

THE ELECTROCHEMICAL OXIDATION OF LIGNIN MODEL COMPOUNDS I.
 OXIDATION OF 3,5-DIMETHOXY-4-HYDROXY- α -METHYLBENZYL ALCOHOL

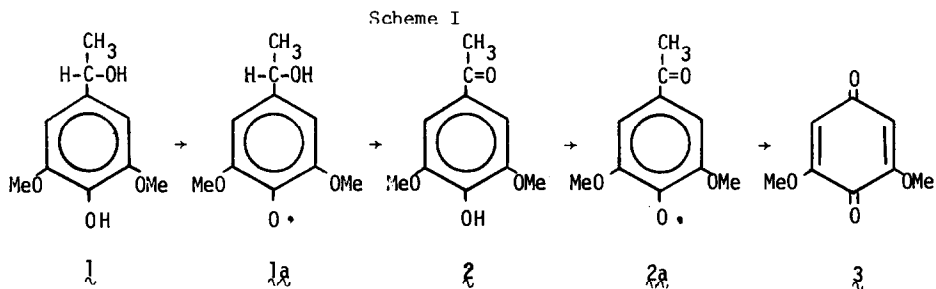
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3,5-Dimethoxy-4-hydroxy- α -methylbenzyl alcohol (1) is a lignin model compound, which represents an important structural unit in hardwood lignin. Understanding the mechanisms of oxidation of the title compound, as well as other lignin models, may help elucidate wood rotting processes and can provide useful information for controlled degradation of crude lignin to useful products.

Steelink and Young (1) reported the peroxidase catalyzed oxidation of 1 with excess H_2O_2 to afford 3,5-dimethoxy-p-benzoquinone (3). Monitoring the oxidation with esr spectroscopy revealed the production of phenoxy radical $1a$ followed by radical $2a$ (See Scheme I). They observed however, that for values of the molar ratio of H_2O_2 to 1 less than unity, the esr spectrum of $2a$ was not detected although 3 was still a product of the reaction. This result led to the suggestion that there was a mechanism leading to 3 without requiring the involvement of $2a$, e.g., through $1a$. We therefore undertook a study of the electrochemical oxidation of 1



and also 2 (2), with the goal of establishing the existence of a species responsible for the formation of 3 . Electrochemistry is ideally suited for a study of this kind; with carefully controlled oxidizing conditions and with the aid of cyclic voltammetry, one can establish the involvement of shortlived intermediates (3).

Fig. 1 depicts the cyclic voltammograms of 1 at two different concentrations in acetonitrile (AN) containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The

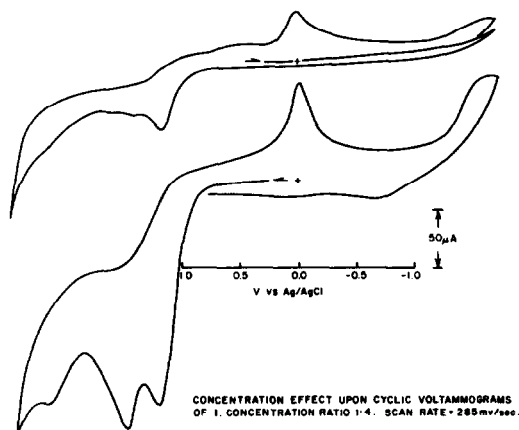


Fig. 1 Cyclic voltammogram of 1 at a Pt. anode

interesting, concentration dependent, second oxidation wave can be tentatively assigned to oxidation of 2 (which is formed in the first oxidation wave) by comparison with the cyclic voltammogram of 2 (Fig. 2). In a related compound the third oxidation wave has been attributed by

