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

N. T. Tsona1, N. Bork1,2, and H. Vehkamäki1

1Division of Atmospheric Sciences, Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland
2Department of Chemistry, University of Copenhagen, 2100, Copenhagen, Denmark

Correspondence to: N. T. Tsona (narcisse.tsonatchinda@helsinki.fi)

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Abstract. The gas phase reaction between SO$_4^-$ (H$_2$O)$_n$ and SO$_2$, $n = 0$–2, is investigated using ab initio calculations and kinetic modelling. Structures of reactants, transition states and products are reported. Our calculations predict that the SO$_2$SO$_4^-$ (H$_2$O)$_n$ cluster ion, which is formed upon SO$_2$ and SO$_4^-$ (H$_2$O)$_n$ collision, can isomerize to SO$_3$SO$_4^-$ (H$_2$O)$_n$. The overall reaction is SO$_2$ oxidation by the SO$_4^-$ (H$_2$O)$_n$ anionic cluster. The results show that SO$_4^-$ (H$_2$O)$_n$ is a good SO$_2$ oxidant, especially at low relative humidity, with a reaction rate constant up to $1.5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. At high relative humidity, instead, the re-evaporation of SO$_2$ from the SO$_2$SO$_4^-$ (H$_2$O)$_n$ cluster ion is favoured.

1 Introduction

The sulfur cycle is one of the most important cycles in the atmosphere as sulfur oxidation products, most notably sulfuric acid ($\text{H}_2\text{SO}_4$), have a significant contribution in the formation of acid rain, aerosols, and clouds. The most abundant sulfurous molecule in the atmosphere is sulfur dioxide ($\text{SO}_2$), emitted from volcanoes and fossil fuel combustion. The major atmospheric sink of $\text{SO}_2$ is its oxidation in the gas phase, mostly by the hydroxyl radical (OH) in a UV-light-induced mechanism. This mechanism is well known to be the predominant source of atmospheric $\text{H}_2\text{SO}_4$. Other important $\text{SO}_2$ oxidation mechanisms involve 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 (Enghoff et al., 2012; Bork et al., 2013a).

The ionic $\text{SO}_2$ oxidation mechanism in the gas phase is more complex than the neutral oxidation since many oxidant SO$_2$ anions can be formed, and each of them may trigger new reactions. In many gas phase laboratory studies, the SO$_3^-$, SO$_4^-$, and SO$_5^-$ anions have been observed as ionic SO$_2$ oxidation products (Fehsenfeld and Ferguson, 1974; Fahey et al., 1982; Möhler et al., 1992). However, their further reactions in the gas phase are still not well known. Using quantum chemical calculations, Bork et al. (2013a) investigated the chemical fate of SO$_5^-$ after collisions with O$_3$, and found that SO$_5^-$ is one of the reaction end products. As opposed to SO$_4^{2-}$, which does not exist in the atmosphere as a free species (Boldyrev and Simons, 1994; Wang et al., 2000), the SO$_4^-$ anion and the other anions mentioned above were recently detected in a boreal forest in Finland (Ehn et al., 2010) and in the CLOUD aerosol chamber (Kirkby et al., 2011). Despite these observations, the further chemistry of SO$_4^-$ in the gas phase remains poorly understood.

The reactive properties of SO$_4^-$ in the gas phase were first studied by Fehsenfeld and Ferguson (1974). They observed that SO$_4^-$ binds efficiently to $\text{SO}_2$, but neither the structure, further outcome, nor the effect of hydration on the resulting cluster was examined. We present an in-depth investigation of the gas phase reaction between SO$_4^-$ and $\text{SO}_2$ at standard conditions, including up to two water molecules. The main pathways in this reaction are depicted in Fig. 1. We used ab initio calculations to determine structures and formation energies of reactants, reactant complexes (RCs), transition states (TSs), and products. The reaction rate constants were calculated, the effect of hydration on the reactions was ex-
and a much higher binding energy, corresponding to reaction (R1) for the latter. We may therefore conclude that the conversion of \( \text{SO}_2\text{SO}_4^- \) to \( \text{SO}_3\text{SO}_3^- \) is not instantaneous since, otherwise, the oxygen transfer reaction would have taken place in the experimental apparatus and a much higher binding energy, corresponding to Reaction (R2), would have been measured.

\[
\text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_2\text{SO}_4^- \quad \text{or to} \quad \text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^- .
\]

However, ab initio calculations clearly indicate that the measured thermodynamics correspond to the former of these reactions, e.g. PW91/aVDZ predicting \(-6.6 \text{ kcal mol}^{-1}\) for the former while \(-9.0 \text{ kcal mol}^{-1}\) for the latter. We may therefore conclude that the conversion of \( \text{SO}_2\text{SO}_4^- \) to \( \text{SO}_3\text{SO}_3^- \) is not instantaneous since, otherwise, the oxygen transfer reaction would have taken place in the experimental apparatus and a much higher binding energy, corresponding to Reaction (R2), would have been measured.

