

## Study on Oxidation of 1,2-Dipropyldisulfane in Oxidative Desulfurization

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DFT calculations were performed for calculation of standard electrode potential for 1,2-dipropyldisulfane sulfone/2-dipropyldisulfane. The electrochemical behaviour of 1,2-dipropyldisulfane at gold electrode was investigated by cyclic voltammetry and the results showed that experimental standard electrode potential for 1,2-dipropyldisulfane sulfone/1,2-dipropyldisulfane is 1.111 V, which is consistent with that of 1.067 V at B3LYP/6-31++g(d, p)-PCM level. The front orbit theory and Mülliken charges of molecular explain well on the oxidation of 1,2-dipropyldisulfane in oxidative desulfurization. According to equilibrium theory the experimental equilibrium constant in the oxidative desulfurization system of 1,2-dipropyldisulfane/H<sub>2</sub>O<sub>2</sub>, is  $2.27 \times 10^{89}$ , which is consistent with the theoretical equilibrium constant is  $2.10 \times 10^{95}$  at B3LYP/6-31++g(d, p)-PCM level, indicating that 1,2-dipropyldisulfane can be oxidized by H<sub>2</sub>O<sub>2</sub>.

**Keywords:** 1,2-Dipropyldisulfane, Standard electrode potential, Oxidative desulfurization.

### INTRODUCTION

In recent years, deep desulfurization of fuel oils has attracted increasing attention worldwide because sulfur compounds such as 1,2-dipropyldisulfane (DPPDF) present in fuel oils lead to SO<sub>x</sub> emission and acid rains<sup>1</sup>. The conventional industrial process removing sulfur-containing compounds from middle distillate fuels is hydrodesulfurization (HDS)<sup>2-4</sup>. To meet new sulfur standards with hydrodesulfurization process, operation at higher temperature and higher pressure with more active catalysts is indispensable, leading to higher investment and operating cost. Therefore, several new processes have been developed to remove these refractory sulfur-containing compounds satisfactorily. Such alternative processes include selective adsorption<sup>5-8</sup>, extractive separation<sup>8</sup>, bio-oxidation<sup>9,10</sup> and oxidative desulfurization (ODS)<sup>11-16</sup> for removal of sulfur from hydrocarbon fuels. Among these alternative processes, the oxidative desulfurization process has received much attention as an alternative process for the desulfurization because of its advantages of mild temperature and pressure conditions. Another important feature of oxidative desulfurization is that benzothiophene (BT), dibenzothiophene (DBT), thiophene (TH) and their derivative<sup>11,12,15</sup> are oxidized to their corresponding sulfoxides and sulfones subsequently. Then, these highly polarized products can be separated by means of solvent extraction or adsorption. Besides, the oxidative desulfurization process is a non-hydrogen consuming desulfurization method.

Thus oxidative desulfurization was considered as one of the most promising alternative desulfurization processes to obtain ultra low sulfur fuels<sup>12,13-16</sup>, more and more attentions have been paid to disulfide in oxidative desulfurization.

The divalent sulfur can be oxidized by the electrophilic addition reaction of oxygen atoms to form the hexavalent sulfur of sulfones<sup>13</sup>. Fig. 1 illustrates the oxidation reaction scheme for 1,2-dipropyldisulfane.

The reaction speed of a reaction is controlled by the catalyst, temperature and content and the equilibrium constant, the reaction limit, is controlled by the standard potential. Therefore, the study on the standard potential of sulfur compounds is very important and indispensable.

DFT using hybrid functionals has emerged as very powerful theoretical method<sup>17-20</sup>, we select a B3LYP method using 6-31g(d, p) and 6-31++g(d, p) basis sets to study the geometries of molecules and the standard electrode potential of half reaction for DPPDF<sub>(O)}/DPPDF<sub>(R)</sub>.</sub>

This paper describes the determination method of standard electrode potential for DPPDF<sub>(O)}/DPPDF<sub>(R)</sub> by cyclic voltammetry and the theoretical calculation of standard electrode potential for DPPDF<sub>(O)}/DPPDF<sub>(R)</sub>.</sub></sub>

### EXPERIMENTAL

All solutions were prepared with distilled-water. 1,2-Dipropyldisulfane was procured from Aldrich. All reagents were of analytical grade.

