Reaction Mechanism of Phenolic Lignin and High Concentration Chlorine Dioxide and Its Application

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**ABSTRACT:** In fact, the chemical reaction rate of traditional chlorine dioxide bleaching of pulp is too fast to observe the intermediate process. The mechanism behind the reaction of 4-hydroxy-3-methoxyacetophenone (APO), a phenolic lignin model compound, with high concentrations of chlorine dioxide was investigated. Individual solutions of each compound and a mixture of the two were analyzed by UV−vis spectrophotometry, and an absorbance band at 260 nm was observed for the stable benzoquinone intermediates at room temperature. Free chlorine dioxide displayed an absorbance at 360 nm and changes in this absorbance were studied with different APO concentrations. A fixed molar ratio of 1:3 was obtained between APO and chlorine dioxide consumption. The intermediate absorbance demonstrated a linear relationship with the APO concentration. The reaction path between APO and chlorine dioxide at high concentrations was speculated, and it was observed that the activity of C1, C2, C3, C5, and C6 on the APO benzene ring was enhanced when high concentrations of chlorine dioxide were present. From these results, a new method for efficient and clean chlorine dioxide bleaching can be developed.

**INTRODUCTION**

Lignin is an abundant natural resource, and significant attention has been paid to its separation, modification, and applications. Lignin has a complex chemical structure and diverse composition and is always associated with cellulose and hemicellulose. Therefore, it is helpful to understand the chemical changes and reaction mechanism of lignin at the molecular level. However, directly isolating lignin for study is difficult because it easily degrades and condenses. There-fore, the chemical structure of natural lignin can be evaluated by studying lignin model compounds with similar structure and functions to those of natural lignin.

Bleaching is a primary chemical reaction for making pulp and paper, and the reaction of lignin with chlorine dioxide is the core reaction of elemental free chlorine (ECF) bleaching, which is a mainstream cleaning and bleaching technology. The reaction mechanism between lignin and chlorine dioxide has been studied using lignin models under simulated bleaching conditions. It is well known that 2 mol of chlorine dioxide reacts with 1 mol of phenol, where chlorine dioxide first reacts with phenol to produce a phenolic radical (and its mesomeric forms) and chlorous acid. Next, another molecule of chlorine dioxide combines with the phenolic radical, usually at the site where there is a methoxy substituent, to form an unstable chlorite ester of an ortho-quinol. This intermediate decomposes to form an ortho quinone, methanol, and another molecule of chlorous acid or to form a muconic acid monomethyl ester, hypochlorous acid, and water. The structure of lignin can be classified as phenolic or non-phenolic, and it is speculated that non-phenolic lignin reacts with chlorine dioxide in a way similar to that of phenol lignin. In previous studies, reducing chlorine dioxide during the bleaching process was considered one of the main methods to achieve efficient, clean bleaching. The mechanism of lignin and chlorine dioxide at low concentrations of chlorine dioxide was studied. Phenolic lignin is highly abundant and reactive, and its reaction with high concentrations of chlorine dioxide has not yet been studied. Understanding the mechanism behind the reaction of phenolic lignin and high concentrations of chlorine dioxide can help elucidate that of the reaction of lignin and chlorine dioxide, making this study highly important. Lignin in woody biomass mainly consists of guaiacyl type (G-units), syringyl type (S-units), and polyhydroxyphenyl type (H-units). The residual lignin in unbleached pulp is mainly G-units. Therefore, G-units and chlorine dioxide are the main reaction in chlorine dioxide bleaching reaction.
methoxyacetophenone (APO) is a highly representative G-unit lignin model compound. In this study, the changes in the absorbance of APO, chlorine dioxide, and mixtures of the two were measured using a UV–vis spectrophotometer at room temperature. The morphological and structural changes of APO and chlorine dioxide in the reaction system were analyzed as well as the relationship between APO and chlorine dioxide concentration consumption. Furthermore, the relationship between the absorbance of the intermediates and the concentration of APO was also analyzed, and the characteristics of the intermediates were identified by gas chromatography–mass spectrometry (GC-MS). Using these analysis techniques, the reaction mechanism between phenolic lignin and high concentrations of chlorine dioxide was determined, which provided insight into the reaction mechanism between natural lignin and chlorine dioxide.

