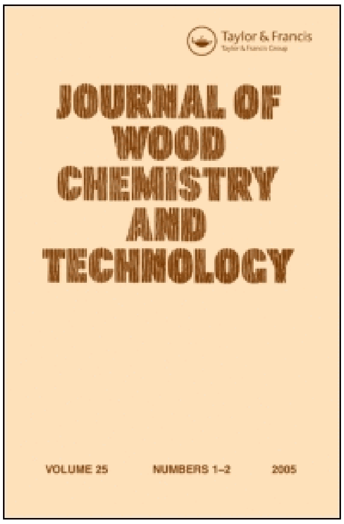

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REACTIVITY OF LIGNIN DIPHENYLMETHANE MODEL DIMERS UNDER MILD ALKALI - 0_2 CONDITIONS

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ABSTRACT

A series of phenolic lignin-model dimers of the guaiacyl diphenylmethane (DPM) type has been shown to be quite reactive under mild alkali-O_2 conditions (0.5 N NaOH, 55°C) giving significant amounts of monomeric products. The reactivity of these dimers varies significantly and decreases in the order of α-5, 5,5', α-6, and α-1 types. Interestingly, the oxidative cleavages of these DPM units, except the α-6 type, all gave the benzyl alcohol products e.g. vanillyl alcohol.

INTRODUCTION

In the current development of elemental chlorine-free (ECF) or totally chlorine-free (TCF) bleaching of chemical pulps, O_2 bleaching has become nearly a standard process following kraft pulping, but it can only readily remove approximately 50% of the residual lignin without causing excessive degradation of the fiber [1,2]. An understanding of the controlling factors involved should provide a firm basis for planning strategy for further improving the O_2 delignification efficiency.

As parts of our attempts to further understand the nature and reactivity of residual lignin, we have studied the behavior of lignin DPM model dimers under oxidative conditions. Recent findings indicated that these dimers were rather reactive under nitrobenzene[3] and permanganate[4] oxidation conditions.

Extensive studies on lignin-related model compounds [5-13] under O_2 bleaching conditions clearly reveal that phenolic and enolic structures are the major reactive sites. The oxidative degradation of these functional groups includes side-chain cleavages and ring opening resulting in the formation of carboxylic acid groups. The reactivity of phenolic units was also significantly influenced by the nature of aromatic nuclei and side-chain units. In addition, the oxidative degradation may be counteracted by coupling reactions.

Although phenolic diphenylmethane (DPM) model dimers have been shown to be reactive in alkali-O_2 solution[12,13], little information is available on the degradation mechanism involved. We reported previously [14] that 6-vanillyl creosol I (Fig. 1), an unsubstituted phenolic α-5 DPM dimer, was very sensitive to molecular oxygen in dilute alkali (0.1-0.5 N NaOH) at 55°C. Interestingly, the major monomeric product formed was vanillyl alcohol instead of vanillin as one would have anticipated under oxidative conditions. In the present study, we have extended similar studies to three other types of DPM model dimers including α-6 (II), α-1 (III), and 5,5' (IV) types (Fig. 1).

RESULTS AND DISCUSSION

Product Analysis

The reaction of four guaiacyl DPM dimers (I-IV) was conducted in dilute alkali (O.5 N NaOH) with a continuous flow of O_2 atmosphere at 55°C under otherwise identical conditions. Table 1 summarizes the yields of monomeric products (Fig. 2), which were obtained after 1 h reaction except 30 min for the α-5 dimer. The products were identified initially on the basis of their mass spectral fragmentation patterns and further confirmed by comparing with authentic compounds.

All the dimers were shown to be reactive under the mild alkali-O_2 conditions. Approximately 80-90% degradation was observed for the α-5 and 5,5'-DPM types

