Reaction Mechanism of Aldehyde Groups during Coal Self-Heating

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ABSTRACT: In order to further understand the mechanism of coal self-heating in the initial stage, the aldehyde group was analyzed by using the quantum chemistry methods. The charge distribution, structural parameters, and molecular orbital were analyzed to determine the active sites existing in the structure of aldehyde group. Then, a chemical reaction model including five elementary reaction sequences was established. In elementary reaction E1, the hydrogen of the aldehyde group is captured by hydroxyl to form the aldehyde radical, which provides the reactant and accumulates heat for the subsequent reaction. In elementary reaction E2, the aldehyde radical further reacts to form a carbon-free radical (R) and CO, which is the main source for CO generation during coal spontaneous combustion. In elementary reaction E3, the aldehyde radical is oxidized to a carboxyl radical, providing the reactant for elementary reaction E4, which is directly related to CO2 generation during coal spontaneous combustion. The thermodynamic parameters of the elementary reactions were further analyzed and confirmed by quantum chemistry methods. The results are helpful for further understanding the pathways of CO generation in the initial stage of coal spontaneous combustion, which provides theoretical support for prediction of coal spontaneous combustion.

1. INTRODUCTION

Coal spontaneous combustion is a complicated physical and chemical reaction.1 It usually results in serious personal injuries or death, economic loss, and environmental pollution.2 Many investigators are focusing on the reaction mechanism of coal spontaneous combustion.

It has been proved that the coal spontaneous combustion is essentially the interaction between coal and oxygen at low temperature.3,4 According to previous research studies on coal spontaneous combustion, the reaction process between coal and oxygen includes physisorption, chemisorption, and chemical reaction.5,6 Some investigators have done a lot of study on this complicated reaction process. Clemens et al.8 proposed a reaction model for the oxygen adsorption by coal, which includes 10 reaction sequences. Based on further study, Dlugogorski et al.7 confirmed some reaction sequences in Clement’s model. Previous literature studies have confirmed that the oxidation reactions mainly occur at the active sites of coal during the process of coal spontaneous combustion.7–16 Dou and Zhong17 analyzed the differences in chemical structures and reactivity of two Chinese coals and explained their differences in coal self-heating rate. Zhang et al. found that the distribution of organic sulfur in coal is related to the degree of metamorphism of coal and the interaction of sulfur-containing functional groups.8,9 and oxygen is mainly physisorption between 30 and 80 °C.10 As one of the oxygen-containing functional groups, the aldehyde group has been studied by many scholars. Xu et al.10 inferred that the aldehyde group in the coal structure is one of the main factors for the redox reaction. Tang11 found that the reaction of the aldehyde group generates CO and CO2 in the initial reaction of coal spontaneous combustion. As known, CO is not only one of the important indexes for predicting coal spontaneous combustion but also one of the main disaster-causing gases in coal mine fire period. In this paper, the reaction mechanism of the aldehyde group in coal spontaneous combustion was further studied by the method of quantum chemistry. In summary, the coal self-heating process is actually the reaction process of various groups in coal. As for the coal with a different metamorphism, the main functional groups are aromatic hydrocarbon, aliphatic hydrocarbon, and oxygen-containing functional groups.1 However, the content of different functional groups in different types of coal varies, and the aldehyde group distributes most in lignite and noncaking coal while less in gas coal and anthracite distribution and medium in coke coal.12,13

