A potential source of atmospheric sulfate from O$_2^-$-induced SO$_2$ oxidation by ozone

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Abstract. It was formerly demonstrated that O$_2$SOO$^-$ 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$_2$SOO$^-$ 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 4.0x10$^{-11}$ cm$^3$ molecule$^{-1}$ 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 modelling 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 (SO\textsubscript{2}), the most abundant sulfur-containing molecule in the atmosphere, is known to oxidize in the gas-phase following different mechanisms to form sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) as the final oxidation species. The main SO\textsubscript{2} oxidizers 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), mineral dust (Harris et al., 2013) and atmospheric ions (Fehsenfeld and Ferguson, 1974; Enghoff et al., 2012; Tsona et al., 2015). Mechanisms involving OH and Criegee intermediates lead to the formation of SO\textsubscript{3} that ultimately forms H\textsubscript{2}SO\textsubscript{4} (Larson et al., 2000), whereas SO\textsubscript{2} reactions with ions are generally more complex. H\textsubscript{2}SO\textsubscript{4} 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), yet the role of ions in this process 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).

The immediate products of SO\textsubscript{2} 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 SO\textsubscript{4}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, and SO\textsubscript{5}\textsuperscript{-}, were detected at relatively high concentrations in the ambient atmosphere (Ehn et al., 2010) and in chamber experiments of SO\textsubscript{2} 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 SO\textsubscript{3}\textsuperscript{-} can form SO\textsubscript{3}, the precursor for H\textsubscript{2}SO\textsubscript{4}, through electron transfer to ozone (O\textsubscript{3}) (Bork et al., 2012). SO\textsubscript{3}\textsuperscript{-} can equally react with O\textsubscript{2} to form SO\textsubscript{4}\textsuperscript{2-} whose atmospheric outcome by reaction with O\textsubscript{3} is H\textsubscript{2}SO\textsubscript{4} formation (Bork et al., 2013). It was also speculated from chamber studies that SO\textsubscript{4}\textsuperscript{2-} 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 SO\textsubscript{4}\textsuperscript{2-} separated by a high energy barrier may exist in the atmosphere (Tsona et al., 2014): the sulfate radical ion henceforth indicated as SO\textsubscript{4}\textsuperscript{2-}, and the peroxy form, O\textsubscript{2}SOO\textsuperscript{-}. Formerly, the two isomers were often misleadingly attributed exclusively to the sulfate radical ion, the most stable form of SO\textsubscript{4}\textsuperscript{2-}. However, their reactive properties greatly differ (Fehsenfeld and Ferguson, 1974).

The formation mechanisms of SO\textsubscript{4}\textsuperscript{2-} in the gas-phase have been largely unknown but, recent studies showed that this ion can be formed by SO\textsubscript{2} reaction with O\textsubscript{3} (Bork et al., 2013) and in a O\textsubscript{3}SOO\textsuperscript{-} isomerization process catalyzed by NO (Tsona et al., 2018). SO\textsubscript{4}\textsuperscript{2-} can also be produced during the chemical transformation of organic compounds, triggered by sulfate salts (Noziere et al., 2010), whereas O\textsubscript{2}SOO\textsuperscript{-} is formed at collision rates upon SO\textsubscript{2} reaction with O\textsubscript{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, it was demonstrated that SO$_4^-$ acts 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$_3$SOO$^-$ is largely unknown but, is potentially important for sulfur chemistry and atmospheric aerosol formation. Fehsenfeld and Ferguson found that O$_3$SOO$^-$ can be decomposed by NO$_2$ into NO$_3^-$ and SO$_3$ (Fehsenfeld and Ferguson, 1974) and it was formerly demonstrated that in the presence of nitrogen oxides (NOx = NO$_2$ + NO), O$_3$SOO$^-$ can be converted into sulfates (Tsona et al., 2018). In mildly polluted environments, the concentration of O$_3$ can be few orders of magnitude higher than that of NOx and the chemical fate of O$_3$SOO$^-$ would then also greatly depend on collisions with O$_3$. In such environments, O$_3$SOO$^-$ could experience much more collisions with O$_3$ than with NOx.

