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Exploration of the Mechanism of the Oxidation of Sulfur Dioxide and Bisulfite by Hydrogen Peroxide in Water Clusters Using *Ab Initio* Methods

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Abstract: Mechanisms for the oxidation of sulfur dioxide and bisulfite by hydrogen peroxide in water droplets have been explored using *ab initio* electronic structure methods. The large barriers that are found for bimolecular reactions are considerably reduced upon the inclusion of explicit water molecules, which provide a proton shuttle mechanism to facilitate the reaction. Further solvation of these clusters, either by a continuum model or by explicit water molecules modeled classically, has little effect on the reaction energetics. The transition state for reaction of bisulfite and hydrogen peroxide effectively involves SO_2 and OH^-, thus leading to acid catalysis for this reaction, analogous to the oxygen exchange in bisulfite in aqueous solution. The possibility of direct formation of sulfur(VI) species in a single step is less likely on energetic grounds.

1. Introduction

Acid rain is one of the most serious ecological problems facing industrial countries today. The major component of acid rain is sulfuric acid, resulting indirectly from the burning of fossil fuels with their small sulfur content to give SO_2. Sulfuric acid is then produced from the gaseous or aqueous phase oxidation of sulfur dioxide in the atmosphere.[1−3] The first stage in the production of sulfuric acid is the uptake of atmospheric SO_2 into cloudwater droplets followed by its oxidation. It is believed that hydrogen peroxide is the dominant oxidant at typical cloudwater pH,[4,5] and several mechanisms have been proposed for the production of hydrogen peroxide in cloudwater, which is known to be seasonally dependent, with higher concentrations observed in the summer months.[6]

Electronic structure calculations have an increasing role in understanding atmospheric chemistry at a molecular level. Indeed, the reaction of SO_3 with H_2O to form sulfuric acid in the gas phase has been extensively studied[7−9] due to its possible implication in the formation of acid rain. On the experimental side, the study of the structure and reactivity of small water clusters containing solute molecules of atmospheric relevance is also providing valuable insight into the interactions that are important in modeling atmospheric reactions.[10]

In this work, we use high-level electronic structure methods to study the aqueous phase oxidation of SO_2 once it has been taken up into the cloud droplet. Given typical cloudwater pH of 4,[2] SO_2 will exist in solution mainly as bisulfite,[11] $HOSO_2^-$,

$$SO_2 + H_2O \rightleftharpoons HOSO_2^- + H^+$$

which will subsequently be oxidized by H_2O_2 to sulfuric acid. Although there have been many experimental studies of the oxidation of bisulfite by H_2O_2,[1−6] there appear to be no theoretical studies to date. The generally accepted mechanism of the oxidation is a two-step process proposed by Hoffmann and Edwards in 1975.[12] This mechanism is consistent with the early isotope labeling studies of Halperin and Taube,[13] which found that two ^{18}O atoms from doubly labeled hydrogen peroxide were present in the product sulfate, although the stoichiometry required transfer of only one. It is also consistent with the general acid catalysis of the reaction observed by Hoffmann and Edwards.[12] The first stage of their mechanism involves nucleophilic attack by hydrogen peroxide on bisulfite to give water and a peroxymonosulfurous intermediate, which then undergoes rearrangement to sulfuric acid:

$$H_2O_2 + HOSO_2^- \rightleftharpoons H_2O + HOOSO_2^-$$

$$HOOSO_2^- \rightarrow HOSO_3^-$$

We having previously explored the potential energy surface in the region of the two low-energy isomers of bisulfite ($H{-}OSO_2^-$ and $H{-}SO_3^-$), with the aim of determining which one is

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most likely to be the reactive form in solution.[14] We found that the hydroxy form was favored in line with NMR measurements,[11] and we have assumed this form in the present study.

In this paper, we present the results of *ab initio* calculations which focus on the oxidation of bisulfite by hydrogen peroxide as well as exploring the possibility of direct oxidation of SO_2 by H_2O_2 without the involvement of bisulfite. Since our calculations are designed to gain an understanding of reactions taking place in water droplets, we pay particular attention to the role of water in these chemical reactions. In reactions which involve proton transfer, water can be intimately involved at the molecular level, as previously modeled for a variety of systems.[8,15] In addition the polar environment of the aqueous medium may modulate the reaction due to the change in the charge distribution during the course of the reaction. Such effects are often successfully modeled by employing a continuum model of the bulk solvent which can readily be incorporated into electronic structure calculations.[16]

2. Computational Methods

The calculations reported were carried out using Gaussian 94.[17] We use both the 6-31g** [18−21] and the more flexible 6-311+g** [22−24] basis to obtain stationary structures on the potential energy surface associated with a number of possible reactions involved in the first step in the formation of sulfuric acid. Electron correlation was included by the use of both density functional theory (B3LYP)[25−27] and Møller−Plesset perturbation theory (MP2).[28] Stationary structures were obtained for both basis sets using the B3LYP functional, but only for the smaller basis using MP2, due to the computational expense required for such calculations using the 6-311+g** basis on the larger clusters studied. All stationary structures were determined by analytic gradient methods, and the transition states were characterized by the calculation of harmonic frequencies.

To conveniently model bulk solvent, we used the polarizable continuum model (PCM) as developed by Tomasi and coworkers[29] and implemented within Gaussian 94 as a range of variants. We here use the IPCM method,[30] in which the electrostatic effect of the solvent is expressed in terms of an apparent charge distribution which is spread on the surface of the cavity containing the solute molecule. These charges are determined self-consistently on the 0.0004 au isodensity surface of the solute. As in our previous study of bisulfite,[14] we have encountered some convergence problems in these calculations and hence have not carried out geometry optimizations within the PCM formalism.

Table 1. Barrier Heights (kcal mol^{-1}) from Hydrogen-Bonded Reactant Complexes[a]

	MP2	B3LYP	
	6-31g**	6-31g**	6-311+g**
$SO_2\cdot H_2O_2$ (1)[b]	33.4 (35.1)	26.4 (27.9)	30.7 (31.9)
$SO_2\cdot H_2O_2$ (2)[c]	43.5 (41.9)	46.2 (45.2)	46.2 (45.9)
$SO_2\cdot H_2O_2\cdot H_2O$ (1)	20.3 (18.6)	15.1 (12.6)	18.8 (16.1)
$SO_2\cdot H_2O_2\cdot H_2O$ (2)	19.8 (17.7)	13.9 (11.4)	18.4 (16.3)
$H_2O_2\cdot HSO_3^-$ (1)[b]	31.4 (27.4)	33.6 (30.7)	26.2 (22.7)
$H_2O_2\cdot HSO_3^-$ (2)[c]	42.5 (35.5)	38.1 (34.4)	30.4 (26.6)
$SO_2\cdot H_2O_2\cdot 2H_2O$ (2)	18.0 (19.7)	14.0 (15.5)	18.5 (17.4)
$SO_2\cdot H_2O_2\cdot 2H_2O$ (1)	11.9 (10.4)	5.5 (5.3)	11.4 (12.2)
$SO_2\cdot H_2O_2\cdot 3H_2O$ (1)			6.8 (3.3)
$SO_2\cdot H_2O_2\cdot 3H_2O$ (2)			6.8 (4.9)
$SO_2\cdot H_2O_2\cdot 4H_2O$			4.5 (5.8)
$2H_2O\cdot H_2O_2\cdot HSO_3^-$	17.4 (17.2)	19.2 (19.7)	14.9 (12.4)
$H_2O\cdot H_2O_2\cdot (HO)_2SO$	36.8 (39.9)	33.3 (35.5)	35.1 (34.8)

[a] The values in parentheses are the corresponding values from the IPCM method. [b] Transition state leads to formation of sulfur(IV) species. [c] Transition state leads to formation of sulfur(VI) species.