From Table 1 it can be seen that PW91 predicts a transition state located 3.8 \text{ kcal mol}^{-1} below the separated reactants, predicting immediate conversion of \( \text{SO}_2\text{SO}_4^- \) to \( \text{SO}_3\text{SO}_3^- \). According to the above considerations, this is inconsistent with the experimental data. It is therefore likely that PW91 underestimates the height of the energy barrier although no quantification can be made.

On the other hand, B3LYP and CAM-B3LYP predict barriers of 7.8 and 9.3 \text{ kcal mol}^{-1}, respectively. In order to obtain a conservative estimate of the atmospheric importance of the \( \text{SO}_2 + \text{SO}_4^- \rightarrow \text{SO}_3\text{SO}_3^- \) reaction rather than an upper limit, we choose the CAM-B3LYP functional for our calculations. However, since the CAM-B3LYP functional, according to Table 1, has a tendency of underbinding it should be noted that CAM-B3LYP is likely to overpredict cluster re-evaporation and hence underpredict the rates of Reactions (R3) and (R2).

It is well known that single-point coupled cluster electronic energy calculations performed on the CAM-B3LYP/aVDZ optimized geometries improve estimates of the Gibbs free energy change (Bork et al., 2014a, b; Tsona et al., 2014). Test calculations were carried out using the explicitly correlated coupled cluster singles, doubles, and perturbative triples method CCSD(T) (Porvis and Bartlett, 1982) with the aVDZ and aVTZ basis sets, and the CCSD(T)-F12 method (Alder et al., 2007; Peterson et al., 2008) with the VDZ-F12 and VTZ-F12 basis sets (Peterson et al., 2008) (see Table 1). All species with an unpaired number of electrons were treated with UCCSD(T) (or UCCSD(T)-F12) based on a restricted open-shell Hartree–Fock reference. The total formation Gibbs free energy \( \Delta G \) of a reaction was calculated as

\[
\Delta G = \Delta G_{\text{DFT}} - \Delta E_{\text{DFT}} + \Delta E_{\text{CCSD(T)}},
\]

where \( \Delta G_{\text{DFT}} \) denotes the Gibbs free energy change of the reaction calculated with DFT, and where \( \Delta E_{\text{DFT}} \) and \( \Delta E_{\text{CCSD(T)}} \) are electronic energy changes calculated with DFT and the CCSD(T) (or CCSD(T)-F12), respectively. Note that the structures are not optimized at the CCSD(T) and CCSD(T)-F12 levels of theory.

From Table 1 it is apparent that no systematic improvement of the DFT results are obtained at increasing quality of the coupled cluster single-point calculations. Although CCSD(T)/aVDZ is the least complex of the tested coupled cluster calculations, we find that this method, when used in combination with CAM-B3LYP/aVDZ on these systems, provides the results in best agreement with the experiment, most likely due to fortunate error cancellation. Considering also the extended computational expense of the different methods, we chose the CCSD(T)/aVDZ method for electronic energy correction throughout this study. The T1 and D1 diagnostic values on CCSD(T)/aVDZ calculations were typically between 0.02 and 0.04, and 0.07 and 0.28, respectively. These values indicate a low to modest multi-reference character for the computed species, and thus the
Energy units are kcal mol\(^{-1}\). Corrected Gibbs free energies are calculated according to Eq. (1). Experimental data from Fehsenfeld and Ferguson (1974) are included.

### Table 1. Comparison of Gibbs free energy changes of the indicated reactions calculated by different DFT functionals, all using the aug-cc-pVDZ (aVDZ) basis set. Electronic energy corrections are performed using the indicated coupled cluster methods and basis sets and the corrected Gibbs free energies are calculated according to Eq. (1). Experimental data from Fehsenfeld and Ferguson (1974) are included. Energy units are kcal mol\(^{-1}\).

