Quantum Chemical Calculation of the Effects of H₂O on Oxygen Functional Groups during Coal Spontaneous Combustion

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ABSTRACT: The effects of H₂O on the low-temperature oxidation characteristics of coal have always been one of the keys in the research of coal spontaneous combustion, but most studies rely on experiments for macroscopic derivation, and theoretical researches at the microlevel are rarely mentioned. In this paper, phenylacetaldehyde, phenylethyl alcohol, phenylacetic acid, and ethylbenzene hydroperoxide were used as modeling compounds of coal molecules containing aldehyde (−CHO), alcohol hydroxyl (−OH), carboxyl (−COOH), and peroxide (−C−O−OH). The surface electrostatic potential (ESP), electron density of atoms in molecules (AIM), and reduced density gradient (RDG) of coal molecules were calculated by density functional theory (DFT), and the thermokinetic parameters of low-temperature oxidation of coal molecules with or without H₂O were analyzed. The results show that the extreme positive and negative ESPs are located at the H and O atoms of oxygen functional groups (OFGs), respectively, which are the active sites for H₂O adsorption. The AIM and RDG show that the phenylacetaldehyde···H₂O complexes have two kinds of adsorption configurations with two and three hydrogen bonds, and that the phenylethyl alcohol···H₂O complexes also have two kinds of adsorption configurations with one and three hydrogen bonds, and that both phenylacetic acid···H₂O and ethylbenzene hydroperoxide···H₂O only have one adsorption configuration, forming two and three hydrogen bonds, respectively. According to electron density ρ(r) and potential energy density V(r), the adsorption strength of H₂O by four kinds of oxygen functional groups is ranked as −C−O−OH > −COOH > −OH > −CHO. The thermokinetic parameters show that H₂O can increase the activation energy (ΔE) of the oxidation reactions of phenylacetaldehyde and phenylethyl alcohol, which can inhibit the reaction and decrease the activation energy (ΔE) of the oxidation reaction of phenylacetic acid and ethylbenzene hydroperoxide, which can promote the reactions.

1. INTRODUCTION

Coal is the main energy source and raw material in the world.¹⁻³ Coal spontaneous combustion is a common disaster phenomenon in the process of coal mining, storage, and utilization, and it could generate CO, CO₂, SO₂, NO, and other toxic and harmful gases. Serious coal spontaneous combustion disaster can even cause coalfield fire and gas explosion, which has a major threat to the safety of staffs’ life and coal mine production.⁴⁻⁵ Therefore, research of the coal spontaneous combustion mechanism and prevention technology is still the key.

Most of the available coal reserves in the world have low metamorphic degree. Compared with high metamorphic coal, low metamorphic coal has a low calorific value, but it has low mining cost, high reactivity, and less sulfur, nitrogen, heavy metals, and other environmental pollutants.⁹ However, low metamorphic coal generally has high H₂O content, leading to more heat loss, large amounts of flue gas, and difficult transportation, which seriously limits the large-scale exploitation and utilization.¹⁰¹¹ The coal molecular structure is very complex and has a lot of pores, so the effect of H₂O on coal spontaneous combustion is multidimensional.¹² H₂O in coal exists in two forms: free and combined H₂O. On the one hand, free H₂O can condense in coal pores and fissures to form a water film on the surface of coal particles, which hinders the dissolution and diffusion of O₂, and the rate of the coal oxidation reaction also decreases.¹³ The evaporation and heat absorption of free H₂O will also hinder the heat storage of coal.¹⁴ On the other hand, H₂O can form complexes with coal molecules under a large number of noncovalent and intermolecular interactions (including hydrogen bonding, van der Waals interaction, and charge transfer) and participate in the oxidation reactions.

The influence of H₂O on the oxidation characteristics of coal at a low temperature has been one of the keys in the study of coal spontaneous combustion. Many scholars have adopted exper-
imental methods for its study, including thermogravimetry (TG), proton nuclear magnetic resonance (1H NMR), differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectrometry.\textsuperscript{19−21} Zhang et al.\textsuperscript{22} studied the influence of H\textsubscript{2}O on coal spontaneous combustion characteristics using DSC, finding that with the increase of H\textsubscript{2}O, the critical temperature of coal spontaneous combustion is basically unchanged, but the time required for coal spontaneous combustion increases, and the coal spontaneous combustion tendency gradually decreases. Ghosh et al.\textsuperscript{23} conducted the same research by FTIR, finding that the initial stage of coal oxidation mostly occurs on the surface of coal, and the types and quantities of oxygen functional groups (OFGs) and H\textsubscript{2}O content are the biggest factors affecting the coal spontaneous combustion characteristics. Küçük\textsuperscript{24} Kadioğlu\textsuperscript{25} and Beamish\textsuperscript{26} found that the oxidation reaction rate of dry coal is the fastest, and the number of OFGs in the wet coal sample is basically the same as that of dry coal, but with the decrease of particle size and the increase of H\textsubscript{2}O content, the spontaneous combustion tendency of coal gradually increases. However, other scholars believe that H\textsubscript{2}O can promote and inhibit coal oxidation at a low temperature at the same time. Vance\textsuperscript{27} applied the adiabatic oxidation method to explore the oxidation process of coal samples with different H\textsubscript{2}O contents in the temperature range of 40−140 °C. The results show that the oxidation reaction rate is the fastest when the H\textsubscript{2}O content is 7% in the same temperature range but decreases when the H\textsubscript{2}O content changes. Clemens et al.\textsuperscript{13} also believed that when a small amount of combined H\textsubscript{2}O exists, the oxidation reaction of coal could be promoted, and the oxidation reaction rate of coal with 5−10% H\textsubscript{2}O content is faster than that of completely dry coal. Gao\textsuperscript{28,29} studied the adsorption characteristics of lignite molecules on H\textsubscript{2}O by the density functional theory (DFT) method. The results showed that H\textsubscript{2}O molecules tend to adsorb around OFGs, where carboxyl has the strongest adsorption capacity and hydrogen bonds play a leading role.

