DFT study on the sulfur migration during benzenethiol pyrolysis in coal

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ABSTRACT

The migration of sulfur resulting in the formation of CS, H_2S and thiophene during benzenethiol pyrolysis has been investigated using the density functional theory method with PW91 functional and DND basis set. The lowest energy path is that H of the thiol group transfers to the ipso C and S radical is eliminated by beta scission reaction, and then the S radical combines with H radical formed during coal pyrolysis and eventually results in the formation of H_2S. The formation of H_2S via benzenthiol pyrolysis is easier than via thiophene by comparing with the kinetic data.

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1. Introduction

The sulfur in coal exists in inorganic and organic forms. The inorganic forms are mostly pyrite and marcasite, with small amounts of sulfates depending on the level of oxidation of the coal [1]. The organic sulfur exists either in aromatic rings or in aliphatic functional groups, usually categorized as thiols (RSH), aliphatic and aryl sulfides (RSR′), disulfides (RSSR′) and thiophenes [2,3]. Benzenethiol (C_6H_5SH) is the simplest aromatic thiol [4], which is often used to investigate the desulfurization as typical thio-alcohol compound [5–7].

The organic sulfur in coal is eliminated as H_2S mainly during coal pyrolysis [8], especially the unstable thiols compounds, which eliminate H_2S at 700–850 °C [9]. Benzenethiol was investigated by flow pyrolysis at 700 °C and vacuum pyrolysis at 800 °C, benzene was identified as one of the major products [10]. Benzene as the major product during benzenethiol decomposition at CO or CO/H_2O condition was also investigated by Van Buren [11]. Meanwhile, the decomposition of benzenethiol was studied in a flow reactor by Bruinsma [12], it could be concluded that the intramolecular H migration in phenol resulting in the formation of cyclopentadiene demonstrated by Cypres [13] was not observed for benzenethiol. But the mass spectrum of the molecular ions produced by electron ionization of neutral benzenethiol was shown that the most intense peaks observed at m/z 84 and 66 (corresponding to the losses of ethyne and carbon monosulfide, respectively) were the reactions already observed without the presence of a collision gas and then resulted from unimolecular

rearrangements of the metastable molecular ions, thiophene and cyclopentadiene ions (m/z 84: m/z 66 = 0.83) were likely to be generated [14], which showed that cyclopentadiene and thiophene might be also the decomposition products of benzenethiol. And some of the thiols being transformed into thiophenes during coal pyrolysis has been investigated in early study [15]. We can see that the sulfur in benzenethiol may be migrated to products CS, H_2S and thiophene from the above experiments. Nevertheless, none of the intermediates has been identified experimentally, or no kinetic data has been got.

In this study, a density functional theory (DFT) method was used to understand the process of sulfur migration to products CS, H_2S and thiophene during benzenethiol pyrolysis, so as to provide information for understanding the coal pyrolysis.

2. Computational details

A DFT method was adopted and calculations were performed using the Dmol^3 program [16] mounted on Materials studio 4.0 package. The reactant, intermediates and products were optimized at the level of the generalized gradient approximation (GGA) using the Perdew–Wang 1991 (PW91) functional [17] and DND basis set. Spin unrestricted was chosen, total SCF tolerance criteria, integration accuracy criteria and orbital cutoff quality criteria were set at medium and multipolar expansion was set at octupole. Then TS search calculations were carried out to find possible transition state structure for every elementary reaction. All the structures were calculated at the same level of theory and vibration analysis was carried out for each structure to characterize it either as an equilibrium structure (no imaginary frequency) or a transition state (one imaginary frequency whose vibration mode corresponds

Table 1
Imaginary frequency of each transition state and the bonds corresponding to normal vibration.

Transition state	Imaginary frequency (cm^{-1})	Bond corresponding to normal vibration
TS1	−1709.21	S7–H13–C4
TS2	−600.30	C4–C6
TS3	−378.66	C5–C6
TS4	−194.12	C5–S7
TS5	−418.33	S7–H13–C5
TS6	−244.57	C5–S7
TS7	−373.32	C2–S7
TS8	−522.05	C2–C3; C4–C5

to the reaction coordinate), imaginary frequency of each transition state and the bonds corresponding to relative normal vibration in the process of benzenethiol pyrolysis are shown in Table 1. TS confirmation calculation was carried out to confirm every transition state leaded to the desired reactant and product. Meanwhile, the electronic energy (E_{elec}), zero point vibration energies (ZPVE) and Mulliken atomic charges were calculated. These parameters and the method are credible to study the pyrolysis mechanism of sulfur-containing model compounds according to our previous study [18,19]. All calculations were performed on HP Proliant DL 380 G5 server system.