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

The CCSD(T)/aVDZ method should describe reasonably well the reactions energetics explored in this study.

Often, anisotropy is an important issue to address when treating sterically hindered collisions. Related to this, our previous molecular dynamics simulation of SO\(_2\) and the \(\text{O}_3^+(\text{H}_2\text{O})_5\) ionic cluster showed an overall sticking probability of ca. 75\% (Bork et al., 2013b). The sticking probability for the \(\text{SO}_2 + \text{SO}_4^- (\text{H}_2\text{O})_n\) collision is likely to be even higher due to the lower number of water molecules. Considering also the uncertainties on the evaporation rates and reaction rates from the ab initio based thermodynamics, anisotropy seems of minor importance. In support of this, experimental studies on numerous ion–dipole reactions reported collision-limited reaction rates (see, e.g. Fehsenfeld and Ferguson, 1974).

The TS structures were obtained by configurational energy scans along the reaction coordinate with a step size down to 0.01 Å starting from the RC. The configurations closest to the TS were thereafter refined using the synchronous transit quasi-Newton method (Peng et al., 1996). A single imaginary frequency, corresponding to the correct reaction coordinate, was found in all TS structures. Finally, intrinsic reaction coordinate calculations (Fukui, 1981) were performed on all TSs to ensure their connectivity to the desired reactants and products. All structure optimizations and vibrational frequency calculations were carried out using the Gaussian 09 package (Frisch et al., 2009) while single-point coupled cluster calculations were performed using the Molpro program (Werner et al., 2012a, b).

### 3 Results and discussions

#### 3.1 Thermodynamics

The initial collisions between SO\(_2\) and SO\(_4^-\) (H\(_2\)O)\(_n\) led to the barrierless formation of SO\(_2\)SO\(_4\)(H\(_2\)O)\(_n\) cluster complexes as

\[
\text{SO}_2 + \text{SO}_4^- (\text{H}_2\text{O})_n \rightarrow \text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n. \tag{R3}
\]

The structures of the SO\(_2\)SO\(_4\)(H\(_2\)O)\(_n\) clusters were thereby optimized and they are shown in Fig. 2a. Regardless of the degree of hydration, one SO\(_4^-\) oxygen atom is clearly coordinating the SO\(_2\) sulfur atom. The Gibbs free energy changes of Reaction (R3) are shown in Fig. 3 and the numerical values are given in the Supplement. In this work we limit the hydration range to two since several of the water molecules initially bound to SO\(_4^-\) will evaporate after collision with SO\(_2\), leaving the SO\(_2\)SO\(_4^-\) cluster ion mostly dehydrated. See also Fig. 4 and Supplement Fig. S2.

Under standard conditions, we determined the binding Gibbs free energy of SO\(_2\) and SO\(_4^-\) (H\(_2\)O)\(_n\) to be \(\Delta G_o(R3) = -5.6, -3.6\), and \(-2.5\) kcal mol\(^{-1}\) for \(n = 0, 1\), and 2, respectively. The decrease in Gibbs free energy gain with increasing degree of hydration is most likely a result of the reduced electrostatic strain of the SO\(_4^-\) (H\(_2\)O)\(_n\) cluster. Experimental data are available from Fehsenfeld and Ferguson (1974), who found \(\Delta G_o(R3) = -6.7\) kcal mol\(^{-1}\) for \(n = 0\). We can conclude that our calculations somewhat underestimate the experimental binding energy of SO\(_2\) and SO\(_4^-\) at standard conditions.

Since Reaction (R3) is distinctly exothermic, the SO\(_2\)SO\(_4\)(H\(_2\)O)\(_n\) clusters are formed with a large amount of excess internal energy, which may lead to partial H\(_2\)O evaporation. The SO\(_2\) in the cluster may thereafter oxidize (Reaction R4a) or re-evaporate to form the initial reactants (Reaction R4b) as

\[
\text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n \rightarrow \begin{cases} 
\text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n, & \text{(a)} \\
\text{SO}_2 + \text{SO}_4^- (\text{H}_2\text{O})_n. & \text{(b)} 
\end{cases} \tag{R4}
\]

