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Structures and reaction rates of the gaseous oxidation of SO$_2$ by an O$_3^-(\text{H}_2\text{O})_{0-5}$ cluster – a density functional theory investigation

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Abstract

Based on density functional theory calculations we present a study of the gaseous oxidation of SO$_2$ to SO$_3$ by an anionic O$_3^-(H_2O)_n$ cluster, $n = 0$–$5$. The configurations of the most relevant reactants, transition states, and products are discussed and compared to previous findings. Two different classes of transition states have been identified. One class is characterized by strong networks of hydrogen bonds, very similar to the reactant complexes. The other class is characterized by loose structures of hydration water and is stabilized by high entropy. At temperatures relevant for atmospheric chemistry, the most energetically favorable class of transition states vary with the number of water molecules attached. A kinetic model is utilized, taking into account the most likely outcomes of the initial SO$_2$O$_3^-(H_2O)_n$ collision complexes. This model shows that the reaction takes place at collision rates regardless of the number of water molecules involved. A lifetime analysis of the collision complexes supports this conclusion. Hereafter, the thermodynamics of water and O$_2$ condensation and evaporation from the product SO$_3^-O_2(H_2O)_n$ cluster is considered and the final products are predicted to be O$_2$SO$_3^-$ and O$_2$SO$_3^-(H_2O)_1$. The low degree of hydration is rationalized through a charge analysis of the relevant complexes. Finally, the thermodynamics of a few relevant reactions of the O$_2$SO$_3^-$ and O$_2$SO$_3^-(H_2O)_1$ complexes are considered.

1 Introduction

One of the most debated subjects within atmospheric chemistry is the mechanisms leading to cloud formation. This is due to the combination of lacking success in constructing predictive models and the high impact of clouds on a variety of atmospheric phenomena (Solomon et al., 2007). Most noticeable is the understanding and forecasting of weather and climate (Simpson and Wiggert, 2009; Rosenfeld, 2006; Spracklen et al., 2008; Carslaw et al., 2002; Marsh and Svensmark, 2000).
A known prerequisite for formation of a cloud droplet is a cloud condensation nucleus (CCN) onto which water vapour may condense. The chemistry and physics behind CCN formation is, however highly complex and may involve both solid and liquid particles (Zhang et al., 2007; Pierce and Adams, 2006; Falsig et al., 2006; Nadykto et al., 2008; Gross et al., 2008; Madsen et al., 2008, 2011) and may be based mainly on organic or inorganic species or a mixture of both (De Gouw and Jimenez, 2009; Kanakidou et al., 2005; Kirkby et al., 2011). One of the most important species involved in CCN formation is sulphuric acid, mainly due to its high water affinity (Liss and Lovelock, 2007; Charlson et al., 1987). The predominant source of atmospheric sulphuric acid is the well known UV light induced oxidation of SO$_2$. Although consisting of several elementary reactions the actual sulphur oxidation step,

$$\text{OH} + \text{SO}_2 \rightarrow \text{HSO}_3,$$

(R1)
is believed to be rate limiting (Seinfeld and Pandis, 1998; Wine et al., 1984).

Clearly complementary to this mechanism, a number of experimental and field based studies have found correlations between cosmic rays intensities and various cloud or aerosol parameters (Kirkby et al., 2011; Svensmark et al., 2009; Enghoff and Svensmark, 2008; Harrison and Carslaw, 2003). Cosmic rays are the primary source of atmospheric ionization and currently, ions are the most likely candidate responsible for these correlations. Although other micro- and macrophysical mechanisms may be important as well, interest have gathered around alternative mechanisms for H$_2$SO$_4$ formation involving the presence of one or more ions (Yu et al., 2008). However, the chemical and physical interactions involved in such a mechanism are still largely unresolved. The lack of knowledge of these fundamental processes is a major constraint towards the final assessment of the importance of ion induced cloud formation (Solomon et al., 2007).

Upon entrance of a cosmic ray into the atmosphere, a cascade of free electrons and various cations are produced. Although both cations and anions may be of interest for atmospheric nucleation, recently, more interest have gathered around the role of the anions and hence the fate of the electrons (Nadykto et al., 2006; Kurtén et al., 2009).
A free electron is thermally unstable and will most likely, rapidly attach to an O$_3$ molecule with a significant energy gain. The O$_3^-$ anion has a high water affinity and will, dependent on humidity and temperature, attract a number of H$_2$O molecules creating a small molecular cluster. Our previous studies show that at least 5 hydration water molecules will be present at usual atmospheric conditions (Bork et al., 2011b). Any subsequent chemistry involving the O$_3^-(H_2O)_n$ clusters will thus, at least initially, involve 5 water molecules.

