Reactivity of Lignin Diphenylmethane Model Dimers Under Alkaline Pulping Conditions

Hui Xu[a]; Yuan-Zong Lai[a]

[a] College of Environmental Science and Forestry, Empire State Paper Research Institute, Faculty of Paper Science and Engineering, State University of New York, Syracuse, NY

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Hui Xu and Yuan-Zong Lai*
Empire State Paper Research Institute
Faculty of Paper Science and Engineering
State University of New York
College of Environmental Science and Forestry
Syracuse, NY 13210

ABSTRACT

The reactivity of a series of phenolic lignin diphenylmethane (DPM) model dimers has been examined in soda and kraft cooks, in an attempt to understand the role of lignin condensation in the alkaline delignification process. These condensed dimers were shown to be rather stable in alkali in the absence of O_2 even at elevated temperatures. In contrast, they were sensitive to traces of O_2 present in air, and the degradation mechanism involved was shown to be different from that occurring under mild alkali-O_2 conditions.

INTRODUCTION

Although lignin condensation reactions are generally thought to be a factor in retarding alkaline delignification processes,[1-6] their chemical nature and impacts still cannot be clearly defined. This situation may be largely attributed to the lack of a suitable technique that can selectively quantify different types of lignin condensed units *in situ*, especially the diphenylmethane (DPM)-types suspected of being generated in the pulping stage.

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Prior studies,[7,8] based on the permanganate oxidation (PMO) method, generally led to the conclusion that the DPM-condensed structures were not the primary factor causing the low reactivity of alkaline pulp residual lignin. On the other hand, Chiang and Funaoka,[2] using the combined alkaline nitrobenzene oxidation (NO) and phenyl nucleus exchange (NE) techniques,[9,10] reported that over 50% of the phenyl nuclei present in extended kraft cooked softwood pulps were associated with the DPM-type structures.

We have been interested in possible causes for the contrasting observations obtained between the NO-NE and the PMO methods on the significance of lignin condensation reactions in alkaline pulping. Thus, we have investigated the reactivity of lignin DPM model dimers, **Ia**, **II**, **IIIa** and **IV** (Figure 1) under a variety of oxidative conditions.[11-15] These phenolic DPM dimers were generally shown to be rather reactive under nitrobenzene oxidation[13] and mild alkali-O_2[11,12] conditions resulting in significant formation of monomeric products.

One of the most interesting findings in mild alkali-O_2 treatments[12] (0.5 M NaOH at 55°C) was that the oxidative cleavages of the α-5 (**I**), α-1 (**IIIa**), and 5,5'-type (**IV**) DPM dimers all gave the alcohol-type products, vanillyl alcohol (**1**) or 5-hydroxymethylcreosol (**2**), whereas the α-6 dimer (**II**) gave the aldehyde products, vanillin (**3**) and 6-formyl creosol (**4**) (Figure 2). The formation of these distinctly different products were explained in terms of a variation in the cleavage of the hydroperoxide intermediates formed from initial oxygenation of the DPM unit.[12]

The reactivity of lignin DPM model dimers under alkaline pulping conditions, however, has not been studied in details. Gierer *et al.*[16] examined the alkaline stability of two α-5 (**Ib** and **Ic**), and two α-1 (**IIIa** and **IIIb**) dimers (Figure 2) in soda (2 M NaOH) and kraft (0.9 M NaOH + 0.4 M Na_2S) liquors at
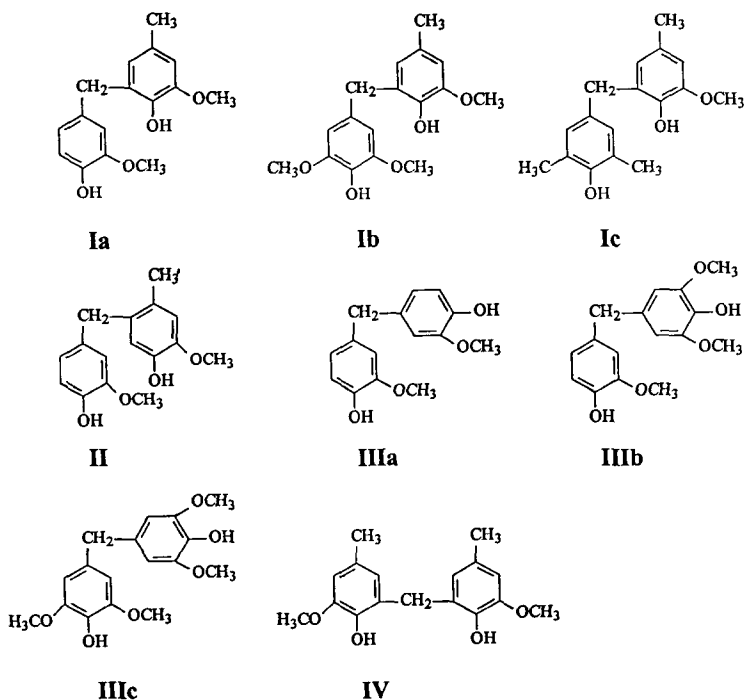
FIGURE 1 Lignin diphenylmethane model dimers.

