

# What are the reacting species in the oxidation of bisulfite by hydrogen peroxide in water clusters?

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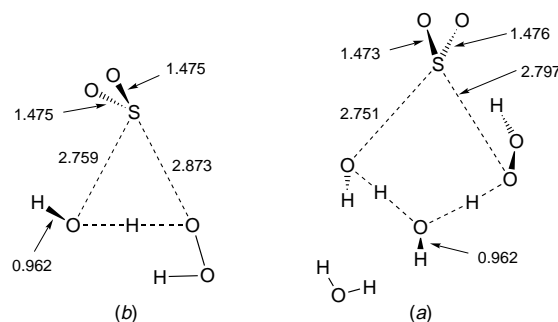
**Ab initio** calculations suggest that in the oxidation of  $\text{HSO}_3^-$  to sulfuric acid by  $\text{H}_2\text{O}_2$  under acid conditions,  $\text{SO}_2$  and not  $\text{HSO}_3^-$ , is the reacting species, a result relevant to modelling the formation of acid rain.

One of the most studied of the multiphase reactions in the troposphere is the oxidation of  $\text{SO}_2$  to sulfuric acid in water droplets by oxidants such as  $\text{H}_2\text{O}_2$ .<sup>1,2</sup> The elucidation of the mechanism of this reaction is naturally central to modelling the formation of acid rain. It is usual to invoke the involvement of the bisulfite anion,  $\text{HSO}_3^-$ , in proposed reaction mechanisms.<sup>3,4</sup> However, the actual mechanism by which the proposed intermediate, the peroxymonosulfite ion, is produced, is unclear. Indeed many  $\text{S}^{\text{IV}}$  species have been proposed to be involved along the reaction pathway.<sup>3,4</sup>

To provide further insight into this reaction we have studied the mechanism by employing high level *ab initio* electronic structure calculations. These were carried out using a 6-311+g\*\* basis<sup>5-7</sup> and included electron correlation at the B3LYP level<sup>8</sup> via the Gaussian 94 suite of programs.<sup>9</sup> Two possible transition states for the reacting  $\text{H}_2\text{O}_2$  and  $\text{HOSO}_2^-$  species, leading to the proposed intermediate peroxymonosulfite ion,<sup>3,4</sup> have been determined. One of the transition states included two explicit water molecules and the other included no solvent (Fig. 1). A similar direct participation of additional water molecules has been invoked in the calculation of the reaction of  $\text{SO}_3$  with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$ .<sup>10</sup>

A common feature of both of these calculated transition states are the two very long S–O bond lengths (2.75–2.87 Å), and two others (1.47–1.48 Å) close to the value in  $\text{SO}_2$  itself (1.46 Å). In addition, in both transition structures there is a well developed hydroxide group. Furthermore, if the unsolvated transition state is located without the  $\text{SO}_2$  being present, the structure changes very little, and involves proton transfer between  $\text{HO}^-$  and  $\text{H}_2\text{O}_2$ . Thus both transition states essentially correspond to the dissociation of the bisulfite ion to  $\text{SO}_2$ . However, it would be expected that in acid solution the developing negative charge on the OH group would be neutralized at an early stage to yield free  $\text{SO}_2$ .

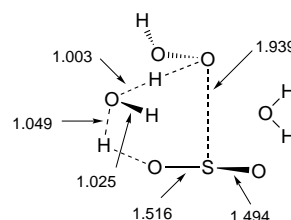
Indeed there is evidence that in the absence of  $\text{H}_2\text{O}_2$  protonation of aqueous bisulfite can lead to the formation of  $\text{SO}_2$ . NMR studies of aqueous bisulfite<sup>11</sup> have demonstrated



**Fig. 1** Transition states for the reaction of  $\text{HOSO}_2^-$  and  $\text{H}_2\text{O}_2$ , (a) with and (b) without water (bond lengths in Å)

exchange of the oxygen atoms associated with the sulfur atom, suggesting ease of formation of  $\text{SO}_2$ . Computationally we have previously found from *ab initio* calculations<sup>12</sup> that protonation of the OH oxygen atom of  $\text{HOSO}_2^-$ , in a small water cluster, also leads to the formation of  $\text{SO}_2$  with little or no barrier, again suggesting the direct involvement of  $\text{SO}_2$ . This latter result is supported by the experimental<sup>11</sup> evidence that exchange of oxygen in the bisulfite ion is first order in both  $\text{H}_3\text{O}^+$  and  $\text{HOSO}_2^-$ .

These results, both experimental and theoretical, suggest that under acid conditions the reacting species in water droplets containing bisulfite is probably  $\text{SO}_2$ . In view of this we have modelled the subsequent reaction of sulfur dioxide and  $\text{H}_2\text{O}_2$ . The corresponding transition state for the reaction leading to peroxymonosulfuric acid, and involving two explicit water molecules was located, and is shown in Fig. 2. This structure



**Fig. 2** Transition state for the reaction of  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  involving two water molecules (bond lengths in Å)

involves somewhat greater perturbation of the  $\text{SO}_2$  moiety than in the corresponding reaction of  $\text{HOSO}_2^-$  (Fig. 1), with a well developed  $\text{H}_3\text{O}^+$  entity acting as a proton shuttle between  $\text{H}_2\text{O}_2$  and  $\text{SO}_2$ . Both this structure and the corresponding transition state for the reaction of  $\text{HOSO}_2^-$  with  $\text{H}_2\text{O}_2$  involve a six-membered ring, which is probably less strained than the cyclic transition state for the reaction without explicit solvation. When this structure is further solvated using a continuum approach<sup>13</sup> the barrier from the hydrogen bonded reactants is calculated to be  $12.3 \text{ kcal mol}^{-1}$  ( $1 \text{ cal} = 4.184 \text{ J}$ ). This value is somewhat larger than the experimental barrier<sup>4</sup> of  $8.8 \text{ kcal mol}^{-1}$ , for the formation of the peroxymonosulfite ion from  $\text{H}_2\text{O}_2$  and  $\text{HOSO}_2^-$  in acid solution.

There are thus compelling reasons to believe that the reactive species involved in the formation of acid rain, from bisulfite and hydrogen peroxide in acid solution, is  $\text{SO}_2$ .

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## Footnote and References

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