

A computational investigation on the oxidation of sulfur

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Abstract

The present work is part of Pegasus [1, 2] project which objective is to develop a novel power cycle for renewable electricity production. Electricity generation may be carried out with the heat generated from sulfur combustion and the process is independent of encasement: Sulfur is a very cost-effective material and can be inexpensively stored outdoor under ambient conditions for long times and in large quantities [1]. The whole process is based on streams of solid particles as heat transfer fluid combined with indirect thermochemical storage of solar energy in elemental sulfur, resulting in a round-the-clock plant electricity production. Our first task is to investigate and develop a sulfur combustor with high power density which will be integrated in a whole process. The second part of our work is to develop a model which describes the oxidation of sulfur with oxygen and later with air. The model should be validated with own experimental data.

In order to find accurate computational methods for use in developing an elementary reaction mechanism for oxidation of sulfur, enthalpy of well-known sulfur species related to sulfur oxidation are estimated using several computational chemistry methods. DFT methods and composite ab-initio methods at different levels are used. Enthalpy of formation was calculated for SO, SO₂, SO₃ and SSO at B3LYP (with several basis sets) and BB1K/GT Large and ab-initio levels (G2, G3, G3MP2, G3B3, G3MP2B3 and CBS-QB3) and compared with literature values. Standard enthalpies are calculated using different isodesmic reactions (hypothetical reactions with similarity in mass and bonding environments for reactant and product sets), whenever possible, in order to provide cancellation of systematic errors and improve the accuracy of the calculations. The results have shown that the calculated values from six composite ab-initio methods show very good agreement with the literature values. The spin value (singlet, triplet) is of crucial importance in the calculation of the energy and consequently in the determination of the thermodynamics and kinetics. We note a deviation of 1 to 4 kcal mol⁻¹ among the composite methods and the literature values.

The series of DFT calculations at six levels (B3LYP at different basis sets and BB1K) were also tested for the enthalpy calculation of SO, SO₂, SO₃ and SSO. All DFT calculations gave poor results for these sulfur species at all basis levels, although all structures parameters (lengths, angles, dihedrals) are in good agreement with literature data [3, 4, 5]. It appears that, for oxygenated sulfur compounds, DFT is not eligible. Therefore, for further investigations in developing an elementary reaction mechanism for oxidation of sulfur, the six composite methods are selected and will be used.

In order to further test the methods, The S—O bond energy (BE) in the SO₃ molecule has been determined at different levels of calculation (DFT and ab-initio). For each method, the bond energy is estimated as the calculated energy difference between the products and adducts and converted into kcal mol⁻¹. The BE values are listed in Table 1. According to reported enthalpies in the literature [6], the S—O bond energy in SO₃ is calculated to be 83.20 kcal mol⁻¹. The different B3LYP methods listed in Table 1 yield lower BE values (62-75 kcal mol⁻¹) while all six composite methods calculations (G2, G3, G3MP2, G3B3, G3MP2B3 and CBS-QB3) are near 81-83 kcal mol⁻¹ which is in very good agreement with

the literature. We note a deviation of only 0.4 and 1.1 kcal mol⁻¹ for CBS-QB3 and G2 values, respectively, from literature.

The S—O bond energy (BE) in the SO₂ molecule has been also determined at different levels of calculation (DFT and ab-initio) and is listed in Table 1. Based on enthalpies reported in the literature [6], the S—O bond energy in SO₂ is calculated to be strong with 130.14 kcal mol⁻¹. As above, all B3LYP methods yield lower BE values (103-120 kcal mol⁻¹) while all six composite methods calculations are very similar by 130-138 kcal mol⁻¹. We note a difference of less than 1 kcal mol⁻¹ between CBS-QB3, G3B3, G3MP2B3 and literature.