Hereby, we investigate the reaction between O$_3$SOO$^-$(H$_2$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 O$_3$SOO$^-$(H$_2$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

All molecules and stationary points in the energy surface were optimized using density functional theory (DFT) based on the M06-2X density functional (Zhao and Truhlar, 2008), and the aug-cc-pVTZ basis set (Dunning Jr et al., 2001). This functional has successfully proven to be adequate for reactions involving transition state (TS) configurations (Elm et al., 2012, 2013b, a). Harmonic vibrational frequencies analysis on the optimized structures were performed (at 298 K and 1 atm) using the M06-2X/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 M06-2X/aug-cc-pVTZ optimized geometries were corrected with the CCSD(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
\[ G = E_{\text{CCSD(T)}} + G_{\text{therm}} \]  

where \( E_{\text{CCSD(T)}} \) is the electronic energy calculated with the CCSD(T)/aug-cc-pVTZ method and \( G_{\text{therm}} \) is the thermal contribution to the Gibbs free energy, calculated at the M06-2X/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 (http://gaussian.com/).

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). 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 \( \text{O}_2\text{SOO}^- \) and \( \text{O}_3 \) 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:

\[ \text{O}_2\text{SOO}^- + \text{O}_3 \leftrightarrow \text{Pre-reactive intermediate} \rightarrow \text{Products} \]  \hspace{1cm} (R1)

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

\[ k = k_{\text{coll}} \frac{k_{\text{reac}}}{k_{\text{reac}} + k_{\text{evap}}} \]  \hspace{1cm} (2)

where \( k_{\text{coll}} \) is the collision frequency for \( \text{O}_2\text{SOO}^-\text{-O}_3 \) collisions, \( k_{\text{evap}} \) is the rate constant for the evaporation of the pre-reactive intermediate back to initial reactants, and \( k_{\text{reac}} \) 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 \( K_{\text{eq}} \) being the equilibrium constant of formation of the pre-reactive intermediate from the reactants. This consideration is, however, not valid for barrierless reactions, 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...
Based on this theory, the overall rate constant \( (k) \) for a reaction channel is expressed in terms of the outer \( (k_{\text{out}}) \) and inner \( (k_{\text{in}}) \) rate constants as:

\[
\frac{1}{k} = \frac{1}{k_{\text{out}}} + \frac{1}{k_{\text{in}}}
\]  

(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 has been demonstrated 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-Määtä 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-Määtä et al., 2013). It is given as

\[
k_{\text{out}} = k_L \times \left( \frac{(x+0.5990)^2}{10.526} + 0.9754 \right)
\]  

(4)

where \( k_L = q\mu^{-1/2}(\alpha a\varepsilon_0)^{1/2} \), \( x = \mu \rho/(8\pi a\alpha k_B T)^{1/2} \), \( q \) is the charge of the ion, \( \mu \) is the reduced mass of the colliding species, \( \varepsilon_0 \) is the vacuum permittivity, \( a \) and \( \alpha \) are the polarizability and dipole moment of the neutral molecule, \( k_B \) is Boltzmann’s constant, and \( T \) is the absolute temperature. The inner rate constant can be written as:

\[
k_{\text{in}} = \frac{k_B T}{h c^0} \times \exp\left( -\frac{\Delta G^a}{R T} \right)
\]  

(5)

where \( \Delta G^a \) 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.

### 3 Results and discussion

Starting with optimized structures of \( \text{O}_2\text{SOO}^+\cdots(\text{H}_2\text{O})_{0-1} \) and \( \text{O}_3 \) shown in Fig. S1, a series of geometry optimizations were performed on \( \text{O}_2\text{SOO}^+\cdots(\text{H}_2\text{O})_{0-1} + \text{O}_3 \) interaction, 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 barrierless formation of a molecular complex in which the SO₂ entity of O₂SOO····(H₂O)₀.₁ is oxidized to SO₃⁻.

