Stimulation Calculation of Desulfurization Mechanisms Dominated by Free Radicals Reactions During Pyrolysis of Thiophenes Under Water Vapor Atmosphere

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Stimulation calculation of desulfurization mechanisms dominated by free radicals reactions during pyrolysis of thiophenes under water vapor atmosphere

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Abstract: The desulfurization mechanisms of thiophene and 2-methyl thiophene were investigated by the density functional theory (DFT) during pyrolysis under water vapor atmosphere. All possible reaction pathways of these desulfurization mechanisms were explored at M06-2X/6-311g (d) level. The Multwfn3.0 and VMD1.9.2 programs were used to analyze weak interactions between thiophene compounds and H_2O molecule. It can be seen that hydrogen bonds can be formed in the reactions of thiophene sulfurs and H_2O. Since H_2O molecule can decompose at higher temperature and generate free radicals, such as • H and • OH, , the desulfurization mechanisms of thiophene and 2-methyl thiophene with free radicals need to be further considered. The reaction energy barriers ($\Delta G^{\neq}$) and reaction energies (ΔG_P) of thiophene and 2-methyl thiophene with H_2O molecule (g) or free radicals (•H and •OH)

have been stimulated and calculated in detail. Based on the transition state theory (TST), the rate constants corresponding to these elementary reactions are also calculated, meanwhile the speed and spontaneity of every reaction can be obtained from the aspect of kinetics. Theoretically, it is found that H_2O (g) directly attacking C-S bonds of thiophene and 2-methyl thiophene cannot easily generate COS and H_2S even at 1200 K in terms of thermodynamics and kinetics. If the desulfurization mechanisms of thiophenes are investigated by free radicals mechanisms under steam atmosphere, their initial energy barriers needing to be overcome significantly reduce. Therefore, desulfurization mechanisms of thiophenes and H_2O (g) are the most possibly dominated by radical reactions at higher temperatures and H_2S is mainly generated.

Keywords: Desulfurization mechanism; Steam atmosphere; Thiophene compounds; Pyrolysis; Free radicals

1. Introduction

China consumes the most coal worldwide. The sulfur and nitrogen heteroatoms in coal would be converted to sulfur-containing gases (COS, H_2S, SO_X) and nitrogen oxides (NO_X)[1]. Thus, massive utilization of coal can cause various environmental issues, such as air pollution and acid rain. Therefore, Sulfur removal before the toxic sulfur compounds are released into the environment is also an important subject [2].

Hydrous pyrolysis was used to simulate desulfurization reaction and the obtained data suggest that water acts like a reactant[3]. But, the detailed desulfurization mechanism under steam atmosphere remains unclear[4]. Aliphatic sulfur compounds,

such as thiols and sulfides, have been found to react during the experiment of hydrothermal simulation in 473-603K. Liu et al.[3] found that the increasing of the feed ratio of water to thiophene facilitates desulfurization and more gases were generated. Abraham and Klein[5] investigated the reaction of benzylphenyl sulfide (BPS) in subcritical water and observed benzaldehyde as the major product, indicating that water was involved as a reactant. Thus, water vapor has been used as an atmosphere to investigate desulfurization behavior during coal pyrolysis. As large quantities of H_2 and expensive catalysts were required during the conventional hydro desulfurization process, water vapor pyrolysis can be considered as a potential alternative desulfurization method to reduce sulfur content in high sulfur coals. Water vapor attacks C-S bond of thiophene which results in the breakage of the C-S bond, and H_2S, CO, CO_2, H_2, light hydrocarbons and other gases are produced during the hydrothermal cracking of thiophene [6,7,8]. Under steam atmosphere, H and OH free radicals are easily formed at high temperature. Wang et al.[9] has focused on the effect of steam on the transformation of sulfur during coal pyrolysis at the range of temperatures from 573 to 1073K. The removal of organic sulfur was found to increase, because the addition of steam above 773K promoted the decomposition of thiophenic sulfur. In addition, steam can generate more •H radicals, promoting the formation of H_2S[9].

There have been several experimental studies about the desulfurization behaviors [10,11,12], but few have focused on the detailed desulfurization mechanism at the micro level. Quantum chemistry can be used to calculate the thermochemical properties of coal, the interaction between coal surface and gas, the desulfurization mechanism of

sulfur-containing model compounds and their pyrolysis reactions[13,14,15,16]. It can also help explaining some unclear phenomena in the experiments at a theoretical level. Yuko Kida et al.[9] used quantum chemistry to calculate the radical reactions of C-S bond cleavage in hexyl sulfide and the addition of water to the C=S bond to form a geminal mercaptoalcohol in the supercritical water (SCW) experiment. The mercaptoalcohol then decomposes into an aldehyde and H_2S either directly or via a water-catalyzed 6-membered ring transition state. So their results showed that H_2O is a reactant and can participate in the decomposition reaction of hexyl sulfide. Other theoretical studies have also shown H_2O can reduce the energy barrier of gas phase single molecular reactions in several systems[17,18,19]. In recent years, interactions between water molecules and coal models have been extensively studied[20,21,22]. Water molecules tend to accumulate around oxygen-containing functional groups of coal models and hydrogen bonds play a leading role in the interaction according to the Reduced Density Gradient (RDG) analysis[23].