The reactivity of O$_3^-(H_2O)_n$ has previously been evaluated with respect to a few chemical species including CO$_2$, CH$_3$CN, N$_2$O$_5$, and DNO$_3$ (Fehsenfeld and Ferguson, 1974; Yang et al., 1991; Wincel et al., 1995, 1996). Of particular interest for sulphuric acid formation is the reaction

$$O_3^- + SO_2 \rightarrow SO_3^- + O_2,$$

which has been investigated by Fehsenfeld and Ferguson (1974). The observed rate constant was determined to $1.7 \times 10^{-9}$ cm s$^{-1}$. However, to the best of our knowledge, no studies of Reaction (R2) has included the effect of hydration. Given our findings concerning the high water affinity of O$_3^-$, this should be performed for obtaining data relevant for atmospheric chemistry.

We have performed a density functional theory investigation of the reactivity of O$_3^-(H_2O)_n$ with SO$_2$, $n = 0$–5. Our main objective was to determine the reaction rate of SO$_2$ oxidation via this mechanism. However, a number of other possible chemical outcomes have been considered as well. These include re-evaporation of SO$_2$, evaporation of O$_3$ and O$_2$ and equilibrium with water. The main reactions are illustrated in Fig. 1.

Initially, the structures of all reactants, transition states, and products are thoroughly investigated and the thermodynamics considered. Hereafter, a simple kinetic model is set up to determine the reaction rates. The distribution of the final products is described and rationalized using molecular charges. Finally, a few relevant reactions of the end products are considered.
2 Computational details

All electronic structure calculations have been performed using the Gaussian 09 package (http://gaussian.com/) and all computational parameters are thoroughly described in a previous paper (Bork et al., 2011b). Here, a brief overview follows.

Ab initio calculations on radical systems, anionic systems, and hydrogen bonded networks require special attention with respect to several parameters in order to ensure reliable results. The extra electrons of anions are known to occupy diffuse, long ranging orbitals and hence require similar basis sets (Jensen, 2010). Also, the most common density functional theory (DFT) functionals have problems in this regard (Yanai et al., 2004).

To address these issues we have utilized the CAM-B3LYP DFT functional (Yanai et al., 2004) and the aug-cc-pVDZ basis set (Dunning, 1989). The CAM-B3LYP functional is a modification to the well known B3LYP functional, including increasing Hartree-Fock exchange at increasing distances. We have previously demonstrated excellent agreement between CAM-B3LYP/aug-cc-pVDZ and benchmark UCCSD(T)-F12/VDZ-F12 calculations (Bork et al., 2011b). Of further interest with respect to this study, it has been shown that CAM-B3LYP is superior to B3LYP with respect to evaluating classical activation barriers (Peach et al., 2006; Yanai et al., 2004).

The presence of multiple water molecules require a thorough sampling of configurational space. For structure optimizations we have utilized the simulated annealing technique which is able, not only to determine the nearest local minima, but also to migrate from minima to minima. Thereby, each calculation scans a large number of different configurations and hence, provide a much better sampling of configurational space (Corana et al., 1987).
Transition states were found using the Synchronous Transit and Quasi-Newton methods (STQN) (Peng et al., 1996) as implemented via the QST keyword. The initial guess for the transition states were obtained partly via structural analyses of the reactants and products and partly via scans of configurational space.

For analyzing the charge distribution of the various clusters, we have utilized the Bader charge partitioning method (Bader, 1998, 1990). The method is based on partitioning the electronic density by zero-flux surfaces and has a much better theoretical basis than most other charge partitioning methods. Previously, this method has successfully been used to describe both charged systems (Bork et al., 2011a) and water containing systems (Henkelman et al., 2006).

3 Results and discussion

3.1 Structures and thermodynamics

Initially, all SO$_2$O$_3^−$(H$_2$O)$_n$, SO$_3^-$(H$_2$O)$_n$, and SO$_2^-$(H$_2$O)$_n$ structures ($n = 0–5$) were thoroughly scanned using simulated annealing at the Hartree-Fock (HF) level. The 5–15 most stable structures were then re-optimized using DFT. In no cases were significant structural discrepancies between the most stable structures at the HF and DFT levels found.

The ground state structures of the initial collision complexes are shown in Fig. 2. In all cases, the O$_3$ and SO$_2$ molecules are found in configurations with one of the O$_3$ oxygen atoms clearly coordinated to the sulfur atom. The bond length is quite short, between 1.92 and 1.97 Å, indicating a relatively strong bond between the molecules. The SO$_2$ and O$_3$ molecules are thus positioned such that transferring an oxygen atom may occur without further structural rearrangement.

In the $n = 0$ and $n = 1$ cases, the remaining atoms of the O$_3$ molecule are turned away from the SO$_2$ molecule. As one more water is added, the O$_3$ arranges as to maximize the number of hydrogen bonds and hence, a more dense configuration is obtained.
Adding the 3rd, 4th and 5th water, the only noticeable difference is the coordination of the water molecules being structured in 3 and 4 membered rings.

We note that many structures are almost iso-energetic, both at 0 Kelvin and at standard conditions. Hence, we conclude that the structures are resembling a liquid phase and that many other structures than the ones presented in Fig. 2 are found at atmospheric conditions.