To more realistically model the energetics of the reaction occurring within a water droplet, we have carried out Monte Carlo simulations of the solvation energies of a number of optimized stationary structures: reactants, transition states, and products. These were solvated with 10 additional water molecules, described by a TIP4P potential. The atom-centered charges used for the solutes in these simulations were obtained by a least-squares fit to the electrostatic potential of the solute. This was achieved by the CHELPG method[31] employing the B3LYP/6-311+g** wave function. Nonbonded parameters employed in these Monte Carlo simulations were taken from the literature.[32] Average enthalpies of interaction were calculated at 298 K following equilibration taking 2.42 × 10^6 configurations and data collection from 2.53 × 10^6 configurations.

3. Prediction of Stationary Structures and Energetics

A summary of the calculated barriers is given in Table 1, and the structures themselves obtained at the B3LYP/6-311+g** level are shown in Figures 1−8. Individual structural parameters quoted in the text are at the B3LYP/6-311+g** level unless otherwise stated.

3a. Reaction of SO_2 and H_2O_2. We first consider the reaction of SO_2 with H_2O_2 to form peroxymonosulfurous acid (HOS(O)OOH). The optimal structures of the isolated reactants

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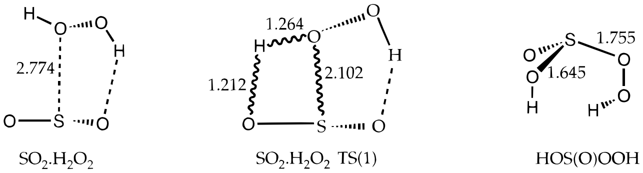


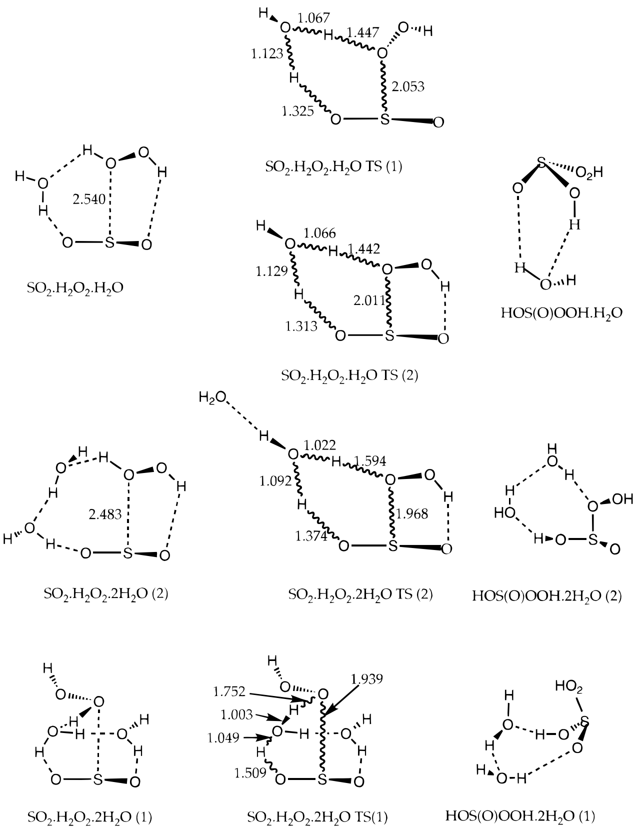
$SO_2.H_2O_2$ $SO_2.H_2O_2$ TS(1) HOS(O)OOH

Figure 1. Stationary structures for the reaction H_2O_2 and SO_2 to form peroxymonosulfurous acid. In all figures, distances are in angstroms.

(SO_2 and H_2O_2) are essentially those obtained by previous studies,[33,34] though the S−O bond lengths at the different levels of theory (1.458−1.478 Å) are longer than perhaps would have been expected compared to experiment (1.431 Å).[35] We find that SO_2 and H_2O_2 form a van der Waals complex (Figure 1: $SO_2{\cdot}H_2O_2$) with a similar structure to the two found from the interaction of SO_2 and H_2O.[36] In the latter case, one structure involves a hydrogen bond between water and an oxygen of SO_2, while in the other, there is a donor−acceptor interaction involving the water lone pair and the π^* orbital of SO_2. Both theoretically and experimentally the second structure is found to be of lower energy.[36,37] In the single $SO_2-H_2O_2$ van der Waals complex that we predict, both of these interactions are present. Thus, an oxygen atom of hydrogen peroxide sits above the sulfur, as in the lowest energy complex of water, while the hydrogen attached to the other oxygen atom is hydrogen bonded to one of the oxygens of SO_2. This involves little conformational change, with the HOOH dihedral angle varying by less than 10°. At the highest level of theory (B3LYP/6-311+g**), we find the interaction energy to be 5.9 kcal mol^{-1} and the S···O distance to be 2.774 Å, compared to an interaction energy for the $H_2O{\cdots}SO_2$ complex of 5.8 kcal mol^{-1} [36] and an S···O length of 2.824 Å.[37]

The product HOS(O)OOH appears not to have been previously studied extensively, and we predict it be less stable than the reactants (H_2O_2 and SO_2) by 4.5−11.3 kcal mol^{-1}. We note that, in its structure, the S−O bond linking the peroxy group to the sulfur is noticably longer (1.726−1.755 Å) than the other single S−O bond (1.643−1.647 Å).

The transition state for this reaction (Figure 1: $SO_2{\cdot}H_2O_2$ TS(1)) involves the addition of one of the OH groups of hydrogen peroxide across one of the sulfur−oxygen double bonds. The distances to the two oxygens from the transferring hydrogen indicate that the transition state is neither particularly early nor particularly late, these distances being 1.212 Å (SO−H) and 1.264 Å (H−OO) at the B3LYP/6-311+g** level, with other levels of theory yielding similar values. We find the O−O bond to be compressed by 0.03−0.05 Å. While this may help to stabilize the hydrogen bond, it probably indicates that the OOH unit resembles an isolated HOO radical, where the O−O bond length is 1.331 Å.[38] The forming S···O bond with a length of 2.023−2.102 Å is further from its equilibrium value than is the developing O···H bond. The calculated barrier is in the range 26.4−33.4 kcal mol^{-1} with respect to the hydrogen-bonded complex $SO_2{\cdot}H_2O_2$ (Table 1). The effect of bulk solvent estimated by employing the PCM treatment does not significantly alter the barrier, with values between 27.9 and 35.1 kcal mol^{-1}.