170°C for 2 h. Based on thin-layer chromatographic (TLC) analysis of the ether extract of the reaction mixture, which was found to contain only the starting dimer, they concluded that all the dimers were essentially stable under alkaline pulping conditions. However, they did not provide any quantitative measurements of the unreacted dimers. Also, it was unclear whether traces of O_2 normally present in cooking liquors would have any effects on the DPM dimers under alkaline pulping conditions. These questions have been pursued in the present study in order to understand the fate of DPM condensed units in the alkaline delignification process.
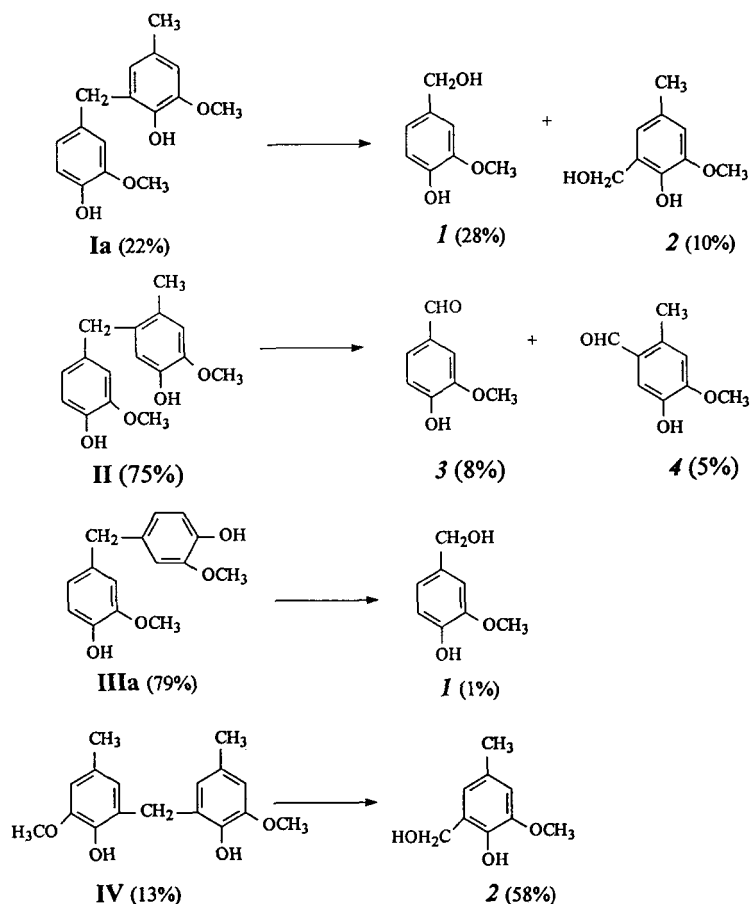
FIGURE 2   Monomeric products formed from mild alkali-O_2 treatments of diphenylmethane model dimers in 0.5 M NaOH at 55°C for 1 h. [1]

RESULTS AND DISCUSSION

The alkaline stability of four phenolic DPM dimers of the guaiacyl type (Ia, II, IIIa, and IV) and one disyringylmethane dimer (IIIc) (Figure 1) were examined in soda (1 M NaOH) and kraft (1 M NaOH + 0.3 M Na_2S) liquors at 170° for 3 h. In one series, the reactions were conducted in the presence of air, whereas in another series, the reaction vessels were purged with and sealed under

N_2 atmosphere. As indicated in Table 1, the DPM dimers were not entirely stable under alkaline pulping conditions, and, in most cases, were sensitive to the molecular O_2 present in the air, especially in the case of the disyringylmethane dimer **IIIc**.

