

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

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Cite This: *ACS Omega* 2021, 6, 30841–30855

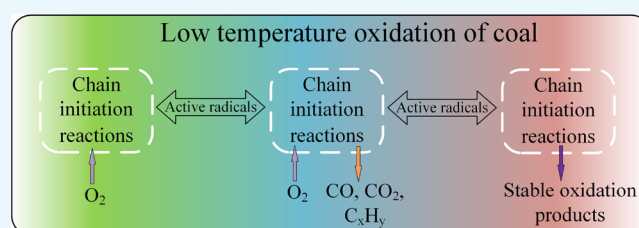
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ABSTRACT: The coal spontaneous combustion phenomenon seriously affects the safety production of coal mines. Aiming at the problem of complex coal molecular structure and incomplete reaction sequences at present, the mechanisms and thermodynamic parameters 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 ($-\text{CH}_3$), methylene ($-\text{CH}_2$), methyne ($-\text{CH}$), phenolic hydroxyl ($-\text{ArOH}$), alcohol hydroxyl ($-\text{ROH}$), carboxyl ($-\text{COOH}$), aldehyde ($-\text{CHO}$), and ether ($-\text{O}-$), 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, O_2 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 ($-\text{C}-\text{O}-\text{O}\cdot$) can produce the key hydroxyl radical ($-\text{O}\cdot$). In the chain propagation reaction stage, O_2 and $-\text{O}\cdot$ continuously consume active sites to accelerate the reaction sequences and increase the temperature of coal, and index gases such as CO and CO_2 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 O_2 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 O_2 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 $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$, while oxygen-containing functional groups include

Received: September 24, 2021

Accepted: October 27, 2021

Published: November 4, 2021



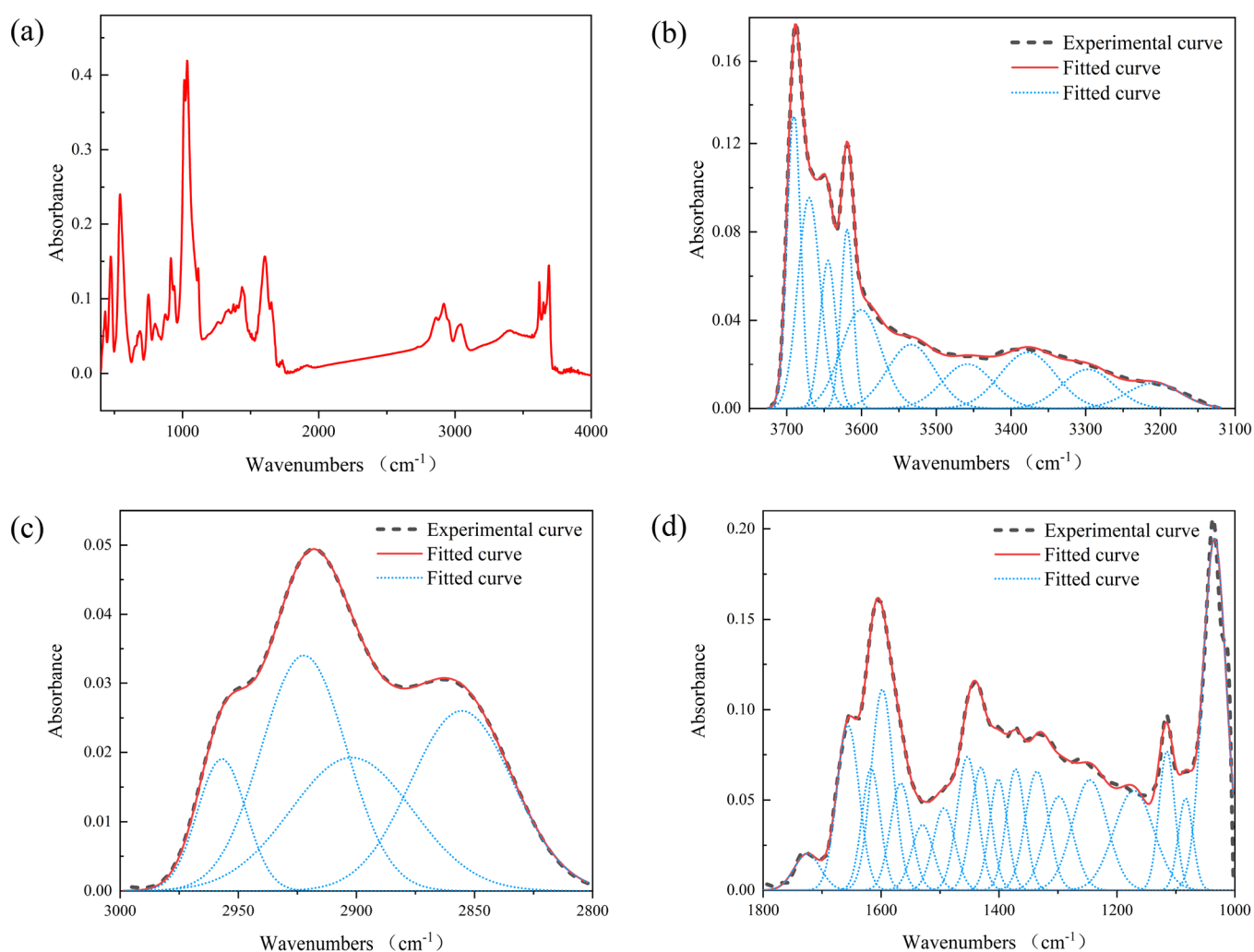


Figure 1. FTIR spectrum and fitting curves of raw coal. (a) Original data of the FTIR spectrum; (b) deconvolution of the region from 3700 to 3100 cm^{-1} in the spectrum; (c) deconvolution of the region from 3000 to 2800 cm^{-1} in the spectrum; (d) deconvolution of the region from 1800 to 1000 cm^{-1} in the spectrum.

–OH, –C=O, –COOH, –CHO, and so on.^{21–25} Not only do the original functional groups have a significant impact on the process of coal spontaneous combustion, but also a large number of radicals²⁶ 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 $-\dot{\text{C}}$, $-\dot{\text{C}}\text{H}$, $-\dot{\text{C}}\text{H}_2$, $-\dot{\text{O}}$, $-\text{CO}\dot{\text{O}}$, $-\dot{\text{C}}\text{O}$, 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,²⁷ carboxyls,^{28,29} hydroxyls,³⁰ and sulfur-containing functional groups,³¹ which deeply expounded the micromechanism of coal spontaneous combustion. Zhu et al.^{9,10} 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.³² believed that $-\dot{\text{C}}$ and $\cdot\text{OH}$ are the key groups in the coal spontaneous combustion process and proposed the chemical chain reaction sequences. Deng³³ 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 simu-

lations and put forward the risk index of coal spontaneous combustion to judge the spontaneous combustion tendency of coal. Wang et al.^{34,35} 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 $-\text{OH}$ stretching vibration, as shown in Figure 1b.³⁶ The absorption band of 3000–2800 cm^{-1} is mainly caused by the stretching vibration of aliphatic $\text{C}-\text{H}$ 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 $\text{C}-\text{H}$ stretching (2891.916 cm^{-1}), and symmetric methylene stretching (2856.349 cm^{-1}).³⁷ 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 $-\text{CH}_2$ is significantly higher than those of $-\text{CH}$ and $-\text{CH}_3$, 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 $-\text{ROH}$, $-\text{ArOH}$, $-\text{COOH}$, and $-\text{CHO}$), as shown in Figure 1d.³⁴ Eighteen fitting peaks were obtained after analysis, where the peak at 1724.976 cm^{-1} corresponds to the $\text{C}=\text{O}$ bond stretching vibration of $-\text{COOH}$ whose vibration intensity is weak, the peak at 1655.995 cm^{-1} corresponds to the vibration of $-\text{CHO}$, the peaks at 1616.855 and 1597.832 cm^{-1} are the stretching vibrations of $\text{C}=\text{C}$ bonds in aromatic or fused rings, and the peaks ranging from 1171.264 to 1246.042 cm^{-1} correspond to the $\text{C}-\text{O}$ bond stretching vibrations of $-\text{ArOH}$, $-\text{ROH}$, $-\text{O}-$, and $-\text{C}=\text{O}$, 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.³⁸ The functional groups in Danhou lignite have been identified by FTIR, including $-\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$, $-\text{ROH}$, $-\text{ArOH}$, $-\text{COOH}$, $-\text{CHO}$, and $-\text{O}-$. A coal molecular model containing all functional groups was constructed based on the aromatic skeleton as the basic unit, and the functional groups mainly exist in the form of side chains. To reduce the interaction between functional groups, they are directly connected to the benzene ring in the same way of connection. The simplified plane model is 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.