Based on our previous studies, the thermodynamics of forming the collision complex, corresponding to

\[ \text{O}_3^-(\text{H}_2\text{O})_n + \text{SO}_2 \rightarrow \text{O}_3^+\text{SO}_2(\text{H}_2\text{O})_n, \]  

(R3)

were hereafter readily available (Bork et al., 2011b). The potential energy surfaces are shown in Fig. 3.

All binding energies are large and positive and the \( \text{SO}_2\text{O}_3^-(\text{H}_2\text{O})_n \) collision complexes are thus likely to form at atmospheric conditions. As expected, the binding energy of the \( \text{SO}_2 \) molecule is largest for small values of \( n \). This is a consequence of the effect of the water molecules in dispersing and stabilizing the charge of the \( \text{O}_3^- \) ion. This stabilization reduces the energy gain of any further clustering.

Following the outline in Fig. 1, the oxygen transfer reaction was investigated,

\[ \text{O}_3^+\text{SO}_2(\text{H}_2\text{O})_n \rightarrow \text{O}_2\text{SO}_3^-(\text{H}_2\text{O})_n. \]  

(R4)

Due to the \( \text{O}_2^-\text{O}-\text{SO}_2 \) configuration of the reactant structures, a series of transition states were readily found and are illustrated in Fig. 4.

Minor structural differences are found, depending on the level of hydration. For \( n = 0–2 \), the \( \text{O}_3 \) molecule is turned away from the \( \text{SO}_2 \) molecule, which yields a minimum S-O distance close to 1.71 Å. For \( n = 3–5 \), the \( \text{O}_3 \) molecule is positioned similar to the ground state structures, inducing longer S-O distances of ca. 1.80 Å. A similar trend in the O-O bond distance is found, here referring to the bond being broken during the reaction. These are found to be around 1.69 Å and 1.75 Å for \( n = 0–2 \) and \( n = 3–5 \), respectively. In all cases, the water molecules are tightly structured and hence, this class of transition states is denoted “tight”.

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Although some configurational differences are found at varying degree of hydration these are not reflected in the corresponding energy barriers, shown in Fig. 5. The free energy activation barrier for the water free system is found to 27.6 kJ mol\(^{-1}\) and is, as expected, decreased by adding the first and second water molecule. However, the addition of more water molecules tend to increase the energy barrier, i.e. stabilize the reactant complexes more than the transition states. This is somewhat surprising since many studies have found an increasing catalytic effect as more water is present (Larson et al., 2000; Niedner-Schatteburg and Bondybey, 2000). However, in this case the lowest barrier is found for the systems containing exactly 2 water molecules. We note that this is regardless of considering \(\Delta H\) or \(\Delta G\) within the temperature region of interest. At standard conditions, the free energy barrier is in the \(n = 2\) case reduced to just 16.6 kJ mol\(^{-1}\) which is a reduction of 11 kJ mol\(^{-1}\) compared to the dehydrated structure.

While scanning configurational space, a second class of transition states was found. Within this class, the transition states are characterized by a much looser structure of hydrogen bonds even though the configurations of the actual reactants (the O\(_2\)S-O-O\(_2\) complex) are very similar. These are shown in Fig. 6 and are denoted “loose” due to the loose structure of the water molecules.

Despite a much less ordered structure, the actual reactant complexes (O\(_2\)-O-SO\(_2\)) are more similar at varying degrees of hydration than within the “tight” class of transition states. In the “loose” transition states, S-O distances of ca. 1.71 Å, and a O-O distances of ca. 1.69 Å are found regardless of the number of water molecules. These distances are almost identical to the ones found in the “tight” transition states for \(n = 0–2\) and may thus be interpreted as the optimal transition state configuration at low degree of water interaction.

Examining the energy barriers of the “loose” transition states, as expected we find the \(\Delta H\) barriers significantly increased. Obviously, this occurs since the stabilization of the hydrogen bonded network of water molecules is lost. This is especially pronounced for \(n \geq 3\), since the \(n = 3\) cluster is the smallest structure capable of forming a ring of
However, considering also entropy at standard conditions we see that the “loose” transition states are in fact more favored for $n = 3$ and 4. The differences are about 8 and 5 kJ mol$^{-1}$ for $n = 3$ and 4, respectively and these “loose” transition states are thus significantly favored at standard conditions. Further, at $n = 5$ the values of $\Delta G$ are practically identical.

The energy barrier for the corresponding, electrically neutral reaction has been evaluated both theoretically and experimentally, albeit not including the effect of water. Using B3LYP and a triple zeta basis set, Jiang et al. (2009) determined the barrier to be around 83 kJ mol$^{-1}$, while Sander et al. (2006), based on time-of-flight mass spectrometry by Davis et al. (1974), suggest an activation barrier of at least 58 kJ mol$^{-1}$. Hence, we conclude that although the reaction may be catalysed by the presence of a few water molecules, the extra electron itself will dramatically enhance the oxidation reaction.