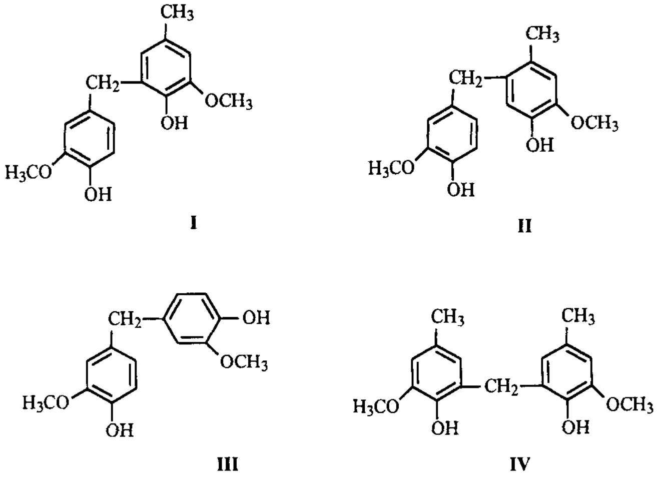


FIGURE 1. Lignin diphenylmethane model dimers.

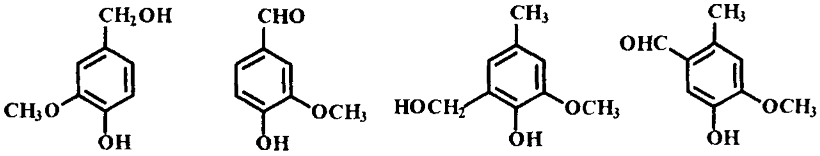
TABLE 1

Product Yields from Alkali-O_2 Treatments of Diphenylmethane Model Dimers in 0.5N NaOH at 55°C for 1h

Compounds	Product Yield, Mole % of Dimer[a] I[b]	II	III	IV
Unreacted dimer	22.4	74.7	79.4	13.1
Vanillyl alcohol	27.6	-	9.7	-
Vanillin	-	8.4	-	-
6-Hydroxymethyl creosol	10.4	-	-	58.2
6-Formylcreosol	-	4.9	-	-

a. Refers to structures in Fig. 1

b. Was treated for 0.5 h instead of 1 h for others.



1 2 3 4

FIGURE 2. Monomeric products identified from alkali-O_2 treatments of lignin diphenylmethane model dimers.

and significantly lower (20-25%) for the α-6 and α-1 dimers. Concerning the nature of monomeric products formed, it is of interest to note that both 5,5' and α-1 dimers like the α-5 unit[14] gave mainly the benzyl alcohol products (vanillyl alcohol and 6-hydroxymethyl creosol), whereas the α-6 dimer yields the aldehyde products (vanillin and 6-formyl creosol).

The benzyl alcohol degradation products, however, cannot be produced simply from a reversed process of the alkaline condensation reactions , because all the dimers were shown to be stable in the alkali under a N_2 atmosphere. Also, all the dimers pre-methylated with dimethyl sulfate to block the phenolic hydroxyl groups were found to be practically stable in alkali-O_2 solution. The apparent stability of these methylated dimers, however, may be partly attributed to their reduced solubility in alkali.

α-5 Dimer (I)

Figure 3 illustrates a proposed reaction scheme to account for the oxidation products of α-5 dimer, vanillyl alcohol and 6-hydroxymethyl creosol. The reaction appears to be initiated from oxygenation at the two ring (C_1 and C_5) positions carrying the methylene groups. These oxygenations facilitated by the phenolic hydroxyl groups likely include an addition of superoxide ion radical to a conjugated phenoxy