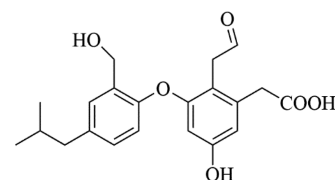


Figure 2. Simplified plane model of a coal molecule.

When coal molecules are subjected to oxidation reaction at low temperatures, O_2 can be used as a nucleophilic reagent attacking H atoms with negative potential first. In general, the H atom region of the functional group is obviously blue, such as H32, H35, and H42 atoms; the potential of this region is positive, which is the active site of nucleophilic reaction. However, part of C atoms and all O atoms are obviously red, such as O16, O13, and O11. The ESPs of these regions are negative, which are the active sites of the electrophilic reaction.³⁹

The value of charge density can reflect the reactivity of the atom, and the greater the absolute value is, the stronger the reaction activity is. Table 1 shows the maximum and minimum charge densities of the functional groups and their corresponding atoms. The largest positively charged atom of each functional group is the H atom, and the largest negatively charged atom is the C or O atom. Because $-\text{O}-$ lacks the active H atom for nucleophilic reaction, it does not easily react with O_2 . The results show that under the same conditions, the charge density order of the nucleophilic reaction site in each coal molecular functional group is $-\text{COOH}$ (0.514) > $-\text{ArOH}$ (0.503) > $-\text{ROH}$ (0.482) > $-\text{CH}$ (0.249) > $-\text{CH}_2$ (0.237) > $-\text{CH}_3$ (0.232) > $-\text{CHO}$ (0.150), which is the same as that of oxidation reaction activity.

2.2.2. Molecular Frontier Orbital. The molecular frontier orbital theory holds that the chemical reaction occurs when the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) between the two reactants attract each other. For this reason, the electrons on the frontier orbitals have stronger reaction characteristics than the others, which are likely to initiate electron transfer, resulting in the formation of reactions by bonding or breaking bonds. Therefore, the bonding properties of chemical reactions depend on the frontier orbital electron activity.⁴⁰ When the chemical reaction occurs, the bond where the HOMO is located is the active bond prone to electrophilic reaction, while the LUMO is the active bond prone to nucleophilic reaction. O_2 can be considered as a nucleophilic reagent during the low-temperature oxidation of coal molecules. However, due to the special trilinear structure of the ground-state O_2 molecule, it becomes an electron-deficient body and easily captures electrons in the process of reaction, which takes precedence over attacking the atom with the largest charge density on HOMO of the coal molecule. However, for radicals, the molecular orbitals can be divided into α and β molecular orbitals, and the single electron orbital of the α orbitals is most likely to cause orbital crossover and electron transfer.

To reduce the interaction among functional groups, the small coal molecular models containing only a single functional group were reconstructed, and the geometric optimization and orbital analyses were carried out for each model. The electron clouds on the molecular orbitals are shown in Figure 4.

The results showed that the largest electron cloud on the HOMO of each coal molecule is located on the benzene ring. However, the bonds of the benzene ring are stable, attributed to

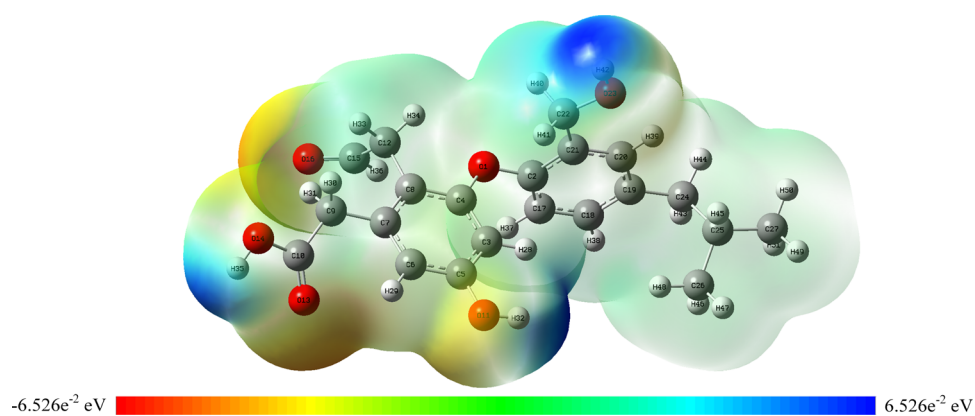


Figure 3. ESP isosurface map of a coal molecule.

Table 1. Charge Density Distributions of Atoms

category	-CH-		-CH ₂ -		-CH ₃		-CHO	
atom	C25	H45	C24	H44	C26	H48	O16	H36
charge	-0.244	0.249	-0.476	0.237	-0.677	0.232	-0.536	0.150
category	-ROH		-ArOH		-COOH		-O-	
atom	O23	H42	O11	H32	O14	H35	O1	
charge	-0.756	0.482	-0.699	0.503	-0.708	0.514	-0.535	

