for H₂SO₄, through electron transfer to ozone (O₃) (Bork et al., 2012). SO₃⁻ can equally react with O₂ to form SO₅⁻ whose atmospheric outcome by reaction with O₃ is H₂SO₄ formation (Bork et al., 2013). It was also speculated from chamber studies that SO₅⁻ could form and stabilize clusters with sulfuric acid in the gas-phase (Kirkby et al., 2011). Reliable predictions of the outcomes of these ions require an exact knowledge of their chemical structures since interactions between molecules or ions depend both on their physical and chemical properties. **A previous study demonstrated that two forms of SO₄⁻ separated by a high energy barrier may exist in the atmosphere (Tsona et al., 2014): the sulfate radical ion henceforth indicated as SO₄⁻, and the peroxy form, O₂SOO⁻, in which the O₂S–OO⁻ bond nature is more dative than covalent.** Formerly, the two isomers were often misleadingly attributed exclusively to the sulfate radical ion, the most stable form of SO₄⁻. However, their reactive properties greatly differ (Fehsenfeld and Ferguson, 1974).

The formation mechanisms of SO_4^- in the gas-phase have been largely unknown but, recent studies showed that this ion can be formed by SO_5^- reaction with O_3 (Bork et al., 2013) and in a O_2SOO^- isomerization process catalyzed by NO (Tsona et al., 2018). SO_4^- can also be produced during the chemical transformation of organic compounds, triggered by sulfate salts (Noziere et al., 2010), whereas O_2SOO^- is formed at collision rates upon SO_2 reaction with O_2^- (Fahey et al., 1982; Tsona et al., 2014). The sulfate radical ion is believed to react with unsaturated compounds to form organosulfates, a major component of secondary organic aerosol (Surratt et al., 2007; Surratt et al., 2008; Schindelka et al., 2013). Using first-principles calculations, SO_4^- was shown to act as a catalyst in SO_2 oxidation to SO_3 by O_3 in the gas-phase and hence, plays a role in atmospheric aerosol formation (Tsona et al., 2015; Tsona et al., 2016). The chemistry of O_2SOO^- is largely unknown, although potentially important for sulfur chemistry and atmospheric aerosol formation. Fehsenfeld and Ferguson found that O_2SOO^- can be decomposed by NO_2 into NO_3^- and SO_3 (Fehsenfeld and Ferguson, 1974) and a recent study showed that in the presence of nitrogen oxides ($\text{NO}_x = \text{NO}_2 + \text{NO}$), O_2SOO^- can be converted into sulfate (Tsona et al., 2018). In mildly polluted environments, the concentration of O_3 can be few orders of magnitude higher than that of NO_x and the chemical fate of O_2SOO^- would then also greatly depend on collisions with O_3 . In such environments, O_2SOO^- could experience much more collisions with O_3 than with NO_x .

Hereby, we investigate the reaction between $\text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$ and O_3 using *ab initio* calculations. By determining the reactions thermodynamics and kinetics, we examine the possible pathways for the reaction and propose the most probable outcome of $\text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$ based on O_3 reaction. Implications of the most relevant pathways in aerosol formation are discussed.

2 Methods

2.1 Geometry optimizations, thermochemical and charge analysis

As the substrate in this study is a radical anion, all stationary points in the energy surface were optimized using density functional theory (DFT) based on the UM06-2X density functional (Zhao and Truhlar, 2008) and the aug-cc-pVTZ basis set (Dunning Jr et al., 2001), setting the charge to -1 and the spin multiplicity to 2. The use of UM06-2X implies using unrestricted wavefunctions to describe the quantum state of the system. Spin contamination often arises from unrestricted density functional theory (DFT) calculations and it is not guaranteed that the electronic states from these calculations are eigenstates of the \hat{S}^2 operator. The spin contamination was then evaluated for all electronic states as $\Delta S = \langle \hat{S}^2 \rangle - \langle \hat{S}^2 \rangle_{\text{ideal}}$, where $\langle \hat{S}^2 \rangle$ is actual value of the expectation value of the \hat{S}^2 operator from DFT calculations and $\langle \hat{S}^2 \rangle_{\text{ideal}}$ is the ideal expectation value. For systems explored in this study, $\langle \hat{S}^2 \rangle_{\text{ideal}} = 0.75$.

The UM06-2X functional has successfully proven to be adequate for reactions involving transition state (TS) configurations (Elm et al., 2012, 2013a, b). Harmonic vibrational frequencies analysis on the optimized structures were performed (at 298 K and 1 atm) using the UM06-2X/aug-cc-pVTZ method under the harmonic oscillator-rigid rotor approximation. These calculations ensured that the obtained stationary points were minima or TS and, also, provided the thermal contributions to the Gibbs free energy and the enthalpy.

Transition states structures were initially located by scanning the reactants configurations. The best TS guesses out of the scans were then refined using the synchronous transit quasi Newton method (Peng et al., 1996), and the final TS structures underwent internal reaction coordinate calculations (Fukui, 1981) to ensure they connected the reactants to desired products.

The electronic energies of the UM06-2X/aug-cc-pVTZ optimized geometries were corrected with the UCCSD(T) method (Purvis and Bartlett, 1982) in conjunction with the aug-cc-pVTZ basis set. The Gibbs free energies, G , of all relevant species were then calculated as

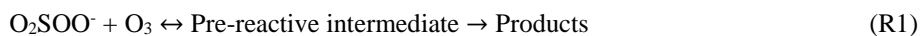
$$G = E_{\text{UCCSD(T)}} + G_{\text{therm}} \quad (1)$$

where $E_{\text{UCCSD(T)}}$ is the electronic energy calculated with the UCCSD(T)/aug-cc-pVTZ method and G_{therm} is the thermal contribution to the Gibbs free energy, calculated at the UM06-2X/aug-cc-pVTZ level of theory. All geometry optimizations, harmonic vibrational frequencies analysis and electronic energies correction calculations were carried out in the Gaussian 09 package (Frisch et al., 2016).

To analyse the distribution of the excess electronic charge over different species and fragments in the optimized systems, we used the Atoms-in-Molecules charge partitioning method presented by Bader (Bader, 1998). This is an intuitive way of dividing the molecules of a system into atoms, which are purely defined in terms of electronic charge density. The Bader charge partitioning assumes that the charge density between atoms of a molecular system reaches a minimum, which is an ideal place to separate atoms from each other. As input, this method requires electronic density and nuclear coordinates from electronic structure calculations. We used the approach implemented in the algorithm developed by Henkelman and co-workers, which has been shown to work well both for charged and water-containing systems (Tang et al., 2009; Bork et al., 2011; Henkelman et al., 2006).

2.2 Reactions kinetics

Regardless of the presence of water, the reaction between $\text{O}_2\text{SOO}^\cdot$ and O_3 begins by forming different van der Waals pre-reactive intermediates, depending on the orientation of the reactants at impact. The pre-reactive intermediate could either decompose to different species or react further through a transition state configuration to form new products:



The traditional approach to determine the rate constant of reaction (R1) relies on the steady-state approximation and leads to the following equation:

$$k = k_{\text{coll}} \frac{k_{\text{reac}}}{k_{\text{reac}} + k_{\text{evap}}} \quad (2)$$

where k_{coll} is the collision frequency for O_2SOO^- - O_3 collisions, k_{evap} is the rate constant for the evaporation of the pre-reactive intermediate back to initial reactants, and k_{reac} is the unimolecular rate constant for the reaction of the pre-reactive intermediate to the products. Moreover, assuming that $k_{\text{evap}} \gg k_{\text{reac}}$, the rate constant of reaction (R1) becomes $k = K_{\text{eq}}k_{\text{reac}}$ over a range of temperatures, with K_{eq} being the equilibrium constant of formation of the pre-reactive intermediate from the reactants. **This consideration is, however, not valid for reactions with submerged barrier, since the pre-reactive intermediate seldom thermally equilibrates.** For such reactions, a two-transition state theory has been introduced, treating two distinct transition state bottlenecks that define the net reactive flux (Klippenstein et al., 1988; Georgievskii and Klippenstein, 2005; Greenwald et al., 2005). The first bottleneck, the “outer” transition state, occurs in the association of the initial reactants to form the pre-reactive intermediate, whereas the second bottleneck, the “inner” transition state, occurs in the transformation of the pre-reactive intermediate to the products. Based on this theory, the overall rate constant (k) for a reaction channel is expressed in terms of the outer (k_{out}) and inner (k_{in}) rate constants as:

$$\frac{1}{k} = \frac{1}{k_{\text{out}}} + \frac{1}{k_{\text{in}}} \quad (3)$$

The outer transition state is treated by the long-range transition state theory approach (Georgievskii and Klippenstein, 2005), while the inner transition state is resolved by the transition state theory. It was shown that for interactions between ions and neutral molecules, due to their long-range attraction, the collision cross section is larger than would be measured from the physical dimensions of the colliding species (Kupiainen-Määttä et al., 2013). To account for this phenomenon, the outer rate constant was determined from the ion-dipole parametrization of Su and Chesnavich who performed trajectory simulations of collisions between a point charge and a rigidly rotating molecule (Su and Chesnavich, 1982). This parametrization is equivalent to a Langevin capture rate constant (k_{L}) scaled by a temperature-dependent term and was found to provide good agreement with experiments (Kupiainen-Määttä et al., 2013). It is given as

$$k_{\text{out}} = k_{\text{L}} \times \left(\frac{(x+0.5090)^2}{10.526} + 0.9754 \right) \quad (4)$$

where $k_L = q\mu^{-1/2}(\pi\alpha/\epsilon_0)^{1/2}$, $x = \mu_D/(8\pi\epsilon_0\alpha k_B T)^{1/2}$, q is the charge of the ion, μ is the reduced mass of the colliding species, ϵ_0 is the vacuum permittivity, α and μ_D are the polarizability and dipole moment of the neutral molecule (ozone), k_B is Boltzmann's constant, and T is the absolute temperature. The inner rate constant can be written as:

