Exploring the atmospheric chemistry of O$_2$SO$_3^-$ and assessing the maximum turnover number of ion-catalysed H$_2$SO$_4$ formation

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Received: 24 August 2012 – Published in Atmos. Chem. Phys. Discuss.: 22 November 2012

Revised: 4 March 2013 – Accepted: 14 March 2013 – Published: 4 April 2013

Abstract. It has recently been demonstrated that the O$_2$SO$_3^-$ ion forms in the atmosphere as a natural consequence of ionization. Here, we present a density functional theory-based study of the reactions of O$_2$SO$_3^-$ with O$_3$. The most important reactions are (a) oxidation to O$_3$SO$_3^-$ and (b) cluster decomposition into SO$_3$, O$_2$ and O$_3^-$. The former reaction is highly exothermic, and the nascent O$_3$SO$_3^-$ will rapidly decompose into SO$_4^-$ and O$_2$. If the origin of O$_2$SO$_3^-$ is SO$_2$ oxidation by O$_3^-$, the latter reaction closes a catalytic cycle wherein SO$_2$ is oxidized to SO$_3$. The relative rate between the two major sinks for O$_2$SO$_3^-$ is assessed, thereby providing a measure of the maximum turnover number of ion-catalysed SO$_2$ oxidation, i.e. how many SO$_2$ can be oxidized per free electron. The rate ratio between reactions (a) and (b) is significantly altered by the presence or absence of a single water molecule, but reaction (b) is in general much more probable. Although we are unable to assess the overall importance of this cycle in the real atmosphere due to the unknown influence of CO$_2$ and NO$_x$, we roughly estimate that ion-induced catalysis may contribute with several percent of H$_2$SO$_4$ levels in typical CO$_2$-free and low NO$_x$ reaction chambers, e.g. the CLOUD chamber at CERN.

1 Introduction

One of the most significant uncertainties in weather and climate forecasts is related to the processes leading to cloud formation (Simpson and Wiggert, 2009; Rosenfeld, 2006; Spracklen et al., 2008; Carslaw et al., 2002). It is well known that each cloud droplet forms around a cloud condensation nucleus (CCN). CCNs may well originate from a solid particle (e.g. soot, salt, or pollen), but recently it has become increasingly clear that a significant part originate from clustering of purely gaseous molecules (Kulmala et al., 2004; Wiedensohler et al., 2009; Yu and Luo, 2009; Kazil et al., 2010).

Although molecular clustering and aerosol particle formation has been intensively studied, fundamental uncertainties prevail. One of the most significant uncertainties concerns the chemical composition of the very smallest molecular clusters. Sulfuric acid has repeatedly been found in atmospheric clusters, and the concentration of sulfuric acid is known to correlate well with nanoparticle formation rates (Sipilä et al., 2010; Nieminen et al., 2009). Traditionally, binary nucleation of H$_2$SO$_4$ and H$_2$O has been the most studied mechanism, but during the last couple of decades it has become evident that a third species (e.g. ammonia or an amine) is needed as well (Kirkby et al., 2011; Ortega et al., 2012). However, the critical importance of sulfuric acid remains undisputed.

The main source of atmospheric sulfuric acid is UV-induced oxidation of SO$_2$, which is emitted from volcanoes and through fossil fuel combustion. The oxidation mechanism involves several elementary reactions, but is relatively well understood (Bondybye and Beyer, 2002). The rate limiting step is the initial S(IV) to S(V) oxidation (Li and McKee, 1997):
SO$_2$ + OH + M $\rightarrow$ HSO$_3$ + M,  \hspace{1cm} (R1)
where $M$ is a stabilizing molecule. HSO$_3$ is then further oxidized to SO$_3$ by O$_2$ before hydration to H$_2$SO$_4$. The final hydration is known to be catalysed by one or more excess water molecules and is the main sink of atmospheric SO$_3$ (Morokuma and Muguruma, 1994). In addition to this, a mechanism where SO$_2$ is oxidized by Criegee biradicals has been proposed (Welz et al., 2012; Mauldin III et al., 2012).