With the development of quantum chemistry, more and more researchers applied quantum chemistry methods in the field of coal spontaneous combustion.14–27 Quantum chemistry calculation becomes an effective method to study detailed reaction
processes and visualize the microscopic molecular geometry. Some investigators have applied this method to calculate the structural transformation characteristics of the reaction in the spontaneous combustion process of coal.\textsuperscript{24,27} Shi et al.\textsuperscript{24,28} attached the functional group to different numbers of benzene rings. The optimized structural parameters for the same active groups were approximately identical, as well as the charges on the active atoms (carbon and hydrogen), despite the difference in the number of aromatic rings. The same results were also observed for the charges on active atoms and their changes after being oxidized. Therefore, it was concluded that the reactivity of functional groups is not affected by the number of benzene rings in coal. Therefore, it is reasonable to simulate the coal structure using functional groups binding with a single benzene ring. Wang et al.\textsuperscript{29} found that the adsorption amount of methane per unit mass of coal decreased with the increase of the number of stacked layers of aromatic units by means of molecular dynamics simulation. Wang et al.\textsuperscript{30} used the quantum chemistry method to optimize the structure of coal and the CH\textsubscript{4} molecular adsorption-associated system and obtained the geometric configuration of the adsorption equilibrium state. Deng et al.\textsuperscript{31} studied and analyzed the mechanism of interaction of Zn\textsuperscript{2+} and α-thiophenol structure in coal through Gaussian 03. Wang et al.\textsuperscript{32} calculated the kinetic characteristics of cyclic chain reaction in the process of coal oxidation, including 12 reaction pathways, and sequenced its activation energy sequence. These studies supply the possibility of using quantum chemistry to calculate the reaction sequence of aldehyde group during coal self-heating.

In consideration of the current investigations, this paper focuses on the reaction sequences of aldehyde groups during the process of coal self-heating. The results will be helpful for further understanding the mechanism of coal spontaneous combustion.

2. COMPUTATIONAL DETAILS

2.1. Establishment of Molecular Model. Shi et al.\textsuperscript{24} calculated the structural parameters and Mulliken atomic charges in coal structure and found out that the reactivity of functional groups is not affected by the number of aromatic rings in coal. Therefore, it is reasonable to simulate the coal structure using functional groups binding with a single benzene ring. Combining with previous studies on functional groups of coal molecules,\textsuperscript{33,52} functional groups were connected with a single benzene ring to simulate the aldehyde group reaction during the coal self-heating process in this paper. What’s more, according to our early simulations, the structural characteristics, charge distribution, active sites, vibration characteristics, and the orbital parameters were described. The aldehyde group on the side chain was found to be more reactive and preferentially involved in the reaction. To keep the calculation simple and the reaction complete, phenyacetaldehyde was selected as the simulation object.

2.2. Quantum Chemistry Method and Methodology. The calculations in this paper were carried out with Gaussian 09 and Gauss View. For getting more accurate data, all calculations in this paper were conducted in the framework of density functional theory (DFT) utilizing the Becke’s three-parameter exchange function (B3LYP) at the 6-311G* basis set level. Gaussian job type and Opt + Freq were used to optimize the geometry and calculate the energy of the molecule. Orbital occupancies and charge delocalization were analyzed with the natural bond orbital analysis. In addition, the diagrams of molecular orbital (MO) surfaces were showed on the MO editor. During the process of obtaining the structure of transition states (TSs), which was verified by a certain imaginary frequency, the QST2 protocol was adopted in this paper. The intrinsic reaction coordinate method is another way to verify whether the TS is correct. In addition, the other parameters were set as default. In addition, it is important to emphasize that the functional groups whose spin multiplicity is not 1 are calculated under open-shell conditions.

3. RESULTS AND DISCUSSION

3.1. Quantum Chemical Analysis of the Aldehyde Groups. In order to characterize the reaction more precisely, this section performed a detailed analysis of the side chain and bridge bond of phenyacetaldehyde. Then, the structural characteristics, charge distribution, active sites, vibration characteristics, and the orbital parameters were described. First, the structure of phenyacetaldehyde was optimized and the functional group energy values were calculated. The results are shown in Figure 1.

According to the optimization results listed in Table 1, the final energy value is −384.774 hartree after operation.

Based on the parameters in Table 2, C7, C8, and O9 carry more charge. The functional group structure unit is mainly composed of the aldehyde group. In order to further study the distribution of functional charge, C8, O9, and H17 were taken as examples for the research studies on their orbital components. The results are presented in Table 3.
According to the orbital component analysis in Table 3, the electrons of the C–O bond, where the hydrogen atoms are attached, are clearly inclined to oxygen atoms. As a result, the oxygen atoms become electrically rich and the carbon atoms become electrically deficient because of the action of double bonds, which is consistent with charge analysis. It indicates that C8 and O9 are the more reactive atoms in the structure.