With the development of computer technology, the quantum chemical simulation method has been applied to the study of coal spontaneous combustion; the active sites, reaction pathways, and thermodynamic parameters can be determined at the microscopic level by this method.\textsuperscript{30−32} Shi et al.\textsuperscript{33} analyzed eight active groups in coal molecules and obtained their optimized geometric configuration and thermodynamic parameters by DFT-B3LYP and ONIOM methods and explored the initial oxidation mechanism of each active group at room temperature. Wu et al.\textsuperscript{11} constructed the coal molecular model and simulated the process of H\textsubscript{2}O adsorbing on coal molecules, then explored the interactions between H\textsubscript{2}O and functional groups. The results showed that hydrogen bonds and van der Waals forces play an important role. Yuan\textsuperscript{34} studied the upgrade of coal by H\textsubscript{2}O by combining experiments with computational quantum chemistry, and it was found that H\textsubscript{2}O could inhibit and promote coal oxidation at a low temperature.

![Figure 1. ESP isosurface maps of coal molecules. (a) Maximum and minimum ESP of phenylacetaldehyde, (b) maximum and minimum ESP of phenylethyl alcohol, (c) maximum and minimum ESP of phenylacetic acid, and (d) maximum and minimum ESP of ethylbenzene hydroperoxide.](https://doi.org/10.1021/acsomega.1c03673)
In the past, scholars generally applied experimental methods to study the role of H2O in the process of coal oxidation at a low temperature. The interaction mechanisms between H2O and the active groups in coal molecules only rely on macroscopic analyses and inferences, and little is known about the descriptions of hydrophilicity of active groups and the noncovalent interactions between H2O and coal at the molecular level. According to the reaction mechanisms of coal spontaneous combustion, the DFT of the quantum chemical calculation method is used to construct the simplified models of coal molecules and to analyze the hydrogen bonds and the interaction mechanisms of coal--H2O complexes, and the reaction pathways of active groups in the presence and absence of H2O are compared. Through the comparison of thermokinetic parameters, the influence mechanism of H2O in the process of coal oxidation at a low temperature is revealed at the microlevel, which can provide theoretical reference for accurate prevention and control of coal spontaneous combustion disaster.
2. RESULTS AND DISCUSSION

2.1. Wave Function Analyses. 2.1.1. Optimized Configurations and Electrostatic Potential (ESP) Analyses of Coal Molecules. When H2O is close to the coal molecule, the positive and negative ESP regions on the surface of H2O and coal molecule attract each other to form a stable complex, which is neutralized by the interactions. The noncovalent hydrogen bond plays a leading role in this process. Relevant literature shows that the positions of the extreme positive ESP (such as the H atom in the OFG) are possible hydrogen bond donors, while the positions of the extreme negative ESP (such as the O atom in the OFG) are possible hydrogen bond acceptors. Therefore, the ESP analysis of coal molecules can provide a reference for establishing the stable structure of the coal–H2O complex.

In this paper, the ESP (electronic density = 0.001 au) of coal molecules is analyzed by the Multiwfn 3.7 software. First, the minimum energy configuration and wave function file of each coal molecule are obtained at the level of density functional M062X-D3/6-31G(d,p), and the ESP isosurface maps are drawn by the VMD1.9.4 program, as shown in Figure 1.

Figure 2. BCPs, bond pathways, and RDG analyses of coal–H2O complexes. (a) Phenylacetaldehyde–H2O complex 1, (b) phenylacetaldehyde–H2O complex 2, (c) phenylethyl alcohol–H2O complex 1, (d) phenylethyl alcohol–H2O complex 2, (e) phenylacetic acid–H2O complex, and (f) ethylbenzene hydroperoxide–H2O complex.
In general, the ESPs of C and H atoms in coal molecules are positive (red), and nucleophilic reactions are easy to occur at these positions, while the ESP in the region of the O atom is negative (blue), which is prone to electrophilic reactions. The extreme negative ESPs of phenylacetaldehyde, phenylethyl alcohol, phenylacetic acid, and ethylbenzene hydroperoxide are located at the O atom of $\text{CH}_2\text{O}$, $\text{OH}$, $\text{COOH}$, and $\text{C}=\text{O}$–$\text{OH}$, and the values are $-33.869$, $-34.533$, $-40.385$, and $-22.884$ kcal/mol, respectively. The benzene ring of each coal molecule has medium negative ESPs due to the enrichment of electron clouds. However, the extreme positive ESPs of the coal molecules are located at the H atoms of OFGs, and the values are $19.744$, $45.382$, $64.117$, and $20.475$ kcal/mol, respectively. The results show that the H and O atoms of OFGs are the dominant adsorption sites of H$_2$O.

2.1.2. Atoms in Molecules (AIM) and Reduced Density Gradient (RDG) Analyses of Coal--H$_2$O Complexes. Based on the results of coal molecular structure optimizations and ESP analysis, the H atom (or O atom) of H$_2$O is placed in the extreme negative (or positive) region of the coal molecule, and the structure of the coal--H$_2$O complex is optimized. It is worth noting that VMD1.9.4 program is used to draw the AIM analysis diagram. The colorful map of RDG corresponding to the electron density $\rho(r)$ multiplied by the eigenvalue sign($\lambda_2(r)$) of the Hessian matrix is also drawn according to the output file of Multiwfn 3.7.