During the last decades, the influence of ions in aerosol formation has been targeted by several chamber studies (Kirby et al., 2011; Enghoff and Svensmark, 2008). Here, it has been firmly established that ions enhance formation of nanometer-sized aerosol particles in SO$_2$- and O$_3$-containing atmospheres under UV exposure. One possible explanation, based on classical nucleation theory, is that the energy barrier of nucleation is lowered by the charge hereby increasing the total nucleation rate (Tohmor and Valmer, 1939; Lovejoy et al., 2004). The lower barrier might result from reduced evaporation rates from ionic clusters due to charge delocalization or from increased collision rates between ionic particles and dipolar molecules or between oppositely charged particles (Su and Bowers, 1973; Kopiainen et al., 2012).

A fundamentally different approach to explain ion-induced nucleation is through ion-induced chemistry altering the composition of the metastable gas phase. This idea is supported by several experimental studies where mainly collision-limited ionic gas-phase chemical reactions were found; see e.g. Fehsenfeld and Ferguson (1974) and references therein. Further, a successful chamber study led Svensmark et al. (2007) to suggest an ion-induced SO$_2$ oxidation mechanism. Despite of this, little research has been dedicated to enhanced nucleation from ion-induced chemistry; see however Sorokin and Arnold (2007, 2009) and Enghoff et al. (2012).

Atmospheric ions are mainly products of radioactivity and galactic cosmic rays. Although both cations and free electrons are produced, most attention has gathered around the influence of the electrons and subsequent anions (Nadyko et al., 2006; Kurtén et al., 2009). It is well known that some of the first stable products are O$_2$ (H$_2$O)$_m$ and O$_3$ (H$_2$O)$_n$ clusters (Luts and Parts, 2002). The first 5 water molecules are strongly bound to the ion, but several more may attach under cold and/or humid conditions (Bork et al., 2011b).

Further, it has been shown that O$_3$ (H$_2$O)$_n$ may oxidize SO$_2$ to SO$_3$ via the reaction
\[ \text{O}_3\text{(H}_2\text{O)}_n\text{+SO}_2\rightarrow\text{SO}_3\text{(H}_2\text{O)}_n\text{+O}_2. \]  \hspace{1cm} (R2)
This reaction is probably the dominant sink of O$_3$ in most reaction chambers since CO$_2$ most often is omitted. Initially, the product cluster might partially decompose due to the large release of internal energy in the oxidation. However, the high concentrations of both O$_2$ and H$_2$O ensure that the equilibrium quickly settles. Hereafter, the predominant products are O$_2$SO$_3^-$ and O$_2$SO$_3$ (H$_2$O) (Bork et al., 2011a; Möhler et al., 1992). This is supported by a recent field study by Ehn et al. (2010), finding that, after HSO$_3^-$, O$_2$SO$_3^-$ is the second most common sulfur-based anion in a boreal forest.

The further chemical fate of O$_2$SO$_3^-$ and the extra electron is largely unknown, but is potentially important. We have investigated the most probable reactions of de- and monohydrated O$_2$SO$_3^-$ under standard conditions focusing mainly on the reaction with O$_3$. The two main reactions are
\[ \text{O}_2\text{SO}_3^--\text{W}_{0-1}+\text{O}_3\rightarrow\begin{cases} \text{O}_3\text{SO}_3^--\text{W}_{0-1}+\text{O}_2 \\ \text{O}_3^-\text{W}_{0-1}+\text{O}_2+\text{SO}_3 \end{cases} \]  \hspace{1cm} (a) (R3)
where $W$ is shorthand for water. The latter reaction is of particular interest since a catalytic cycle of SO$_2$ oxidation thereby is closed (see Fig. 1).

Using ab initio calculations we have determined the structures, energies and thermodynamics of reactants, transition states and products. We proceed to evaluate the rates of the relevant reactions and hereby evaluate the total turnover number, i.e. how many SO$_2$ oxidations a single electron on average will induce. Finally, we estimate the maximum fraction of H$_2$SO$_4$ originating from ionic catalysis under typical conditions in CO$_2$-free reaction chambers.

