The reactions of SO3 with HO2 radical and H2O···HO2 radical complex. Theoretical study on the atmospheric formation of HSO5 and H2SO4†

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The influence of a single water molecule on the gas-phase reactivity of the HO2 radical has been investigated by studying the reactions of SO3 with the HO2 radical and with the H2O···HO2 radical complex. The naked reaction leads to the formation of the HSO5 radical, with a computed binding energy that is computed to be 4.76 kcal mol\(^{-1}\) more stable than the SO3 + H2O···HO2 reactants (\(\Delta(E + ZPE)\) at 0K) and an estimated branching ratio of about 34% at 298K and (b) sulfuric acid and the hydroperoxyl radical, which is computed to be 10.51 kcal mol\(^{-1}\) below the energy of the reactants (\(\Delta(E + ZPE)\) at 0K), with an estimated branching ratio of about 66% at 298K. The fact that one of the products is H2SO4 may have relevance in the chemistry of the atmosphere. Interestingly, the water molecule acts as a catalyst, [as it occurs in (a)] or as a reactant [as it occurs in (b)]. For a sake of completeness we have also calculated the anharmonic vibrational frequencies for HO2, HSO5, the HSO5···H2O hydrogen bonded complex, H2SO4, and two H2SO4···H2O complexes, in order to help with the possible experimental identification of some of these species.

Introduction

Water vapour is very important in the Earth’s atmosphere. It is the most abundant atmospheric greenhouse gas\(^1\) and it also has a key role in the chemistry of the atmosphere, showing a plethora of effects. The water molecule reacts with atomic oxygen (O, \(^{1}\)D) making it the main source of the atmospheric hydroxyl radical,\(^2\) but it can also act as a collision partner, collisionally stabilizing many reaction intermediates. Moreover, the water molecule can form hydrogen-bonded complexes with many atmospheric species, modifying their stability and changing their photochemical features.\(^3\)–\(^9\) The mean lifetime of such complexes can be quite large and consequently an important fraction of a given molecule can be “kidnapped” by a single water molecule. This occurs, for instance, in the case of the hydroperoxyl radical (HO2), where about 30% of the total HO2 concentration can be in form of the HO2···H2O complex.\(^10,11\) A single water molecule can have a catalytic effect, as occurs in the HO2 self-reaction\(^11,12\) or in the oxidation of formaldehyde by the hydroxyl radical\(^13\) and it can also produce a change in the product distribution as predicted for the HCOOH + HO reaction catalyzed by a single water molecule.\(^14\) However, it can act in the opposite direction reducing, for instance, the ability of the hydroxyl radical to oxidize methane.\(^15\) In addition, water itself can act as a reactant, reacting with SO3 to form sulfuric acid\(^16\)–\(^18\) or by reacting with carbonyl oxides (intermediates of alkene ozonolysis) producing carboxylic acids or H2O2 in a non-radical process.\(^19\)–\(^21\) In the last case, a second water molecule catalyzes the reaction. All these data clearly suggest that the role that the water vapour plays in the Earth’s atmosphere is still not well understood and deserves further research.

In this work we investigate how the water molecule affects the reactivity of the hydroperoxyl radical by studying the reaction between SO3 and HO2, and the reaction between SO3 and the HO2···H2O complex as well. This reaction has been chosen because SO3 is an important intermediate in the atmospheric formation of sulfuric acid and it is formed by oxidation of SO2 with the hydroxyl radical in a first step (reaction 1) forming the bisulphite radical (HOSO2), followed by reaction of HOSO2 with O2 (reaction 2),\(^22\) the last can occur through the HOSO2 intermediate radical,\(^23,24\) and is followed also by reaction of SO3 with water vapour (reaction 3).\(^16\)–\(^18,25–29\)

\[
\begin{align*}
\text{SO}_3 + \text{HO} &\rightarrow \text{HOSO}_2  \\
\text{HOSO}_2 + \text{O}_2 &\rightarrow \text{SO}_3 + \text{HO}_2  \\
\text{SO}_3 + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{SO}_4
\end{align*}
\]