After optimization analysis, it can be known that there are two optimal adsorption configurations of the phenylacetaldehyde::H$_2$O complex, and the bond critical points (BCPs), bond pathways, and RDG analyses diagrams are shown in Figure 2a,b. There are also two optimal adsorption configurations of the phenylethyl alcohol::H$_2$O complex, and the BCPs, bond pathways, and RDG analyses diagrams are shown in Figure 2c,d. There is only one optimal adsorption configuration of the phenylacetic acid::H$_2$O complex and ethylbenzene hydroperoxide::H$_2$O complex, respectively, and the BCPs, bond pathways, and RDG analyses diagrams are shown in Figure 2e,f. Both the BCPs and the corresponding bond pathways between BCPs and two interacting atoms (H and O atom) can be found in the figures, which indicates that hydrogen bonds exist. The RDG analysis results of each complex can be used to determine the multiple weak interactions between coal molecules and H$_2$O by the colorful isosurface map according to the value of sign($\lambda_2$)/$\rho$. The sign of sign($\lambda_2$)/$\rho$ can be used to distinguish attraction and mutual exclusion, while its absolute value can be used as an index of bonding strength. When sign($\lambda_2$)/$\rho$ is negative and the absolute value is large, it indicates attraction (such as hydrogen bond and halogen bond); when sign($\lambda_2$)/$\rho$ is positive and the absolute value is large, it means mutual exclusion (such as the steric effect in the ring and cage); and when sign($\lambda_2$)/$\rho$ is close to 0, it means a weak van der Waals effect.

There are two spikes in the ranges of $-0.03$ to $-0.02$ and $-0.02$ to $-0.01$ au for complex (a), which correspond to the bond pathways La1 (O18--H19--O16) and La2 (O18--H17--C8), respectively. It shows that phenylacetaldehyde and H$_2$O are connected by two hydrogen bonds and the isosurface of La1 is blue, while the isosurface of La2 is green, so the strength of La1 is greater than that of La2. Complex (b) has one spike in the range of $-0.03$ to $-0.02$ au corresponding to the bond pathway Lb1 (O16--H20--O18), and there are two spikes in the range of $-0.02$ to $-0.01$ au, which correspond to the bond pathways Lb2 (O18--H15--C7) and Lb3 (O18--H12--C4). The results indicate that the hydrogen bond strength is ordered as Lb1 > Lb2 > Lb3 according to the color of the isosurfaces. There is one spike in the range of $-0.03$ to $-0.02$ au for complex (c) corresponding to the blue isosurface bond pathway Lc1 (O9--H20--O21). There is one spike in the range of $-0.02$ to $-0.01$ au corresponding to the bond pathway Lc2 (O21--H15--C7) with a dark green isosurface, and there is also one spike in the range of $-0.01$ to $0$ au corresponding to the light green isosurface bond pathway Lc3 (O21--H13--C4). The results indicate that there are three hydrogen bonds between phenylethyl alcohol and H$_2$O and their strength order is Lc1 > Lc2 > Lc3. There is only one spike in the range of $-0.03$ to $-0.02$ au for complex (d) corresponding to the blue isosurface bond pathway Ld1 (O21--H19--O9) whose strength is strong. In the ranges of $-0.04$ to $-0.03$ and $-0.02$ to $-0.01$ au, complex (e) has two spikes corresponding to the bond pathways Le1 (O19--H18--O9) and Le2 (O19--H16--C7), indicating that phenylacetic acid and H$_2$O are connected by two hydrogen bonds and the strength of Le1 is greater than that of Le2. There are two spikes in the range of $-0.03$ to $-0.02$ au for complex (f), which correspond to the bond pathways Lf1 (O21--H20--O10) and Lf2 (O9--H23--O21), respectively, and the RDG isosurface of the complex is blue, so the intensity is high.

The AIM quantitative analyses of coal::H$_2$O complexes are shown in Table 1. According to different donors, hydrogen bonds can be divided into two types: O--H--O and O--H--C. The distance between H and O atoms of O--H--O is 1.80--1.94 Å, and the distance between H and O atoms of O--H--C is 2.33--2.71 Å. Both the types of H--O distances are significantly smaller than the sum of the van der Waals radii of H and O atoms.
so the existence of hydrogen bonds is verified. The hydrogen bond angles of O···H−O and O···H−C are 145.28°−174.79° and 109.71°−142.98°, respectively. The results show that the distances of O···H−O are generally smaller than those of O···H−C, and the hydrogen bond angles are just the opposite, indicating that the hydrogen bonds with smaller distance and larger angle have greater bonding strength.

Figure 3. Oxidation reaction processes of (a) phenylacetaldehyde and phenylacetaldehyde···H2O complexes (b) 1 and (c) 2.
To calculate the energies of hydrogen bonds, the electron density ρ(r) and potential energy density V(r) of BCPs are calculated and shown in Table 1. The interacting ρ(r) of O--H--O and O--H--C are distributed in the ranges of 0.0242–0.0342 and 0.0064–0.0128 au, respectively. The relationship between the hydrogen bond energy (E) and V(r) can be expressed as $E = V_{\text{HOO}}(\text{ECP})/2$, and the V(r) of O--H--O and O--H--C are −27.032 to −35.562 and −5.249 to −12.598 kJ/mol, respectively. The literature points out that the stronger hydrogen bond formed by H2O and hydroxyl (−OOH radical) is easy to break in the subsequent reaction to form the *OH radical. Comparing the transition-state structure parameters of the three reaction processes, it can be seen that the adsorption of H2O on −CHO causes regular changes in the transition state: the distance between the transferred H17 and O18 bond gradually extends. After H2O adsorbs on −CHO, the oxidation activation energies of the two complexes increase from 149.53 to 169.98 and 166.69 kJ/mol, respectively.