2 Computational details
As always when treating weakly bound systems, anionic systems and radical reactions, special care must be taken to ensure reliable results. Of special interest of this study is the relative adiabatic electron affinity of SO$_3$ and O$_3$ since this energy difference will be the thermodynamic driving force behind Reaction (R3b). The experimental electron affinity of O$_3$ has been determined to 202.9 kJ mol$^{-1}$ with high certainty (Novick et al., 1979; Arnold et al., 1994). On the contrary, despite several studies, the electron affinity of SO$_3$ remains highly uncertain. The most recent studies find values of 183 ± 10 kJ mol$^{-1}$ (Gleason, 1987) and 190 ± 10 kJ mol$^{-1}$ (Dobrin et al., 2000) suggesting that, most likely, the electron affinity of O$_3$ exceeds that of SO$_3$ by ca. 15 kJ mol$^{-1}$. 

![Fig. 1. Schematic of a simple catalytic SO$_2$ oxidation cycle. The net reaction is O$_3$ + SO$_2$ → O$_2$ + SO$_3$, and the catalyst is the electron. All reaction rates are mainly collision-limited.](image-url)
While scanning a variety of methods, we found that most ab initio methods actually predict a larger electron affinity of SO$_3$ than of O$_3$, despite large basis sets. However, the CAM-B3LYP functional is an exception to this (Yanai et al., 2004). At basis sets of at least triple zeta quality, both the order and magnitude of the electron affinity difference are in accordance with the experimental value. Therefore, we have used the CAM-B3LYP functional with aug-cc-pVTZ basis set throughout (Dunning, 1989), predicting an electron affinity difference between O$_3$ and SO$_3$ to be 18 kJ mol$^{-1}$. We note that adding further $d$ functions, as normally preferable for third period elements, is not desirable since we found that the otherwise accurate aug-cc-pV(T+d)Z basis set predicted the electron affinity difference to $-35$ kJ mol$^{-1}$. Further, it has been shown that CAM-B3LYP is superior to B3LYP with respect to determining activation energies for a range of typical chemical reactions (Peach et al., 2006; Yanai et al., 2004; Elm et al., 2012). All density function theory (DFT) calculations were performed using the Gaussian09 package (http://gaussian.com/), and all clusters were corrected for basis set superposition error using the counterpoise method (Boys and Bernardi, 1970).

The present reactions involve both neutral and charged ozone as well as highly oxidized sulfur species with unknown electronic properties. Therefore, we have performed CCSD(T)-F12 calculations with the VDZ-F12 basis set to test the DFT results (Adler et al., 2007; Peterson et al., 2008). These calculations have been performed using the MOLPRO package (http://molpro.net/) and are described in detail elsewhere (Bork et al., 2011b).

Energy barriers were determined by scans of the potential energy surface and confirmed by frequency analyses showing exactly one imaginary frequency. Further, by following the reaction coordinate in both directions, it was ensured that transition states indeed connected the desired reactants and products.

The temperature-dependent reaction rate constants, $k(T)$, were determined using harmonic transition state theory (Hänegi et al., 1990; Billing and Mikkelsen, 1996):

$$k(T) = A \times \exp \left( \frac{-E_A}{RT} \right),$$

where

$$A = \frac{\prod \nu_{\text{react}}}{\prod \nu_{\text{TS}}},$$

$E_A$ is energy barrier separating reactants and products, $R$ the molar gas constant and $\nu$ the harmonic frequencies for the reactant and transition state. The $\dagger$ indicates that the imaginary frequency should be omitted.

We finally stress that all reactants and products are radicals and hence electronic doublets. In all cases, molecular oxygen is treated as an electronic triplet but, due to the pairing with the doublet state of the ionic radical, all reactions are spin-allowed. Further, none of the considered pre-reactive complexes contains any symmetry.

