

THE THERMODYNAMIC STUDY ON THE SULFUR-CONTAINING COMPOUND IN COAL USING QUANTUM CHEMISTRY

Ling Lixia, Zhao Lijuan, and Wang Baojun

Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

Introduction

As one of main energy sources in China, coal has contributed to the development of national economy. But the release of SO₂, NO_x during the use of coal has seriously influenced the quality of environment and the development of zoology. Nowadays, several methods have been developed to remove sulfur, such as biochemistry desulfuration^[1] and electrochemistry desulfuration^[2] etc. But so far completely satisfactory solution has not been found.

Coal pyrolysis is the basic process of all coal conversions including combustion, gasification, carbonization and liquefaction, etc. It is a useful tool for the elucidation of coal structure and the assessment of its molecular reactivity^[3]. The understanding of physical and chemical transformation of sulfur in coal during pyrolysis is very important for the rational utilization of coal and also for environmental protection^[4]. In the process of coal pyrolysis, the cleavage of chemical bond is the most elementary behavior. In order to well understand this process, appropriate thermodynamic data are needed, such as internal energy, the bond dissociation energy (BDE), etc. With the development of technology, the quantum chemistry calculation method is more and more widely applied to the study of pyrolysis mechanism. About the calculation of compounds containing sulfur, some research have been developed^[5], and the results show that the calculation results are good agreement with the experimental results. But seldom research has been reported on the study of the compounds containing sulfur in coal.

Sulfur in coal is found in both inorganic and organic forms. The inorganic sulfur is relatively simple, mostly pyrite (FeS₂) and sulfates, but the organic sulfur is more complex and is hard to remove, which may exist in forms of various functional groups, such as thiophene, sulfur ether and thiol structure^[6]. Zhu Z P^[7] considers that sulfur exists in the form of connecting two macromolecular structures in coal. Considering the computation time and capacity, the naphthyl benzyl sulfide was chosen as the study model in this paper.

The Design of Reaction Paths and the Calculation Method

To well understand the pyrolysis of naphthyl benzyl sulfide, the designed reaction paths are shown in Figure 1. The number of every atom of reactant and a partial number of radical are also shown in Figure 1.

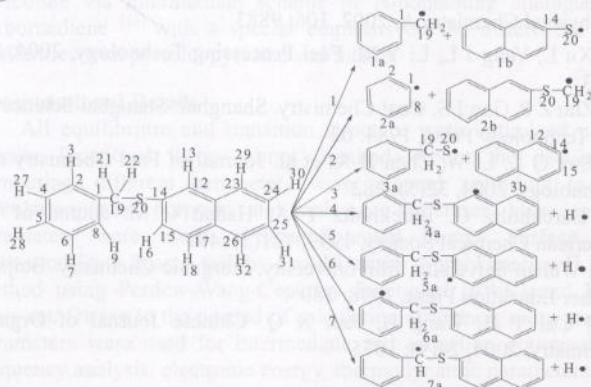


Figure 1 The designed reaction paths of naphthyl benzyl sulfide

The bond dissociation energy (BDE) is a thermodynamic quantity in token of thermal stability of molecular^[8], which is defined as the enthalpy change of the reaction required to break the specific bond of reactant to form two radicals^[9], as the following reaction: $R-X \rightarrow R+X\cdot$

The BDE can be expressed as Eq 1.

$$BDE(R-X) \equiv \Delta H^\theta(R-X) = \Delta H^\theta(R\cdot) + \Delta H^\theta(X\cdot) - \Delta H^\theta(R-X) \quad (1)$$

In order to choose appropriate calculation method, five model compounds were chosen in this paper, and the BDE were calculated using AM1, PM3 and Dmol³ methods respectively when the bond connecting to sulfur atom was cleaved. It can be concluded that the calculation results of BDE using AM1 and PM3 methods have more lager deviation with experiment results, while the calculation results employing Dmol³ method is in agreement with the experiment results. So Dmol³ method is chosen in this paper, parameters are shown as following: Method is Local DFT; Basis Set is DND; The Medium convergence criteria is used, Energy: 1.00×10^{-5} (Ha), Gradient: 1.00×10^{-3} (Ha·Bohr⁻¹), Displament: 1.00×10^{-3} (Bohr); Spin Polarization: Unrestricted; Numerical Integration Grid: Medium; Multipolar Expansion of Density: Octopole; Occupation: Thermal; SCF Convergence Criteria: Brief.

