Quantum Chemistry Calculation Study on Chain Reaction Mechanisms and Thermodynamic Characteristics of Coal Spontaneous Combustion at Low Temperatures

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ABSTRACT: The coal spontaneous combustion phenomenon seriously affects the safety production of coal mines. Aiming at the problem of complex coal molecular structure and incomplete reaction sequences at present, the mechanisms and thermodynamic parameters of coal spontaneous combustion chain reactions were explored by combining experimental detections and molecular simulations. First, the active groups on the surface of coal were obtained by Fourier transform infrared spectroscopy (FTIR), mainly including methyl (−CH₃), methylene (−CH₂), methyne (−CH), phenolic hydroxyl (−ArOH), alcohol hydroxyl (−ROH), carboxyl (−COOH), aldehyde (−CHO), and ether (−O−), and the coal molecular models containing functional groups and radicals were established. According to the charge density, electrostatic potential, and frontier orbital theories, the active sites and active bonds were obtained, and a series of reactions were given. The thermodynamic and structural parameters of each reaction were explored. In the chain initiation reaction stage, O₂ chemisorption and the self-reaction of radicals play a leading role. In this stage, heat gradually accumulates and various radicals begin to generate, where the intramolecular hydrogen transfer reaction of a peroxide radical (−O−O−) can produce the key hydroxyl radical (−OH). In the chain propagation reaction stage, O₂ and −O− continuously consume active sites to accelerate the reaction sequences and increase the temperature of coal, and index gases such as CO and CO₂ generate, causing the chain cycle reactions to gradually form. The chain termination reaction stage is the formation of stable compounds such as ethers, esters, and quinones, which can inhibit the development of chain reactions. The results can further explain the reaction mechanism of coal spontaneous combustion and provide references for the development and utilization of chemical inhibitors.

1. INTRODUCTION
Coal is the important basic energy all over the world.¹⁻³ It is well known that coal spontaneous combustion is a major hazard in the mining industry, and serious coal spontaneous combustion can burn mining machines and even cause major safety accidents.⁴⁻⁷ The essence of coal spontaneous combustion is chemical reactions. Therefore, it is necessary to conduct scientific research based on the inherent mechanisms of coal chemical reactions. Thermodynamic analysis of these chemical reactions can be used to obtain their activation energy and other parameters, which is of great significance to understand the mechanism of coal spontaneous combustion, and is the hinge to the coal mine safety production.⁸⁻¹²

The chemical reaction process of spontaneous combustion of coal is very complicated. For quite some time, domestic and foreign scholars have done a lot of research on its internal mechanism, where the coal−oxygen interaction hypothesis has been widely recognized.¹³,¹⁴ The theory holds that coal oxidation at low temperatures is due to the interaction of coal with O₂ in the air (physical adsorption, chemical adsorption, and chemical reaction). When the heat accumulates to the point that it cannot be released in time, the coal will combust spontaneously.¹⁵⁻¹⁷ Under certain conditions, only some groups with active properties can undergo chemisorption with O₂ and further react, which are called active groups or functional groups. Wang,¹⁸ Xu et al.,¹⁹ and Ge et al.²⁰ studied the functional groups on the coal surface by chemical extraction, FTIR, nuclear magnetic resonance (NMR), and automatic imaging. The conclusions made it clear that coal molecules are rich in active groups, and the active groups are most widely distributed in low rank coals. Because the coal molecules contain less S and N, aliphatic and oxygen-containing functional groups play an important role in the coal spontaneous combustion process. Aliphatic functional groups mainly include −CH₁, −CH₂, and −CH₃, while oxygen-containing functional groups include...
Not only do the original functional groups have a significant impact on the process of coal spontaneous combustion, but also a large number of radicals can be produced by the covalent bonds breaking in coal macromolecules during the process of coal fragmentation and the reactions of the original functional groups. They can also participate in the oxidation reactions at low temperatures as active groups and have stronger reactivity, mainly including $-\cdot C$, $-\cdot CH$, $-\cdot CH_2$, $-O$, $-\cdot COO$, $-\cdot CO$, etc.

Many scholars have explored the reaction sequences of coal spontaneous combustion at low temperatures on the basis of studying the active sites. Qi et al. brought forward the reaction processes of aliphatic hydrocarbons, carboxyls, hydroxyls, and sulfur-containing functional groups, which deeply expounded the micromechanism of coal spontaneous combustion. Zhu et al. explored the pathways of the oxidation reactions when the aldehyde and hydroxyl in coal molecules are located at different sites by applying the quantum chemical calculation method. Clemens et al. believed that $-\cdot C$ and $-\cdot OH$ are the key groups in the coal spontaneous combustion process and proposed the chemical chain reaction sequences. Deng explored the generation mechanisms of $H_2O$, $CH_4$, $CO$, $CO_2$, and other gas products during the process of coal spontaneous combustion by combining experiments and numerical simulations and put forward the risk index of coal spontaneous combustion to judge the spontaneous combustion tendency of coal. Wang et al. put forward the reaction sequences during low-temperature oxidation of coal and successfully integrated the conclusions into the cognition of coal spontaneous combustion and the research and development of chemical inhibitors.

Although many studies on low-temperature oxidation of coal have been carried out, the current research studies did not consider the electronic transition and distribution characteristics of frontier orbitals, which led to the inaccurate exploration of the active bonds of active groups and the deviation of the proposed chemical reaction pathways. Meanwhile, incomplete analyses resulted in poor continuity of the reaction sequences. The combination of experimental tests and quantum chemical simulation calculations was less, and the emphasis of experimental research studies led to the finding that although the temperature and concentration of key products such as index gases can be measured, the formation mechanisms were not clear. In this paper, the active sites in coal molecules were obtained by FTIR, and the coal molecular model was reconstructed to ensure the close combination of experiment and simulation. The reaction characteristics of the active sites were analyzed by the quantum chemistry calculation method.
from the aspects of ESP, charge density, and molecular frontier orbital. The proposed reaction sequences were more accurate and complete, the formation mechanisms of index gases were more scientific and clearer, and the calculations of reaction thermodynamic parameters were more accurate.

2. RESULTS AND DISCUSSION

2.1. Analyses of Coal Molecular Active Groups. Taking Danhou lignite raw coal as the sample, FTIR was carried out under normal temperature and pressure. The detection spectrum and its fitting curves are shown in Figure 1.