Table 1. S—O Bond energy in SO₃ and SO₂ in kcal mol⁻¹

<i>SO₃ → SO₂ + O Literature = 83.20 [6]</i>			
Method-basis set	BE (kcal mol ⁻¹)	Method-basis set	BE (kcal mol ⁻¹)
B3LYP/6-311G(d,p)	62.07	CBS-QB3	82.83
B3LYP/6-311+G(d,p)	58.94	G2	82.06
B3LYP/6-311G+(2d,p)	68.18	G3	81.73
B3LYP/6-311G++(3df,2p)	75.88	G3B3	81.22
B3LYP/CBSB7	70.0	G3MP2	80.63
BB1K	73.64	G3MP2B3	80.34
<i>SO₂ → SO + O Literature = 130.14 [6]</i>			
Method-basis set	BE (kcal mol ⁻¹)	Method-basis set	BE (kcal mol ⁻¹)
B3LYP/6-311G(d,p)	103.2	CBS-QB3	130.61
B3LYP/6-311+G(d,p)	101.57	G2	132.26
B3LYP/6-311G+(2d,p)	112.61	G3	128.28
B3LYP/6-311G++(3df,2p)	119.9	G3B3	129.32
B3LYP/CBSB7	112.13	G3MP2	138.73
BB1K	120.06	G3MP2B3	129.59

New pathways for the formation of SO₂

The calculations have shown new pathways for the formation of SO₂. New transition state structures have been identified as illustrated in Figures 1-3.

There are several reaction paths for the formation of SO₂ reported in the literature [7, 8, 9]. In the present work we report three new paths calculated at G3 and G3B3 levels. The first one (Figure 1) is obtained from the association of ³S₂ + ³O₂. One oxygen will bond to one sulfur atom, forming SSOO and expected to occur without barrier. The exact structure of the SSOO needs to be thoroughly investigated and requires new calculations in a future study. TS1 illustrated in Figure 1 shows the intramolecular shift of the peroxy oxygen atom to the centered sulfur atom to form a stable SS(=O)=O at -42 kcal mol⁻¹ (see Figures 1). G3B3 calculations show clearly the displacement of the oxygen toward the sulfur atom. The new formed molecule (SS(=O)=O) reacts further by cleaving one sulfur atom to form SO₂ and S (TS2) over about 63 kcal mol⁻¹ energy barrier relative to SS(=O)=O. This reaction could be explained by the S—S bond energy in SS(=O)=O at 38.6 kcal mol⁻¹ which is weak when compared to the S—S bond in S₂ at 102 kcal mol⁻¹. It is important to point out that the ³S₂ + ³O₂, which is a complicated association, leads to the formation of different products and undergoes different transition state structures depending on the structure of the intermediate S₂O₂ formed. This investigation will be reported in a future work.

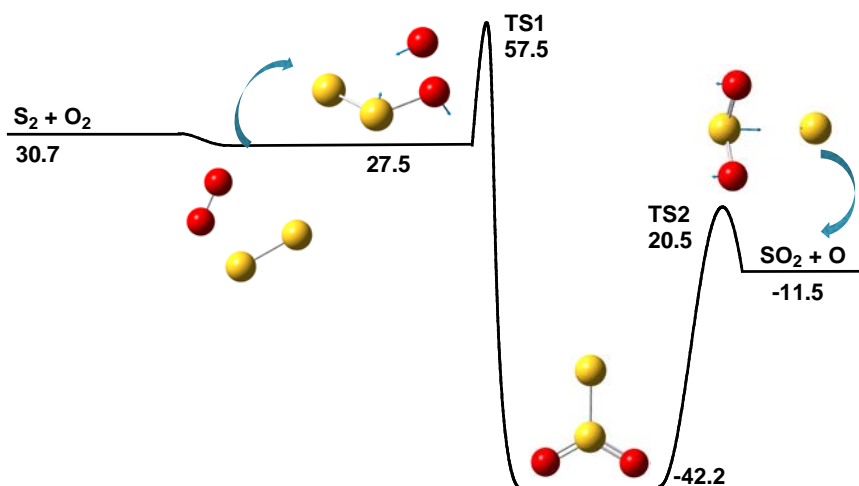


Fig. 1 Formation of SO_2 from $\text{S}_2 + \text{O}_2$ association

A second path for the formation of SO_2 is possible by association of two SO_3 . Enthalpy of intermediates and transition state structures relative to these reactions has been calculated at different levels. As illustrated in Figure 2, one oxygen atom attacks the sulfur atom of the second SO_3 and forms a stable molecule (O_3SOSO_2) at $-135 \text{ kcal mol}^{-1}$. This addition (TS1) is endothermic by approximately 46 kcal mol^{-1} relative to SO_3 . This formed molecule undergoes a S—O (TS2) dissociation and forms SO_2 and SO_4 . The barrier needed for this dissociation is near 56 kcal mol^{-1} relative to O_3SOSO_2 . The new formed SO_4 may further dissociate to $\text{SO}_2 + \text{O}_2$.