In order to determine the specific reaction site, C8, O9, and H17 were taken as examples for the analysis on their natural atomic orbital (NAO). The calculation results are shown in Table 4.

As shown in Table 4, the minimum energy of the carbon atom appears in the 2P orbital, which is ~0.04953 eV. In addition, the minimum energy of the hydrogen atom appears in the 1S orbital. Therefore, the bonding orbital of the two atoms is distributed on 2P and 1S, and the bonding type is σ bond.

For further study on the electron transfer in the reaction, quantum chemical frontier orbitals were analyzed. The frontier MOs include the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital. The partial MO diagrams are shown in Figure 2.

According to the MO structure obtained above, the frontier orbitals of Ar–CH2–CHO are the π bond and π* bond on the benzene ring. However, the next highest occupied MO following HOMO is the σ-p bonding orbital between C8 and the H17. Therefore, it can be thought of that, in the case where the π bond of the benzene ring is not easy to react, C8 and H17 will be the next reaction centers.

The molecule reactivity is mainly reflected in the frontier MO and the charge distribution. Therefore, according to the above analysis, the reaction of the aldehyde structural units is mainly concentrated in the C–H bonding orbital.

3.2. Oxidation Process of the Aldehyde Groups. Based on the analysis in the previous section, the reaction equations of the aldehyde groups in the process of coal spontaneous combustion were suggested as follows.

There are many free radicals such as hydroxyl radicals during coal heating. These free radicals are formed in one process and then participate in other reactions. This paper focused on the reactions related to aldehyde groups. According to the property of hydrogen on the aldehyde group and the dissociation energy of hydrocarbon bond, the reaction ability of hydrogen capture is not easy to react, C8 and H17 will be the next reaction centers.

The molecule reactivity is mainly reflected in the frontier MO and the charge distribution. Therefore, according to the above analysis, the reaction of the aldehyde structural units is mainly concentrated in the C–H bonding orbital.
reaction E5 is difficult to occur in the initial stage and the transition stage of coal oxidation at low temperatures.

3.2.1. Hydrogen Is Captured by the Hydroxyl Groups. The elementary reaction E1 provides reactants for the elementary reactions E2 and E3, which is the key step for the generation of CO and CO2 during coal spontaneous combustion. Therefore, it is necessary to study this elementary reaction.

3.2.1.1. Geometry Optimization. DFT was utilized to find the TS at the level of B3LYP/6-311G* by QST2. In addition, the geometry of reactants, products, and transition molecules was optimized. Their frequencies were calculated. Because the ground state of an oxygen molecule is a triple state, the spin of all reactions is a triple state. The optimized reactant, TS, and product configuration are shown in Figure 3.

During the process of the elementary reaction, the conversion process from the reactant to the TS to the product is mainly reflected in the change of structure, and the main structural change is shown in Table 5.

According to the changes of the key structural parameters in Table 5, it can be seen that the C8−H18 bond in the aldehyde group gradually elongates. In contrast, the length of the O10−

H18 bond is decreasing. Hydrogen atoms are finally captured by hydroxyl to form water molecules.

3.2.1.2. IRC Response Path Analysis. In the calculation, the saddle point was the center and 10 points before and after the saddle point were obtained. Changes of potential energy during the intrinsic reaction coordinate (IRC) calculation process are shown in Figure 4. The results show that the reaction mechanism is correct and feasible. In addition, it indicates that this process overcomes an energy barrier during the reaction process.

Figure 4. Potential energy variation during the IRC calculation process of reaction E1.

3.2.1.3. Thermodynamic Quantities and Reaction Activation Energy Analysis. In order to analyze the conditions and reaction rate, the thermodynamic quantities of reactants, TSs, and products were analyzed. Their thermodynamic data are shown in Table 6.