Figure 1a shows the original data obtained from the experiment. According to the fitting results of FTIR, the absorption band of 3700–3100 cm\(^{-1}\) is mainly caused by −OH stretching vibration, as shown in Figure 1b. The absorption band of 3000–2800 cm\(^{-1}\) is mainly caused by the stretching vibration of aliphatic −H bonds, as shown in Figure 1c. The obtained four fitting peaks are attributed to asymmetric methyl stretching (2956.429 cm\(^{-1}\)), asymmetric methylene stretching (2921.22 cm\(^{-1}\)), aliphatic C−H stretching (2891.916 cm\(^{-1}\)), and symmetric methylene stretching (2856.349 cm\(^{-1}\)). Among them, the order of absorption peaks areas is 2921.22 cm\(^{-1}\) > 2856.349 cm\(^{-1}\) > 2891.916 cm\(^{-1}\) > 2956.429 cm\(^{-1}\), that is, the number of −CH\(_2\) is significantly higher than those of −CH and −CH\(_3\), indicating that the aliphatic side-chain structures are mostly long chains.

The absorption band of 1800–1000 cm\(^{-1}\) corresponds to oxygen-containing functional groups (such as −ROH, −ArOH, −COOH, and −CHO), as shown in Figure 1d. Eighteen fitting peaks were obtained after analysis, where the peak at 1724.976 cm\(^{-1}\) corresponds to the C==O bond stretching vibration of −COOH whose vibration intensity is weak, the peak at 1655.995 cm\(^{-1}\) corresponds to the vibration of −CHO, the peaks at 1616.855 and 1597.832 cm\(^{-1}\) are the stretching vibrations of C==C bonds in aromatic or fused rings, and the peaks ranging from 1171.264 to 1246.042 cm\(^{-1}\) correspond to the C−O bond stretching vibrations of −ArOH, −ROH, −O−, and −C==O, respectively, where the vibration intensities at 1171.264 and 1246.042 cm\(^{-1}\) are relatively large. The results show that the peak fitted results are in good agreement with the original spectra, which proves the feasibility of the method.

2.2. Active Sites and Active Bonds of Coal Molecules.

2.2.1. ESP and Reactivity of Active Sites. During a chemical reaction, the most vulnerable position in the molecule is called the active site, mainly located in the functional groups and radicals. The functional groups in Danhou lignite have been identified by FTIR, including −CH, −CH\(_2\), −CH\(_3\), −ROH, −ArOH, −COOH, −CHO, and −O−. The ESP isosurface map are shown in Figure 2.

Combined with the charge density of each atom in the coal molecule, the ESP isosurface map can be used to explore the positions that are prone to nucleophilic and electrophilic reactions. This method was applied to calculate the charge density and reaction activity of each atom in the coal molecular model, and the known active sites were modified. After geometric optimization, the coal molecular configuration and ESP isosurface map are shown in Figure 3.

Figure 2. Simplified plane model of a coal molecule.
the existence of the $\pi-\pi^*$ conjugation effect on the benzene ring, which do not easily react. The atoms on the side chains do not have the above restrictions; they have stronger reaction characteristics than those on the benzene ring. For $-\text{CH}, -\text{CH}_2,$ and $-\text{CH}_3,$ the second largest electron clouds are located on their C–H bonds, indicating that C–H bonds are the active bonds, which are easy to break to form aliphatic radicals. The second largest electron clouds of $-\text{ROH}$ and $-\text{ArOH}$ are

### Table 1. Charge Density Distributions of Atoms

| category | $-\text{CH}$ | $-\text{CH}_2$ | $-\text{CH}_3$ | $-\text{CHO}$ |
|----------|--------------|----------------|----------------|---------------|
| atom     | C25          | H45            | C24            | H44           |
| charge   | $-0.244$     | 0.249          | $-0.476$       | 0.237         |
| atom     | O23          | H42            | O11            | H32           |
| charge   | $-0.756$     | 0.482          | $-0.699$       | 0.503         |

Figure 3. ESP isosurface map of a coal molecule.

Figure 4. Electron cloud distributions on the HOMO of coal molecules with functional groups. (a) Ar–CH(–CH$_3$)–CH$_3$; (b) Ar–CH$_2$–CH$_3$; (c) Ar–CH$_3$; (d) Ar–CH$_2$–OH; (e) Ar–OH; (f) Ar–CH$_2$–CHO; (g) Ar–CH$_2$–COOH.

Table 1. Charge Density Distributions of Atoms

| atom     | $-\text{ROH}$ | $-\text{ArOH}$ | $-\text{COOH}$ | $-\text{O}$ |
|----------|----------------|----------------|----------------|-------------|
| charge   | $-0.536$       | 0.150          | $-0.536$       | 0.535       |
located on O\textendash}H, which are the active bonds. The second electron cloud of \textendash}CHO is located on C8\textendash}H17, which is its active bond. The second largest electron cloud of \textendash}COOH is located on C8\textendash}O9, but C8 is hybridized with O9 to form a \(\sigma\) bond by sp2 type, and the unhybridized p orbital forms a \(\pi\) bond with the p orbital of the O9 atom. Due to the conjugation effect of the C\textendash}O bond, its chemical properties are very stable; the active bond is the third electron cloud, that is, the O10\textendash}H19 bond.

Due to the limitation of the existing technology, the experimental test can only get the total concentration of radicals instead of the distinction of their species effectively. Therefore, based on previous studies, small coal molecular models containing radicals were established, mainly including \textendash}C, \textendash}\cdot \textendash}CH, \textendash}\cdot \textendash}CH2, \textendash}\cdot \textendash}RO, \textendash}\cdot \textendash}ArO, \textendash}\cdot \textendash}CO, \textendash}\cdot \textendash}COO, and \textendash}O\textendash}O. The electron clouds on the bonding orbitals are shown in Figure 5.

