Ab initio study of the electronic structure of the $(SO_2)(SO_2^-)$ dimer. A one-electron S–S bond formation?

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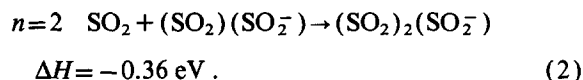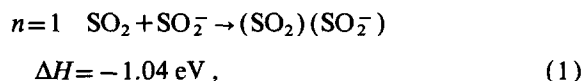*Laboratoire de Chimie Théorique, URA 506 (ICMO), Université de Paris-Sud, Bâtiment 490, 91405 Orsay Cedex, France*

Abstract

The structure of the $(SO_2)(SO_2^-)$ anion with a S–S linkage is studied by means of ab initio calculations at the PUMP4/6-31+G*//UMP2/6-31+G* level. The trans structure is found to be a minimum on the potential energy surface and is mainly characterized by a long (286 pm) one-electron SS bond. The theoretical dimerization enthalpy is in agreement with experiment. Moreover, this structure in which the unpaired electron is used to bind the sulfur atoms might well explain the smaller enthalpy variations associated with further addition of SO_2 molecules.

1. Introduction

The experimental study of the formation and the stability of the negative ion clusters $(SO_2)_n(SO_2^-)$ shows that the exothermicity of the clustering reaction falls drastically between $n=1$ (dimerization reaction (1) below, $\Delta H = -1.04$ eV) and $n=2$ ($\Delta H = -0.36$ eV, see (2) below) [1]. For $n=3$ to 10, the enthalpy variation slowly decreases from 0.27 to 0.13 eV [2]

$$n=1 \quad SO_2 + SO_2^- \rightarrow (SO_2)(SO_2^-)$$

$$\Delta H = -1.04 \text{ eV}, \tag{1}$$

$$n=2 \quad SO_2 + (SO_2)(SO_2^-) \rightarrow (SO_2)_2(SO_2^-)$$

$$\Delta H = -0.36 \text{ eV}. \tag{2}$$

These results suggest that the binding interaction in the dimer $(SO_2)(SO_2^-)$ is of covalent nature while adding one or more (SO_2) units would only result in weaker electrostatic interactions. Note, however, that the enthalpy of formation of the dimer (1.04 eV) [1], whose structure is not known, seems too low to be associated with a usual two-electron covalent bond.

The purpose of this Letter is to study, by means of ab initio calculations, the structures of the dimer in which a sulfur–sulfur bonding takes place through an interaction of the π systems of the reacting molecules. The reason for this lies in the electronic structure of SO_2 and SO_2^-. Both species are triatomic bent molecules with four and five π electrons, respectively. The shape and the energy ordering of the π MOs are similar to those of the well-known allyl parent molecule, with one bonding (π_1), one non-bonding (π_2) and one antibonding (π_3) orbital (Fig. 1). In SO_2, both π_1 and π_2 are doubly occupied and in SO_2^- the extra electron lies in the antibonding π_3 orbital.

The simple picture of the electronic structure of the reactants in Fig. 1 suggests that a good way to create a covalent bond might be to bring together the reactants such that the highest singly occupied MO of
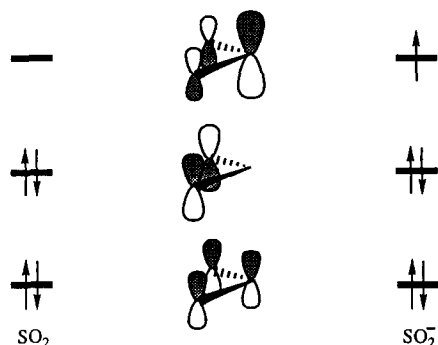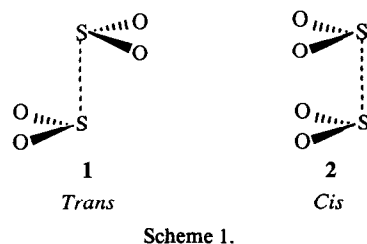
Fig. 1. π electronic configuration of SO_2 and SO_2^-.

Scheme 1.

SO_2^- (π_3) interacts strongly with the lowest unoccupied MO of SO_2 (π_3). Since the π_3 orbital is mainly developed on the central sulfur atom, even more than in the parent allyl species as the sulfur is less electronegative than the oxygen, this interaction can be achieved by forming a sulfur–sulfur bond through a parallel or a quasi-parallel approach of the two reactants. Two limit structures can be built in this way, depending on the relative orientation of the two SO_2 units (trans, **1** and cis, **2**) (Scheme 1). Note that the S–S bond associated with these structures contains a single electron which occupies the bonding combination of the two π_3 fragment orbitals.