### 3 Results and discussion

#### 3.1 Self dissociation

The simplest reaction of O$_2$SO$_3^-$ based clusters is spontaneous dissociation into O$_2$ and SO$_3^-_{}$:

$$\text{O}_2\text{SO}_3^-_{} - W_{0\rightarrow1} \rightarrow \text{SO}_3^-_{} - W_{0\rightarrow1} + \text{O}_2.$$  \hspace{1cm} (R4)

This reaction is potentially important since the reaction

$$\text{SO}_3^-_{} - W_{0\rightarrow1} + \text{O}_3 \rightarrow \text{SO}_3^-_{} + \text{O}_3 - W_{0\rightarrow1}$$ \hspace{1cm} (R5)

is distinctly exothermic, thus providing a direct path to complete the catalytic cycle in Fig. 1. Further, both SO$_3^-$ and O$_2$SO$_3^-$ have recently been measured by Ehn et al. (2010) in a Finnish boreal forest, where typical ratios of 1:10 were found, suggesting that this reaction may be significant.

After optimizing all species we found free O$_2$ binding energies of 48.9 and 39.8 kJ mol$^{-1}$ for the de- and monohydrated clusters at standard conditions, respectively. Little experimental data is available, but Möhler et al. (1992), based on mass spectro-metrical data, concluded that O$_2$ is bound stronger to SO$_3^-$ than H$_2$O is to CO$_3^-$, HCO$_3^-$, and NO$_3^-$. This implies that $\Delta G(R4) \leq -25$ kJ mol$^{-1}$ at room temperature (Keesee et al., 1979; Payzant et al., 1971).

These binding energies suggest much lower [SO$_3^-$]:[O$_2$SO$_3^-$] ratios than the observed ratio of 1:10. Although several factors may contribute to this discrepancy, it appears most likely that SO$_3^-$ may be stabilized in configurations not considered here, preventing O$_2$SO$_3^-$ formation. Some of the most obvious candidates include OH, HO$_2$, other radicals, and/or clusters containing more than one water. It is well known that weakly bound clusters may evaporate inside spectrometers. In accordance with this, it seems that the reported field-based concentrations of unclustered SO$_3^-$ are overestimated.

We conclude that, although some SO$_3^-$ exists, the population of O$_2$SO$_3^-$ is significantly higher and we will thus focus on this species in the remainder of this article. Finally, we note that, contrary to previous studies, we generally avoid referring to O$_2$SO$_3^-$ as SO$_3^-$ since the O$_2$--SO$_3^-$ bond resembles that of a molecular cluster more than a molecular covalent bond, concerning both distance and strength.

#### 3.2 O$_3$ collision and formation of O$_2$SO$_3^-_{} - W_{0\rightarrow1} \cdot$O$_3$

First, the O$_2$SO$_3^-_{} \cdot$O$_3$ and O$_2$SO$_3^-_{} \cdot$W$\cdot$O$_3$ molecular complexes were optimized (see Fig. 2). In the dehydrated system, only a few different stable configurations were found, while at least 10 stable configurations were found in the monohydrated cluster. Most configurations were within 10 kJ mol$^{-1}$ and are thus predicted to co-exist at typical atmospheric temperatures. However, for the remainder of this article, mainly the single most stable configurations with respect to $\Delta G^\circ$ will be considered.
Structurally, only small changes were apparent upon ozonation since the binding preferences of the O₃ and H₂O are very different. In accordance with this, the binding energy of O₃ to O₂SO⁻₃ is only minutely affected by hydration. Considering the equilibrium,

\[ \text{O}_2\text{SO}_3^-\text{W}_{0-1} + \text{O}_3 \rightleftharpoons \text{O}_2\text{SO}_3^-\text{W}_{0-1}\text{O}_3. \quad (R6) \]

Regardless of the presence or absence of water, we found \( \Delta H_{(R6)} \) values of ca. −12 kJ mol\(^{-1}\) and \( \Delta G_{(R6)}^0 \) values of ca. +12 kJ mol\(^{-1}\) implying a short lifetime towards de-ozonation since no energy barrier is present. See Ortega et al. (2012) for a description of the link between binding energies and lifetime.