Because of the variably complicated three-dimensional macromolecular structure of coal, it is difficult to build coal itself via modeling tools. The homolytic energy of monocyclic aromatic compounds often can be used to predict the homolytic energy of polycyclic aromatic compounds with similar structures. Thus, in this study, thiophene and 2-methyl thiophene were selected to represent the difficult-to-remove coal-based sulfur species and to investigate their detailed desulfurization mechanisms during pyrolysis under steam atmosphere. All possible desulfurization pathways of these thiophenes were calculated and analyzed from the perspective of thermodynamics and

kinetics. Therefore, the detailed desulfurization mechanisms of these thiophenes can be obtained under steam atmosphere. This can provide some theoretical basis for coal desulfurization during coal utilization under steam atmosphere.

2. Calculation methods

2.1 Geometry optimization and energy evaluation

All quantum chemistry calculations were carried out using the Gaussian 09 software package[24]. Geometry optimization of various reactants, products, intermediate (IMn) and transition states (TSn) were calculated by using the mixed element exchange correlation function M06-2X[25,26] with the standard base group 6-311g(d) in density fun ctional theory (DFT), and the thermodynamic correction was calculated at the same theoretical level. M06-2X with Grimme's DFT-D3 dispersion correction using the Becke-Johnson damping function is highly suitable and reliable for noncovalent interaction calculations[27,28]. Moreover, for each transition state calculations of intrinsic reaction coordinate (IRC) and vibration analysis, using a same basis set for computational rationality (M06-2X/6-311g(d)), were used to confirm the connections between the reactants and products correspondingly. The transition state has only one imaginary frequency[18,29,30], and all other species have real frequency. M06-2X/def2tzvp was used to calculate the single point energy which was added to the thermodynamic correction amount to obtain the energy barrier ($\Delta G^{\neq}$) of each step reaction. Reaction energy (ΔG_{p}) was used to judge whether the reaction is spontaneous. All relative energy barrier ($\Delta G^{\neq}$) and reaction energy (ΔG_{p}) were obtained via equations (1) and (2)

$$\Delta G^{\neq} = G^{TS} - G^{IM} \quad (1)$$

$$\Delta G_P = G_P - G_R \quad (2)$$

where G_P, G_R, G_{TS}, G_{IM} are the Gibbs free energy of the corresponding product (P), reactant (R), transition state (TSn) and intermediate (IMn) of a pathway, respectively.

2.2 The Reduced Density Gradient (RDG) Analysis

The Reduced Density Gradient (RDG)[31] method was used to define a real space function, and the points in space and the sign [λ2 (r)]ρ(r) function were used as coordinates to make a RDG diagram by the wave function program Multiwfn3.4.1[32] and the visualization program VMD1.9.2[33]. The RDG diagram can manifest weak interaction areas between molecules and inter molecules. The smaller value [λ_2 (r)] ρ(r) of the scatter (ρ>0, λ_2<0) indicates that the interaction is of stronger attractive (H-bonds). The higher sign [λ_2 (r)] ρ(r) of the scatter (ρ>0, λ_2>0) indicates that the interaction is a repulsive force. If the sign [λ_2 (r)] ρ(r) of the scatter is close to zero (ρ≈0, λ_2≈0), this interaction is Van der Waals (vdW) forces. The complex structures of thiophene sulfurs and H_2O have been optimized at the M06-2X/6-311g (d) level and used for RDG analysis. The RDG function equation is

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/2}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}}$$

where ρ(r) is the electron density varing with r.

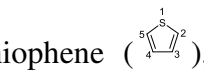
2.3 Reaction rate constant calculation

The rate constants of reactions of thiophene sulfurs and water vapor can be obtained according to the following equation[34],

$$k(T) = \frac{K_B T}{h}\left(\frac{Q_{TS}}{Q_R}\right) exp\left(-\frac{E_a}{K_B T}\right)$$

where K_B, T, and Ea are the Boltzmann constant, reaction temperature (298 K), and activation energy, respectively. Q_{TS} and Q_R are the partition functions per unit volume for a TS and a reactant, respectively.

3 Results and discussion

In this study, thiophene (), 2-methyl thiophene () were selected to investigate their desulfurization mechanisms during pyrolysis under steam atmosphere. During pyrolysis, water vapor maybe directly attack C-S bonds, or water vapor dissociates and forms free radicals (•H and •OH). Free radicals then attack C-S bonds or / and other carbon sites, and H_2S, CO, H_2, light hydrocarbons and other gases could be generated [3]. Therefore, we aim to investigate the addition reactions of H_2O and C-S bonds of thiophene sulfurs and radical reactions of free radicals and thiophenes and obtained the most possible desulfurization mechanisms of thiophenes and H_2O.

