ON THE REACTIVITY OF LIGNIN MODELS WITH OXYGEN-CENTERED RADICALS. I. COMPUTATIONS OF PROTON AND ELECTRON AFFINITIES AND O-H BOND DISSOCIATION ENERGIES

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Dedicated with respect to Professor
David Goring on the occasion of his 85th birthday

The electronic structures of three lignin model compounds were computed by means of semi-empirical (PM3) and density functional methods (B3LYP), both *in vacuo* and in solution. The computed values of proton affinities, electron affinities and O-H bond dissociation energies for 4-methylphenol, 2-methoxy-4-methylphenol and 2,6-dimethoxy-4-methylphenol were compared with those of the oxygen-derived radicals, hydroxyl radical, superoxide radical anion, hydroperoxyl radical, oxyl radical anion and triplet oxygen. The data suggest that the hydroxyl radical is the strongest oxidizing and dehydrogenating reagent, followed by the oxyl radical anion and the hydroperoxyl radical. These three radicals could oxidize or dehydrogenate the lignin models at an appropriate pH. The superoxide radical anion and the triplet oxygen are somewhat weaker reagents. Thermodynamic calculations indicate that formation of aromatic peroxides is to be expected during peroxide bleaching and that the pK_a of the phenolic hydroxyls significantly decreases when these peroxides are formed. The results obtained demonstrate the usefulness of molecular orbital calculations for elucidating the radical reactions in pulp bleaching, in the attempt to improve the selectivity of alkaline oxygen and peroxide delignification processes.
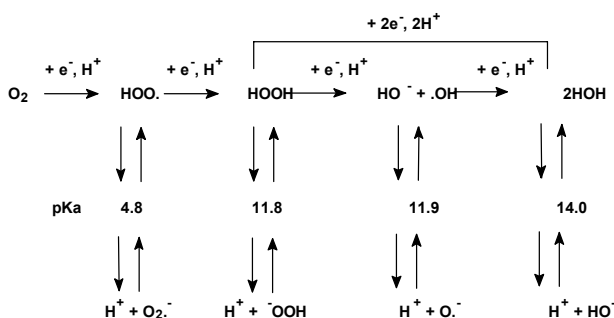
INTRODUCTION

Lignin removal from pulp using oxygen or hydrogen peroxide in the presence of alkali is an attractive method of bleaching for the production of high brightness paper. The main reasons for the interest in this bleaching process are its environmental appeal (no chlorine is used) and the low cost of oxygen. The disadvantage is the low selectivity of lignin. Consequently, the process must be carefully controlled, often at the cost of incomplete lignin removal, in order to protect cellulose from a detrimental loss of strength. An important part of the drive towards a better bleaching process has been the extensive investigation of the chemical mechanisms involved in oxygen bleaching.

It has been recognized that the oxygen radicals formed under alkaline conditions from both molecular oxygen and hydrogen peroxide play an important role in bleaching.[1,4] Scheme 1 shows[2,3] how these radicals are formed by oxygen reduction during oxygen delignification. The hydroxyl radical (HO[•]) is the most reactive one, if judging by its radical strength,[5] followed closely by its conjugate base, O[•-]. The hydroperoxyl radical, HOO[•], and its conjugate base, superoxide, OO[•-], have substantially lower radical strength values.

Kratzl *et al.*[1] considered that the attack by HO• or O•⁻ is the first step in the sequence of reactions, which leads to the oxidative decomposition of lignin model compounds such as cresol and bicresol. Based on the analysis of the reaction kinetics and of the pattern of the degradation products, these authors consider that this first reaction is also the rate determining one.

$$O_2 \xrightarrow{+ e^-, H^+} HOO\cdot \xrightarrow{+ e^-, H^+} HOOH \xrightarrow{+ e^-, H^+} HO^- + \cdot OH \xrightarrow{+ e^-, H^+} 2HOH$$

+ 2e⁻, 2H⁺

pKa   4.8   11.8   11.9   14.0

H⁺ + O₂⁻   H⁺ + ⁻OOH   H⁺ + O⁻   H⁺ + HO⁻

Scheme 1: Radicals derived from the reduction of oxygen

Gierer[4] believes that the main role of HO• and O•⁻ is to generate radical sites on lignin. These radical sites then undergo coupling reactions with other oxygen radicals, such as HOO• and OO•⁻ (superoxide), leading to the formation of, e.g., organic peroxides, whose transformations result in aromatic ring cleavages and scissions of the aliphatic side chains.