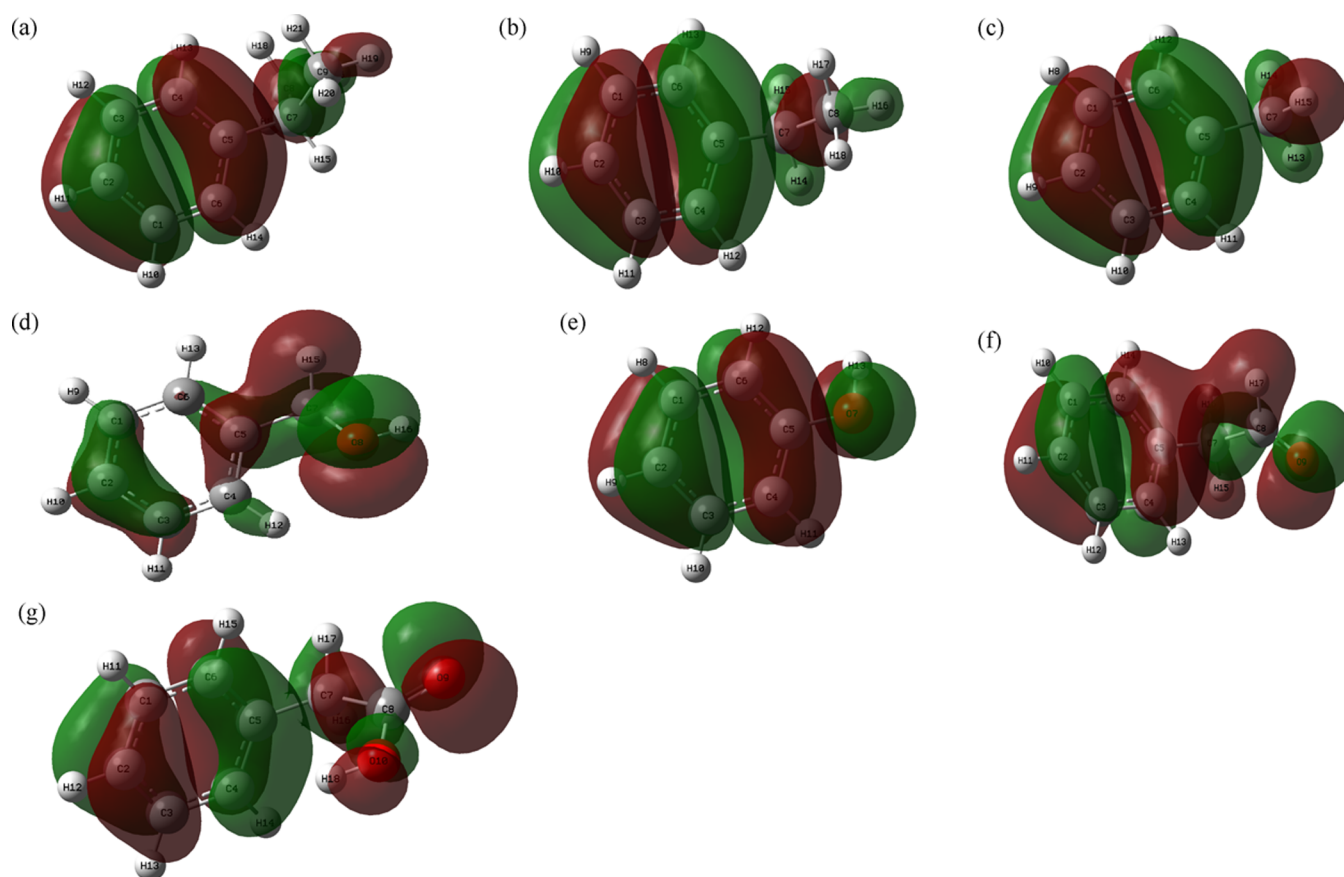


Figure 4. Electron cloud distributions on the HOMO of coal molecules with functional groups. (a) Ar-CH(-CH₃)-CH₃; (b) Ar-CH₂-CH₃; (c) Ar-CH₃; (d) Ar-CH₂-OH; (e) Ar-OH; (f) Ar-CH₂-CHO; (g) Ar-CH₂-COOH.

the existence of the π - π^* 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 -CH, -CH₂,

and -CH₃, 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 -ROH and -ArOH are

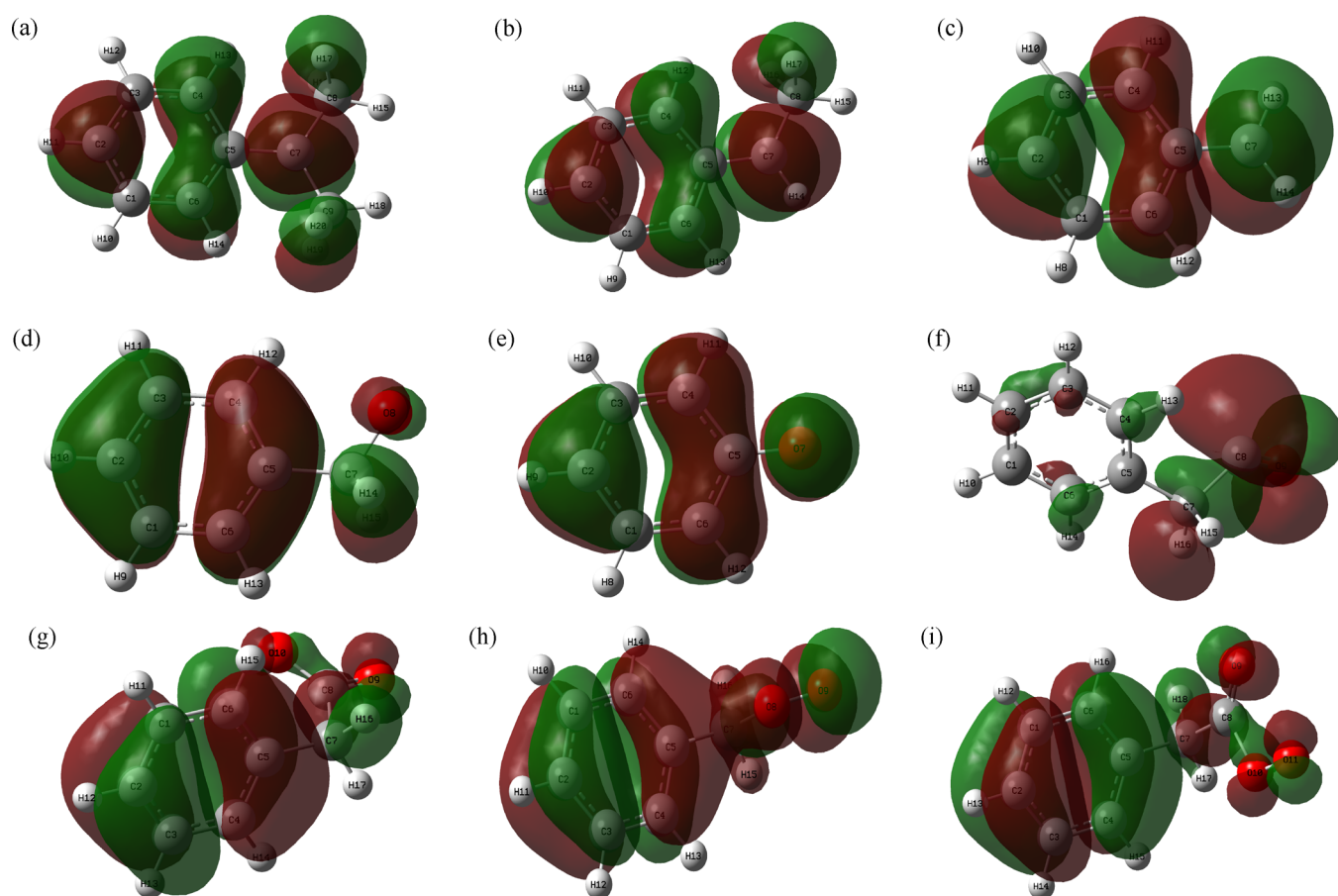


Figure 5. Electron cloud distributions on the α single electron orbital of coal molecules with radicals. (a) $\text{Ar}-\text{C}(-\text{CH}_3)-\text{CH}_3$; (b) $\text{Ar}-\dot{\text{C}}\text{H}-\text{CH}_3$; (c) $\text{Ar}-\dot{\text{C}}\text{H}_2$; (d) $\text{Ar}-\text{CH}_2-\text{O}\cdot$; (e) $\text{Ar}-\text{O}\cdot$; (f) $\text{Ar}-\text{CH}_2-\text{CO}\cdot$; (g) $\text{Ar}-\text{CH}_2-\text{COO}\cdot$; (h) $\text{Ar}-\text{CH}_2-\text{C}-\text{O}-\text{O}\cdot$; (i) $\text{Ar}-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{O}\cdot$.

located on O–H, which are the active bonds. The second electron cloud of $-\text{CHO}$ is located on C8–H17, which is its active bond. The second largest electron cloud of $-\text{COOH}$ is located on C8=O9, but C8 is hybridized with O9 to form a σ bond by sp^2 type, and the unhybridized p orbital forms a π bond with the p orbital of the O9 atom. Due to the conjugation effect of the C=O bond, its chemical properties are very stable; the active bond is the third electron cloud, that is, the O10–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 $-\dot{\text{C}}\cdot$, $-\dot{\text{C}}\text{H}\cdot$, $-\dot{\text{C}}\text{H}_2\cdot$, $-\text{RO}\cdot$, $-\text{ArO}\cdot$, $-\dot{\text{C}}\text{O}\cdot$, $-\text{COO}\cdot$, and $-\text{O}-\text{O}\cdot$. The electron clouds on the bonding orbitals are shown in Figure 5.