Guaiacyl DPM Dimers

Under normal soda cooking conditions in the presence of air, the percent degradation for four guaiacyl dimers (**Ia**, **II**, **IIIa**, and **IV**) was in the 42-46% range. However, the degradation was drastically reduced to 8-10% with a N_2 purge of the reaction mixture prior to heating. The reactivity of these dimers was shown to decrease slightly in the order of α-5 (**Ia**), 5,5' (**IV**), α-6 (**II**), and α-1 (**IIIa**) types, as similarly observed[12] for their mild alkali-O_2 reactions at low temperatures (50-70°C).

However, extensive reactions of these dimers in soda cooks, unlike the mild alkali-O_2 reactions (Figure 2), resulted in little formation of monomeric products detectable by GC analysis and are likely to involve some unknown condensation processes. The latter possibility was supported by the appearance of immobile components on TLC analysis of the product mixtures.

Also, it was evident that the DPM dimers were considerably more stable in kraft liquor which contains sodium sulfide than in soda liquor under otherwise similar cooking conditions. For example, in the kraft liquor the degradation of α-5 dimer (**Ia**) was reduced from 46 to 11%, relative to the soda liquor. Since these dimers were shown previously to be very sensitive to oxygen in dilute alkali,[12] the stabilizing effect of sodium sulfide may be partly attributable to its ability to react with molecular O_2 at elevated temperatures. This contention is also consistent with the finding that the dimer stability in kraft cooks, like in soda cooks, can be further improved by a N_2 purge of the reaction vessels prior to heating.

TABLE 1

Alkaline Stability of Diphenylmethane Lignin Model Dimers[a] in Soda
(1 M NaOH) and in Kraft (1 M NaOH + 0.3 M Na_2S) Liquors at 170°C for 3 h

Dimer	Dimer Remained, %			
	Soda		Kraft	
	Air	N_2	Air	N_2
Ia	53.7	82.9	88.8	95.8
II	57.8	89.8	100	100
IIIa	58.4	91.7	100	100
IIIc	8.9	72.5	89.3	93.1
IV	56.3	88.8	89.4	96.9

[a]Structures are shown in Figure 1.

Disyringylmethane Dimer

As shown in Table 1, the α-1 disyringylmethane dimer (IIIc) was considerably more reactive than the corresponding guaiacyl dimer (IIIa) under alkaline pulping conditions (170°C for 3 h). For example, degradations of 42 and 91% were observed for dimers IIIa and IIIc, respectively, under otherwise similar soda cooking conditions in the presence of air. Interestingly, the syringyl dimer IIIc, in contrast to the corresponding guaiacyl dimer IIIa, gave significant amounts of an aldehyde product, (syringylaldehyde, 11), 2,6-dimethoxyphenol (12), and a dimeric product, (disyringylmethaneketone, 13).

Table 2 also indicates that the syringyl α-1 dimer (IIIc) was very reactive under mild alkali-O_2 condition (0.5 M NaOH at 70°C). A short reaction (6 min) resulted in a high degree of dimer degradation (69%) and a high yield of syringyl alcohol 8 (47%). As noted earlier, the guaiacyl α-1 dimer (IIIa) on a similar alkali-O_2 treatment also gave the alcohol-type product, vanillyl alcohol (1) (Figure 2). Thus, it appears that reaction of the syringyl α-1 dimer (IIIc) and the corresponding guaiacyl dimer (IIIa) under mild alkali-O_2 conditions are quite similar in mechanism and differ only in the reaction rate. A higher reactivity for

the syringyl dimer was also reported previously by Sultanov *et al.*[17] but the oxidation products were not examined.

However, the nature of products obtained from the syringyl α-1 dimer (**IIIc**) varied considerably with the oxidation conditions as indicated in Table 2. A low temperature reaction gave mainly syringyl alcohol, whereas syringaldehyde was obtained from a high temperature reaction. Thus, temperature appears to have a profound influence on the degradation mechanism of DPM units in an alkali-O_2 system.

Reaction Mechanisms

Interestingly, the oxidative cleavage products of α-1 disyringylmethane dimer **IIIc** observed in an alkali-O_2 system (Table 2) varied widely from syringyl alcohol to syringaldehyde depending on the reaction conditions. Figure 3 illustrates two possible mechanisms to accommodate the formation of these products. A key difference between these two mechanisms is in the transformation of the hydroperoxide adducts **5** and **5a** (Figure 3) following initial oxygenation at ring positions adjacent to the methylene carbon.