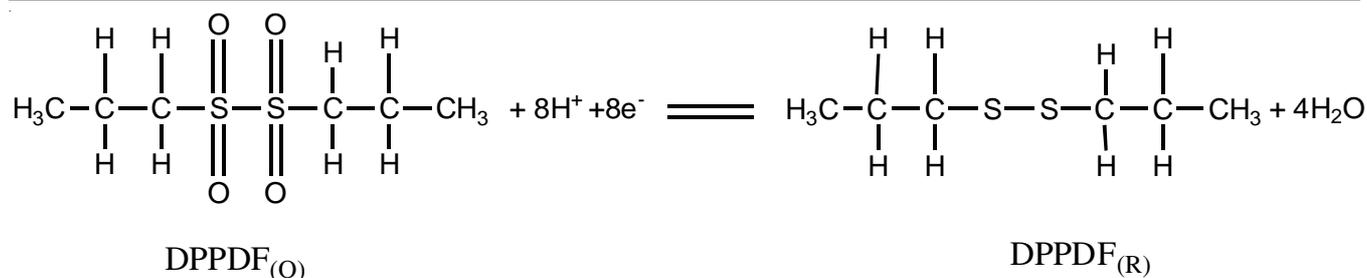


Fig. 1. Reaction scheme for the oxidation of 1,2-dipropyldisulfane

**Electrode preparation:** A cylindrical glass electrode, 3 mm in diameter and 50 mm in length, was used for the preparation of the modified electrode as follows. The glass electrodes were prepared for the experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with 1 and 0.3 alumina slurry on micro cloth pads (Buehler, USA). The glass electrode was activated by holding the potential in 0.1 M H<sub>2</sub>SO<sub>4</sub> at +2 V for 5 s and then at -0.35 V for 10 s, followed by potential cycling between -0.35 and +1.5 V at 4 V s<sup>-1</sup> for 1 min. Finally, the CV characteristic of a clean gold electrode was recorded.

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The electrochemical cells consisted of a three electrode, a saturated calomel electrode (SCE), a platinum wire and a glass electrode, were used as the reference, auxiliary and working electrode, respectively. All CV experiments were carried out at 25 °C.

**Calculation methods:** All the calculations were performed by using the DFT method (B3LYP)<sup>21</sup> with the split-polarised 6-31g(d, p) and diffusion function 6-31++ g(d, p) basis sets using the Gaussian 09 suite of programs<sup>22</sup>. Optimized geometries of DPPDF<sub>(O)</sub>, DPPDF<sub>(R)</sub>, HBQ, BQ and H<sub>2</sub>O in water with no geometrical restriction were calculated using the polarizable continuum model (PCM)<sup>23-25</sup>. All optimized geometries were further examined through vibrational frequency analysis.

## RESULTS AND DISCUSSION

**Electrochemical investigation of DPPDF<sub>(R)</sub> at glass electrode:** 2 μL of DPPDF<sub>(R)</sub> was added into the surface of glass electrode and the glass electrode insert into 1 M HCl aqueous solution. The cyclic voltammogram (CVs) of DPPDF<sub>(R)</sub> at glass electrode in 1 M HCl aqueous solution are shown in Fig. 2, the first cyclic voltammogram scan toward positive direction was performed, an oxidation peak of DPPDF<sub>(R)</sub> at the glass electrode appeared at 0.869 V (vs. SCE), no peaks at about 0.869 V for bare glass electrode were found.

