Chapter 18

Polyoxometalate Oxidation of Phenolic Lignin Models

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A new environmentally friendly technology for wood pulp delignification, based on the use of polyoxometalates (POMs) and oxygen, is being developed. Polyoxometalate solutions that selectively oxidize lignin under anaerobic conditions can be reoxidized by oxygen and also catalyze the aerobic mineralization of the lignin fragments to CO₂ and H₂O, making possible the closed-mill manufacture of paper. Model studies on the oxidation of various lignin-like soluble compounds with POMs suggest that single-electron oxidation of phenolic substructures occurs first, followed by the hydrolysis of cationic intermediates. Detailed physico-chemical studies of the solutions of the alkali-metal salts of POMs show a correlation between the reduction potentials of POMs and the rate of oxidation of a phenolic lignin model that is ascribed to ion pairing between alkali-metal cations and POM anions.

The delignification of wood is a major process in the manufacturing of paper, one of the largest industries in the world. The goal of the delignification process is to chemically remove lignin (the component of wood that in residual quantities deteriorates the quality of paper) and to leave cellulose (the desirable component of wood) undamaged. The search for selective and environmentally
friendly pulp bleaching technologies that can be used to achieve effluent free (closed-mill) manufacturing is a current challenge for the paper industry worldwide. The use of polyoxometalates (POMs) as reusable oxidants to achieve these goals was first reported in 1996 in (I). The chemical selectivity and economic feasibility of the newly developed process of pulp delignification by POMs makes it quite competitive with conventional chlorine-based and with alternative totally chlorine free (TCF) delignification technologies (2-5).

Polyoxometalates

Polyoxometalates are structurally diverse anionic clusters consisting of d⁰ metal cations, particularly W(VI), Mo(VI), V(V) and Nb(V) and oxygen anions arranged in MO₆ octahedral units (6,7). The attributes of POMs such as low cost, commercial availability, and synthetic tractability (acidity, solubility, thermal stability and redox potentials can be controlled) make them attractive for the use as acid or oxidation catalysts (8-10). One of the best studied POM families is Keggin-type heteropolyoxoanions of general formula XM´₆M´´¹₂₋₁ₐOₘ⁻ where X⁺ is a d- or p- block “heteroatom”, M´ and M´´ are d⁰ and dⁿ metal centers, respectively (Figure 1). They have prominent advantages that can be attractive for oxidation reactions including delignification processes. First, many physical properties such as redox potential, solubility or molecular charge can be controlled by the choice of synthetic precursors or reaction conditions. Second, they can be reversibly reduced by one or more electrons. Third, the d⁰ metal cations of parent POMs can be substituted by other d metal ions thus affording a multitude of POMs that exhibit a wide range of physical and chemical properties.

POM Delignification

Delignification technology based on POM catalysts is being developed at the Forest Products Laboratory of the U.S. Department of Agriculture, Forest Service, the Emory University Department of Chemistry and the University of Wisconsin-Madison, Department of Chemical Engineering. The overall wood pulp bleaching process is accomplished in 2 steps. First, unbleached pulp is heated in an aqueous solution of a fully oxidized POM (POM,') under anaerobic conditions to yield soluble oxidized lignin fragments (Lignin,') and the reduced POM (POM,red) (Scheme 1, Step 1). The blched cellulose is then separated and the reduced bleaching liquor is treated with O₂ at elevated temperature and pressure (Scheme 1, Step 2). During this POM reoxidation step, the POM simultaneously catalyzes the O₂ oxidation of the dissolved lignin fragments to
Figure 1. Polyhedral representation of monosubstituted Keggin-type POM $[X^n\text{VW}_{11}\text{O}_{40}]^{8-}$ where the central tetrahedron represents the XO$_4$ ($X^n = \text{Al}^{3+}$, $\text{Si}^{4+}$ or $\text{P}^{5+}$) unit, the shaded octahedron represents the VO$_6$ unit and the unshaded octahedra represent the WO$_6$ units,
CO₂ and H₂O (aerobic mineralization). Thus, the net reaction for POM-mediated delignification is the selective transfer of electrons from lignin to O₂. The POM must possess a reduction potential positive enough to effectively oxidize lignin in Step 1 and sufficiently negative for spontaneous (i.e., thermodynamically favorable) reoxidation by O₂ in Step 2.