5

$$k_{in} = \frac{k_B T}{hc^0} \times \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (5)$$

where ΔG^\ddagger is the Gibbs free energy barrier separating the pre-reactive intermediate and the products, h is the Planck's constant, R is the molar gas constant, and c^0 is the standard gas-phase concentration. **The constants and variables in Eq. (4) and Eq. (5) are given in centimetre-gram-second (CGS) system of units and International System (SI) units, respectively. Details on these units are given in the Supplement.**

10

3 Results and discussion

Starting with optimized structures of $O_2SOO\cdots(H_2O)_{0-1}$ and O_3 shown in Fig. S1, a series of geometry optimizations were performed on the $O_2SOO\cdots(H_2O)_{0-1} + O_3$ system, taking into account different spatial orientations of the reactants at impact. These optimizations led to two main chemical processes, depending on the initial orientation of the reactants, with potentially different outcomes. The first process is the formation of a van der Waals complex followed by its direct decomposition to other species. **The second process is the low-lying formation of a molecular complex in which the SO_2 entity of $O_2SOO\cdots(H_2O)_{0-1}$ is oxidized to SO_3^- .**

20 3.1 Cluster formation and decomposition of $O_2SOO\cdots(H_2O)_{0-1}$

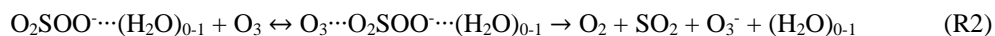
As O_3 approaches $O_2SOO\cdots(H_2O)_{0-1}$ towards the oxygen atoms of the peroxy fragment or the oxygen atom of the SO_2 moiety, the immediate outcome of $O_2SOO\cdots(H_2O)_{0-1}$ and O_3 collisions is the formation of the van der Waals $O_3\cdots O_2SOO\cdots(H_2O)_{0-1}$ complex in which O_3 interacts with O_2SOO^- . Among the different stable configurations found upon optimizations, we solely report the most stable one with respect to the Gibbs free energy, which is henceforth denoted RC1 and RCW1 for the unhydrated and monohydrated, respectively, shown in Fig. 1. Exploration of the RC1 and RCW1 structures reveals that $O_2SOO\cdots(H_2O)_{0-1}$ basically keeps its configuration upon clustering with O_3 . **The spin contaminations for RC1 and RCW1 are negligible, being 0.0086 and 0.0081, respectively. The electronic energies of formation of RC1 and RCW1 are -5.1 and -4.6 kcal mol⁻¹, respectively. Despite these complexes may form at 0 K, the Gibbs free energies of their formation under atmospheric pressure and 298 K (4.5 and 4.7 kcal mol⁻¹, respectively) indicate that their formation is endergonic under atmospherically relevant conditions.** These Gibbs free energy values indicate that, if formed, these complexes would not live long and will rather decompose either to initial reactants or to different species. **Hence, the Gibbs free energies of formation of RC1 and**

30

RCW1 define the lowest states at which O_2SOO^- can interact with O_3 to allow electron transfer and $\text{O}_2\text{S}-\text{OO}$ decomposition, and thus represent the energy barrier towards $\text{O}_2 + \text{SO}_2 + \text{O}_3^-$ formation. Inspecting the vibrational modes of RC1 and RCW1, two vibrations are found that would clearly lead to the dissociation of O_2SOO^- within the complex. The analysis of the charge distribution over $\text{O}_3 \cdots \text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$ shows that the extra electron initially located on O_2SOO in the reactants has migrated to the O_3 molecule in the van der Waals product complex, as can be observed in Fig. S2. This is as expected, given the high electronegativity of O_3 relative to those of O_2 and SO_2 (Rothe et al., 1975). The charge distribution over the different atoms of the optimized complex is weakly affected by the presence of water, as previously demonstrated by Bork and co-workers (Bork et al., 2011).

The most likely fates of RC1 and RCW1 are, therefore, decomposition into O_2 , SO_2 and O_3^- as follows:

10



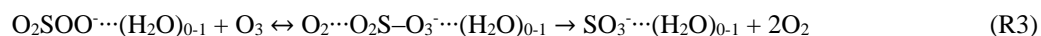
The numerical values of the formation energies of all intermediate species in reaction (R2) are given in Table 1 and the energy surfaces are plotted in Fig. 2. RC1 and RCW1 decompositions are highly exergonic at 298 K, occurring with -18.1 and -16.7 kcal mol⁻¹ Gibbs free energy changes, respectively. These processes are, therefore, likely to occur in the atmosphere upon formation of $\text{O}_3 \cdots \text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$.

The limiting step in reaction (R2) is the formation of RC1 and RCW1, whose formation energies indicated above can then be considered as the only barrier to the formation of $\text{O}_2 + \text{SO}_2 + \text{O}_3^-$. This leads to overall rate constants (according to Eq. 5) of 1.4×10^{-10} and 9.9×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K for the unhydrated and monohydrated reaction, respectively. Both reactions are, in principle, collision-limited and the effect of hydration on the kinetics is found to be negligible. The atmospheric relevance of reaction (R2) has been determined earlier (Bork et al., 2012; Bork et al., 2013; Enghoff et al., 2012).

3.2 $\text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$ reaction with O_3

When O_3 approaches $\text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$ from the sulfur atom side, the formation of a more stable cluster than found above prevails. The incoming O_3 molecule strongly interacts with $\text{O}_2\text{SOO}^- \cdots (\text{H}_2\text{O})_{0-1}$ by forming a coordination bond with the sulfur atom and hereby, inducing the ejection of the O_2 molecule that remains in interaction with the remainder of the system. This process leads to the formation of the $\text{O}_2 \cdots \text{O}_2\text{S}-\text{O}_3^- \cdots (\text{H}_2\text{O})_{0-1}$ complex which further transforms, through an intramolecular SO_2 oxidation, into $\text{SO}_3^- \cdots (\text{H}_2\text{O})_{0-1} + 2\text{O}_2$ according to the following equation:

30



The configurations of the most stable intermediate structures in reaction (R3) are given in Fig. 1. The charge analysis on this system indicates that the electronic charge on the pre-reactive complex is essentially on two oxygen atoms of the O₃ moiety that is coordinated to SO₂ as can be seen in Fig. 3(a). The net charge on these two oxygen atoms is 1.04e, whereas the net charge on the free O₂ molecule is 0.01e. The latter value shows that the O₂ molecule formed in the pre-reactive complex has no unpaired electrons, and hence is a singlet. Although the charge is still on the O₃ moiety in the transition state configuration, it is mostly located on the oxygen atom bound to sulfur (**Fig. 3(b)**). The net charge on the two outer oxygen atoms of the O₃ moiety in the transition state has substantially decreased to 0.30e while the charge on the free O₂ molecule has slightly increased to 0.04e. The strong decrease in the charge of the two outer oxygen atoms of O₃ from the pre-reactive complex to the transition state suggests that the O₂ molecule to form in the product will likely be a singlet. In the products (**Fig. 3(c)**), the old free O₂ molecule has a net charge of 1.99e, whereas the charge on the newly formed O₂ is 0.06e. The 1.99e charge on the old free O₂ molecule indicates the presence of unpaired electrons in its configuration, meaning that the singlet O₂ has been transformed into triplet. This clearly shows that a spin flip has occurred in O₂ during further optimization of the products. The newly formed O₂ with 0.06e charge is obviously a singlet. This analysis shows for the unhydrated system that the singlet O₂ initially formed in the pre-reactive complex transforms into triplet in the products state, while a new singlet O₂ is also formed. In the monohydrated system, the singlet O₂ initially formed in the pre-reactive complex remains as singlet in the products state and a triplet O₂ is also released. Overall, the two forms of O₂ (singlet and triplet) are formed in the studied reaction, despite following different mechanisms. Although the water molecule in the monohydrated system does not retain any electric charge, it most likely stabilizes the initially formed singlet O₂ and prevents the spin flip.