Laviron's equation for an irreversible redox couple is given as<sup>26,27</sup>

$$E_p = E^{of} + \frac{RT}{\alpha nF} \ln \frac{RTk_s}{\alpha nF} + \frac{RT}{\alpha nF} \ln v$$

where  $\alpha$  is transfer coefficient,  $E_p$  is peak potential,  $k_s$  is standard rate constant of the surface reaction,  $v$  is scan rate,  $E^{of}$  is the conditional potential,  $n$  is electron transfer number involved in rate determining step,  $R$  is the gas constant,  $T$  is the absolute temperature and  $F$  is the Faraday constant. When the scan rate is close to zero,  $E_p$  equates  $E^{of}$ <sup>26-30</sup>.

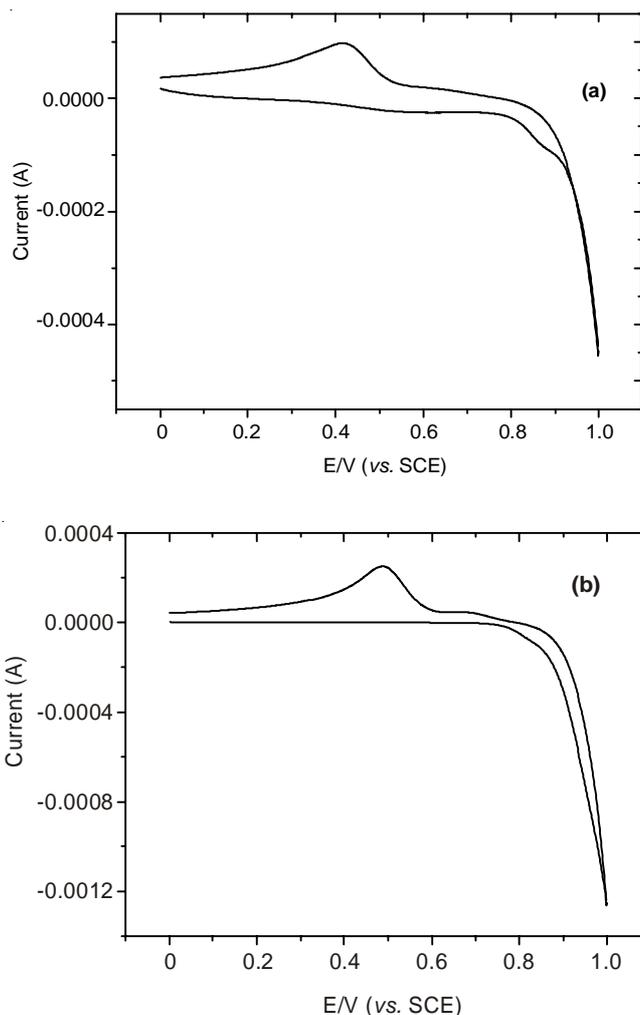


Fig. 2. Cyclic voltammogram of 1,2-dipropyldisulfane at glass electrode (a) and bare glass electrode (b) at scan rate of 10 mV/s in 1 M HCl aqueous solution

According to Nernst's equation the peak potential for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> can be written as

$$E_p = E_{\text{DPPDF}_{(\text{O})}/\text{DPPDF}_{(\text{R})}}^{of} + \frac{0.059}{4} \lg \frac{c_{\text{H}^+}^4 c_{\text{DPPDF}_{(\text{O})}}}{c_{\text{DPPDF}_{(\text{R})}}} \quad (25 \text{ }^\circ\text{C})$$

If the activities of hydrogen ion is given as  $c_{\text{H}^+} = 1 \text{ mol/L}$ ,

