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Triplet state promoted reaction of SO_2 with H_2O by competition between proton coupled electron transfer (pcet) and hydrogen atom transfer (hat) processes†

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The SO_2 + H_2O reaction is proposed to be the starting process for the oxidation of sulfur dioxide to sulfate in liquid water, although the thermal reaction displays a high activation barrier. Recent studies have suggested that the reaction can be promoted by light absorption in the near UV. We report *ab initio* calculations showing that the SO_2 excited triplet state is unstable in water, as it immediately reacts with H_2O through a water-assisted proton coupled electron transfer mechanism forming OH and HOSO radicals. The work provides new insights for a general class of excited-state promoted reactions of related YXY compounds with water, where Y is a chalcogen atom and X is either an atom or a functional group, which opens up interesting chemical perspectives in technological applications of photoinduced H-transfer.

Introduction

Hydrogen atom transfer originated by radicals is one of the most fundamental processes for several areas of chemistry, from biological processes, to chemical synthesis, materials science, hydrocarbon combustion or atmospheric chemistry.[1–12] In the context of the chemistry of the troposphere, the oxidation processes involving abstraction of hydrogen atoms by radicals are among the most important reactions and many of these processes are well known.[7,13] Very recently, it has been shown that the triplet excited state of SO_2 can react with water producing hydroxyl radicals and is the most oxidizing species in the Earth's atmosphere,[14] and it has also been predicted that this reaction is enhanced by several orders of magnitude at the air–water (air–clouds) interface.[15] Because the SO_2 molecule is an air pollutant formed as a byproduct of fossil fuel combustion, there is broad interest in the chemistry of SO_2 ranging from its industrial clean-up to understanding the chemistry associated with its oxidation to sulfuric acid, a major constituent of acid rain.[7,16,17] On a fundamental level, the oxidation of SO_2 is thought to proceed by the following steps in the gas-phase:

$$SO_2(g) + OH(g) \rightarrow HOSO_2(g) \quad (1)$$

$$HOSO_2(g) + O_2(g) \rightarrow SO_3(g) + HO_2(g) \quad (2)$$

$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g) \quad (3)$$

or an aqueous-phase

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq) \quad (4)$$

$$H_2SO_3(aq) + H_2O_2(aq) \rightarrow H_2O(l) + H_2SO_4(aq) \quad (5)$$

Studies in the literature have focused on reactions (1)–(3),[18,19] sometimes assuming a water dimer (ref. 17), but those that have addressed the reaction of SO_2 with H_2O have been few. Recently, Kroll *et al.*[14] proposed that SO_2 driven by sunlight could initiate the reaction producing HOSO and OH radicals. However, details on the electronic features triggering the reaction mechanism were not analyzed. In the present work we show that the reaction of the triplet exited state of sulfur dioxide with water yielding HOSO and OH radicals belongs to a subcategory of proton coupled electron transfer (pcet) processes that involve photo-excitation of SO_2 followed by intersystem crossing to a triplet state. The effect of further water molecules on these reactions has been also investigated because it has interest in modeling how these processes behave in different environments, such as

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for instance at the air–water interface, where we have predicted an enhancement of the reaction rate by several orders of magnitude,[15] or in the bulk.

Results and discussion

Our investigation has been carried out by doing calculations with B3LYP[20] density functional theory and coupled cluster with single, double and extrapolation to triple excitations (CCSD(T)),[21] along with the 6-311+G(2df,2p), aug-cc-pVTZ, aug-cc-pVQZ and complete CBS basis sets.[22–26] The bonding interactions have been analyzed within the framework of atoms in molecules (AIM),[27] and for some elementary reactions we have calculated the corresponding rate constants according to transition state theory. Full details of the theoretical methods employed are discussed in the ESI.†

The reaction of the SO_2 (X^1A_1) ground state with H_2O

The interaction between SO_2 and H_2O in the gas phase first forms a complex. Computational studies have determined conformational structures for the SO_2–H_2O complex.[28,29] It is established that the global-minimum has C_s symmetry with H_2O lying above the plane of SO_2. Such a structure stems mainly from the interaction between the S atom of SO_2 and the O atom in H_2O. Both theoretical and experimental gas phase microwave spectroscopy and frozen matrix infrared spectroscopy studies[30–32] have confirmed and validated this picture. The binding energy of SO_2 to H_2O was estimated to be between 3.5 and 5.5 kcal mol^{-1}.[29,32]

The transition state for addition of H_2O to SO_2 to form sulfurous acid, H_2SO_3, involves a four-centered transition state in which the O–H bond in water is broken while forming a new O–H bond on the SO_2, and the OH from water forms an S–OH bond with the SO_2. The activation barrier for the addition of H_2O to SO_2 to form H_2SO_3 is calculated to be 30–33.9 kcal mol^{-1}.[29,33,34] All theoretical computations show a high reaction barrier and suggest that SO_2 does not react with H_2O in the gas phase and no experimental studies have observed the H_2SO_3 product in the gas phase; nor has it been isolated in a matrix.