3.1 Cluster formation and decomposition of O₂SOO····(H₂O)₀.₁

As O₃ approaches O₂SOO····(H₂O)₀.₁ towards the oxygen atoms of the peroxy fragment or the oxygen atom of the SO₂ entity, the immediate outcome of O₂SOO····(H₂O)₀.₁ and O₃ collisions is the formation of the van der Waals O₃····O₂SOO····(H₂O)₀.₁ complex in which O₃ interacts with O₂SOO⁻. 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 RC1 and RCW1 structures reveals that O₂SOO····(H₂O)₀.₁ basically keeps its configuration upon clustering with O₃. Their formations are endergonic at most atmospheric temperature, with Gibbs free energy changes of 4.5 and 4.7 kcal mol⁻¹, respectively, at 298 K. These values indicate that, when formed, these complexes would not live long and will rather decompose either to initial reactants or to different species. Inspecting the vibrational modes of RC1 and RCW1, two vibrations are found that would clearly lead to the dissociation of O₂SOO⁻ within the cluster. The analysis of the charge distribution over O₃····O₂SOO····(H₂O)₀.₁ shows that the extra electron initially located on O₂SOO⁻ in the reactants has partially migrated to the O₃ molecule in the van der Waals product complex, as can be observed in Fig. S2. This is as expected, given the high electronegativity of O₃ relative to those of O₂ and SO₂ (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 O₂, SO₂ and O₃⁻ as follows:

\[
O₂SOO····(H₂O)₀.₁ + O₃ \leftrightarrow O₃····O₂SOO····(H₂O)₀.₁ \rightarrow O₂ + SO₂ + O₃⁻ + (H₂O)₀.₁ \quad (R2)
\]

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 O₃····O₂SOO····(H₂O)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 O₂ + SO₂ + O₃⁻. 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 $\text{O}_2\text{SOO}^-\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ reaction with $\text{O}_3$

When $\text{O}_3$ approaches $\text{O}_2\text{SOO}^-\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ from the sulfur atom side, the formation of a more stable cluster than found above prevails. The incoming $\text{O}_3$ molecule strongly interacts with $\text{O}_2\text{SOO}^-\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ by forming a coordination bond with the sulfur atom and hereby, inducing the ejection of the $\text{O}_2$ molecule that remains in interaction with the remainder of the system. This process leads to the formation of the $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ complex which further transforms, through an intramolecular $\text{SO}_2$ oxidation, into $\text{SO}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1} + 2\text{O}_2$ according to the following equation:

$$\text{O}_2\text{SOO}^-\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1} + \text{O}_3 \leftrightarrow \text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1} \rightarrow \text{SO}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1} + 2\text{O}_2$$  \hspace{1cm} (R3)

The configurations of the most stable intermediate structures in reaction (R3) are given in Fig. 1. The charge analysis indicated that the oxygen molecules released in the products are in the singlet state. Though the necessity to determine the electronic structure of the $\text{O}_2$ molecule in the singlet state $^1\Delta_g$ has been demonstrated to be useful (Buttar and Hirst, 1994), obtaining a reliable electronic energy for $\text{O}_2^1\Delta_g$ 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 $\text{O}_2$ to the computed electronic energy of the triplet $\text{O}_2$ (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 $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ 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 $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot\text{SO}_2$ configuration results from $\text{O}_3$ being switched by $\text{O}_3$ in the $\text{O}_2\text{SOO}^-$ molecular ion. In the optimized $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot\text{SO}_2$ structure, the $\text{O}_3$ atom of $\text{O}_3$ points towards the S atom of $\text{O}_2\text{SOO}^-$, forming $\text{S}\cdot\cdot\cdot\text{O}_3$ 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 $\text{SO}_3$ and 1.46 Å in $\text{H}_2\text{SO}_4$. The $\text{S}\cdot\cdot\cdot\text{O}_3$ coordination bond distances in RC2 and RCW2 are shorter by 0.04 and 0.03 Å than $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot\text{O}_3$ bond distances in unhydrated and monohydrated $\text{O}_2\text{SOO}^-$ forms. This indicates stronger interaction between $\text{O}_3$ and $\text{SO}_2$, and hence higher stability of $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot\text{O}_3$ relative to $\text{O}_2\text{SOO}^-$. 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. $\text{SO}_2$ oxidation can readily occur within the $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ cluster and lead to $\text{SO}_3$ formation. In principle, to form the products of reaction (R3), the $\text{O}_3$ atom of the $\text{O}_3$ fragment in $\text{O}_2\cdot\cdot\cdot\text{O}_3\cdot\cdot\cdot(\text{H}_2\text{O})_{0.1}$ transfers, through transition state configurations, to $\text{SO}_2$ and form $\text{SO}_3$ followed by the ejection of the $\text{O}_2$ 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. The S-O3 bonds in RCW2 and TSW2 are shorter by ~0.03 Å than in RC2 and TS2.