2.2. Effects of H2O on the Characteristics of Coal Oxidation. Based on the above conclusions, the transition-state (TS) (Berny) method is used to find the transition-state structures of reactions 1–4, and compared with the reactions without H2O, and the thermokinetic characteristics of the effects of H2O on the reactions were analyzed. Since O2 has a trilinear structure, the spin multiplicity is set to 3, and the calculation is carried out in the open-shell system. When the transition-state structure has a unique virtual frequency and the vibration directions correspond to the reactant and product, the transition-state search can be considered correct.

2.2.1. Effects of H2O on the Reaction of Aldehyde with O2. Figure 3a shows the intrinsic reaction coordinate (IRC) curve of the oxidation reaction of phenylacetaldehyde and the configurations of the reactants, transition states, and products. The active site of the reaction is the H17 atom of aldehyde, and O2 first adsorbs near the H17 atom and abstracts it to form the *OOH radical.

Figure 3b,c shows the IRC curves of the oxidation reactions of two phenylacetaldehyde−H2O complexes with O2 and the configurations of reactants, transition states, and products. In these two transition states, H2O maintains O−H−O and O−H−C hydrogen bonds with aldehydes, and the adsorption positions of O2 are basically the same as those before H2O adsorption, so do the active sites and reaction pathways of these reactions.

Table 2 shows the structural and thermokinetic parameters of the coal molecules in each state during the three reactions. It is found that the C8−H17 bond breaks first and the H17 atom moves toward the O18 atom, which indicates that the H17 atom has broken away from the bonding of the C8 atom. Compared with the transition state, the O18−H17 bond of the product further shortens, while the O18−O19 bond gradually extends. This phenomenon indicates that the O18−O19 bond of the *OOH radical is easy to break in the subsequent reaction to form the *OH radical. Comparing the transition-state structure parameters of the three reaction processes, it can be seen that the transition-state structure of the reaction of phenylacetaldehyde and the con-
between the lone pair electrons of O atom and the $\sigma$ orbital of adjacent C–H bonds will weaken and the strengths of O–H or C–H bonds will increase, leading to an enhancement of the stability of the carbon radical and an increase in $\Delta E$ of the reaction.

2.2.3. Effects of H$_2$O on the Reaction of Carboxyl with O$_2$.

Figure 5a,b shows the IRC curves of the reactions of (a) phenylethyl alcohol and phenylethyl alcohol···H$_2$O complexes (b) 1 and (c) 2.
Table 3. Changes of Structure and Thermodynamic Parameters before and after adsorption of H₂O by −OH

| categories | state       | R(O9−H19) (Å) | R(O20−H19) (Å) | R(O20−O21) (Å) | single-point energy E (hartree) | activation energy ΔE (kJ/mol) | enthalpy change ΔH (kJ/mol) |
|------------|-------------|----------------|----------------|----------------|-------------------------------|------------------------------|-----------------------------|
| phenylethanol | reactant     | 0.967          | 2.445          | 1.215          | −536.425420                  | 181.29                       | 177.23                      |
|             | transition state | 1.529          | 1.038          | 1.318          | −536.356372                  |                              |                             |
| phenylethanol−H₂O complex 1 | product     | 1.714          | 1.002          | 1.332          | −536.357916                  |                              |                             |
|             | reactant     | 0.964          | 2.381          | 1.198          | −612.587762                  | 220.36                       | 207.86                      |
|             | transition state | 1.504          | 1.033          | 1.295          | −612.503833                  |                              |                             |
| phenylethanol−H₂O complex 2 | product     | 1.771          | 0.991          | 1.311          | −612.508592                  |                              |                             |
|             | reactant     | 0.966          | 2.290          | 1.197          | −612.586659                  | 216.14                       | 194.71                      |
|             | transition state | 1.475          | 1.033          | 1.296          | −612.504336                  |                              |                             |
|             | product      | 1.685          | 0.999          | 1.307          | −612.512499                  |                              |                             |

phenylacetic acid and phenylacetic acid−H₂O complex with O₂, as well as the reactant, transition state, and product configurations. In the transition state of the phenylacetic acid−H₂O complex reaction, H₂O also maintains O−H−O and O−H−C hydrogen bonds with carboxyl and the active site and reaction pathway remain unchanged.

Table 4 shows the structural and thermokinetic parameters of coal molecules in the two reaction processes. The results indicate that the mechanisms of the reactions are similar to those of aldehyde and hydroxyl, where O₂ abstracts the H₁₈ atom resulting in the breaking of the O₉−H₁₉ bond and the formation of the °OOH radical. In the phenylacetic acid−H₂O complex, the O−H−O hydrogen bond formed by H₂O and carboxyl occupies the position of O₂ in the reaction process, which hinders the formation of a similar transition-state structure, so the position of O₂ reverses.

Comparing the transition-state structure parameters of the two reaction processes, it can be seen that both R(O9−H18) and R(O9−H18) of the phenylacetic acid−H₂O complex increase in varying degrees, while R(O19−O20) basically remains unchanged. After H₂O adsors on carboxyl, ΔE decreases to 186.28 kJ/mol. The above changes are mainly caused by the fact that the H₁₈ atom has positive charge, while the local charges on C₈ and O₉ atoms of carboxyl at the reaction center are both negative, and there is electrostatic mutual exclusion between them, which is not conducive to the stability of the transition state. However, when H₂O is adsorbed by phenylacetic acid, the electronegativity of C₈ and O₉ atoms weakens and the positive charge transfer to H₁₈ atoms increases due to the influence of hydrogen bonds, and the electrostatic mutual repulsion between C₉ and O₉ weakens, thus forming a more stable transition-state structure.