As shown in Figure 5, the largest electron clouds on \(\alpha\) single electron orbitals of coal molecules with radicals are located on the benzene rings. The second largest electron clouds of the \textendash}C, \textendash}CH, and \textendash}CH2 are all located on the C atoms without H atoms, which are the active bonds of the aliphatic radicals. The second largest electron cloud of the \textendash}RO is located on C7\textendash}H14(C7\textendash}H15) near the benzene ring, which is the active bond. The \textendash}ArO is not stable, and the second electron cloud is located on the C\textendash}H bond of the para position due to the electron transfer to form a ketone group, which is the active bond. The second largest electron clouds of \textendash}CO and \textendash}COO are located on C7\textendash}C8 bonds, which are the active bonds. The second largest electron clouds of the two peroxide radicals are located on the bonds of the outermost O atoms in the side chains.

2.3. IRC Analyses and Thermodynamic Parameter Calculations. The reactions between functional groups, radicals, and O2 constitute and promote the reaction sequence of coal spontaneous combustion together,35 and the reaction process can be deduced based on the coal molecular reactivity sites obtained in Section 3.2. The elementary reactions of coal spontaneous combustion can be divided into (1) the reactions between functional groups and O2, (2) the reactions between functional groups and free \(\cdot\)OH, (3) the reactions between functional groups and radicals, (4) the adsorption reactions between radicals and O2, and (5) the self-reactions between functional radicals. According to the above classifications, the microreaction processes of various elementary reactions are discussed.

2.3.1. Elementary Reactions between Functional Groups and O2. 2.3.1.1. Elementary Reactions between Aliphatic Functional Groups and O2. The elementary reactions between the aliphatic functional groups and O2 can be summarized as O2 capturing the H atom of the C\textendash}H bonds to generate aliphatic radicals and \(\cdot\)OOH, while the \(\cdot\)OOH is not stable. In the subsequent reactions, the O\textendash}O bond of \(\cdot\)OOH is easy to break to form free \(\cdot\)OH, which can continue to react next. Considering the properties of O2 adsorbed by coal small molecules, the reaction sequences of \(\cdot\)CH, \(\cdot\)CH2, and \(\cdot\)CH3 with O2 are proposed as shown in reactions 1\textendash}3.
Taking −CH as an example and Ar−CH−CH₃(−CH₃) as the model compound, the mechanism of the reaction between −CH and O₂ was calculated by quantum chemical theory. The structural parameters and energy changes in the reaction process are shown in Figure 6.

By comparing the structural characteristics of the reactant, transition state, and product, it can be seen that the C7−H15 breaks, and H15 moves toward O₂ along the vibration direction, showing that H15 has been divorced from the bonding effect of C7. In comparison with the transition state structure, the product’s O22−H15 further shortens, whereas the O22−O23 spreads step by step. This change suggests that the O22−O23 in ·OOH is likely to split in subsequent reactions to...

Figure 6. IRC calculation of reaction 1.

Figure 7. IRC calculation of reaction 4.

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In addition, the hybridization mode of C7 also changed, that is, sp3 hybridization changed to sp2 hybridization, and the side chain twists and changes from the original three-dimensional configuration to the planar configuration in this process. The other product is $-\text{C}_2$, whose chemical property is very active and will continue to take part in the subsequent chain reaction.

According to the calculation, the $\Delta H$ is 96.60 kJ/mol and the $\Delta E$ is 106.68 kJ/mol. The results show that the energy required for the reaction is high and it does not easily occur in the initial stage of coal spontaneous combustion at low temperatures. The reaction has great heat absorption, and although it cannot enhance the self-heating of coal, it can generate key reactive groups, which is an important reaction pathway in the process of coal spontaneous combustion.

### 2.3.1.2. Elementary Reactions between Oxygen-Containing Functional Groups and O$_2$

The oxygen-containing functional groups of coal molecules that can react with O$_2$ at low temperatures are mainly $-\text{CHO}$, $-\text{COOH}$, $-\text{ROH}$, and $-\text{ArOH}$. Similar to the reaction mechanism between aliphatic functional groups and O$_2$, the H atoms at the active sites in the oxygen-containing functional groups can also be captured by O$_2$ to generate oxygen-containing radicals and $\cdot\text{OH}$, and the reaction sequences are shown in reactions 4–7.

Taking $-\text{CHO}$ as an example and Ar$-\text{CH}_2-\text{CHO}$ as the model compound, the mechanism of the reaction between $-\text{CHO}$ and O$_2$ was calculated by quantum chemical theory. The structural parameters and energy changes in the reaction process are shown in Figure 7.

It is found that the mechanism of this reaction is similar to that of reaction 3, which is the hydrogen abstraction reaction of O$_2$. Due to space limitation, the specific details will not be repeated. However, unlike reaction 3, the other product of this reaction is $-\text{CO}$, which can be used as a new active center for chemical O$_2$ absorption and dealdeldehyde reaction.

The calculated results show that the $\Delta H$ of the reaction is 136.87 kJ/mol and the $\Delta E$ is 149.53 kJ/mol. The results indicate that the activation energy required for the reaction is very high, and the reaction will not occur before the reaction accumulates a certain amount of heat, which generally occurs in the middle stage of coal spontaneous combustion. The heat absorption of the reaction is very large and has obvious thermal effects.

### 2.3.2. Elementary Reactions between Functional Groups and Free $\cdot\text{OH}$

#### 2.3.2.1. Elementary Reactions between Aliphatic Groups and Free $\cdot\text{OH}$

The $\cdot\text{OH}$ is very active in chemical properties, which can capture the H in the C–H to generate aliphatic radicals and H$_2$O. Based on these, the reaction sequences between $-\text{CH}_2$, $-\text{CH}_2$, $-\text{CH}_3$, and $\cdot\text{OH}$ are shown in reactions 8–10.

Taking $-\text{CH}_3$ as an example and Ar$-\text{CH}_2-\text{CH}_3$ as the model compound, the mechanism of the reaction between $-\text{CH}_3$ and $\cdot\text{OH}$ was calculated by quantum chemical theory. The structural parameters and energy changes are shown in Figure 8.

In this reaction, the bond of C8$-\text{H}16$ breaks progressively, increasing from 1.102 Å to 2.273 Å. In comparison with the reactant and transition state structure, the product’s O19–H16...
shortens further, while the O19–H20 is basically unchanged, and their lengths are stable at 0.974 Å. The bond angle of H20–O19–H16 gradually increases from 91.38° to 104.48°, which is similar to that of H2O. Since the hybrid orbital electron cloud occupied by the lone pair electrons is denser, the hybrid orbital occupied by the bonding electron pair is repelled and compressed so that the H–O–H angle twists to 104.48°, which forms a V-shaped structure. The results show that H2O has formed a stable structure completely.