Based on TS2 and TSW2 energies, the unimolecular decomposition of O$_2$···O$_2$S···O$_3$ at 298 K was found to occur at rate constants of 3.1×10$^5$ s$^{-1}$ and 6.5×10$^{15}$ s$^{-1}$, corresponding to atmospheric lifetimes of 3.3×10$^3$ ns and 1.5×10$^{-7}$ ns for the unhydrated and monohydrated systems, respectively. The obtained short lifetimes indicate that O$_2$···O$_2$S···O$_3$ 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 O$_2$···O$_2$S···O$_3$ is decomposition to the products of reaction (R3), which are formed with about -23 kcal mol$^{-1}$ overall Gibbs free energy at 298 K. The net reaction is an O$_2$-initiated SO$_2$ oxidation to SO$_3$ by O$_3$.

The charge analysis clearly indicates that the extra electron, initially confined on the atoms of the O$_3$ fragment of O$_2$···O$_2$S···O$_3$ (RC2 structure), is partially distributed over other atoms in the transition state (TS2) and is finally located on SO$_3$ in the product (see Fig. 3). Apparent also from Fig. 3 is the antibonding orbital of the singlet O$_2$ molecule.

The overall rate constants of reaction (R3), determined at 298.15 K using Eq. (3), are 1.3×10$^{-14}$ and 8.0×10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the unhydrated and monohydrated reactions, respectively. The values of the different components ($k_{\text{out}}$ and $k_{\text{in}}$) 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 dominated bottleneck to the rate constant of the monohydrated reaction.

The effective effect of water on the rate constant can be evaluated by taking into account the stability of O$_2$SOO···H$_2$O (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,

$$J_{(R3w)} = k_{(R3w)} \times [O_2SOO\cdots H_2O] \times [O_3]$$  \hspace{1cm} (6)

$$= k'_{(R3w)} \times [O_2SOO] \times [O_3]$$ \hspace{1cm} (7)
where $k_{(R3w)}$ is the overall rate constant for the hydrated reaction, determined using Eq. (3), $k_{\text{eff}(R3w)}$ is the effective reaction rate constant calculated as $k_{\text{eff}(R3w)} = k_{(R3w)} \times K_{\text{eq}} \times p_{\text{H}_2\text{O}}$. $K_{\text{eq}}$ is the equilibrium constant for the $\text{O}_2\text{SOO}^- + \text{H}_2\text{O} \leftrightarrow \text{O}_2\text{SOO}^\cdot\cdots\text{H}_2\text{O}$ reaction and $[\text{H}_2\text{O}]$ the actual water vapor pressure. Details on the determination of $K_{\text{eq}}$ and $p_{\text{H}_2\text{O}}$ are given in the Supplement.

At 298 K and 50 % relative humidity, the effective rate constant of the monohydrated reaction is $1.7 \times 10^{10}$ cm$^3$ molecule$^{-1}$ 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 $\text{O}_2\text{SOO}^- + \text{H}_2\text{O} \leftrightarrow \text{O}_2\text{SOO}^\cdot\cdots\text{H}_2\text{O}$ hydrates. Using the law of mass action, we find that $\text{O}_2\text{SOO}^- + \text{H}_2\text{O} \leftrightarrow \text{O}_2\text{SOO}^\cdot\cdots\text{H}_2\text{O}$ mostly exists as a dry species, constituting 77% of the total population, whereas the monohydrated species is formed at 23%. The net rate constant of reaction (R3) is then determined to be $4.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ 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 $\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3^\cdot + \text{O}_2$ reaction (Fehsenfeld and Ferguson, 1974; Bork et al., 2012). Despite this difference, the oxidation process follows a similar mechanism to the one presented by Bork et al. for the $\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3^\cdot + \text{O}_2$ reaction, consisting of the oxygen transfer from $\text{O}_3$ to $\text{SO}_2$ (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 $\text{SO}_2$ in the current study, which tends to stabilize the $\text{O}_2\cdots\text{O}_2\text{S}–\text{O}_3^\cdot$ pre-reactive complex. The presence of the O–O fragment seemingly deactivates $\text{SO}_2$ for the upcoming O transfer from $\text{O}_3$ to form $\text{SO}_3^\cdot$. However, this situation is rapidly reversed with the presence of water as the reaction becomes much faster, proceeding nearly at collision rate.