2.2.4. Effects of H₂O on the Decomposition Reaction of Peroxide. Peroxide is an initial product of low-temperature oxidation of coal and −C=O−OH can generate alkoxyl (−CO°) and hydroxyl (°OH) radicals, which is an important chain branching reaction in the process of coal oxidation. Wang et al. estimated that the dissociation energy of the −C=O−OH bond is about 180 kJ/mol, and believed that the reaction rate is very slow at a low temperature, which is the decisive step of the coal oxidation reaction. After inference, H₂O and ethylbenzene hydroperoxide can form one complex configuration, where H₂O can form two O−H−O hydrogen bonds with H₂O and O₉ in the peroxide, while H₂O can combine with the °OH radical coming from the decomposition of −C=O−OH to form a stable °OH−H₂O complex. Figure 6 shows the configurations of ethylbenzene hydroperoxide and ethylbenzene hydroperoxide−H₂O complex.

As shown in Table 5, R(O9−H10) of ethylbenzene hydroperoxide is 1.425 Å, while in the ethylbenzene hydroperoxide−H₂O complex, the bond length of O₉−O₁₀ increases to 1.453 Å, indicating that the strength of the O−O bond tends to weaken after H₂O adsorption. To describe the strength of the O−O bond accurately, the Laplacian bond order (LBO) and activation free energy (ΔG) of the decomposition reaction is calculated. Since there is no transition-state structure in the reaction, ΔG can be applied to replace ΔE to measure the difficulty of the reaction. The LBO has good applicability to organic systems, which can accurately describe the strength of the bond, and the smaller the bond level, the worse the thermal stability of the bond.

3. CONCLUSIONS

In this paper, phenylacetaldehyde, phenylethyl alcohol, phenylacetic acid, and ethylbenzene hydroperoxide were selected as coal molecular models containing −CHO, −OH, −COOH, and −C=O−OH, respectively. At the same time, coal−H₂O complex configurations and the influence mechanisms of H₂O on oxidation reactions of OFGs in coal at a low temperature were analyzed by the quantum chemistry method.

(1) ESP analyses show that the extreme negative ESPs of coal molecules are located at the positions of O atoms (red) in the OFGs, while the extreme positive ESPs are located at the positions of H atoms (blue) in the OFGs, so H and O atoms of OFGs are the active adsorption sites of H₂O by coal molecules, which easily form two kinds of hydrogen bonds (O−H−O and O−H−C), and the bond strengths of the former are significantly greater than those of the latter.

(2) Colorful RDG isosurface maps can be used to reflect the noncovalent interactions of coal−H₂O complexes accurately. AIM and RDG analyses show that there are two adsorption configurations of H₂O on phenylacetaldehyde, forming two and three hydrogen bonds, respectively, and the phenylethyl alcohol−H₂O complex also has two adsorption configurations, forming one and three hydrogen bonds, respectively, while there is only one adsorption configuration of H₂O adsorbing on phenylacetic acid and ethylbenzene peroxide, forming two and three hydrogen bonds, respectively. According to ρ(r) and V(r), the order of H₂O adsorption intensity by four OFGs is −C=O−OH > −COOH > −OH > −CHO.
TS searches and IRC verifications of the oxidation processes of phenylacetaldehyde, phenylethyl alcohol, phenylacetic acid, ethylbenzene peroxide, and their corresponding coal···H₂O complexes at a low temperature show that the adsorption of H₂O does not change the active sites and reaction pathways. However, under the action of hydrogen bonds, the adsorption of H₂O can promote the intramolecular electron transfer of coal molecules or change the adsorption configuration of O₂, which can change the reaction energy barrier. The calculation results show that H₂O increases ΔE of the phenylacetaldehyde and phenylethyl alcohol oxidation reactions and decreases ΔE of phenylacetic acid and ethylbenzene peroxide, which leads to inhibition and promotion effects, respectively.

Figure 5. Oxidation reaction processes of (a) phenylacetic acid and (b) phenylacetic acid···H₂O complex.
4. COMPUTATIONAL DETAILS

All of the computations in this study are completed in Gaussian 16A and GaussView 6.0 software.

4.1. Computational Contents. Alkyl side chains,42,43 bridge bonds,44 and OFGs32,45−48 are typical active groups on the coal surface. Alkyl side chains and bridge bonds are hydrophobic groups whose interactions with H2O are weak. The OFGs such as −CHO, −OH, −COOH, and −C−O−OH have strong hydrophilicity and can form hydrogen bonds with H2O, which are the dominant adsorption sites on the coal surface.47 Under the influence of hydrogen bonds, H2O and hydrophilic groups on the surface of coal first form coal···H2O complexes and participate in the coal oxidation reactions.

Since the coal macromolecular model is very complex, it is difficult to calculate the oxidation reaction process of each active group directly. According to previous studies, the properties of aromatic rings in coal molecules are very stable, and the chemical properties of active groups are basically not affected by aromatic rings.33 Therefore, coal small molecular models with hydrophilic groups such as phenylacetaldehyde, phenylethyl alcohol, phenylacetic acid, and ethylbenzene hydroperoxide are selected as the models of coal molecules instead of alkyl side chains and bridge bonds. According to our previous research3,32,47−49 aldehyde, hydroxyl, and carboxyl can react directly with O2 under certain conditions. O2 can directly capture the H atom of the active site in each OFG and generate radicals. Peroxide can also break easily to generate radicals due to its instability. Therefore, reaction eqs 1−4 can be obtained

![Chemical reaction images]

4.1.1. Optimization of Coal Molecular Structures. DFT is a kind of quantum chemical calculation method, which can be used to calculate the energy and electronic structure of the target system.50 The M062X method in DFT is used to describe the

| categories                  | state          | R(O9−H18) (Å) | R(O19−H18) (Å) | R(O19−O20) (Å) | single-point energy ΔE (hartree) | activation energy ΔE (kJ/mol) | enthalpy change ΔH (kJ/mol) |
|-----------------------------|----------------|---------------|----------------|----------------|----------------------------------|-----------------------------|----------------------------|
| phenylacetic acid           | reactant       | 0.964         | 2.884          | 1.198          | −610.203393                      | 229.78                      | 217.09                     |
|                             | transition state| 1.278         | 1.045          | 1.284          | −610.115875                      |                             |                            |
|                             | product        | 1.730         | 0.992          | 1.309          | −610.120704                      |                             |                            |
| phenylacetic acid···H2O complex | reactant     | 0.962         | 1.845          | 1.196          | −686.590913                      | 186.28                      | 165.96                     |
|                             | transition state| 1.398         | 1.127          | 1.282          | −686.518062                      |                             |                            |
|                             | product        | 1.586         | 1.011          | 1.308          | −686.525799                      |                             |                            |

