

SO₂ Hydrolysis: *Ab initio* MD Study of the Formation of Bisulfite Ion

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Ab initio molecular dynamics simulations have been performed to study the dissolution of SO₂ in water. It has been obtained that the hydrated SO₂ is surrounded by the water molecules without any S-H hydrogen bond, restraining the sulfonate anion formation but allowing the bisulfite isomer formation. The metadynamics method has been employed to explore the free energy surface of the SO₂ + H₂O reaction. The simulations revealed that the hydrated SO₂ forms bisulfite anion and hydronium cation after overcoming a ca. 17 kcal/mol free energy barrier. Direct, one-step H₂SO₃ formation could not be observed, in sharp contrast with earlier cluster calculations. These findings indicate a step-wise H₂SO₃ formation in water. The presence of the sulfur lone pair represents an important constraint on the mechanism: the nucleophilic H₂O attack can occur only from certain angles as shown by the reactive trajectories.

1 Introduction

SO₂ and its reactions play a very important role in environmental and atmospheric chemistry and also in the global sulfur cycle [1]. In particular, the various products of the SO₂ hydrolysis received considerable attention, because they are critical in corrosion processes or in the formation of sulfur containing aerosols and acid rains [1,2]. In solutions SO₂ forms SHO₃⁻ anion featuring two constitutions: the sulfonate ion and the bisulfite ion [3,4].



In the first form the proton is attached to the sulfur atom, whereas in the second form the H is bonded to one of the oxygens. According to experiments both ionic forms are present in aqueous solutions and they undergo continuous interconversion [3,4]. The corresponding acids have not yet been isolated [5], although H₂SO₃ could be detected by mass-spectrometry [6]. Experiments provided important insights into the chemistry of the sulfur species in solutions. Kinetic [4,7] and spectroscopic [8,9] measurements have been performed to study the speciation of the dissolved SO₂. It has been revealed that the stabilities of the two forms of SHO₃⁻ anion are comparable, and the bisulfite anion is the dominant form [4]. XANES studies also

supported this finding [8].

A large number of computational studies have also been done in order to provide theoretical insight into the chemistry of aqueous SO₂. Cluster calculations on gas-phase models of SO₂ and water molecules yielded different results concerning the stability of the two form of the SHO₃⁻ anion [10–14]. Some studies predicted the sulfonate form to be more stable [11,13], whereas others showed that the bisulfite form is more favorable [12,14]. The effect of the solvent taken into account in an implicit manner has not altered the conclusions [11,12]. In a very recent DFT and G3X (MP2) study [14], where the hydration has been represented with up to 8 explicit water molecules, again the bisulfite anion was predicted to be the dominant form, in accordance with experiments. Several computational studies have addressed the problem of the mechanism of the SO₂ dissolution in water [15–20]. Both the reaction energetics and the activation barriers have been calculated. These studies employed a single SO₂ molecule interacting with 1, 2, or 3 water molecules and the reaction product was H₂SO₃ molecule. While experiments suggest the direct formation of the SHO₃⁻ anion (both possible configurations) and a H₃O⁺ ion, these small clusters cannot account for any ionic separation. Nevertheless, the calculations showed the catalytic role of the additional water molecules as the predicted activation barriers decreased when

the number of water molecules was larger. For instance G3 (MP2) calculations combined with PCM B3LYP/6-31+G* solvent corrections yielded 42.5, 23.3 and 19.2 kcal/mol activation energies in the presence of 1, 2 and 3 water molecules, respectively [20]. Activation free energies are more relevant in comparison with experiment and the best estimate has been so far 31 kcal/mol for $\text{SO}_2 + 2 \text{H}_2\text{O}$ (Ref. 15) which seems too high as experiments predict relatively fast hydrolysis as compared to CO_2 hydrolysis [3,4].

In the present study I address the mechanism of the SO_2 hydrolysis in water. In order to take into account the effect of the solvent and temperature, Ab initio molecule dynamics (MD) simulations have been performed which provide realistic description of the system. The aim of the present study is to obtain a mechanistic insight into the first step of this process, where the new S-O bond formation takes place. The present simulations yielded the formation of the bisulfite anion and the release of a hydronium ion into the bulk water. This is in analogy with the formation of bicarbonate ion where the H_2CO_3 formation is preceded by the HCO_3^- formation [3,21,22]. Further studies however necessary for a detailed comparison of the possible routes, in particular to address the formation of the sulfonate anion.