The reaction of the SO_2 (a^3B_1) excited state with H_2O

The lowest triplet state of SO_2 (a^3B_1) may be accessed by near-UV solar excitation (absorption band extending from 240 to 330 nm) to its excited $^1B_1$ state followed by rapid intersystem crossing.[35–39] The lifetime of the lowest triplet state of SO_2 has been estimated to be $\tau = (7.9 \pm 1.7) \times 10^{-4}$ s.[40] Because of the long lifetime, the triplet state has been suggested to react with water to form H_2SO_3 in the gas phase[41] or OH + HOSO.[14]

The potential energy surface for the reaction of SO_2 (a^3B_1) with water is shown in Fig. 1. Only the most stable structures involving the (a^3B_1) excited state are discussed here but other structures are reported as ESI† (Tables S1, S2 and Fig. S1, S2). We have found that there are two different kinds of processes leading to product formation of HOSO + OH. Fig. 1 shows that the transition state structure having the lowest energy barrier (**ATS1**) lies 6.53 kcal mol^{-1} above the energy of the separate reactants and compares quite well with the data reported very

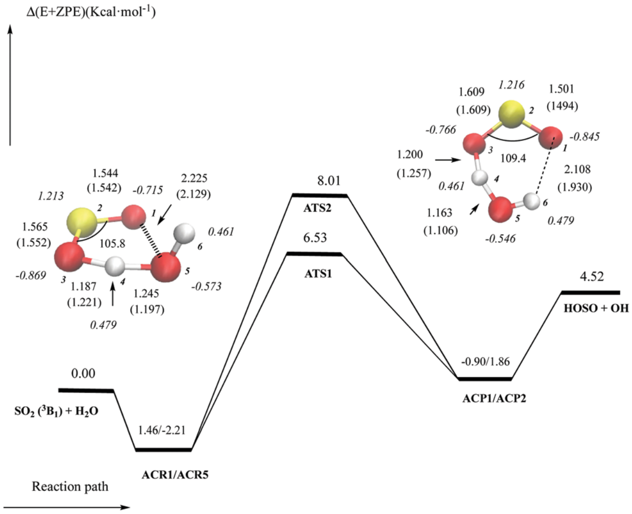

Fig. 1 Schematic potential energy surface (CCSDT/CBS//B3LYP/aug-cc-pVTZ) for the SO_2 (a^3B_1) + H_2O reaction. Energies (kcal mol^{-1}) include zero-point energies. Interatomic distances (in Å), OSO angles (degrees) computed at the B3LYP (plain numbers) and at the CCSD(T) level (in parenthesis), and net atomic charges (italics, in a.u.) for the transition state structures are indicated.

recently by Kroll and coworkers.[14] In addition, Fig. 1 also shows the existence of a second reaction path (*via* **ATS2**) whose energy barrier is 1.48 kcal mol^{-1} higher. Both elementary processes have different electronic features and we have plotted in Fig. 2 an orbital diagram to illustrate them.

In the process going through **ATS1**, the reaction between SO_2 (a^3B_1) and water (X^1A_1) involves the interaction of the $8a_1$ singly occupied orbital of the triplet state of SO_2 with a lone pair of water, so that the doubly occupied 20a and the singly occupied 22a orbitals are formed in **ATS1**. The structure and electronic features of this transition state allow the electronic density of the lone pair of water to interact with the electronic density of the unpaired electron of SO_2 (orbital $8a_1$) localized over the terminal oxygen atom of sulfur dioxide opposite the oxygen