The reaction of SO3 with HO2 is the reverse of reaction 2. It can be important for atmospheric purposes provided that the atmospheric concentration of the hydroperoxyl radical is about 50 times that of HO radical,\(^2\) and this reaction leads to the formation of HSO5.\(^30\) As far as we know, the reaction of
SO$_3$ with the H$_2$O···HO$_2$ complex has not been studied yet, in spite of the fact that its atmospheric concentration is about 15 times higher than that of the OH radical. This reaction can produce the hydrated HSO$_3$ radical, but it also opens the possibility of forming H$_2$SO$_4$, which is of great interest in the chemistry of the atmosphere.

Technical details of the calculations

The geometries for all stationary points have been optimized using the 6-311 + G(2df,2p) basis set$^{31,32}$ employing the unrestricted density functional Becke’s three-parameter and Lee–Yang–Parr functional (B3LYP) method.$^{33}$ At each stationary point we have performed harmonic frequency calculations to verify the nature of the corresponding stationary point (minima or transition state), and to provide the zero-point vibrational energy (ZPE) and the thermodynamic contributions to the enthalpy and free energy for $T = 298\text{K}$. In addition, intrinsic reaction coordinate calculations$^{34–36}$ have been performed to ensure that the transition states connect the desired reactants and products. For some selected minima of interest, we have also carried out anharmonic frequency calculations in order to help possible experimental identification of these species. The anharmonic corrections have been evaluated at the same level of theory by the second-order perturbative treatment implemented by Barone.$^{37,38}$ and the requested third and fourth energy derivatives with respect to normal coordinates have been calculated by numerical differentiation of the analytical Hessians. In recent years, several studies have pointed out the need of considerable computational effort for obtaining accurate geometries and energies of SO$_x$-containing compounds$^{39–42}$ and therefore we have performed additional geometry optimizations at the QCISD/6-311 + G(2df,2p) level of theory$^{43}$ for the stationary points involved in the SO$_3$ + HO$_2$ reaction. The final energies were obtained by performing single-point CCSD(T)$^{44,47}$ calculations at the optimized geometries using the more flexible cc-pVTZ basis set and the aug-cc-pVTZ basis set in some cases.$^{48,49}$ These calculations were done using the Gaussian 03 program package.$^{50}$

For several stationary points of interest, we have also analyzed the bonding features by using the atoms in molecules (AIM) theory by Bader.$^{51}$ This analysis was done over the B3LYP/6-311 + G(2df,2p) wave function by using the AIMPAC package.$^{52}$ Following the AIM theory, the topological properties of a bond are characterized by the existence of a bond critical point (bcp) and the values of the electron density ($\rho_{bc}$), its Laplacian ($\nabla^2 \rho_{bc}$), and the energy density ($H(\rho)$) at the bcp. A bond critical point has $\nabla \rho_{bc} = 0$ and the Laplacian of the electronic density describes two different situations. $\nabla^2 \rho_{bc} < 0$ indicates that the density is locally concentrated and characterizes a covalent bond. $\nabla^2 \rho_{bc} > 0$ indicates that the density is locally depleted and characterizes closed-shell interactions as found in ionic bonds, hydrogen bonds, dative bonds, and van der Waals interactions. For instance, a strong hydrogen bond will be associated with large values of the electron density (around 0.035 a.u.) and positive and large values of the Laplacian of the electron density (around 0.139 a.u.) at the bcp.$^{53}$ The energy density (which is the sum of the kinetic and potential energy) determines whether the accumulation of charge is stabilizing (negative values) or destabilizing (positive values).$^{54–56}$ The Molden program$^{57}$ has been used to visualize the geometrical and wave function features of the different stationary points. Finally, we have also computed the rate constants for two reactions of interest using the Rice–Ramsperger–Kassel–Marcus (RRKM) and conventional transition state theories. In these cases, the UNIMOL and Polyrate programs$^{58}$ have been employed.