As shown in Figure 5, the largest electron clouds on α single electron orbitals of coal molecules with radicals are also located on the benzene rings. The second largest electron clouds of the $-\dot{\text{C}}\cdot$, $-\dot{\text{C}}\text{H}\cdot$, and $-\dot{\text{C}}\text{H}_2\cdot$ 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 $-\text{RO}\cdot$ is located on C7–H14 (C7–H15) near the benzene ring, which is the active bond. The $-\text{ArO}\cdot$ is not stable, and the second electron cloud is located on the C–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 $-\dot{\text{C}}\text{O}\cdot$ and $-\text{COO}\cdot$ are located on C7–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 O_2 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 O_2 , (2) the reactions between functional groups and free $\cdot\text{OH}$, (3) the reactions between functional groups and radicals, (4) the adsorption reactions between radicals and O_2 , 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 O_2 . **2.3.1.1. Elementary Reactions between Aliphatic Functional Groups and O_2 .** The elementary reactions between the aliphatic functional groups and O_2 can be summarized as O_2 capturing the H atom of the C–H bonds to generate aliphatic radicals and $\cdot\text{OOH}$, while the $\cdot\text{OOH}$ is not stable. In the subsequent reactions, the O–O bond of $\cdot\text{OOH}$ is easy to break to form free $\cdot\text{OH}$, which can continue to react next. Considering the properties of O_2 adsorbed by coal small molecules, the reaction sequences of $-\text{CH}\cdot$, $-\text{CH}_2\cdot$, and $-\text{CH}_3\cdot$ with O_2 are proposed as shown in reactions 1–3.

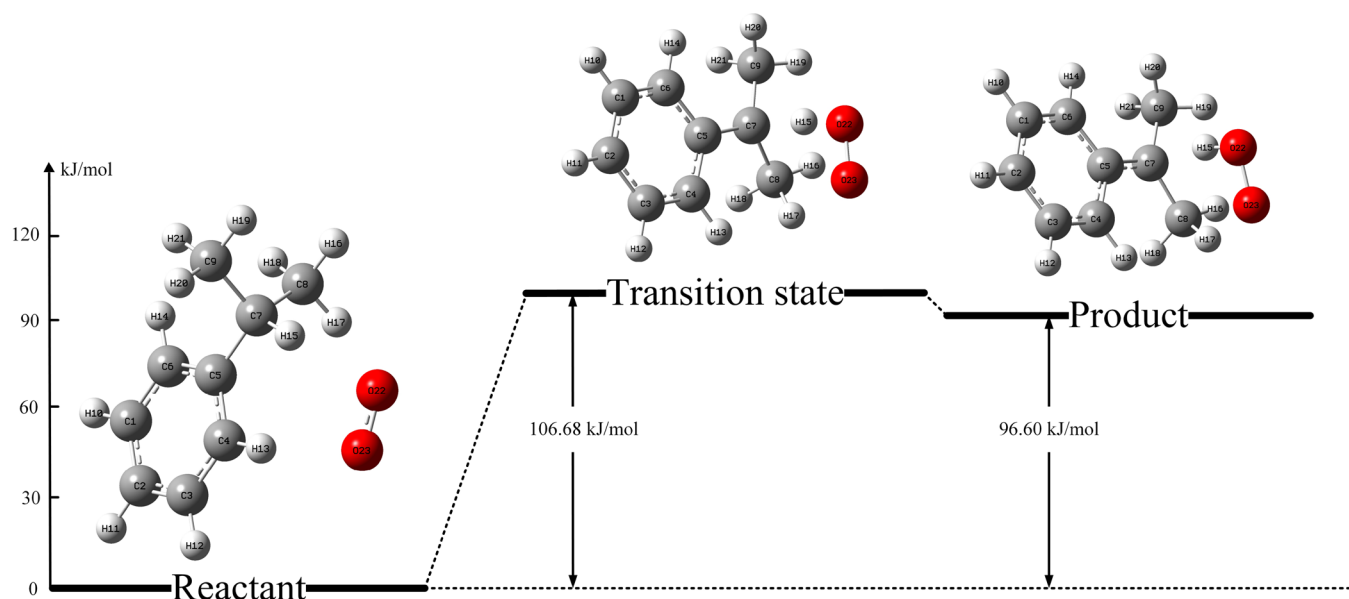


Figure 6. IRC calculation of reaction 1.

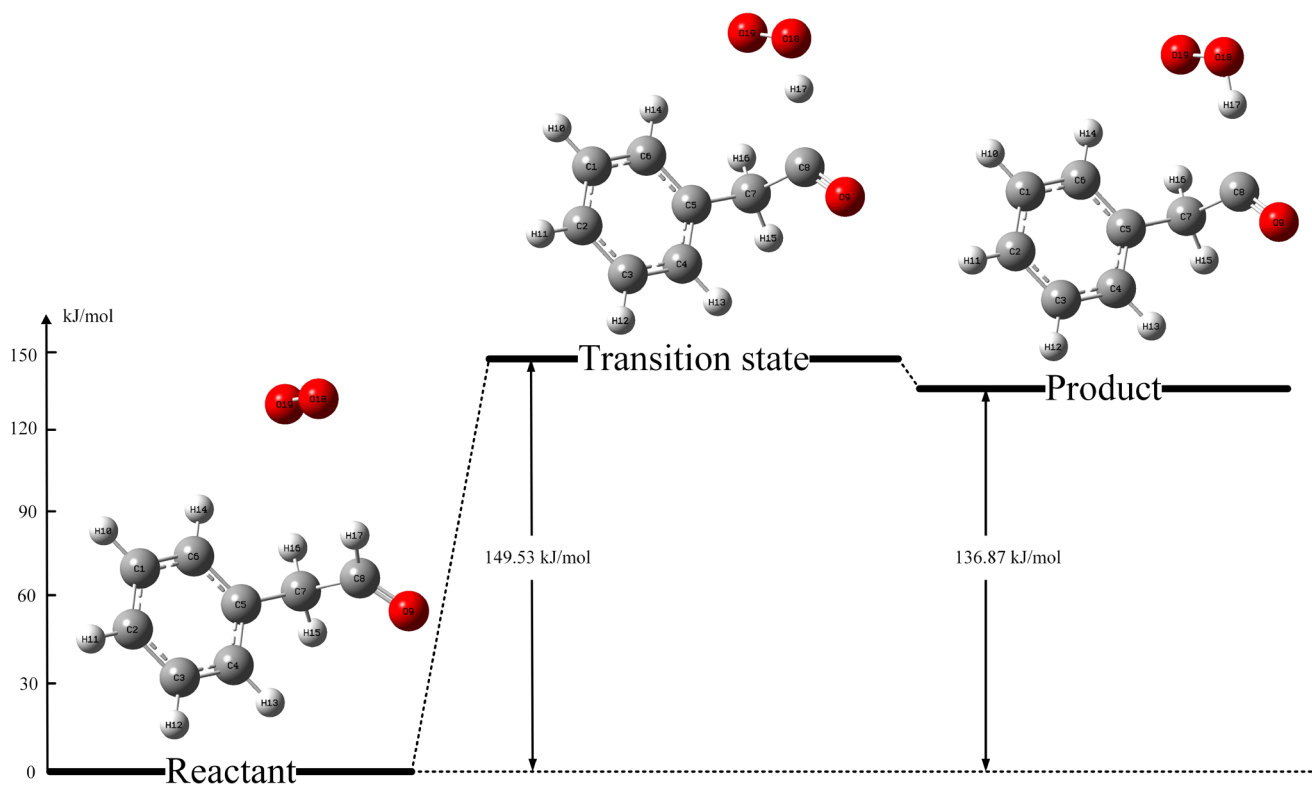
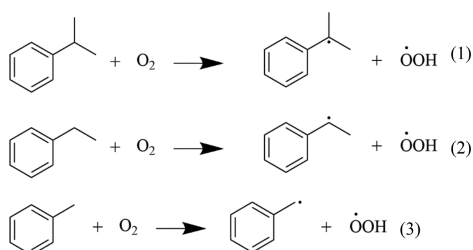


Figure 7. IRC calculation of reaction 4.