Though the necessity to determine the electronic structure of the O₂ molecule in the singlet state (¹Δ_g) has been demonstrated to be useful (Buttar and Hirst, 1994), obtaining a reliable electronic energy for O₂(¹Δ_g) is difficult (Drougas and Kosmas, 2005). An alternative approach to determine this energy is to add the experimental energy spacing (22.5 kcal mol⁻¹) between triplet and singlet states of O₂ to the computed electronic energy of the triplet O₂ (Schweitzer and Schmidt, 2003; Drougas and Kosmas, 2005). We used this approach to determine the energies of the products of reaction (R3). The numerical values of the formation energies of all intermediate species in reaction (R3) are thus given in Table 1 and the energy surfaces are plotted in Fig. 2. The most stable optimized structures of O₂⋯O₂S–O₃⋯(H₂O)₀₋₁ according to our calculations are denoted as RC2 and RCW2 for the unhydrated and monohydrated systems, respectively and are shown in Fig. 1. Regardless of the presence of water, the O₂⋯O₂SO₃⁻ configuration results from O₂ being switched by O₃ in the O₂SOO⁻ molecular ion. In the optimized O₂⋯O₂S–O₃⁻ structure, the O₃ atom of O₃ points towards the S atom of O₂SOO⁻, forming S–O₃ bonds at distances of 1.90 and 1.87 Å in the absence and presence of water, respectively. These bonds are coordination bonds in nature since the S–O covalent bond in e.g., 1.43 Å in SO₃ and 1.46 Å in H₂SO₄. The S–O₃ coordination bond distances in RC2 and RCW2 are shorter by 0.04 and 0.03 Å than O₂S–OO⁻ bond distances in unhydrated and monohydrated O₂SOO⁻ forms. This indicates stronger interaction between O₃ and SO₂, and hence higher stability of O₂⋯O₂S–O₃⁻ relative to O₂SOO⁻.

The formations of RC2 and RCW2 are highly exergonic, with Gibbs free energy changes at 298 K of -14.7 and -12.4 kcal mol⁻¹, respectively. These values, with corresponding electronic energies and enthalpies are shown in Table 1. These Gibbs free energy changes for the formation of RC2 and RCW2 are about 19 kcal mol⁻¹ lower than those of RC1 and RCW1 at similar conditions, indicating the higher stability of RC2 and RCW2, and the highly favourable switching reaction at ambient conditions. SO₂ oxidation can readily occur within the O₂⋯O₂S-O₃⁻⋯(H₂O)₀₋₁ cluster and lead to SO₃⁻ formation. In principle, to form the products of reaction (R3), the O3 atom of the O₃ moiety in O₂⋯O₂S-O₃⁻⋯(H₂O)₀₋₁ transfers, through transition state configurations, to SO₂ and form SO₃⁻ followed by the ejection of the O₂ molecule. The transition states are denoted TS2 and TSW2 for the unhydrated and monohydrated systems, respectively, and their structures are presented in Fig. 1. While RC2 and RCW2 are formed with similar Gibbs free energies within 2 kcal mol⁻¹ difference, the formation Gibbs free energies of their transition states at similar conditions greatly differ. TS2 is located at 10 kcal mol⁻¹ Gibbs free energy above RC2, while TSW2 is located at -4 kcal mol⁻¹ below RCW2. It is speculated that the low energy barrier in the monohydrated reaction is the result of a strong stabilisation of the transition state due to hydration, with the S-O3 bonds in RCW2 and TSW2 shorter by ~0.03 Å than in RC2 and TS2. Another reason for this substantial drop in energy barrier is the difference in the electronic configurations of the two outer oxygen atoms of the O₃ moiety in the two transition states that form O₂ with different multiplicities in the products.

Based on the TS2 energy, the unimolecular decomposition of O₂⋯O₂S-O₃⁻ at 298 K in the absence of water was found to occur at a rate constant of 3.1×10⁵ s⁻¹, corresponding to an atmospheric lifetime of 3.3 μs. Both this short lifetime and the negative energy barrier of the monohydrated reaction indicate that O₂⋯O₂S-O₃⁻ would not live long enough to experience collisions with other atmospheric oxidants. It should be noted that few to no collisions with nitrogen can, however, be achieved. It follows that the most likely outcome of O₂⋯O₂S-O₃⁻ is decomposition to the products of reaction (R3), which are formed with about -46 kcal mol⁻¹ overall Gibbs free energy at 298 K. The net reaction is an O₂⁻-initiated SO₂ oxidation to SO₃⁻ by O₃.

The spin contamination for electronic states in reaction (R3) is quite significant, being 1.0122, 1.4666, and 2.0374 for the pre-reactive complex, transition state and product, respectively, and is almost insensitive to the presence of water. The actual values of the expectation values of the \hat{S}^2 operator for all electronic states obtained from our calculations are given in the Supplement, along with their cartesian coordinates. The high values of spin contamination likely reflect the formation of O₂ with different multiplicities within the system. As the charge analysis indicates, starting with singlet O₂ in the pre-reactive complexes of reaction (R3), both singlet and triplet O₂ are formed in the final products.

The overall rate constants of reaction (R3), determined at 298 K using Eq. (3), are 1.3×10⁻¹⁴ and 8.0×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for the unhydrated and monohydrated reactions, respectively. The values of the different components (k_{out} and k_{in}) are listed in Table S1 of the Supplement. It is observed from Table S1 that the inner transition state provides the dominant bottleneck to the

rate constant of the unhydrated reaction, whereas the outer transition state provides the **dominant** bottleneck to the rate constant of the monohydrated reaction.

5 The effective effect of water on the rate constant can be evaluated by taking into account the stability of $O_2SOO\cdots H_2O$ (which is formed at the entrance channel of the reaction in the presence of water before colliding with O_3) and the equilibrium vapor pressure of water. Starting from the definition of the reaction rate for the hydrated reaction,

$$J_{(R3w)} = k_{(R3w)} \times [O_2SOO\cdots H_2O] \times [O_3] \quad (6)$$

$$= k_{(R3w)}^{eff} \times [O_2SOO^-] \times [O_3] \quad (7)$$

10

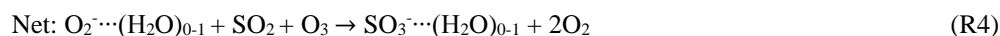
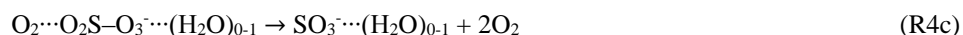
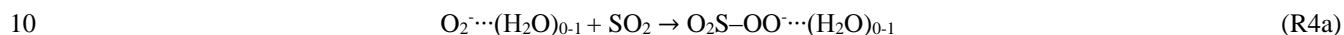
where $k_{(R3w)}$ is the overall rate constant for the hydrated reaction, determined using Eq. (3), $k_{(R3w)}^{eff}$ is the effective reaction rate constant calculated as $k_{(R3w)}^{eff} = k_{(R3w)} \times K_{eq} \times p_{H_2O}$. K_{eq} is the equilibrium constant for the $O_2SOO^- + H_2O \leftrightarrow O_2SOO\cdots H_2O$ reaction and p_{H_2O} the actual water vapor pressure. Details on the determination of K_{eq} and p_{H_2O} are given in the Supplement.

15 At 298 K and 50 % relative humidity, the effective rate constant of the monohydrated reaction is $1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, four orders of magnitude higher than the rate constant of the unhydrated reaction. Therefore, water plays a catalytic role on the kinetics of reaction (R3). The net rate constant of reaction (R3) can be obtained by weighing the rate constants of the unhydrated and monohydrated reactions to corresponding equilibrium concentrations of $O_2\cdots O_2S-O_3^-$ hydrates. Using the law of mass action, we find that $O_2\cdots O_2S-O_3^-$ mostly exists as a dry species, constituting 77% of the total population, whereas the
20 monohydrated species forms 23% of the total population. The net rate constant of reaction (R3) is then determined to be $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Considering only the unhydrated process of reaction (R3), the rate constant is 4-5 orders of magnitude lower than the rate constant obtained for the $SO_2 + O_3^- \rightarrow SO_3^- + O_2$ reaction (Fehsenfeld and Ferguson, 1974; Bork et al., 2012). Despite this
25 difference, the oxidation process follows a similar mechanism to the one presented by Bork et al. for the $SO_2 + O_3^- \rightarrow SO_3^- + O_2$ reaction, consisting of the oxygen transfer from O_3 to SO_2 (Bork et al., 2012). The discrepancy between the two results is associated with the effect of the presence of the O-O fragment initially coordinated to SO_2 in the current study, which tends to stabilize the $O_2\cdots O_2S-O_3^-$ pre-reactive complex. The presence of the O-O fragment seemingly deactivates SO_2 for the upcoming O transfer from O_3 to form SO_3^- . However, this situation is rapidly reversed with the presence of water as the reaction
30 becomes much faster, proceeding nearly at collision rate.