The structures of the TSs and the products of Reaction (R4a) were optimized and their geometries are shown in Fig. 2b and c, respectively. Reaction (R4a) is exothermic (\(\Delta G_o(R4a) = -3.9, -3.6\), and \(-2.6\) kcal mol\(^{-1}\) for \(n = 0, 1, 2\), respectively), albeit there exists an energy barrier towards the formation of the products. The Gibbs free energy barriers for \(n = 0, 1, 2\) were determined to be 10.0, 8.8, and 10.8 kcal mol\(^{-1}\), respectively. In Reaction (R4a), one SO\(_4^-\)
oxygen atom is transferred to the SO₂ sulfur atom by forming a SOS linkage through a TS configuration. The S–O bond lengths in the SOS linkage of the TS are ca. 1.65 Å and 2.06 Å on the SO₄ and SO₂ sides, respectively, and they are weakly altered by the hydration. The structures of the TS and SO₃SO₃⁻(H₂O)ₙ clusters are very similar; they mostly differ by the lengths of S–O bonds in the SOS linkage. For the SO₃SO₃⁻(H₂O)ₙ structures, the S–O bonds in the SOS linkage are longer on the former SO₄ side than on the for-

Figure 2. Configurations of the most stable structures of (a) SO₂SO₄⁻(H₂O)₀₋₂, (b) TS, and (c) SO₃SO₃⁻(H₂O)₀₋₂. Descriptive bond lengths (in angstroms) in the SOS linkage are included. The colour coding is red for oxygen, yellow for sulfur, and white for hydrogen.

Figure 3. Gibbs free energies of formation of the most stable species involved in the reaction between SO₂ and SO₄⁻(H₂O)ₙ. All the Gibbs free energies are calculated relative to SO₂ + SO₄⁻(H₂O)ₙ. “TS” denotes the transition state. Numerical values are given in the Supplement.

Figure 4. Hydration Gibbs free energy of the SO₄⁻, SO₂SO₄⁻, and SO₃SO₃⁻ ions at standard conditions. The black dotted line delimits the domains where water condensation is favoured (below the dotted line) and where water evaporation is favoured (above the dotted line).
mer SO₂ side. The SO₃SO₄⁻(H₂O)ₙ clusters can thus be regarded as SO₃⁻(H₂O)ₙ and SO₃ donor–acceptor interaction products.

3.2 Kinetics

Considering Reactions (R3), (R4a), and (R4b), we can use the steady-state approximation for SO₂SO₄⁻(H₂O)ₙ and obtain

\[ k_{\text{coll},(R3)}[\text{SO}_2][\text{SO}_4^- (\text{H}_2\text{O})_n] = (k_{\text{ox},(R4a)} + k_{\text{evap},(R4b)})[\text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n], \]

where \( k_{\text{coll},(R3)} \) is the collision rate constant of SO₂ and SO₄⁻(H₂O)ₙ, \( k_{\text{ox},(R4a)} \) is the rate constant of SO₂ oxidation in the RC, and \( k_{\text{evap},(R4b)} \) is the rate constant of RC dissociation to form the initial reactants.

The reaction rate of SO₂ oxidation in the SO₂SO₄⁻(H₂O)ₙ complex can be written as

\[ r_{\text{ox},(R4a)} = k_{\text{ox},(R4a)}[\text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n], \]

\[ = k_{\text{ox, bimol}}[\text{SO}_2][\text{SO}_4^- (\text{H}_2\text{O})_n], \]

where the bimolecular rate constant \( k_{\text{ox, bimol}} \) of the SO₂ + SO₄⁻(H₂O)ₙ reaction is obtained by combining Eqs. (2) and (3) as

\[ k_{\text{ox, bimol}} = k_{\text{coll}, (R3)} \frac{k_{\text{ox},(R4a)}}{k_{\text{ox},(R4a)} + k_{\text{evap},(R4b)}}. \]

The evaporation rate constant, \( k_{\text{evap},(R4b)} \), is determined from the detailed balance condition (Vehkamäki, 2006; Ortega et al., 2012) as

\[ k_{\text{evap},(R4b)} = k_{\text{coll},(R3)} \times \rho_{\text{atm}} \times \exp \left( -\frac{\Delta G_{\text{evap},(R4b)}^0}{R T} \right), \]

where \( \rho_{\text{atm}} \) is the standard density (at \( T = 298.15 \) K and \( p = 1 \) atm, \( \rho_{\text{atm}} = 2.5 \times 10^{19} \) molecule cm⁻³) and \( R \) is the molar gas constant.