The ΔE for this reaction is pretty small, which is 10.628 kJ/mol, and the ΔH is 40.76 kJ/mol. The results make it clear that the reaction does not need to overcome the high reaction energy barrier and can carry out at room temperature; in addition, a certain amount of heat release plays a great role in increasing the temperature of the oxidation process. As the key reaction sequence of consuming ·OH and generating new radicals, this reaction has significant effects on promoting the occurrence of coal spontaneous combustion.

2.3.2.2. Elementary Reactions between Oxygen-Containing Functional Groups and Free ·OH. Free ·OH can also react with oxygen-containing functional groups and capture the H atom of the active site to generate H2O. The reactions are shown in reactions 11–14.

Taking −ROH as an example and Ar−CH2−OH as the model compound, the mechanism of the reaction between −ROH and ·OH was calculated by quantum chemical theory. The structural parameters and energy changes in the reaction process are shown in Figure 9.

It is found that the O8–H16 breaks gradually, which indicates that H16 has separated from the adsorption of O8 and gradually moves along the vibration direction to connect with O17, and finally forms a H2O molecule. The calculated ΔE is 8.14 kJ/mol, which is less than 40 kJ/mol, showing that the reaction can occur spontaneously at room temperature. Moreover, the ΔH is −47.76 kJ/mol, indicating that the reaction has a large exothermic capacity and contributes to the self-heating of coal. At the same time, the reaction can clearly explain the source of H2O during coal spontaneous combustion.

2.3.3. Elementary Reactions between Functional Groups and Radicals. There are a lot of original and derivative radicals in coal, including −C, −CH, −CH2, −RO, −ArO, −COO, −CO, and −O−O. Due to the absence of electrons, radicals have strong reactivity. When the single electron orbital of a radical and the highest-level orbital of a functional group have similar energy, the H of the active site can be captured by the radical directly. Based on this, the reaction sequence between functional groups and radicals is proposed as shown in reactions 15–20.
Taking $-\text{CHO}$ and $-\text{CH}_2$ as examples and $\text{Ar}-\text{CH}_2-\text{CHO}$ and $\text{Ar}-\text{CH}_2$ as the model compounds, the mechanism of the reaction between $-\text{CHO}$ and $-\cdot\text{CH}_2$ was calculated by quantum chemical theory. The structural parameters and energy changes are shown in Figure 10.

In the reaction, the H17 moves toward C24, which increases the distance between C8 and H17 to 2.878 Å, resulting in the breaking of the C–H bond. The C24 changes from sp$^2$ hybridization to sp$^3$ hybridization after capturing H17, and a $\sigma$ bond of 1.098 Å forms between C24 and H17 by s–sp$^3$ hybridization. At the same time, the angle of H31–C24–H30 in the $-\cdot\text{CH}_2$ twists from 117.623° to 109.466° and the angle between C24–C22 and H30–C24–H31 planes twists from the plane structure to 122.807°. The microscopic parameters of the product are consistent with the known $-\text{CH}_3$ parameters, indicating that H17 has completely separated from $-\text{CHO}$ and the $-\text{CH}_3$ at the stable state generates.

Through calculation, the $\Delta H$ is $-5.63$ kJ/mol, and $\Delta E$ values are $-5.63$ and $63.76$ kJ/mol, respectively, indicating that the activation energy required for the reaction is large, the heat release is very small, and the effect of increasing the temperature is not obvious.

2.3.4. Elementary Reaction between Radicals and O$_2$.

According to the reaction characteristics of radicals, the radicals cannot only adsorb O$_2$ molecules or free single O atoms to form peroxide radicals. When an O directly attaches to the benzene ring, the reaction activity of H at the same site is enhanced so it can be captured by O$_2$. Based on the above, the reaction sequences are proposed as reactions 21–26.
Take the reaction of $\cdot CH_2$ adsorbing $O_2$ as an example and $Ar\cdot CH_2$ as the model compound, and the mechanism of the reaction between $\cdot CH_2$ and $O_2$ was calculated by quantum chemical theory. The structural parameters and energy changes in the reaction process are shown in Figure 11.

Before the reaction occurs, $O_2$ is adsorbed on the $Ar\cdot CH_2$ molecule, the distance between $C8$ and $O9$ is 2.35 Å, and the bond length of $O9\cdot O10$ is 1.214 Å. When the reaction occurs, the $O2$ molecule moves toward the $\cdot CH_2$. The $O9$ links to $C8$ to form a peroxide radical, in which the equilibrium distance of $C8\cdot O9$ shortens to 1.456 Å and that of $O9\cdot O10$ increases from 1.214 Å to 1.322 Å.

Because the reaction only involves the formation instead of the breaking of the bond, it is a chemical adsorption reaction, there is no transition state, that is, the $\Delta E$ is 0, and it can occur directly at room temperature and pressure. The $\Delta H$ of the reaction is 147.028 kJ/mol, indicating that it is an exothermic reaction, and the exothermic energy is very large, which can significantly improve the self-heating of coal. It is an important process to start the chain reactions of coal spontaneous combustion at low temperatures.

### 2.3.5. Self-reactions between Radicals

The self-reactions between radicals mainly include the desorption reactions of radicals, the reactions between radicals and free $\cdot OH$, and the reactions between radicals. Therefore, the reaction sequences are proposed as shown in reactions 27–33.

Take the dealdehyde reaction of $\cdot CO$ generating CO as an example and $Ar\cdot CH_2\cdot CO$ as the model compound, and the structural parameters and energy changes are shown in Figure 12.

The change process of the coal molecular structure indicates that the hybridization mode of $C7$ changes from sp3 to sp2 as soon as $C7\cdot C8$ breaks, and the configuration of $H16\cdot C7\cdot H15$
low-temperature oxidation of coal.41,42 Heating of coal is not obvious, it is the main source of CO during spontaneous combustion. The reaction is 43.69 kJ/mol, indicating that the energy required for the reaction is low, which can occur in the early stage of coal heating and promote the occurrence of other reactions. With the accumulation of heat, the reactions between original functional groups and radicals in coal molecules start first, mainly the reactions between original oxygen-containing functional groups and aliphatic radicals. It is worth noting that the peroxide OH bond can directly break to generate free ·OH due to the low bond dissociation energy. So far, the number of free radicals in coal has greatly increased, which makes adequate preparations for the occurrence of subsequent reaction sequences.