$SO_2.H_2O_2.H_2O$ TS (1)

$SO_2.H_2O_2.H_2O$

$SO_2.H_2O_2.H_2O$ TS (2)

$HOS(O)OOH.H_2O$

$SO_2.H_2O_2.2H_2O$ (2) $SO_2.H_2O_2.2H_2O$ TS (2) $HOS(O)OOH.2H_2O$ (2)

$SO_2.H_2O_2.2H_2O$ (1) $SO_2.H_2O_2.2H_2O$ TS(1) $HOS(O)OOH.2H_2O$ (1)

Figure 2. Stationary structures for the reaction of H_2O_2 and SO_2 to form peroxymonosulfurous acid involving one or two water molecules.

We now describe the effect of the participation of a single water molecule on this reaction. The minimum energy structure of the reactant $SO_2{\cdot}H_2O_2{\cdot}H_2O$ (Figure 2) is that of $SO_2{\cdot}H_2O_2$ with a water molecule hydrogen bonded to the free hydrogen of hydrogen peroxide. One hydrogen of the water also weakly interacts with the SO_2 molecule. This structure closely resembles the structure of the complex $SO_2{\cdot}2H_2O$, where the two water molecules do not sandwich sulfur dioxide but form a six-membered ring, each molecule contributing two atoms to the ring.[36] The effect of this solvating water molecule is to reduce the S···O distance from 2.774 to 2.540 Å, which is a considerable step in the reaction direction. Energetically this complex is stabilized by 16.3 kcal mol^{-1} (B3LYP/6-311+g**) with respect to the isolated molecules.

The corresponding product complex $HOS(O)OOH{\cdot}H_2O$ involving a single water molecule has the water molecule double hydrogen bonded between the (S)OH group and the S═O group of peroxymonosulfurous acid to form a six-membered ring (Figure 2: $HOS(O)OOH{\cdot}H_2O$). One would expect that this sulfur−oxyacid would be a relative strong acid. This is in line with the short hydrogen bond distance from the water to the OH group (1.731 Å) and the longer O−H bond (0.999 Å) compared to 0.969 Å for the other O−H bond of this acid. Energetically the $SO_2{\cdot}H_2O_2{\cdot}H_2O$ complex is more stable than the reaction product $HOS(O)OOH{\cdot}H_2O$ by 3.7−8.5 kcal mol^{-1}, while solvation reduces this difference somewhat to between 3.1 and 8.3 kcal mol^{-1}.

The calculated transition state for the reaction without water (Figure 1: $SO_2{\cdot}H_2O_2$ TS(1)) shows a four-membered ring, which is presumably quite strained. This strain can be relieved by participation of a water molecule to give a six-membered ring structure, as has been found previously for the hydration

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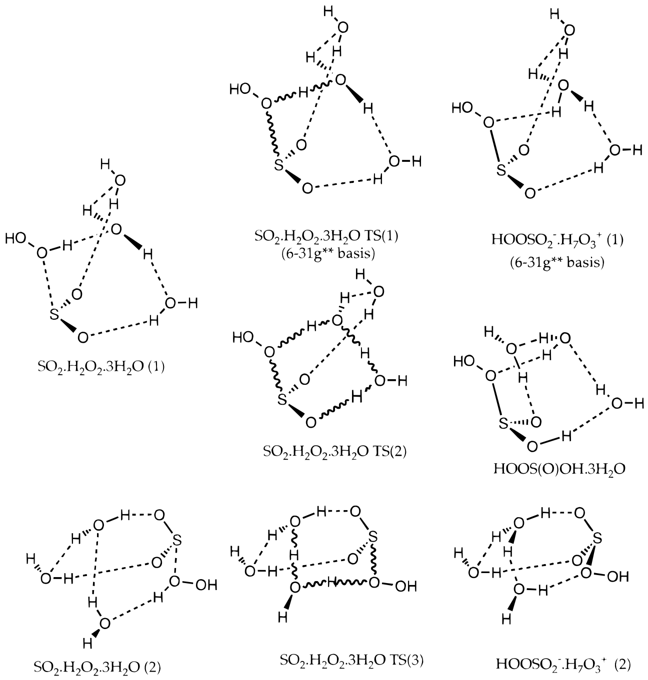
of SO_3.[7,8,39,40] There are two interesting features of this transition-state structure (Figure 2: $SO_2\cdot H_2O_2\cdot H_2O$ TS(1)). First, the $O\cdots H\cdots O$ angles are much more open than the other angles in the six-membered ring, being between 154° and 157°, and second, both migrating hydrogens are close to the catalytic water, giving a structure similar to that of $H_3O^+\cdot HO_2^-\cdot SO_2$, though a population analysis indicates only a small charge buildup on the terminal peroxy oxygen. The concept of an early, symmetric, or late transition state seems to be less easily defined for this system than for the addition of H_2O_2 to sulfur dioxide. Thus, one hydrogen is transferred to the catalytic water (O−H, 1.067−1.091 Å) while the leaving one has yet to be stretched to the point of breaking (O−H, 1.102−1.123 Å). The forming $S\cdots O$ bond is a little shorter than in the uncatalyzed transition state, being between 1.966 and 2.053 Å.

We have located a second transition state for the water-assisted oxidation of SO_2 by H_2O_2. In this structure (Figure 2: $SO_2\cdot H_2O_2\cdot H_2O$ TS(2)), the hydrogen of the peroxy group is hydrogen bonded to the passive oxygen of the SO_2 molecule. In the first transition state (Figure 2: $SO_2\cdot H_2O_2\cdot H_2O$ TS(1)), there is no such hydrogen bond, and in a droplet, the O−H group would no doubt be solvated by water. These are probably not the only transition states as different conformations of this OH group are possible. Furthermore, the atoms that are not part of the six-membered ring could be cis or trans with respect to each other. While some of these conformational possibilities may collapse to other transition states, it highlights the complexities that can arise even for the relatively small system being studied here. The effect of the internal hydrogen bond on the structure of the second transition state is to make it slightly more product-like, though at the highest level (B3LYP/6-311+g**), the only structural parameter changing significantly is the forming $S\cdots O$ bond, which is about 0.04 Å shorter. Energetically the barriers associated with both transition states are quite similar, although the internal hydrogen bond in the second transition state lowers the barrier by 0.4−1.2 kcal mol^{-1} compared to the first. The barrier heights from hydrogen-bonded reactant complexes (Table 1) for this water-assisted reaction via the second transition state are 13.9−19.8 kcal mol^{-1}, some 12 kcal mol^{-1} lower than for the reaction in the absence of water. Turning to the effect of solvation by the PCM method of these structures having a single explicit water molecule, we find that the activation barrier is consistently lower than for the unsolvated systems, being in the range 11.4−18.6 kcal mol^{-1} compared to 13.9−20.3 kcal mol^{-1} in the absence of continuum solvation. This is consistent with the polarity of the transition state arising from the proton transfer to give a structure close to that of $H_3O^+\cdot HO_2^-\cdot SO_2$ as previously discussed.