The structures of the product complexes were investigated as well and are shown in Fig. 7. In all cases, the same configuration of the SO$_3$ and O$_2$ molecules were found, forming an O$_3$S-O$_2$ complex. The S-O distances are between 1.81 and 1.85 Å and given the stability of the HSO$_4^-$ ion, these configurations may be of relevance for the further outcome of these complexes. At 0 Kelvin, all the most stable structures display a strong network of hydrogen bonds while other, less ordered structures become relevant at elevated temperatures. As expected, we find Reaction (R4) highly exothermic at values between 135 and 175 kJ mol$^{-1}$. It is thus clear that the reverse reaction will be without relevance.

Another theoretically possible outcome of the initial collision complex is evaporation of O$_3$, leaving a SO$_2^-(H_2O)_n$ cluster behind. Although not performing a full simulated annealing configurational analysis of the clusters, we conclude that this reaction is at least 130 kJ mol$^{-1}$ endothermic and hence without relevance under atmospheric conditions.
Besides discarding the relevance of O₃ evaporation from the O₃⁻SO₂(H₂O)ₙ cluster, these calculations can be used for an evaluation of the accuracy of the calculational methods. Considering the n = 0 systems, i.e. the reaction

\[ \text{O}_3^- + \text{SO}_2 \rightarrow \text{O}_3 + \text{SO}_2^-, \]  

we find that this is 92.1 kJ mol⁻¹ endothermic. We also note that this energy equals the difference between the electronegativities of O₃ and SO₂, given as 96 kJ mol⁻¹ (Lide, 1997). This very good agreement between theoretical and experimental values is a strong argument in favor of the quality of the present results.

Finally, the structures of the SO₃⁻(H₂O)ₙ clusters were examined since evaporation of O₂ is an obvious possibility,

\[ \text{SO}_3^-\text{O}_2(\text{H}_2\text{O})_n \rightarrow \text{SO}_3^-\text{(H}_2\text{O})_n + \text{O}_2. \]  

The structures were similar to the product clusters shown in Fig. 7 just without the O₂ species, and have all maintained a strong hydrogen bonded network. The structures are shown in the Supplement.

The thermodynamics of O₂ evaporation were hereby available and it is thus clear that the bond between SO₃⁻ and O₂ is quite weak for \( n \geq 2 \), but quite strong for \( n \leq 1 \). Considering the large release of internal energy due to the oxidation, the O₂ molecule will have a high probability of evaporating, but given the large concentration of atmospheric O₂ the equilibrium will quickly settle. See also Sect. 3.4.

Finally, the thermodynamics of the entire reaction chain, as illustrated in Fig. 1, are available,

\[ \text{O}_3^-\text{(H}_2\text{O})_n + \text{SO}_2 \rightarrow \text{SO}_3^-\text{(H}_2\text{O})_n + \text{O}_2. \]  

Hereby, we are able to make a second assessment of the quality of the results by considering the \( n = 0 \) reaction as the sum of the reactions

\[ \text{O}_3^- \rightarrow \text{O}_3 + \text{e}^- \]  

(R8)
O₃ + SO₂ → SO₃ + O₂  \hspace{1cm} (R9)
SO₃ + e⁻ → SO₃⁻. \hspace{1cm} (R10)

Hereby, can compare our value of −217 kJ mol⁻¹ to the experimental ΔG° of −196 kJ mol⁻¹ (Lide, 1997). Considering the inherent difficulties within DFT of describing charge transfer reactions and the potential multireference problems of O₂ and O₃, the agreement is very satisfactory.

3.2 Kinetics

The main objective of this study is to examine the kinetics of SO₂ oxidation to SO₃ by an O₃⁻(H₂O)ₙ cluster. Having established the thermodynamic properties of the reactants, products and transition states we proceed to this point.

To determine the total rate of oxidation, steady state for the pre-reactive complex, O₃⁻SO₂(H₂O)ₙ, is assumed. Hereby we obtain the following set of reactions

\[ \frac{\partial [O₃⁻SO₂(H₂O)ₙ]}{\partial t} = 0 \]

\[ = Z_{\text{coll}} - r_{\text{ox}} - r_{\text{SO₂ evap}} \]

where \( r_{\text{ox}} \) and \( r_{\text{SO₂ evap}} \) are the reaction rates of the oxidation and SO₂ evaporation processes, respectively. \( Z_{\text{coll}} \) is the rate of collisions leading to formation of the collision complex. Recall that evaporation of O₃ is highly endothermic and may be disregarded. At this point we consider only fixed values of \( n \), since it later can be concluded that varying hydration will not alter the kinetics. See Sects. 3.3 and 3.4 for further analysis.