3. INFERENCE OF CHAIN REACTIONS OF COAL SPONTANEOUS COMBUSTION

The 33 reaction kinetic models proposed were explored and verified by using quantum chemistry theory, and the ΔE and ΔH of the reaction were calculated, as shown in Table 2. According to the ΔE of all reactions, the reaction sequences can be inferred, that is, they gradually occur from small to large. According to previous experimental analyses,35,43,44 when ΔE = 0, the reaction can occur spontaneously. When ΔE < 40 kJ/mol, the reaction can occur at room temperature and pressure (T < 30 °C). When 40 kJ/mol < ΔE < 180 kJ/mol, the reaction can occur at 30−70 °C. When ΔE > 180 kJ/mol, the reaction can occur at 70−120 °C. According to statistics, the ΔE values of reactions 21–25, 32, and 33 are 0, which are chemical adsorption reactions, so they can occur spontaneously because there are no energy barriers. The ΔE values of reactions 8–10, 11–14, and 31 are less than 40 kJ/mol and can occur at room temperature and pressure. The ΔE values of others are greater than 40 kJ/mol, which can only occur under the stimulation of higher external temperatures.

3.1. Chain Initiation Reaction. Chain initiation reactions are characterized by the formation of radicals. In the process of coal crushing, a large number of radicals can be generated due to the breaking of coal macromolecular covalent bonds, most of which are aliphatic radicals. All of them can adsorb chemically with O2 (E21−E23) to form peroxide radicals and release a lot of heat (−147.03 to −149.72 kJ/mol). The role of this kind of reaction is to continuously provide heat to improve coal self-heating and promote the occurrence of other reactions. With the accumulation of heat, the reactions between original functional groups and radicals in coal molecules start first, mainly the reactions between original oxygen-containing functional groups and aliphatic radicals. It is worth noting that the peroxide generated by reaction E19 is not stable, and its O−OH bond can directly break to generate free ·OH due to the low bond dissociation energy. So far, the number of free radicals in coal has greatly increased, which makes adequate preparations for the occurrence of subsequent reaction sequences.

3.2. Chain Propagation Reactions. Chain propagation reactions are characterized by the gradual formation of cycle reactions, which can be divided into four parallel sequences. (1) Because free ·OH have high reaction activity, they can first react with the functional groups in coal molecules (E8−E14) to generate a large number of radicals and H2O. Although the activation energy required for these reactions is very low (1.97−32.41 kJ/mol) and can occur spontaneously at room temper-
nature, they will not occur before E19 due to the lack of key active groups -OH. Most of these reactions are exothermic reactions, which can also continuously improve the energy of the reaction system and raise the temperature. (2) Reactions E17 and E18 can produce —CO and ketone compounds, which will continue to adsorb O₂ or O (E24 and E25) and release heat (−51.47 to −121.04 kJ/mol), continuously promoting the occurrence of subsequent reactions. At the same time, the product of E24 constitutes the reactant of E20, which promotes E20 occurrence and releases heat (−26.69 kJ/mol) again and generates -OH. The -OH can aggravate the occurrences of E8–E14, while the radicals generated by E8–E10 can reverse-promote the occurrences of E15–E20, which constitute a cyclic reaction. (3) The peroxide radicals generated by chemical adsorption reactions can undergo intramolecular H transfer reaction (E27) to generate -OH, while the oxygen-containing radicals can undergo desorption reactions (E28–E30) to generate various index gases, such as CO, CO₂, and C₂H₆. Among them, the ΔE (43.49 kJ/mol) of the CO formation reaction (E28) is significantly smaller than those of the other two (56.98–73.11 kJ/mol), which is consistent with the experimental result that CO can generate earlier.¹³ (4) With the accumulation of heat, the temperature of the reaction system gradually increases, and the E1–E7 reaction sequence starts. Among them, O₂ can react with various functional groups to generate a large number of radicals and ·OH again, which continue to participate in other reaction sequences and promote the chain reactions.

### 3.3. Chain Termination Reactions

The chain termination reactions are characterized by the formation of stable compounds, which are difficult to continuously react, such as ethers, esters, and quinones (E26 and E31–E33). These reactions are exothermic (−4.55 to −34.19 kJ/mol), which can accumulate heat at the initial stage of the reactions. The stable oxidation products not only block the transmission of the reaction chain but also inhibit the oxidation of surrounding active groups after the accumulation on the coal surface. It is reasonable to study the precise prevention and control of coal spontaneous combustion disasters based on promoting the formation of such substances. At present, the commonly used inhibitor for blocking the chain reactions of coal low-temperature oxidation is mainly an antioxidant, which is composed of phenolic substances.⁴⁵ The H atom of hydroxyl on the benzene ring is easy to separate and combine with an oxygen radical, which changes the oxygen radical into a stable product and loses its activity, so as to terminate the chain reactions. Common antioxidants include butylated hydroxytoluene (BHT), triphenyl, catechin, 2,2,6,6-tetramethyl-1-piperidine-N-oxyl free radical (TEMPO), etc. However, their inhibition effects are different. After research,¹⁶ BHT and TEMPO have the best inhibition effect. The aqueous solution of their mixture can be used as the inhibition to promote the chain termination reactions.

Through quantum chemical calculation and analyses, all elementary reaction pathways are summarized as Figure 13.

### 4. CONCLUSIONS

(1) FTIR was used to accurately measure the active groups in coal molecules. The results show that Danhou lignite molecules are mostly aromatic rings or fused rings, aliphatic structures, and oxygen-containing functional groups. Among them, the aliphatic structure and oxygen-containing functional groups are the active groups of the coal spontaneous combustion reactions, and the number of −CH₂ in the aliphatic structure is significantly higher than those of −CH and −CH₃, indicating that the aliphatic structures are mostly long chains, while the oxygen-containing functional groups are mostly −ROH, −ArOH, −COOH, −CHO, and −O−.