3.1 RDG analysis of thiophenes and H_2O

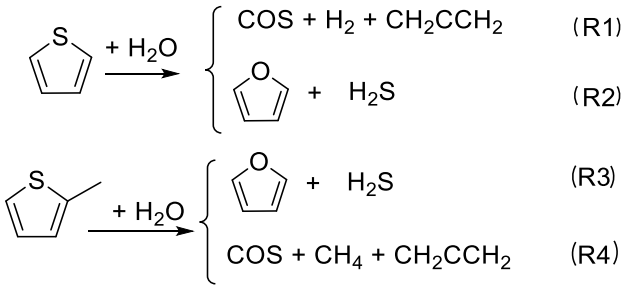
Fig. 1 shows the RDG diagrams of complexes (i.e., A and B) formed by two typical thiophenes with H_2O (g). The RDG diagram of complex A is of thiophene and H_2O (g). The large green or brown-green isosurface indicates that the weak vdW interaction in complex A is quite obvious, corresponding to the spikes at the scattered value range from -0.01 a.u. to 0.01 a.u. The fusiform red isosurface in the thiophene ring indicates that the ring itself has spatial repulsion (see the spike at the range from 0.035 a.u. to 0.040 a.u.).

The RDG diagram of complex B is of H_2O and 2-methyl thiophene. For complex B,

S atom of 2-methyl thiophene and H atom of H_2O can form distinct H-bond at the scattered value of -0.040 a.u. to -0.035 a.u., and there also is a large spatial repulsive force between O in H_2O and C5 on 2-methylthiophene, corresponding to the spikes at the value ranging from 0.020 a.u. to 0.030 a.u..

3.2 Desulfurization mechanisms of thiophenes with H_2O (g) addition reactions

Recently, for the better desulfurization effect and higher tar yield of coal, the supplement of hydrogen source is the most effective method. Water vapor used for pyrolysis desulfurization is a relative cheap and easily available hydrogen source. Thus, in order to investigate the effect of water molecules on desulfurization mechanisms, the reaction mechanisms of H_2O (g) or free radicals (• H and • OH) with thiophenes were calculated and investigated. The most possible pathways of thiophenes and H_2O (g) are considered as follows:



3.2.1 Desulfurization mechanisms of thiophenes with H_2O

Fig. 2 illustrates the energy diagrams of thiophene and H_2O forming COS (R1) and H_2S (R2) at 1200 K. For R1, H_2O firstly attacks C2 site in thiophene and forms intermediate IM1 by overcoming the energy barrier (145.6 kcal/mol) of TS1, meanwhile one molecule of H_2 is removed. Then, IM2 is formed through TS2 after overcoming a 64.9 kcal/mol energy barrier. Subsequently, H migration occurs from C4 to C5 in IM2 and then IM3 is generated. Lastly, C-S, C-C bonds of IM3 are

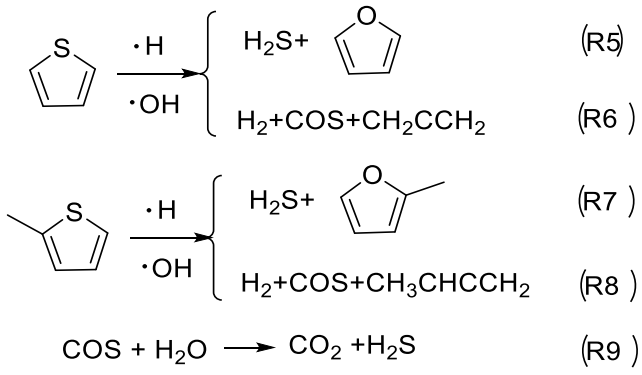
broken, and COS, H_2 and CH_2CCH_2 are generated. In R2, the H···OH bond in H_2O is extended from the original 0.97Å to 1.02Å by the transition state TS1 and is added to the C-S bond of thiophene to form intermediate IM1. Then, H migration in IM1 occurs after overcoming a 46.6 kcal/mol barrier and IM2 is formed. Lastly, IM2 undergoes the closed-loop reaction and forms furan, meanwhile one molecular H_2S is removed. Thermodynamically and dynamically, H_2O (g) attacking C-S bonds of thiophene cannot easily generate COS and H_2S at 1200 K, as the ΔG_p of R1 and R2 are 2.8 kcal/mol and 11.8 kcal/mol, respectively.

Fig. 3 is the energy diagram of 2-methyl thiophene and H_2O (g) forming H_2S (R3) and COS (R4) at 1200 K. In R3 and R4, the formation of their IM1s needs to overcome the higher initial reaction energy barriers of 116.3 kcal/mol and 147.3 kcal/mol, respectively. For R3, IM1 undergoes an closed-loop reaction and intramolecular hydrogen migration and C-S bonds cleavage to form 2-methylfuran and H_2S. The ΔG_p of R3 is 3.9 kcal/mol. IM1 in R4 undergoes two-step H migration and IM3 is generated. Then, C-S, C-C bonds of IM3 are broken and COS, CH_4 and CH_2CCH_2 are generated. R3 are thermodynamically non-spontaneous. Although reaction R4 (ΔG_p= -13.4 kcal/mol) is thermodynamically spontaneous, it needs to overcome a very high energy barrier. Thus, it is also not easy to generate H_2S and COS at 1200 K for H_2O with thiophene and 2-methyl thiophene through R3 and R4.