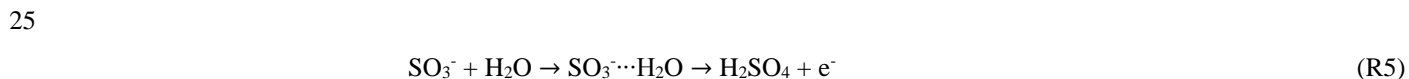
3.3 Further chemistry

In real atmospheric and ionized conditions, despite O_2 has lower electron affinity than O_3 , it would likely ionize faster than O_3 owing to its much higher concentration. Considering for example chamber experiments, upon interaction of ionizing particles with the gas, electrons can transfer from one species to another and, e.g., O_2^- can form and rapidly hydrate within one nanosecond (Svensmark et al., 2007; Fahey et al., 1982). Furthermore, Fahey et al. showed that $O_2^- \cdots (H_2O)_{0-1}$ association reaction with SO_2 is faster than the electron transfer from $O_2^- \cdots (H_2O)_{0-1}$ to O_3 (Fahey et al., 1982). This means that in an ionized environment containing O_2 , O_3 , and SO_2 , the formation of O_2S-OO^- resulting from SO_2 and O_2^- association will happen faster than O_3^- formation. O_2S-OO^- would react thereafter with O_3 and the following stepwise process could take place



The Gibbs free energy change of this net reaction at 298 K is about $-40 \text{ kcal mol}^{-1}$ more negative than that of the $SO_2 + O_3^- \rightarrow SO_3^- + O_2$ reaction at similar conditions. Given that the intermediate steps of reaction (R4) are significantly fast, this reaction is believed to be an important process in most environments of SO_2 ion-induced oxidation to SO_3^- or more oxidized species. The limiting step in the process of reaction (R4) is reaction (R4c) for which an energy barrier has to be overcome before the products are released.

SO_3^- is an identified stable ion detected in the atmosphere and in experiments (Ehn et al., 2010; Kirkby et al., 2011; Kirkby et al., 2016). The chemical fate of SO_3^- is fundamentally different from that of SO_3 that forms H_2SO_4 by hydration. Likely outcomes of SO_3^- are hydrolysis, electron transfer by collision with O_3 , reaction with O_2 and H_2O and, possibly, radicals, according to the following equations



Fehsenfeld and Ferguson showed that H_2SO_4 formation could occur in the $SO_3^- \cdots H_2O$ cluster, releasing a free electron (Reaction (R5)) (Fehsenfeld and Ferguson, 1974). Owing to the high electron affinity of O_3 relative to SO_3 (Rothe et al., 1975), the electron can transfer from SO_3 to O_3 and lead to the formation of SO_3 , the precursor for sulfuric acid in the atmosphere.

Moreover, the free electron released and the O_3^- formed in reactions (R5) and (R6), respectively, are potential triggers of new SO_2 oxidations with implication in aerosol formation (Svensmark et al., 2007; Enghoff and Svensmark, 2008; Bork et al., 2013). Reactions (R7) and (R8) are potential outcomes for SO_3^- as well, forming the highly stable HSO_4^- species that would terminate the oxidation process of SO_2 initiated by a free electron. Reactions (R5)–(R8) are likely competitive processes upon SO_3^- formation in the gas-phase, and their different rates would determine the number of SO_2 oxidations induced by a free electron. However, they have no other fate than HSO_4^- or H_2SO_4 , the most oxidized sulfur species in the atmosphere, which both share many properties and play a central role in atmospheric particle formation.

Experimental studies have shown that in atmospheres heavily enriched in SO_2 and O_3 , a free electron could initiate SO_2 oxidation and induce the formation of $\sim 10^7 \text{ cm}^{-3}$ sulfates in the absence of UV light, clearly indicating the importance of other ionic SO_2 oxidation mechanisms than UV-induced (Enghoff and Svensmark, 2008). To evaluate the importance of the mechanism presented in this study in the formation of sulfate, it is necessary to identify the scavengers that terminate the SO_2 oxidation initiated by O_2^- . Possible scavengers include radicals, NO_x , acids, cations and other particles. **The main ones are likely NO_x , OH, HO_2 and organic acids, which lead to the formation of the stable NO_3^- , HSO_4^- , and CO_3^- species.** If the ion concentration was known, the contribution of reaction (R4) to H_2SO_4 formation could be determined by comparing its formation rates from ionic and electrically neutral mechanisms. Alternatively, it can be assumed that reaction (R4) is terminated when the ion cluster hits a scavenger. The free electron which acts as catalyst is then scavenged. The average catalytic turnover number (TON) is defined as (Kozuch and Martin, 2012):

$$TON = \frac{\text{concentration of limiting reacted molecules}}{\text{concentration of the catalyst}} \quad (8)$$

The concentration of the catalyst can be approximated to the concentration of the scavengers and, considering that at most atmospheric conditions $[O_3^-] > [SO_2]$, SO_2 is the limiting species in reaction (R4). Equation (8) can then be re-written as

$$TON \approx \frac{[SO_2]}{[OH] + [HO_2] + [NO_x] + [\text{organic acids}]} \quad (9)$$

The catalytic efficiency of SO_2 ion-induced oxidation is then given as

$$J_{ion} = k_{ion} \times TON \quad (10)$$

Where k_{ion} is the ion production rate. Depending on the tropospheric temperature and altitude, measurements at the **Cosmics Leaving Outdoor Droplets chamber at CERN** found $k_{ion} = 2\text{--}100 \text{ cm}^{-3} \text{ s}^{-1}$, covering the typical ionization range in the troposphere (Franchin et al., 2015). **We assume nearly pristine conditions with $[SO_2] = 5 \text{ ppb} = 1.2 \times 10^{11} \text{ molecule cm}^{-3}$, $[NO_x] = 200 \text{ ppt} = 4.9 \times 10^9 \text{ molecule cm}^{-3}$, $[OH] = 5.0 \times 10^5 \text{ molecule cm}^{-3}$ (day and night average), and $[HO_2] = 10^8$**

molecule cm^{-3} (Dusanter et al., 2009; Holland et al., 2003). Noting that formic acid and acetic acid are the most abundant organic acids in the atmosphere, their concentrations are considered in Eq. (9) as representative examples for organic acids, $[\text{organic acids}] = 110 \text{ ppt} = 2.7 \times 10^9 \text{ molecule cm}^{-3}$ (Le Breton et al., 2012; Baasandorj et al., 2015). We then determine J_{ion} in the range $3.2 \times 10^1 - 1.6 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$. The rate of the UV-induced SO_2 oxidation by OH is

5

$$J_{\text{UV}} = k_{\text{UV}} \times [\text{SO}_2] \times [\text{OH}] \quad (11)$$

With $k_{\text{UV}} = 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004), $J_{\text{UV}} = 7.9 \times 10^4 \text{ molecule cm}^{-3} \text{ s}^{-1}$, and the proportion of H_2SO_4 formed from ion-induced oxidation can be estimated from the following equation

10

$$\frac{[\text{H}_2\text{SO}_4]_{\text{ion}}}{[\text{H}_2\text{SO}_4]_{\text{total}}} = \frac{J_{\text{ion}}}{J_{\text{UV}} + J_{\text{ion}}} \quad (12)$$

We find that the contribution of ion-induced SO_2 oxidation to H_2SO_4 formation can range from 0.1 to 2.0% of the total formation rate. This estimate could be improved by considering also the SO_2 oxidation by Criegee Intermediates, another important channel for H_2SO_4 formation.

15

3 Conclusions

This study highlights the role of the superoxide ions (O_2^-) in SO_2 oxidation. Our previous study demonstrated that SO_2 interacts with O_2^- and forms O_2SOO^- whose atmospheric fate remains unelucidated (Tsona et al., 2014). In this study, we used ab initio calculations to assess the chemical fate of O_2SOO^- by collisions with O_3 . Regardless of the presence of water, two main mechanisms are observed, leading to fundamentally different products. The first mechanism is characterized by electron transfer followed by O_2SOO^- decomposition, leading to O_3^- formation and releasing SO_2 . The chemistry of $\text{SO}_2 + \text{O}_3^-$ has been explored elsewhere. The second mechanism is characterized by SO_2 oxidation and proceeds through formation of a pre-reactive complex that subsequently reacts to form the products by overcoming a relatively low energy barrier. The overall reaction, $\text{O}_2^- + \text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3^- + 2\text{O}_2$, is faster and more energetically favourable than the $\text{SO}_2 + \text{O}_3^- \rightarrow \text{SO}_3^- + \text{O}_2$ reaction, thereby highlighting the positive role of O_2^- in SO_2 ionic oxidation. Hence, the two reactions may compete in chamber experiments and in the atmosphere.

20

25

While for the electron transfer and O_2SOO^- decomposition process the reaction is hindered by the presence of water, the oxidation reaction is catalysed instead as the rate constant is increased by 6 orders of magnitude with the presence of water. Weighing the rate constants of unhydrated and monohydrated reactions to the equilibrium concentrations of hydrates of corresponding pre-reactive complexes leads to the net rate constant of $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K for the oxidation reaction. Hence, this reaction proceeds nearly at collision rate. The main species (SO_3^-) in the end products of the studied

30

reaction has been proved to form both in the atmosphere and in experiments, where it definitely plays a role in atmospheric sulfur chemistry and particle formation. The contribution of this mechanism to the total atmospheric sulfuric acid formation is estimated. The studied reaction further deepens the understanding of ion-induced SO₂ oxidation, with implications in aerosol formation.

5 Author contributions

NTT and LD designed the work. NTT performed all calculations and analysed the data. NTT wrote the whole manuscript and LD edited it.

Competing interests

The authors declare that they have no conflict of interest.