### 3.3 Further chemistry

In real atmospheric and ionized conditions, despite $\text{O}_2$ has lower electron affinity than $\text{O}_3$, it would likely ionize faster than $\text{O}_3$ 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., $\text{O}_2^-$ can form and rapidly hydrate within one nanosecond (Svensmark et al., 2007; Fahey et al., 1982). Furthermore, Fahey et al. showed that $\text{O}_2\cdots(\text{H}_2\text{O})_{0.1}$ association reaction with $\text{SO}_2$ is faster than the electron transfer from $\text{O}_2\cdots(\text{H}_2\text{O})_{0.1}$ to $\text{O}_3$ (Fahey et al., 1982). This means that in an ionized environment containing $\text{O}_2$, $\text{O}_3$, and $\text{SO}_2$, the formation of $\text{O}_2\text{SOO}^-$ resulting from $\text{SO}_2$ and $\text{O}_2^-$ association will happen faster than $\text{O}_3^-$ formation. $\text{O}_2\text{SOO}^-$ would react thereafter with $\text{O}_3$ and the following stepwise process could take place

\[
\text{O}_2\cdots(\text{H}_2\text{O})_{0.1} + \text{SO}_2 \rightarrow \text{O}_2\text{SOO}^-\cdots(\text{H}_2\text{O})_{0.1} \quad \text{(R4a)}
\]
\[
\text{O}_2\text{SOO}^-\cdots(\text{H}_2\text{O})_{0.1} + \text{O}_3 \rightarrow \text{O}_2\cdots\text{O}_2\text{SO}_3^-\cdots(\text{H}_2\text{O})_{0.1} \quad \text{(R4b)}
\]
The Gibbs free energy change of this net reaction at 298 K is about -20 kcal mol$^{-1}$ more negative than that of the SO$_2$ + O$_3$ → 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$_3$ 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$_2$SO$_4$ by hydration. Likely outcomes of SO$_3^-$ are hydrolysis, electron transfer by collision with O$_3$, reaction with O$_2$ and H$_2$O and, possibly, radicals, according to the following equations

$$\text{SO}_3^- + \text{H}_2\text{O} \rightarrow \text{SO}_3\ldots\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + e^- \quad \text{(R5)}$$

$$\text{SO}_3^- + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_3^- \quad \text{(R6)}$$

$$\text{SO}_3^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{HO}_2 \quad \text{(R7)}$$

$$\text{SO}_3^- + \text{OH} \rightarrow \text{HSO}_4^- \quad \text{(R8)}$$

Fehsenfeld and Ferguson showed that H$_2$SO$_4$ formation could occur in the SO$_3\ldots\text{H}_2\text{O}$ 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$_2$SO$_4$, the most oxidized forms of sulfur 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 $\sim 10^7$ 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 sulfates, it is necessary to identify the scavengers that terminate the SO$_2$ oxidation initiated by O$_2$. Possible scavengers include radicals, NOx, acids, cations and other particles. The main ones are...
likely NOx and OH, which lead to the formation of the stable NO\textsubscript{3} and HSO\textsubscript{4}\textsuperscript{-} species. If the ion concentration was known, the contribution of reaction (R4) to H\textsubscript{2}SO\textsubscript{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):

$$\text{TON} = \frac{\text{concentration of limiting reacted molecules}}{\text{concentration of the catalyst}}$$ \hspace{1cm} (8)

The concentration of the catalyst can be approximated to the concentration of the scavengers and, assuming [O\textsubscript{3}]>>[SO\textsubscript{2}], SO\textsubscript{2} is the limiting species in reaction (R4). Equation (8) can then be re-written as

$$\text{TON} \approx \frac{[\text{SO}_2]}{[\text{OH}]+[\text{NO}_x]}$$ \hspace{1cm} (9)

The catalytic efficiency of SO\textsubscript{2} ion-induced oxidation is then given as

$$J_{\text{ion}} = k_{\text{ion}} \times \text{TON}$$ \hspace{1cm} (10)

Where $k_{\text{ion}}$ is the ion production rate. Depending on the tropospheric temperature and altitude, measurements at the CLOUD chamber experiments found $k_{\text{ion}} = 2$–100 cm\textsuperscript{-3} s\textsuperscript{-1}, covering the typical ionization range in the troposphere (Franchin et al., 2015). Assuming nearly pristine conditions with [SO\textsubscript{2}] = 5 ppb = 1.2×10\textsuperscript{11} molecule cm\textsuperscript{-3}, [NO\textsubscript{x}] = 200 ppt = 4.9×10\textsuperscript{9} molecule cm\textsuperscript{-3}, and [OH] = 5.0×10\textsuperscript{5} molecule cm\textsuperscript{-3} (day and night average), we determine $J_{\text{ion}}$ in the range 5.0×10\textsuperscript{1}–2.5×10\textsuperscript{3} cm\textsuperscript{-3} s\textsuperscript{-1}. The rate of the UV-induced SO\textsubscript{2} oxidation by OH is

$$J_{\text{UV}} = k_{\text{UV}} \times [\text{SO}_2] \times [\text{OH}]$$ \hspace{1cm} (11)