2 Computational details

For the present study I applied a periodic box of $12.416 \times 12.416 \times 12.416 \text{ \AA}^3$. This simulation box has been filled with 63 water molecules and a single SO_2 . This setup represents satisfactorily an SO_2 solution. The initial configuration was obtained from classical simulation and was subject to further equilibration for 10 ps with the quantum chemical setup. The simulations have been carried out with the Car-Parrinello method [23] using the CPMD program package [24]. The BLYP exchange-correlation functional [25] has been employed. The atomic cores have been replaced with ultrasoft pseudopotentials and the electronic orbitals have been expanded on a plane-wave basis set up to 27 Ry energy cutoff at the Γ point. The fictitious electronic mass was 700 au, the time step for integrating the Verlet equations was 5 au. The hydrogens have been replaced by deuterium atoms in order to improve the decoupling between the ionic and electronic subsystems. A similar setup has been applied successfully for the dissolution of CO_2 in water at neutral [21] and high pH [26].

Chemical reactions are rare events on the time scale of the simulations, hence special techniques are necessary to steer them. There are a vast number of such methods [27]. In the present study I use the metadynamics method [28] which has

been already applied successfully for exploring reactive free energy surfaces (FES-s) [29]. Since there are excellent reviews on metadynamics [30], here I give only the relevant details to the simulations. In metadynamics we explore the FES of the reaction as a function of a few reaction coordinates (called also collective variables, CV-s). In the present case I use only a single CV which describes the coordination number of the sulfur atom with respect of the water oxygen atoms. The form of this coordinate is given in Eq. 1:

$$CV = \sum_{i \in O_w} \frac{1 - \left(\frac{r_i}{r_c}\right)^p}{1 - \left(\frac{r_i}{r_c}\right)^q} \quad (1)$$

where r_i is the distance between the sulfur atom and the i th water oxygen (O_w), r_c is a suitably selected cutoff distance (in the present case $r_c = 1.95 \text{ \AA}$), whereas the exponents p and q are 6 and 14, respectively. This CV is close to zero, when the SO_2 molecule has not formed bond with the water molecules and has a large, slightly fluctuating value between the 0.7–1 interval when a new S-O bond is present. During the metadynamics simulations we use a history dependent bias potential in the space of the CVs. Under the action of this potential the system explores the underlying FES around the reactants' minimum, finds the lowest activation free barrier and starts the exploration of the products' free energy well. A particularly important feature of the method is that the FES can be reconstructed from the time dependent potential. In this study the simulations have been carried out till the first barrier crossing occurred and the product region was sampled only for a short period [31]. Several runs have been initiated for a better statistics. In analogy with earlier simulations [21,22,26], the error of the metadynamics sampling is estimated to be around 2 kcal/mol ($\sim 3k_B T$).

3 Results and discussions

The first stage of the study is to characterize the physical hydration of the SO_2 molecule. Figure 1 shows the S-O and the S-H radial distribution functions ($g(r)$ -s). The S-O $g(r)$ shows a large peak at 1.5 \AA , which corresponds to the two oxygen atoms of the SO_2 . The first hydration shell starts at 2.3 \AA as a broad peak till 3.1 \AA and then continues with a larger and broader peak between 3.1 and 4.2 \AA . These shells contain *ca.* 2–3 and 9–10 water molecules on average. Similar but somewhat more structured hydration structure has been predicted by QM/MM simulations where the quantum region was described by Hartree-Fock method [32]. The S-H $g(r)$ gives additional insight into the hydration. It is seen that the broad first peak