In a recent study on the radical species employed in peroxide bleaching, Smith and Argyropoulos[6] revealed a surprisingly abundant presence of the superoxide anion. Petlicki and van de Ven[7] demonstrated a feasible mechanism for superoxide formation *via* the reduction of oxygen by alkaline hydrogen peroxide (HOO⁻ + HO⁻).

One of the research methods used to investigate the bleaching mechanisms is computation of the molecular orbital (MO) energies. An early attempt to correlate the critical oxidation potential (COP) values with the highest occupied molecular orbital (HOMO) energies, by Kratzl *et al.*,[1,2] was only partially successful. Chlorine dioxide bleaching mechanisms have been investigated, by means of MO computations, by Garver.[8] Computational analysis of alkaline hydrogen peroxide bleaching pathways performed on lignin model compounds[9] suggested that the formation of dioxetane structures is the main barrier, rather than the initial reaction with HO• or O•⁻. The computed results were in agreement with the experimental values of the activation energies. The purpose of the present work is to investigate, by MO calculations, the possible primary reactions of various oxygen radicals in the presence of alkali with model compounds representing phenolic moieties of softwood lignin.

COMPUTATIONAL METHODS

The initial structures of all compounds were drawn with a model builder (HyperChem 5.11 Professional, HyperCube, Inc.). Where applicable, hydrogen bonding was facilitated by an appropriate manipulation during model building. The structures were then subjected to preliminary geometry optimization with molecular mechanics.[10] The force field used was MM+ (HyperChem) and the optimization proceeded up to root mean square, RMS, gradient 0.06 kcal·mol⁻¹Å⁻¹. A short (10 cycles) semi-empirical PM3 (the 3rd parametrization method [11]) geometry optimization was then performed to assign partial charges on all atoms. The charges permitted to use an improved MM+ force field, based on non-bonded electrostatic interactions. By the application of this force field, the starting structures have been generated by simulated annealing (molecular dynamics under increasing and, respectively, decreasing temperature). The starting geometries were then optimized with MM+, followed by the PM3 semi-empirical method with self-consistent-field convergence set to 0.01 and the optimization convergence to RMS gradient 0.06 kcal·mol⁻¹Å⁻¹. The unrestricted Hartree-Fock (UHF) algorithm was used for PM3 calculations.

The PM3 geometries of the compounds served as starting structures for higher-level geometry optimizations using the B3LYP/6-31G(d) method - as implemented[12] by Gaussian 98. B3LYP is a density functional method created by Becke,[13] as based on the results of Lee, Yang, and Parr.[14] The optimized structures were further subjected to calculations in aqueous solution using the self-consistent reaction field (SCRF). To this end, B3LYP/6-31+G(d) was applied by an isodensity polarized continuum IPCM model.[15] Frequency calculations were also performed using B3LYP/6-31G(d) at 298 K, for

obtaining thermodynamic data on the reactions of some of the optimized structures.

RESULTS AND DISCUSSION
Lignin models

Three lignin models were used in this study: 4-methylphenol (1), 2-methoxy-4-methylphenol (2) and 2,6-dimethoxy-4-methylphenol (3) (Scheme 2).
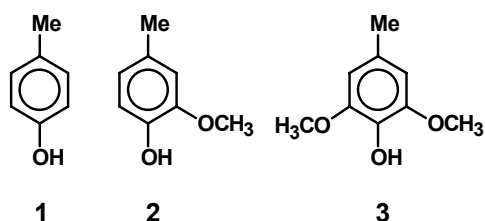
Scheme 2: Lignin model compounds