(2) In this paper, a coal molecular model containing various active groups was constructed, and the active site and reaction activity of each were explored. The results show that the active sites of functional groups are H atoms. The ESPs of atoms show that the charge density order of the active site is −COOH (0.514) > −ArOH (0.503) > −ROH (0.482) > −CH (0.249) > −CH₃ (0.237) > −CH₂ (0.232) > −CHO (0.150). Therefore, when reacting with O₂, the order of reaction activity is the same.

(3) The coal molecular models containing various functional groups and radicals were constructed. The frontier orbital analyses show that the active bonds of aliphatic hydrocarbons are C–H bonds, and those of oxygen-
containing functional groups are C–H or O–H bonds. The H atom on the activity bond of functional groups can be directly captured to form radicals under certain conditions. The active bonds of radicals are C=C or C–H bonds whose H atom is missing, and those of peroxy radicals are O–O bonds.

(4) The chain reaction sequences of coal spontaneous combustion at low temperatures were studied by the quantum chemical method, which can be divided into chain initiation reactions, chain propagation reactions, and chain termination reactions. In the chain initiation reaction stage, aliphatic radicals react with O2 to generate peroxy radicals and a large amount of heat. With the accumulation of heat, the self-reaction sequence between functional groups and radicals starts, the number of free radicals gradually increases, and the generation of free -OH further promotes the chain reaction. After entering the chain propagation reaction stage, free -OH and O2 continuously consume active groups and generate a large number of radicals; thus, the reaction sequence is further intensified, and the index gases such as CO and CO2 begin to generate through desorption reactions in this stage. The stage lasts until the active sites are completely consumed. In the chain termination reaction stage, radicals can combine with each other to form stable compounds such as ethers, esters, and quinones to inhibit the reactions. Therefore, based on this, the inhibitors can be developed to promote the formation of such compounds and control the chain reactions of coal spontaneous combustion.

5. EXPERIMENTS AND METHODOLOGY

5.1. FTIR Test. 5.1.1. Coal Sample Preparation. Considering the difference of functional groups in different kinds of coals, the functional groups in lignite are the most abundant, and the spontaneous combustion reactions are more complex and comprehensive. Therefore, a lignite sample from the Danhou mine was selected as the representative experimental coal sample. First, the exterior part of the large fresh lump coal was removed and the rest was crushed into 60–80 mesh pulverized coal. Second, the treated pulverized coal was put into a vacuum drying oven for 24 h. Finally, the dry pulverized coal was put into the sealed glass bottle for standby.

5.1.2. Coal Sample Test. The experiment was carried out in the Fourier transform infrared spectrometer (TENSOR27) produced by Bruker Company in Germany. First, 0.001 g of pulverized coal was weighed, mixed with potassium bromide (KBr) powder in the ratio of 1:150 (i.e., 1 mg of pulverized coal and 150 mg of KBr powder), and ground for 20 min. The fully ground powder was put into the tablet press and pressed to 10 MP, and then the film was taken off after pressing for 1 min. A transparent sheet with a diameter of 0.9 mm and a thickness of 0.1 mm was obtained. Then, it was put into the sample chamber of the Fourier transform infrared spectrometer for scanning test. The wavenumber range was 4000–400 cm⁻¹, the resolution was 4.0 cm⁻¹, and the cumulative scanning times were 64.

5.2. Contents and Methods of Quantum Chemistry Calculation. Since the macromolecular structure of coal is very sophisticated, it is very expensive to treat the macromolecular structure by quantum chemistry. The study of Shi et al. shows that the benzene ring structures are quite stable and do not easily participate in chemical reactions. Therefore, a small molecular fragment composed of a benzene ring and active group can be used as a model of coal. Based on the quantum chemistry theory, the ESP, molecular orbital, and thermodynamic parameters of coal small molecule models were calculated to explore the reaction characteristics of coal molecules, providing the theoretical basis for the study of coal spontaneous combustion mechanism and the development of inhibitors. The calculations were carried out on Gaussian 16W.

5.2.1. Molecular Structure and Frontier Orbital Analysis of Coal. Density functional theory (DFT) is important in the field of computational chemistry and is provided with the little calculation quantity but excellent precision and determination, so it can be utilized to work out the electronic constitution and energy of the object system. The B3LYP technique in DFT was applied to depict the electron exchange and associated functions, and the 6-31G(d,p) basis set level was picked. The ground-state method was utilized to optimize molecular models, and the natural bond orbital (NBO) was used to analyze molecular frontier orbitals and charge delocalization.

5.2.2. ESP Analysis. Molecular surface quantitative analysis is of great importance for forecasting the reactive sites, binding styles, and thermodynamic characteristics of molecules. ESP is an important characterization parameter that describes charges’ interaction energy, and it can be illustrated as follows. In this paper, the van der Waals distribution of molecular ESP was used to predict the electrophilic and nucleophilic reaction centers of molecules.

\[
V_{	ext{tot}}(r) = V_{	ext{nuc}}(r) + V_{	ext{ele}}(r) = \sum_{\alpha} \frac{Z_{\alpha}}{|r - R_{\alpha}|} - \int \frac{\rho(r')}{|r - r'|} \text{d}r'
\]

where \(R_{\alpha}\) is the nucleus coordinates of atom \(\alpha\), \(Z_{\alpha}\) represents the nuclear charges, and \(\rho(r)\) is the electron density.

5.2.3. Transition State Analysis. On the basis of the structure peculiarity of coal molecules, an optimization task was selected to conduct the search for transition state, and the keywords (TS/QST2,Calcfc,Noeigen) were added. TS/QST2 meant to find the transition states by only guessing the initial structures or giving both the reactants and products. Calcfc represented the accurate calculation of the Hessian matrix at first, and Noeigen meant that the accurate calculation of Hessian matrix eigenvalues does not need to be carried out at every step. The intrinsic reaction coordinate (IRC) method was utilized to confirm the correctness of reaction pathways. The keywords of IRC were Calcfc, Maxpoints = 20, Recalc = 5, Stepsize = 10, and LQA; it meant that the LQA algorithm was applied to calculate 20 points in the positive and negative directions, and the step size was 0.05 Bohr/s. Recalc = 5 represented that the program calculated the Hessian matrix every five steps. The method to verify the accuracy of IRC is to calculate the frequency of the coal molecular transition state. If there is only a unique virtual frequency and the vibration direction corresponds to the reactant and product, the transition state is accurate. It ought to be mentioned that both IRC analysis and TS searching were carried out on the B3LYP/6-31G(d,p) level.