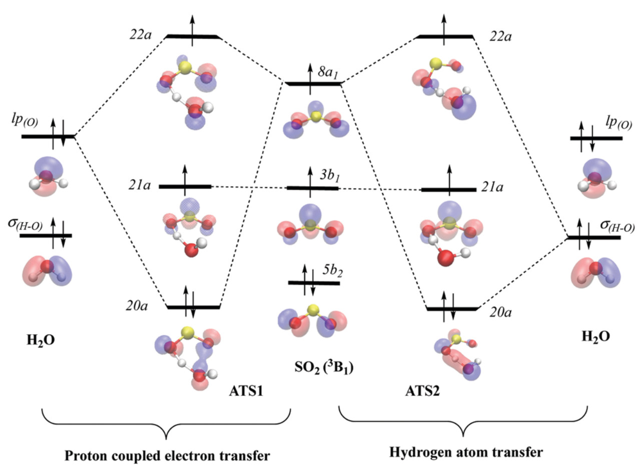

Fig. 2 Orbital diagram for the pcet and hat mechanisms for the SO_2 (a^3B_1) + H_2O reaction, along with a picture of the natural orbitals involved in these processes.

atom of the water moiety. Fig. 2 shows that in the doubly occupied orbital 20a of **ATS1**, the electron density is shared between the oxygen atom of the water moiety and the terminal oxygen atom of SO_2, whereas in the singly occupied 22a orbital the anti-bonding combination is formed. This situation corresponds to a two-center three-electron structure in which an electron is transferred from the lone pair of water to the terminal oxygen atom of SO_2. This originates a simultaneous jump of a proton from water to the other oxygen atom of SO_2 so that the whole process can be described as a proton coupled electron transfer (pcet) mechanism. The $3b_1$ orbital of SO_2 converts into the 21a orbital of **ATS1**; it has no interaction with water and consequently acts as a spectator in the reaction. Its sole role is to maintain the triplet multiplicity. It is worth pointing out that the electronic features of this pcet mechanism are the same as those described for the oxidation of organic and inorganic species by radicals.[9,42–51]

The process *via* **ATS2** occurs in a different way. Fig. 2 shows that it takes place by interaction of the $8a_1$ orbital of SO_2 and the (O–H) σ bond of water forming the doubly occupied 20a orbital with bonding character and the singly occupied 22a orbital with anti-bonding character. This situation corresponds to a three-center three-electron system where the electronic density lies over the O–H–O moiety and describes the well-known hydrogen atom transfer mechanism (hat), in which simultaneous breaking and forming of the covalent bonds (OS)O–H–O(H) occurs. It is also interesting to point out that only small differences are found in the natural atomic charges of both transition states, which can be attributed to a minor role played by the unpaired electron in these processes. One should note however that the two oxygen atoms of the SO_2 moiety bear different net charge in the two transition structures. Thus, in the case of **ATS1**, the largest negative charge corresponds to the H^+-acceptor O atom. Conversely, in the case of **ATS2**, the H-acceptor O atom bears the lowest negative charge, and the remaining charge is accumulated on the opposite O atom because it is involved in a H-bond with water.

The electronic features of these two reaction mechanisms are also supported by the bonding analysis according to the AIM theory, which points out the existence of a bond critical point between O1 and O5 in the case of **ATS1** and a hydrogen bond interaction between O1 and H6 in the case of **ATS2**, as discussed in previous work on related systems[9] (see also the ESI†). It is also worth mentioning that pcet and hat processes involved in hydrogen transfer reactions have been identified by the electronic features of the orbitals involved and according the vibronic coupling in the self-exchange reactions between these processes.[52–54]

Fig. 1 shows that the elementary reaction going *via* the pcet mechanism (**ATS1**) is more favorable than the process taking place through the hat mechanism (**ATS2**), despite the last one being additionally stabilized by a hydrogen bond between the terminal oxygen atom of SO_2 and one hydrogen of the water moiety. Indeed, elementary reactions occurring through a pcet mechanism in the oxidation of organic and inorganic species by radicals have been found to be more favorable than the oxidation processes taking place *via* a hat mechanism,[9,42–51] which can be easily rationalized looking at the pictorial canonical forms in the transition states. For the hat process, Zavitsas and co-workers[55–58] pointed out that the three-center three-electron structure in the transition state can be described by the four canonical forms (a = X↑↓H···Y↑; b = ↑X···H↓↑Y; c = X↑···H↓···↑Y; and d = [X···H···Y]), where X and Y are the two atoms between which the hydrogen atom is being transferred, namely two oxygen atoms in the present case. a and b describe the bonding of the H to both X and Y; c corresponds to the triplet repulsion (antibonding) between X and Y and d describes the resonance of one electron delocalization between the three atoms. Thus, the corresponding energy barrier is related to the triplet repulsion energy of the X/Y pair (canonical form c) in the transition state structure. In the case of the pcet mechanism, the electrons are transferred from the Z to the Y atoms (both oxygen atoms in this case) in a two center three electron mechanism so that we could write two canonical forms for this process, namely e = Z↑↓···↑Y; and f = $Z↑^{+}$···↓↑Y^{-}. Thus, it turns out that the pcet mechanism avoids the triplet repulsion occurring in hat, which, in general, results in a lower energy barrier for the proton coupled electron transfer reactions compared to the conventional hydrogen atom transfer processes.