Proton affinity

Proton affinity (A_p) can be computed as the energy gained when a compound is protonated. The pK$_a$ is directly related to the free energy of the deprotonation reaction.[16] To predict the pK$_a$ values of various compounds, the A_p values had been calculated as differences between the electronic energies of acids and anions (Table 1), while the experimental pK$_a$ values of formic and acetic acid, hydroperoxyl radical, acetyl and phenyl peroxide, hydrogen peroxide, hydroxyl radical, and water[5] were plotted against A_p (Fig. 1).
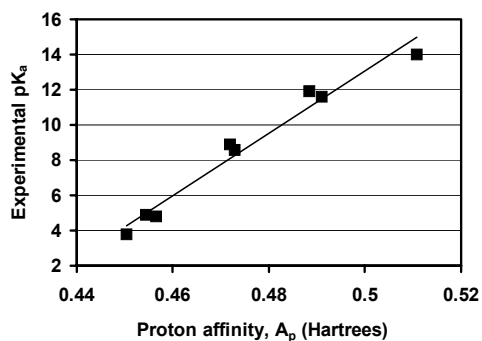

Figure 1: pKa *versus* proton affinity

The equation of this calibration line is:
pK$_a$ = A_p (Hartrees) x 177.2 – -75.5
r^2 = 0.96; standard error = 0.72

The equation can be used to estimate the pK$_a$ of any unknown compound, provided that A_p is computed by the same method as the standards.

This procedure was applied to evaluate the effect of hydrogen abstraction from 2, followed by a coupling reaction with peroxyl radical or superoxide on the ionization of the phenolic hydroxyl group of the model compound.
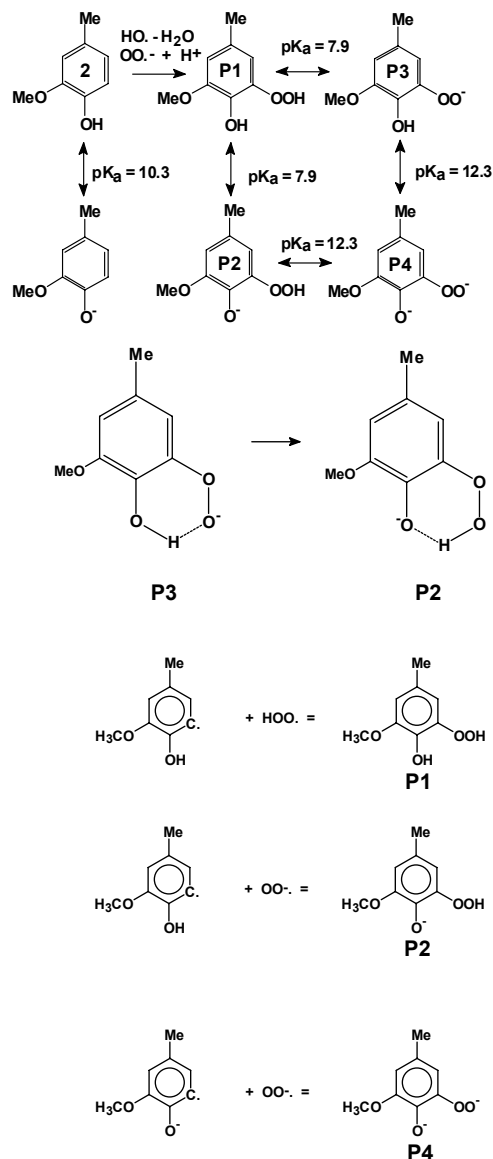
Scheme 3: pK values of peroxides derived from 2

The results summarized in Scheme 3 show that once 2 is derivatized to yield P1, the pK$_a$ of the phenolic hydroxyl drops from 10.3 to 7.9. Inspection of the structures

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revealed that, on geometry optimization, P3 converted into P2, suggesting that the proton from the phenolic hydroxyl would migrate within the hydrogen bonded structure to the peroxyl group if the groups were ionized. The consequence of lowering the pK_a of the phenolic hydroxyl seems to be that, for example, at moderate alkalinity (pH 9), the phenolic hydroxyl of P1 is almost fully ionized. Comparatively, 2 is almost fully protonated. If hypothetical phenolic peroxides are formed during bleaching, then changes in the pK_a values may play a role in the bleaching reactions.