5.2.4. Thermodynamic Parameter Calculations. From the aspect of chemical science, thermodynamic characteristic parameters are very necessary for the analysis of chemical reactions, where the enthalpy change (\(\Delta H\)) and activation energy (\(\Delta E\)) are two parameters of great importance. \(\Delta E\) can indicate the difficulty of the reaction, which is obtained by the
difference between the total energy of the transition state and reactant. $\Delta H$ is an important index to judge the endothermic or exothermic reaction. Its calculation method is the total energy of the product minus that of the reactant.

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**Notes**

The authors declare no competing financial interest.

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# REFERENCES

1. Atalay, F.; Tercan, A. E. Coal resource estimation using Gaussian copula. *Int. J. Coal. Geol.* 2017, 175, 1–9.
2. Deng, J.; Xiao, Y.; Lu, J.; Wen, H.; Jin, Y. Application of composite fly ash gel to extinguish outcrop coal fires in China. *Nat. Hazards* 2015, 79, 881–898.
3. Solomon, P. R.; Fletcher, T.; Pugmire, R. Progress in coal pyrolysis. *Fuel* 1993, 72, 587–597.
4. Wang, H.; Dlugogorski, B. Z.; Kennedy, E. M. Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. *Prog. Energy Combust.* 2003, 29, 487–513.
5. Wang, H.; Chen, C. Experimental Study on Greenhouse Gas Emissions Caused by Spontaneous Coal Combustion. *Energy Fuels* 2015, 29, S213–S221.
6. Zeng, Q.; Tiyp, T.; Wuttke, M. W.; Guan, W. Modeling of the equivalent permeability for an underground coal fire zone, Xinjiang region, China. *Nat. Hazards* 2015, 78, 957–971.
7. Niu, H.; Deng, X.; Li, S.; Cai, K.; Zhu, H.; Li, F.; Deng, J. Experiment study of optimization on prediction index gases of coal spontaneous combustion. *J. Cent. South Univ.* 2016, 23, 2321–2328.
8. Zhu, H.; Huo, Y.; He, X.; Wang, W.; Fang, S.; Zhang, Y. Molecular model construction of Danhoud lignite and study on adsorption of CH4 by oxygen functional groups. *Environ. Sci. Pollut. Res. Int.* 2021, 28, 25368–25381.
9. Zhu, H.; Huo, Y.; Wang, W.; He, X.; Fang, S.; Zhang, Y. Quantum chemical calculation of reaction characteristics of hydroxyl at different positions during coal spontaneous combustion. *Process Saf. Environ. Prot.* 2021, 148, 624–635.
10. Zhu, H.; Huo, Y.; Fang, S.; He, X.; Wang, W.; Zhang, Y. Quantum Chemical Calculation of Original Aldehyde Groups Reaction Mechanism in Coal Spontaneous Combustion. *Energy Fuels* 2020, 34, 14776–14785.
11. Zhu, H.; He, X.; Xie, Y.; Guo, S.; Huo, Y.; Wang, W. A Study on the Effect of Coal Metamorphism on the Adsorption Characteristics of a Binary Component System: CO2 and N2. *ACS Omega* 2021, 6, 523–532.
12. Zhu, H.; Wang, W.; Huo, Y.; He, X.; Zhao, H.; Wang, H. Molecular Simulation Study on Adsorption and Diffusion Behaviors of CO2/N2 in Lignite. *ACS Omega* 2020, 5, 29416–29426.
13. Fei, Y.; Aziz, A. A.; Nasir, S.; Jackson, W. R.; Marshall, M.; Hulston, J.; Chaffee, A. L. The spontaneous combustion behavior of some low rank coals and a range of dried products. *Fuel* 2009, 88, 1650–1655.
14. Qu, Z.; Sun, F.; Gao, J.; Pei, T.; Qie, Z.; Wang, L.; Pi, X.; Zhao, G.; Wu, S. A new insight into the role of coal adsorbed water in low-temperature oxidation: Enhanced-OH radical generation. *Combust. Flame* 2019, 208, 27–36.
15. Wang, H.; Dlugogorski, B. Z.; Kennedy, E. M. Thermal decomposition of solid oxygenated complexes formed by coal oxidation at low temperatures. *Fuel* 2002, 81, 1913–1923.
16. Wang, H.; Dlugogorski, B. Z.; Kennedy, E. M. Kinetic modeling of low-temperature oxidation of coal. *Combust. Flame* 2002, 131, 452–464.
17. Itay, M.; Hill, C. R.; Glasser, D. A study of the low temperature oxidation of coal. *Fuel Proc. Technol.* 1989, 21, 81–97.
18. Wang, D. The coal oxidation dynamics theory and application; Science press: Beijing, 2012.
19. Xu, J.; Zhang, L.; Wen, H.; Deng, J. Procedure of reaction between coal and oxygen at low temperature adn calculation of its heat emitting intensity. *J. China Univ. Ming. Technol.* 2000, 29, 253–257.
20. Ge, L.; Xue, H.; Xu, J.; Deng, J.; Zhang, X. Procedure of reaction between coal and oxygen at Low temperature and calculation of its heat emitting intensity. *Coal Coners.* 2001, 24, 23–28.
21. Kus, J.; Misz-Kennan, M. Coal weathering and laboratory (artificial) coal oxidation. *Int. J. Coal Geol.* 2017, 171, 12–36.
22. Ibarra, J. V.; Miranda, J. L. Detection of weathering in stockpiled coals by Fourier transform infrared spectroscopy. *Vib. Spectrosc.* 1996, 10, 311–318.
23. Fujisataka, H.; Ashida, R.; Kawase, M.; Miura, K. Examination of Low-Temperature Oxidation of Low-Rank Coals, Aiming at Understanding Their Self-Ignition Tendency. *Energy Fuels* 2014, 28, 2402–2407.
24. Gao, Z.; Ma, C.; Lv, G.; Li, A.; Li, X.; Liu, X.; Yang, W. Car-Parrinello molecular dynamics study on the interaction between lignite and water molecules. *Fuel* 2019, 258, 116189.
25. Gao, Z.; Ding, Y. DFT study of CO2 and H2O co-adsorption on carbon models of coal surface. *J. Mol. Model.* 2017, 23, 187.
26. Chen, L.; Qi, X.; Tang, J.; Xue, H.; Liang, Z. Reaction pathways and cyclic chain model of free radicals during coal spontaneous combustion. *Fuel* 2021, 293, 120436.
27. Qi, X.; Chen, L.; Xue, H.; Ji, Y.; Bai, C.; Song, R.; Xue, H.; Liu, F. Reaction Mechanism and Thermodynamic Properties of Aliphatic Hydrocarbon Groups during Coal Self-Heating. *Energy Fuels* 2018, 32, 10469–10477.
28. Qi, X.; Xue, H.; Xue, H.; Bai, Z. Quantum chemistry calculation of reaction pathways of carboxyl groups during coal self-heating. *Can. J. Chem.* 2017, 95, 824–829.
29. Qi, X.; Wang, D.; Xue, H.; Jin, L.; Su, B.; Xue, H. Oxidation and Self-Reaction of Carboxyl Groups During Coal Spontaneous Combustion. *Spectros. Lett.* 2014, 48, 173–178.
30. Qi, X.; Xue, H.; Xue, H.; Wei, C. Reaction pathways of hydroxyl groups during coal spontaneous combustion. *Can. J. Chem.* 2016, 94, 494–500.
(31) Zhang, L.; Li, Z.; He, W.; Li, J.; Qi, X.; Zhu, J.; Zhao, L.; Zhang, X. Study on the change of organic sulfur forms in coal during low-temperature oxidation process. *Fuel* 2018, 222, 350–361.