**Table 4. Changes of Structure and Thermodynamic Parameters before and after Adsorption of H2O by −COOH**

**Table 5. Changes of Structure and Thermodynamic Parameters before and after Adsorption of H2O by −C−O−OH**

| categories                  | R(O9−O10) (Å) | LBO  | ΔG (kJ/mol) |
|-----------------------------|---------------|------|-------------|
| ethylbenzene hydroperoxide  | 1.425         | 0.073| 128.76      |
| ethylbenzene hydroperoxide···H2O complex | 1.453 | 0.068 | 112.24 |

**Figure 6. Configurations of (a) ethylbenzene hydroperoxide and (b) ethylbenzene hydroperoxide···H2O complex.**
electron exchange and related functional, and the Becke–Johnson damping function is used in combination with Grimme’s DFT-D3 algorithm for dispersion corrections, which can accurately calculate the noncovalent interactions. The 6-31G(d,p) basis set level is applied to optimize the geometry structure of the molecules. The spin multiplicity is the difference between the number of α and β electrons plus 1, and when the spin multiplicity is greater than 1, the calculation was carried out in the open-shell system.

4.1.2. Optimization of Coal···H$_2$O Complex Structures. The hydrogen bonds between hydrophilic groups on the coal surface and H$_2$O are mainly O···H–O and O···H–C, which correspond to the hydrogen bonds between the O atom in OFG and H$_2$O and the hydrogen bond between the O atom in H$_2$O and the C···H bond in the coal molecule, respectively. According to the characteristics of the hydrogen bond between OFG and H$_2$O, the H atom (O atom) of H$_2$O is placed toward the O atom (H atom) of OFG, and the geometry optimization is also carried out at the level of M062X-D3/6-31G(d,p) to obtain a stable coal···H$_2$O complex configuration with the lowest total energy.

4.2. Wave Function Analyses of Coal···H$_2$O Complexes. 4.2.1. ESP Analyses of Coal Molecules. The quantitative analysis of the molecular surface is of great significance to predict the reactive sites, the binding modes, and the thermokinetic properties of molecules. ESP is an index describing the interaction energy of charges in a molecular system at a certain point, which is defined as follows:

$$ V_{\text{int}}(r) = V_{\text{nuc}}(r) + V_{\text{el}}(r) = \sum_{A} \frac{Z_A}{r - R_A} - \int \frac{\rho(r')}{|r - r'|} \, dr' $$

where $R_A$ is the nucleus coordinate of atom $A$, $Z_A$ represents the nuclear charges, and $\rho(r)$ is the electron density.

4.2.2. Laplacian Bond Order (LBO) Analyses. Bond order is the simplest and most explicit index to measure the characteristics of atomic interactions, which is widely applied to predict the reactivity, aromaticity, and stability of molecules. LBO is a definition of the covalent bond order, which is obtained by integrating the negative value of the Laplacian function of electron density in the overlapping space of fuzzy atoms. It is quite suitable for organic systems and is closely related to the bond strength and has been proved that it has a good correlation with bond dissociation energy (BDE). LBO is defined as

$$ \text{LBO}_{A-B} = -10 \times \int_{V^2p < 0} w_A(r)w_B(r)V^2\rho(r) \, dr $$

where $w$ is a smoothly varying weighting function proposed by Becke, which represents fuzzy atomic space, while $w_A$ and $w_B$ correspond to fuzzy overlap space between $A$ and $B$. Note that the integration is only restricted to the negative part of $V^2\rho$. The physical basis of LBO is that the larger the magnitude of the integral of negative $V^2\rho$ in the fuzzy overlap space, the more intense the electron density concentrated in the bonding region and therefore the stronger the covalent bonding.

4.2.3. AIM Analyses. In the field of computational quantum chemistry, topological analysis is widely used to analyze real space functions, where the most typical theory is AIM. In the AIM, the critical points (CPs) are defined as the positions where the electron density gradients disappear. According to the sign of the eigenvalues of the Hessian matrix, CPs can be divided into four types. Among them, the bond critical points (BCPs) are the saddle points of first order in the scalar field of electron density whose Hessian matrix has two negative eigenvalues, most of which appear between the attractive atomic pairs. Nevertheless, the ring critical points have only one negative eigenvalue, which usually appears in the center of the ring structures, showing spatial repulsions. Bond pathways are defined as the maximum gradient pathways connecting a BCP and two attractive atoms, which can be used to reveal the atomic interaction pathways of all types of bonds.

4.2.4. RDG Analyses. The RDG is a basic dimensionless quantity used to identify noncovalent bond interactions, which can be applied to determine the region of weak intermolecular interactions. The RDG is shown in formula (7)

$$ \text{RDG}(r) = \frac{1}{2(3\pi^2)^{3/5}} \frac{|V\rho(r)|}{\rho(r)^{1/5}} $$

where $\rho(r)$ and $V\rho(r)$ are the electron density and its first derivative, respectively.