Of the many POMs formulated and evaluated for effectiveness in delignification (Step 1), [SiV\textsuperscript{IV}W\textsubscript{11}O\textsubscript{40}]\textsuperscript{5-} (1) is among the most selective (3). For effectiveness in the overall cycle (Scheme 1), the POM must be reoxidized by O₂ (Step 2). Though thermodynamically favorable, the reoxidation of reduced 1, [SiV\textsuperscript{IV}W\textsubscript{11}O\textsubscript{40}]\textsuperscript{6-} (1\textsubscript{red}), is extremely slow on an industrial time scale even at 200 °C and several atmospheres of oxygen. While new equilibrating POM systems designed for optimum effectiveness in both Steps 1 and 2 have been developed (the unique and complex self-buffering chemistry of these new systems will be reported elsewhere), 1 remains an ideal starting point for detailed mechanistic study of POM delignification (11,13).

In this chapter, reactions of 1 are used to address mechanistic aspects of oxidative delignification by POMs (Step 1). Studies included here include the investigation of the reactions of 1 (chosen for quantititative lignin-model studies as it is not only very effective in delignification, but also readily available in chemically and isomerically pure form) with lignin model compounds, and physico-chemical studies of several isostructural POMs and correlations between their thermodynamic (reduction potentials) and kinetic (reactivity with a phenolic lignin model) properties.
Results and Discussion

Oxidation of Lignin Models by Polyoxometalates

Lignin has a polymeric structure consisting of cross-linked hydroxylated (ca. 15%) and methoxylated phenylpropane monomers. In kraft lignin, the amount of hydroxylated phenyl structures increases to ca. 20-40 % as a result of the cleavage of aryl ether bonds during kraft pulping (12). Preliminary studies of the oxidation of various lignin models, reported in a recent publication (3), showed that phenolic substructures are substrates for oxidation by 1. Under actual delignification conditions (pH 7 phosphate buffer, 3 h at 125 °C), the phenolic β-aryl ether lignin dimer model 3 undergoes a rapid oxidative cleavage by 1. Oxidation of the non-phenolic analogue 4 is under investigation.

Further studies of the oxidation of lignin-like phenolic compounds with no ortho substituents (i.e., R₂ = H) indicate that phenoxyl radicals are likely intermediates (13). At room temperature, the oxidation of 5 by 1 results in the rapid oligomerization of 5, a result consistent with coupling of phenoxyl radical intermediates. Phenoxyl radicals are also very likely intermediates in the delignification of pulp; relative to solutions, however, radical coupling is less likely in media of restricted molecular mobility, such as within the ligninocellulosic matrix of the cell wall.

In order to study the cleavage reaction of a phenolic model under the conditions wherein competing oligomerization processes are minimized, the substituted phenolic model, 3, was used. At room temperature, 3 was rapidly oxidized by 1 to yield an approximately 1:1:1 mixture of 6,7 and 8 (Scheme 2).
The \( \alpha \)-ketone, 6, results from dehydrogenation of the benzylic hydroxyl group of 3, while compounds 7 and 8 result from repeated oxidation and hydrolysis of 3 and subsequent intermediates. To give a 1:1 ratio of two-electron (6) and four-electron (7 and 8) oxidation products, three equivalents of 1 would be consumed per equivalent of 3. This was confirmed experimentally.

The phenolic diphenylmethane, 9 (Scheme 3), which is believed to form under alkaline pulping conditions, rapidly reacts with 1 at room temperature. The alcohol 10, along with small amounts of \( \text{para} \)-benzoquinone, 11, and...
3,4,5-trimethoxybenzaldehyde, 12, were found among the reaction products. After reaction at elevated temperature, the alcohol, 10, a possible intermediate in further oxidative cleavage, was not detected.

These results strongly suggest that phenol oxidation reactions are crucial in delignification of native and residual kraft lignins by 1. Oxidation reactions of non-phenolic lignin components remain under investigation. Experimental details of the results summarized in Schemes 2 and 3 are reported in ref. (13).