Since both \( r_{\text{ox}} \) and \( r_{\text{SO₂ evap}} \) must depend linearly on the concentration of O₃⁻SO₂(H₂O)ₙ we obtain

\[ Z_{\text{coll}} - [O₃⁻SO₂(H₂O)ₙ] (k_{\text{ox}} + k_{\text{SO₂ evap}}) = 0, \]  \hspace{1cm} (3)

where “\( k \)” denote the corresponding rate constants.
Further, since the oxidation is highly exothermic no backwards reaction is possible and hence, the total reaction rate can be obtained as

\[ r_{\text{tot}} = r_{\text{ox}} \]
\[ = k_{\text{ox}} [O_3^-SO_2(H_2O)_n] \]
\[ = Z_{\text{coll}} \left(1 + \frac{k_{\text{SO}_2 \text{ evap}}}{k_{\text{ox}}} \right)^{-1} \]

(4) (5) (6)

where the final equation is obtained by inserting the expression for \([O_3^-SO_2(H_2O)_n]\) from Eq. (3). Further assuming that both oxidation and \(SO_2\) evaporation can be described by Arrhenius equations we obtain

\[ \frac{r_{\text{tot}}}{Z_{\text{coll}}} = \left(1 + \frac{A_{\text{SO}_2 \text{ evap}}}{A_{\text{ox}}} \exp \left(-\frac{\Delta E_{\text{SO}_2 \text{ evap}} - \Delta E_{\text{ox}}}{RT} \right) \right)^{-1} \]

(7)

where the ratio \(r_{\text{tot}}/Z_{\text{coll}}\) denote the fraction of \(O_3^-SO_2(H_2O)\) complexes, in which \(SO_2\) is oxidized.

The differences in activation energies, \(\Delta E_{\text{SO}_2 \text{ evap}} - \Delta E_{\text{ox}}\), are directly obtained from Fig. 3. The prefactors were obtained using transition state theory in the harmonic approximation (Hänngi et al., 1990; Billing and Mikkelsen, 1996). The prefactor of oxidation is then given as

\[ A_{\text{ox}} = \frac{\Pi \nu_{\text{reac}}}{\Pi \nu_{\text{TS}}} \]

(8)

where “\(\nu\)” denote the vibrational frequencies of the reactants and transition states. The \(^{\dagger}\) symbol indicate that the imaginary frequency should be omitted.

We here note that the reactant configuration, should be the first stable configuration into which the transition state falls upon relaxation and not necessarily the absolute ground state. In the class of “tight” transition states, the configuration actually relaxes...
into the ground state, but in the class of “loose” transition states this is not the case. These relax into a configuration, not much different from the transition state itself.

Since evaporation of SO$_2$ is barrierless, there were no transition states in which to evaluate the frequencies. In stead, we loosely estimated these by gradually moving the SO$_2$ away from the cluster and continuously evaluating the resulting frequencies. Although this method is rough, we emphasize that the accuracy is adequate for the present purpose, namely to evaluate the fraction of reactive collisions from Eq. (7). This was ensured by a sensitivity analysis showing no major discrepancies, even considering an error of two orders of magnitude. All relevant frequencies are given in the Supplement.

Finally, we evaluate the fraction of reactive collisions at standard conditions. Regardless of the number of water molecules we find that

$$\frac{r_{\text{tot}}}{Z_{\text{coll}}} > 0.995,$$

(9)
i.e. practically all collisions will lead to oxidation. The main reason is not a particularly small energy barrier but rather that any other chemical fate shown in Fig. 1 requires a significantly higher activation energy.

The rate of oxidation of SO$_2$ by an anionic O$_3$\(^-\)(H$_2$O)$_n$ cluster may thus simply be estimated using classical collision theory,

$$Z_{\text{coll}} = N_{\text{SO}_2} N_{\text{cluster}} \pi d^2 \sqrt{\frac{8 k_B T}{\mu \pi}}$$

(10)

where $N$ is the number of species pr. unit volume, $d = d_{\text{SO}_2} + d_{\text{cluster}}$ is the total collision cross section, $k_B$ is Boltzmann’s constant, and $\mu$ is the reduced mass (Atkins, 2001; Billing and Mikkelsen, 1996).

Comparison with experimental data is only possible for the dehydrated system where Fehsenfeld and Ferguson (1974) measured the rate constant to $1.7 \times 10^{-9}$ cm$^3$ s$^{-1}$ at $T = 296$ K. In this case, assuming $d = 5.5$ Å, we obtain a rate constant of $1.1 \times$
10^{-10} \text{ cm}^3 \text{ s}^{-1}. \ We \ consider \ it \ most \ likely \ that \ the \ order \ of \ magnitude \ difference \ reflects \ a \ net \ attractive \ potential \ between \ the \ O_3^- \ ion \ and \ SO_2 \ increasing \ the \ collision \ rates. \ Alternatively, \ inaccuracies \ in \ the \ original \ experimental \ measurements \ may \ be \ the \ reason. \ In \ any \ case, \ the \ results \ are \ in \ reasonable \ accordance \ and \ oxidation \ of \ SO_2 \ by \ an \ O_3^-(H_2O)_n \ cluster \ is \ undoubtedly \ fast \ and \ should \ be \ considered \ when \ studying \ ionic \ atmospheric \ chemistry.