4.3. Thermokinetic Analyses of the Effects of H$_2$O on Coal Oxidation. 4.3.1. Transition-State (TS) Search and Intrinsic Reaction Coordinate (IRC) Analysis. According to the molecular characteristics of reactants and products, the TS (Berny) method is selected to find the transition state, and Opt (TS, Calcfc, Noeigen) is selected as the keyword to calculate the initial transition state. Opt = TS is one of the most important algorithms to search the transition state, where Calcfc represents calculating the Hessian matrix of the initial structure accurately, and Noeigen means that the number of eigenvalues of the Hessian matrix is not tested at every step in the optimization process.

The IRC method is usually used to analyze the reaction pathways. In the IRC analysis, the LQA algorithm is utilized to track 20 points in the directions of product and reactant by a step size of 0.05 b/s, and the Hessian matrix is calculated accurately every five steps, while other parameters remain default. It should be confirmed that the reactant and product have no virtual frequencies, the transition state has a unique virtual frequency, and the vibrational directions of transition state correspond to the reactant and product. It should be noted that both TS search and IRC analysis use the M062X-D3/6-31G(d,p) method.

4.3.2. Computation of Thermokinetic Parameters. Enthalpy ($H$) and activation energy ($\Delta E$) are two important characteristic parameters of the reaction activity in thermodynamics. The enthalpy change ($\Delta H$) is the difference between the $H$ of the product and the reactant. $\Delta E$ can be defined as the difference between the $H$ of the transition state and the reactant, that is, the maximum energy barrier to overcome for the reaction. For any reaction, $\Delta H > 0$ and $< 0$ indicate that the reaction is endothermic and exothermic, respectively, and $\Delta E > 0$ and $< 0$ indicate that the reaction is not spontaneous and spontaneous, respectively. Based on this theory, the thermodynamic parameters of the reactions proposed in this study are calculated.
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Notes
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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) Lu, X.; Zhu, H.; Wang, D.; Hu, C.; Zhao, H.; Huo, Y. Flow characteristic investigation of inhibition foam used for fire extinguishment in the underground goaf. Process Saf. Environ. Prot. 2018, 116, 159–168.
(3) 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, S23–S32.
(4) Guo, J.; Wen, H.; Zheng, X.; Liu, Y.; Cheng, X. A method for evaluating the spontaneous combustion of coal by monitoring various gases. Process Saf. Environ. Prot. 2019, 126, 223–231.
(5) Wang, H.; Chen, C. Experimental Study on Greenhouse Gas Emissions Caused by Spontaneous Coal Combustion. Energy Fuels 2015, 29, S213–S221.
(6) Wang, H.; Tan, B.; Shao, Z.; Guo, Y.; Zhang, Z.; Xu, C. Influence of different content of FeS2 on spontaneous combustion characteristics of coal. Fuel 2021, 288, No. 119582.
(7) Yao, Y.; Cheng, X.; Zhang, S.; Zhu, K.; Zhang, H.; Shi, L. Maximum smoke temperature beneath the ceiling in an enclosed channel with different fire locations. Appl. Therm. Eng. 2017, 111, 30–38.
(8) Zeng, Q.; Tiyp, T.; Wutkte, M. W.; Guan, W. Modeling of the equivalent permeability for an underground coal fire zone, Xinjiang region, China. Nat. Hazards 2015, 78, 957–971.
(9) Yu, Y.; Liu, J.; Hu, Y.; Gao, F.; Zhou, J.; Cen, K. The properties of Chinese typical brown coal water slurries. Energy Sources, Part A 2016, 38, 1176–1182.
(10) Yu, J.; Tahmasebi, A.; Han, Y.; Yin, F.; Li, X. A review on water in low rank coals: The existence, interaction with coal structure and effects on coal utilization. Fuel Process. Technol. 2013, 106, 9–20.
(11) Wu, J.; Liu, J.; Yuan, S.; Wang, Z.; Zhou, J.; Cen, K. Theoretical Investigation of Noncovalent Interactions between Low-Rank Coal and Water. Energy Fuels 2016, 30, 7118–7124.
(12) Tang, H.; Wang, X.; Feng, L.; Cao, Z.; Liu, X. Theoretical Study on the Interactions between the Lignite Monomer and Water Molecules. Russ. J. Phys. Chem. A 2015, 89, 1605–1613.
(13) Clemens, A. H.; Matheson, T. W. The role of moisture in the self-heating of low-rank coals. Fuel 1996, 75, 891–895.
(14) Hayashi, J.; Norinaga, K.; Kudo, N.; Chiba, T. Estimation of size and shape of pores in moist coal utilizing sorbed water as a molecular probe. Energy Fuels 2001, 15, 903–909.
(15) Larsen, J. W.; Baskar, A. J. Hydrogen bonds from a subbituminous coal to sorbed solvents. An infrared study. Energy Fuels 1987, 1, 230–232.
(16) Iino, M.; Takenohashi, T.; Shishido, T.; Saito, I.; Kumagai, H. Increase in extraction yields of coals by water treatment: Beulah-Zap lignite. Energy Fuels 2017, 21, 205–208.
(17) Liu, F.; Wei, X.; Fan, M.; Zong, Z. Separation and structural characterization of the value-added chemicals from mild degradation of lignites: A review. Appl. Energy 2016, 170, 415–436.
(18) Xiong, J. C.; Maciel, G. E. Interactions between pyridine and coal at the molecular level: Insights from variable-temperature (1)H NMR studies of pyridine-saturated coal. Energy Fuels 2002, 16, 497–509.
(19) Norinaga, K.; Kumagai, H.; Hayashi, J.-i.; Chiba, T. Classification of Water Sorbed in Coal on the Basis of Congelation Characteristics. Energy Fuels 1998, 12, 574–579.
(20) Miura, K.; Mae, K.; Li, W.; Kusakawa, T.; Morozumi, F.; Kumanou, A. Estimation of Hydrogen Bond Distribution in Coal through the Analysis of OH Stretching Bands in Diffuse Reflectance Infrared Spectrum Measured by in-Situ Technique. Energy Fuels 2001, 15, 599–610.
(21) Tahmasebi, A.; Yu, J.; Su, H.; Han, Y.; Lucas, J.; Zheng, H.; Wall, T. A differential scanning calorimetric (DSC) study on the characteristics and behavior of water in low-rank coals. Fuel 2014, 133, 245–252.
(22) Zhang, K.; You, C. Effect of Upgraded Lignite Product Water Content on the Propensity for Spontaneous Ignition. Energy Fuels 2013, 27, 20–26.
(23) Ghosh, A. K.; Choudhury, D. Spontaneous Combustion in Relation to Drying of Low Rank Coal. Int. J. Coal Prep. Util. 2020, 1–14.
(24) Kiiçik, A.; Kadioglu, Y.; Gulaboglu, M. S. A study of spontaneous combustion characteristics of a turkish lignite: particle size, moisture of coal, humidity of air. Combust. Flame 2003, 133, 255–261.
(25) Kadioglu, Y.; Varamaz, M. The effect of moisture content and air-drying on spontaneous combustion characteristics of two Turkish lignites. Fuel 2003, 82, 1685–1693.
(26) Beamish, B. B.; Hamilton, G. R. Effect of moisture content on the R70 self-heating rate of Callide coal. Int. J. Coal Geol. 2005, 64, 133–138.
(27) Vance, W. E.; Chen, X. D.; Scott, S. C. The rate of temperature rise of a subbituminous coal during spontaneous combustion in an adiabatic device: The effect of moisture content and drying methods. Combust. Flame 1996, 106, 261–270.
(28) 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, No. 116189.
(29) Gao, Z.; Deng, Y.; Yang, W.; Han, W. DFT study of water adsorption on lignite molecular surface. J. Mol. Model. 2017, 23, No. 27.
(30) Xiong, J.; Zhao, P.; Zheng, C. Theoretical study of different speciation of mercury adsorption on CaO (0 0 1) surface. Proc. Combust. Inst. 2009, 32, 2693–2699.
(31) Sun, X.; Hwang, J.-Y.; Xie, S. Density functional study of elemental mercury adsorption on surfactants. Fuel 2011, 90, 1061–1068.
(32) 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.
(33) 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.
(34) Yuan, S. Fundamental Study on Reaction Mechanism and Effect of Up Grading Treatment on Spontaneous Combustion of Lignite. Zhejiang University, 2018.
(35) Hagelin, H.; Murray, J. S.; Politzer, P.; Brinck, T.; Berthelot, M. Family-independent relationships between computed molecular sur-
face quantities and solute hydrogen bond acidity/basicity and solute-induced methanol O−H infrared frequency shifts. *Can. J. Chem.* 1995, 73, 483−488.