As shown in Table 6, the activation energy of the reaction is 28.88 kJ/mol, and the enthalpy of the reaction is −52.51 kJ/mol. The thermodynamic calculation results show that reaction E1 is exothermic and the activation energy is relatively low. Therefore, reaction E1 can react spontaneously at a normal pressure and...
3.2.2. CO Detaches from the Aldehyde Groups. The elementary reaction E2 is an important generation pathway of CO during coal spontaneous combustion. CO is not only one of the important indexes for predicting coal spontaneous combustion but also one of the main disaster-causing gases in coal mine fire period. The elementary reaction E2 was analyzed in detail.

3.2.2.1. Geometry Optimization. According to the method described above, the TS is obtained, and then geometrical optimization of reactants, TSs, and products was carried out. In addition, the main structural changes were calculated. The results are shown in Figure 6 and Table 7.

According to the changes of key structural parameters in Table 7, it can be concluded that the C7–C8 bond group gradually elongates. In contrast, the length of the C8–O9 bond is decreasing. The C–O bond eventually breaks off the aldehyde group to form CO, which is an important reason for the CO production at the initial stage of coal spontaneous combustion.

3.2.2.2. IRC Response Path Analysis. As mentioned above, the IRC path diagram of elementary reaction E2 is shown in Figure 7.

The results show that the reaction mechanism proposed above is correct and feasible. In addition, it indicates that this reaction process overcomes an energy barrier during the reaction process.

3.2.2.3. Thermodynamic Quantities and Reaction Activation Energy Analysis. Based on calculation, the energy, thermodynamic parameters, and activation energy in the reaction process were obtained, as shown in Table 8.

As shown in Table 8, the activation energy of reaction E2 is 42.00 kJ/mol, which is relatively small, and the enthalpy of the reaction becomes 18.38 kJ/mol. It indicates that reaction E2 is endothermic. However, the change of enthalpy is small. Therefore, it still can be thought that it reacts spontaneously at room temperature and pressure, which is consistent with the initial formation temperature of CO during coal spontaneous combustion. The schematic diagram of reaction E2 is presented in Figure 8.

3.2.3. Combination between the Aldehyde Radical and Oxygen. The elementary reaction E3 is a combination of free radical and oxygen. There is no bond rupture during this process.
reaction, which can also occur spontaneously and easily. It has no TS, which means it can occur without activation energy. According to the foregoing, the elementary reaction E3 was also analyzed by the method of quantum chemistry. The results are shown in Table 9 and Figure 9.

According to the above data, the elementary reaction E3 is an exothermic reaction with a change in enthalpy of 55.14 kJ/mol. There is no TS during the process of reaction, which means reaction E3 does not have to cross the energy barrier. Therefore, the elementary reaction E3 can also occur spontaneously at room temperature and pressure. The schematic diagram of reaction E3 is presented in Figure 10.

3.2.4. Decarboxylation Reaction. The free radical produced by the elementary reaction E3 is not stable, and the two C–O bonds gradually break away from the benzene ring to form CO2, which is the process of elementary reaction E4. The elementary reaction E4 was analyzed by quantum chemistry method, and the results are shown in Table 10 and Figure 11.

Based on the above data, the elementary reaction E4 is an endothermic reaction with a change in enthalpy of 44.63 kJ/mol. In addition, the activation energy of the reaction is 60.39 kJ/mol. Therefore, the reaction cannot be spontaneous at room temperature and pressure. In addition, the reaction is directly related to the generation of CO2 during coal spontaneous combustion. In view of the above, the generation of CO2 needs to accumulate certain heat in the process of coal spontaneous combustion, which is consistent with the reality. The schematic diagram of reaction E4 is presented in Figure 12.

3.3. Reaction Model of Aliphatic Aldehyde Groups during Coal Spontaneous Combustion. Based on the above analysis, the aldehyde groups will take part in different reaction sequences in the development of coal spontaneous combustion. The thermal properties of the elementary E1 reactions E1–E4 are shown in Table 11.