Results and Discussion

The bond length analysis. The structure of naphthyl benzyl sulfide and all radicals were optimized using the above method, partial bond lengths of optimized structure were shown in Table 1.

Table 1 Partial bond lengths of optimized structure

Bond length of naphthyl benzyl sulfur					
Bond	Bond length	Bond	Bond length	Bond	Bond length
C1-C19	1.495	C1-C2	1.391	C19-S20	1.803
C14-S20	1.751	C1-C8	1.394	C12-C14	1.384
C2-C3	1.099	C4-H27	1.097	C14-C15	1.407
C5-H28	1.097	C6-H7	1.097	C8-H9	1.099
C12-H13	1.099	C15-H16	1.098	C17-H18	1.098
C19-H21	1.106	C19-H22	1.108	C23-H29	1.098
C24-H30	1.097	C25-H31	1.097	C26-H32	1.098
Bond length of radicals					
1aC1-H19	1.391	2aC1-H2	1.370	3aC1-H19	1.495
1bC14-H20	1.714	2aC1-H8	1.370	3aC19-S20	1.790
		2bC19-S20	1.705	3bC14-C15	1.382
				3bC12-C14	1.358

It can be seen from the optimized naphthyl benzyl sulfide that the bond length of C19-S20 is the longest, C14-S20 is the second and C1-C19 is the third. It is well known that the shorter the bond length is, the stronger the bond is^[10], vice versa. It can be found that the bond length of bond connecting to radicals is shorter than the length corresponding to reactant structure, because the steric effect is weaker with the formation of radical as the bond cleavage. So the reaction of path 1 occurs firstly, then path 3, path 2. According to the comparison of bond lengths of all C-H, the bond lengths of C2-H3, C12-H13, C15-H16, C19-H21 and C19-H22 are longer than other bond lengths, and the length of C19-H22 is the longest in all bonds, so the bond of C19-H22 is cleaved easily. That can be explained that H21 and H22 are connected to aliphatic C, while other H are connected to aromatic C resulting in the combination between C and H more closed.

The Mayer bond orders were calculated using the same method, the similar conclusion was gotten from the analysis of bond order.

The microcosmic parameters of optimized structure can provide

some information for understanding the properties such as the stability of molecular and the strength of bond, but we must consider the thermodynamic property if we want to understand the thermally stability of molecular and the reaction of the above paths.

Thermodynamic calculation. According to the above method, the electronic energy of every structure (E_{elec}), statistic entropy (S_m^θ) and statistic enthalpy (h_m^θ) at different temperatures could be gotten. The calculated ΔE , ΔH , ΔG , ΔS of every path at different temperatures are shown in **Table 2**.

Table 2 The thermodynamic function change of the 7 reaction paths

	Path 1	Path 2	Path 3	Path 4	Path 5	Path 6	Path 7
298.15K							
ΔE	195.63	433.02	330.10	467.65	458.09	474.17	333.78
ΔH	198.11	435.50	332.58	470.13	460.57	476.65	336.26
ΔG	145.74	381.70	283.68	438.18	424.33	442.43	301.00
ΔS	175.66	180.45	164.00	107.16	121.51	114.78	118.28
400K							
ΔE	195.49	432.77	328.71	469.47	460.01	476.14	335.92
ΔH	198.81	436.09	332.04	472.80	463.34	479.47	339.24
ΔG	128.71	364.20	268.04	427.82	412.50	431.28	289.46
ΔS	175.26	179.74	159.99	112.44	127.09	120.48	124.45
600K							
ΔE	194.47	431.20	325.41	472.32	463.01	479.22	339.32
ΔH	199.46	436.19	330.40	477.31	468.00	484.21	344.31
ΔG	95.50	330.20	238.39	406.34	388.05	408.13	265.45
ΔS	173.26	176.66	153.35	118.28	133.24	126.80	131.43
800K							
ΔE	192.63	428.49	321.58	474.39	465.19	481.45	341.74
ΔH	199.28	435.15	328.26	481.05	471.84	488.10	348.39
ΔG	62.76	296.91	209.95	384.02	362.72	384.08	240.44
ΔS	170.65	172.79	147.86	121.29	136.39	130.02	134.94
825K							
ΔE	192.36	428.09	321.08	474.60	465.41	481.67	341.98
ΔH	199.22	434.95	327.94	481.46	472.27	488.53	348.84
ΔG	58.71	292.80	206.47	381.18	359.51	381.03	237.27
ΔS	170.31	172.30	147.24	121.55	136.67	130.31	135.24
1000K							
ΔE	190.27	425.05	317.43	475.87	466.73	483.02	343.40
ΔH	198.59	433.36	325.75	484.19	475.04	491.34	351.72
ΔG	30.57	264.40	182.51	361.24	336.91	359.55	214.90
ΔS	168.02	168.96	143.23	122.95	138.13	131.79	136.81