10 Acknowledgements

This work was supported by the National Natural Science Foundation of China (21707080, 91644214), the Postdoctoral Science Foundation of China (2017M612276), Shandong Natural Science Fund for Distinguished Young Scholars (JQ201705) and the International Postdoctoral Exchange Fellowship Program. We acknowledge the High-Performance Computing Center of Shandong University for providing the computational resources.

15

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species, *Atmos. Chem. Phys.*, 4, 1461-1738, doi:10.5194/acp-4-1461-2004, 2004.
- 20 Baasandorj, M., Millet, D. B., Hu, L., Mitroo, D., and Williams, B. J.: Measuring acetic and formic acid by proton-transfer-reaction mass spectrometry: sensitivity, humidity dependence, and quantifying interferences, *Atmos. Meas. Tech.*, 8, 1303-1321, doi:10.5194/amt-8-1303-2015, 2015.
- Bader, R. F. W.: A Bond Path: A Universal Indicator of Bonded Interactions, *J. Phys. Chem. A*, 102, 7314-7323, doi:10.1021/jp981794v, 1998.
- 25 Bork, N., Kurtén, T., Enghoff, M., Pedersen, J. O. P., Mikkelsen, K. V., and Svensmark, H.: Ab initio studies of O₂⁻(H₂O)_n and O₃⁻(H₂O)_n anionic molecular clusters, n ≤ 12, *Atmos. Chem. Phys.*, 11, 7133-7142, doi:10.5194/acp-11-7133-2011, 2011.

- Bork, N., Kurtén, T., Enghoff, M., Pedersen, J. O. P., Mikkelsen, K. V., and Svensmark, H.: Structures and reaction rates of the gaseous oxidation of SO₂ by an O₃⁻(H₂O)_{0.5} cluster – a density functional theory investigation, *Atmos. Chem. Phys.*, 12, 3639-3652, doi:10.5194/acp-12-3639-2012, 2012.
- 5 Bork, N., Kurtén, T., and Vehkamäki, H.: Exploring the atmospheric chemistry of O₂SO₃⁻ and assessing the maximum turnover number of ion-catalysed H₂SO₄ formation, *Atmos. Chem. Phys.*, 13, 3695-3703, doi:10.5194/acp-13-3695-2013, 2013.
- Buttar, D., and Hirst, D. M.: Ab initio quantum chemistry study of the gas-phase reaction of ClO with HO₂, *J. Chem. Soc. Faraday Trans.*, 90, 1811-1817, doi:10.1039/FT9949001811, 1994.
- Caffrey, P., Hoppel, W., Frick, G., Pasternack, L., Fitzgerald, J., Hegg, D., Gao, S., Leaitch, R., Shantz, N., Albrecht, T., and Ambrusko, J.: In-cloud oxidation of SO₂ by O₃ and H₂O₂: Cloud chamber measurements and modeling of particle growth, 10 *J. Geophys. Res.-Atmos.*, 106, 27587-27601, doi:10.1029/2000jd900844, 2001.
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Sci. Adv.*, 2, e1601530, doi:10.1126/sciadv.1601530, 2016.
- Drougas, E., and Kosmas, A. M.: Computational studies of (HIO₃) isomers and the HO₂+IO reaction pathways, *J. Phys. Chem.* 15 *A*, 109, 3887-3892, doi:10.1021/jp044197j, 2005.
- Dunning Jr, T. H., Peterson, K. A., and Wilson, A. K.: Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited, *J. Chem. Phys.*, 114, 9244-9253, doi:10.1063/1.1367373, 2001.
- Dusanter, S., Vimal, D., Stevens, P. S., Volkamer, R., Molina, L. T., Baker, A., Meinardi, S., Blake, D., Sheehy, P., Merten, A., Zhang, R., Zheng, J., Fortner, E. C., Junkermann, W., Dubey, M., Rahn, T., Eichinger, B., Lewandowski, P., Prueger, J., 20 and Holder, H.: Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign - Part 2: Model comparison and radical budget, *Atmos. Chem. Phys.*, 9, 6655-6675, doi:10.5194/acp-9-6655-2009, 2009.
- Ehn, M., Junninen, H., Petäjä, T., Kurtén, T., Kerminen, V.-M., Schobesberger, S., Manninen, H., Ortega, I., Vehkamäki, H., and Kulmala, M.: Composition and temporal behavior of ambient ions in the boreal forest, *Atmos. Chem. Phys.*, 10, 8513-8530, doi:10.5194/acp-10-8513-2010, 2010.
- 25 Eisele, F. L., Lovejoy, E. R., Kosciuch, E., Moore, K. F., Mauldin III, R. L., Smith, J. N., McMurry, P. H., and Iida, K.: Negative atmospheric ions and their potential role in ion-induced nucleation, *J. Geophys. Res.-Atmos.*, 111, D04305, doi:10.1029/2005jd006568, 2006.
- Elm, J., Bilde, M., and Mikkelsen, K. V.: Assessment of Density Functional Theory in Predicting Structures and Free Energies of Reaction of Atmospheric Prenucleation Clusters, *J. Chem. Theory Comput.*, 8, 2071-2077, doi:10.1021/ct300192p, 2012.
- 30 Elm, J., Bilde, M., and Mikkelsen, K. V.: Assessment of binding energies of atmospherically relevant clusters, *Phys. Chem. Chem. Phys.*, 15, 16442-16445, doi:10.1039/c3cp52616j, 2013a.
- Elm, J., Bilde, M., and Mikkelsen, K. V.: Influence of Nucleation Precursors on the Reaction Kinetics of Methanol with the OH Radical, *J. Phys. Chem. A*, 117, 6695-6701, doi:10.1021/jp4051269, 2013b.

- Enghoff, M., and Svensmark, H.: The role of atmospheric ions in aerosol nucleation—a review, *Atmos. Chem. Phys.*, 8, 4911-4923, doi:10.5194/acp-8-4911-2008, 2008.
- Enghoff, M. B., Bork, N., Hattori, S., Meusinger, C., Nakagawa, M., Pedersen, J. O. P., Danielache, S., Ueno, Y., Johnson, M. S., Yoshida, N., and Svensmark, H.: An isotopic analysis of ionising radiation as a source of sulphuric acid, *Atmos. Chem. Phys.*, 12, 5319-5327, doi:10.5194/acp-12-5319-2012, 2012.
- Fahey, D., Böhringer, H., Fehsenfeld, F., and Ferguson, E.: Reaction rate constants for $O_2^-(H_2O)_n$ ions $n=0$ to 4, with O_3 , NO , SO_2 , and CO_2 , *J. Chem. Phys.*, 76, 1799-1805, doi:10.1063/1.443220, 1982.
- Fehsenfeld, F., and Ferguson, E.: Laboratory studies of negative ion reactions with atmospheric trace constituents, *J. Chem. Phys.*, 61, 3181-3193, doi:10.1063/1.1682474, 1974.
- Franchin, A., Ehrhart, S., Leppä, J., Nieminen, T., Gagné, S., Schobesberger, S., Wimmer, D., Duplissy, J., Riccobono, F., Dunne, E. M., Rondo, L., Downard, A., Bianchi, F., Kupc, A., Tsagkogeorgas, G., Lehtipalo, K., Manninen, H. E., Almeida, J., Amorim, A., Wagner, P. E., Hansel, A., Kirkby, J., Kürten, A., Donahue, N. M., Makhmutov, V., Mathot, S., Metzger, A., Petäjä, T., Schnitzhofer, R., Sipilä, M., Stozhkov, Y., Tome, A., Kerminen, V. M., Carslaw, K., Curtius, J., Baltensperger, U., and Kulmala, M.: Experimental investigation of ion-ion recombination under atmospheric conditions, *Atmos. Chem. Phys.*, 15, 7203-7216, doi:10.5194/acp-15-7203-2015, 2015.
- Fukui, K.: The path of chemical reactions—the IRC approach, *Acc. Chem. Res.*, 14, 363-368, doi:10.1021/ar00072a001, 1981.
- Georgievskii, Y., and Klippenstein, S. J.: Long-range transition state theory, *J. Chem. Phys.*, 122, doi:10.1063/1.1899603, 2005.
- Greenwald, E. E., North, S. W., Georgievskii, Y., and Klippenstein, S. J.: A two transition state model for radical-molecule reactions: A case study of the addition of OH to C_2H_4 , *J. Phys. Chem. A*, 109, 6031-6044, doi:10.1021/jp058041a, 2005.
- Harris, E., Sinha, B., Hoppe, P., Crowley, J. N., Ono, S., and Foley, S.: Sulfur isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H_2O_2 , O_3 and iron catalysis, *Atmos. Chem. Phys.*, 12, 407-423, doi:10.5194/acp-12-407-2012, 2012.
- Harris, E., Sinha, B., van Pinxteren, D., Tilgner, A., Fomba, K. W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., and Herrmann, H.: Enhanced Role of Transition Metal Ion Catalysis During In-Cloud Oxidation of SO_2 , *Science*, 340, 727-730, doi:10.1126/science.1230911, 2013.
- Hegg, D. A., Majeed, R., Yuen, P. F., Baker, M. B., and Larson, T. V.: The impacts of SO_2 oxidation in cloud drops and in haze particles on aerosol light scattering and CCN activity, *Geophys. Res. Lett.*, 23, 2613-2616, doi:10.1029/96gl02419, 1996.
- Henkelman, G., Arnaldsson, A., and Jónsson, H.: A fast and robust algorithm for Bader decomposition of charge density, *Comput. Mater. Sci.*, 36, 354-360, doi:10.1016/j.commatsci.2005.04.010, 2006.
- Hirsikko, A., Nieminen, T., Gagné, S., Lehtipalo, K., Manninen, H. E., Ehn, M., Hörrak, U., Kerminen, V. M., Laakso, L., McMurry, P. H., Mirme, A., Mirme, S., Petäjä, T., Tammet, H., Vakkari, V., Vana, M., and Kulmala, M.: Atmospheric ions and nucleation: a review of observations, *Atmos. Chem. Phys.*, 11, 767-798, doi:10.5194/acp-11-767-2011, 2011.