Several parameterizations of the ion–dipole collision rate have been presented. Here we use the version by Su and Chesnavich (1982), which we find to yield collision rates within 10 to 20% of the parameterizations presented by Su and Bowers (1973) and Nadykto and Yu (2003). The Su and Chesnavich parameterization is given by

\[ k_{\text{coll},(R3)} = \beta_L \times (0.4767x + 0.6200), \]

where \( \beta_L = q \mu^{-1/2}(\pi \alpha/\varepsilon_0)^{1/2} \times \mu_D/(8 \pi \varepsilon_0 \sigma k_B T)^{1/2} \) is the charge of the ion, \( \mu \) is the reduced mass of the colliding species, \( \sigma \) and \( \mu_D \) are the polarizability and dipole moment of the polar molecule, and \( k_B \) is Boltzmann’s constant. Finally we obtain evaporation rate constants of 2.3 × 10^9, 6.1 × 10^7 and 4.1 × 10^8 s⁻¹ for \( n = 0, 1 \) and 2, respectively.

Table 2. Bimolecular rate constant \( (k_{\text{ox, bimol}}) \) of the SO₂ + SO₄⁻(H₂O)ₙ → SO₂SO₄⁻(H₂O)ₙ reaction. The computational benchmarking (Table 1) suggests that these values are more likely to be underestimated than overestimated.

| \( n \) | \( k_{\text{ox, bimol}} \text{(cm}^3\text{molecule}^{-1}\text{s}^{-1}) \) |
|------|------------------|
| 0    | 1.5 × 10⁻¹⁰     |
| 1    | 4.9 × 10⁻¹¹     |
| 2    | 2.6 × 10⁻¹³     |

The oxidation rate constant, \( k_{\text{ox},(R4a)} \), is calculated using Eyring’s equation (Eyring, 1935) as

\[ k_{\text{ox},(R4a)} = \frac{k_B T}{h} \times \exp \left( -\frac{\Delta G_{\text{ox},(R4a)}^0}{R T} \right), \]

where \( \Delta G_{\text{ox},(R4a)}^0 \) is the Gibbs free energy of activation and \( h \) is Planck’s constant. The obtained values of \( k_{\text{ox},(R4a)} \) are 2.8 × 10⁶, 2.2 × 10⁶, and 7.7 × 10⁴ s⁻¹, corresponding to atmospheric half-lives of 3, 1, and 9 µs for de-, mono- and di-hydrated systems respectively. These values, in addition to those obtained for Reaction (R4b), indicate that SO₂SO₄⁻(H₂O)ₙ would react well before any collision with the most abundant atmospheric oxidants.

The values of \( k_{\text{ox, bimol}} \) were obtained and they are given in Table 2. It can be seen from Table 2 that the formation of SO₃SO₃⁻(H₂O)ₙ from the SO₂ + SO₄⁻(H₂O)ₙ reaction is relatively fast at low relative humidity (RH). To the best of our knowledge, there are no experimental data available for direct comparison. However, we found that the rate constant, \( 1.5 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \), of the unhydrated reaction is close to the rate constants of other similar reactions involving either SO₂ or SO₄⁻. For the SO₂ oxidation reaction by the CO₅ anion, Fehsenfeld and Ferguson (1974) and Möhler et al. (1992) reported reaction rate constants of 2.3 × 10⁻¹⁰ and 4.7 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹, respectively. Furthermore, Fehsenfeld and Ferguson (1974) investigated the SO₄⁻ + NO₂ reaction and determined a rate constant \( < 2 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \).

Considering the high computed rate constant of Reaction (R4a) at low RH, it is likely that SO₂SO₄⁻(H₂O)ₙ will form from the SO₂ and SO₄⁻(H₂O)ₙ collision at standard conditions. To evaluate the stability of the SO₃SO₃⁻(H₂O)ₙ clusters we considered its decomposition through two main processes: evaporation of a SO₂ molecule (Reaction R5a) and formation of SO₂SO₄⁻(H₂O)ₙ by the reverse direction of Reaction (R4a) (i.e. Reaction R5b).

\[ \text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n \rightarrow \begin{cases} \text{SO}_3 + \text{SO}_3^- (\text{H}_2\text{O})_n, \\ \text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n. \end{cases} \quad (\text{R5}) \]

We found Reaction (R5a) to be highly endothermic with Gibbs free energy changes 21.4, 17.6, and 15.0 kcal mol⁻¹.