The unit of ΔE , ΔH , ΔG is $\text{kJ}\cdot\text{mol}^{-1}$, the unit of ΔS is $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

It can be seen from the **Table 2** that the order of the thermodynamic changes ΔE , ΔH , ΔG of different paths is path 1 < path 3 < path 7 < path 2 < path 5 < path 4 < path 6, and the

thermodynamic changes of path 2, path 5, path 4 and path 6 are larger than path 1, path 3 and path 7. As far as energy is concerned, the smaller of the value of internal energy and enthalpy change, the easier reaction occurs. And as far as equilibrium is concerned, the smaller of the value of Gibbs free energy change, the easier reaction occurs and the equilibrium reaches. So it can be seen that the bond cleavage occurs at S-C_{al} firstly, then at S-C_{ar}, the C-C bond between methylene and benzene cleavages finally either by energy or by equilibrium. This can be explained that the p - π conjugation system is formed between C and benzene, which leads to the C-C bond connecting to benzene possess the property of double bond to a certain extent^[11]. Path 4, 5, 6, 7 are dehydrogenation paths, it can be concluded from the thermodynamic change of the four paths that the H atom of methylene is broken off firstly, then the H atom of conjugate ring is broken off, and every thermodynamic change of path 4, 5, 6 is more larger than that of path 7. This is reasonable that the C of benzene employs sp^2 hybridization resulting in the combination of C and H closer than other C-H bonds, and C of methylene employs sp^3 hybridization.

At the temperature of 400K, 600K, 800K, there is no change in the order of thermodynamic reaction paths with increasing temperature. But above 825K, the free energy change ΔG of reaction path 4 changes from less than that of path 6 to more than that of path 6. When the temperature reaches 1000K, the ratio of equilibrium constants path 6 and path 4, K_6^θ/K_4^θ changes from 0.18 at 298.15K to 1.23 at 1000K. These values clearly indicate that the main reaction change from path 4 to path 6 as temperature increases.

It can also be seen from the Table 4 that improving temperature has a great influence on ΔG , but has a little influence on ΔE and ΔH . For every path, the ΔG decreases with improving temperature, it can be concluded that improving temperature is advantageous to pyrolysis reaction by equilibrium.

Acknowledgments

This work was supported by the National Basic Research Program of China (No. 2005CB221203), the National Natural Science Foundation of China (No. 20476069, 20576087) and the Foundation of Shanxi Province (No. 2006011022)

References

- [1] Jürgen K. Biodegradation, 1998, 9: 293
- [2] Wang Z C, Yao W R, Cui P, et al. Journal of Fuel Chemistry and Technology, 2003, 31(5): 509
- [3] Arenillas A, Pevida C, Rubiera F, et al. Journal of Applied Pyrolysis, 2004, 71: 747
- [4] Yasushi S, Mitsunori M, et al. Fuel, 1998, 77(9-10): 907
- [5] Borges dos Santos R M, Muralha V S F, Correia C F, et al. Journal of Physical Chemistry A, 2002, 106: 9883
- [6] Xu L, Yang J L, Li Y M. Fuel Processing Technology, 2004, 85: 1013
- [7] Zhu Z P, Gao J S. Coal Chemistry. Shanghai: Shanghai Science and Technology Press, 1984: 62
- [8] Sun Q L, Li W, Chen H K, et al. Journal of Fuel Chemistry and Technology, 2004, 32(3): 282
- [9] Barckholtz C, Barckholtz T A, Hadad C M. Journal of the American Chemical Society, 1999, 121(3): 491
- [10] Wuhan university, Jilin university. Inorganic Chemistry. Beijing: Higher Education Press, 1998: 180
- [11] Cui Y B, Wang H, Ran X Q. Chinese Journal of Organic Chemistry, 2004, 24(9): 1075