- Holland, F., Hofzumahaus, A., Schafer, R., Kraus, A., and Patz, H. W.: Measurements of OH and HO₂ radical concentrations and photolysis frequencies during BERLIOZ, *J. Geophys. Res.-Atmos.*, 108, D4, 8246, doi:10.1029/2001jd001393, 2003.
- Hoyle, C. R., Fuchs, C., Järvinen, E., Saathoff, H., Dias, A., El Haddad, I., Gysel, M., Coburn, S. C., Tröstl, J., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Corbin, J. C., Craven, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Frege, C., Gordon, H., Höppel, N., Heinritzi, M., Kristensen, T. B., Molteni, U., Nichman, L., Pinterich, T., Prévôt, A. S. H., Simon, M., Slowik, J. G., Steiner, G., Tomé, A., Vogel, A. L., Volkamer, R., Wagner, A. C., Wagner, R., Wexler, A. S., Williamson, C., Winkler, P. M., Yan, C., Amorim, A., Dommen, J., Curtius, J., Gallagher, M. W., Flagan, R. C., Hansel, A., Kirkby, J., Kulmala, M., Möhler, O., Stratmann, F., Worsnop, D. R., and Baltensperger, U.: Aqueous phase oxidation of sulphur dioxide by ozone in cloud droplets, *Atmos. Chem. Phys.*, 16, 1693-1712, doi:10.5194/acp-16-1693-2016, 2016.
- 10 Hvelplund, P., Pedersen, J. O. P., Stochkel, K., Enghoff, M. B., and Kurten, T.: Experimental studies of the formation of cluster ions formed by corona discharge in an atmosphere containing SO₂, NH₃, and H₂O, *Int. J. Mass Spectrom.*, 341, 1-6, doi:10.1016/j.ijms.2013.03.001, 2013.
- Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature*, 476, 429-433, doi:10.1038/nature10343, 2011.
- Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521, doi:10.1038/nature17953, 2016.
- 30 Klippenstein, S. J., Khundkar, L. R., Zewail, A. H., and Marcus, R. A.: Application of unimolecular reaction-rate theory for highly flexible transition-states to the dissociation of NCNO into NC and NO, *J. Chem. Phys.*, 89, 4761-4770, doi:10.1063/1.455670, 1988.
- Kozuch, S., and Martin, J. M. L.: "Turning Over" Definitions in Catalytic Cycles, *Acs Catalysis*, 2, 2787-2794, doi:10.1021/cs3005264, 2012.
- 35 Kuang, C., McMurry, P. H., McCormick, A. V., and Eisele, F. L.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.-Atmos.*, 113, D10209, doi:10.1029/2007jd009253, 2008.

- Kulmala, M., Pirjola, L., and Mäkelä, J. M.: Stable sulphate clusters as a source of new atmospheric particles, *Nature*, 404, 66-69, doi:10.1038/35003550, 2000.
- Kupiainen-Määttä, O., Olenius, T., Kurtén, T., and Vehkamäki, H.: CIMS sulfuric acid detection efficiency enhanced by amines due to higher dipole moments: a computational study, *J. Phys. Chem. A*, 117, 14109-14119, doi:10.1021/jp4049764, 5 2013.
- Larson, L. J., Kuno, M., and Tao, F.-M.: Hydrolysis of sulfur trioxide to form sulfuric acid in small water clusters, *J. Chem. Phys.*, 112, 8830-8838, doi:10.1063/1.481532, 2000.
- Le Breton, M., McGillen, M. R., Muller, J. B. A., Bacak, A., Shallcross, D. E., Xiao, P., Huey, L. G., Tanner, D., Coe, H., and Percival, C. J.: Airborne observations of formic acid using a chemical ionization mass spectrometer, *Atmos. Meas. Tech.*, 5, 10 3029-3039, doi:10.5194/amt-5-3029-2012, 2012.
- Manninen, H. E., Nieminen, T., Asmi, E., Gagné, S., Häkkinen, S., Lehtipalo, K., Aalto, P., Vana, M., Mirme, A., Mirme, S., Hörrak, U., Plass-Dülmer, C., Stange, G., Kiss, G., Hoffer, A., Törö, N., Moerman, M., Henzing, B., de Leeuw, G., Brinkenberg, M., Kouvarakis, G. N., Bougiatioti, A., Mihalopoulos, N., O'Dowd, C., Ceburnis, D., Arneth, A., Svenningsson, B., Swietlicki, E., Tarozzi, L., Decesari, S., Facchini, M. C., Birmili, W., Sonntag, A., Wiedensohler, A., Boulon, J., Sellegri, 15 K., Laj, P., Gysel, M., Bukowiecki, N., Weingartner, E., Wehrle, G., Laaksonen, A., Hamed, A., Joutsensaari, J., Petäjä, T., Kerminen, V. M., and Kulmala, M.: EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, *Atmos. Chem. Phys.*, 10, 7907-7927, doi:10.5194/acp-10-7907-2010, 2010.
- Mauldin III, R. L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V.-M., and Kulmala, M.: A new atmospherically relevant oxidant of sulphur dioxide, *Nature*, 488, 193-196, doi:10.1038/nature11278, 20 2012.
- Möhler, O., Reiner, T., and Arnold, F.: The formation of SO_5^- by gas phase ion–molecule reactions, *J. Chem. Phys.*, 97, 8233-8239, doi:10.1063/1.463394, 1992.
- Nagato, K., Kim, C. S., Adachi, M., and Okuyama, K.: An experimental study of ion-induced nucleation using a drift tube ion, mobility spectrometer/mass spectrometer and a cluster-differential mobility analyzer/Faraday cup electrometer, *J. Aerosol Sci.*, 25 36, 1036-1049, doi:10.1016/j.jaerosci.2004.12.006, 2005.
- Nieminen, T., Manninen, H., Sihto, S.-L., Yli-Juuti, T., Mauldin III, R. L., Petäjä, T., Riipinen, I., Kerminen, V.-M., and Kulmala, M.: Connection of sulfuric acid to atmospheric nucleation in boreal forest, *Environ. Sci. Technol.*, 43, 4715-4721, doi: 10.1021/es803152j, 2009.
- Noziere, B., Ekstrom, S., Alsberg, T., and Holmstrom, S.: Radical-initiated formation of organosulfates and surfactants in atmospheric aerosols, *Geophys. Res. Lett.*, 37, doi:10.1029/2009gl041683, 2010.
- Peng, C., Ayala, P. Y., Schlegel, H. B., and Frisch, M. J.: Using redundant internal coordinates to optimize equilibrium geometries and transition states, *J. Comput. Chem.*, 17, 49-56, 1996.
- Purvis, G. D., and Bartlett, R. J.: A full coupled-cluster singles and doubles model - the inclusion of disconnected triples, *J. Chem. Phys.*, 76, 1910-1918, doi:10.1063/1.443164, 1982.