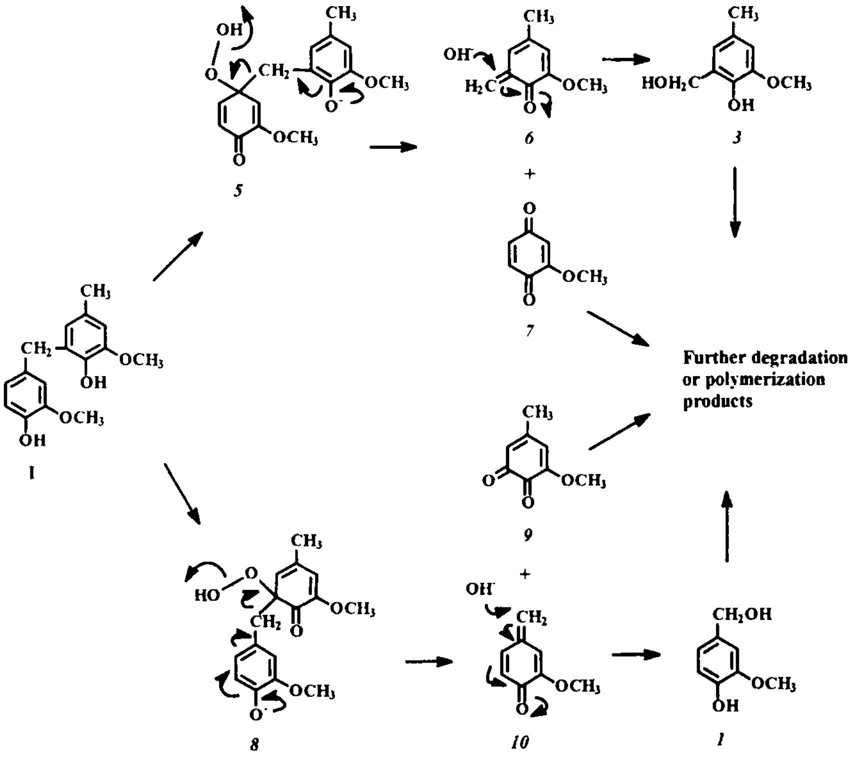


FIGURE 3. A proposed degradation mechanism of α-5 dimer I in alkali-O_2 solution.

radical intermediate. The resulting hydroperoxides 5 and 8 then undergo intramolecular fragmentation to give the quinonemethides (6 and 10) and quinones (7 and 9) derivatives. A hydroxide addition to the p- and o-quinonemethides then yields vanillyl alcohol and 6-hydroxymethyl creosol, respectively. It is evident that the combined yield of these two products was considerably less than the theoretical value based on the dimer degradation (38 vs 78%).

In separate experiments with authentic compounds under similar alkali-O_2 conditions, both vanillyl alcohol and 6-hydroxymethyl creosol were shown to be relatively stable, and they displayed only a 20 and 12% degradation, respectively after 1 h reaction in 0.5 M NaOH at 70°C. Sultanov *et al.*[12] also previously noted that vanillyl alcohol was relatively stable in alkali-O_2 solution (1M KOH at 70°C for 1 h). Consequently, the apparent low yield of vanillyl alcohol and 6-hydroxymethyl cresol may indicate a significant formation of other unknown products under the prevailing oxidation conditions. Radical reactions were likely to be involved, and are supported by the detection of two dimeric products during the alkali-O_2 treatment of the α-5 dimer I[14].

Since both vanillyl alcohol and 6-hydroxymethyl creosol were relatively stable in the alkali-O_2 solution, the observed significantly high yield of vanillyl alcohol may suggest that the initial oxygenation occurs preferentially at the C_5 position over the C_1 position; or the intramolecular cleavage of hydroperoxide 8 proceeds more readily than that of intermediate 5. As indicated in Fig. 3, the proposed intramolecular cleavage reactions can be applied only to intermediates with an undissociated hydroperoxy group. This contention is supported by an observation that the alkali-O_2 degradation of α-5 dimer was significantly affected by the alkalinity used, being higher in 0.1 N than in 0.5 N alkali solution.

α-6 Dimer (II)

A proposed mechanism of formation of vanillin and 5-formyl creosol from the alkali-O_2 treatment of α-6 dimer II is illustrated in Figure 4. Although the basic principle involved seems to be similar for both α-5 and α-6 dimers, they gave entirely different types of products. It appears that initial oxygenation of the α-6 dimer occurs preferentially at the C_1 position of the DPM unit. The resulting hydroperoxide 11 may undergo elimination of water to yield the DPM-type quinonemethide intermediate 12, which after hydroxide addition leads to the formation of diguaiacycarbinol 13.

Conceptually, the carbinol intermediate 13 is a likely precursor of the aldehyde products, 5-formyl creosol 4 and vanillin. The α-6 dimer II, as noted earlier (Table