Taking $-\dot{\text{C}}\text{H}$ as an example and $\text{Ar}-\text{CH}-\text{CH}_3$ ($-\text{CH}_3$) as the model compound, the mechanism of the reaction between $-\dot{\text{C}}\text{H}$

and O_2 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 $\text{C}7-\text{H}15$ breaks, and $\text{H}15$ moves toward $\text{O}22$ along the vibration direction, showing that $\text{H}15$ has been divorced from the bonding effect of $\text{C}7$. In comparison with the transition state structure, the product's $\text{O}22-\text{H}15$ further shortens, whereas the $\text{O}22-\text{O}23$ spreads step by step. This change suggests that the $\text{O}22-\text{O}23$ in $\cdot\text{OOH}$ is likely to split in subsequent reactions to

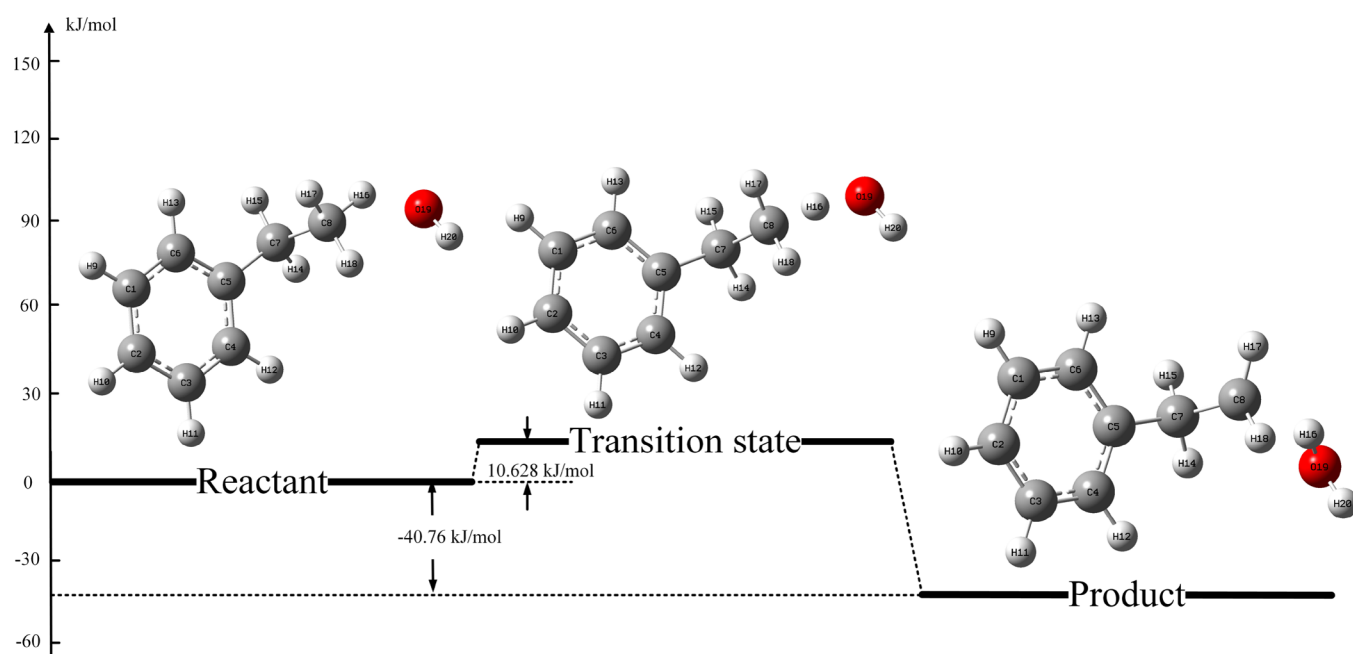
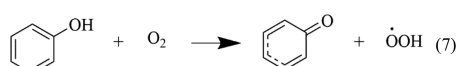
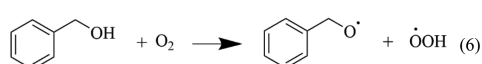
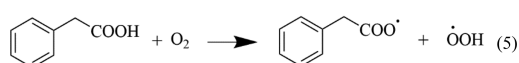
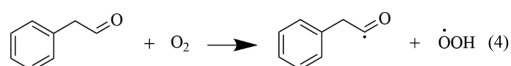


Figure 8. IRC calculation of reaction 10.

form $\cdot\text{OH}$. In addition, the hybridization mode of C7 also changed, that is, sp^3 hybridization changed to sp^2 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 $-\text{C}\cdot$, whose chemical property is very active and will continue to take part in the subsequent chain reaction.

According to the calculation, the ΔH is 96.60 kJ/mol and the ΔE 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.



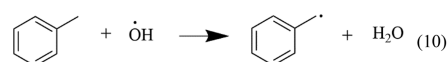
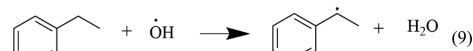
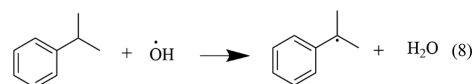
Taking $-\text{CHO}$ as an example and $\text{Ar}-\text{CH}_2-\text{CHO}$ as the model compound, the mechanism of the reaction between $-\text{CHO}$ and O_2 was calculated by quantum chemical theory. The

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 $-\text{CO}\cdot$, which can be used as a new active center for chemical O_2 absorption and dealdehyde reaction.

The calculated results show that the ΔH of the reaction is 136.87 kJ/mol and the ΔE 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 $\text{C}-\text{H}$ to generate aliphatic radicals and H_2O . Based on these, the reaction sequences between $-\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$, and $\cdot\text{OH}$ are shown in reactions 8–10.