From an energetic point of view, Fig. 1 and Table S2 (ESI†) show that our calculations predict the SO_2 (a^3B_1) + H_2O → HOSO + OH reaction to be endothermic by 4.52 kcal mol^{-1} or endoergic by 3.81 kcal mol^{-1} in terms of free energy at 298 K, whereas **ATS1** and **ATS2** are predicted to lie 8.53 and 8.01 kcal mol^{-1}, respectively, above the energy of the separate reactants, or 15.39 and 16.44 kcal mol^{-1} in terms of free energy at 298 K, which makes the reaction feasible in the atmosphere despite the endothermicity of the whole reaction. For this reaction, Kroll *et al.*[14] report an estimated rate constant of (5–16) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} following photochemical experiments and in the range between 10^{-14} and 10^{-16} cm^3 $molecule^{-1}$ s^{-1} according to theoretical calculations employing transition state theory. Employing the same level of kinetic calculations and our theoretical results, we obtain a rate constant of 4.7 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1} for the elementary reaction through **ATS1** and 2.6 × 10^{-20} cm^3 $molecule^{-1}$ s^{-1} for the elementary reaction through **ATS2**, indicating that the whole reaction takes place *via* the pcet mechanism.

Finally, for the sake of completeness, we have also optimized the reactants SO_2 (a^3B_1) and H_2O and the **ATS1** and **ATS2** transition states at the CCSD(T) level of theory and their geometrical parameters compare quite well with those obtained at the DFT level (see Fig. 1). Moreover, the corresponding relative energies obtained with both the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ and CCSD(T)/CBS//CCSD(T)/6-311+G(2df,2p) levels of theory differ by less than 0.2 kcal mol^{-1} (see Table S2 of the ESI†).

Impact of multiple H_2O on the excited state reaction

We now look at the effect of additional water molecules interacting with the $SO_2 \cdot H_2O$ system by taking into account the interaction of SO_2 (a^3B_1) with a water dimer, trimer and tetramer.

Fig. 3 displays schematically the zero-point energy corrected potential energy surfaces for the reaction SO_2 (a^3B_1) + $(H_2O)_2$, as well as the structures corresponding to the hat and pcet transition states. As shown, hydrogen-bonding with water produces a huge stabilization of the pcet and hat transition structures (respectively **BTS1** and **BTS2**), which lie now only 0.62 and 1.60 kcal mol^{-1} above the energy of the separated reactants.

The geometry obtained for the transition state structures shows that the additional water molecules essentially play a solvation role, and are not directly involved in the elementary H$^{\bullet}$, H^{+} and e^{-} transfer processes. To rationalize the strong stabilizing solvation effect in this case, it is interesting to look at the geometrical parameters and charge distributions reported in Fig. 1 and 3.

The transition state structure involved in the hat mechanism (**BTS2**) is a single ring-type structure whose stabilization stems from a cooperative hydrogen-bond network. Remarkably, the hydrogen-bond distance between the two water molecules is very short (1.62 Å) compared to the same bond length in the isolated water dimer (around 1.9 Å). Apart from the hydrogen-bond contribution, the stability of **BTS2** can be explained by the relaxation of the strain energy in **ATS2** providing greater geometrical flexibility for the atoms involved in the H-transfer.

