Kinetics of Alkaline Cleavage of β-Aryl Ether Bonds in Lignin Models: Significance to Delignification

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Introduction
Although the century-old kraft process is the major source of chemical wood pulp, only recently has an attempt been made to explain the delignification rate in terms of specific bond cleavage between arylpropane units in the lignin portion of the pulpwood (Ljunggren 1980). This is surprising because kinetic studies of wood delignification had been conducted much earlier and the major lignin cleavage reactions of phenolic β-0-4 aryl ethers (Adler et al. 1964; Gierer, Lenz, and Wallin 1964) and of non-phenolic β-0-4 aryl ethers (Gierer and Norén 1962) have been known for nearly 20 years. However, investigations of the rate of β-ether cleavage in anthraquinone/lignin-model systems (Obst and Sanyer 1980) and soda pulping with amines (Obst 1981a) raised questions regarding results obtained in alkali/water/organic-solvent systems. A continuation of a study of lignin-model/soda-amine reactions (Obst 1981b) led to a re-examination of the soda cleavage rates of nonphenolic β-aryl ethers. These results now require a new appraisal of the correlation of bond cleavage in simple model systems to delignification kinetics.

Materials and Methods
All model cooks were with 10 ml of liquor in 9.5 ID x 70 mm stainless steel bombs. Homogeneous cooks were with 30 to 40 mg of model. Bombs were placed in an oil bath at 170 °C and tumbled. Four minutes warmup time was subtracted for all times at temperature. Reaction products were isolated as before (Obst and Sanyer 1980).

Gluaycol analysis was performed by gas chromatography (Varian Vista 44) on a 2-m 3% OV-1column using 2,6-dimethoxynaphthal as internal standard. Acetylation (acetic anhydride/pyridine) was required for analysis of unreacted II. In all cases the amount of recovered starting material was measured: the sum of the

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guaiacol yield and percent recovery of starting material was always between 94 and 100%.

The 60:40 *erythro*:threo mixture of II was obtained by sodium borohydride reduction of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxypropanone in 95% ethanol. The ratio of the stereoisomers was determined by $^{13}$C NMR at 15 MHz and by $^1$H NMR at 270 MHz of II-diacetate.

**Results and Discussion**

Veratrylglycol-β-guaiacyl ether (I) and veratrylglycerol-β-guaiacyl ether (II) (Fig. 1) are commonly used as models in studies of cleavage of β-aryl ether bonds between non-phenolic units in lignin. Of the two, the glycerol ether is more appropriate because it more closely resembles the actual structural units in lignin. Although the reactions of I and II are similar, their rates of ether cleavage are not the same. Notably, the presence of the terminal hydroxymethyl group in II results in *erythro-* and *threo-* stereoisomers that have markedly different rates of alkaline cleavage (Miksche 1972). However, compound I has been widely used as a lignin model and its rate of soda cleavage has been used to explain the rate of bulk delignification in kraft pulping (Ljunggren 1980).

![Fig. 1. Lignin model compounds veratrylglycol-β-guaiacyl ether (I) and veratrylglycerol-β-guaiacyl ether (II).](image)

**Effect of solvent on alkaline cleavage of veratrylglycol-β-guaiacyl ether**

Veratrylglycol-β-guaiacyl ether (I) is not soluble in aqueous alkali at ambient temperature; water-soluble organic solvents, such as *p*-dioxane (Miksche 1972; Obst and Sanyer 1980) and methyl cellosolve (Gierer and Ljunggren 1979), can be added to produce homogenous solutions. However, difficulties arise in alkali/water/organic-solvent systems by the occurrence of phase separation either at ambient or pulping temperatures (Obst and Sanyer 1980; Obst 1981a). For example, 0.5N sodium hydroxide in 50% aqueous dioxane is one phase at 20°C but forms two phases on heating to 170°C, as is easily observed in a sealed glass tube. Fortuitously, the inclusion of bleached hardwood pulp and glucose in 50% dioxane cooks of I with 0.5N sodium hydroxide (Obst and Sanyer 1980) consumes/adsorbs enough alkali to maintain one phase at cooking temperature. Another difficulty in alkali/water/organic-solvent systems is the effect of the solvent on reaction rates. Although dioxane and methyl cellosolve have been assumed to have no effect on the cleavage rate of nonphenolic 0-aryl ethers in model systems, there are no data to support this assumption.