3.2.2 Desulfurization mechanisms of thiophenes with free radicals (•H and •OH)

Free radicals play a crucial role in coal pyrolysis process[35]. H and OH free radicals generation, stabilization and condensation easily occur during water vapor treatment

196 and coal pyrolysis progress[36,37]. The removal of organic sulfur was found to increase,
197 because the addition of steam results in generating more H free radicals promoting the
198 generation of H_2S[9]. Based on these results, desulfurization reactions of thiophenes
199 with free radicals (•H and •OH) were proposed and investigated under steam
200 atmosphere. The possible desulfurization pathways of thiophene, 2-methyl thiophene
201 and free radicals are considered as follows:



202

203 Fig. 4 shows energy diagrams of thiophene and • H and • OH forming H_2S (R5) and
204 COS (R6) at 1200 K. H and OH radicals are mainly derived from the decomposition
205 of water vapor [36] and coal [37]. For R5, firstly, H radical is adsorbed on the C2 site
206 of thiophene, and the unstable cyclic thiophene radical (R) is formed after overcoming
207 a 1.9 kcal/mol energy barrier. Then, OH radical combines with the C5 site in R with
208 only a 41.7 kcal/mol barrier and IM1 is generated. Subsequently, IM3 is formed by
209 two steps of hydrogen transferring. Lastly, IM3 transforms into H_2S and furan through
210 C-S bond breakage with a low energy barrier of 20.2 kcal/mol. For R6, the energy
211 barrier of transition state from IM1 to IM2 (80.3 kcal/mol) is very high. Then, IM2
212 undergoes H migrations from C3 site to C4 site and IM3 is formed through
213 overcoming an energy barrier of 72.8 kcal/mol. Lastly, COS, H_2 and CH_2CCH_2 are

formed by C-C and C-S bonds cleavage of IM3. As of its high energy barrier, it is also impossible for R6 to occur. Thus, H_2S is the main product during thiophene desulfurization under steam atmosphere. Compared with the reactions of thiophene with H_2O, its desulfurization mechanism should be dominated by radical reactions at high temperatures in water vapor atmosphere. These results can further prove that the hydrogen radicals significantly reduce the energy barrier of thiophene desulfurization reaction. The reason is that • H can damage the aromaticity of thiophene according to the anisotropy of the induced current density (ACID) analysis [15] to form unstable complex cyclic thiophene radical (R).

Fig. 5 lists the energy diagrams of 2-methyl thiophene with • H and • OH forming H_2S (R7) and COS (R8) at 1200 K. For R7 and R8, dynamically, • H firstly combines with C2 or C5 sites of 2-methyl thiophene to form 2-methyl thiophene radical (R) by overcoming only a 8.0 or 3.1 kcal/mol energy barrier, respectively. And this energy barrier is lower than the total reactants energy of 2-methyl thiophene and • H. OH radical then attacks C5 or C2 sites to form a complex IM1 after overcoming the energy barrier of 45.0 or 47.6 kcal/mol, respectively. IM1 in R7 undergoes two-step H migration and IM3 is generated. Then, a closed-loop reaction occurs and a molecule of H_2S is removed through TS4 to form H_2S and 2-methyl furan after overcoming a low energy barrier of 23.8 kcal/mol. For R8, IM1 undergoes similar reaction steps as R6 and generates COS, H_2 and CH_3CHCCH_2. These calculated results show that thiophenes reacting with • H and • OH can generate COS, H_2S and small molecular hydrocarbons. But, COS is unstable compared with H_2S[38], as it can be converted to

H_2S (R9) in steam atmosphere in the reactor[39]. Consistent with some previous experimental conclusions, sulfur-containing gases are mainly H_2S during pyrolysis of thiophenes in water vapor system[3,9]. Therefore, at higher temperatures, thiophenes desulfurization mechanisms are most likely dominated by radical reactions under steam atmosphere.