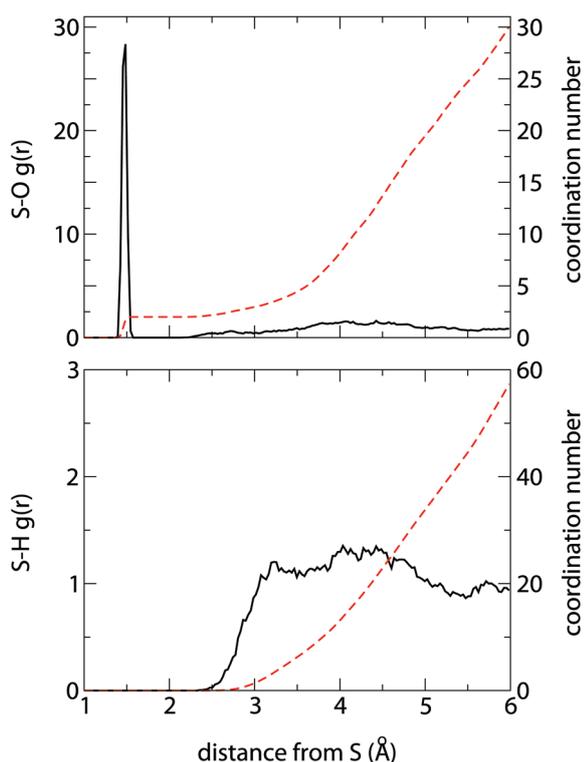


Figure 1. Radial distribution functions and the corresponding running coordination numbers for the O and H atoms around the sulfur atom.

starts only at 2.5 Å, i.e., somewhat later than the S-O $g(r)$. This indicates that the surrounding water molecules prefer orientations where they do not form H-bonds with the sulfur atom. This shows that for the water H atoms the participation in the water H-bond network is more favorable than approaching the SO₂ molecule at the sulfur side. This observation has important implications for the direct formation of the H-SO₃⁻ sulfonate anion: the eventual activation barrier of the reaction has to involve the work of breaking the H-bond network and the rotation of a water molecule. On the other hand, the simulated $g(r)$ -s show that the hydration shell around the SO₂ molecule features the reactant water molecules in proper orientation for the formation of an S-O bond.

The next step in this study is to simulate the attack of a water molecule on SO₂. The CV employed here does not bias any water molecule, hence the predicted activation free energy properly accounts for the configurational entropy arising from the hydration configurations. A typical FES obtained from the metadynamics simulation is shown in Figure 2. Inspection of the trajectories shows that the reaction is initiated by attempts

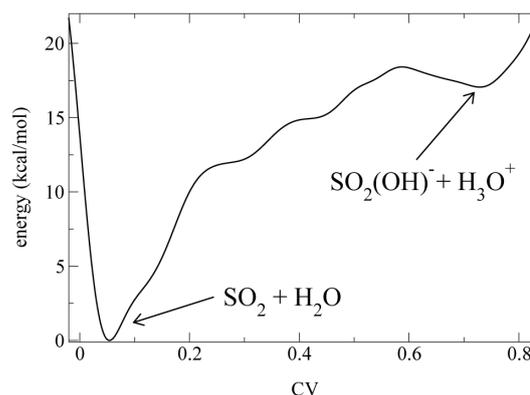


Figure 2. FES for the $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2\text{OH}^- + \text{H}_3\text{O}^+$ reaction.

from a nearby water molecule from the first hydration shell to form S-O bond. An important characteristic of these H₂O molecules is that they participate in H-bonds mostly as only donors and seldom as acceptors in the moment of the attack. When the S-O bond starts to form, the O-H bonds of the attacking water molecule elongate and hydronium ion formation can occur. When an O-H bond breaks, an ion pair (SO₂OH⁻ + H₃O⁺) forms and for a few tenths of ps they remain together, then they recombine. When the system overcomes the barrier the ion pair does not recombine, but dissociates and the hydronium ion diffuses away into the bulk. It is important to note that I could not observe a single-step formation of H₂SO₃ predicted by cluster calculations. This is because cluster calculations are strongly biased toward neutral products even when implicit, polarizable solvent models are applied and spontaneous ionic separations in small models are not possible. While in clusters the presence of a suitable H-bond chain drives the reaction toward the neutral H₂SO₃ product, in the present, extended model the presence of such H-bond chain is not a sufficient condition for H₂SO₃ formation. This clearly shows that in the presence of a large hydration sphere the reaction mechanism can significantly differ from that operating in a small gas-phase cluster of SO₂ + n H₂O.