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for n = 0, 1, and 2, respectively (see Fig. 3). Thereby, decomposition of SO$_3$SO$_3^-$ (H$_2$O)$_n$ by SO$_3$ evaporation is negligible at standard conditions.

Reaction (R5b) has energy barriers of 14.0, 12.4, and 13.4 kcal mol$^{-1}$ for n = 0, 1, and 2, respectively. The rate constants of this reaction at 298.15 K are 3.9 $\times$ 10$^5$, 4.8 $\times$ 10$^3$, and 8.9 $\times$ 10$^2$ s$^{-1}$, corresponding to half-lives of 1760, 145, and 782 $\mu$s for n = 0, 1, and 2, respectively. These lifetimes are comparable to collision rates between SO$_3$SO$_3^-$ and O$_3$. It is therefore likely that SO$_3$SO$_3^-$ will react with O$_3$, e.g., forming SO$_4^-$, SO$_3^-$, and O$_2$, irreversibly preventing Reaction (R5). We therefore consider the SO$_3$SO$_3^-$ cluster ion as a terminal sink for the SO$_2$ + SO$_4^-$ collision.

### 3.3 Equilibria and cluster distribution

Although ionic species in the atmosphere are mostly detected unhydrated, probably due to evaporation of water in the mass spectrometers, many anions are known to bind a few water molecules at typical tropospheric conditions (Seta, 2003; Husar et al., 2012; Bork et al., 2011). It is well known that the degree of solvation of chemical species affects their further reaction in the atmosphere. We therefore proceeded to examine the hydration state of the most stable anionic species studied in this work.

Upon SO$_2$ and SO$_4^-$ (H$_2$O)$_n$ collisions, the resulting product clusters will most likely undergo water condensation and evaporation in order for the thermal equilibrium to settle. In addition to Reactions (R3) and (R4a), the other relevant equilibria (as also shown in Fig. 1) are given below

\[
\begin{align*}
\text{SO}_4^- (\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} & \rightleftharpoons \text{SO}_4^- (\text{H}_2\text{O})_n, \quad \text{(R6)} \\
\text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} & \rightleftharpoons \text{SO}_2\text{SO}_4^- (\text{H}_2\text{O})_n, \quad \text{(R7)} \\
\text{SO}_3\text{SO}_3^- (\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} & \rightleftharpoons \text{SO}_3\text{SO}_3^- (\text{H}_2\text{O})_n. \quad \text{(R8)}
\end{align*}
\]

For Reaction (R6), we found that two water molecules bind with similar strength to the SO$_4^-$ ion. The Gibbs free energy changes are determined to be $\Delta G_{(R6)}^o = -3.3$ and $-3.1$ kcal mol$^{-1}$ for n = 1 and 2, respectively (see Fig. 4). The comparison of the first hydration Gibbs free energy to the $-5.1$ kcal mol$^{-1}$ experimental value (Fehsenfeld and Ferguson, 1974) shows that we might be somewhat underestimating the hydration of SO$_4^-$ at standard conditions. However, the values of the Gibbs free energy changes of Reaction (R6) indicate that the SO$_4^-$ ion most likely binds at least two water molecules at standard conditions since the binding Gibbs free energies are more negative than the critical clustering energy. The critical clustering energy (represented as a dotted line on Fig. 4) calculated at 298.15 K and 50 % RH is $RT \times \ln([\text{H}_2\text{O}]) = -2.5$ kcal mol$^{-1}$.

Although the additions of the first and second water molecules to either SO$_2$SO$_4^-$ or SO$_3$SO$_3^-$ are thermodynamically favourable at standard conditions, the hydration energies of these species are less negative than the hydration energies of SO$_4^-$. Further, the Gibbs free energies of the first and second water addition to SO$_2$SO$_4^-$ and SO$_3$SO$_3^-$ are both less negative than the critical clustering energy (see Fig. 4), and these ions are thus predicted to be mostly unhydrated at standard conditions.

The binding energies of larger hydrates were investigated using the B3LYP, CAM-B3LYP and PW91 functionals, although not CCSD(T)/aVDZ corrected due to computational expense. These data are shown in Figs. S2, S3 and S4 and indicate that the sulfur anions considered here are unlikely to bind more than a few water molecules. One possible exception to this is the SO$_3$SO$_3^-$ cluster which is seen to form a somewhat stable tetrahydrate (e.g., $\Delta G_{R6,n=3}^o = -2.1$ kcal mol$^{-1}$ for PW91/aVDZ), which may be present in noticeable concentrations.