## RESULTS AND DISCUSSION

### Reaction System of APO with High Concentration Chlorine Dioxide

The reaction rate between lignin and chlorine dioxide is so fast that intermediates cannot be observed under normal chlorine dioxide bleaching conditions.\(^{27}\) Furthermore, this reaction rate increases rapidly with reaction temperature; therefore, decreasing the reaction temperature is helpful for observing the reaction process between lignin and chlorine dioxide. The concentrations of the APO and chlorine dioxide solutions were 0.01 and 0.15 mmol·L\(^{-1}\), respectively. The UV–vis spectra of the solutions showed absorbance for APO, chlorine dioxide, and an equal volumes mixture of the two at 25 °C. The morphological transformations of APO, chlorine dioxide, and their mixtures were investigated, and the reaction process between them was speculated. The results are shown in Figure 1a.

Figure 1a shows that the pure chlorine dioxide solution exhibited full wavelength absorption, and its maximum absorbance was at 360 nm. In addition, the pure APO solution showed characteristic absorbances at 205, 227, 280, and 305 nm, the last of which corresponded to the benzene ring and the carbonyl group on a branched chain of benzene rings.\(^{29}\) The absorbance spectrum of the reaction solution changed significantly when APO and chlorine dioxide were mixed. First, the characteristic absorption bands of APO at 205, 227, 280, and 305 nm were altered significantly, which indicated that the structure of APO was changed by the addition of chlorine dioxide. The absorbance maximum at 280 nm shifted to 260 nm, which was due to stable intermediates forming from the degradation of APO.\(^{30,31}\) However, chlorite and chlorate was formed as products when chlorine dioxide reacts with organic compounds. Chlorite has a distinctive band at 260 nm.\(^{32}\) Chlorite ester was formed in the reaction of chlorine dioxide with phenol. However, it was quickly converted to benzoquinone because of its instability in an acidic environment.\(^{18,19}\) Therefore, the absorbance at 260 nm was attributed to the new stable intermediate. The absorption intensity observed for pure chlorine dioxide at 360 nm also decreased, indicating that the morphology of the chlorine dioxide was slightly altered.\(^{33}\) In fact, two forms of chlorine dioxide existed in the reaction system, where a portion of it remained unassociated (free chlorine dioxide) and the remainder coordinated with APO to form intermediates. This intermediate formation was due to an increase in the reactivity of APO caused by the high concentration of chlorine dioxide. These reaction characteristics of APO due to the chlorine dioxide were then analyzed.

### Reaction Product Identification

The reaction products were qualitatively analyzed by GC-MS, where equal volumes of 0.20 mmol·L\(^{-1}\) APO and 1.00 mmol·L\(^{-1}\) chlorine dioxide were mixed and allowed to react. The results are shown in Figure 1b.

The reaction solution was adsorbed and purified. The observed peaks in Figure 1b were compared with the standard spectrogram database in the Nist MS search software, and if a matched-degree was larger than 90%, then the peak can be attributed to the corresponding compound. The results indicate that the products were mainly 4-methoxy-m-resorcinone and 2-methoxy-p-benzoquinone.\(^{34}\) To support...
the chromatographic peak assignment, the standard solutions of 4-methoxy-m-resorcinone and 2-methoxy-p-benzoquinone were detected by GC-MS. It showed that their peaks appeared at the same retention time. Therefore, the results confirmed the existence of stable intermediate benzoquinone in the reaction of APO with high concentration chlorine dioxide.