- Rothe, E. W., Tang, S. Y., and Reck, G. P.: Measurement of electron affinities of O₃, SO₂, and SO₃ by collisional ionization, *J. Chem. Phys.*, 62, 3829-3831, doi:10.1063/1.430941, 1975.
- Schindelka, J., Iinuma, Y., Hoffmann, D., and Herrmann, H.: Sulfate radical-initiated formation of isoprene-derived organosulfates in atmospheric aerosols, *Faraday Discuss.*, 165, 237-259, doi:10.1039/c3fd00042g, 2013.
- 5 Schweitzer, C., and Schmidt, R.: Physical mechanisms of generation and deactivation of singlet oxygen, *Chem. Rev.*, 103, 1685-1757, doi:10.1021/cr010371d, 2003.
- Seinfeld, J. H., and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 3rd Edition, John Wiley & Sons, Inc., 2016.
- Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin III, R. L., Hyvarinen, A.-P.,
10 Lihavainen, H., and Kulmala, M.: The Role of Sulfuric Acid in Atmospheric Nucleation, *Science*, 327, 1243-1246, doi:10.1126/science.1180315, 2010.
- Su, T., and Chesnavich, W. J.: Parametrization of the ion-polar molecule collision rate-constant by trajectory calculations, *J. Chem. Phys.*, 76, 5183-5185, doi:10.1063/1.442828, 1982.
- Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of
15 acidity on secondary organic aerosol formation from isoprene, *Environ. Sci. Technol.*, 41, 5363-5369, doi:10.1021/es0704176, 2007.
- Surratt, J. D., Gomez-Gonzalez, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, 112, 8345-8378, doi:10.1021/jp802310p, 2008.
- 20 Svensmark, H., Pedersen, J. O. P., Marsh, N. D., Enghoff, M. B., and Uggerhoj, U. I.: Experimental evidence for the role of ions in particle nucleation under atmospheric conditions, *Proc. R. Soc. A*, 463, 385-396, doi:10.1098/rspa.2006.1773, 2007.
- Tang, W., Sanville, E., and Henkelman, G.: A grid-based Bader analysis algorithm without lattice bias, *J. Phys. Condens. Matter*, 21, doi:10.1088/0953-8984/21/8/084204, 2009.
- Tsona, N., Bork, N., and Vehkamäki, H.: Exploring the chemical fate of the sulfate radical anion by reaction with sulfur dioxide
25 in the gas phase, *Atmos. Chem. Phys.*, 15, 495-503, doi:10.5194/acp-15-495-2015, 2015.
- Tsona, N. T., Bork, N., and Vehkamäki, H.: On the gas-phase reaction between SO₂ and O₂⁻(H₂O)₀₋₃ clusters – an ab initio study, *Phys. Chem. Chem. Phys.*, 16, 5987-5992, doi:10.1039/c3cp54715a, 2014.
- Tsona, N. T., Bork, N., Loukonen, V., and Vehkamäki, H.: A Closure Study of the Reaction between Sulfur Dioxide and the Sulfate Radical Ion from First-Principles Molecular Dynamics Simulations, *J. Phys. Chem. A*, 120, 1046-1050, doi:
30 10.1021/acs.jpca.5b12395, 2016.
- Tsona, N. T., Li, J., and Du, L.: From O₂⁻-Initiated SO₂ oxidation to sulfate formation in the gas-phase, *J. Phys. Chem. A*, 122, 5781-5788, doi:10.1021/acs.jpca.8b03381, 2018.

- Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO₂, and SO₂, and their fate in the atmosphere, *Phys. Chem. Chem. Phys.*, 14, 14682-14695, doi:10.1039/c2cp42300f, 2012.
- Wagner, R., Yan, C., Lehtipalo, K., Duplissy, J., Nieminen, T., Kangasluoma, J., Ahonen, L. R., Dada, L., Kontkanen, J., Manninen, H. E., Dias, A., Amorim, A., Bauer, P. S., Bergen, A., Bernhammer, A. K., Bianchi, F., Brilke, S., Mazon, S. B.,
5 Chen, X., Draper, D. C., Fischer, L., Frege, C., Fuchs, C., Garmash, O., Gordon, H., Hakala, J., Heikkinen, L., Heinritzi, M., Hofbauer, V., Hoyle, C. R., Kirkby, J., Kürten, A., Kvashnin, A. N., Laurila, T., Lawler, M. J., Mai, H., Makhmutov, V., Mauldin Iii, R. L., Molteni, U., Nichman, L., Nie, W., Ojdanic, A., Onnela, A., Piel, F., Quéléver, L. L. J., Rissanen, M. P., Sarnela, N., Schallhart, S., Sengupta, K., Simon, M., Stolzenburg, D., Stozhkov, Y., Tröstl, J., Viisanen, Y., Vogel, A. L., Wagner, A. C., Xiao, M., Ye, P., Baltensperger, U., Curtius, J., Donahue, N. M., Flagan, R. C., Gallagher, M., Hansel, A.,
10 Smith, J. N., Tomé, A., Winkler, P. M., Worsnop, D., Ehn, M., Sipilä, M., Kerminen, V. M., Petäjä, T., and Kulmala, M.: The role of ions in new particle formation in the CLOUD chamber, *Atmos. Chem. Phys.*, 17, 15181-15197, doi:10.5194/acp-17-15181-2017, 2017.
- Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du,
15 Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, *Proc. Natl. Acad. Sci.*, 113, 13630, doi:10.1073/pnas.1616540113, 2016.
- Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct kinetic measurements of Criegee intermediate (CH₂OO) formed by reaction of CH₂I with O₂, *Science*, 335, 204-207,
20 doi:10.1126/science.1213229, 2012.
- Yan, C., Dada, L., Rose, C., Jokinen, T., Nie, W., Schobesberger, S., Junninen, H., Lehtipalo, K., Sarnela, N., Makkonen, U., Garmash, O., Wang, Y., Zha, Q., Paasonen, P., Bianchi, F., Sipilä, M., Ehn, M., Petäjä, T., Kerminen, V. M., Worsnop, D. R., and Kulmala, M.: The role of H₂SO₄-NH₃ anion clusters in ion-induced aerosol nucleation mechanisms in the boreal forest, *Atmos. Chem. Phys.*, 18, 13231-13243, doi:10.5194/acp-18-13231-2018, 2018.
- 25 Yu, F.: From molecular clusters to nanoparticles: second-generation ion-mediated nucleation model, *Atmos. Chem. Phys.*, 6, 5193-5211, doi:10.5194/acp-6-5193-2006, 2006.
- Yu, F. Q., and Turco, R. P.: Ultrafine aerosol formation via ion-mediated nucleation, *Geophys. Res. Lett.*, 27, 883-886, doi:10.1029/1999gl011151, 2000.
- Yu, F. Q., and Turco, R. P.: From molecular clusters to nanoparticles: Role of ambient ionization in tropospheric aerosol
30 formation, *J. Geophys. Res.-Atmos.*, 106, 4797-4814, doi:10.1029/2000jd900539, 2001.
- Yu, T., Zhao, D., Song, X., and Zhu, T.: NO₂-initiated multiphase oxidation of SO₂ by O₂ on CaCO₃ particles, *Atmos. Chem. Phys.*, 18, 6679-6689, doi:10.5194/acp-18-6679-2018, 2018.
- Zhang, H., Chen, S., Zhong, J., Zhang, S., Zhang, Y., Zhang, X., Li, Z., and Zeng, X. C.: Formation of aqueous-phase sulfate during the haze period in China: Kinetics and atmospheric implications, *Atmos. Env.*, 177, 93-99,
35 doi:10.1016/j.atmosenv.2018.01.017, 2018.

Zhao, D., Song, X., Zhu, T., Zhang, Z., Liu, Y., and Shang, J.: Multiphase oxidation of SO₂ by NO₂ on CaCO₃ particles, *Atmos. Chem. Phys.*, 18, 2481-2493, doi:10.5194/acp-18-2481-2018, 2018.

5 Zhao, Y., and Truhlar, D. G.: The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Account.*, 120, 215-241, doi:10.1007/s00214-007-0310-x, 2008.

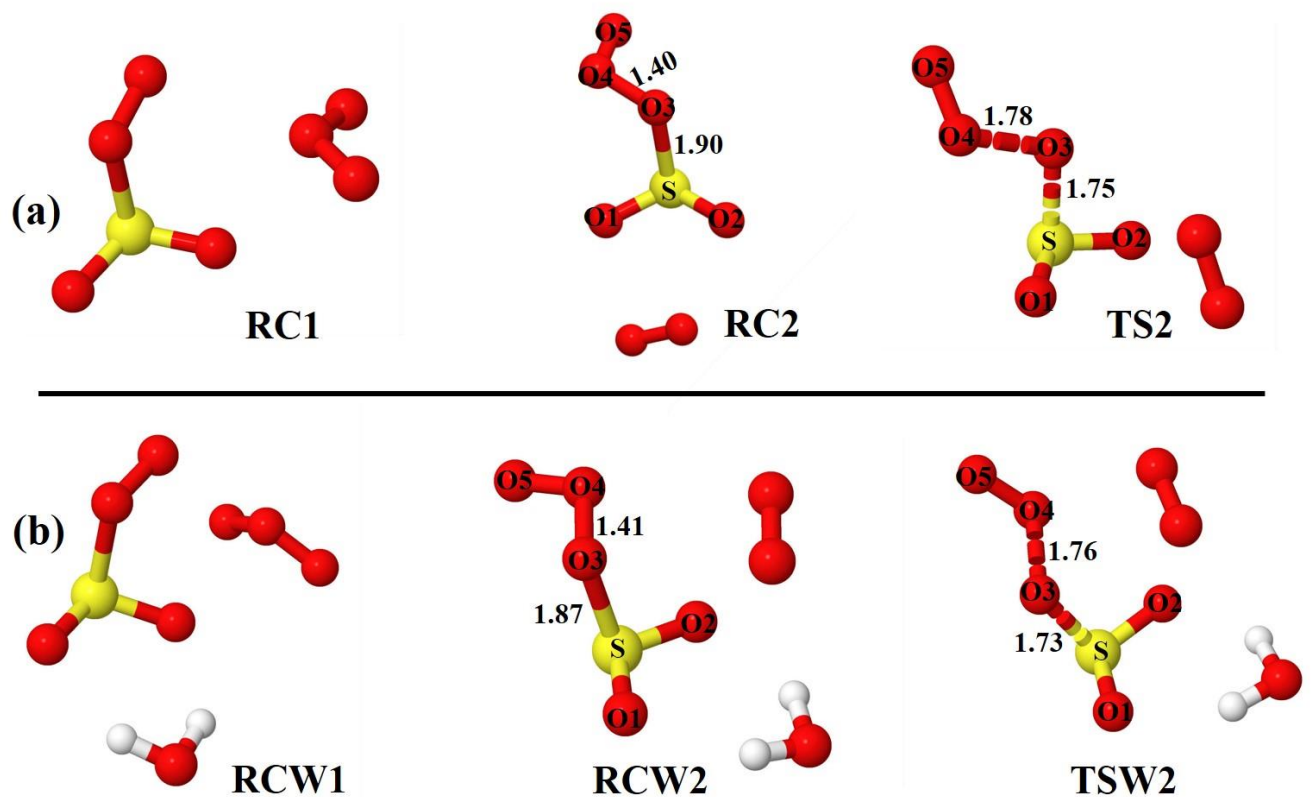


Figure 1: Optimized structures of the most stable intermediates in the $\text{O}_2\text{SOO} + \text{O}_3$ reaction (a) in the absence and (b) in the presence of a single water molecule. Optimizations were performed at the **UM06-2X/aug-cc-pVTZ** level of theory. Lengths (in Å) of some descriptive bonds are indicated. The color coding is yellow for sulfur, red for oxygen and white for hydrogen.