In the case of the pcet transition state structure (**BTS1**), instead, the solvating water molecule forms a second ring and two cooperative hydrogen-bonds with the reacting system. The main effect of this solvating water molecule is a significant enhancement of the electron charge transfer between the oxygen atoms (compare net charges on linked O-atoms in **BTS1** and **ATS1**, Fig. 1 and 3). Thus, electron transfer in the transition state structure is sustained by water solvation, and accordingly, the activation barrier decreases. Overall, the solvating water molecule bears a non-negligible positive charge (0.0311 a.u.), which suggests that its role as a proton acceptor prevails over its role as a proton donor, which is also reflected in the H-bond distances. Our results displayed in Fig. 3 and Table S4 (ESI†) show that the formation of HOSO + $H_2O\cdots OH$ is endothermic by 3.72 kcal mol^{-1}. In terms of free energy at 298 K, the formation of these products is also

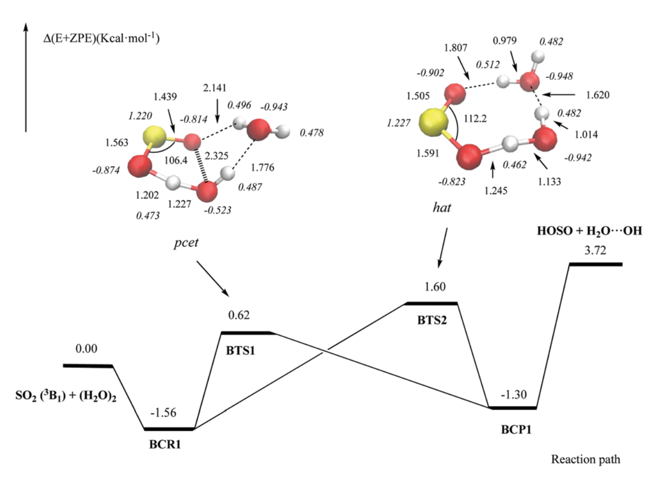

Fig. 3 Schematic potential energy surface (CCSDT/CBS//B3LYP/aug-cc-pVTZ) for the SO_2 (a^3B_1) + $(H_2O)_2$ reaction. Energies (kcal mol^{-1}) include zero-point energies. Interatomic distances (in Å), OSO angles (degrees) and net atomic charges (italics, in a.u.) for the transition state structures are indicated.

endoergic by 2.94 kcal mol^{-1}, but the production of HOSO + H_2O + OH is endoergic by about 1 kcal mol^{-1}. Our calculations also predict the transition states *via* pcet and hat to lie between 0.6 and 1.8 kcal mol^{-1}, or between 12.1 and 13.0 kcal mol^{-1} in terms of free energy at 298 K, and the corresponding rate constants are computed to be 5.8×10^{-15} cm^3 molecule^{-1} s^{-1} *via* the pcet reaction mechanism, and 2.1×10^{-15} cm^3 molecule^{-1} s^{-1} *via* the hat reaction mechanism, with a total value of 7.9×10^{-15} cm^3 molecule^{-1} s^{-1}. This means that 74% of the reaction goes through a pcet mechanism and 26% goes *via* a hat mechanism. The calculated rate constant for the reaction with a water dimer is two orders of magnitude greater than the value computed for the reaction with a single water molecule. However, its importance in the chemistry of the atmosphere is negligible, given the smaller concentration of water dimers compared to the concentration of single water molecules. Only in very hot and humid conditions, where $[(H_2O)_2]$ is about 2.5×10^2 times smaller than $[(H_2O)]$,[59] could the reaction with a water dimer play a minor role.

Regarding the reaction with a water trimer, our calculations reveal that the pcet mechanism is even more stabilized than in the case of a water dimer. The corresponding transition state structure (**CTS1**) is more stable than the separated reactants (−2.75 kcal mol^{-1}, Table S5 and Fig. S5, ESI†). As in the case of **BTS1**, the two additional water molecules act as a solvent forming a second ring in the transition state structure, which allows the geometry of the transition state to be less strained and results in a more effective interaction of the reactant moiety with the solvent. In contrast, adding a further water molecule does not lead to additional stabilization of the transition state structure of the hat mechanism (**CTS2**), which lies 2.05 kcal mol^{-1} above the separate reactants, and similar results are obtained when considering four water molecules (see also Table S5 and Fig. S5 of the ESI†).

It is worth pointing out that the gas phase reactivity of SO_2 (a^3B_1) with a water trimer and tetramer has less interest for gas phase atmospheric purposes, because of the low atmospheric concentration of these water clusters.[59] However, these results may be useful for predicting the reactivity of SO_2 in the condensed phase. Indeed, in previous work, we have shown that SO_2 displays a significant affinity for the air–water interface and that the photo-induced reaction with water at the surface of cloud water droplets has large atmospheric significance.[15] The clusters with three or four water molecules studied here represent a simple microsolvation model for these condensed phase reactions, in which relative free energies with respect to the initial SO_2–water complexes are the relevant quantities. In Fig. 4, the free energy profiles of the pcet process *via* **CTS1** or **DTS1** are shown (see also Table S5 and S6 of the ESI†). As shown, the free energy barriers are very small, 0.79 and 0.70 kcal mol^{-1} at 298 K for **CTS1** and **DTS1**, respectively, the processes being almost isoergonic. These results indicates therefore that a very fast reaction of triplet SO_2 with water should take place in the condensed phase.