**Absorbance Changes of the Reaction System.** The structural transformations of the reactants and products were analyzed based on the changes in their characteristic absorptions. The concentration of APO in the reaction system was fixed at 0.20 mmol L$^{-1}$. The change in absorbance of the reaction solution was studied by varying the chlorine dioxide concentration, and the results are shown in Figure 1c.

Figure 1c shows that the characteristic absorbance of APO at 205, 227, 280, and 305 nm were gradually weakened as the chlorine dioxide concentration were increased, suggesting that APO was slowly being consumed. The changes of the band at 260 nm were most pronounced at a chlorine dioxide concentration of 0.14 mmol L$^{-1}$. It means that this absorbance was affected by the formation of the stable intermediate. The absorbance at 360 nm increased with increasing chlorine dioxide concentration. The amount of chlorine dioxide consumed by the complete reaction with APO was fixed; therefore, the reaction between APO and chlorine dioxide is not a traditional first-order reaction. First, APO is rapidly converted into a phenolic radical by high concentrations of chlorine dioxide, which is then converted to benzoquinone. This has been confirmed in previous studies,$^{10,13,26}$ but in this study, the formed intermediates were stable and observable.

Changes in the absorbances at 260 and 360 nm were primarily noted as the chlorine dioxide concentration was varied. The absorbance changes of the intermediates and free chlorine dioxide with different APO concentrations were also analyzed, where the concentration of chlorine dioxide was fixed at 1.83 mmol L$^{-1}$. The results are shown in Figure 1d.

The absorbance at 260 nm was thought to be the sum of the contributions from chlorine dioxide,$^{35}$ the branched chain of APO$^{36}$ and benzoquinone. However, since APO was completely converted under conditions with excess chlorine dioxide, this absorbance is likely a result of the benzoquinone intermediates and chlorine dioxide. In addition, it shows that the absorbance at 260 nm changed significantly when the concentration of chlorine dioxide exceeded 0.14 mmol L$^{-1}$. It suggests that this absorbance is completely attributed to the stable intermediates. Therefore, the absorption at 360 nm corresponds to free chlorine dioxide. It was observed that the absorbance at 260 nm gradually increased as the APO concentration increased due to the increase in intermediate formation. The consumption of chlorine dioxide also increased with the increase in APO concentration, which reduced the absorbance at 360 nm.

**Analysis of the Absorbance at 360 Nm.** The absorbance at 360 nm was studied with a fixed APO concentration and varying concentrations of chlorine dioxide, establishing the relationship between the absorbance and the chlorine dioxide concentration. The amount of chlorine dioxide consumed by 0.20 mmol L$^{-1}$ APO was analyzed under different conditions, and the results are shown in Figure 2a.

Figure 2a shows that the absorbance at 360 nm increased gradually as the concentration of chlorine dioxide was slowly increased, indicating that with a fixed APO concentration the free chlorine dioxide concentration increases gradually with that of chlorine dioxide. The absorbance curve of chlorine dioxide concentration at 360 nm with and without APO was also established (Figure 2b). The linear regression equation of the absorbance of pure chlorine dioxide solution (at 360 nm) as a function of its concentration was $y = 0.85x$ with a linearly dependent coefficient $R^2$ of 0.9997. The same equation was obtained for the reaction solution (at 360 nm) and was determined to be $y = 0.85x - 0.51$ with an $R^2$ value of 0.9995. The two regression curves have the same slope, indicating that the amount of chlorine dioxide consumed by the fixed amount of APO was also a fixed value. The intercept difference between the two regression curves was 0.51, and the consumption of chlorine dioxide corresponding to this 0.51 decrease in absorbance was 0.60 mmol L$^{-1}$. All chlorine...
dioxide consumed by the reaction system was involved in the formation of the phenolic-oxygen free radical and the stable intermediates. In this series of experiments, the concentration of APO participating in the reaction was 0.20 mmol-L⁻¹, and the consumption of chlorine dioxide was 0.60 mmol-L⁻¹. Therefore, the constant molar ratio of APO to consumed chlorine dioxide was 1:3, respectively. These results also confirm the oxidation removal of APO by high concentrations of chlorine dioxide at room temperature.