3.3 Lifetime of SO_2O_3^-(H_2O)_n

Although \ there \ is \ no \ other \ likely \ fate \ of \ the \ isolated \ SO_2O_3^-(H_2O)_n \ complex \ other \ than \ SO_2 \ oxidation, \ collision \ with \ other \ atmospheric \ species \ could \ induce \ other \ possible \ end \ products. \ This \ is \ dependent \ of \ the \ expected \ lifetime \ of \ the \ SO_2O_3^-(H_2O)_n \ complex \ which \ was \ evaluated \ using \ hTST. \ The \ lifetime, \ \tau, \ is \ thus \ given \ as

\[\tau = k_{\text{ox}}^{-1} = A_{\text{ox}}^{-1} \times \exp \left( \frac{\Delta E_{\text{ox}}}{RT} \right) \tag{11}\]

where \ A_{\text{ox}} \ is \ given \ in \ Eq. \ (8). \ Hereby, \ the \ lifetimes \ are \ evaluated \ to \ be \ in \ the \ picosecond \ regime, \ illustrated \ in \ Fig. \ 8. \ For \ comparison, \ the \ average \ times \ between \ collisions \ with \ N_2, \ O_2 \ and \ H_2O \ (50\% \ relative \ humidity) \ are \ illustrated \ as \ well.

From \ this \ it \ is \ apparent \ that \ the \ most \ reactive \ complexes, \ i.e. \ the \ n = 2, 3 \ and \ 4 \ complexes, \ typically \ reacts \ before \ colliding \ with \ any \ other \ species. \ The \ remaining \ complexes \ will \ experience \ a \ few \ N_2 \ collisions \ and \ perhaps \ a \ single \ collision \ with \ O_2. \ Collision \ with \ any \ other \ species, \ including \ H_2O \ is \ rarely \ experienced.

We \ thus \ conclude \ that \ the \ most \ likely \ fate \ of \ the \ SO_2O_3^-(H_2O)_n \ complex \ undoubtedly \ is \ SO_2 \ oxidation \ since \ any \ other \ outcome \ require \ a \ large \ extra \ activation \ energy \ and \ since \ the \ complex \ is \ too \ short \ lived \ to \ experience \ collision \ with \ another \ molecule \ which \ may \ induce \ pathways \ not \ considered \ here.
3.4 Equilibrium with H₂O and O₂

From the previous section, growth via stepwise water condensation on the SO₂O₃⁻(H₂O)ₙ cluster has been excluded due to kinetics, i.e. the cluster is too short lived for the equilibrium to settle. Even though some water molecules possibly may evaporate from the cluster prior to Reaction (R4), we note that this will not alter the overall kinetics, since the reaction will take place at collision rates regardless of the number of attached water molecules. In other words, once the collision complex is formed no other fate than Reaction (R4) is possible, regardless of the state of hydration. Consequently, the degree of hydration of the SO₂O₃⁻(H₂O)ₙ cluster is not of immediate interest.

After the reaction, both the SO₃⁻O₂(H₂O)ₙ and SO₃⁻(H₂O)ₙ clusters will, most likely, be stable enough to reach thermal equilibrium via H₂O and O₂ evaporation and condensation. The thermodynamics of these equilibria, i.e.

\[
\text{SO}_3^- (\text{H}_2\text{O})_n + \text{O}_2 \leftrightarrow \text{SO}_3^- \text{O}_2 (\text{H}_2\text{O})_n \quad (R11) \\
\text{SO}_3^-(\text{H}_2\text{O})_n + \text{H}_2\text{O} \leftrightarrow \text{SO}_3^- \text{O}_2 (\text{H}_2\text{O})_{n+1} \quad (R12) \\
\text{SO}_3^- (\text{H}_2\text{O})_n + \text{H}_2\text{O} \leftrightarrow \text{SO}_3^- (\text{H}_2\text{O})_{n+1} \quad (R13)
\]

are therefore considered. All values are available from the previous calculations and are shown in Fig. 9.

Considering first the equilibrium with oxygen, i.e. Reaction (R11), we see that the oxygen binding energy to the dehydrated SO₃⁻ anion is quite strong, but also that it quickly and smoothly converges to a value of ca. −4 kJ mol⁻¹ as water is added. Considering the equilibrium with water, i.e. Reactions (R12) and (R13), we observe that the thermodynamics of water condensation is considerably weaker than expected and even weaker than the O₂ binding energies. Although binding energies are positive for the smallest clusters, the binding energy becomes negative for condensation of the 4th and 5th water molecule and hence, large clusters are destabilized.
Experimental data is available for Reaction (R13) in the \( n = 0 \) case. Fehsenfeld and Ferguson (1974) determined this \( \Delta G \) to be \(-24.7 \text{ kJ mol}^{-1}\) in fairly good accordance with the ca. \(-17 \text{ kJ mol}^{-1}\) found here.

A likely outcome of the reactants is thus as follows. Immediately after the reaction the clusters have a large amount of excess energy due to the thermodynamics. The cluster will most likely not be able to accommodate this energy and evaporation of \( \text{O}_2 \) and one or more \( \text{H}_2\text{O} \) will occur. The clusters considered here bind \( \text{O}_2 \) stronger than \( \text{H}_2\text{O} \) and further due to the higher concentration of \( \text{O}_2 \), this equilibrium will settle first.