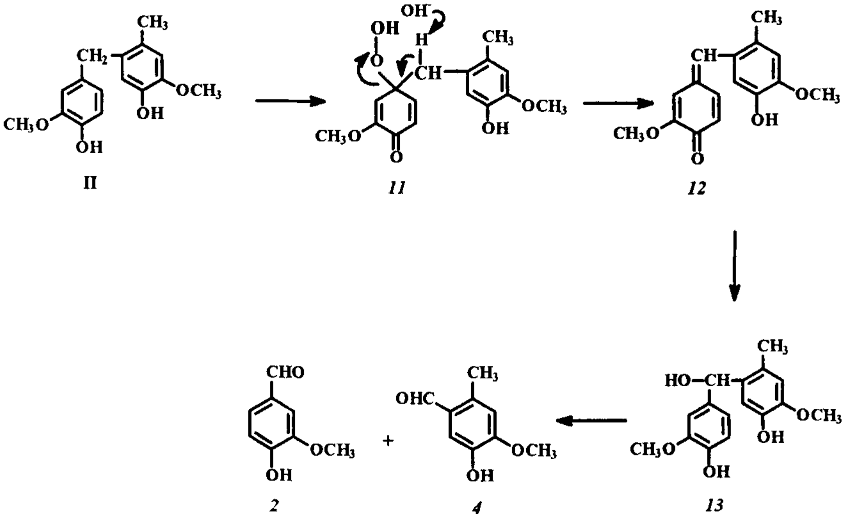


FIGURE 4. A proposed degradation mechanism of α-6 dimer II in alkali-O_2 solution.

1), was more stable than the α-5 dimer I, and its reduced reactivity may be partly attributed to the formation of DPM quinonemethide 12 from hydroperoxide 11 being a very slow reaction. Also, an intramolecular cleavage of the latter hydroperoxide 11, unlike those derived from α-5 dimer 5 and8 (Fig. 3), may be difficult to proceed without the assistance of a conjugated phenolic hydroxyl group.

α-1 Dimer (III)

Similarly, the formation of vanillyl alcohol from the α-1 dimer III may be explained in terms of initial oxygenation at the C_1 position followed by cleavage of the hydroperoxide adduct 14 and hydroxide addition to the DPM quinonemethide intermediate 10 as illustrated in Figure 5. Although the α-1 dimer is closely related to the α-5 dimer in functionality, it displayed a considerably lower reactivity (Table

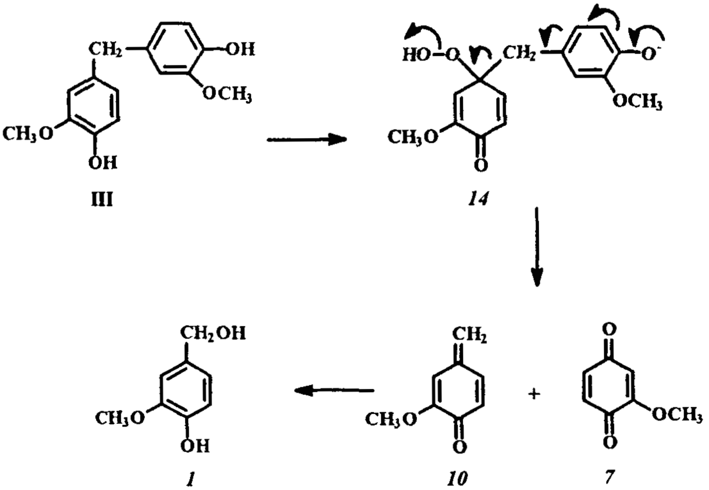


FIGURE 5. A proposed degradation mechanism of α-1 dimer III in alkali-O_2 solution.

1). It appears that the phenoxide-promoted cleavage of the hydroperoxide adduct facilitated by a para hydroxyl group 14 may not be as effective as an ortho phenolic unit 5.

5,5' DPM Dimer (IV)

The reaction of the 5,5'-DPM IV under mild alkali-O_2 conditions was quite similar to that of the α-5 dimer in reactivity (Table 1). It gave a higher yield of 6-hydroxymethyl creosol, and this may be largely attributed to its two guaiacyl units being identical in substitution pattern.