3. Results and discussion

Four different paths were proposed to describe the migration process of sulfur, two of which were for the sulfur migration eventually resulting in H₂S. All these are shown in Fig. 1. The optimized

structures and the atom numbers of all the stationary points (reactant, intermediates, transition states and products) during benzenethiol pyrolysis are shown in Fig. 2, and the relative energies of the stationary points of the four paths are shown in Fig. 3.

3.1. Sulfur migration yielding CS

A mechanism with a six-member ring changing into a five-member ring describes the sulfur migration yielding CS (Path 1). In the first step, the S7–H13 bond is elongated and the C4–H13 bond in R is shortened resulting in the formation of IM1 via TS1, which has one imaginary frequency of −1709.21 cm^{-1}. In this step, an energy barrier of 228.18 kJ/mol is needed. Then C4 and C6 in IM1 combine followed by a six-member ring changing into a five-member ring, the rearrangement of IM1 → IM2 is structurally similar to the cyclization 1 → 2 in the decomposition process of phenoxy radical. The cyclopentadiene radical is formed (Fig. 4) [20]. In this step, the bond length of C4–C6 changes from 2.512 to 1.536 Å via TS2 resulting in the formation of IM2. TS2 has one imaginary frequency corresponding to the stretch mode of C4–C6 bond, which is 395.41 kJ/mol higher than benzenethiol. IM2 has an unpaired electron locating in C1 and the other electron locating in C5. The last step is C5–C6 bond cleavage, cyclopentadiene is formed followed by CS leaving, and the length of the C5–C6 bond is increased to 3.142 Å from 1.467 Å via TS3. TS3 is 348.45 kJ/mol higher in energy than benzenethiol.

3.2. Sulfur migration yielding H₂S

Two paths are provided for the formation of H₂S, one of which is that C5–S7 bond in benzenethiol cleaves resulting in the formation
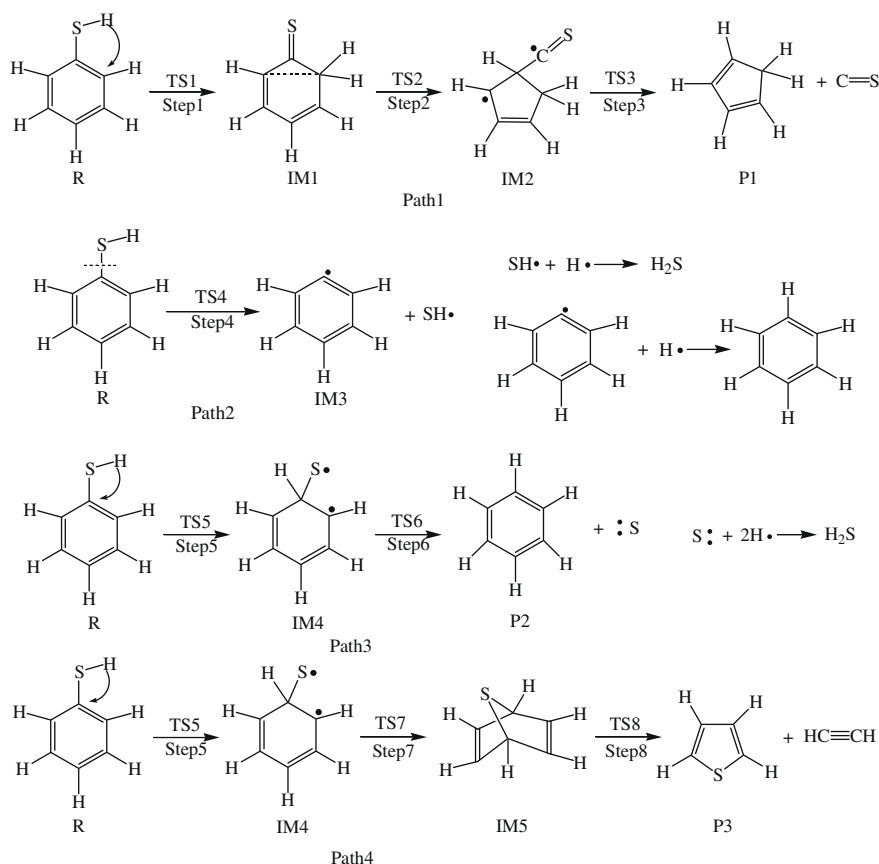