$c_{\text{DPPDF}_{(\text{O})}} = C_{\text{DPPDF}_{(\text{R})}}$ , then the peak potential and standard electrode potential for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> can be written as

$$E_p = E_{\text{DPPDF}_{(\text{O})}/\text{DPPDF}_{(\text{R})}}^{of}$$

If the activity of hydrogen ion is given as  $\alpha_{H^+} = 1$  mol/L the relationship between the conditional potential and standard electrode potential for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> can be written as

$$E_{DPPDF_{(O)}/DPPDF_{(R)}}^{of} = E_{DPPDF_{(O)}/DPPDF_{(R)}}^{\circ} + \frac{0.059}{4} \log \frac{\gamma_{DPPDF_{(O)}} \alpha_{DPPDF_{(R)}}}{\gamma_{DPPDF_{(R)}} \alpha_{DPPDF_{(O)}}} \quad (25^{\circ}C)$$

where  $\gamma$ ,  $\alpha$  and  $E^{\circ}$  represent activity coefficient, side reaction coefficient and standard electrode potential, respectively. Because DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> are neutral molecules the activity coefficient, side reaction coefficient and standard electrode potential can be written as  $\gamma_{DPPDF_{(O)}} = \gamma_{DPPDF_{(R)}} = 1$ ,

$$\alpha_{DPPDF_{(O)}} = \alpha_{DPPDF_{(R)}} = 1 \quad \text{and} \quad E_{DPPDF_{(O)}/DPPDF_{(R)}}^{of} = E_{DPPDF_{(O)}/DPPDF_{(R)}}^{\circ}$$

The standard electrode potential ( $E^{\circ}$ ) versus normal hydrogen electrode (NHE) for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> is calculated as<sup>31</sup>

$$E_{vs,SHE}^{\circ} = E_{vs,SCE}^{\circ} + E_{SCE} (0.242V)$$

Therefore, the oxidation potential at 10 mV/s for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> is close to the conditional potential, the calculated standard potential as above method for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> is 1.111 V (vs. SHE).

**Geometry of 1,2-dipropyl disulfane:** The molecular geometries of DPPDF<sub>(O)</sub> and DPPDF<sub>(R)</sub> are important because the properties are controlled by the geometries, the geometries and numeration of atoms in both DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> are shown in Fig. 3. The selected bond lengths and bond angles of both DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> optimized at the BLYP/6-31g(d, p)-PCM and B3PP/6-31++g(d, p)-PCM levels are also listed in Table-1. Table-1 showed that the bond lengths and bond angles of the same molecule at BLYP/6-31g(d, p)-PCM level are in a good agreement with the those at B3LYP/6-31++g(d, p)-PCM level.

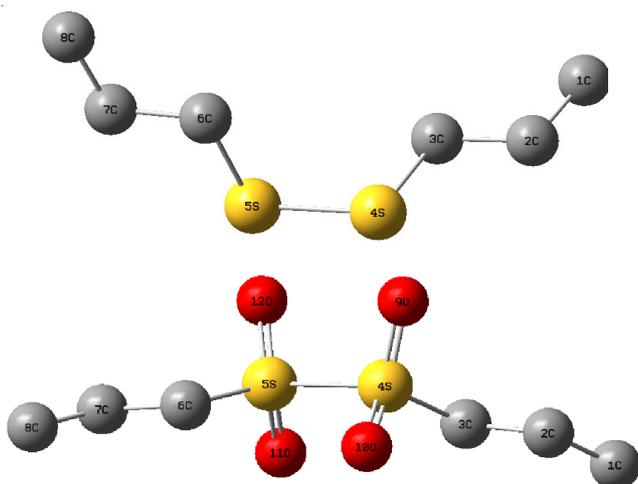


Fig. 3. Numbering in both DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> and geometries optimized at B3LYP/6-31++g(d, p)-PCM level

**Eigenvalues of LUMO and HOMO:** The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and energies gap of HOMO and

LUMO for DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> are shown in Table-2. The eigenvalues of LUMO and HOMO and its energies gap reflect the chemical activity of molecule. From Table-2 the results show that the energies of HOMO for DPPDF<sub>(R)</sub> are higher than that of DPPDF<sub>(O)</sub>, indicating that DPPDF<sub>(R)</sub> donates electrons easily. As a result, the oxidation reaction occurs in DPPDF<sub>(R)</sub>.