The reaction between SO$_3$ and HO$_2$

Fig. 1 shows a schematic potential energy surface for the SO$_3$ + HO$_2$ reaction and the most relevant geometrical parameters of the stationary points are displayed in Fig. 1 and S1 of the ESI.$^\dagger$ The relative energies, enthalpies, and free energies are contained in Table 1.

The reaction starts with the formation of the Cr1 complex, for which our best results provide a computed binding energy of 10.48 kcal mol$^{-1}$. After the Cr1 complex the reaction proceeds through Ts1, with a very small computed energy barrier (0.80 kcal mol$^{-1}$ at 0K) and forms the HSO$_3$ (M1) radical, which is computed to be 13.81 kcal mol$^{-1}$ more stable than the separate SO$_3$ + HO$_2$ reactants. In addition, the HOSO$_2$ + O$_2$ channel (opposite of reaction 2) is computed to lie 2.82 kcal mol$^{-1}$ below the energy of SO$_3$ + HO$_2$. The reliability of our calculations can be also checked by comparing the computed enthalpy of the reaction SO$_3$ + HO$_2$ → HOSO$_2$ + O$_2$ at 298K (−2.69 kcal mol$^{-1}$, see Table 1) with the experimental value (−0.349 kcal mol$^{-1}$) obtained taking into account the experimental values of the enthalpies of formation at 298K.$^{59–62}$

From a technical point of view, Figs. 1 and S1 show that the optimized geometries obtained using B3LYP and QCISD

![Fig. 1 Schematic potential energy surface for the reaction between SO$_3$ and HO$_2$. Distances are in Angstroms at the B3LYP and QCISD (in brackets) levels of theory. The energy values correspond to calculations at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311 + G(2df,2p) level of theory.](image-url)
Table 1  Zero-point energies (ZPE in kcal mol\(^{-1}\)), Entropies (S in e.u.), and relative energies, energies plus ZPE, enthalpies, and free energies (in kcal mol\(^{-1}\)) calculated for the reaction between SO\(_3\) and HO\(_2\)\(^a\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M(^a)</th>
<th>ZPE</th>
<th>S</th>
<th>(\Delta E)</th>
<th>(\Delta(E + \text{ZPE}))</th>
<th>(\Delta H) (298K)</th>
<th>(\Delta G) (298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_3) + HO(_2)</td>
<td>A</td>
<td>16.5</td>
<td>116.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr1</td>
<td>A</td>
<td>18.7</td>
<td>81.3</td>
<td>−11.66</td>
<td>−9.44</td>
<td>−10.08</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>−12.70</td>
<td>−10.48</td>
<td>−11.12</td>
<td>−0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>−11.59</td>
<td>−9.28</td>
<td>−9.92</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ts1</td>
<td>A</td>
<td>16.5</td>
<td>76.8</td>
<td>−8.69</td>
<td>−8.67</td>
<td>−9.91</td>
<td>1.81</td>
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<tr>
<td></td>
<td>B</td>
<td>−9.70</td>
<td>−9.68</td>
<td>−10.92</td>
<td>0.80</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>C</td>
<td>−8.96</td>
<td>−8.93</td>
<td>−10.17</td>
<td>1.55</td>
<td></td>
<td></td>
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<tr>
<td>M1</td>
<td>A</td>
<td>18.6</td>
<td>79.9</td>
<td>−14.75</td>
<td>−12.64</td>
<td>−13.36</td>
<td>−2.58</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>−15.93</td>
<td>−13.81</td>
<td>−14.54</td>
<td>−3.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>−14.62</td>
<td>−12.51</td>
<td>−13.23</td>
<td>−2.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOSO(_2) + O(_2)</td>
<td>A</td>
<td>16.1</td>
<td>118.0</td>
<td>−1.33</td>
<td>−1.77</td>
<td>−1.64</td>
<td>−2.22</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>−2.38</td>
<td>−2.82</td>
<td>−2.69</td>
<td>−3.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>−1.38</td>
<td>−1.82</td>
<td>−1.69</td>
<td>−2.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) In all cases the ZPE, S, and the enthalpic and entropic corrections correspond to calculations at the B3LYP/6-311+G(2df,2p) level of theory. \(^b\) M stands for method: A: CCSD(T)/cc-pVTZ//B3LYP/6-311+G(2df,2p); B: CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(2df,2p), and C: CCSD(T)/cc-pVTZ//QCISD/6-311+G(2df,2p).