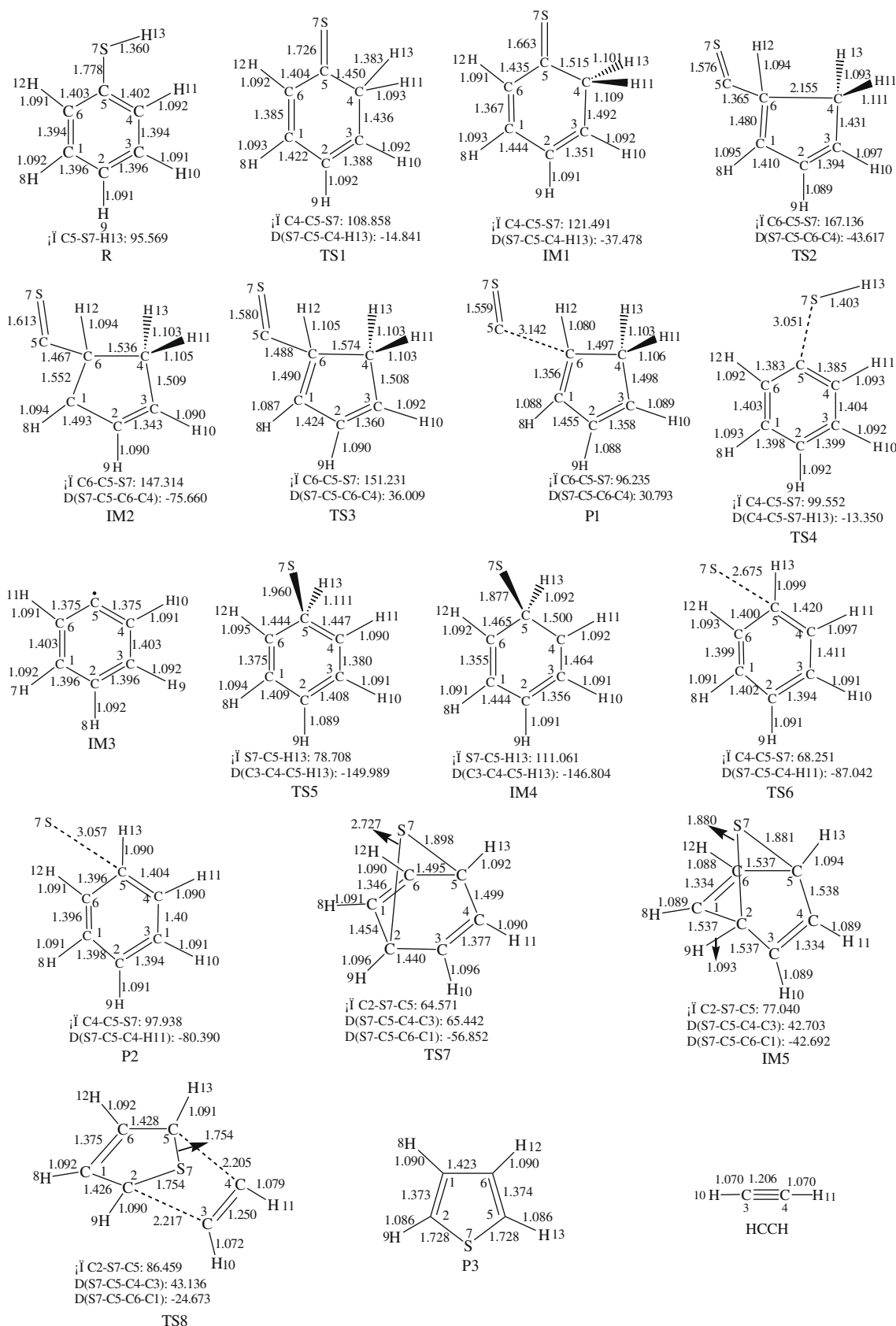**Fig. 1.** The proposed sulfur migration mechanisms during benzenethiol pyrolysis.

Fig. 2. The optimized geometries[a] of all reactant, intermediates, transition states and products during benzenethiol pyrolysis. [a]Bond lengths are in angstroms, and angles are in degrees.

of SH radical in Path 2, then the SH radical combines with H radical formed by the homolysis of weak R–H (R may be alkyl) bonds or released in the process of polymerization during coal pyrolysis [21–23] resulting in the formation of H_2S. The energy barrier of

343.56 kJ/mol is needed in the fission of C5–S7 bond. The radical combination can occur without energy barrier, and the reaction energy of SH radical combining with H radical leading to the formation of H_2S is −383.95 kJ/mol. In the process of H_2S formation, the phenyl radical can also abstract an H radical leading to the formation of benzene, which is also a process without energy barrier, and the reaction energy is −488.22 kJ/mol.