An important finding of our calculation is that the transition state for the reaction of $SO_2\cdot H_2O_2\cdot H_2O$ resembles $H_3O^+\cdot HO_2^-\cdot SO_2$, with a hydrogen of the H_3O^+ entity pointing into free space, which is expected to be strongly solvated. For this reason, we have added a second water molecule to both transition states to explore the effect of explicit solvation on these structures. It will be seen that adding a water to the transition state, $SO_2\cdot H_2O_2\cdot H_2O$ TS(2) (Figure 2), produces a structure very much as would be expected. A water molecule hydrogen bonds to the free hydrogen, though various orientations of it are calculated, depending on the theoretical level. However, adding a water to the other transition state (Figure 2: $SO_2\cdot H_2O_2\cdot H_2O$ TS(1)) yields a structure (Figure 2: $SO_2\cdot H_2O_2\cdot 2H_2O$ TS(1)) that is perhaps somewhat unexpected. The added water is positioned so that it can hydrogen bond to the free oxygen of sulfur dioxide. In the case of the other transition state ($SO_2\cdot H_2O_2\cdot 2H_2O$ TS(2)), this cannot happen due to the internal hydrogen bond between the peroxy group and this oxygen. Energetically transition state $SO_2\cdot H_2O_2\cdot 2H_2O$ TS(1) is the most stable, even though it is formally derived from the less stable transition state $SO_2\cdot H_2O_2\cdot H_2O$ TS(1). The barriers to reaction are between 14.0 and 18.5 kcal mol^{-1} for TS(2) and between 5.5 and 11.9 kcal mol^{-1} for TS(1), with the corresponding reactant structures $SO_2\cdot H_2O_2\cdot 2H_2O$ (1) and (2) differing in energy by only 1.3 kcal mol^{-1} (B3LYP/6-311+g**), (2) being the more stable. Comparing these barriers with the corresponding values for $SO_2\cdot H_2O_2\cdot H_2O$, there is little difference for the internally hydrogen bonded form (2), where the barrier lies between 13.9 and 19.8 kcal mol^{-1}. However, there is a significant reduction in the barrier for structures (1), from between 15.1 and 20.3 kcal mol^{-1} for the structure with a single water molecule to 5.5−11.9 kcal mol^{-1} on the involvement of a second water molecule (Table 1).


$SO_2.H_2O_2.3H_2O$ (1)

$SO_2.H_2O_2.3H_2O$ TS(1)
(6-31g** basis)

$HOOSO_2^-.H_7O_3^+$ (1)
(6-31g** basis)

$SO_2.H_2O_2.3H_2O$ TS(2)

HOOS(O)OH.$3H_2O$

$SO_2.H_2O_2.3H_2O$ (2)

$SO_2.H_2O_2.3H_2O$ TS(3)

$HOOSO_2^-.H_7O_3^+$ (2)

Figure 3. Stationary structures for the reaction of H_2O_2 and SO_2 involving three water molecules to form peroxymonosulfurous acid and the corresponding ions.

Monte Carlo simulations of the solvation with 10 additional water molecules were carried out for the transition-state structure $SO_2\cdot H_2O_2\cdot 2H_2O$ TS(1), corresponding to the lower energy pathway, and the reactant $SO_2\cdot H_2O_2\cdot 2H_2O$ (1) and product HOOS(O)OH$\cdot 2H_2O$ (1). These give average solvation energies of 71.5, 72.5, and 59.8 kcal mol^{-1} for the reactant, transition state, and product, respectively. Thus, further solvation of the two water structures has little effect on the barrier but preferentially stabilizes the reactants over the products by ∼10 kcal mol^{-1}. Including solvation by the continuum model for the lowest energy transition state has similarly little effect, giving a barrier between 5.3 and 12.2 kcal mol^{-1} (Table 1), and again favors the reactants by 6.5 kcal mol^{-1} (B3LYP/6-311+g**).

In view of the noteable effect of adding a second water molecule, we have introduced a third explicit water molecule into the quantum mechanical model to give $SO_2\cdot H_2O_2\cdot 3H_2O$. Two reactant structures were considered $SO_2\cdot H_2O_2\cdot 3H_2O$ (1) and (2) (Figure 3), (2) being lower in energy by 0.1 kcal mol^{-1}. Unfortunately, the structures of the corresponding transition

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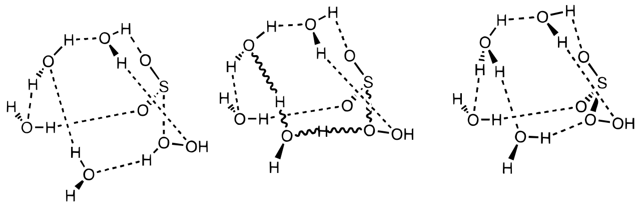
(40) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1313−1315.

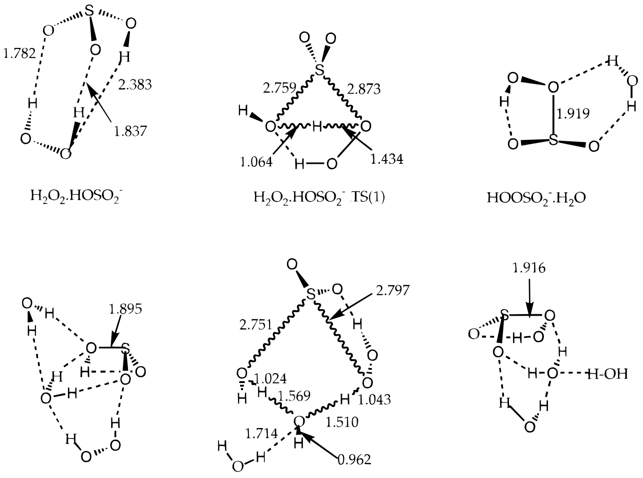


$SO_2.H_2O_2.4H_2O$ $SO_2.H_2O_2.4H_2O$ TS $HOOSO_2^-.H_9O_4^+$

Figure 4. Stationary structures for the reaction of H_2O_2 and SO_2 involving four water molecules to form the peroxymonosulfite ion.