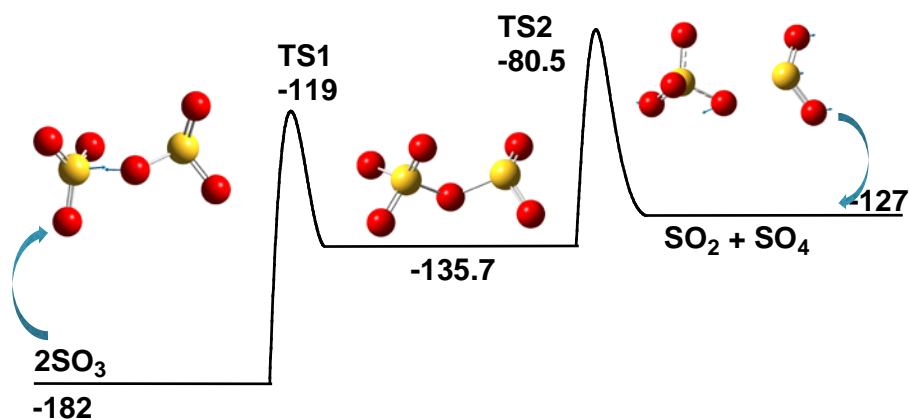


Fig. 2 Formation of SO_2 from $\text{SO}_3 + \text{SO}_3$ association

The association of $^3\text{SO} + \text{O}$ has shown an interesting transition state structure (see Figure 3) calculated with the six composite methods. TS1 in Figure 3 shows clearly the migration of one triplet oxygen atom towards the SO molecule over 62 kcal mol^{-1} (at G3B3 level) relative to the entrance channel and form SOO at lower energy. The six composite calculations have shown that the most favorable structure is when the $\text{SOO}^\#$ moiety is bent as illustrated in Figure 3. The $\text{SOO}^\#$ formed at TS1 has sufficient energy to pass over TS2 to form a more stable SO_2 by undergoing an intramolecular rearrangement. The terminal oxygen undergoes an oxygen-shift (TS2 in Figure 3) and moves to the sulfur atom to form the low energy SO_2 at about $-71 \text{ kcal mol}^{-1}$. This isomerization was found to have a barrier of 70 kcal mol^{-1} (at G3B3 level) relative to SOO .

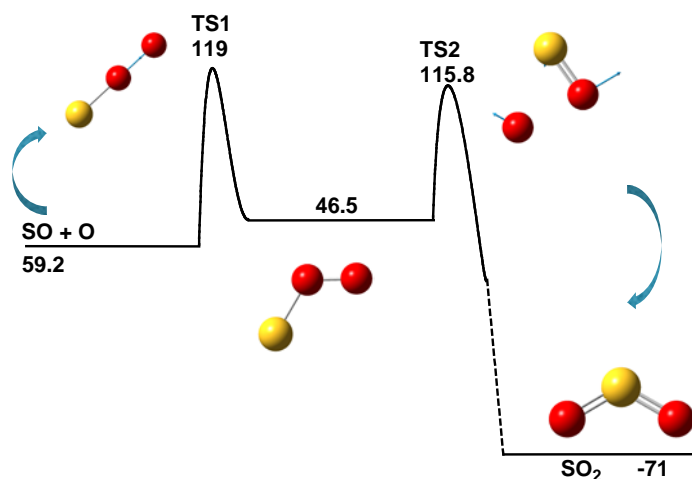


Fig. 3 Formation of SO_2 from $\text{SO} + \text{O}$ association

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