The data in Table 1 evidence a large discrepancy between the experimental and the predicted pK_a values of model compounds 1 and 3. MO computations suggest that proton affinity of the model compounds grows as the number of methoxyl groups increases from compound 1 to 3. This would agree with the intuitive notion of increasing electronegativity, due to the addition of the methoxyl groups. This hypothesis would explain the predicted gradual increase of pK_a. However, this idea is not borne with the experimental values compiled by Ragnar *et al.*,[17] showing only small pK_a differences among compounds 1-3. To examine the feasibility of the coupling reactions leading to the formation of peroxides derived from model compound 2, a series of frequency calculations was conducted at 298 K. The results are summarized in Table 2. Thermodynamic calculations of enthalpies and Gibbs free energies of some of the reactions suggest that the coupling reactions between the C5-centered radical and either peroxyl radical or superoxide would be spontaneous (the predicted $Ä_rG°$ (298 K) is –66 and –100 kcal/mol, respectively). However, the coupling reaction between the C5 centered radical derived from a phenolate of compound 2 and the superoxide does not appear spontaneously ($Ä_rG°$ (298 K) = +18 kcal/mol).

Electron affinity

Electron affinity is defined as the energy gained when a compound attracts an electron. It can be interpreted as the direct measure of the one-electron oxidation power of a compound. Electron affinities (A_e) were computed as the difference between the electronic energies of the radical of a compound and its corresponding anion. A plot (Fig. 2) of the experimental[18] redox potentials (E_O) of 4-aminophenol, 1,4-dihydroxybenzene, 4-methylphenol, 4-acetylphenol, and 4-hydroxybenzonitrile against the computed electron affinities appears as a straight line described by equation:

E_O (mV) = A_e (eV) x 754.9 – -2629.4
r^2= 0.998498; standard error = 14.5 mV.

With this equation, the redox potentials of our lignin models and of the oxygen-derived radicals (Table 3) have been computed. The predicted redox potential of the phenolate derived from compound 1 is substantially higher than the E_O of the other two lignin model phenolates, suggesting that the *p*-hydroxyphenyl moieties in lignin might be more resistant to oxidative bleaching than the guaiacyl and syringyl ones (Fig. 3). Comparison of the redox potentials also suggests that the lignin model phenolates can be oxidized only by hydroxyl and oxyl radicals.
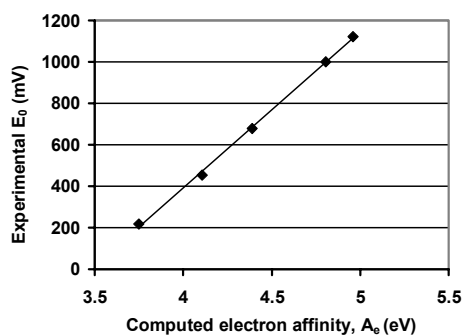

Figure 2: Experimental redox potentials (E_O) *versus* computed electron affinity

Table 1

Calculation of proton affinity and prediction of pK_a

| Compound	$Å_O$ (Hartrees)		A_p (Hartrees)	Experimental pK_a	Predicted pK_a
Peroxide acid/ base couples	Acid	Anion			
P1/P2	-611.695	-611.224	0.471		7.9
P1/P3	-611.695	-611.224	0.471		7.9
P2/P4	-611.224	-610.728	0.496		12.3
P3/P4	-611.224	-610.728	0.496		12.3
Lignin models					
Compound 1	-346.811	-346.338	0.473	10.1	8.2
Compound 2	-461.339	-460.857	0.483	10.3	10.0
Compound 3	-575.867	-575.378	0.489	10	11.2
Standards					
Formic acid	-189.777	-189.327	0.450	3.8	4.3
Acetic acid	-229.104	-228.647	0.457	4.8	5.4
HOO$^\bullet$	-150.920	-150.466	0.454	4.9	5.0
AcOOH	-304.234	-303.761	0.473	8.6	8.3
PhOOH	-382.617	-382.145	0.472	8.9	8.1
HOOH	-151.561	-151.070	0.491	11.6	11.5
HO$^\bullet$	-75.742	-75.253	0.488	11.9	11.0
H_2O	-76.435	-75.924	0.511	14	15.0