In a preliminary study on the effect of organic solvents on the rate of cleavage of I, it was observed that, unexpectedly, the highest rate of cleavage was with water as the only solvent. Although I was insoluble in aqueous alkali at ambient temperature it dissolved as 170°C was approached. However, the initial rate of soda cleavage of I in water at 170°C was slower than expected from first-order kinetics, presumably because some material was initially undissolved. This was verified by the decreasing rate of β-ether cleavage with increasing concentration of I as measured by guaiacol yields (Fig. 2).

![Fig. 2. Effect of concentration on the extent of cleavage of veratrylglycol-β-guaiacyl ether (I) (0.25N NaOH, water solvent, 170°C, 1 hr).](image)

Because model I was soluble in aqueous alkali at lower concentrations, a direct comparison was made between treatments in aqueous and aqueous-organic solvent systems. The rate of β-ether cleavage of I with 0.5N sodium hydroxide at 170°C, as determined by guaiacol yields, was faster in water than in 30% methyl cellosolve (Fig. 3). The effect of varying the amount and type of organic solvent on the amount of guaiacol released by ether cleavage within 1 hour was also determined (Fig. 4). A reduction of the cleavage rate with methyl cellosolve occurred up to about 30% addition. Increasing the concentration of methyl cellosolve beyond 30% did not significantly further reduce the cleavage rate. Additions of dioxane to the soda cook of I reduced the yield of guaiacol even more than did methyl cellosolve; the greatest rate suppression also occurred up to about 30% concentration as measured by guaiacol yields (Fig. 4). Between 50% and 60% concentration of dioxane in the liquor a major reduction in rate was observed which resulted from phase separation. Although I is soluble at 170°C in such a two-phase system, I would be more soluble in the dioxane layer. Because the dioxane layer contained only a small amount of the total alkali (Obst and Sanyer 1980), a low yield of guaiacol would be expected.

Because commercial kraft and soda wood cooks are performed with water as the only solvent, correlation of the rate of nonphenolic β-ether cleavage of a lignin model in
Kinetics of Alkaline Cleavage of β-Aryl Ether Bonds in Lignin Models

Fig. 3. Guaiacol yield from β-ether cleavage of veratrylglycerol-β-guaiacyl ether (I) with 0.5N NaOH at 170°C in water and aqueous methyl cellosolve or dioxane to wood delignification would be erroneous. However, comparisons of the rates of cleavage of bonds within model systems is valid for example, comparison of the rate of alkaline cleavage of the O-aryl ether bond in I in dioxane-water with and without anthraquinone (Obst and Sanyer 1980).

Fig. 4. Soda cleavage of veratrylglycerol-β-guaiacyl ether (I) with varying amounts of methyl cellosolve and p-dioxane (0.25N NaOH, 170°C).

Alkaline cleavage of veratrylglycerol-β-guaiacyl ether

Veratrylglycerol-β-guaiacyl ether (II) is a more appropriate lignin model than I; moreover, erythro-II undergoes alkaline cleavage faster than does threo-II (Miksche 1972). If erythro- and threo- forms of phenylglycerol units with β-aryl ethers occur in lignin in about equal amounts (Nimz and Lüdeman 1976) then it is of interest to examine the alkaline cleavage rates not only of the pure isomers but also that of an erythro- + threo-mixture of II. Such a mixture was prepared by borohydride reduction of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxypropanone to give a 60:40 erythro/threo mixture. Due to its hydroxymethyl group, model II is even more soluble in aqueous alkali at 170°C than I; comparisons of alkaline treatments in water, 30% methyl cellosolve, and 30% dioxane were made (Fig. 5). The cleavage rate of II was essentially unaffected by 30% methyl cellosolve. The rate was slowed by 30% dioxane but not as much as for I under the same conditions.