It can be seen from Fig. 4 that the electronic density in the HOMO states of DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> is associated with carbon and sulfur atoms. However, the electronic density in the HOMO states of DPPDF<sub>(R)</sub> is associated with S atom, which lost electrons easily. The sulfur atoms in HOMO state with p- $\pi$  and  $\pi$ - $\pi$  conjugate of S=O for DPPDF<sub>(O)</sub> lost electrons difficultly. Therefore, when the oxidation reaction begins, the sulfur atoms in DPPDF<sub>(R)</sub> can be oxidized easily.

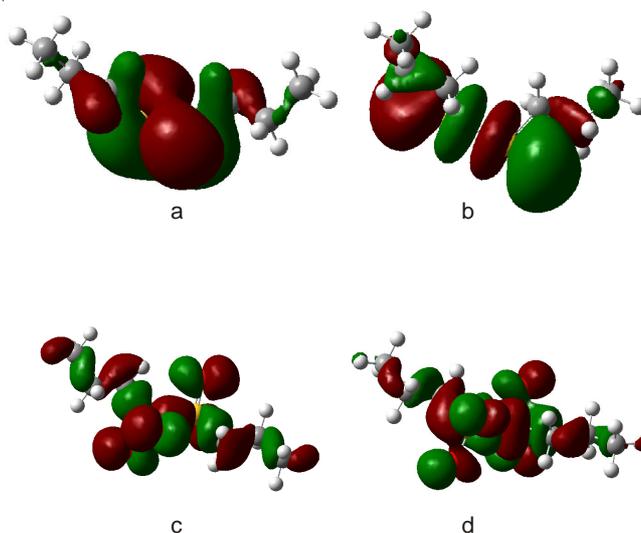


Fig. 4. Electronic density in the HOMO and LUMO states of DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> calculated by B3LYP/6-31++g(d, p)-PCM method: (a) HOMO orbital for DPPDF<sub>(R)</sub>; (b) LUMO orbital for DPPDF<sub>(R)</sub>; (c) HOMO orbital for DPPDF<sub>(O)</sub>; (d) LUMO orbital for DPPDF<sub>(O)</sub>.

#### Distribution of Mülliken charge and dipole moment:

To remove of sulfur compounds in hydrocarbon fuels, the oxidation products of sulfur compounds in ODS system must be solvable in water. The solubility of a compound is controlled by the dipole moments. Thus, the dipole moments of DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> are discussed here. The total dipole moments of DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> at B3LYP/6-31g(d, p) level are 3.2293 and 3.2081 Debye, respectively, which are consistent with those of 3.2584 for DPPDF<sub>(R)</sub> and 3.1422 for DPPDF<sub>(O)</sub> at B3LYP/6-31++g(d, p) level, indicating that DPPDF<sub>(R)</sub> and DPPDF<sub>(O)</sub> are weak polar molecules. The charges of the compound affects on its polarity, thus the charges of atoms are discussed. Distribution of Mülliken charges of molecules are shown in Table-3. From Table-3 the Mülliken charges of S in DPPDF<sub>(O)</sub> are more positive than that of S in DPPDF<sub>(R)</sub>, and the Mülliken charges of O<sub>14</sub> and O<sub>15</sub> in DPPDF<sub>(O)</sub> are markedly more negative than the other atoms. However, the framework group of both DPPDF<sub>(O)</sub> and DPPDF<sub>(R)</sub> are C<sub>1</sub>. Hence, DPPDF<sub>(O)</sub> is insoluble in water and separable from oil difficultly. The oxidation reaction for DPPDF<sub>(R)</sub> in aqueous solution occurs difficultly, a carrier must be presented in ODS for transferring DPPDF<sub>(R)</sub> from oil to aqueous solution.