(36) Lu, T.; Chen, F. Multiwf: a multifunctional wavefunction analyzer. *J. Comput. Chem.* 2012, 33, 580−592.

(37) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* 1996, 14, 33−38.

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

(39) Espinosa, E.; Molins, E.; Lecomte, C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chem. Phys. Lett.* 1998, 285, 170−173.

(40) Salamone, M.; Bietti, M. Tuning reactivity and selectivity in hydrogen atom transfer from aliphatic C-H bonds to alkoxyl radicals: role of structural and medium effects. *Acc. Chem. Res.* 2015, 48, 2895−2903.

(41) 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. Sci.* 2003, 29, 487−513.

(42) Chen, L.; Qi, X.; Zhang, Y.; Xin, H.; Liang, Z. Reaction activity and mechanism of R3-CH structure oxidation in coal self-heating. *Fuel* 2021, 290, No. 119797.

(43) Qi, X.; Chen, L.; Xin, 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.

(44) Qi, X.; Wang, D.; Xue, H.; Jin, L.; Su, B.; Xin, H. Oxidation and Self-Reaction of Carboxyl Groups During Coal Spontaneous Combustion. *Spectrosc. Lett.* 2015, 48, 173−178.

(45) Qi, X.; Xue, H.; Xin, H.; Bai, Z. Quantum chemistry calculation of reaction pathways of carboxyl groups during coal self-heating. *Can. J. Chem.* 2017, 95, 824−829.

(46) Qi, X.; Xue, H.; Xin, H.; Wei, C. Reaction pathways of hydroxyl groups during coal spontaneous combustion. *Can. J. Chem.* 2016, 94, 494−500.

(47) Zhu, H.; Huo, Y.; He, X.; Wang, W.; Fang, S.; Zhang, Y. Molecular model construction of Danhou lignite and study on adsorption of CH4 by oxygen functional groups. *Environ. Sci. Pollut. Res. Int.* 2021, 28, 25368−25381.

(48) 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.

(49) 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.

(50) 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.

(51) Grimme, S. Density functional theory with London dispersion correction. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2011, 1, 211−228.

(52) 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, No. 154104.

(53) Wu, J.; Wang, J.; Liu, J.; Yang, Y.; Cheng, J.; Wang, Z.; Zhou, J.; Cen, K. Moisture removal mechanism of low-rank coal by hydrothermal dewatering: Physicochemical property analysis and DFT calculation. *Fuel* 2017, 187, 242−249.

(54) 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.

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

(56) Lu, T.; Chen, F. Bond order analysis based on the Laplacian of electron density in fuzzy overlap space. *J. Phys. Chem. A* 2013, 117, 3100−3108.

(57) Manzetti, S.; Lu, T. The geometry and electronic structure of Aristolochic acid: possible implications for a frozen resonance. *J. Phys. Org. Chem.* 2013, 26, 473−483.

(58) Johnson, E.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A.; Yang, W. Revealing Non-Covalent Interactions. *J. Am. Chem. Soc.* 2010, 132, 6498−6506.

(59) 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.