Table 2. Imaginary Frequencies (cm^{-1}) of the Transition States

	MP2	B3LYP	
	6-31g**	6-31g**	6-311+g**
$SO_2{\cdot}H_2O_2$ (1)	1515	1495	1533
$SO_2{\cdot}H_2O_2$ (2)	823	915	873
$SO_2{\cdot}H_2O_2{\cdot}H_2O$ (1)	674	676	769
$H_2O_2{\cdot}HSO_3^-$ (1)	238	411	234
$H_2O_2{\cdot}HSO_3^-$ (2)	442	291	213
$SO_2{\cdot}H_2O_2{\cdot}2H_2O$ (2)	238	240	341
$SO_2{\cdot}H_2O_2{\cdot}2H_2O$ (1)	159	114	160
$SO_2{\cdot}H_2O_2{\cdot}3H_2O$ (1)			264
$SO_2{\cdot}H_2O_2{\cdot}3H_2O$ (2)			429
$SO_2{\cdot}H_2O_2{\cdot}4H_2O$			435
$2H_2O{\cdot}H_2O_2{\cdot}HSO_3^-$	65	108	82
$H_2O{\cdot}H_2O_2{\cdot}(HO)_2SO$	551	466	781



$H_2O_2.HOSO_2^-$ $H_2O_2.HOSO_2^-$ TS(1) $HOOSO_2^-.H_2O$

$H_2O_2.HOSO_2^-.2H_2O$ $H_2O_2.HOSO_2^-.2H_2O$ TS $HOOSO_2^-.3H_2O$

Figure 5. Stationary structures for the reaction of $HOSO_2^-$ and H_2O_2 to form the peroxymonosulfite ion, with and without direct involvement of water molecules.

states and products for this supermolecule are very basis set dependent. Thus, for example, both MP2 and B3LYP yield an ion pair as the product (Figure 3: $HOOSO_2^-{\cdot}H_7O_3^+$ (1)) with the 6-31g** basis set. However, the larger basis set (B3LYP/6-311+g**) predicts this ion pair structure to be a region of low gradient where no stationary point could be located except that of the reactants. In view of this, only the large basis set results will be discussed. Two transition states of $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ have been determined at this level, both of very different character. They both involve the H_3O^+ ion, but one arises from a two-proton shift (Figure 3: $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(2)) and gives rise to the hydrated acid, $HOOS(O)OH{\cdot}3H_2O$ as the product. The other (Figure 3: $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(3)) involves a single-proton shift and gives rise to an ionic product (Figure 3: $HOOSO_2^-{\cdot}H_7O_3^+$ (2)). This latter case is similar to those with a smaller number of water molecules in that the hydrogen peroxide gives up a proton to its closest water to form the transition state. However, in the former case (Figure 3: $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(2)), the water closest to H_2O_2 receives the proton but passes one of its own protons on to an adjacent water. Given that the shape of this part of the potential energy surface is very basis set dependent, there may not be a simple explanation as to why this occurs. However, the results do indicate that the movement of protons within the hydrogen-bonded framework of the water, sulfur dioxide, and hydrogen peroxide is a low-energy process. The calculated activation energy for this reaction is 6.8 kcal mol^{-1}, and 3.3 kcal mol^{-1} including continuum solvation effects. For the other transition state (Figure 3: $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(3)), the interest is in the product, where an ion pair is formed (Figure 3: $HOOSO_2^-{\cdot}H_7O_3^+$ (2)). Here the H_3O^+ ion is in contact with the $HOOSO_2^-$ ion, but solvated to give $(H_2O)_2{\cdot}H_3O^+$, and is thus less acidic than $HOOS(O)OH$. The energy needed to form this transition state (Figure 3: $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(3)) is 6.8 kcal mol^{-1} (4.9 kcal mol^{-1} with solvation), close to the values for the other transition state (Figure 3: $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(2)). The two different transition states and products of the $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ system show how crucial the arrangement of the solvating waters is in determining the course of the reaction.

Our final consideration of the sulfur dioxide, hydrogen peroxide, and water system consists of an investigation of $SO_2{\cdot}H_2O_2{\cdot}4H_2O$. Given the problems with the 6-31g** basis set for $SO_2{\cdot}H_2O_2{\cdot}3H_2O$, we consider only results from the 6-311+g** basis set. The transition state involves an H_3O^+ ion (Figure 4: $SO_2{\cdot}H_2O_2{\cdot}4H_2O$ TS), which lies between the proton-donating hydrogen peroxide and the water that will receive a proton to form the H_3O^+ in the product. This is similar to the situation for $SO_2{\cdot}H_2O_2{\cdot}3H_2O$ TS(3), and in fact, the similar value for the imaginary frequency of the transition state of these two structures (Table 2) implies that the surfaces have a similar shape in this region. It requires 4.5 kcal mol^{-1} to form this transition state and 5.8 kcal mol^{-1} if bulk solvent effects (PCM) are taken into account (Table 1). This value of 4.5 kcal mol^{-1} is the lowest barrier predicted for any of the transition states and arises from the effect of explicit solvation. The ionic product consists of an H_3O^+ ion with three waters hydrogen bonded to each of the hydrogens to give the $H_9O_4^+$ ion. These waters in turn are hydrogen bonded to the negative ion $HOOSO_2^-$. Energetically this zwitterion lies slightly above the reactants by 1.0 kcal mol^{-1}, a value that is not altered by solvation with the PCM approach. In comparison, it is of note that our Monte Carlo calculations of the solvation energetics of reactants and products for $SO_2{\cdot}H_2O_2{\cdot}2H_2O$ (1) (Figure 2) and $HOS(O)OOH{\cdot}2H_2O$ (1) favor the reactants by ~10 kcal mol^{-1}, leading to an energy difference between reactants and products of ~17 kcal mol^{-1}. Thus, the need for the direct participation of solvating molecules to produce the ionic product and facilitate reaction by forming the appropriate transition state cannot be overestimated.

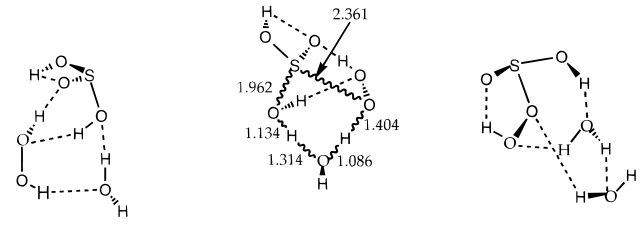
We have further examined the effect of zero-point and thermodynamic corrections to the barrier for the reaction of the cluster $SO_2{\cdot}H_2O_2{\cdot}4H_2O$, being the largest system we have studied. Whereas the zero-point terms reduce the barrier from 4.5 to 2.6 kcal mol^{-1}, the further inclusion of thermodynamic corrections yields a free energy difference between reactants and transition state of 4.8 kcal mol^{-1} at 298 K. Thus, these corrections do not radically alter the calculated barriers reported herein.