Fig. 5. Guaiacol yield from β-ether cleavage of veratrylglycerol-β-guaiacyl ether (60:40 erythro/threo-II) with 0.25N NaOH at 170°C in water, 30% methyl cellosolve or 30% p-dioxane.

Although it had been established (Miksche 1972) that alkaline cleavage of the pure stereoisomers of II was pseudo first-order, the rate of alkaline hydrolysis of the erythro- + threo-mixture of II was not first-order (Fig. 6). Using the rate constants from the plots of the pure erythro- and threo-isomers, the simulated rate data for a 60:40 erythro:threo mixture were calculated, plotted, and found to agree with the experimentally determined rate (Fig. 6). The nonlinearity is explained by the fact that the overall rate is a result of two significantly different pseudo first-order reactions. The erythro:threo ratio is changing throughout the cook: the erythro-isomer reacts faster resulting in an enrichment of threo-II. Accordingly, the rate of production of guaiacol is fast in the early stages of the cook whereas, toward the end, the mixture is composed of mainly threo- isomer with a resulting slow cleavage rate.

Fig. 6. First-order cleavage-rate plots of veratrylglycerol-β-guaiacyl ether (II) in aqueous 0.25N NaOH at 170°C. Experimental: o; Calculated: A.
Significance of $\beta$-aryl ether cleavage to delignification rate

The validity of directly applying the results of kinetic studies with models to lignin depolymerization in the pulping of wood is untested. However, it has been postulated that the rate-determining step during bulk delignification in kraft wood pulping is cleavage of nonphenolic $\beta$-aryl ethers in lignin (Ljunggren 1980). This postulate requires several assumptions, including one that the rate of $\beta$-aryl ether cleavage in nonphenolic units in wood lignin is the same as in the model systems. This seems unlikely: bond cleavage in the homogeneous model system ought to be faster than in the heterogeneous, polymeric wood system. Another assumption is that the cleavage rate of a 50:50 mixture of erythro- and threo-veratryl-glycerol-$\beta$-guaiacyl ether is the same as that of the glycol model (Ljunggren 1980). This assumption has now been shown to be incorrect because not only does the glycol-$\beta$-aryl ether exhibit different cleavage rates in water and 30% methyl cellosolve but, more importantly, alkaline cleavage of the $\beta$-ether bonds in erythro/threo mixtures of glycerol-$\beta$-aryl ethers do not follow first-order kinetics. The significance of this is that the kinetics of the cleavage of $\alpha$-aryl ethers in the model system does not correlate to the well-established apparent first-order kinetics of bulk delignification (Marton 1971; Axegård and Wilken 1981).

Only one attempt has been made to correlate model cleavage kinetics to delignification kinetics (Gierer and Norén 1980); results obtained by premethylation of wood by various methods followed by kraft pulping were claimed as supportive. However, care must be exercised in equating the dissolution of methylated lignin with lignin depolymerization. For example, milled wood lignin methylated with diazomethane does not dissolve in aqueous alkali and the low reactivity of diazomethane-methylated wood in alkaline pulping may be due, at least partly, to the poorer swelling and dissolution properties of methylated lignin (Obst, Landucci, and Sanyer 1979; Obst and Sanyer 1980). Therefore the lack of an initial fast delignification phase (Gierer and Norén 1980) upon pulping of wood subjected to diazomethane methylation may alternatively be explained by the insufficient phenolic content of the lignin necessary to effect dissolution.

Study of lignin model systems has shown that the major difference between soda reactions and sulfide and anthraquinone reactions was the increased cleavage of free phenolic $\beta$-ethers observed with the additives (Obst and San-