**Relationship between APO Consumption and Chlorine Dioxide Consumption.** The fixed ratio of APO to consumed chlorine dioxide is needed to be further verified, which was done by studying the variation in the chlorine dioxide consumption as a result of the chlorine dioxide concentration under different APO concentrations. The concentrations of APO used were 0, 0.02, 0.06, 0.12, and 0.20 mmol-L⁻¹. The chlorine dioxide concentrations varied from 0.91 to 2.28 mmol-L⁻¹. The change in the absorbance of the free chlorine dioxide at 360 nm was analyzed, and the results are shown in Figure 2c.

Figure 2c demonstrates the changes in the free chlorine dioxide absorbance band as a function of the chlorine dioxide concentration in the presence of different APO concentrations. The absorbance of 360 nm gradually increased with the increase in chlorine dioxide concentration. The linear relationship between the absorbance of free chlorine dioxide and the concentration of chlorine dioxide was determined with varying APO concentrations present. The regression equations are shown in Table 1, where they were different for each fitting curve. Based on the linear regression equations, the absorbance at 360 nm was calculated with a fixed chlorine dioxide concentration but different APO concentrations. The reduction in absorbance at 360 nm at different APO concentrations was calculated and compared with the pure chlorine dioxide solution at the same concentration. The effect of different chlorine dioxide concentrations on the absorbance at 360 nm with a fixed APO concentration was also analyzed, and the details are shown in Table 2. The results indicate that the reduction in absorbance at 360 nm was independent of the concentration of chlorine dioxide, and the consumption of chlorine dioxide in the reaction system was directly related to the APO concentration.

The effect of the APO concentration on the absorbance reduction at 360 nm was investigated as well as the relationship between the concentration of APO and the amount of chlorine dioxide consumed. To study the effect of the APO concentration on the band at 360 nm, APO concentrations of 0, 0.02, 0.06, 0.12, and 0.20 mmol-L⁻¹ were used. The concentration of chlorine dioxide was fixed at 2.50 mmol-L⁻¹. The decrease in absorbance of the band at 360 nm in different reaction systems was obtained, and based on the standard curve fitting equation (Figure 2b), the consumption of chlorine dioxide was calculated. The change in chlorine dioxide consumption with varying APO concentrations is shown in Figure 2d.

A curve representing the relationship between the concentration of APO and the concentration of chlorine dioxide consumed was established. The linear regression equation was \( y = 3x \) with an \( R^2 \) value of 0.9987. This supports the fixed molar ratio of 1:3 that was obtained between APO and the consumption of chlorine dioxide, respectively. It is well known that 2 mol of chlorine dioxide reacts with 1 mol of phenol. Our results differ from previous studies mainly in that the reactivity of APO was enhanced by high concentrations of chlorine dioxide. The phenolic-oxygen free radical was rapidly formed, and the activities of the C1, C2, C3, CS, and C6 on the APO benzene ring were enhanced. The phenolic-oxygen radicals were produced by the reaction of 1 mol of APO with 2 mol of chlorine dioxide, and subsequent reaction of the phenolic oxygen with 1 mol of chlorine dioxide resulted in unstable chlorite esters, which converted to benzoquinone. In fact, the absorption peak at 260 nm is the acromion. It is not a single substance; it is a mixture with the same structure. First of all, different kinds of APO free radicals were rapidly generated. They were transformed into corresponding benzoquinones under the action of chlorine dioxide. However, due to the difference in stability, the final stable intermediate products were 4-methoxy-m-resorcinone and 2-methoxy-p-benzoquinone. The presence of these two substances was confirmed by GC-MS, and they have the same absorption wavelength. Based on these results, a reaction pathway is proposed in Scheme 1.