3b. Reaction of $HOSO_2^-$ and H_2O_2. Our study of the oxidation of bisulfite by hydrogen peroxide follows that of SO_2 described previously. Figure 5 shows the structures of the stationary points. We first discuss the reaction in the absence of explicit water molecules. The charge on the bisulfite ion results in it being more strongly bound to H_2O_2 than was found for SO_2 (24.1 kcal mol^{-1}, B3LYP/6-311+g**). In the reactant complex, we find two short hydrogen bonds (1.837 and 1.782 Å) to the two terminal oxygens of the bisulfite group from H_2O_2, accounting for most of this stabilization energy, though there is a longer hydrogen bond from the O−H group of $HOSO_2^-$ to one of the oxygens of H_2O_2. The O−H lengths of hydrogen peroxide are correspondingly increased somewhat (by ~0.02 Å) by forming these short hydrogen bonds.

A central feature of the predicted transition state for the formation of the peroxymonosulfite ion from the bisulfite ion, shown by all levels of theory, is that the SO_2 fragment is quite far away from the HOO···H···OH fragment. In fact, the S···O bond-breaking and -forming distances (2.759 and 2.873 Å) are longer than the S···O distance in the neutral reactant complex SO_2·H_2O_2·H_2O (2.540 Å). We have confirmed by an intrinsic reaction coordinate calculation that the product from this transition state is indeed the peroxymonosulfite ion. We may thus picture the reaction to occur first by formation of SO_2 and OH^- from bisulfite, followed by proton transfer from H_2O_2 to the OH^- entity. The resulting HO_2^- ion then forms a complex with the sulfur dioxide to give the $HOOSO_2^-$ ion. A calculation of the transition state for the transfer of a proton from H_2O_2 to HO^- without the SO_2 being present gives only slightly different hydrogen−oxygen distances. For the O−H bond being formed, the length (1.064 Å) is unchanged, while for the breaking O−H bond, a length of 1.472 Å is calculated compared to 1.434 Å. The strength of the interaction between the bisulfite ion and hydrogen peroxide in the reactant structure is high and helps stabilize the charge; this means, however, that the barrier to reaction is large and found to lie between 26.2 and 33.6 kcal mol^{-1} (Table 1). The effect of bulk solvent as given by the PCM method is to reduce this barrier to between 22.7 and 30.7 kcal mol^{-1}.

The product of the reaction is the peroxymonosulfite ion, which shows considerable structural differences from the parent acid. While it is no surprise that the terminal S−O bonds have similar lengths (1.492 and 1.512 Å), the considerable increase in the length of the other S−O bond is unexpected (1.894 Å as opposed to 1.755 Å in the parent acid). Miaskiewicz and Steudel[41] noted that certain compounds of the formula XSO_2^- can be described as Lewis adducts of sulfur dioxide and X^-. While our previous study[14] of $HOSO_2^-$ gave a sufficiently short (H)O−S bond that the description as a complex of HO^- and SO_2 was not necessarily warranted, the difficulty to accurately predict the vibrational frequency of this bond and the larger than expected change in its length on solvation[14] suggests that the electronic structure of this bond is not straightforward. It appears that $HOOSO_2^-$ is best described as a complex of HOO^- and SO_2, a view consistent with the transition state being dissociative. In the product complex being considered here, $HOOSO_2^-$·H_2O, interaction with the water molecule lengthens this S−O distance to 1.919 Å from 1.894 Å. We find the energies of the reactant H_2O_2·$HOSO_2^-$ and product $HOOSO_2^-$·H_2O complexes to be close, with the three levels of theory giving energy differences of −2.1 to 2.8 kcal mol^{-1}.

We turn now to the water-assisted reaction of $HOSO_2^-$ and H_2O_2 (Figure 5). A transition state has been located involving one catalytic water molecule, leading to a six-membered ring transition state, which is further stabilized by interacting with a second water molecule. The water molecule in the ring provides a shuttle mechanism for proton transfer to the OH^- derived from $HOSO_2^-$. This catalytic water molecule has largely dissociated, with O···H distances involving ring hydrogen atoms close to 1.5 Å and a third O−H distance of 0.962 Å. This developing OH^- group is stabilized by hydrogen bonding to the second explicit water molecule.



$(HO)_2SO.H_2O_2.H_2O$ $(HO)_2SO.H_2O_2.H_2O$ TS $(HOO)S(O)OH.2H_2O$

Figure 6. Stationary structures on the $(HO)_2SO$·H_2O_2·H_2O potential energy surface.

The important feature of the transition state for the reaction with no explicit water, namely that dissociation of bisulfite to SO_2 is well advanced, is also found in the transition state with two explicit water molecules present. Indeed, the four S−O distances are very similar in the two transition states. However, the barrier to the reaction is considerably reduced by ~11 kcal mol^{-1} on expansion of the ring from four- to six-membered. Monte Carlo simulations, as previously described, which include 10 water molecules described classically in addition to the two involved in the quantum mechanical cluster, yield interaction energies of 87.4, 87.7, and 81.9 kcal mol^{-1} for reactant, transition state, and product, respectively. Thus the barrier to reaction is essentially unaltered by further solvation, although the reactants are somewhat stabilized with respect to the products.

3c. Reaction of $(HO)_2SO$, H_2O_2, and H_2O. Although most of the sulfur(IV) in solution is solvated SO_2 or $HOSO_2^-$, a small amount of the parent acid is expected to be available as a potential reacting species. We have thus investigated sulfurous acid [$(HO)_2SO$] reacting with H_2O_2 and water. We note that experimentally the site of the hydrogen of the bisulfite ion can be on either oxygen[11] or sulfur[42] depending on the condensed-phase environment. In the solid state the sulfur is protonated, while in the aqueous medium one of the oxygens is protonated. Our modeling of explicit solvation[14] showed that there was a better arrangement of hydrogen bonds in the aqueous medium if the hydrogen was on the oxygen rather than the sulfur atom. Thus in solution we would expect that the acid would be $(HO)_2SO$ and not H−S(OH)O_2. Calculations[43] confirm this to be the structure without explicit solvation.

The structure of the reactant complex is very much as expected (Figure 6). There is a six- and a seven-membered ring of hydrogen bonds linking the water, hydrogen peroxide, and sulfurous acid with a long internal hydrogen bond in the acid. The O−H group of the acid involved in hydrogen bonding to the peroxide has lengthened (by 0.025−0.033 Å) compared to the other O−H bond of the acid (involved in a intramolecular hydrogen bond only), showing the expected strong proton-donating ability of oxy−sulfur acids.

The transition state for the sulfurous acid, hydrogen peroxide, and water reaction, though only differing by a proton from the (H_2O·H_2O_2·HSO_3^-) transition state (ignoring the solvating water), is considerably more compact. In the present case, the breaking S−O bond is 1.913−1.962 Å in length and the forming

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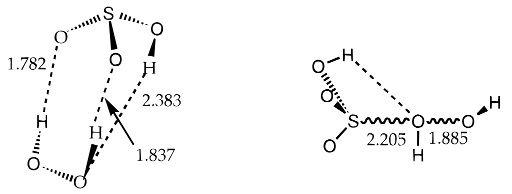
[41] Miaskiewicz, K.; Steudel, R. *J. Chem. Soc., Dalton Trans.* **1994**, 2919−2923.