Via the law of mass action,

\[
\frac{[\text{SO}_3\text{O}_2(\text{H}_2\text{O})_n]}{[\text{SO}_3\text{O}_2(\text{H}_2\text{O})_{n-1}]} = [\text{H}_2\text{O}] \times \exp\left(-\frac{\Delta G}{RT}\right)
\]

(12)

it is realized that the main product is dehydrated. Assuming standard conditions and 50% relative humidity, this configuration constitutes ca. 80–90% of the resulting clusters, depending on altitude. The remaining 20–10% of the clusters are mainly found as \( \text{SO}_3\text{O}_2(\text{H}_2\text{O})_1 \) with any other constitution populating less than 1%.

### 3.5 Charge analysis

Comparing the results of the previous section to other modeling and theoretical studies, it is surprising that the most stable configuration is without water. Most other studies on both cations and anions have found a tendency to attract at least a few water molecules at standard conditions. The best explanation is found via a molecular charge analysis of the systems, shown in Fig. 10. Included for comparison is our previous results for the \( \text{O}_3^- \) based clusters.

From this, a clear correlation between the charge and the binding energy of the water is seen. If a large amount of charge is distributed to the water molecules, proportional reductions in the electrostatic energy are obtained yielding a stronger binding energy. This is fully in line with our previous findings (Bork et al., 2011b).
It is also apparent that the size of the non-water part of the cluster is important. This is due to the extra electron being more delocalized in larger molecules, reducing the electrostatic stress on the system and hence reducing the need for further electronic delocalization through cluster growth.

Apparently, the $\text{O}_2\text{SO}_3^-$ cluster is almost large enough to facilitate the extra electron by itself, since only about 0.03 e is being distributed to the first water molecule. Consequently, the binding energy is just ca. 8 kJ mol$^{-1}$ which is below the critical energy of cluster growth. This corresponds to the value of $\Delta G$ where Eq. (12) equals 1, separating the regimes of cluster growth and evaporation.

### 3.6 Further chemistry of $\text{SO}_3\text{O}_2$

During charge neutral, photo induced, atmospheric $\text{H}_2\text{SO}_4$ synthesis, the rate determining step is oxidation of $\text{SO}_2$ to $\text{SO}_3$, shown in Reaction (R1) (Seinfeld and Pandis, 1998; Wine et al., 1984). Hence, once the neutral $\text{SO}_3$ molecule is formed, the mechanism leading to $\text{H}_2\text{SO}_4$ is well known and the formation is relatively fast.

Originating from a $\text{SO}_3^-$ based cluster, non-charged $\text{SO}_3$ may readily form by collision with $\text{O}_3$. Considering their electronegativities, the charge transfer reaction

$$\text{SO}_3^- + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_3^- \tag{R14}$$

will be ca. 40 kJ mol$^{-1}$ exothermic but should be studied further with respect to the effects of $\text{O}_2$ and $\text{H}_2\text{O}$ (Lide, 1997). We note that formation of $\text{O}_3^-$ will enable the oxidation process to repeat and hence, close a catalytic cycle. Exploring electronic induced catalysis in $\text{SO}_3$ and $\text{H}_2\text{SO}_4$ formation is of particular interest for explaining the observed correlations between cloud and aerosol parameters and cosmic ray influx (Kirkby et al., 2011; Svensmark et al., 2009; Enghoff and Svensmark, 2008; Harrison and Carslaw, 2003).

However, the chemical fate of $\text{O}_2\text{SO}_3^-$ may be different from neutral $\text{SO}_3$ and subsequently neutral $\text{H}_2\text{SO}_4$. Here, we note that the species $\text{H}_2\text{SO}_4^-$ is without atmospheric relevance since the HOMO orbital is very high in energy (NIST, 2011).
The most obvious other outcome is synthesis of $\text{HSO}_4^-$ via reaction with $\text{O}_2$ and $\text{H}_2\text{O}$,

$$\text{SO}_3^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{HO}_2.$$  \hfill (R15)

Even though this reaction is ternary and may have a significant energy barrier and complex dynamics, the necessary reactants are all abundant and therefore, this reaction is a likely candidate as well.

Naturally, $\text{HSO}_4^-$ and $\text{H}_2\text{SO}_4$ are closely related and share many properties, but should Reaction (R15) occur, the catalytic effect of the electron will terminate due to the high stability of the $\text{HSO}_4^-$ ion. The competing rates of Reactions (R14) and (R15) will thus ultimately determine how many $\text{SO}_2$ oxidations each free electron may induce.

4 Conclusions

The role of ion-induced $\text{H}_2\text{SO}_4$ formation has for a long time lacked a proper explanation of the chemical and physical mechanism. We have performed density functional theory calculations of one of the most important reactions in a proposed mechanism for ion induced $\text{SO}_2$ oxidation (Fig. 1).

Motivated by a previous study (Bork et al., 2011b), we find that $\text{O}_3^-(\text{H}_2\text{O})_n$ clusters are capable of further clustering with $\text{SO}_2$, creating $\text{O}_3^-\text{SO}_2(\text{H}_2\text{O})_n$ clusters (Fig. 2). A variety of possible outcomes of these clusters have been examined. The most likely outcome, requiring the smallest activation energy, is oxidation of $\text{SO}_2$ to $\text{SO}_3^-$. Two classes of transition states were identified. One characterized by a network of hydrogen bonds and one characterized by high entropy (Figs. 4 and 6). At standard conditions, both are important and will significantly contribute to the total reaction rate (Fig. 5).

