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BENZOSEMIQUINONE RADICALS IN ALKALINE SOLUTIONS OF HARDWOOD LIGNINS

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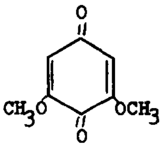
Lignin, the ubiquitous component of terrestrial plants, has been shown to be paramagnetic[1,2,3]. The paramgnetism of lignin preparations increases with the extent of chemical or enzymatic degradation.[4] Hardwood lignins (which contain a high proportion of 3,5-dimethoxy-4-hydroxy-phenyl groups) have a higher spin content than analogous softwood lignins (which have 3-methoxy-4-hydroxyphenyl elements as the chief constituent). Alkali or soda lignins show the highest radical content of all preparations. Because of the lack of hyperfine splitting in the single-line ESR spectra of these solids, however, no deduction could be made concerning the nature of the radical species.

To obtain structural information from the ESR technique, we dissolved lignin samples in dilute aqueous NaOH and examined the solution with high resolution ESR spectrometry. All hardwood samples gave the same spectrum (Figure 1a); the only variation was in the signal intensity. Commercial specimens such as Meadol, Indulin and Kraft products, were used. Softwood alkali lignins gave weak, unresolved spectra. In strong base (0.1 M to 1.0 M NaOH) spectrum 1a changed rapidly to spectrum 1b. For a 5% mixture of Meadol and 0.1 M base, the signal intensity corresponded to a radical concentration of 2×10^{-4} M or approximately 1 mole percent of the parent substance. The signal intensities were pH dependent, increasing from zero at pH 10 to a maximum at pH 13.

When native aspen lignin (a hardwood) was treated with 0.1 M base as above, a very weak signal was obtained. After the solution was boiled for one hour, a strong signal of spectrum 1a appeared. Continued boiling served to increase the amount of the radical species 1a. This would suggest that alkaline cleavage of hardwood lignin is a free radical process.[5]

The spectrum of the free radical species 1a corresponds to structure II, which could arise from several sources. We observed the ESR spectrum of this radical (Fig. 1a) using a solution of 2,6-dimethoxyhydroquinone exposed to air, as well as by a similar aerial oxidation of a 2,6-dimethoxyphenol solution. Since 2,6-dimethoxyquinone (I) in aqueous base gives the same spectrum, and can be demonstrated by thin-layer chromatography to be present in the aqueous extracts of lignin preparations (Meadol, Krafts, etc.), this compound was chosen as the best model for our investigation.

The primary radical (II) results from I in aqueous sodium hydroxide or buffer solutions exposed to air only when the concentration of I is sufficient to cause scavenging of dissolved oxygen by the resulting radicals. Excess air exposure was found to destroy the semiquinone. To eliminate this variable, experiments were conducted on 1×10^{-3} M concentrations of the quinone (I) in aqueous base at various pH values in a closed apparatus filled with nitrogen.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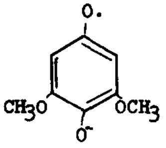
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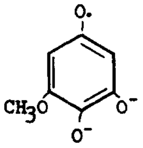
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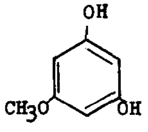
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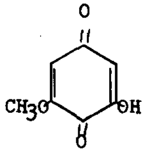
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The aqueous base was purged with nitrogen before mixing it with the quinone. The results are highly dependent on the pH as shown in Table 1.

Table 1

Effect of pH on Radical Concentrations

pH	Observed Spectrum
9.18 (Buffer)	Very weak; develops strong signal of II on overnight (17 hours) standing.
11.98 (NaOH)	Moderately strong signal of II, increasing in intensity over 3 hours. Overnight standing (17 hours) produces spectrum of III (Fig. 1b).
13 (0.1M NaOH)	Strong signal of II changing to III after 2.5 hours.
14 (1.0M NaOH)	Spectrum of III almost immediately.

The details of the mechanism of formation of the primary radical II from the quinone I is the subject of our continuing investigation, but it is reasonable to assume that it involves addition of the OH^- ion to the quinone to produce a phenolic anion which can participate in a redox reaction with the quinone (as shown by the work of M Eigen and P. Matthies[6]). In this regard, we have found more intense ESR signals resulting from alkaline mixtures of the quinone I and other monohydric phenols than with the quinone alone. Although we did not observe a radical intermediate due to the oxidized phenolic anion, it is quite possible that its existence is transitory. (Vankataraman and Fraenkel[7] did observe mixed spectra with alkaline solutions of p-benzoquinone, which they attributed to the presence of an hydroxyhydroquinone anion radical).

As the pH is increased (Table 1) a sixteen-line secondary radical spectrum appears (Fig. 1b). Interpretation of this spectrum shows that the unpaired electron interacts with three equivalent and two non-equivalent protons. This indicates the loss or exchange of a methoxy group, consistent with the results of Pilar, Buben and Pospisil[8] on 2-tert-butyl-6-methoxy-p-semiquinone. Therefore, we assign structure III to this radical species.

To confirm the above assignment (III), the monomethyl ether of phloroglucinol (IV) was prepared according to the method of Rodighiero and Antello[9] and this was oxidized with Fremy's Salt to 2-hydroxy-6-methoxy-p-benzoquinone, V. The resulting yellow oxidation solution was made alkaline (pH, 11-12) with NaOH, without isolating the quinone; its ESR spectrum was identical to that for the secondary radical (III) resulting from compound I and base.