The FES profile shows that the calculated activation free energy barrier is around 17 kcal/mol. Since experimental value is not available I compare it with the free energy barriers obtained for CO₂ hydrolysis (experimental value (Ref. 33): 21 kcal/mol, theory (Ref. 21): 19 kcal/mol). The present calculations predict a slightly lower barrier for SO₂ hydrolysis than that obtained for CO₂ hydrolysis, in agreement with the larger rate constant of the SO₂ dissolution [3,4,33]. The predicted activation free energy is much smaller than that obtained from cluster calculations (31 kcal/mol, Ref. 15). I attribute the difference to the bet-

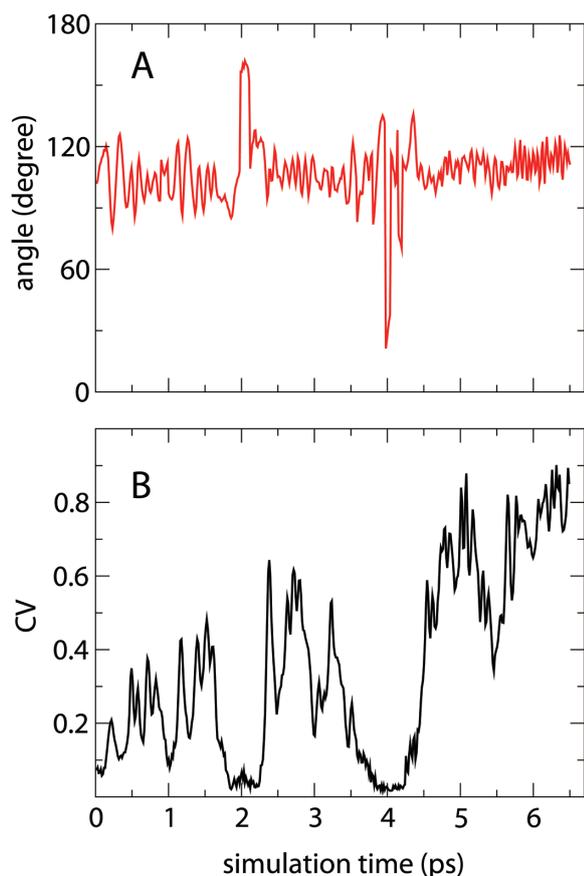


Figure 3. A: Evolution of the angle between the line defined by the S atom and the O atom of the closest water molecule and the plane of the SO_2 molecule. B: Evolution of the collective variable (CV) during the simulation.

ter treatment of the entropy contributions in the present model. Note that the FES profile in Figure 2 features two shallow oscillations at $CV = 0.3$ and $CV = 0.5$. They might be attributed to weak $\text{SO}_2\text{-H}_2\text{O}$ associations but further simulations are necessary to fully explore these regions on the FES.

Although the stoichiometry suggests similarities for CO_2 and SO_2 , the simulations showed remarkable differences in the hydrolysis mechanism. An important difference between the parent SO_2 and CO_2 molecules is their geometry: CO_2 is linear, whereas SO_2 is bent. This is because the sulfur atom has a lone pair which requires room in the ligand sphere. When the CO_2 forms HCO_3^- in water, the linear molecule transforms to a planar one. In the case of SO_2 the situation is different as shown in Figure 3. In this Figure the angle between the plane of the SO_2 molecule and the line defined by the S atom and the oxygen of the closest H_2O is plotted along with the variation of the CV. Clearly, the SO_2 undergoes almost exclusively a side"-attack,

whereas in-plane attempts are excluded. This is due to the presence of the lone pair orbital which lies in the plane of the molecule. Occasionally the closest water molecule has a large or a very small angle direction, but this is due to a temporarily expanded hydration sphere as shown by the very small value of the CV at those moments. We can conclude that the SO_2 hydrolysis occurs by a side attack from the first hydration shell, in sharp contrast with the mechanism of the bicarbonate formation [21].

4 Conclusions

Ab initio metadynamics simulations have been carried out to study the first step of the SO_2 hydrolysis. At equilibrium simulations the orientation of the water molecules in the hydration shell of SO_2 suggests an easier formation of the bisulfite anion than the sulfonate isomer. The metadynamics calculations yielded $\text{SO}_2\text{OH}^- + \text{H}_3\text{O}^+$ formation, whereas the one-step formation of H_2SO_3 could not be obtained. The activation free energy of the bisulfite formation is around 17 kcal/mol. The presence of the sulfur lone pair represents a strong constraint on the possible directions of the nucleophilic attack of the water molecules: the angle between the plane of the SO_2 molecule and the S-O (H_2) axis has to be between $80\text{--}120^\circ$. Further studies are ongoing to reveal additional details of the mechanism and to explore the other reaction steps of the bisulfite-sulfonate- H_2SO_3 equilibria.

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