$Å_O$, total electronic energy
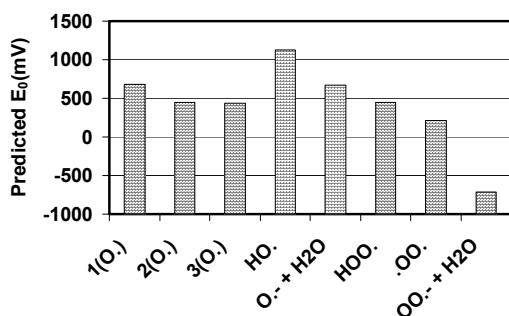
Figure 3: Predicted redox potential for different lignin model compounds

The E_O values for the peroxyl radical and the triplet oxygen are slightly lower than those of the lignin models, while the superoxide radical anion appears to be a much weaker oxidizing agent. Redox potential calculations of the oxyl radical and superoxide included water, to permit the formation of hydroxyl and hydroperoxyl anions, respectively, upon the reduction of radicals.

Table 2

Frequency calculations on the formation of peroxides

Compound	Å_O (Hartrees)	$\text{Å}_O + H_{corr}$ (Hartrees)	$\text{Å}_O + G_{corr}$ (Hartrees)
P1	-611.641	-611.456	-611.508
P2	-611.093	-610.922	-610.972
P4	-610.332	-610.175	-610.225
Compound 2 (C5 radical)	-460.611	-460.447	-460.495
Compound 2 (4-phenolate, C5 radical)	-460.039	-459.89	-459.936
peroxyl radical	-150.899	-150.881	-150.907
superoxide	-150.3	-150.294	-150.317
Energies of reactions			
		$Ä_rH°$(298 K)	$Ä_rG°$(298 K)
Reaction: Compound 2 (C5 radical) + $HOO^•$ = P1			
Hartrees		-0.1268	-0.1055
kcal/mol		-79.5	-66.2
Reaction: Compound 2 (C5 radical) + $OO^{•-}$.= P3 = P2			
Hartrees		-0.1807	-0.1601
kcal/mol		-113.4	-100.5
Reaction: Compound 2 (4-phenolate, C5 radical) + $OO^{•-}$ = P4			
Hartrees		0.008442989	0.028145989
kcal/mol		5.3	17.7

Å_O - total electronic energy; H_{corr} - correction to the enthalpy due to internal energy; G_{corr} - correction to the Gibbs free energy due to internal energy; $Ä_rH°$ (298 K) - enthalpy of reaction; $Ä_rG°$ (298 K) - Gibbs free energy of reaction

Table 3
Calculation of electron affinity (A_e) and prediction of the one-electron reduction potential

	Å_O (Hartrees)		A_e (Hartrees) radical-anion	A_e (eV)	Experimental (mV)	Calculated (mV)
Compound	radical	anion				
Compound 1	-346.1772	-346.3382	0.1611	4.383		679.5
Compound 2	-460.7066	-460.8565	0.1500	4.081		451.4
Compound 3	-575.2283	-575.3775	0.1492	4.060		435.5
$HO^•/HO-$	-75.7415	-75.9245	0.1829	4.978		1128.6
$HOO^•/HOO-$	-150.9203	-151.0699	0.1496	4.071		443.9
$^•OO^•/OO^{•-}$	-150.3276	-150.4659	0.1383	3.763		211.3
$O^{•-}/O^{--}$	-75.2531	-75.2887	0.0356	0.968		-1898.5
$OO^{•-}/OO^{--}$	-150.4659	-150.5120	0.0461	1.255		-1682.2
$O^{•-}+H_2O/2HO^-$	-151.6884	-151.8489	0.1606	4.369		668.8
$OO^{•-}+H_2O/HOO^-+HO^-$	-226.9011	-226.9944	0.0933	2.539		-712.8
Standards						
4-aminophenol	-362.2364	-362.3743	0.1378	3.751	217	202.1
1,4-dihydroxybenzene	-382.0936	-382.2446	0.1510	4.109	454	472.5
4-methylphenol	-346.1772	-346.3385	0.1613	4.389	680	684.2
4-acetylphenol	-459.5126	-459.6893	0.1766	4.807	1000	999.2
4-hydroxybenzonitrile	-399.1022	-399.2844	0.1822	4.957	1120	1113.0