Reaction **A** involves an intramolecular cleavage of the hydroperoxide intermediate **5** to yield a quinone **6** and a quinonemethide **7**. The latter intermediate (**7**) adds water to yield syringyl alcohol (**8**). This reaction pathway appears to be dominant for the reaction of the α-5 (**I**), α-1 (**IIIa**) and 5,5' (**IV**) DPM dimers under mild alkali-O_2 conditions at low temperatures (Figure 2). Having a phenolic hydroxyl group at the *para* or *ortho* position relative to the methylene carbon facilitates this intramolecular cleavage process.

In contrast, reaction **B** involves an alkali-catalyzed intramolecular elimination of perhydroxyl anion to yield the disyringyl quinonemethide intermediate **9**. The latter intermediate (**9**) adds water to yield the

TABLE 2

Product Yields From Alkali Treatments of α-1 Disyringylmethane Dimer **IIIc**
Under Mild Alkali-O_2 (A) and Soda Cooking (B) Conditions[a]

Compounds[b]	Product Yield, Mole % of Dimer		
	Mild Alkali-O_2	Soda (Air)	Soda (N_2)
Unreacted dimer (**IIIc**)	30.6	8.9	72.5
Syringyl alcohol (**8**)	46.8	-	-
Syringyl aldehyde (**11**)	-	37.4	6.7
2,6-Dimethoxyphenol (**12**)	-	4.9	0.8
α-1 Disyringylketone (**13**)	-	8.9	3.2

[a]A - 0.5 M NaOH at 70°C under O_2 flow for 6 min;
B - 1 M NaOH at 170°C for 3h in the presence of air or N_2.
[b]Structures are shown in Figure 3.

disyringylcarbinol **10**, which is a likely precursor of several products which were obtained including syringaldehyde (**11**), 2,6-dimethoxyphenol (**12**), and disyringylketone (**13**). This pathway is clearly dominant for the reaction of the disyringyl α-1 dimer **IIIc** under alkaline pulping conditions at elevated temperatures. It is also a pathway in the oxidative cleavage of the diguaiacyl α-6 dimer **II** under mild alkali-O_2 conditions.[12] It is possible that reaction **B** is also operative in the degradation of other DPM units, especially for those hydroperoxide adducts lacking a conjugated phenolic hydroxyl group. This contention is being investigated further.

CONCLUSIONS

This study demonstrates that process conditions and structural factors can play dominant roles in the degradation mechanisms of DPM units in alkali-O_2 systems. This was clearly reflected in the oxidative products of disyringyl α-1 dimer **IIIc** whose products varied from an alcohol type at low temperatures to an aldehyde type at elevated temperatures.
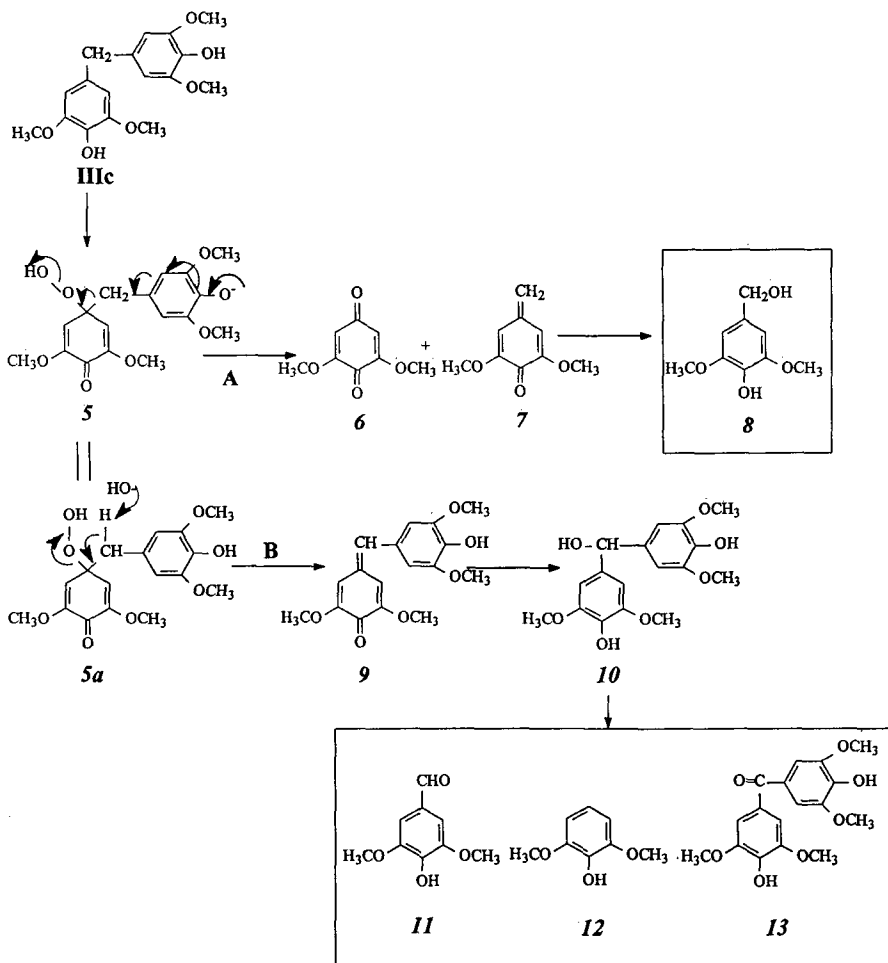
FIGURE 3   Proposed   mechanisms   for   the   degradation   of   α-1 disyringylmethane dimer **IIIc** in mild alkali-O₂ (A) and in soda cooking (B).