Taking $-\text{CH}_3$ as an example and $\text{Ar}-\text{CH}_2-\text{CH}_3$ 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 C_8-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 $\text{O}_{19}-\text{H}_{16}$

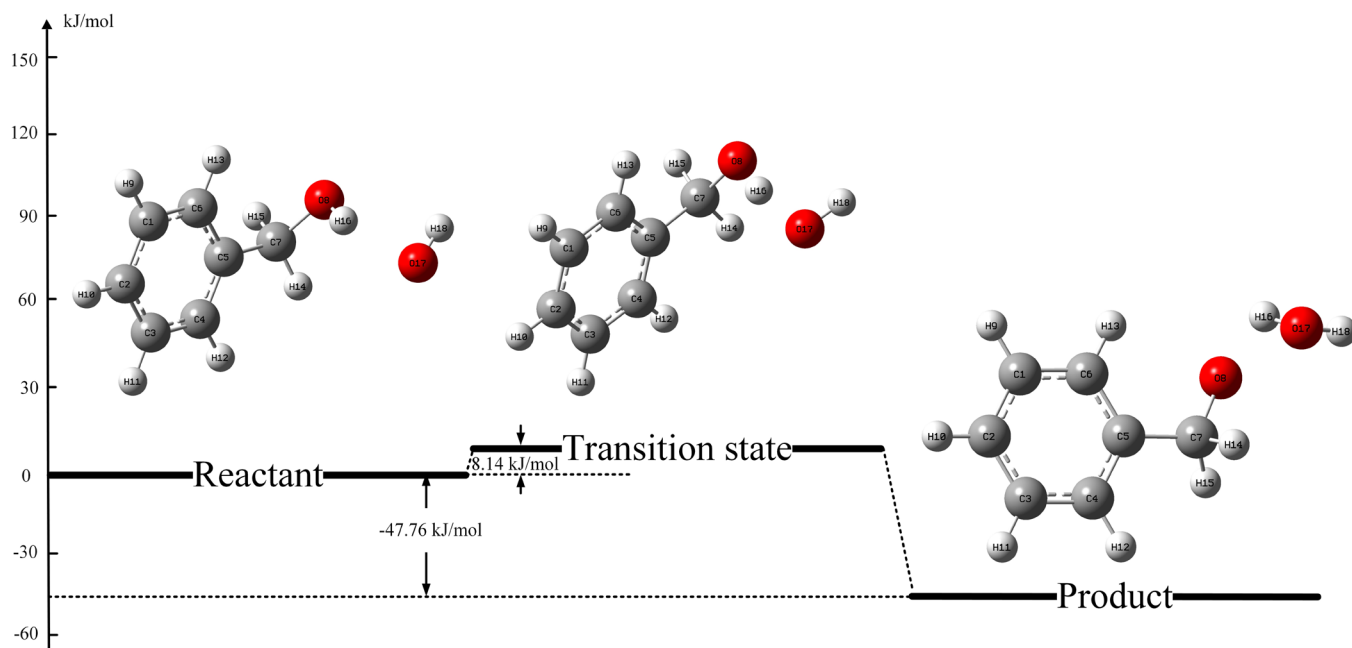
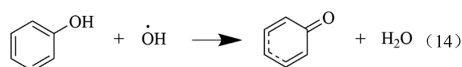
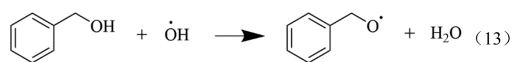
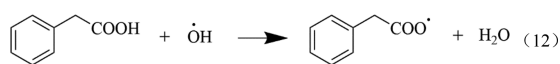
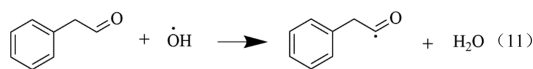


Figure 9. IRC calculation of reaction 13.

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 $\cdot\text{OH}$ 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 $\cdot\text{OH}$. Free $\cdot\text{OH}$ 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 $-\text{ROH}$ as an example and $\text{Ar}-\text{CH}_2-\text{OH}$ as the model compound, the mechanism of the reaction between $-\text{ROH}$ and $\cdot\text{OH}$ 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 $-\text{C}\cdot$, $-\text{CH}\cdot$, $-\text{CH}_2\cdot$, $-\text{RO}\cdot$, $-\text{ArO}\cdot$, $-\text{COO}\cdot$, $-\cdot\text{CO}$, and $-\text{O}-\text{O}\cdot$. 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.

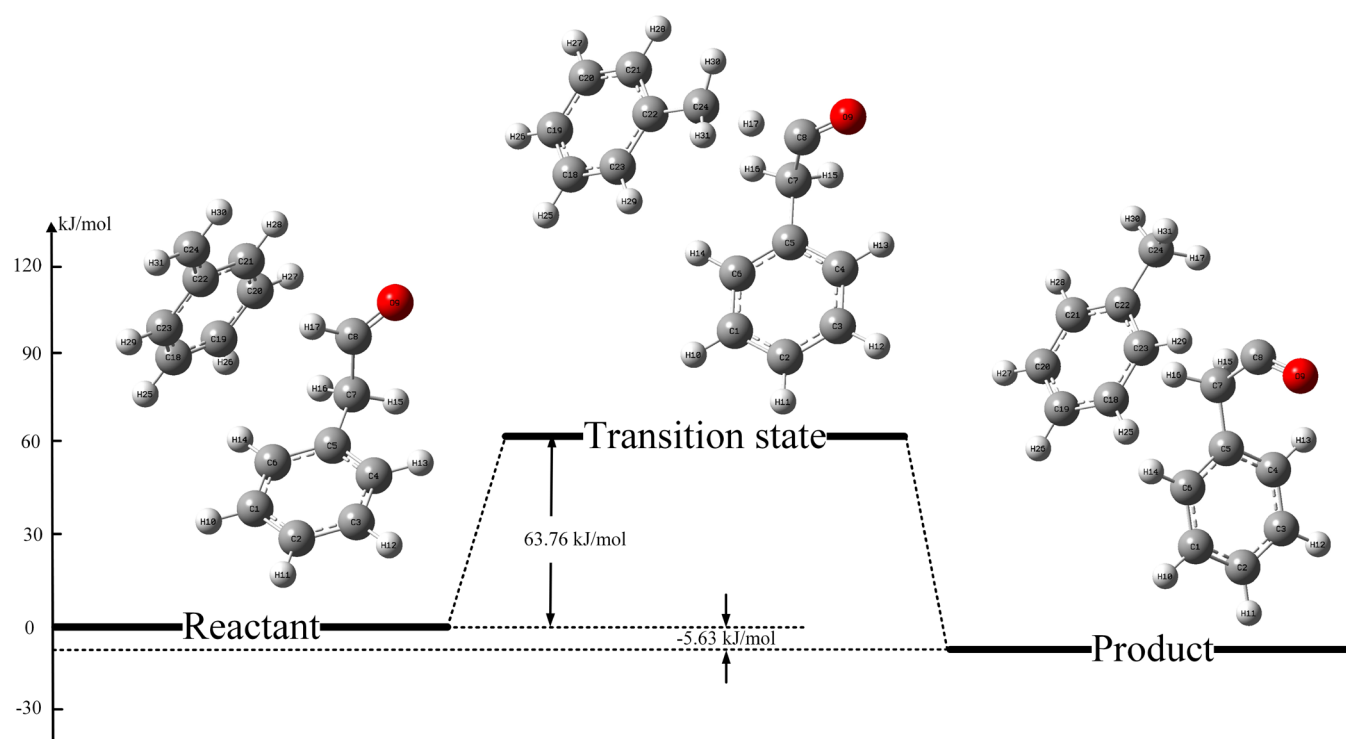
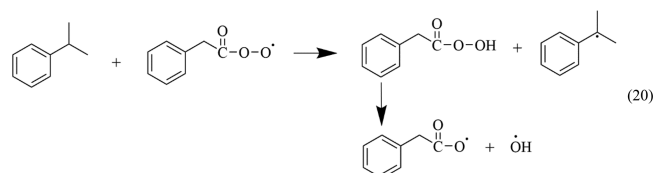
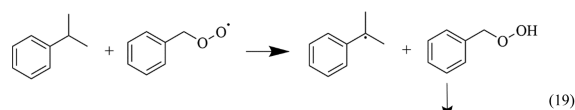
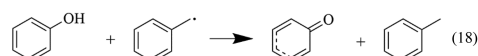
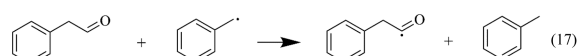
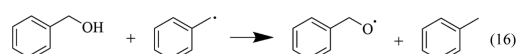


Figure 10. IRC calculation of reaction 17.