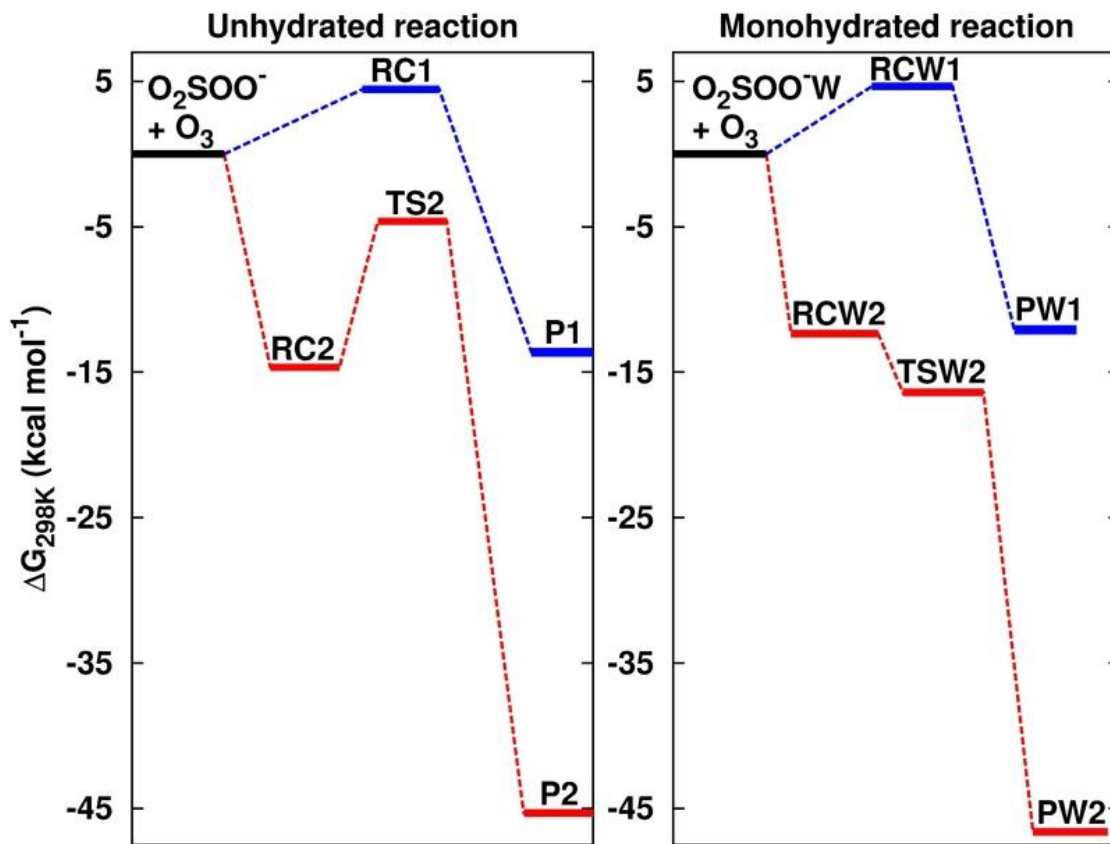


Figure 2: Formation Gibbs free energies of the most stable intermediate species in the $\text{O}_2\text{SOO}^- + \text{O}_3$ reaction in the absence and in the presence of water. “W” is the shorthand notation for water. RC1, RC2, TS2, RCW1, RCW2, and TSW2 structures are shown in Fig. 1. P1 = $\text{O}_2 + \text{SO}_2 + \text{O}_3$, P2 = $\text{SO}_3 + 2\text{O}_2$, PW1 = $\text{O}_2 + \text{SO}_2 + \text{O}_3 + \text{H}_2\text{O}$ and PW2 = $\text{SO}_3 \cdots \text{H}_2\text{O} + 2\text{O}_2$. Calculations were performed at the **UCCSD(T)/aug-cc-pVTZ//UM06-2X/aug-cc-pVTZ** level of theory.

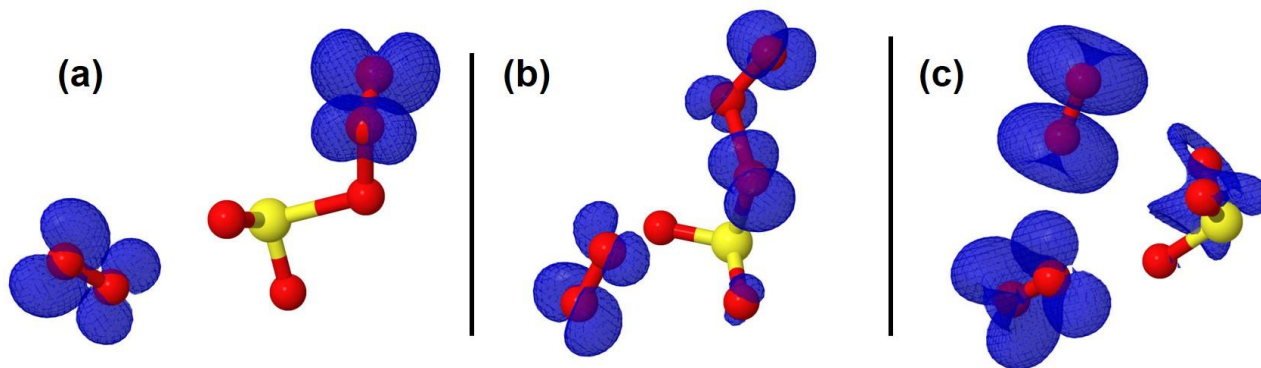


Figure 3: Representation of the spin density (in blue color) on intermediate structures in the $\text{O}_2\text{SOO}^- + \text{O}_3$ reaction. The spin density clearly indicates that the extra electron is progressively distributed over all the atoms from (a) the pre-reactive complex through (b) the transition state to (c) the product complex.

5 Table 1: Electronic energies (ΔE), enthalpies ($\Delta H_{298\text{K}}$) and Gibbs free energies ($\Delta G_{298\text{K}}$) of the different states in the $\text{O}_2\text{SOO}^- + \text{O}_3$ reaction both in the absence and in the presence of water, calculated relative to the energy of initial reactants at the **UCCSD(T)/aug-cc-pVTZ//UM06-2X/aug-cc-pVTZ** level of theory.

Species	ΔE	$\Delta H_{298\text{K}}$	$\Delta G_{298\text{K}}$
Unhydrated reaction			
$\text{O}_2\text{SOO}^- + \text{O}_3$	0	0	0
RC1 = $\text{O}_3 \cdots \text{O}_2\text{SOO}^-$	-5.1	-3.9	4.5
RC2 = $\text{O}_2 \cdots \text{O}_2\text{S}-\text{O}_3^-$	-21.9	-21.0	-14.7
TS2	-11.6	-11.9	-4.6
$\text{SO}_3^- + 2\text{O}_2$	-35.8	-36.4	-45.3
$\text{O}_2 + \text{SO}_2 + \text{O}_3^-$	-1.7	-3.2	-13.6
Monohydrated reaction			
$\text{O}_2\text{SOO}^- \cdots \text{H}_2\text{O} + \text{O}_3$	0	0	0
RCW1 = $\text{O}_3 \cdots \text{O}_2\text{SOO}^- \cdots \text{H}_2\text{O}$	-4.6	-3.4	4.7
RCW2 = $\text{O}_2 \cdots \text{O}_2\text{S}-\text{O}_3^- \cdots \text{H}_2\text{O}$	-21.9	-20.9	-12.4
TSW2	-25.3	-25.4	-16.4
$\text{SO}_3^- \cdots \text{H}_2\text{O} + 2\text{O}_2$	-36.7	-37.4	-46.6
$\text{O}_2 + \text{SO}_2 + \text{O}_3^- + \text{H}_2\text{O}$	10.3	7.1	-12.1