Neither does the water molecule change the thermodynamics of ozonation, nor does the ozone change the thermodynamics of hydration. Considering the condensation–evaporation equilibrium, i.e.

\[ \text{O}_2\text{SO}_3^-\text{(O}_3\text{)}_{0-1} + \text{W} \rightleftharpoons \text{O}_2\text{SO}_3^-\text{(O}_3\text{)}_{0-1}\text{W}. \quad (R7) \]

we find \( \Delta H_{(R7)} \) and \( \Delta G_{(R7)}^0 \) of −42 and −7 kJ mol\(^{-1}\), respectively. Also this reaction was investigated by Möhler et al. (1992), who determined \( \Delta G_{(R7)}^0 \) to −17.2 kJ mol\(^{-1}\). To clarify this discrepancy, we optimized all relevant species with CCSD(T)-F12 and found an electronic binding energy of 51.3 kJ mol\(^{-1}\). Assuming \( \Delta S_{(R7)} \approx -120 \text{ J mol}^{-1} \text{ K}^{-1} \), which is typical of water condensation reactions, we find \( \Delta G_{(R7)}^0 = -15 \text{ kJ mol}^{-1} \), in good accordance with Möhler et al. (1992).

Using the law of mass action,

\[
\frac{[\text{O}_2\text{SO}_3^- \text{W}]}{[\text{O}_2\text{SO}_3^-]} = [W] \times \exp\left(-\frac{\Delta G}{RT}\right). \quad (3)
\]

we find that roughly 90% of O₂SO₃⁻ are hydrated at \( T = 298 \text{ K} \) and 50% relative humidity, and the fate of the hydrated cluster is thus of primary importance. However, in all but extremely dry conditions both hydrated and dehydrated clusters co-exist and should both be considered when evaluating Reactions (R3a) and (R3b).

Having established the structures and relative populations of the relevant clusters, we proceed to evaluate the possible chemical reactions.

### 3.3 Cluster decomposition

The most important reaction considered here is decomposition of the reactant cluster as

\[
\text{O}_3\cdot\text{O}_2\text{SO}_3^-\text{W}_{0-1} \rightarrow \text{O}_3\text{W}_{0-1} + \text{O}_2 + \text{SO}_3. \quad (R8)
\]

As mentioned, the Gibbs free binding energy of the O₂SO₃⁻ cluster is at least 25 kJ mol\(^{-1}\), which is only partially compensated by the transferring of the electron, and the dehydrated Reaction (R5) is ca. 15 kJ mol\(^{-1}\) exothermic.

However, the water molecule is bound significantly stronger to the O₃ ion than to the SO₃⁻ ion. Considering also this effect we find that the monohydrated cluster decomposition reaction is ca. 10 kJ mol\(^{-1}\) exothermic at \( T = 298 \text{ K} \). The Gibbs free potential energy surface is shown in Fig. 3 for \( T = 298 \text{ K} \) and tabulated in the Supplement.
Considering first the dehydrated reaction, we identified three vibrational modes of the \( \text{O}_2\text{SO}_3^-\text{O}_3 \) clusters clearly leading towards dissociation via

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

(R9)

These modes are shown in Fig. 2. All modes will be active at all times, and their combined magnitude at time, \( t \), is given by

\[
f(t) = \sum_{\nu=464,504,364} d_{\nu} \cos(\nu t),
\]

where \( d_{\nu} \) is the displacement vector of vibration \( \nu \). Assuming that all modes are all in their ground states and that their displacement vectors are of similar magnitudes, we find an effective frequency of \( 540 \text{ cm}^{-1} \) by functional analysis of \( f(t) \).

By analysing the Mulliken charges (Mulliken, 1955) during these vibrations, it was confirmed that electronic density was smoothly being transferred to \( \text{O}_3 \) from \( \text{SO}_3^- \) during a vibration and that no electronic barrier separated the charge transfer Reaction (R5). Hence, the minimum energy required to dissociate the dehydrated cluster is exactly the energy of the net reaction, here 30.5 kJ mol\(^{-1}\) above the reactants. This implies an overall rate constant of \( 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at \( T = 298 \text{ K} \) (see also Fig. 4).