Path3 is the other path to yield H_2S. In Path 3, H13 of the thiol group transfers from S7 to the ipso C5 followed by S7–H13 bond cleavage and then C5–H13 bond formation via TS5 with an energy barrier of 239.62 kJ/mol, which is 11.44 kJ/mol higher than Step 1. It results from the Mulliken atom charge of C5 in benzenethiol being positive, and charge of C4 being negative, which indicates that C5 is more difficult than C4 to undergo nucleophilic reaction. The steric effect can also show that H13 is unfavorable to transfer to C5 yielding IM4. IM4 has an unpaired electron locating in S7 and the other electron locating in C4. Then the C5–S7 bond cleaves resulting in the formation of benzene and S radical via TS6, which has one imaginary frequency corresponding to the stretch mode of C5–S7 bond. TS6 is 242.14 kJ/mol higher than benzenethiol. The S radical is active, which can combine with H radical formed by homolysis of some weak R–H (R may be alkyl) bonds or released in the process of polymerization during coal pyrolysis [21–23] resulting in the formation of H_2S. This step is also a process without energy barrier, and the reaction energy is −749.87 kJ/mol.

The radical combination reactions occur without energy barrier, including the SH + H and S + 2H leading to the formation of H_2S, respectively. They have not influences on the reaction process of benzenethiol pyrolysis from a kinetic point of view. We have not shown these steps in Fig. 3.

3.3. Sulfur migration yielding thiophene

Reaction path involving a bridge intermediate is designed to describe the sulfur migration yielding thiophene (Path 4). H migration in benzenethiol first leads to the formation of IM4, then S7 in IM4 bonds with C2 via TS7 with one imaginary frequency corresponding to the stretch mode of C2–S7 bond. This results in the formation of IM5 with a bridge bond and C_{2v} symmetry. From the Mulliken atomic charges of IM5 in Table 2, we can see that the charges of C1, C3, C4 and C6 are similar, and the charges of C2 and C5 are also the same. TS7 is 319.03 kJ/mol higher than benzenethiol. Then thiophene and acetylene are formed via C4–C5 and C2–C3 bonds cleavage at the same time. The transition state TS8 has one imaginary frequency corresponding to the stretch mode of C4–C5 and C2–C3 bonds. The TS is 387.60 kJ/mol higher than benzenethiol. The Mulliken atomic charges of thiophene in Table 2 show that C1, C2, C5 and C6 have the similar charges.

3.4. Comparison on every sulfur migration path

From the relative energies of the stationary points for sulfur migration resulting in the formation of CS, H_2S and thiophene, respectively, in Fig. 3, we see that the highest energy barrier along the sulfur migration yielding CS occurs at TS2, which is 395.41 kJ/mol higher than benzenethiol. In the two paths of H_2S formation, the highest energy barrier of one of which occurs at C5–S7 bond cleavage in benzenethiol to SH radical via TS4, and the energy is 343.56 kJ/mol higher than benzenethiol. The second path to H_2S formation is Path3, and the highest energy barrier occurs at TS6, which is 242.14 kJ/mol higher in energy than benzenethiol. The highest energy barrier along the sulfur migration yielding thiophene occurs at TS8, which is 387.60 kJ/mol higher in energy than benzenethiol. The lowest energy path is Path3, that is, H of the thiol group transfers to the ipso C and S radical is eliminated by beta scission reaction. The S radical abstracts H atoms or combines with
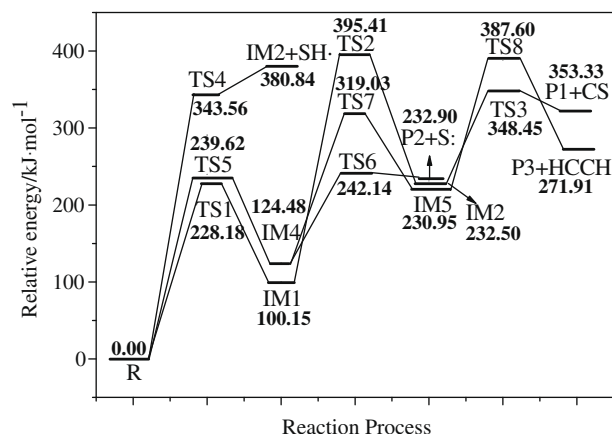