**Analysis of Absorbance at 260 nm.** The absorbance of the intermediate (260 nm) with the concentration of chlorine dioxide is shown in Figure 3a. In order to avoid the contingency of experimental results, different APO concentrations were adopted. The concentrations of APO were 0.02, 0.04, and 0.06 mmol-L⁻¹, respectively. In the control group, APO was not added. The concentration of chlorine dioxide in the different reaction systems ranged from 0.08 to 3.04 mmol-L⁻¹.

The absorbance at 260 nm increased with the concentration of chlorine dioxide, as shown in Figure 3a. The relationship between the concentration of chlorine dioxide and the absorbance at 260 nm with different APO concentrations was also analyzed, and the details are shown in Table 3. The data fitting results show that the different curves have the same slope but different intercepts, which suggests that the absorbance of the intermediates was independent of the chlorine dioxide concentration. However, it was affected by the concentration of APO in the presence of high concentrations.

| APO concentration (mmol-L⁻¹) | chlorinate dioxide concentration (mmol-L⁻¹) | reduction in absorbance at 360 nm |
|-----------------------------|------------------------------------------|----------------------------------|
|                            |                                          | 1.00                             |
|                            |                                          | 1.50                             |
|                            |                                          | 2.00                             |
| 0.02                       |                                          | 0.05                             |
| 0.06                       |                                          | 0.13                             |
| 0.12                       |                                          | 0.33                             |
| 0.20                       |                                          | 0.51                             |

Table 2. Effect of Chlorine Dioxide Concentration on the Decrease in the Absorbance at 360 nm in the Presence of a Fixed APO Concentration
of chlorine dioxide. Therefore, the effect of varying APO concentration on the absorbance of the intermediates was studied, where APO concentrations of 0, 0.02, 0.04, and 0.06 mmol·L⁻¹ were used. The concentration of chlorine dioxide was kept at 2.50 mmol·L⁻¹, and the results are shown in Figure 3b.

A linear regression relationship between the absorbance of the intermediates at 260 nm and the APO concentration was determined, where the regression equation was \( y = 5.00x \), as shown in Figure 3b, and its \( R^2 \) was 0.9979. The existence of the intermediates was confirmed by this regression curve.

**High Concentration Chlorine Dioxide Bleaching.** APO was activated and its oxidative degradation was promoted at high concentrations of chlorine dioxide. Bleaching reactions are carried out by adding different concentrations of chlorine dioxide. The effect of chlorine dioxide concentration on AOX formation was studied. The results are shown in Figure 4.

Figure 4 shows that AOX formation decreases with the increase in chlorine dioxide concentration. The AOX formation was 3.77 mg·L⁻¹ at 0.26 g·L⁻¹ chlorine dioxide. It decreased to 2.78 mg·L⁻¹ at 2.20 g·L⁻¹ chlorine dioxide. It was reduced by 30%. At this point, the ratio of APO concentration to chlorine dioxide concentration was 1:3. The change of AOX formation tends to be stable when the concentration of chlorine dioxide continues to increase. This means that the oxidation of APO was promoted as the concentration of chlorine dioxide increases. The chlorination of APO was inhibited, and the AOX formation was reduced. APO was completely consumed when the ratio of APO concentration to chlorine dioxide concentration was 1:3. This was the inherent reason why the formation of AOX remains unchanged at the concentration of chlorine dioxide exceeding 2.20 g·L⁻¹. There are side reactions of chlorine gas formation during the preparation of chlorine dioxide solution. Some chlorine gas is present in chlorine dioxide solution. The oxidation degradation reaction between lignin and chlorine dioxide is the main reaction, while the chlorination reaction between hypochlorous acid (chlorine gas) and lignin also exists in chlorine dioxide bleaching. This is the main source of adsorbable organic halogens (AOX), and it was difficult to degrade and toxic. Therefore, the oxidation degradation and chlorination of lignin exist simultaneously in chlorine dioxide bleaching. The current research is mainly to reduce the amount of AOX by reducing the amount of chlorine dioxide. In fact, it was found that phenolic lignin model APO was highly activated under high concentrations of chlorine dioxide. This results in rapid oxidative degradation of APO. The oxidative degradation of lignin was promoted, while the opposite chlorination reaction was inhibited at high concentrations of chlorine dioxide. A new AOX reduction method was found based on the reaction mechanism between APO and high concentration chlorine dioxide. It has a strong industrial application value.