Contrary to the dehydrated cluster, in the monohydrated cluster the dissociation into \( \text{O}_3\text{, O}_2, \) and \( \text{O}_3\text{W} \) is almost thermoneutral. In this case the rate limiting step is formation of the \( \text{O}_3\text{O}_2\text{SO}_3^-\text{W} \) cluster itself and the effective barrier is hence just 12.9 kJ mol\(^{-1}\) at 298 K. The mechanism leading to cluster decomposition is however identical to the dehydrated cluster, and the modes leading to dissociation are almost identical. These are given in parentheses in Fig. 2. Due to the small energy barrier, we find that this reaction essentially is collision-limited (see also Fig. 4).

Comparing the decomposition rates of the dehydrated and monohydrated systems, we see that the water molecule is significantly facilitating cluster decomposition. The main reason is the more favourable thermodynamics since \( \text{H}_2\text{O} \) is bound significantly stronger to \( \text{O}_3^- \) than to \( \text{O}_2\text{SO}_3^- \).

### 3.3.1 Formation of \( \text{O}_3\text{SO}_3^- \)

The other major reaction sink of \( \text{O}_2\text{SO}_3^- \) considered here is oxidation by \( \text{O}_3 \). The sulfur is already tetrahedrally coordinated by oxygen, so the only possible oxidation is from further O–O binding. Most likely is the formation of \( \text{O}_3\text{SO}_3^- \) since the reaction

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

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

is ca. 174 kJ mol\(^{-1}\) exothermic. The de- and monohydrated \( \text{O}_3\text{SO}_3^- \) structures are shown in the Supplement.

The two transition states of Reaction (R10) were then determined, and the monohydrated structure is shown in Fig. 5a. Besides the absent water molecule, the dehydrated structure differs only slightly from the monohydrated and is shown in the Supplement. However, considering the barrier heights, the effect of water is very significant. At standard conditions the de- and monohydrated energy barriers are 28.8 and 35.1 kJ mol\(^{-1}\) respectively, implying that the water is significantly hindering the oxygen transfer due to destabilisation of the transition state (see Fig. 3). Finally, the pre-factors (Eq. 2) were determined to \( 3.12 \times 10^{10} \text{ s}^{-1} \) and \( 7.40 \times 10^9 \text{ s}^{-1} \) respectively.

The reaction rate constant of Reaction (R10) was readily determined from Eq. (1) using the parameters described above (see Fig. 4). It is thus clear that the water molecule, while favouring charge transfer, effectively is hindering the oxidation of \( \text{O}_2\text{SO}_3^- \). The main reason is the increased energy barrier.

To our knowledge \( \text{O}_3\text{SO}_3^- \) has not previously been described in the literature, nor has it been observed in
experiments or in field studies. This suggests that $O_3SO_3^-$ is reactive and has too short of a lifetime to allow for observation. We therefore proceeded to investigate the possible decomposition of $O_3SO_3^-$ via

$$O_3SO_3^- W_{0-1} \rightarrow SO_4^- W_{0-1} + O_2.$$  \hspace{1cm} (R11)

The monohydrated transition state is shown in Fig. 5b, and the dehydrated transition state is shown in the Supplement. We hereby determine the energy barrier to ca. 13 kJ mol$^{-1}$ at standard conditions, practically independent of hydration (see Fig. 3). Since the energy release of Reaction (R10) is so much larger than the energy barrier, it is evident that Reaction (R11) is almost instantaneous.

### 3.4 Overall catalytic turnover

The presence of an ion-catalysed SO$_2$ oxidation cycle is of interest since an extra source of atmospheric H$_2$SO$_4$ significantly may alter the conditions for aerosol particle formation and growth. Although this assessment is the overall goal of this line of studies, several unresolved factors remain.

Considering the real atmosphere the most noticeable shortcoming is the influence of CO$_2$. This is known to be the dominant sink of O$_3$ via

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2.$$  \hspace{1cm} (R12)

and cannot be neglected in any realistic model (Dotan et al., 1977; Luts and Parts, 2002). The chemical fate of CO$_3^-$ is uncertain although the reaction

$$CO_3^- + SO_2 \rightarrow CO_2 + SO_3^-$$  \hspace{1cm} (R13)

is known to proceed at collision rates, similar to Reaction (R2) (Fehsenfeld and Ferguson, 1974). However, extending the catalytic cycle in Fig. 1 to include these reactions is beyond the scope of this study.