3.3 Rate constant analysis

In order to investigate the effect of reaction temperatures and H_2O (g) / radicals on desulfurization mechanisms of thiophene and 2-methyl thiophene, the reaction rate constant of each path was calculated between 700K - 1200K by transition state theory[39] (TST) and listed in Table 1. R1, R2 and R3 are thermodynamically unfeasible even at 1200 K, so their reaction rate constants are not considered. As shown in Table 1, R4 is the reaction path of thiophene sulfur and H_2O (g) for forming COS. R5 and R7 are the paths of thiophene and 2-methyl thiophene with free radicals for generating H_2S, respectively. R6 and R8 are the paths of thiophene and 2-methyl thiophene with free radicals to generate COS, respectively. All these rate constants increase with the increasing of the reaction temperatures from 700K and 1200 K. The rate constants rank of generating H_2S and COS is: k[R7] > k[R5] > k[R6]> k[R8]> k[R4] at 1200K. For R5 (R7), the rate constant for generating H_2S is higher about10-10^3 times than that of COS (R6 and R8) at 1200K. This further indicates that the sulfur-containing gases generated by the reaction of thiophenes and free radicals are mainly H_2S. The rate constants of COS formation in R6 and R8 are about 3×10^{10} times higher than that of

R4 at 1200 K. This further proves that ·OH/·H participation is more beneficial for COS formation than H_2O (g) during thiophenes desulfurization.

4. Conclusions

The desulfurization mechanisms of thiophene and 2-methyl thiophene under steam atmosphere have been investigated in detail. The following conclusions can be drawn:

H_2O attacking C-S bond of thiophene and 2-methyl thiophene cannot kinetically and thermodynamically form H_2S and COS even at 1200 K, as their higher reaction energy barriers need to be overcome. The reaction energies of these thiophenes with free radicals can reduce significantly compared with H_2O molecule.

At higher temperature, thiophenes and free radicals can kinetically and thermodynamically react and form H_2S and COS. And H_2S is the main sulfur-containing gases, its rate constant further proves that rate of generating H_2S is faster than COS. Therefore, the most possible mechanisms for the removal of thiophenes are dominated by free radical reaction mechanisms in water vapor atmosphere at high temperatures. This can provide some theoretical basis for the desulfurization mechanisms of sulfurs in coals during pyrolysis.