With $k_{\text{UV}} = 1.3 \times 10\textsuperscript{-12}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} (Atkinson et al., 2004), $J_{\text{UV}} = 7.9 \times 10\textsuperscript{4}$ molecule cm\textsuperscript{-3} s\textsuperscript{-1}, and the proportion of H\textsubscript{2}SO\textsubscript{4} formed from ion-induced oxidation can be estimated from the following equation

$$\frac{[\text{H}_2\text{SO}_4]_{\text{ion}}}{[\text{H}_2\text{SO}_4]_{\text{total}}} = \frac{J_{\text{ion}}}{J_{\text{ion}} + J_{\text{UV}}/(\text{ion})}$$ \hspace{1cm} (12)
We find that the contribution of ion-induced SO₂ oxidation to H₂SO₄ formation can range from 0.1 to 3.1% of the total formation rate. This estimate could be improved by considering also the SO₂ oxidation by Criegee Intermediates, another important channel for H₂SO₄ formation.

3 Conclusions

This study highlights the role of the superoxide ions (O₂⁻) in SO₂ oxidation. Our previous study demonstrated that SO₂ interacts with O₂⁻ and forms O₂SOO⁻ whose atmospheric fate remains unelucidated (Tsona et al., 2014). In this study, we used ab initio calculations to assess the chemical fate of O₂SOO⁻ by collisions with O₃. 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 O₂SOO decomposition, leading to O₁⁻ formation and releasing SO₂. The chemistry of SO₂ + O₃⁻ has been explored elsewhere. The second mechanism is characterized by SO₂ 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, O₂⁻ + SO₂ + O₃⁻ → SO₃⁻ + 2O₂, is faster and more energetically favorable than the SO₂ + O₃⁻ → SO₃⁻ + O₂ reaction, thereby highlighting the positive role of O₂⁻ in SO₂ ionic oxidation. Hence, the two reactions may compete in chamber experiments and in the atmosphere.

While for the electron transfer and O₂SOO 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 4.0×10⁻¹² cm³ molecule⁻¹ s⁻¹ at 298 K for the oxidation reaction. Hence, this reaction proceeds nearly at collision rate. The main species (SO₃⁻) in the end products of the studied 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.

Author contributions

NTT and LD designed the work. NTT performed all calculations and wrote the manuscript. LD edited the manuscript.

Competing interests

The authors declare that they have no conflict of interest.
Acknowledgements

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Figure 1: Optimized structures of the most stable intermediates in the $\text{O}_2\text{SOO}^- + \text{O}_3$ reaction in the absence (a) and in the presence (b) of a single water molecule. Optimizations were performed at the M06-2X/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 = \( \text{SO}_3^-\cdot\cdot\cdot\text{H}_2\text{O} + 2\text{O}_2 \). Calculations were performed at the CCSD(T)/aug-cc-pVTZ//M06-2X/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.
Table 1: Electronic energies ($\Delta E$), enthalpies ($\Delta H_{298K}$) and Gibbs free energies ($\Delta G_{298K}$) of the different states in the O$_2$SOO$^-$ + O$_3$ reaction both in the absence and in the presence of water, calculated relative to the energy of initial reactants at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta E$</th>
<th>$\Delta H_{298K}$</th>
<th>$\Delta G_{298K}$</th>
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<tr>
<td><strong>Unhydrated reaction</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>O$_2$SOO$^-$ + O$_3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>RC1=O$_3$⋯O$_2$SOO$^-$</td>
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<tr>
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<td>-21.0</td>
<td>-14.7</td>
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<td>-11.9</td>
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</tr>
<tr>
<td>SO$_3^-$ + 2O$_2$</td>
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<td>-13.9</td>
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<tr>
<td><strong>Monohydrated reaction</strong></td>
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<td>0</td>
<td>0</td>
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<td>-20.9</td>
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<td>7.1</td>
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