The degradation of the 5,5'-DPM dimer is also consistent with the involvement of initial oxygenation followed by cleavage of the hydroperoxide adduct 15 as indicated in Figure 6. The observed comparable reactivity between the 5,5' and α-5 dimers further supports the contention that the cleavage of the proposed hydro-

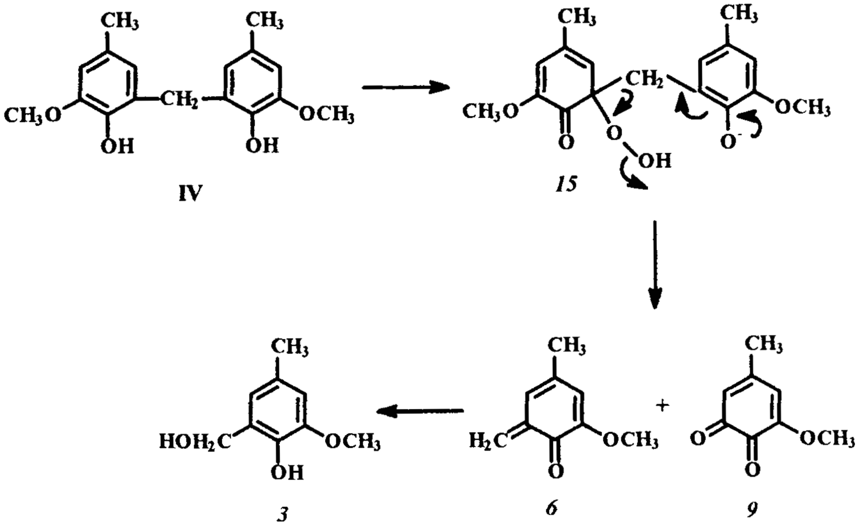


FIGURE 6. A proposed degradation mechanism of 5,5'-DPM dimer IV in alkali-O_2 solution.

peroxide adduct is significantly promoted by having a phenolic hydroxyl groups at the ortho position.

CONCLUSIONS

The phenolic DPM model dimers have been shown to be rather reactive under mild alkali-O_2 solutions, and gave significant amounts of monomeric products. A major reaction appears to be initiated from oxygenation at the ring positions adjacent to the methylene carbon. Further reaction or transformation of the resulting hydroperoxide adducts appears to be a key to the overall degradation of the DPM units, and their reactivities were significantly influenced by position of the phenolic hydroxyl groups present in the ring.

The hydroperoxide adducts from the α-5, α-1 and 5,5' dimers seem to favor an intramolecular cleavage process resulting in the formation of benzyl alcohol products (vanillyl alcohol and 5-hydroxymethyl creosol), whereas the α-6 derived adduct may undergo rearrangement reactions leading to the formation of diguaiacylcarbinol intermediate, which is a likely precursor of the aldehyde products (vanillin and 6-formyl creosol).

EXPERIMENTAL

Synthesis of Lignin Model Dimers

Reported procedures were used to prepare the four phenolic DPM lignin model dimers (Fig. 1) The α-5 dimer I prepared from the alkaline condensation of vanillyl alcohol and creosol [15] was obtained as crystal, m.p. 99-100°C. The α-6 dimer II was obtained from an acid-catalyzed condensation of vanillyl alcohol and creosol, and has m.p. 107-108°C (lit.[16] 112-115°C). The α-1 dimer III was prepared from alkaline condensaion of vanillyl alcohol, and has m.p. 108-109°C (lit.[17] 109-110°C). The 5,5'-DPM dimer IV, prepared from alkaline condensation of creosol with formaldehyde, has m.p. 131-132°C as compared to a reported value[18] of 132-133°C.

The 6-hydroxymethyl creosol 3 was obtained from alkaline condensation of creosol and formaldehyde[19], and has m.p. 50.1-51.8°C (lit. 50.5-51.5°C). The 5-formyl creosol 4 was synthesized based on the method of Scarpati et al.[20], and has a m.p. of 94.3-95.7°C.

Alkali Treatments of Lignin Model Dimers

In general, a solution of lignin model dimer (10 mg) dissolved in 10 mL of dilute alkali (0.5 N NaOH) was placed in a small pearl-shaped flask and heated isothermally in a water bath at 55°C for 30 or 60 min. with a continuous flow of N_2 or O_2 bubbling through the system. The mixture after acidification with a 3.5 N HCl solution to pH 3-4 was extracted with chloroform thrice. The combined extract after drying over Na_2SO_4 was evaporated to dryness under reduced pressure. The products after silylation with BSTFA were analyzed by GC. In the case of the GC/MS analysis, the products were acetylated instead of silylated. The identified products were then further confirmed by comparing with authentic compounds.

ACKNOWLEDGEMENTS

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