The computed geometrical parameters of M1 are displayed in Fig. S1 of the ESI\(^\dagger\) and compare quite well with the recently reported values from the literature.\(^{23,41}\) Because of the importance of the HOSO\(_2\) (M1) radical intermediate, we have also calculated the corresponding anharmonic frequencies that are contained in Table S3 of the ESI. Our computed values agree quite well with the calculated results reported recently by González-García \textit{et al.},\(^{41}\) and a more detailed discussion will be given below. For the sake of completeness we have also considered the possibility that Cr1 could dissociate into SO\(_3\) + HO. Our calculations predict the formation of these products to be endothermic by 59.5 kcal mol\(^{-1}\), so this process will not occur under atmospheric conditions.

The reaction between SO\(_3\) and the HO\(_2\)···H\(_2\)O complex

The reaction between SO\(_3\) and the HO\(_2\)···H\(_2\)O complex can occur in two different ways [(a) and (b)], depending on how the HO\(_2\)···H\(_2\)O reactant approaches to SO\(_3\). The schematic potential energy surfaces of these reactions have been drawn in Figs. 2 and 3. The energy, enthalpy, and free energy values tabulated in Table 2 and Fig. 2 show the formation of these products to be endothermic by 59.5 kcal mol\(^{-1}\), so this process will not occur under atmospheric conditions.
energy of Cr1a, pointing out the difficulty of employing a dual level in predicting the correct energies. Please note that in this case, the imaginary frequency of the transition state is only 10 cm$^{-1}$, which corresponds to a very flat potential energy surface involving the breakdown of a very weak hydrogen bond in the H$_2$O···HO$_2$ moiety and the formation of a stronger O···S bond in Cr2a. However, when the entropy contributions have been taking into account, TS1a lies above Cr1a (see $\Delta G$ (298K) values in Table 2).

Cr2a has a seven-membered-ring structure and the terminal oxygen of the hydroxyperoxide moiety in HO$_2$···H$_2$O bonds the sulfur atom of SO$_3$, whereas one of the hydrogen atoms of the H$_2$O moiety links one of the oxygen atoms of SO$_3$ through a hydrogen bond. The S···O(OH) bond distance is computed to be 2.162 Å and the topological analysis of the wave function ($\rho = 0.0709$, $\nabla^2\rho = 0.1146$, and $H = -0.0127$ a.u.) indicates that it is a weak interaction, with the same features as discussed above for Cr1. The reaction proceeds through
The process from Cr2a to M1a involves the formation of a covalent S–O(OH) bond and, at the same time, a double proton transfer, from the hydroperoxide moiety to the water moiety. The computed S–O(OH) bond length is 2.119 Å, more stable than the reactants (SO3 + H2O complex is held by a van der Waals interaction between the sulfur atom of SO3 and the oxygen of the water moiety). It is important to remark here that, as above, the whole reaction takes place without the participation of the unpaired electron. The computed energy barrier is 1.71 kcal mol⁻¹ and the process leads to the formation of Cp1b, which is predicted to lie 19.38 kcal mol⁻¹ below the energy of the SO3 + H2O complex. For Cp1b we have computed a binding energy of 8.87 kcal mol⁻¹ relative to H2SO4 + HO2. However, it must be pointed out that this is not the most stable hydrogen-bonded complex formed between sulfuric acid and the hydroperoxyl radical species. For Cp2b we have computed a binding energy of 14.14 kcal mol⁻¹ relative to H2SO4 + HO2. However, it must be pointed out that this is not the most stable hydrogen-bonded complex formed between sulfuric acid and the hydroperoxyl radical. For the sake of completeness, the most stable H2SO4····HO2 complex (named as Cp2b) is also reported here, for which we have computed a binding energy of 8.67 kcal mol⁻¹ relative to H2SO4 + HO2. Combining this value with the experimental ∆Hf (298) values for the formation of the H2O····HO2 complex, we estimate the ∆Hf (298) of this complex to be −63.49 kcal mol⁻¹. 