(32) Clemens, A. H.; Matheson, T. W.; Rogers, D. E. Low temperature oxidation studies of dried New Zealand coals. *Fuel* 1991, 70, 215–221.

(33) Deng, C. Study on coal spontaneous combustion mechanisms and the spontaneous combustion danger index; Liaoning Technical University, 2006.

(34) Wang, D.; Xin, H.; Qi, X.; Dou, G.; Zhong, X. Mechanism and relationships of elementary reactions in spontaneous combustion of coal: The coal oxidation kinetics theory and application. *J. China coal soc.* 2014, 39, 1667–1674.

(35) Wang, D.; Xin, H.; Qi, X.; Dou, G.; Qi, G.; Ma, L. Reaction pathway of coal oxidation at low temperatures: a model of cyclic chain reactions and kinetic characteristics. *Combust. Flame* 2016, 163, 447–460.

(36) Xi, Z.; Gao, K.; Guo, X.; Li, M.; Ren, C. Mechanistic Study of the Inhibition of Active Radicals in Coal by Catechin. *Combust. Sci. Technol.* 2020, 193, 1931–1948.

(37) Dou, G.; Wang, D.; Zhong, X.; Qin, B. Effectiveness of catechin and poly(ethylene glycol) at inhibiting the spontaneous combustion of coal. *Fuel Process. Technol.* 2014, 120, 123–127.

(38) Xin, H. Exploring of stage evolution characteristics and mechanism of oxygen-len combustion in coal fire; China university of mining and technology, 2016.

(39) Lin, S. K. Advanced Organic Chemistry. Part A: Structure and Mechanisms. Fourth Edition. by Francis A. Carey. *Molecules* 2000, 5, 1528–1528.

(40) Li, X.; Tang, Y.; Wang, C.; Zhang, H.; Cheng, X. A DFT Investigation on Hydrogen Adsorption Based on Alkali-metal Organic Complexes. *Chin. J. Struct. Chem.* 2010, 29, 1404–1410.

(41) Yuan, S. Fundamental study on reaction mechanism and effect of upgrading treatment on spontaneous combustion of lignite; Zhejiang University, 2018.

(42) Qi, X. Oxidation and self-reaction of active groups in coal; China university of mining and technology, 2011.

(43) Xi, Z.; Li, X.; Xi, K. Study on the reactivity of oxygen-containing functional groups in coal with and without adsorbed water in low-temperature oxidation. *Fuel* 2021, 304, 121454.

(44) Xi, Z.; Jin, B.; Shan, Z. Reaction mechanisms involving peroxy radical in the low-temperature oxidation of coal. *Fuel* 2021, 300, 120943.

(45) Ma, L.; Wang, D.; Wang, Y.; Xin, H.; Dou, G.; Xu, C. Experimental Investigation on a Sustained Release Type of Inhibitor for Retarding the Spontaneous Combustion of Coal. *Energy Fuels* 2016, 30, 8904–8914.

(46) Li, J.; Li, Z.; Yang, Y.; Zhang, X.; Yan, D.; Liu, L. Inhibitive Effects of Antioxidants on Coal Spontaneous Combustion. *Energy Fuels* 2017, 31, 14180–14190.

(47) Shi, T.; Wang, X.; Deng, J.; Wen, Z. The mechanism at the initial stage of the room-temperature oxidation of coal. *Combust. Flame* 2005, 140, 332–345.

(48) Yu, S.; Bo, J.; Fengjuan, L. Competitive adsorption of CO2/N2/CH4 onto coal vitrinite macromolecular: Effects of electrostatic interactions and oxygen functionalities. *Fuel* 2019, 235, 23–38.

(49) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* 2010, 132, 154104.

(50) Grimme, S. Density functional theory with London dispersion corrections. *WIREs Comput. Mol. Sci.* 2011, 1, 211–228.

(51) Xin, H.; Wang, D.; Qi, X.; Xu, T.; Dou, G.; Zhong, X. Distribution and quantum chemical analysis of lignite surface functional groups. *J. Univ. Sci. Technol. Beijing* 2013, 35, 135–139.

(52) Lu, T.; Chen, F. Quantitative analysis of molecular surface based on improved Marching Tetrahedra algorithm. *J. Mol. Graphics Modell.* 2012, 38, 314–323.

(53) Deng, J.; Li, Y.; Zhang, Y.; Yang, C.; Zhang, J.; Shi, X. Effects of hydroxyl on oxidation characteristics of side chain active groups in coal. *J. China Coal Soc.* 2020, 45, 232–240.