2. Method of calculation

In a set of calculations, the potential energy surface was explored at the ROHF level. Since anionic species are involved, we have used the 6-31+G* [3] basis set. All the stationary points were fully optimized at this level and their nature was characterized by diagonalization of the Hessian matrix.

Minima and transition states were reoptimized at the UMP2 level with the same basis set. Since some

spin contamination appears in the doublet wavefunction of SO_2^- and $S_2O_4^-$, the results are given after projection on the lowest doublet state (PUMP2). Finally, UMP4 calculations were carried out on the extrema located at the UMP2 level and projected (PUMP4) results are given. This highest level of calculation is therefore PUMP4(SDTQ)/6-31+G*// UMP2/6-31+G*. All calculations were made with the help of the GAUSSIAN 92 suite of programs [4].

3. Results

The geometries of the reactants SO_2 and SO_2^- were optimized. The UMP2 optimized OSO angle values are close to the experimental ones for both SO_2 [5] (119.3° instead of 119.5°) and SO_2^- [6] (115.3° instead of 115.6°). However, the S–O bond lengths are slightly overestimated: 148.2 pm for SO_2 (exp.: 143.2 pm) and 154.9 pm for SO_2^- (exp.: 152 pm) [#1].

Important to our problem is the computed value for the electron affinity (EA) of SO_2 since the dimer formation involves an anionic partner. The results at the various levels of calculation are given in Table 1. The theoretical values of EA (SO_2) are between 0.87 and 0.94 eV, slightly lower than the experimental one (1.10 eV) [6] but the difference seems to be small enough to allow a proper description of the dimerization reaction. It is, however, possible to get a more reliable EA by improving the calculation of the correlation energy: SAC-CI or G2 computations lead to 1.027 eV [8] and 1.155 eV [7] values, respectively, in better agreement with the experimental one. However, the size of the system under study forbids the use of such calculations.

[#1] Such an overestimation at the MP2 level has already been noted for the S–O bond lengths in SO_2 and SO_2^- (see ref. [7]). For other calculations on SO_2^-, see refs. [8–13].

Table 1
Energies of SO_2 and SO_2^- (au) electron affinity (eV) of SO_2 at the various levels of calculation (see text)

	ROHF	PUMP2	PUMP4
SO_2	−547.17569	−547.69839	−547.72829
SO_2^-	−547.21103	−547.73288	−547.76035
EA	0.96	0.94	0.87

The two structures **1** and **2** are stationary points on the ROHF potential energy surface. However, while the trans conformation is a minimum, the cis one is a transition state (characterization by diagonalization of the Hessian matrix). The reaction coordinate associated with the negative eigenvalue is mainly the rotation angle around the S–S bond which allows the interconversion of two equivalent trans minima through the cis transition state structure.

The geometry of the trans (**1**) and cis (**2**) conformations of the dimer has been fully reoptimized at the UMP2 level, the geometrical parameters associated with each structure being given in Fig. 2. The trans structure is actually of C_{2h} symmetry, the OSO angle value (115.8°) and the S–O bond length (151 pm) being intermediate between the values found for the isolated species SO_2 and SO_2^-. It is noteworthy that the optimized S–S bond length (286 pm) is significantly longer than that of a usual sulfur–sulfur bond (about 205 pm) because it is a one-electron two-center bond. As expected from the qualitative analysis given above, the single occupied MO of the trans structure **1** results from the in-phase combination of the π_3 fragment orbitals of each monomer (Fig. 3). In the parent dianion $S_2O_4^{2-}$, the optimized S–S bond length in the analogous trans structure is much shorter (between 217 [13] and 213 [14] pm depending on the computational level). Moreover, the extra electron allows the formation of a usual two-electron sulfur–sulfur bond through the double occupancy of the bonding combination of the π_3 fragment orbitals of the two SO_2^- units.

The cis conformation is actually of C_{2v} symmetry. In this conformation, the distance between the sulfur atoms is even longer (298 pm), probably due to the larger repulsion between the occupied π_1 and π_2 orbitals which carry large coefficients on the oxygen atoms.
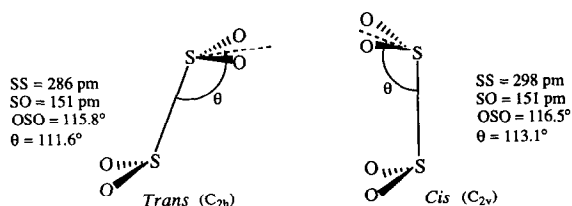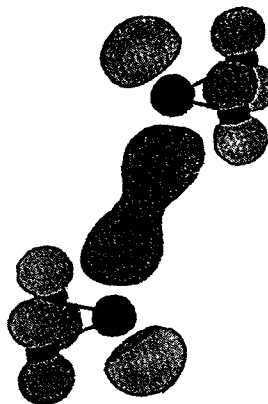

Fig. 3. Single occupied MO of the trans structure **1** obtained from ab initio calculations.