Table 2: Zero-point energies (ZPE in kcal mol⁻¹), Entropies (S in e.u.) and relative energies, energies plus ZPE, enthalpies and free energies (in kcal mol⁻¹) calculated for the reaction between SO3 and the H2O····HO2 radical complex^a^

<table>
<thead>
<tr>
<th>Compound</th>
<th>ZPE</th>
<th>S</th>
<th>∆E</th>
<th>(E + ZPE)</th>
<th>∆H (298K)</th>
<th>∆G (298K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO3 + H2O····HO2</td>
<td>32.5</td>
<td>133.9</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(a) Formation of HSO3····H2O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr1a</td>
<td>33.0</td>
<td>121.7</td>
<td>−2.50</td>
<td>−1.99</td>
<td>−0.18</td>
<td>2.45</td>
</tr>
<tr>
<td>Ts1a</td>
<td>33.0</td>
<td>112.7</td>
<td>−2.56</td>
<td>−2.07</td>
<td>−0.83</td>
<td>4.50</td>
</tr>
<tr>
<td>Cr2a</td>
<td>34.3</td>
<td>94.8</td>
<td>−13.18</td>
<td>−11.36</td>
<td>−11.91</td>
<td>−0.25</td>
</tr>
<tr>
<td>Ts2a</td>
<td>33.4</td>
<td>86.2</td>
<td>−10.40</td>
<td>−9.49</td>
<td>−11.14</td>
<td>3.09</td>
</tr>
<tr>
<td>M1a</td>
<td>34.2</td>
<td>94.4</td>
<td>−19.25</td>
<td>−17.56</td>
<td>−18.16</td>
<td>−6.38</td>
</tr>
<tr>
<td>(b) Formation of H2SO4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr1b</td>
<td>33.9</td>
<td>105.2</td>
<td>−9.65</td>
<td>−6.27</td>
<td>−6.20</td>
<td>2.35</td>
</tr>
<tr>
<td>Ts1b</td>
<td>33.9</td>
<td>98.2</td>
<td>−7.47</td>
<td>−6.11</td>
<td>−6.59</td>
<td>4.06</td>
</tr>
<tr>
<td>Cr2b</td>
<td>34.8</td>
<td>95.8</td>
<td>−12.82</td>
<td>−10.48</td>
<td>−11.13</td>
<td>0.22</td>
</tr>
<tr>
<td>Ts2b</td>
<td>32.1</td>
<td>87.1</td>
<td>−8.37</td>
<td>−8.77</td>
<td>−10.49</td>
<td>3.48</td>
</tr>
<tr>
<td>Cp1b</td>
<td>35.2</td>
<td>92.3</td>
<td>−22.12</td>
<td>−19.38</td>
<td>−20.33</td>
<td>−7.95</td>
</tr>
<tr>
<td>Cp2b</td>
<td>35.3</td>
<td>91.3</td>
<td>−27.41</td>
<td>−24.65</td>
<td>−25.76</td>
<td>−13.08</td>
</tr>
<tr>
<td>H2SO4 + HO2</td>
<td>33.3</td>
<td>125.8</td>
<td>−11.31</td>
<td>−10.51</td>
<td>−11.09</td>
<td>−8.67</td>
</tr>
</tbody>
</table>

^a^ Energies computed at the CCSD(T)/cc-pVTZ//B3LYP/6-311 + G(2df,2p) level of theory. The ZPE, S, and the enthalpic and entropic corrections correspond to calculations at the B3LYP/6-311 + G(2df,2p) level of theory.
of SO₃, H₂SO₄, and HO₂, we estimate a reaction enthalpy for reaction (b) of −14.68 kcal mol⁻¹, which compares well with the −11.09 kcal mol⁻¹ computed in this work (see Table 2).⁵⁹–⁶²

Finally, we have also considered the possibility that this reaction could produce H₂O₂ and HSO₄ radical and our calculations predict this channel to be endothermic by 14.0 kcal mol⁻¹ (relative to the SO₃ + H₂O ⋅ HO₂ channel), so that we conclude that these species will not be formed under atmospheric conditions as a consequence of reaction (b).