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Figures

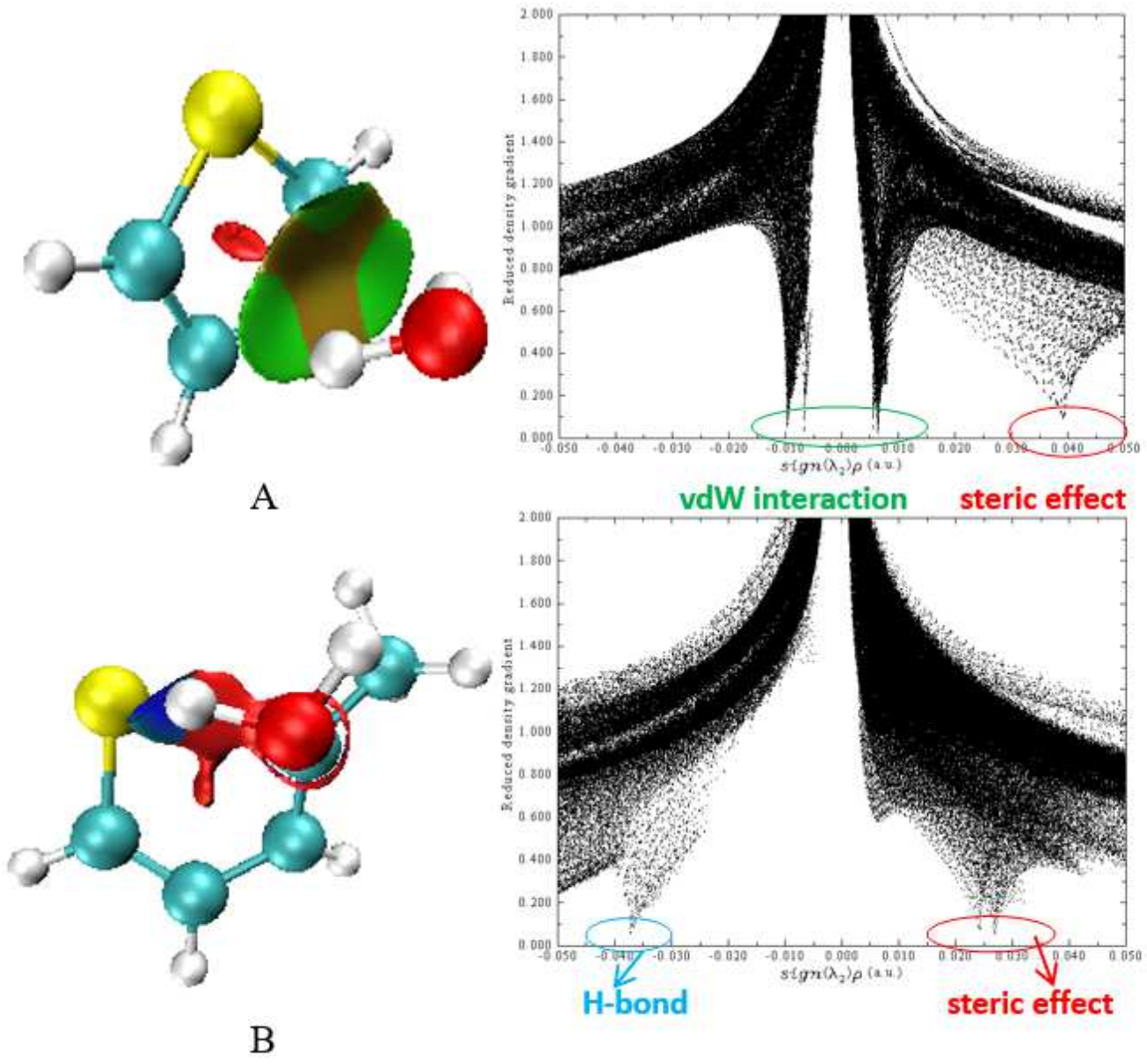

Figure 1

The RDG diagrams of complexes (i.e., complex Aand B) formed by two typical thiophene sulfurs with H2O (complex A is about the complex of thiophene and mono-H2O; complex B is about the complex of mono-H2O and 2-methyl thiophene.)

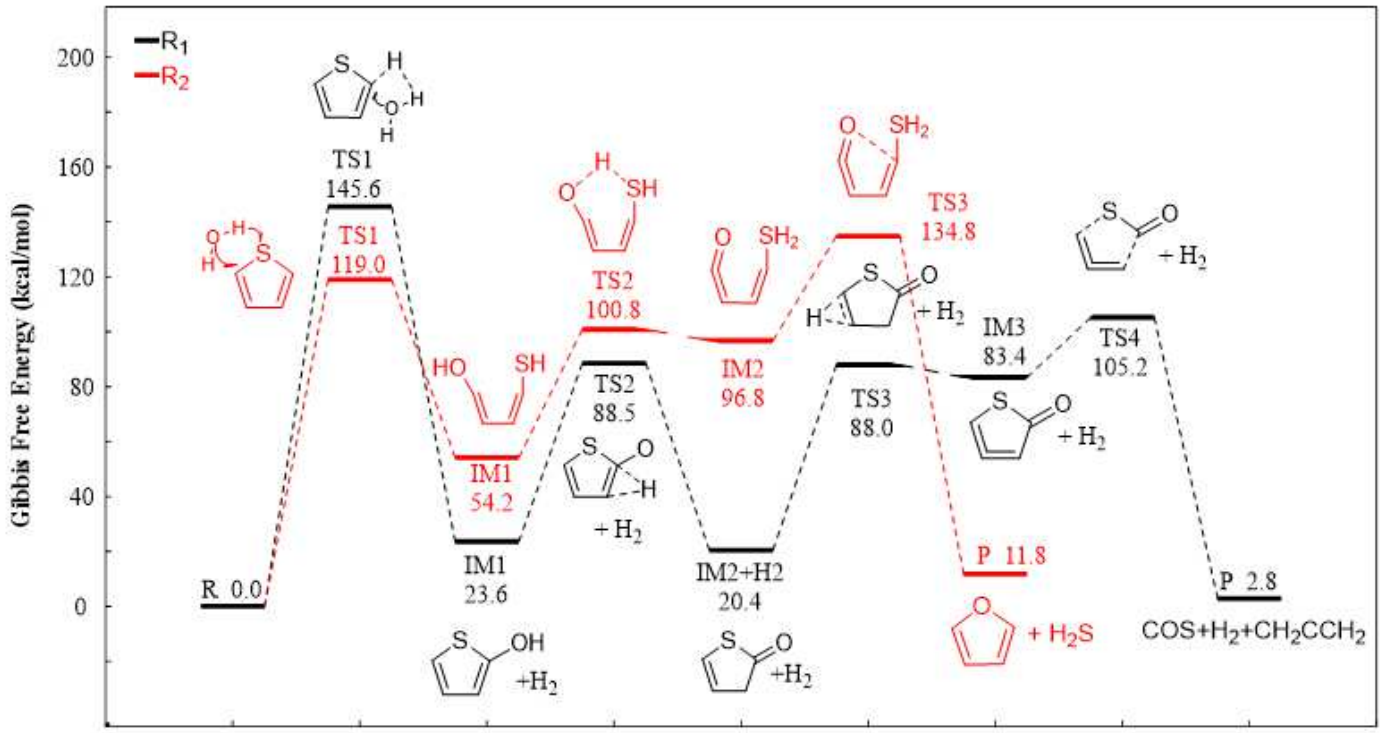

Figure 2

The energy diagram of thiophene and mono-H2O forming COS (R1) and H2S (R2) at 1200K