If the above quinone solution is made alkaline with a saturated solution of $Ca(OH)_2$, an eight-line spectrum results (Fig. 1c). We observed the same spectrum for the secondary radical when compound I is treated with $Ca(OH)_2$ solution. These results are consistent with the known[10] chelation behaviour of O-semiquinones in the presence of Group II ions. Marked changes in the ring coupling constants of semiquinones over the non-chelated radicals are produced with Group II ions. Presumably, complex formation in the case of radical III has sufficiently reduced the coupling of one of the ring protons, so that it is not observed.

We can conclude tentatively that aerobic alkaline degradation of hardwood lignins produces I, which rapidly yields stable radical species II and III. Apparently the reaction sequence for softwood lignins follows an entirely different course. The reaction of I to II to III in base is accelerated by the presence of numerous phenolic groups in lignin, as well as by the concentration of base and the absence of oxygen. A detailed mechanism for this reaction is the subject of continuing investigation.

TABLE 2

Hyperfine Splitting Constants of Semiquinones (in gauss)

Semiquinone	$a^H_{OCH_3}$	a^H_{ring}
2,6-dimethoxy-p-benzosemiquinone	0.80	1.49
2-hydroxy-6-methoxy-p-benzosemiquinone	0.70	2.50 0.20[a]
2-hydroxy-6-methoxy-p-benzosemiquinone (Ca complex)	0.70	2.76[a]

(a) Ring protons not specifically assigned.

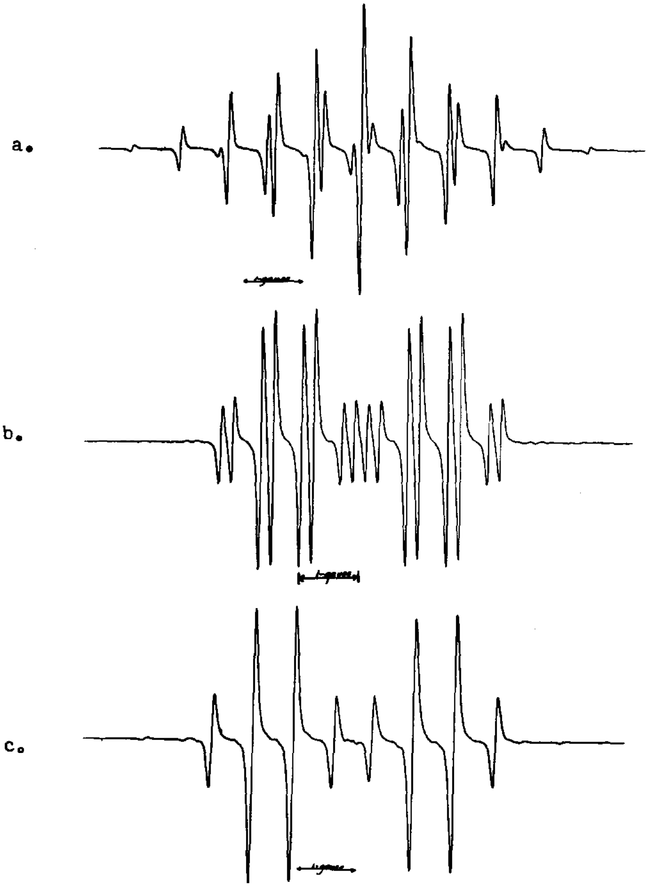

Figure 1

a. ESR spectrum of semiquinone II produced by treatment of 1 x 10^{-3}M 2,6-dimethoxyquinone in aqueous sodium hydroxide under nitrogen; b. ESR spectrum of the secondary radical (III) occurring in the treatment of 1 x 10^{-3}M 2,6-dimethoxyquinone in aqueous sodium hydroxide under nitrogen; c. ESR spectrum of the secondary radical (III) occurring in the treatment of 1 x 10^{-3}M 2,6-dimethoxyquinone in saturated calcium hydroxide under nitrogen.

REFERENCES

1. R.W. Rex, Nature, 188, 1185 (1960)
2. a. C. Steelink, Adv. in Chem., 59, 51 (1966)
   b. C. Steelink and G. Tollin, Biochim. Biophys. Acta, 112, 377 (1966)
   c. C. Steelink, T. Reid and G. Tollin, J. Am. Chem. Soc., 85, 4048 (1963)
3. T.N. Kleinert, TAPPI, 50, 120 (1967)
4. C. Steelink, Geochimica et. Cosmochimica Acta, 28, 1615 (1964)
5. K. Kratz, W. Schafer, P. Claus, J. Gratzl and P. Schilling, Monatsche, 98, 891 (1967)
6. M. Eigen and P. Matthies, Chem. Ber., 94, 3309 (1961)
7. B. Venkataraman and G. Fraenkel, J. Am. Chem. Soc., 77, 2707 (1957)
8. J. Pilar, I. Buben and J. Pospisil, Tetrahedron Letters, 39, 4203 (1968)
9. G. Rodighiero and C. Antonello, II Farmaco (Paria), Ed. Sci., 10, 889 (1955)
10. D.R. Eaton, Inorg. Chem., 3, 1268 (1964)