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**Table 8. Thermodynamic Parameters of the Reactant, TS, and Product in Reaction E2**

| type     | enthalpy $H$/hartree | thermal energy $E$/hartree | heat release $\Delta H$/kJ/mol | activation energy $E_a$/kJ/mol |
|----------|----------------------|---------------------------|-------------------------------|-------------------------------|
| reactant | $-383.992$           | $-383.993$                | 18.38                         | 42.00                         |
| TS       | $-383.976$           | $-383.977$                |                               |                               |
| product  | $-383.985$           | $-383.986$                |                               |                               |

**Table 9. Thermodynamic Parameters of the Reactant and Product in Reaction E3**

| type     | enthalpy $H$/hartree | thermal energy $E$/hartree | heat release $\Delta H$/kJ/mol |
|----------|----------------------|---------------------------|--------------------------------|
| reactant | $-534.311$           | $-534.312$                | $-55.14$                       |
| product  | $-534.333$           | $-534.333$                |                                |

**Figure 8. Schematic diagram of reaction E2.**

**Figure 9. Optimized structures during reaction E3: (a) reactant and (b) product.**

**Figure 10. Schematic diagram of reaction E3.**

**Table 10. Thermodynamic Parameters of the Reactant, TS, and Product in Reaction E4**

| type     | enthalpy $H$/hartree | thermal energy $E$/hartree | heat release $\Delta H$/kJ/mol | activation energy $E_a$/kJ/mol |
|----------|----------------------|---------------------------|-------------------------------|-------------------------------|
| reactant | $-459.342$           | $-459.343$                | 44.63                         | 60.39                         |
| TS       | $-459.320$           | $-459.320$                |                               |                               |
| product  | $-459.325$           | $-459.325$                |                               |                               |

**Figure 11. Optimized structures during reaction E4: (a) reactant and (b) product.**

**Figure 12. Schematic diagram of reaction E4.**

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In the process of elementary reaction E1, the hydrogen on the aldehyde group is captured by the hydroxyl (–OH), forming the
aldehyde radical that provides the reactant for elementary reactions E2 and E3. In addition, the elementary reaction is an exothermic reaction, which accumulates heat for subsequent reactions. Therefore, the basic reaction E1 is a critical step in the initial stage of coal spontaneous combustion. It can be seen from the activation energy and reaction enthalpy change of the elementary reaction E2 that the reaction is in the critical state of spontaneous reaction at normal temperature and pressure, which is of great significance to study the generation of CO in the initial period of coal spontaneous combustion. The aldehyde radical is oxidized by oxygen to form the carboxyl radical, which further reacts to form CO2. The basic reaction E4 is directly related to the generation of CO2 during coal spontaneous combustion. In addition, it can be seen from the thermodynamic parameters that the generation of CO2 needs to accumulate certain heat in the process of coal spontaneous combustion. The main reaction pathways of aldehyde and its relationship during the coal spontaneous combustion process are shown in Figure 13.

### 4. CONCLUSIONS

(1) The chemical reaction model of the aldehyde group reaction has been established based on the quantum chemistry method. According to the established model, the hydrogen of the aldehyde group is captured by the hydroxyl to form the aldehyde radical. The aldehyde radical further reacts to form the carbon-free radical (R·) or is oxidized to the carboxyl radical, and the carboxyl radical reacts to form the carbon-free radical (R·). Active sites are constantly being created to participate in new reactions. It provided a theoretical model for studying the reaction of aldehyde group during coal self-heating.

(2) The elementary reactions E1 and the elementary reaction E2 were studied. In the process of dehydrogenation by the hydroxyl, the resulting aldehyde radicals are involved in the elementary reaction E2, which is an important source of CO during coal spontaneous combustion. In addition, the elementary reaction E1 also accumulates heat for subsequent reactions. The spontaneous reaction E2 at normal temperature and pressure proves why CO can be detected at the initial stage of coal spontaneous combustion.
combustion. It provides theoretical support for the prediction of coal spontaneous combustion disaster.

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**Notes**

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