O-H bond dissociation energy

In this study, the assumption was made that hydrogen abstraction from the model compounds occurred at the phenolic hydroxyls, yielding phenoxyl radicals. MO calculations served to estimate the O-H bond dissociation energies (ΔH_{DBE}). For each of the compounds, the energy change, $\Delta\varepsilon_O$, was calculated by summing up the total electronic energy (ε_O) for the radical (*e.g.*, HO$^\bullet$) and the hydrogen atom (H$^\bullet$), and by subtracting ε_O of the corresponding hydrogenated structure (*e.g.*, H_2O). The $\Delta\varepsilon_O$ values represent biased estimates of the bond dissociation energies, since no corrections (*e.g.*, for temperature) have been included. For obtaining more representative values, the experimental ΔH_{DBE} values of six compounds (phenol (O-H), methanethiol (S-H), hydrogen sulfide, propane (*vs*. n-propyl), methane, and benzene) were plotted[5] against the corresponding $\Delta\varepsilon_O$ values (Fig. 4).

The equation of the calibration line:

ΔH_{DBE}(kcal/mol) = $\Delta\varepsilon_O$ (kcal/mol) x 0.729 + 24.109

r^2 = 0.98; standard error = 1.36 kcal/mol was used to calculate the ΔH_{DBE} values for the lignin models and for a number of reagents.
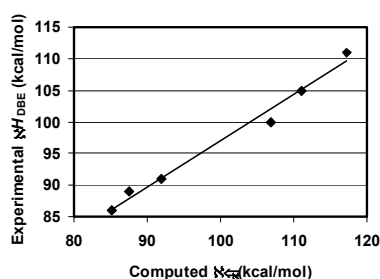

Figure 4: Experimental dissociation energies *versus* total electronic energy

The results (Fig. 5) suggest that the hydroxyl, oxyl and hydroperoxyl radicals could produce phenoxyl radicals from the lignin model compounds, provided that the pH permits appropriate ionization states.

Thus, for example, the hydroperoxyl radical could be effective only at a pH below 6, while the oxyl radical co-exists with the lignin models only to a limited degree, because of the incompatible pK_a values. Our current research also includes a study on the thermodynamics of the bleaching reactions with lignin models, biphenyl and diphenylmethane dimers included, whose structures approximate the properties of residual kraft lignin.
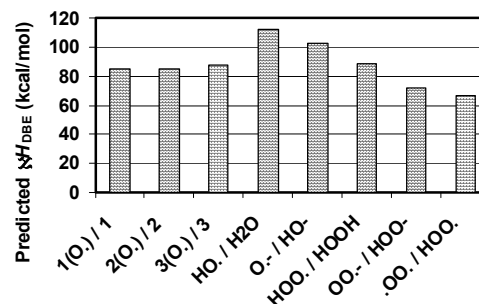

Figure 5: Predicted dissociation energies for some model lignin compouds

CONCLUSIONS

The computations performed suggest that the reactivities of the phenolic hydroxyls of the lignin model compounds 2 and 3 are similar to one another, while compound 1 is estimated to be more difficult to oxidize.

The computed redox potentials suggest that, from among the oxygen-derived radicals, only the hydroxyl and oxyl radicals can oxidize the lignin model phenolates to phenoxy radicals. Hydrogen abstractions from the lignin models could be performed by hydroxyl, oxyl and hydroperoxyl radicals.

Hypothetical coupling reactions of phenoxyl radicals with the superoxide, leading to the formation of peroxides, appear thermodynamically favourable. These reactions could affect the dissociation of the phenolic hydroxyls and, consequently, influence the subsequent bleaching reactions.

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