After determining the thermodynamics of the above reactions, we can use the law of mass action,

\[
\frac{[\text{SO}_4^- (\text{H}_2\text{O})_n]}{[\text{SO}_4^- (\text{H}_2\text{O})_{n-1}]} = [\text{H}_2\text{O}] \times \exp \left( -\frac{\Delta G_{(R6)}^o}{RT} \right),
\]  

(9)

to calculate the relative concentrations of the different hydrates at given concentrations. Equation (9) is written for Reaction (R6) and similar equations exist for Reactions (R3), (R4a), (R7), and (R8). Combining these, we can determine the relative abundance of all the hydrates at thermal equilibrium. The distribution at two different SO$_2$ concentrations, 2 ppb and 200 ppb, corresponding approximately to continental background air and urban air, respectively, and three different RHs (10, 50, and 90 %) are shown in Fig. 5. Similar figures assuming either a general underbinding or overbinding of 1 kcal mol$^{-1}$ are shown in Figs. S6 and S7, respectively. These reveal that the general hydration patterns of the SO$_4^-$, SO$_2$SO$_4^-$, and SO$_3$SO$_3^-$ anions are quite insensitive to variations in binding energy of this magnitude. At 2 ppb of SO$_2$, the equilibrium cluster population consists mostly of the SO$_4^-$ hydrates regardless of the RH. When the concentration of SO$_2$ is 200 ppb, the SO$_4^-$ hydrates still dominate the distribution at all RHs, but the SO$_2$SO$_4^-$ hydrates are present in a moderate proportion. Further, an important feature is observed at 10 % RH where the unhydrated SO$_3$SO$_3^-$ ion is the most abundant species (45 % of the total population). This result can be explained by three reasons:

- SO$_2$ and water concentrations are different only by 4 orders of magnitude under these conditions, compared to the 6 orders of magnitude in the case of 2 ppb of SO$_2$.
- SO$_2$ binds more strongly to SO$_4^-$ than water does.
- the concentrations of SO$_2$SO$_4^-$, SO$_3$SO$_3^-$, and separated SO$_4^-$ and SO$_2$ are in thermal equilibrium.

Our results suggest that SO$_2$ oxidation in the SO$_2$SO$_3^-$ complex would be most important in regions with low RH and high SO$_2$ concentration.
4 Conclusions

In this study, the chemical fate of atmospheric SO$_4^{2-}$ (H$_2$O)$_n$ anionic clusters has been investigated by exploring its reaction with SO$_2$ using ab initio calculations and kinetic modelling. Geometries and formation Gibbs free energies of the products, were determined. The reaction leads to immediate formation of the SO$_2$SO$_4^{2-}$ (H$_2$O)$_n$ reactant complex which is found to isomerize at standard conditions to SO$_2$SO$_3^{-}$ (H$_2$O)$_n$ by overcoming an energy barrier. The overall reaction is SO$_2$ oxidation by the SO$_4^{2-}$ (H$_2$O)$_n$ anion.

In the SO$_2$SO$_4^{2-}$ (H$_2$O)$_n$ isomerization to SO$_3$SO$_3^{-}$ (H$_2$O)$_n$, the transition state is slightly stabilized by the presence of a single water molecule, but destabilized when the reactant complex binds two water molecules. Instead, the presence of two water molecules favours the decomposition of the reactant complex to form the initial reactants. At standard conditions, the bimolecular oxidation rate constants are determined to $1.5 \times 10^{-10}$, $4.9 \times 10^{-11}$, and $2.6 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, for $n = 0$, 1, and 2, respectively. Discrepancies within the available ab initio data (Table 1) suggest that the reaction rate constants could, in fact, be significantly higher.

At a given temperature, the equilibrium distribution of the clusters depends on the SO$_2$ concentration and the relative humidity. At 298.15 K, the concentration of SO$_3$SO$_3^{-}$ at equilibrium is highest for high SO$_2$ concentration (200 ppb) and low relative humidity (10%). Under these conditions, SO$_3$SO$_3^{-}$ is the most abundant species at thermal equilibrium in the SO$_2$ + SO$_4^{2-}$ (H$_2$O)$_n$ reaction, and constitutes 45% of the total population.

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