Using a simple kinetic model, we determined that the reaction takes place at collision rates, in accordance with the available experimental data. Further, the lifetime of the collision complex were determined to exclude other possible outcomes, induced by collision with other reactants (Fig. 8).
Assuming thermal equilibrium, we determined the composition of the resulting products by considering their equilibrium with H$_2$O and O$_2$ (Fig. 9). Using the law of mass action, the most likely products were determined to be SO$_3^{-}$O$_2$ and SO$_3^{-}$O$_2$(H$_2$O)$_n$ (Fig. 7) at ca. 80–90% and 10–20% population, respectively, dependent on altitude.

Finally, these results were rationalized using molecular charge analysis showing a reduced tendency of charge delocalization for these clusters. In accordance with previous results, the degree of charge delocalization was proportional to the binding energies and the low degree of hydration could be explained (Fig. 10).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/29647/2011/acpd-11-29647-2011-supplement.pdf.

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$$\text{SO}_2 + \text{O}_3 (\text{H}_2\text{O})_n \rightarrow \text{SO}_3^- (\text{H}_2\text{O})_n + \text{O}_2$$

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Fig. 1. Schematic overview of the investigated reactions. “W” is shorthand for water and up to 5 water are here included. Under standard conditions and 50 % relative humidity, the main products are $\text{SO}_3\text{O}_2$ and $\text{SO}_3\text{O}_2\text{W}_1$. 

$$\text{SO}_2 + \text{O}_3(\text{H}_2\text{O})_n \rightarrow \text{SO}_3(\text{H}_2\text{O})_n + \text{O}_2$$
Fig. 2. Ground state structures of the initial collision complexes, \( \text{SO}_2\text{O}_3^-(\text{H}_2\text{O})_n, n = 0–5 \). For all water containing structures, a strong hydrogen bonded network is preferred. Hence, many 3 and 4 membered rings are formed. Sulfur (yellow), oxygen (red), hydrogen (white).
Fig. 3. Relative potential energy of the most important structures involved in the oxidation of SO₂ to SO₃ by an anionic O⁻₃(H₂O)ₙ cluster, n = 0–5. “W” is shorthand for water. The values are tabulized in the Supplement.
Fig. 4. Structures of the class of transition state complexes characterized by a strong network of hydrogen bonds. These are very similar to the reactant complexes, shown in Fig. 2, and are denoted “tight” due to the tight water structures. The water free structure is included for completeness. The dashed bonds indicate the bonds which are active in the reaction. Sulfur (yellow), oxygen (red), hydrogen (white).
Fig. 5. $\Delta H$ and $\Delta G$ of the two classes of transition states as function of number of water molecules, $n$, at standard conditions. The structures of the “tight” and “loose” transition states are shown in Figs. 4 and 6, respectively. The barrier of the charge neutral reaction is at least 58 kJ mol$^{-1}$ for $n = 0$. The values are tabulized in the Supplement.
Fig. 6. Structures of the class of transition state complexes characterized by high entropy. These are denoted “loose” due to the loose water structures. The water free structure is included for completeness. The dashed bonds indicate the bonds which are active in the reaction. Sulfur (yellow), oxygen (red), hydrogen (white).
Fig. 7. Configuration of the product complexes $\text{SO}_3\text{O}_2(\text{H}_2\text{O})_n$. The $\text{O}_2$ species is coordinated to the sulfur atom with S-O distances between 1.81 and 1.85 Å. The high concentration of atmospheric $\text{O}_2$ ensures a high population of these complexes. See also Sect. 3.4.
Fig. 8. Lifetime of the reactant complexes, $O_3^-SO_2(H_2O)_n$ at standard conditions. For comparison, the average times between collisions, $\tau$, with $N_2$, $O_2$ and $H_2O$ (50 % RH) are shown.
Fig. 9. Gibbs free energies of growth of the clusters via H\textsubscript{2}O and O\textsubscript{2} condensation. “W” is shorthand for water. The regimes of evaporation and condensation under standard conditions and 50% relative humidity are illustrated, determined using Eq. (12). Assuming thermal equilibrium, the final products are mainly O\textsubscript{2}SO\textsubscript{3}\textsuperscript{-} and O\textsubscript{2}SO\textsubscript{3}\textsuperscript{-}(H\textsubscript{2}O)\textsubscript{1}. The experimental data is from Fehsenfeld and Ferguson (1974).
Fig. 10. Accumulated Bader charges on the water molecules (W\textsubscript{n}) in SO\textsubscript{3}O\textsubscript{2}, SO\textsubscript{3} and O\textsubscript{3} based clusters. This charge is proportional to the binding energies and the larger the non-water part of the cluster, the less charge on the water molecules and hence, the weaker the binding.