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Fig. 7. Cleavage of a key $\beta$-aryl ether in lignin. Cleavage may occur: 1 Directly from a nonphenolic $\beta$-ether, 2 Directly from a phenolic $\beta$-ether, or subsequently, from a phenolic $\beta$-ether 2 resulting from cleavage of a nonphenolic $\beta$-ether 2a.
The rate of cleavage of nonphenolic $\beta$-ethers depended only on the alkali concentration (Obst and Sanyer 1980). If the direct application of simple model kinetics to wood delignification rates were valid, bulk delignification rates for kraft and soda pulping should be the same at identical alkali concentrations. Although this prediction is incorrect, it is reasonable to assume that the major chemical reaction controlling the rate of delignification in any of these systems is cleavage of $\beta$-aryl ether linkages. However, as previously suggested (Obst and Sanyer 1980), not all cleavages of $\beta$-aryl ethers in lignin contribute equally to delignification. Certain “key” $\beta$-aryl ethers, either nonphenolic or phenolic, may be defined as those whose cleavage results in significant dissolution of lignin by depolymerization (Fig. 7, Routes 1,2). Some $\beta$-ether cleavages enhance delignification merely by increasing the phenolic content of lignin and, therefore, its solubility in the liquor. Other $\beta$-ether cleavages minimally assist delignification by removal of small superficial end-groups or oligomers (a kind of lignin “peeling” (Ljunggren 1980)). The importance of key $\beta$-ether linkages, or of any other interunit linkage, is speculative but not unreasonable. For example, cleavage of a nonphenolic $\beta$-aryl ether in a high molecular weight lignin (Fig. 7, Route 2a) does not result in delignification by molecular weight reduction because of cross-linking. However, if the resulting free phenolic $\beta$-ether is subsequently cleaved (approximate relative extent: soda 0.2, kraft or anthraquinone 0.44, and kraft and anthraquinone 0.52 (Obst, Landucci, and Sanyer 1979)), a key interunit linkage is broken and two soluble lignin fragments of lower molecular weight result (Fig. 7, Routes 2a,2).

New phenolic $\beta$-ethers may be generated during delignification (Fig. 7, Route 2a). The rate of cleavage of key nonphenolic $\beta$-ethers may be increased by increasing the alkali concentration (Obst and Sanyer 1980). The claim that the subsequent fast cleavage of newly formed free phenolic $\beta$-ethers has no influence on the rate of delignification (Ljunggren 1980; Gierer 1981) is untenable, considering earlier results: for example, when anthraquinone was added to soda cooks of southern pine after various times, the bulk delignification rate increased (Obst, Landucci, and Sanyer 1979). Cleavage rates of key phenolic $\beta$-ethers may be increased by increasing alkali concentration (Obst and Sanyer 1980) or by adding sulfide or anthraquinone or both. An additional beneficial effect in kraft and anthraquinone cooks is that reactions of additives with quinone methides may reduce lignin condensation reactions and thereby increase delignification rates.

The overall rate of depolymerization of lignin is influenced largely by several concurrent and consecutive $\beta$-ether cleavage reactions of greatly varying rates. The similarity of the apparent pseudo first-order rate of bulk delignification in alkaline pulping and the rate of first-order cleavage of certain $\beta$-ethers in model systems is coincidental and would be misleading in understanding the mechanism of delignification. The dissolution of lignin of increasing molecular weight in the course of digestion is the consequence of the highly heterogeneous nature of cleavage reactions that involve mostly $\beta$-ethers. The delignification rate is further influenced, however, by the polymeric and colloidal properties of the reaction substrate such as the diffusion of lignin fragments and the surface properties and pore structure of the fiber (Szabo and Goring 1968; Yan and Johnson 1981) all of which require additional quantification.

Observations

Veratrylglycol-$\beta$-guaiacyl ether (I) was sufficiently soluble in water at 170°C to allow comparison of aqueous alkali treatment to dioxane/water and methyl cellosolve/water alkaline treatments. Both organic solvent systems depress the rate of guaiacol formation from I. In similar treatments of veratrylglycerol-$\beta$-guaiacyl ether (II) only dioxane reduced the alkaline cleavage rate and then only slightly. More important, the rate of alkaline cleavage of a 60:40 erythro/threo mixture of II was not first-order. Rate data for a 60:40 mixture were calculated from the rates of cleavage of the pure isomers and agreed closely with those determined experimentally. These results did not support the supposition that the kraft delignification rate of wood may be described by the kinetics of simple lignin models. Rather, wood delignification is more complex and must be evaluated on the basis of lignin depolymerization.

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References