Implications

The reported results provide useful information to discuss the actual outcome of the process, which may differ in different

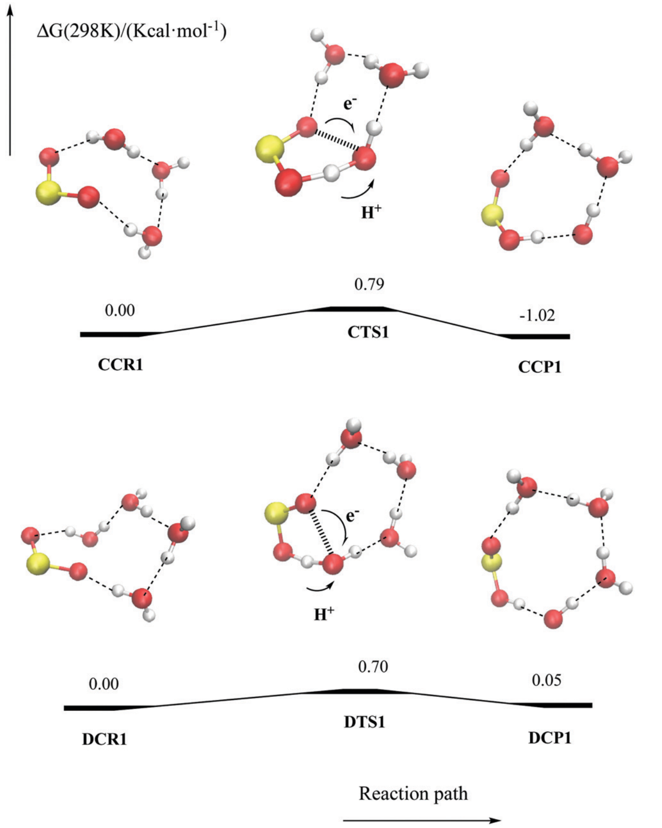

Fig. 4 Schematic free energy surface at 298 K (CCSDT/aug-cc-pVTS//B3LYP/aug-cc-pVTZ, values in kcal mol^{-1}) for the reaction of SO_2 (a^3B_1) with three and four water molecule clusters.

environments (gas *vs.* condensed phase). Overall, they emphasize the fact that in the reaction of triplet SO_2 with water, environmental water molecules may act as a catalyst of the pcet mechanism by expediting charge transfer.

The pcet reactions cover a wide range of chemical processes that have attracted increasing interest over the last decades because they play a key role in biological processes, photocatalysis and solar energy conversion.[3,5,10,12] The mechanism discussed in this work for the reaction of sulfur dioxide with water to yield HOSO and OH radicals belongs to a subcategory of bimolecular pcet processes that involve prior photoexcitation followed by intersystem crossing to a triplet state. We have shown that in this reaction pathway a very low activation barrier needs to be overcome, in contrast to the high stability of SO_2 in its ground electronic state. Since, in addition, the reaction is favored through hydrogen-bonding interactions with additional surrounding water molecules, the photoinduced pcet mechanism is expected to be particularly relevant for SO_2 exposed to sunlight at the air–water interface and in aqueous environments, which presumably should have significant implications for the atmospheric chemistry of sulfur dioxide adsorbed on cloud droplets or other aqueous aerosols.[15]

Nevertheless, the implications of the studied process are much wider. Indeed, our results suggest that pcet mechanisms would be involved in the conversion of other YXY systems to the corresponding HYXY products, where X is an atom or possibly a complex functional group, Y is oxygen or another chalcogen atom, and the YXY system must display an open-shell structure. Interestingly, the reaction of water with NO_2 in its doublet ground state has been previously studied[49] and proceeds through a pcet mechanism that significantly lowers the activation barrier with respect to the traditional H-atom transfer. The data reported here provide chemical insights into such a new general class of reactions by which the electronic excited-state promotes the process. This route opens up interesting chemical perspectives in technological applications of photoinduced H-transfer reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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