**Oxidation of a Phenolic Lignin Model by a POM. Kinetics Studies.**

While investigation of the oxidation of the solubilized lignin models under homogeneous conditions does not allow for assessment of mass-transfer limitations that may be operable during reactions in wood fibers, it does provide considerable information about the redox and fragmentation chemistry. However, the dimeric lignin-like models described above are difficult to use for detailed kinetic (mechanistic) studies of their oxidations by 1 because the reactions give rise to product distributions. As noted above, unsubstituted phenols are prone to couple upon one-electron oxidation. Moreover, other functional groups (-CHOH, -CH₂-, etc.) can also undergo oxidation. Thus, the ideal model for studying oxidation of the phenolic moiety should possess a reactive phenolic group attached to a substituted phenyl ring that is otherwise resistant to oxidation by 1. Of the many compounds evaluated for their suitability in detailed kinetic studies, 3,3',4,4'-tetra-tert-butyldiphenyl-1,1'-diol (13, diphenol, abbreviated (PhO)₂H₂) was found to optimally satisfy these requirements. This diphenol reacts with Li₅SiVₓW₄O₄₀ (Li₁) in tert-butanol/water (3:2, v/v) at 60 °C under argon to give a single organic product 3,3’,4,4’-tetra-tert-butyldiphenylenone, 14, and SiVₓW₄O₄₀⁻ (1₄₋), by the stoichiometry shown in eq 1. One equivalent of 1₄ (quantified by ¹H NMR) and 2 equivalents of 1₄₋ (determined by UV-vis spectroscopy) are formed per equivalent of 13 consumed. During the reaction, 2 equivalents of H⁺ should be generated; therefore, the aqueous component of the solvent mixture was buffered with 0.1 M LiOAc/HOAc (pH 4.76) prior to mixing with tert-butanol.

The reaction kinetics were monitored using UV-vis spectroscopy by following the characteristic absorbance of 1₄₋ (λ = 520 nm, ε = 619 L mol⁻¹ cm⁻¹). The rate law determined by the initial rate method, \( \frac{d[1₄₋]}{dt} = k_{\text{app}}[(\text{PhO})₂H₂][1] \), is first order in both substrate (13, (PhO)₂H₂) and oxidant (1) and effectively zero order in both 1₄₋ and acetate anion. These results suggest that the rate limiting step (r.l.s.) is bimolecular, the forward reaction for the reduction of 1 is much faster than the reverse. One under the reaction conditions
used, and subsequent proton abstraction by acetate (acting as a base), if it occurs, is significantly faster than the r.l.s.

The reaction rate is independent of ionic strength, but dependent on the Li⁺ concentration. Therefore, when the amounts of 1, 1_red or LiOAc were varied in kinetic studies, the concentrations of the alkali-metal cations were carefully controlled by adding the corresponding amounts of LiCl in order to keep the Li⁺ concentration constant. The dependence on Li⁺ concentration is attributed to ion pairing between 1 and Li⁺. Ion pairing in polyoxometalate solutions is discussed in the next section and also addressed in recent work (14,15).

The apparent second-order rate constant, determined as $k_{app} = (\frac{d[1\text{red}]}{dt}) / ([1\text{red}][\text{oxidant}])$, is dependent on the proton concentration (Figure 2). The observed data indicate parallel pathways for the reduction of 1. Such a complex dependence of the reaction rate on [H⁺] is characteristic for phenol oxidation reactions in aqueous or mixed solutions where both a phenol molecule and a phenolate ion are in equilibrium with each other and compete for the oxidant (16-18). Under the reaction conditions used in this study, the protonated diphenol molecules (PhO)_2H_2 are the dominant species (in tert-butanol/water (3/2, v/v) at 60 °C, $pK_a$ of the diphenol were estimated to be ca. 13.5-14.5 and 14.0-15.0, respectively). Oxidations of fully protonated (PhO)_2H_2 and of monoprotonated (PhO)_2H both contribute to the reaction rate; while oxidation of fully deprotonated (PhO)_2^2⁻ is not kinetically significant (see Figure 2, inset, and discussion below). A mechanism for the phenol and monophenolate oxidation by 1 consistent with the data is given in eqs 2-5.
Under these reaction conditions, 1 is a single-electron oxidant; therefore both the diphenol and the monophenolate are likely to react with 1 in parallel pathways (eqs 3 and 4) to give phenoxy radicals, the initial one-electron oxidation intermediates. Given that steps 3 and 4 are rate limiting, the steady-state approximation applied to the concentrations of the intermediates can be used to derive the dependence of the reaction rate on the concentrations of the reactants (eq. 6):