Judging from the behavior of the DPM dimers, it is anticipated that most of the phenolic DPM units, if they are generated in kraft pulping, would survive the harsh cooking conditions and remain in the pulp residual lignin. However, in the presence of molecular O_2, they could be transformed into a variety of products including stable condensed structures. Thus, the extent of such transformations would vary with the availability of molecular O_2 present in a pulping system, and it may play a role in affecting the reactivity of residual pulp lignin.

EXPERIMENTAL

Synthesis of Lignin Model Dimers

Reported procedures were used to prepare four guaiacyl type phenolic lignin DPM model dimers of (**Ia, II, IIIa**, and **IV**) and one syringyl type dimer **IIIc** (Figure 1). The α-5 dimer **Ia** prepared from the alkaline condensation of vanillyl alcohol and creosol[18] was obtained as crystals, m.p. 99-100°C. The α-6 dimer **II** was obtained from an acid-catalyzed condensation of vanilyl alcohol and creosol, and had m.p. 107-108°C (lit.[19] 112-115°C). The guaiacyl α-1 dimer **IIIa** was prepared from alkaline condensation of vanillyl alcohol, and had m.p. 108-109°C (lit.[20] 109-110°C). The 5,5'-DPM dimer **IV**, prepared from alkaline condensation of creosol with formaldehyde, had m.p. 131-132°C (lit.[21] 132-133°C). The syringyl α-1 dimer **IIIc** was obtained from alkaline condensation of 2,6-dimethoxyphenol and formaldehyde as a cotton-like crystal; m.p. 110-112°C (lit.[22] 111-112°C). In addition, an α-1 disyringylketone **13** was synthesized according to a procedure reported by Connors et al.,[23] and obtained as crystals with m.p. 166-167°C.

Alkali Treatments of Lignin Model Dimers

In general, a solution of lignin model dimer (10 mg) dissolved in 10 mL of cooking liquor was used. The alkali treatments with soda (1 M NaOH) and with kraft (1 M NaOH + 0.3 M Na_2S) liquors were conducted in small stainless-steel

autoclaves at 170°C for 3 h. In one series, the reaction vessels were sealed under ambient conditions, whereas in another series, the reaction vessels were purged with and sealed under a N_2 atmosphere. The alkali-O_2 treatments at low temperatures were conducted in small pearl-shaped flasks heated isothermally in a water bath at 70°C for 6 min. with a continuous flow of O_2 bubbling through the system.

For product analysis, the reaction mixture was acidified with 3.5 M HCl to pH 3-4 and extracted three times with $CHCl_3$. The combined $CHCl_3$ extracts were dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The products were silylated with BSTFA and analyzed by GC. For GC/MS analysis, the products were acetylated instead of silylated. Product identifications were confirmed by comparison with authentic compounds.

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