Presently, we are able to assess the overall catalytic turnover in CO$_2$-free atmospheres, including most of the until now conducted chamber studies of ion-induced nucleation. Taking all investigated clusters, their relative concentrations, and all reactions into account, we find that the probability for cluster decomposition through Reaction (R3b) is $10^{5}-10^{6}$ times more likely than other reactions between $O_3SO_3^- W_{0-1}$ and O$_3$. Details are presented in the Supplement. This thus suggests that each free electron may induce up to $10^5-10^6$ SO$_2$ oxidations in atmospheres consisting of N$_2$, O$_2$, O$_3$, H$_2$O and SO$_2$ only.

This is consistent with recent experimental results from Enghoff et al. (2012). In the absence of UV light, it was found that each electron yielded a production of $10^6$ sulfates in atmospheres heavily enriched in SO$_2$ and O$_3$. Further it was found that the isotopic fingerprint of this ion-produced sulfate was very different of sulfate from UV-induced SO$_2$ oxidation, clearly pointing at two different chemical mechanisms.

More commonly chamber atmospheres are made to resemble typical atmospheric conditions, and hence various pollutants become important. In those cases, the catalytic cycle may be terminated by mechanisms different from the ones presented so far, most likely involving species different from SO$_2$ and O$_3$. Considering, for example, a collision between O$_3$ (H$_2$O)$_n$ and a NO$_2$ radical, this will rapidly be oxidized to NO$_3^-$ with large energy gain,

$$O_3^- W_n + NO_2 \rightarrow NO_3^- W_n + O_2.$$  \hspace{1cm} (R14)

Due to the stability of NO$_3^-$, the catalytic cycle for that particular electron is most likely terminated. Other potential scavengers include any species in which an electron may be more stabilized than on O$_3$ or O$_3SO_3^-$, either through immediate charge transfer or after some chemical reaction. These may include radicals and acids, NO$_x$, cations and pre-existing aerosol particles or molecular clusters. Typically, NO$_x$ and HNO$_3$ will be the dominant electron scavengers.

We here outline two methods of determining the rate of ion-induced H$_2$SO$_4$ formation. Most simply, if the actual concentrations of the involved ions are known, the rate of ion-induced H$_2$SO$_4$ formation may be determined based on the mechanism outlined in Fig. 1. Assuming [O$_3$] $\gg$ [SO$_2$] we obtain

$$r_{\text{ion cat.}} = Z \times [O_3^- (H_2O)_n] \times [SO_2].$$  \hspace{1cm} (4)

where Z denotes the collision rate.

Alternatively, the ion-induced H$_2$SO$_4$ formation rate may be determined by realising that the incoming flux of electrons, $J_{\text{ion}}$, is the primary limiting factor. As shown in Fig. 1, the electron will remain catalytically active until scavenged, which occurs when theionic cluster is hit by a scavenger. Again assuming [O$_3$] $\gg$ [SO$_2$] and that NO$_x$ and HNO$_3$ are the dominant scavengers, the average number of catalytic cycles per electron is thus determined as

$$\text{Avg.cyc.} = \frac{Z(SO_2)}{Z(\text{electron scavenger})} \times \frac{[SO_2]}{[NO_x] + [HNO_3]}.$$  \hspace{1cm} (5)

where Z denotes the collision rate. The overall catalytic efficiency is then given as

$$r_{\text{ion cat.}} = J_{\text{ion}} \times \text{Avg.cyc.}.$$  \hspace{1cm} (7)