\[
\text{The derived rate expression, eq 6, is the same as the empirical rate law with the apparent rate constant } k_{\text{app}} = 2 \left( k(\text{PhO})_2\text{H}_2 + k((\text{PhO})_2\text{H}) \cdot K_a/[\text{H}^+] \right), \text{ which validates the approximations made. Rigorously, including } K_a, \text{ } k_{\text{app}} = 2 \left( k(\text{PhO})_2\text{H}_2 + k((\text{PhO})_2\text{H}) \cdot K_a/[\text{H}^+] + k((\text{PhO})_2\text{H}) \cdot K_a \cdot K_a/[\text{H}^+] \right). \text{ However, the plot of } k_{\text{eq}} \text{ vs. } 1/[\text{H}^+] \text{ (Figure 2, inset) gives a straight line rather than a parabolic curve, which demonstrates that the third term (due to oxidation of the}
di-anion, \((\text{PhO})_2^{2-}\) is not kinetically significant. From the linearized function \((k_{\text{app}} \text{ vs. } 1/[\text{H}^+])\), \(k((\text{PhO})_2\text{H})\) and \(K_a\) are obtained. Thus, the reactivity of the monophenolate towards 1 \((k((\text{PhO})_2\text{H})= \text{ca.} 10^5-10^6 \text{L mol}^{-1} \text{s}^{-1})\) is roughly \(10^5-10^6\) times higher than that of the diphenol \((k((\text{PhO})_2\text{H}_2)=0.02 \text{L mol}^{-1} \text{s}^{-1})\).

The empirical rate law (eq 6), established only for the initial rates, can be extrapolated up to 90-95% conversion of phenol by using the integrated dependence of the absorbance vs. time (eq 7), where \(E\) is the extinction coefficient of \([\text{I}_{\text{red}}]\), \([\text{I}]_0\) and \([\text{I}]_o\) are initial concentrations of the diphenol and \([\text{I}]\), and \(A_t\) and \(A_o\) are the initial absorbance and the absorbance at time \(t\), respectively, and \(l\) is the pathlength.

\[
A_t = e \left\{ \frac{[\text{I}]_0 - \frac{[\text{I}]}{2}}{[\text{I}]_o \exp \left[ k_{\text{app}} \left( \frac{[\text{I}]}{2} \right) \right] - \frac{1}{2}} \right\} l + A_o
\]

Eq 7 is the Lambert-Beer's law \(A_t = [\text{I}_{\text{red}}]_t + A_o\), where the expression for the concentration of \([\text{I}]\) at time \(t\) was obtained by integration of the differential equation \(d[\text{I}_{\text{red}}]/dt = k_{\text{app}}([\text{I}]_0)\) (empirical rate law) given the stoichiometry\([\text{O}]:[\text{I}] = 1:2\) (eq 1).

The experimental data were fitted to eq 7 by varying the \(k_{\text{app}}\) values in order to minimize the sum of the squares of the deviations. From Figure 3, one can see that the model holds up to 90-95% conversion of diphenol, after which point the steady-state approximation itself is no longer valid. Thus, the proposed mechanism (eqs 2-5) is valid for nearly the entire reaction.

In order to establish the more intimate mechanistic details of the reaction, kinetic isotope studies with the diphenol deuterated in OH-positions were carried out. The deuterated diphenol \((\text{PhO})_2\text{D}_2\) was generated in situ by using the deuterated solvent mixture tert-BuOD/D\(_2\)O (pD of the D\(_2\)O component = 3.90). The reactions were run at low pH (pD) to eliminate the contribution of the monophenolate oxidation in the apparent rate constant. The determined \(k_D/k_o\) value of 1.2 ± 0.2 indicates that hydrogen atom transfer is unlikely to occur in the activation complex.

The possible mechanisms are narrowed further by determination of the activation parameters associated with the rate-limiting step. From the plot of \(\ln(k((\text{PhO})_2\text{H})/T)\) vs. \(T\) (50-85 °C), the enthalpy of activation \((H^\ddagger)\) and the entropy of activation \((S^\ddagger)\) were found to be \(8.5 ± 1.4 \text{ kcal mol}^{-1}\) and \(-39 ± 5 \text{ esu}\), respectively. The low \(H^\ddagger\) is characteristic of outer-sphere electron transfer reactions. The negative \(S^\ddagger\) value is consistent with a bimolecular r.i.s. (eq 3). The absolute value of the entropy of activation is unusually high for an outer-
Figure 2. Plot of $k_{\text{app}}$ vs. $[H^+]$: $[H^+]_{\text{eq}} = 6.5 \times 10^6 - 1.3 \times 10^7$ (measured in tert-butanol/water mixture), $[\text{LiI}] = 0.48$ mM, $[\text{PhOH}] = 2.86$ mM, $[\text{LiOAc}] = 0.1$ M, $[\text{HOAc}] = 0.1$ M. 60 °C. Inset: plot of $k_{\text{app}}$ vs. $1/[H^+]$.