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 $-\text{CH}_2$ 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 σ 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 $-\text{CH}_2$ 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 ΔH is -5.63 kJ/mol, and ΔE 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.

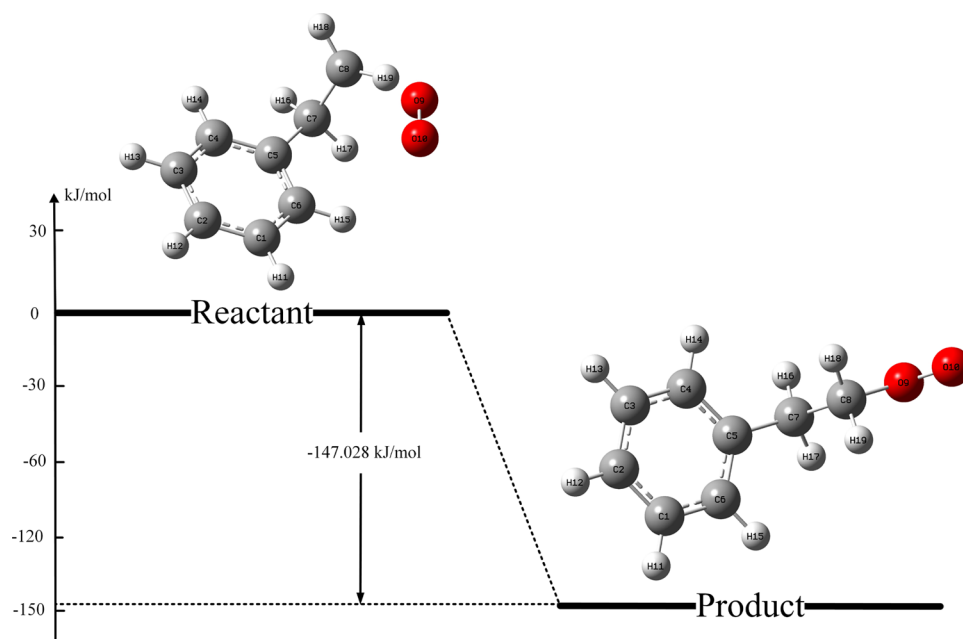
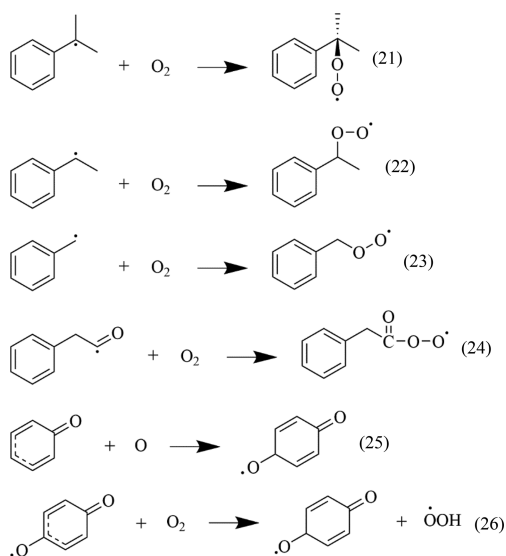


Figure 11. IRC calculation of reaction 23.



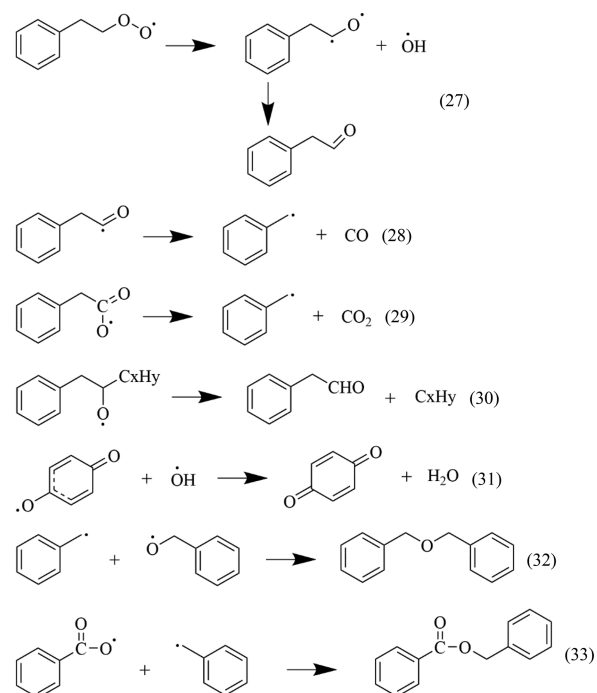
Take the reaction of $-\text{CH}_2$ adsorbing O_2 as an example and $\text{Ar}-\text{CH}_2-\text{CH}_2$ as the model compound, and the mechanism of the reaction between $-\text{CH}_2$ and O_2 was calculated by quantum chemical theory. The structural parameters and energy changes in the reaction process are shown in Figure 11.

Before the reaction occurs, O_2 is adsorbed on the $\text{Ar}-\text{CH}_2-\text{CH}_2$ molecule, the distance between C8 and O9 is 2.35 Å, and the bond length of O9–O10 is 1.214 Å. When the reaction occurs, the O_2 molecule moves toward the $-\text{CH}_2$. The O9 links to C8 to form a peroxide radical, in which the equilibrium distance of C8–O9 shortens to 1.456 Å and that of O9–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 ΔE is 0, and it can occur directly at room temperature and pressure. The ΔH 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 $\cdot\text{OH}$, and the reactions between radicals. Therefore, the reaction sequences are proposed as shown in reactions 27–33.



Take the dealdehyde reaction of $-\text{CO}\cdot$ generating CO as an example and $\text{Ar}-\text{CH}_2-\text{CO}\cdot$ 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 sp^3 to sp^2 as soon as C7–C8 breaks, and the configuration of H16–C7–H15

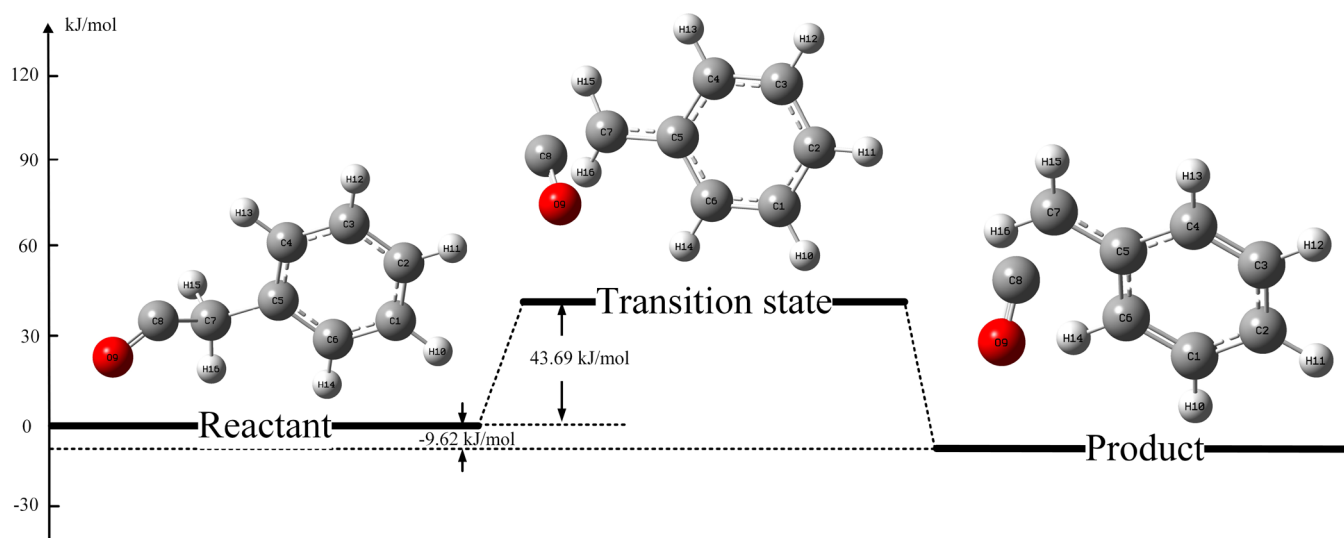


Figure 12. IRC calculation of reaction 28.