We now proceed to evaluate the relevance of ion-catalysed SO$_2$ oxidation in a typical CO$_2$-free chamber. Since we have no data for the ionic concentrations, we will use the latter approach. The well-known UV-induced H$_2$SO$_4$ production rate via Reaction (R1) is

$$r_{\text{UV}} = k_{\text{UV}} \times [OH] \times [SO_2].$$  \hspace{1cm} (8)

where $k_{\text{UV}} = 1.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2004).
We here assume the following conditions: \([\text{OH}] = 5 \times 10^5 \text{ cm}^{-3}\) (day and night average), \([\text{NO}_3] + [\text{HNO}_3] = 10 \text{ ppt} = 2.5 \times 10^8 \text{ cm}^{-3}\) (pristine), \([\text{SO}_2] = 5 \text{ ppb} = 1.25 \times 10^{11} \text{ cm}^{-3}\), \([\text{O}_3] \gg [\text{SO}_2]\), and \(J_{\text{ion}} = 5 \text{ ion pairs cm}^{-3} \text{ s}^{-1}\) (middle or lower troposphere). We thus obtain \(\text{Avg.cyc.} = 500\), and further obtain the contribution of \(\text{H}_2\text{SO}_4\) from ion catalysis as

\[
\frac{[\text{H}_2\text{SO}_4]_{\text{ion.cat.}}}{[\text{H}_2\text{SO}_4]_{\text{total}}} = \frac{r_{\text{ion.cat.}}}{r_{\text{ion.cat.}} + r_{\text{UV}}} = 2.5\%.
\]

Obviously, this is merely a rough estimate intended mainly as an illustrative example. However, variations in \([\text{H}_2\text{SO}_4]\) on the order of a few percent are important, and the lack of this contribution in models of gaseous sulfur chemistry may lead to significant inaccuracies in predicting aerosol formation and growth rates.

4 Conclusions

It has previously been determined that de- or monohydrated clusters of \(\text{O}_2\text{SO}_3^-\) are natural products of free atmospheric electrons. We have investigated the chemical fate of \(\text{O}_2\text{SO}_3^-\) after various reactions with \(\text{O}_3\).

We find two major reaction mechanisms leading to fundamentally different products, shown in Fig. 3. The first mechanism is a normal reaction eventually leading to \(\text{SO}_4^-\) with large energy gain. However, significant energy barriers must be overcome, and we find that this reaction is of minor importance. Of primary importance is the transfer of the electron from \(\text{O}_2\text{SO}_3^-\) to \(\text{O}_3\). In the dehydrated system this is distinctly endothermic but still requires a lower energy than crossing the energy barrier of oxidation. In the hydrated systems, the water molecule can transfer with the charge from \(\text{O}_2\text{SO}_3^-\) to \(\text{O}_3\). We find that this path is \(10^3\) to \(10^6\) times more probable than \(\text{O}_2\text{SO}_3^-\) (H2O) oxidation. This reaction closes a catalytic cycle of \(\text{SO}_2\) oxidation shown in Fig. 1. Both the chemical mechanism and the catalytic turnover number are in accordance with a recent chamber study by Enghoff et al. (2012).

Considering also the concentrations of other typical reactants, we conclude that the cycle is more probable to terminate due to reactions with an electron scavenger, most likely \(\text{NO}_3\) or \(\text{HNO}_3\), than due to its own inherent side reactions. We are unable to assess the influence of this cycle in the real atmosphere, most noticeable due to \(\text{CO}_2\). In chamber studies under UV exposure and in realistic gas mixtures, we roughly estimate the contribution of ion-catalysed \(\text{H}_2\text{SO}_4\) to be on the order of several percent.

Besides being a source of atmospheric \(\text{H}_2\text{SO}_4\), we note that the previously unknown origin of both \(\text{O}_2\text{SO}_3^-\) and \(\text{SO}_4^-\), seen in several experiments and field studies, readily is explained through this mechanism. Finally, this mechanism is also in accordance with the absence of \(\text{SO}_6^-\) from any observations since it explains why \(\text{SO}_6^-\) immediately decomposes to \(\text{SO}_4^-\) and \(\text{O}_2\).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/13/3695/2013/aepc-13-3695-2013-supplement.pdf.

Acknowledgements. The authors thank the Academy of Finland for funding and the CSC IT Centre for Science in Espoo, Finland, for computer time. We acknowledge the Villum foundation, University of Helsinki Chancellors travel grant, the Academy of Finland (CoE Project No. 1118615, LASTU Project No. 135054), ERC Project No. 257360-MOCAPAF for funding. We finally thank Martin B. Enghoff and Henrik Svensmark for valuable comments.

Edited by: A. Laaksonen

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