Figure 3. Absorbance at 520 nm as a function of reaction time for the oxidation of diphenol by Li:1 (open circles) and kinetic model fitting to eq 7 (solid line); $k_{\text{app}} = 0.0412$ L mol$^{-1}$ s$^{-1}$, sum of standardized square residuals = $4.4 \times 10^4$. 
sphere electron transfer process, but can be rationalized by a sterically restricted activated complex. The steric constraint arises from the very low ratio of the size of the COH and V=O moieties relative to the total surface area of the two large reacting molecules, diphenol and 1 (ca. 0.002 and 0.0004, respectively). That is, for electron transfer to occur, the reacting species must collide in a very specific and restricted orientation involving the close proximity of the OH-group and the V=O moiety of 1, which greatly increases the entropy of activation.

These detailed kinetic data indicate that this diphenolic lignin model is oxidized by 1 via an outer-sphere single-electron transfer mechanism. Highly reactive phenoxy1 radicals are likely generated in the bimolecular rate-limiting step. At high pH, the parallel pathway involving oxidation of the monophenolate anion, that is significantly more reactive than the parent phenol, contributes to the overall rate. Clearly, under actual delignification conditions (water and neutral or basic pH), oxidation of phenolic substructures is likely to involve reactions of both protonated and deprotonated phenolic groups.

**IonPairinginPOMSolutions**

As discussed above, the reaction rate increases with an increase in alkali-metal cation concentration (Figure 4). Detailed kinetic and physico-chemical studies of this phenomenon show that in tert-butanol/water (3:2, v/v), 1:1 ion pairing between 1 and Li⁺ occurs (14,15).

Both unpaired and paired POM anions (1 and Li₁) are believed to react with the diphenol in parallel pathways (eqs 9 and 10).

\[
1 + (\text{PhO})_2\text{H}_2 \xrightarrow{k_0} 1_{\text{red}} + (\text{PhO})_2\text{H}^+ + \text{H}^+ \quad (9)
\]

\[
\text{Li}_{1} + (\text{PhO})_2\text{H}_2 \xrightarrow{k_1} \text{Li}_{1_{\text{red}}} + (\text{PhO})_2\text{H}^+ + \text{H}^+ \quad (10)
\]

Based on the modified reaction mechanism (eqs 8-10), the functional dependence of the apparent rate constant (\(k_{\text{app}}\)) on Li⁺ concentration was derived:
Figure 4. Plot of $k_{\text{app}}$ vs. $[\text{Li}^+]$: $[\text{Li}^+] = [\text{LiCl}] + 5[\text{LiI}] + [\text{LiOAc}]$, $[\text{LiCl}] = 0.0 - 0.2 \text{ M}$, $[\text{LiI}] = 1.0 \text{ mM}$, $[\text{PhOH}] = 2.0 \text{ mM}$, $[\text{LiOAc}] = 1 \text{ mM}$, $[\text{HAc}] = 1 \text{ mM}$, 60 °C, argon. Inset: plot of $E_{1/2}$ vs. $[\text{Li}^+]$, same conditions except no PhOH present; $E_{1/2}$ vs. Ag/AgCl electrode. The solid lines are the best fits to eqs 11 and 12, sum of standardized square residuals = $6.4 \cdot 10^{-5}$. 
where \( k_o \) and \( k_1 \) are the rate constants for the oxidation of the diphenol with unpaired and paired POM anions, respectively, and \( K_{IP} \) is an ion pair formation constant. Experimental rate data were successfully fitted to the model (eq 11) by non-linear least square regression (three parameters, \( k_o, k_1 \), and \( K_{IP} \) were allowed to vary to minimize the sum of squares of the deviations). A similar functional dependence of the observed reduction potentials of \( \mathbf{1} \) on Li\(^+\) concentration was also observed (Figure 4, inset). Under the same experimental conditions as those used in the kinetic studies, the curve in Figure 4, representing the functional dependence of the weighted-mean reduction potential, \( E \), on [Li\(^+\)], reaches a plateau. Moreover, the kinetic and electrochemical data in Figure 4 were both simultaneously fit to the corresponding model equations 11 and 12 by varying the parameters \( K_{IP} \) (identical in both eqs 11 and 12), \( k_o, k_1, E_o \), and \( E_1 \).

\[
k_{app} = \frac{k_o + k_1 K_{IP}[\text{Li}^+]}{1 + K_{IP}[\text{Li}^+]} \tag{11}
\]

The excellent fits (\( K_{IP} = 34 \text{ L mol}^{-1}, k_o = 0.012 \text{ L mol}^{-1} \text{s}^{-1}, k_1 = 0.050 \text{ L mol}^{-1} \text{s}^{-1}, E_o = 0.19 \text{ V}, E_1 = 0.34 \text{ V} \)) shown in Figure 4 support the proposed mechanism involving 1:1 ion pairs (eqs. 8-10).