### Table 3. Relationship between the Absorbance at 260 nm and the Concentration of Chlorine Dioxide at Different APO Concentrations

| APO concentration (mmol·L⁻¹) | regression equation | \( R^2 \) |
|-------------------------------|---------------------|----------|
| 0                             | \( y = 0.03x \)     | 0.9954   |
| 0.02                          | \( y = 0.03x + 0.09 \) | 0.9928   |
| 0.04                          | \( y = 0.03x + 0.20 \) | 0.9954   |
| 0.06                          | \( y = 0.03x + 0.30 \) | 0.9961   |

### Figure 4. Effect of chlorine dioxide concentration on AOX formation.
CONCLUSIONS
The reaction mechanism between APO and high concentrations of chlorine dioxide was studied, and stable benzoquinone intermediates were observed in the reaction system at 25 °C. The results showed that APO was activated by high concentrations of chlorine dioxide, and it was quickly converted into benzoquinone. This means that the oxidative degradation of lignin was promoted, and the chlorination reaction was inhibited in the bleaching of high concentration chlorine dioxide. AOX formation was further reduced. These results offer the potential for a new, efficient, and clean chlorine dioxide bleaching method to be developed.

MATERIALS AND METHODS
Materials. APO (GC, >98%), sodium chlorite, hydrochloric acid, sodium hydroxide, sulfuric acid, potassium iodide, and sodium thiosulfate were purchased from Aladdin Biotechnology Co., Ltd. (Shanghai, China). All assay reagents were obtained from Sigma-Aldrich (USA). All chemicals used were of analytical grade.

Preparation of Chlorine Dioxide. The preparation process of chlorine dioxide was as follows:39 Sodium chlorite was dissolved in water and reacted with sulfuric acid. The chlorine dioxide generated was absorbed using ice-cold distilled water. A small amount of chlorine was generated before the absorption of the chlorine dioxide. The purity of the chlorine dioxide exceeded 99.50%, and the solution (11.00 g·L<sup>-1</sup>) was stored in a cryogenically sealed brown bottle to avoid light exposure.

Chemical Reaction and UV Spectra Collection. A UV–vis spectrophotometer (SPECORD 50 PLUS, Analytikjena, Germany) equipped with a jacketed 1.0 cm quartz cell was used to acquire the absorbance spectra. Solutions with different concentrations of APO were prepared and added to separate flasks. The reactions were initiated by adding chlorine dioxide to the APO solutions, and all reactions were carried out at room temperature (25 °C). A small amount of each sample (1 mL) was pipetted into the jacketed quartz cell and analyzed by UV spectroscopy.

Chemical Composition Analysis of the Reaction Solutions. The chemical composition of each reaction solution was determined by GC-MS (6890-5973, Agilent, USA), and the reaction products of APO and high concentrations of chlorine dioxide were qualitatively analyzed. The detailed operating conditions for the GC-MS analysis have been described in a previous study.13

Chlorine Dioxide Bleaching. The bleaching reaction was carried out in a sealed polyethylene bag. Five milliliters of 0.7 g·L<sup>-1</sup> APO solution was added. The pH of the solution was adjusted to 3–4 by sulfuric acid solution. A 100 mL reaction solution was configured by adding different concentrations of chlorine dioxide solution. The reaction was maintained at 65 °C for 1 h. The excess chlorine dioxide in the reaction solution was blown out using nitrogen gas. It can be absorbed and reused. The effect of residual chlorine dioxide in the reaction solution was analyzed by using the Multi-X2500 AOX analyzer (Germany). The basic method and process are described in our previous study.13

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Notes
The authors declare no competing financial interest.

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