[42] Johansson, L.-G.; Lindqvist, O.; Vannerberg, N.-G. *Acta Crystallogr. B* **1980**, *36*, 2523−2526.

[43] Baird, N. C.; Taylor, K. F. *J. Comput. Chem.* **1981**, *2*, 225−230.



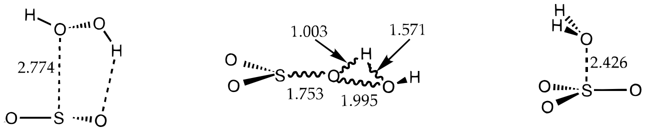
$H_2O_2.HOSO_2^-$ $H_2O_2.HOSO_2^-$ TS(2)

Figure 7. Reactant and transition state of the oxidation of $HOSO_2^-$ by H_2O_2.

S−O bond is 2.215−2.361 Å long, while for the charged transition-state case, both bonds are much longer, between 2.666 and 2.826 Å. In addition there is a considerable increase in the curvature of the potential energy surface on moving from the charged transition state to the neutral one, shown by the associated changes in the imaginary frequencies from 65i, 108i, and 82i cm^{-1} to 551i, 466i, and 781i cm^{-1}, at the three levels of theory employed (Table 2). In this reaction the explicit water molecule acts as expected, by donating a proton to the leaving O−H group of the acid and accepting a proton from the hydrogen peroxide. The transition state is late, as shown by the breaking O−H bond of water to be between 1.314 and 1.348 Å, while the forming bond is between 1.057 and 1.086 Å. Calculated barriers from the hydrogen-bonded reactant complexes lie between 33.3 and 36.8 kcal mol^{-1}. If bulk solvation effects are included, the barrier changes little (34.8 and 39.8 kcal mol^{-1}). The heat of reaction calculated from the hydrogen-bonded reactants and products is calculated to lie between 5.3 and 8.1 kcal mol^{-1} in favor of the products.

3d. Direct Formation of Sulfur(VI) from H_2O_2 and $HOSO_2^-$ or SO_2. The reaction schemes considered so far have followed the view from experiment that the aqueous-phase oxidation of bisulfite proceeds through a peroxy species, which subsequently rearranges to give the bisulfate ion. It is, nevertheless, of interest to investigate the possibility of the direct formation of sulfur(VI) species in a single step. We consider two possible routes, one involving SO_2 and the other involving $HOSO_2^-$. The transition state of this latter case, shown schematically in Figure 7 ($H_2O_2 \cdot HOSO_2^-$ TS(2)) and referred to in the tables as $H_2O_2 \cdot HSO_3^-$ (2), corresponds to a classic S_N2-type reaction which proceeds by attack of the sulfur lone pair on one of hydrogen peroxide oxygen atoms, displacing a hydroxide ion and leaving sulfuric acid. In this transition state, the forming S···O bond is calculated to be between 2.143 and 2.283 Å and the breaking O···O bond to be between 1.751 and 1.918 Å. However, the difference in these values from the MP2 and B3LYP methods indicates that this transition state is not without problems in the way it should be described. The barrier to reaction from the hydrogen-bonded complex is between 30.4 and 42.5 kcal mol^{-1}. If bulk solvent is included via the PCM model, the barrier to reaction from the complexes is between 26.6 and 35.5 kcal mol^{-1}. The product of the reaction is $H_2SO_4 \cdot HO^-$, which would no doubt react to give the bisulfate ion and water. The bisulfate ion ($HOSO_3^-$) ion is much lower in energy than the isomer, the peroxymonosulfite ion ($HOOSO_2^-$), by 52.2 kcal mol^{-1} at the B3LYP/6-311+g** level.

For the other one-step reaction to give a sulfur(VI) species ($SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$), the reaction proceeds through a transition state involving sulfur dioxide attacking hydrogen peroxide via the sulfur lone pairs (Figure 8). This scenario is somewhat similar to the transition state just discussed, but there are significant differences. The S···O forming bond is shorter by at least 0.25 Å being between 1.753 and 1.853 Å, while the leaving oxygen is closer to the hydrogen of the oxygen being attacked (Figure 8), this distance being between 1.528 and 1.876 Å. These latter two values are quite dissimilar, indicating that MP2 theory gives a later formation of the new O···H bond than does B3LYP. The O−H length of the breaking bond is 0.982 Å at the MP2 level as opposed to 1.009 Å at the B3LYP level, also confirming this view. Energetically the barrier to reaction from hydrogen-bonded reactants is between 43.5 and 46.2 kcal mol^{-1}, though the continuum models reduce this very slightly to between 41.9 and 45.9 kcal mol^{-1}. The products of the reaction are SO_3 and H_2O, which subsequently form a complex by the interaction of water lone pairs with the sulfur atom of sulfur trioxide, not too dissimilar to that found for SO_2 and H_2O_2.



$SO_2.H_2O_2$ $SO_2.H_2O_2$ TS(2) $SO_3.H_2O$

Figure 8. Stationary points involved in the formation of hydrous SO_3 from SO_2 and H_2O_2.

Morokuma[8] and Steudel,[40] building on the work of Moore Plummer[39] and von Schleyer,[7] have computationally studied the formation of H_2SO_4 from $SO_3 \cdot H_2O$ via water catalysis. In line with the studies described here, they find considerable lowering of the barrier on inclusion of a second explicit water molecule. We have studied the effect of further solvation on the $SO_3 \cdot 2H_2O$ potential energy surface[9] by using Monte Carlo methods. We find that the addition of 10 water molecules effectively eliminates the barrier found in the $SO_3 \cdot 2H_2O$ system. This is in contrast to the systems studied here where further solvation has only a small effect. This can be associated with the fact that the transition state for hydrate SO_3 is very polar (dipole moment of 6.4 D, MP2/6-311+g**), while the reactants $SO_3 \cdot 2H_2O$ have a considerably smaller dipole (3.3 D, MP2/6-311+g**). However, in contrast to this for our largest system $SO_2 \cdot H_2O_2 \cdot 4H_2O$, the reactants have a somewhat larger dipole (3.8 D) compared to the transition state (2.2 D).

4. Discussion

We first comment on the trends observed in the predicted barriers from different basis sets and models of electron correlation. We find that the use of density functional theory generally gives a lower barrier than that from MP2 theory. This is in line with a detailed study of water-assisted proton transfer by Zhang et al.[44] The larger basis gives a somewhat higher barrier than the smaller basis, except for the case of the charged species, where the additional diffuse functions are presumably important. However, our general conclusions hold for all three sets of calculations carrier out.

The calculations described herein reveal a number of important features of the reaction pathways for the formation of peroxymonosulfurous acid or the corresponding anion from SO_2 or bisulfite. The calculated barriers (summarized in Figure 9) show that the low-energy routes to the formation of a peroxysulfur(IV) species are via $SO_2 \cdot H_2O_2 \cdot xH_2O$ and $HSO_3^- \cdot H_2O_2 \cdot 2H_2O$, which involve catalytic water molecules. Which of these species is present depends on the pH. Without the explicit involvement of catalytic water molecules, the corresponding barriers are considerably higher. Further solva-

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(44) Zhang, Q.; Bell, R.; Truong, T. N. *J. Phys. Chem.* **1995**, *99*, 592−599.