The results of the present section lead us to conclude that water introduces different features with respect to the naked reaction, acting as a catalyst, but also producing a new reactivity.

Infrared spectra
Several of the species investigated in the present work are relevant for atmospheric purposes and this fact has led us to compute their anharmonic frequencies in order to help possible experimental identification. Figs. 4–6 show the anharmonic computed IR spectra, whereas the calculated values, along the computed harmonic frequencies, relative intensities, and a tentative assignation of the vibrational modes, have been included in the ESI (Tables S1–S6). The corresponding harmonic and anharmonic rotational constants have been also included in the ESI (Table S7). In what follows, only the anharmonic frequencies will be considered. In this work we have also considered the anharmonic spectra of H₂SO₄ and the HO₂ radical, which are in a very good agreement with the experimentally observed frequencies,⁶⁸–⁷² given that the differences between the calculated and observed values smaller than 30 cm⁻¹ on average.

It is very interesting to compare, in a first step, the IR spectra of the HSO₅ (M₁) radical with that of the sulfuric acid, that have been drawn in Fig. 4. The dotted line corresponds to the H₂SO₄ spectra and the solid line corresponds to the HSO₅ (M₁) spectra. Please note that both species have structural similarities (one OH bond in sulfuric acid is substituted by an OO bond in M₁) and consequently, it is expected that the IR spectra of both compounds show some common features. A look at both spectra (Fig. 4) indicates that there are many similarities, mainly in the region of the most intense bands, what makes it difficult to distinguish between both species. The O–H stretch in M₁ appears in the same region (about 50 cm⁻¹ red-shifted with respect to H₂SO₄). Perhaps the clearest way to distinguish between the spectra is to look in the 620–830 cm⁻¹ region. The two S–O(H) stretchings in H₂SO₄ are predicted to appear at 781–832 cm⁻¹. For M₁, the S–O(H) stretching band is predicted to be at 825 cm⁻¹ and the S–O(O) stretching band, that could be considered as a signature for this species, is predicted to appear at 622 cm⁻¹.

It is also interesting to compare the predicted spectra for M₁ and M₁a, in order to see the effect of the water in forming a complex with the HSO₅ radical. The computed IR spectra of both species have been drawn in Fig. 5; the dotted line corresponds to M₁ and the solid line corresponds to M₁a. The (S)O–H stretching in M₁ is calculated to appear at 3540 cm⁻¹, but this band is predicted to be red-shifted by 780 cm⁻¹ as a consequence of the hydrogen-bond interaction in M₁a, so that it appears at 2761 cm⁻¹, whereas its intensity is predicted to be enhanced almost 12 times. This band can be considered as a signature for identifying the M₁a radical complex. The two bands in the M₁a spectra, at 3700 and 3590 cm⁻¹, respectively, correspond to the O–H stretching of the water moiety. The different S–O stretching bands appear between 600 and 1400 cm⁻¹ in both compounds and, according to the results of Fig. 5, it would be difficult to distinguish between them. Finally, it is also interesting to note the (H)O–S–O bending band that appears around 450 cm⁻¹.

![Fig. 4](image-url) Computed anharmonic spectra for the H₂SO₄ (dotted line) and M₁ (HSO₅, solid line) compounds, obtained at the B3LYP/6-311+G(2df,2p) level of theory.
can be clearly observed for M1a, but not for M1 (its intensity being computed to be almost unappreciable).