Table 2
Binding energies (eV) of the dimer $(SO_2)(SO_2^-)$ in trans (**1**) and cis (**2**) conformations relative to the isolated monomers SO_2 and SO_2^-

	ROHF	PUMP2	PUMP4
trans (1)	0.51	0.85	0.87
cis (2)	0.34	0.75	0.78

The binding energy of each structure relative to the isolated monomers is given in Table 2 at the various levels of calculations. For the trans minimum, the binding energy increases when correlation is taken into account (from 0.51 to 0.87 eV). At the PUMP4 level, it is in reasonable agreement with the experimental dimer enthalpy formation value (1.04 eV [1]). Taking into account that the electron affinity of SO_2 is underestimated by 0.2–0.3 eV in our calculations, these computed values lead us to believe that the trans conformer is a good candidate for the actual structure of the $(SO_2)(SO_2^-)$ dimer. Moreover, since the unpaired electron binds the two sulfur atoms in the dimer, it is no longer available to bind a new SO_2 unit in a similar way. It may well explain the drastic fall in the enthalpy formation when one more SO_2 molecule is added (reaction (2)). Note, finally, that the cis conformer is found to lie 0.09 eV (PUMP4 level) above the minimum. This energy difference is smaller than that found in the parent $S_2O_4^{2-}$ dianion (0.41 eV) [14]. It probably comes from the lengthening of the S–S bond distance which decreases the four-electron repulsion between the oxygen π lone-pairs.

SS = 286 pm
SO = 151 pm
OSO = 115.8°
θ = 111.6°

Trans (C_{2h})

SS = 298 pm
SO = 151 pm
OSO = 116.5°
θ = 113.1°

Cis (C_{2v})

Fig. 2. Optimized geometrical parameters (UMP2 level) of the trans (**1**) and cis (**2**) conformations of the dimer $(SO_2)(SO_2^-)$.

The dissociation of the trans dimer into the isolated monomers has been studied at the ROHF level by increasing the S–S distance up to 700 pm, the S–O bond lengths and O–S–O angles being optimized. The total energy increases (Fig. 4) but it is never higher than that of the isolated SO_2 and SO_2^- species which means that the reverse dimerization reaction proceeds without any activation energy.

The basis set superposition error (BSSE) was computed for a few points of this dissociation curve. Using the formula needed for fully optimized dimers [15], the correction is found to be equal to only 0.08 eV in the minimum energy structure **1** at the ROHF level. It decreases to 0.03 and 0.01 eV for S–S distances equal to 360 and 460 pm, respectively. Therefore, the BSSE correction does not modify the overall shape of the dissociation energy curve given in Fig. 4. For the cis transition state structure **2**, the correction is 0.05 eV.

In conclusion, the dimer structure **1** has been characterized as a minimum on the potential energy surface associated with the interaction of SO_2 and SO_2^- monomers. In this structure, there is a covalent one-electron bond between the two sulfur atoms and the binding energy is nor far from the enthalpy formation measured experimentally for the dimer $(SO_2)(SO_2^-)$. Since the unpaired antibonding electron of SO_2^- unit is used to bind the sulfur atoms in **1**, a further SO_2 molecule cannot develop the same type of bonding with the dimer. Finally, no activation energy is required to form this dimer from SO_2 and SO_2^- units. All these results make the trans dimer **1** a good candidate to account for the experimental results. We are now investigating in more detail the potential energy surface in order to check if there are other structures which may explain the experimental data, in particular those involving O–O and S–O bonds between the two monomers as has been suggested in a previous experimental study [16].

Acknowledgement

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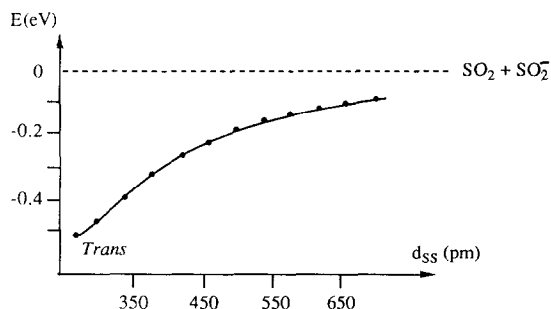[16] H.-S. Kim and M.T. Bowers, J. Chem. Phys. 85 (1986) 2718.

Fig. 4. Dissociation energy curve (ROHF level) of the trans dimer **1** into SO_2 and SO_2^- species.