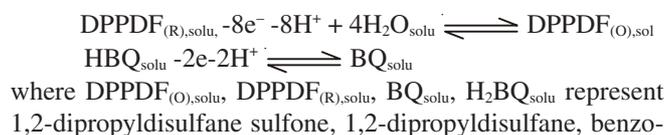
TABLE-1  
 GEOMETRY PARAMETER OF DPPDF<sub>(R)</sub> AND DPPDF<sub>(O)</sub>

Compound	DPPDF <sub>(R)</sub>		DPPDF <sub>(O)</sub>	
	6-31g(d, p)	6-31++g(d,p)	6-31g(d, p)	6-31++g(d,p)
Bond length (Å)				
R(1,2)	1.534	1.535	1.533	1.535
R(2,3)	1.531	1.532	1.534	1.535
R(3,4)	1.852	1.852	1.820	1.826
R(4,5)	2.083	2.085	2.295	2.325
R(5,6)	1.852	1.852	1.820	1.826
R(6,7)	1.531	1.532	1.534	1.535
R(7,8)	1.534	1.535	1.533	1.535
R(4,9)	-	-	1.474	1.477
R(4,10)	-	-	1.477	1.479
R(5,11)	-	-	1.477	1.479
R(5,12)	-	-	1.474	1.477
Angle (°)				
A(1,2,3)	111.6	111.6	110.5	110.1
A(2,3,4)	109.4	109.5	110.5	110.9
A(3,4,5)	104.1	104.0	102.1	102.4
A(4,5,6)	104.1	104.0	102.1	102.4
A(5,6,7)	109.4	109.5	110.5	110.9
A(6,7,8)	111.6	111.6	110.5	110.1
A(3,4,9)	-	-	110.2	110.3
A(3,4,10)	-	-	109.7	110.1
A(5,4,9)	-	-	107.0	107.2
A(5,4,10)	-	-	105.7	105.4
A(9,4,10)	-	-	120.4	119.9
A(4,5,11)	-	-	105.6	105.4
A(4,5,12)	-	-	107.0	2
A(6,5,11)	-	-	109.7	110.1
A(6,5,12)	-	-	110.2	110.3
A(11,5,12)	-	-	120.4	119.9
Dihedral angles (Å)				
D(1,2,3,4)	-179.8	-179.9	-180.0	-179.9
D(2,3,4,5)	-177.2	-177.0	-176.0	-178.1
D(3,4,5,6)	-87.1	-87.3	144.1	148.0
D(4,5,6,7)	-177.2	-177.0	-176.0	-178.1
D(5,6,7,8)	-179.8	-179.9	-180.0	-179.9
D(2,3,4,9)	-	-	70.6	68.1
D(2,3,4,10)	-	-	-64.2	-66.4
D(3,4,5,11)	-	-	29.4	32.8
D(3,4,5,12)	-	-	-100.1	-95.9
D(9,4,5,6)	-	-	-100.1	-95.9
D(9,4,5,11)	-	-	145.2	148.9
D(9,4,5,12)	-	-	15.7	20.2
D(10,4,5,6)	-	-	29.4	32.8
D(10,4,5,11)	-	-	-85.3	-82.4
D(10,4,5,12)	-	-	145.2	148.9
D(11,5,6,7)	-	-	-64.2	-66.4
D(12,5,6,7)	-	-	70.6	68.1

 TABLE-2  
 EIGENVALUES OF LUMO AND HOMO AND ENERGY GAP OF HOMO AND LUMO

Compound	DPPDF <sub>(O)</sub>		DPPDF <sub>(R)</sub>	
	6-31g(d, p)	6-31++g(d, p)	6-31g(d, p)	6-31++g(d, p)
E <sub>HOMO</sub> (eV)	-6.640	-7.790	-6.520	-7.482
E <sub>LUMO</sub> (eV)	-0.959	-2.483	-0.714	-1.895
E <sub>LUMO</sub> - E <sub>HOMO</sub> (eV)	5.680	5.307	5.806	5.587

**Calculated standard electrode potential:** The theoretical calculation of standard electrode potential for DPPDF<sub>(O)</sub>/DPPDF<sub>(R)</sub> versus benzoquinone (BQ)/hydroquinone (HBQ) (E<sub>BQ/HBQ</sub><sup>o</sup> = 0.699V [31]) can be designed as





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