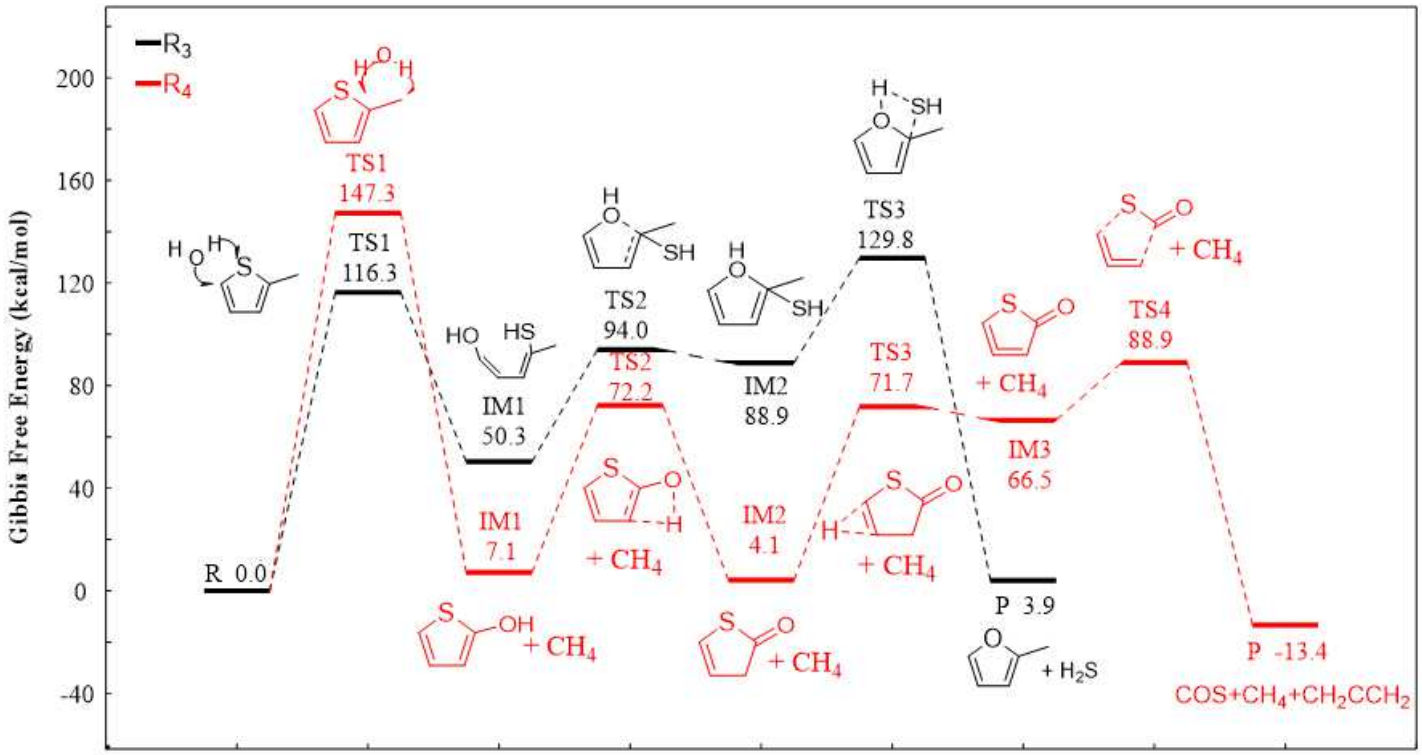

Figure 3

The energy diagram of 2-methyl thiophene and mono-H2O forming H2S (R3) and COS (R4) at 1200K.