The different kind of interactions between the two H$_2$SO$_4$ · HO$_2$ complexes (Cp1b and Cp2b, see Fig. 3) produce differences in the corresponding IR spectra that allow an easy identification. The predicted spectra of both complexes have been drawn in Fig. 6; the solid line corresponds to Cp1b and the dotted line corresponds to Cp2b, where it can be clearly seen that the main differences are found at the 2700–3300 cm$^{-1}$ region, which is the region where the most O–H stretching bands appear. The Cp1b complex is held together by interaction between the terminal oxygen of the HO$_2$ radical and one of the hydrogen atoms of H$_2$SO$_4$ and by interaction between the hydrogen atom of HO$_2$ and one of the oxygen atoms of the OH groups in sulfuric acid and these two hydrogen bonds produce a red-shift in the corresponding O–H stretching frequencies. Thus, the (O)O–H stretching of the hydroperoxyl radical moiety is predicted to appear at 3237 cm$^{-1}$ with a red-shift of 174 cm$^{-1}$ relative to the free HO$_2$ radical, whereas one of the S–O(H) stretching appears at
interactions are stronger than those occurring in \( \text{Cp1b} \) RRKM calculations on the limiting steps for the \( \text{SO}_3 + \text{H}_2\text{O}_2 \) reaction. Consequently, the branching ratio is computed to be 66.7\% for the \( \text{HO}_2 \) radical, whereas one of the S–O(H) stretching bands appears at 2695 cm\(^{-1}\) with a red-shift of 894 cm\(^{-1}\) relative to the free sulfuric acid. Consequently, the stretching band at 3237 cm\(^{-1}\) identifies \( \text{Cp1b} \) and the stretching band at 2695 cm\(^{-1}\) identifies \( \text{Cp2b} \). A detailed comparison between the \( \text{Cp2b} \) and \( \text{H}_2\text{SO}_4 \) spectra can be also found in ref. 67.

Atmospheric relevance of the results

The mechanistic study carried out in the present work has pointed out that the reaction between \( \text{SO}_3 \) and \( \text{H}_2\text{O} \cdot \text{HO}_2 \) can lead to the formation of either (a) \( \text{HSO}_5 \) and/or (b) \( \text{H}_2\text{SO}_4 \). Our results displayed in Table 2 show that, in both cases, the limiting step corresponds to the first transition state (\( \text{Ts1a} \) and \( \text{Ts1b} \), respectively, see the \( \Delta G \) (298) values in Table 2) and at this point it is interesting to estimate the activation of both reaction channels, (a) and (b). To do this we have performed RRKM calculations on the limiting steps for the \( \text{SO}_3 + \text{H}_2\text{O} \cdot \text{HO}_2 \) reactions at 298K and our computed values are 2.31×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for reaction (a) and 4.37×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for reaction (b). Then the total rate constant is computed to be 6.68×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). According to these results the branching ratio is computed to be 65.4\% for the formation of \( \text{H}_2\text{SO}_4 \) [reaction (b)] and 34.6\% for the formation of \( \text{HSO}_5 \) [reaction (a)]. Similar results are obtained applying the conventional transition state theory at 298K. In this case, the computed values for the rate constants are 1.46×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for reaction (a), 2.92×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for reaction (b), and 4.38×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for the total rate constant. Then the branching ratio is computed to be 66.7\% for the formation of \( \text{H}_2\text{SO}_4 \) and 33.3\% for the formation of \( \text{HSO}_5 \), in good agreement with the values obtained from RRKM calculations.