Fig. 3. Energies sketch of the stationary points for benzenethiol pyrolysis. The numbers given are single point energy with ZPVE correction relative to benzenethiol (R) whose total energy is −630.3147 Ha. All of equilibrium structures and transition states are given in Fig. 1.
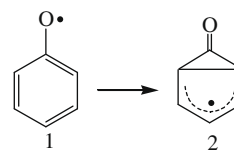

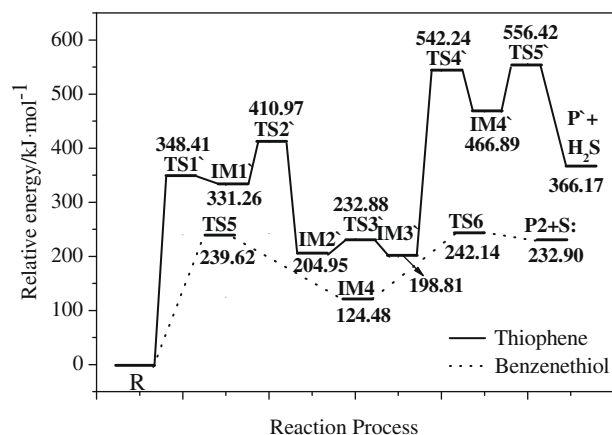**Fig. 4.** The reaction step in the decomposition of phenoxyl radical.

Fig. 5. Energies sketch of the stationary points for the favorable paths of forming H_2S via thiophene and benzenethiol pyrolysis.

Table 2
Mulliken atomic charges of some species during benzenethiol pyrolysis.

	C1	C2	C3	C4	C5	C6	S7
R	−0.163	−0.177	−0.160	−0.214	0.179	−0.209	−0.332
TS5	−0.163	−0.147	−0.164	−0.081	−0.222	−0.092	−0.343
IM4	−0.161	−0.161	−0.122	−0.141	−0.144	−0.118	−0.260
TS7	−0.139	−0.179	−0.129	−0.094	−0.246	−0.102	−0.222
IM5	−0.098	−0.254	−0.099	−0.100	−0.252	−0.100	−0.161
TS8	−0.105	−0.182	−0.193	−0.193	−0.183	−0.106	−0.116
P3	−0.145	−0.151	−0.197	−0.204	−0.145	−0.146	−0.104

H radicals formed during coal pyrolysis resulting in the formation of H_2S. The sulfur migrations leading to the formation of CS and thiophene are more difficult. The products benzene, cyclopentadiene and acetylene are also formed in the process of the sulfur

migration. Benzene is formed easily, which is the reason that a large amount of benzene is found by flow pyrolysis of benzenethiol at 700 °C [10].

3.5. Comparison of the formation of H_2S via benzenethiol and thiophene pyrolysis

Thiophene and benzenethiol are both the organic sulfur-containing compounds, which are commonly as the representation of sulfur-containing models in coal to investigate the desulfurization. In our previous study [19], the pyrolysis mechanism of thiophene was investigated with the same calculation method as this study, the favorable energy path was the α-H in thiophene migrated to S, and then the β-H migrated to the α-C followed by C–S bond cleavage. H_2S was formed via H migration. The relative energies of the favorable paths of forming H_2S via thiophene and benzenethiol pyrolysis are shown in Fig. 5. In the process of benzenethiol pyrolysis, the lowest energy path of H_2S formation is H of the thiol group transfers to the ipso C and S radical is eliminated by beta scission reaction, then the S radical combines with H radical formed during coal pyrolysis. The highest energy barrier is 242.14 kJ/mol higher than benzenethiol, which is smaller than that in thiophene pyrolysis. It can be concluded that the formation of H_2S via benzenthiol pyrolysis is easier than via thiophene, which explains the experimental fact that thiophene was pyrolyzed at higher temperature [24] than that of benzenethiol [10] from a kinetic point of view.

4. Conclusions

The migration of sulfur during benzenethiol pyrolysis was investigated using density functional theory method, the calculated structural microscopic parameters and kinetic data show that:

1. The four paths of sulfur migration resulting in the formation of CS, H_2S and thiophene during benzenethiol pyrolysis have been determined. The lowest energy path is that H of the thiol group transfers to the ipso C and S radical is eliminated by beta scission reaction, and then the S radical combines with H radical formed during coal pyrolysis leading to the formation of H_2S.

2. A large amount of benzene has been found during the pyrolysis of benzenethiol, when sulfur migration leads to the formation of H_2S.

3. The formation of H_2S via benzenthiol pyrolysis is easier than via thiophene from a kinetic point of view.

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