Three independent lines of evidence in support of the 1:1 ion-pair stoichiometry shown in eqs 8 and 10 were obtained (15). Further kinetic and electrochemical studies of ion-pairing with various alkali-metal cations (K\(^+\), Na\(^+\), and Li\(^+\)) and the POM anions PVW\(_{11}\)O\(_{40}\)^{4-}, SiVW\(_{11}\)O\(_{40}\)^{5-}, and AlVW\(_{11}\)O\(_{40}\)^{6-} demonstrate similar rectangular hyperbolic dependencies of rate constants and reduction potentials on alkali-metal cation concentrations (14, 15). Both the reduction potential of each ion pair (\( E_i \)) and the rate constant (\( k_i \)) for its reduction by the diphenol increase in the order: Li\(^+\) < Na\(^+\) < K\(^+\). This trend is rationalized in terms of the relative sizes of the ion pairs. The effective hydrodynamic radii (\( r \)) of the ion pairs were calculated using the Stokes-Einstein equation: \( D = kT/6 \pi \eta r \) where diffusion coefficients (\( D \)) were determined by chronoamperometry, and solvent viscosity (\( \eta \)) was measured by the capillary-flow method. For the ion pairs \( \{\text{M}^+\text{SiVW}_{11}\text{O}_{40}\}^+ \) in tert-butanol/water (3:2, v/v) at 60 °C, the effective radii were found to decrease in the order: M\(^+\) = Li\(^+\) > Na\(^+\) > K\(^+\) (8.3, 7.7 and 6.8 Å, respectively; standard deviation ± 4 %). As the effective crystallographic radii of hexacoordinated alkali-metal cations increase in the order: Li\(^+\) < Na\(^+\) < K\(^+\) (19), the charge densities and hence solvated radii of these ions decrease in the same order (20). Thus, the alkali-metal cations with
larger atomic numbers have smaller solvated radii and form more intimate ion pairs, which possess larger electron affinities.

These discussed results establish that alkali-metal cations and POM anions can form association complexes (ion pairs) in mixed organic - aqueous solutions and that ion-pair formation accelerates phenol oxidation. Ion pairing also occurs in pure water (used in POM delignification) at high concentrations of POMs and/or alkali metal salts. Additional studies on ion association in aqueous POM solutions are needed to quantify these associations.

Experimental

**Materials.** The potassium-salts of 1 and 1red were synthesized according to the literature method (21). The lithium- and sodium-salts of 1 were prepared from the corresponding potassium-salt by cation exchange chromatography using Amberlite IR-120 (plus) ion exchange resin. The preparation of lignin models 3-5 and 9 has been described (13). The diphenol 13 (99% purity) was used as received from Polysciences, Inc. All other materials were reagent grade.

**Methods.** Kinetics data were collected using a Hewlett Packard 8451A diode array spectrometer equipped with both a thermostat (± 0.1 °C) and a stirrer. Quartz cuvettes equipped with Schlenk-type tops were used to degas the solutions prior to reaction. Cyclic voltammetry experiments were carried out under argon using a BAS CV-50W voltametric analyzer. A three electrode cell with a glassy carbon working electrode, a platinum auxiliary electrode and a Ag/AgCl (3M NaCl) reference electrode was used. Non-linear square fits were performed using the Solver Function in Microsoft Excel-98.

Conclusions

The phenolic lignin substructures, modeled by lignin-like dimer compounds, were found to be reactive substrates towards oxidative cleavage by 1. Under actual delignification conditions, outer-sphere oxidation of both phenols and phenolates is likely to occur. Alkali-metal cation - POM anion association in solution increases the electron affinity of POMs and accelerates the rate of phenol oxidation.

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References

Problem 1 New technologies to delignify wood for the production of pulp in ways that will eliminate contamination of our air and waterways.

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