A very important point for atmospheric purposes is to consider whether the reactions investigated in this work may play a role in the chemistry of the Earth’s atmosphere. It is well known that the gas-phase formation of \( \text{H}_2\text{SO}_4 \) occurs by the reaction of \( \text{SO}_3 \) with \( \text{H}_2\text{O} \) (reaction 3) and the atmospheric concentration of water vapour is much higher than that of the hydroperoxyl radical. Experimental results from the literature indicate that the preferred value for the rate constant of reaction 3 is 5.7×10\(^{10}\) s\(^{-1}\) at 298K and 50\% of relative humidity.\(^{73}\) The inferred upper limits for the bimolecular rate constant at 298K are 2.4×10\(^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) and 5.7×10\(^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \(^{74,75}\) whereas further experimental studies suggest a second-order dependence of the rate constant with respect to the water vapour, with a rate constant of 2.0–3.0×10\(^{-33}\) cm\(^6\) s\(^{-1}\) at 300K.\(^{26,27,29}\) It has been pointed out in the literature that the gas-phase formation of \( \text{H}_2\text{SO}_4 \) involves the reaction of \( \text{SO}_3 \) with water dimmers,\(^{16–18,26,28}\) and we will analyze here whether this reaction can compete to any extent with the reactions investigated in the present work. As pointed out above, the estimated rate constant for the \( \text{SO}_3 + \text{H}_2\text{O} \cdot \text{HO}_2 \) reaction is 6.68×10\(^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), which is about 10\(^6\) times faster than the inferred experimental value for \( \text{SO}_3 + \text{H}_2\text{O} \) reaction (see above). At 298K and with 50\% relative humidity, the gas-phase concentration of \( \text{H}_2\text{O} \) is 3.85×10\(^{17}\) molecules cm\(^{-3}\) and the gas-phase concentration of \( \text{(H}_2\text{O})_2 \) can be estimated in 1.8×10\(^{14}\) molecules cm\(^{-3}\). With a typical gas phase concentration of \( \text{HO}_2 \) radical of 3×10\(^9\) molecules cm\(^{-3}\) and taking into account that about 30\% of it could be found in a complexed form with water,\(^{11}\) we can estimate a gas-phase concentration of \( \text{H}_2\text{O} \cdot \text{HO}_2 \) close to 10\(^6\) molecules cm\(^{-3}\), which is about 10\(^8\) times smaller than the concentration of water dimer. This is approximately the same proportion as the relation between the rate constants discussed above and consequently we can conclude that the reactions investigated in the present work could play a role in the chemistry of the Earth’s atmosphere.

Conclusions

We have investigated the reactions between \( \text{SO}_3 \) and the \( \text{HO}_2 \) radical and with the \( \text{H}_2\text{O} \cdot \text{HO}_2 \) radical complex and the results of this work lead us to the following conclusions:

(a) The reaction between \( \text{SO}_3 \) and \( \text{HO}_2 \) brings about the formation of the \( \text{HSO}_5 \) radical, but the introduction of a single water molecule, namely the reaction between \( \text{SO}_3 \) and the \( \text{H}_2\text{O} \cdot \text{HO}_2 \) radical complex, leads to two different kinds of products, the hydrated \( \text{HSO}_5 \) radical and \( \text{H}_2\text{SO}_4 \) plus the \( \text{HO}_2 \) radical. The fact that one of the products of the reaction is \( \text{H}_2\text{SO}_4 \) may have relevance in the chemistry of the Earth’s atmosphere.

(b) A single water molecule introduces different features with respect to the naked reaction. The water can act as a catalyst (forming the \( \text{HSO}_5 \cdot \text{H}_2\text{O} \) complex) or as a reactant, forming sulfuric acid and hydroperoxyl radical.

(c) All elementary reactions investigated in this work, in which the \( \text{HO}_2 \) radical takes place; occur without participation of the unpaired electron, which seems to be a quite common feature in the gas-phase reactivity of the hydroperoxyl radical.

(d) For \( \text{H}_2\text{SO}_4 \), \( \text{M1}, \text{M1a}, \text{Cp1b}, \text{Cp2b} \), and \( \text{HO}_2 \), we have computed the anharmonic frequencies. A comparison of the corresponding calculated spectra will help the identification in possible experimental observation of these species.

(e) Kinetic studies derived from the calculations reported in this work estimate that at 298K, the reaction between \( \text{SO}_3 \) and \( \text{H}_2\text{O} \cdot \text{HO}_2 \) will produce approximately 66\% of \( \text{H}_2\text{SO}_4 \) and 34\% of \( \text{HSO}_5 \). Our calculations also suggest that this reaction could play a role in the chemistry of the Earth’s atmosphere.

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