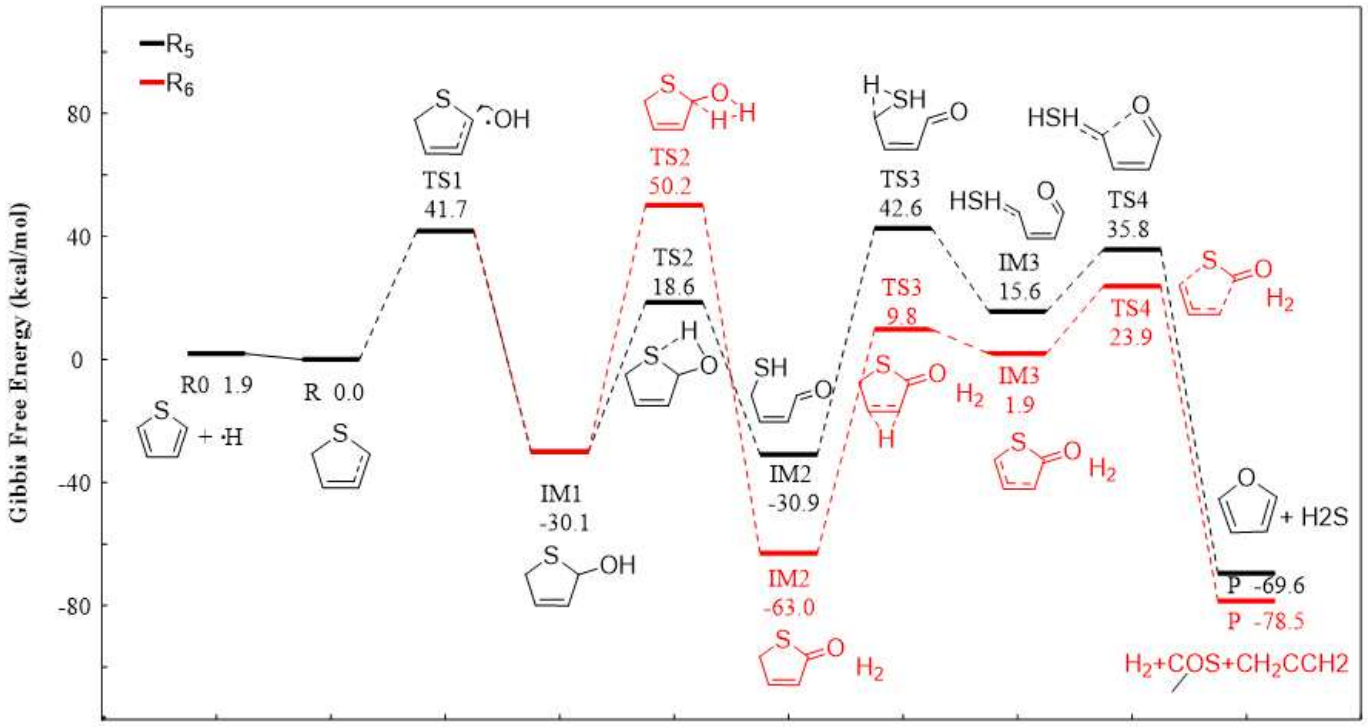

Figure 4

The energy diagram of thiophene and free radicals forming H2S (R5) and COS (R6) at 1200 K

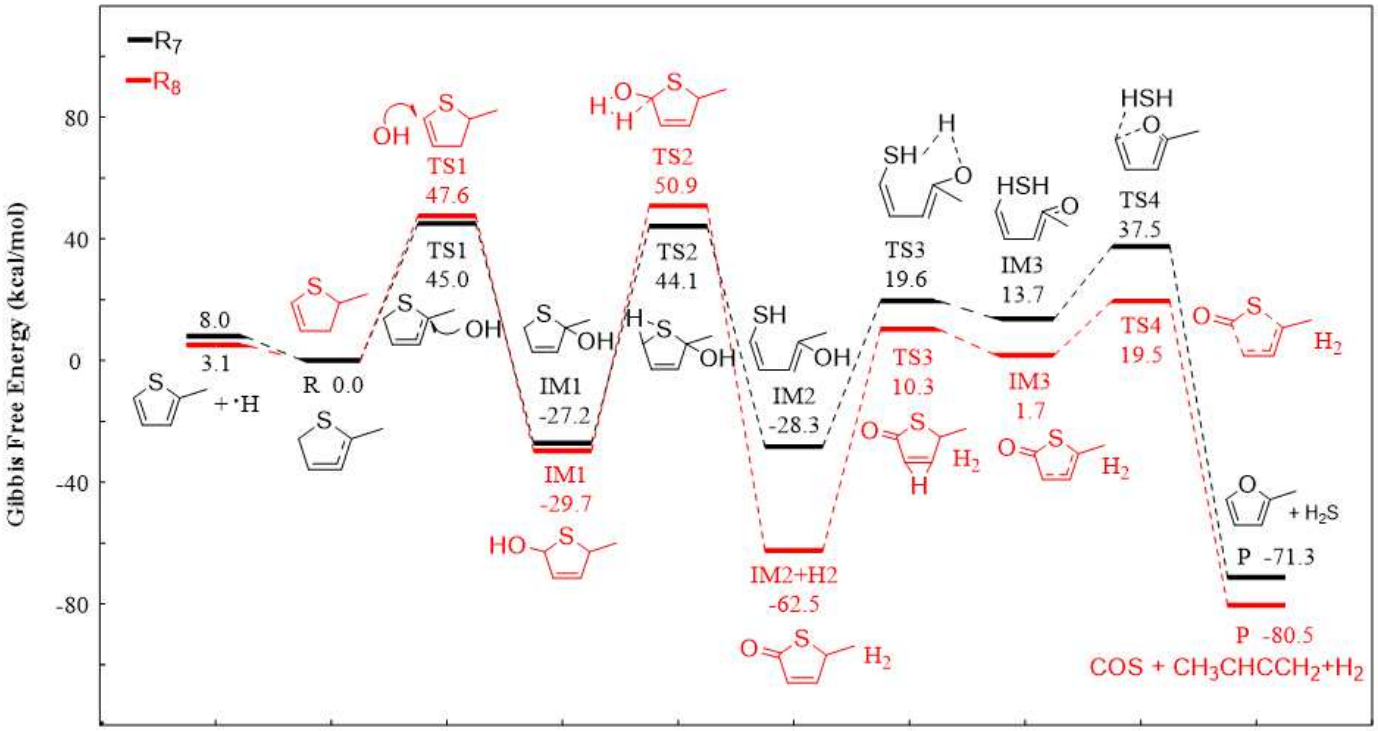

Figure 5

The energy diagram of 2-methyl thiophene and free radicals forming H2S (R7) and COS (R8) at 1200 K