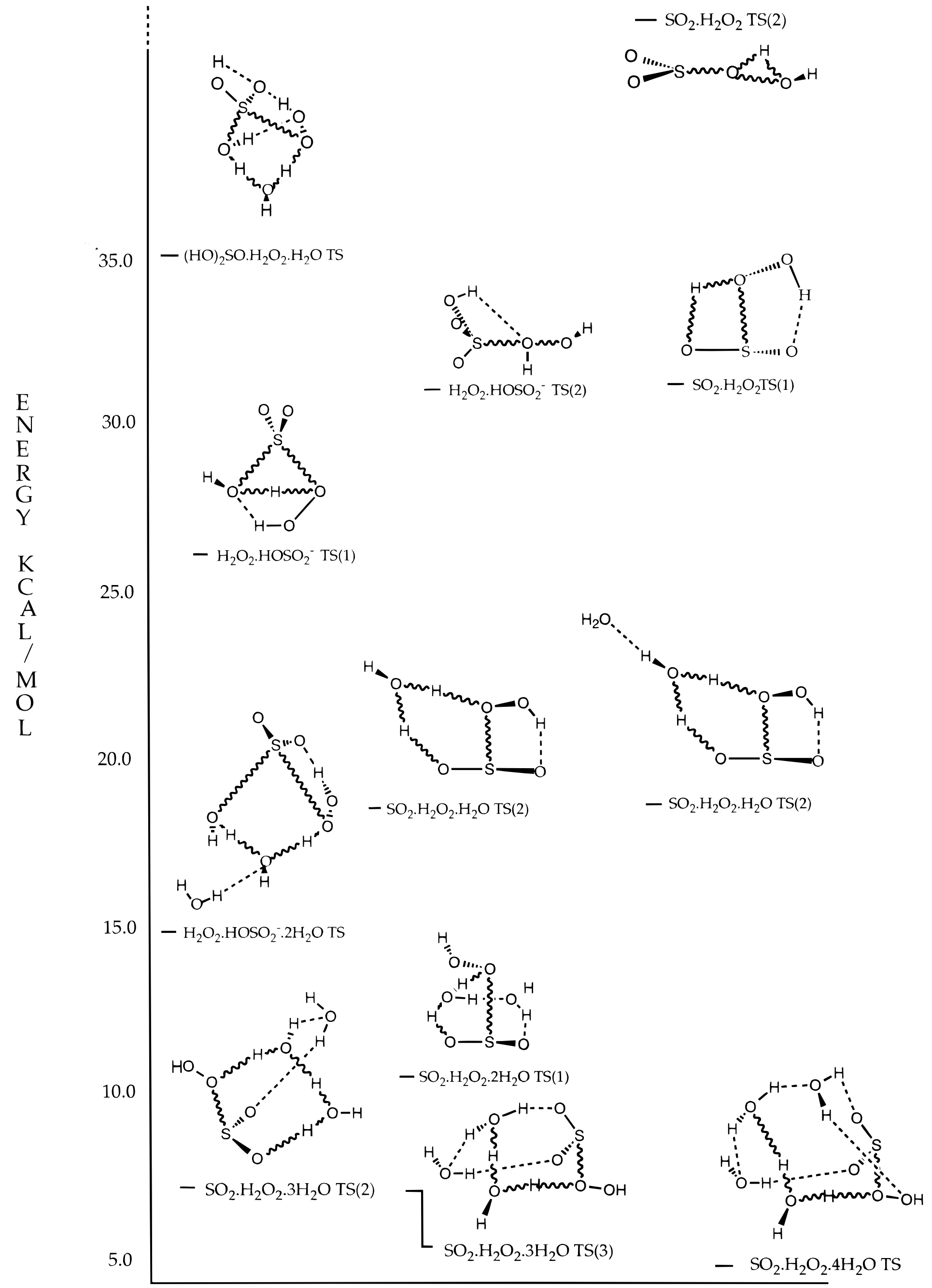

Figure 9. Relative ordering of the transition states with respect to their corresponding hydrogen-bonded reactants.

tion of these complexes using either a continuum model or explicit water molecules has little effect on the barrier.

A central feature of our calculated transition state for the oxidation of bisulfite by hydrogen peroxide is that the bisulfite is effectively dissociated into SO_2 and OH^-. In acid solution we would expect this developing charge on the OH group to be neutralized at an early stage to yield free SO_2. Hydrogen peroxide, with the direct involvement of a few water molecules, then reacts with the free sulfur dioxide, as discussed here. This explains the experimentally observed acid catalysis of the reaction. A similar effect is found in the acid-catalyzed oxygen exchange in aqueous bisulfite studied experimentally by NMR.[11] Such exchange is interpreted in terms of protonation of the hydroxy group of $HOSO_2^-$, followed by dissociation to water and SO_2, the latter being rehydrated to yield bisulfite again. The ease of this acid-catalyzed dissociation of bisulfite has been confirmed by theoretical work, which indicates little or no barrier.[14]

We now turn to a discussion of the experimental energetics of the reaction. McArdle and Hoffmann[45] have obtained a barrier (ΔH) for the formation of $HOOSO_2^-$ from $HOSO_2^-$ and H_2O_2 of 8.8 kcal mol^{-1}. In view of the trend that we have identified of B3LYP calculations underestimating the barrier, compared to MP2 results, and the work of Zhang et al.,[44] we have calculated the barrier using the larger basis at the MP2 level, utilizing the B3LYP stationary structures (MP2/6-311+g**//B3LYP/6-311+g**) which are suggested to be appropriate.[44] For the two reactions of most interest, the one involving $SO_2{\cdot}H_2O_2{\cdot}4H_2O$, which we believe occurs under acid conditions, yields a barrier (ΔE) of 9.3 kcal mol^{-1}, a value greater

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[45] McArdle, J. V.; Hoffmann, M. R. *J. Phys. Chem.* **1983**, *87*, 5425–5249.

than the B3LYP result. The reaction of $2H_2O{\cdot}H_2O_2{\cdot}HSO_3^-$, which is appropriate to basic conditions, now has a barrier of 10.7 kcal mol^{-1}, although this value is now, somewhat surprisingly, lower than the B3LYP result. Thus, the barrier is now predicted to be similar in both acid and base and to be close to the experimental value.

As far as alternative mechanisms are concerned we find that the direct formation of sulfur(VI) species from bisulfite or sulfur dioxide and hydrogen peroxide in a single step has a significantly higher barrier and is not considered to be a feasible mechanism in the condensed phase. This is in line with the experimental observation that both the oxygen atoms of hydrogen peroxide are incorporated into the sulfate ion.[13]

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