Table 2. ΔE and ΔH of All Reactions

number	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
ΔE (kJ/mol)	106.68	147.77	160.19	149.53	113.44	181.28	98.01	7.98	9.14	10.62	32.41
ΔH (kJ/mol)	96.60	72.31	65.47	136.87	-21.09	177.23	88.67	-50.44	-53.15	-40.32	17.66
number	E12	E13	E14	E15	E16	E17	E18	E19	E20	E21	E22
ΔE (kJ/mol)	6.47	8.14	1.97	52.31	46.23	63.76	40.12	57.89	44.06	0	0
ΔH (kJ/mol)	10.84	-47.76	-124.48	50.09	24.48	-5.63	-11.47	9.02	-26.69	-149.72	-147.91
number	E23	E24	E25	E26	E27	E28	E29	E30	E31	E32	E33
ΔE (kJ/mol)	0	0	0	65.78	57.69	43.69	73.11	56.89	5.26	0	0
ΔH (kJ/mol)	-147.02	-121.04	-51.47	-34.19	10.13	9.62	55.69	28.07	-123.68	-6.42	-4.55

changes from the original structure to the planar structure. At the same time, the outer electrons of C8 and O9 transfer and redistribute. The electrons in the outermost orbitals of C8 and O9 transfer; as a result, their lone pair electrons pair with each other to form a $2px\pi$ bond, a $2px\sigma$ bond, and a $2py\pi$ coordination bond. So far, the stable CO structure completely forms. According to the thermodynamic parameters, the ΔE of 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 spontaneous combustion. The ΔH is -9.62 kJ/mol, so the heat absorption is low. Although the effect of this reaction on the self-heating of coal is not obvious, it is the main source of CO during low-temperature oxidation of coal.^{41,42}

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 $\Delta E = 0$, the reaction can occur spontaneously. When $\Delta E < 40$ kJ/mol, the reaction can occur at room temperature and pressure ($T < 30$ °C). When 40 kJ/mol $< \Delta E < 180$ kJ/mol, the reaction can occur at 30–70 °C. When $\Delta E > 180$ 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 O_2 (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 $\cdot OH$ 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 $\cdot OH$ 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 H_2O . Although the activation energy required for these reactions is very low (1.97–32.41 kJ/mol) and can occur spontaneously at room temper-

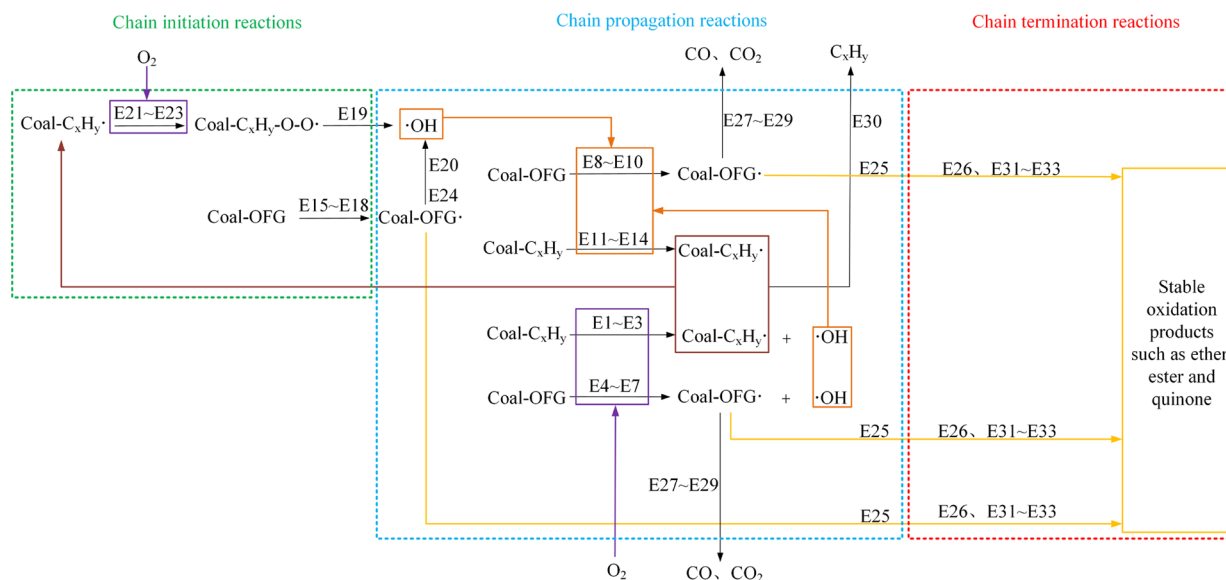


Figure 13. Chain circulation reaction mechanism of coal molecules.

ature, they will not occur before E19 due to the lack of key active groups $\cdot\text{OH}$. 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 $-\text{CO}$ and ketone compounds, which will continue to adsorb O_2 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 $\cdot\text{OH}$. The $\cdot\text{OH}$ 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 $\cdot\text{OH}$, while the oxygen-containing radicals can undergo desorption reactions (E28–E30) to generate various index gases, such as CO , CO_2 , and C_xH_y . 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, O_2 can react with various functional groups to generate a large number of radicals and $\cdot\text{OH}$ 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,⁴⁶ 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 $-\text{CH}_2$ in the aliphatic structure is significantly higher than those of $-\text{CH}$ and $-\text{CH}_3$, indicating that the aliphatic structures are mostly long chains, while the oxygen-containing functional groups are mostly $-\text{ROH}$, $-\text{ArOH}$, $-\text{COOH}$, $-\text{CHO}$, and $-\text{O}-$.
- (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 $-\text{COOH}$ (0.514) > $-\text{ArOH}$ (0.503) > $-\text{ROH}$ (0.482) > $-\text{CH}$ (0.249) > $-\text{CH}_2$ (0.237) > $-\text{CH}_3$ (0.232) > $-\text{CHO}$ (0.150). Therefore, when reacting with O_2 , 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 peroxide 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 peroxide 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.⁴⁷ 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.⁴⁸ 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.^{49,50} 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.^{39,51} In this paper, the van der Waals distribution of molecular ESP was used to predict the electrophilic and nucleophilic reaction centers of molecules.⁵²

$$V_{\text{tot}}(r) = V_{\text{nuc}}(r) + V_{\text{ele}}(r) \\ = \sum_A \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r')}{|r - r'|} dr'$$

where R_A is the nucleus coordinates of atom A, Z_A 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.²⁶ 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 (ΔH) and activation energy (ΔE) are two parameters of great importance.⁵³ ΔE can indicate the difficulty of the reaction, which is obtained by the

difference between the total energy of the transition state and reactant. ΔH 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.

ACKNOWLEDGMENTS

This study was funded by the National Key R&D Program of China (grant no. 2016YFC0801800), the National Natural Science Foundation of China (grant nos. 51704299, 51804311, and 52074304), and the Open Research Fund of State Key Laboratory of Coal Mine Safety Technology (project no. sklcmst102).

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