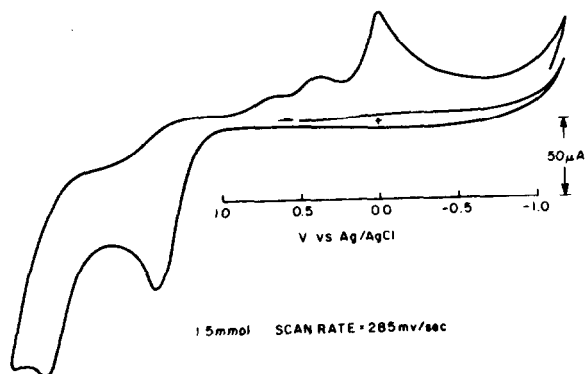
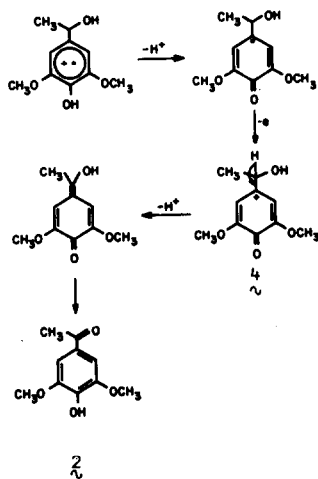


Fig. 2 Cyclic voltammogram of 2 at a Pt. anode.

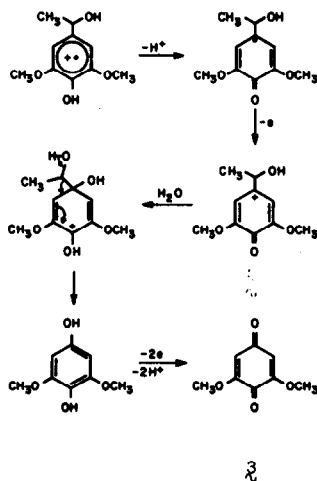
Lund to oxidative cleavage of the side chain (4). A reasonable mechanism based upon electrochemical precedent (5) can be written for the formation of 2 (Scheme II). Studies upon the electrochemical oxidation of 1 at various concentrations of water in AN favor this cationic mechanism as opposed to a mechanism involving the disproportionation of 1_2 , *vide infra*, although the latter mechanism is also supported by the concentration dependence for the second oxidation wave, *vide supra*. Controlled potential electrolysis at 1.1 V (this corresponds to the first oxidation wave of 1) in damp AN affords a 48% yield of 2 while 2 is not formed under

these conditions. Scheme III is a proposed mechanism for the formation of 3 and is supported by a similar observation reported by Sainsbury (6). Acetaldehyde is also predicted as a product of this reaction and is indeed confirmed by gas chromatographic analysis of the electrolysis solution.

Scheme II



Scheme III



Repeating the oxidation of 1 in carefully dried AN (1), under the same conditions results in suppressed yield of 3 (5.8% isolated) while the major product is 2 . These data are all consistent with an ECE process forming 4 (8). Loss of a benzylic proton from 4 leads to formation of 2 , while nucleophilic attack by water leads to 3 .

These data can also explain the apparent concentration dependence for the second oxidation wave of 1 . At high concentrations of 1 , the cation 4 scavenges available water. The remaining unreacted 4 being formed at the electrode can then follow the pathway represented in Scheme II to give compound 2 , the species responsible for the second oxidation wave of 1 observed at high concentrations.

In conclusion, it appears that the quinone 3 can be formed in a four-electron oxidation by an indirect mechanism not requiring the existence of 2 as an intermediate. Thus, side chain cleavage of 1 can be favored over side chain oxidation by controlling the concentration of water.

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References

- 1) Maria Young and Cornelius Steelink, Phytochemistry, **12**, 2851 (1973).
- 2) Wayne E. Britton and Cornelius Steelink, Tetrahedron Lett., following communication.
- 3) Albert J. Fry, "Synthetic Organic Electrochemistry", Harper and Row, New York, 1972, pp 17,82
- 4) Lund, Acts. Chem. Scand., **11**, 491 (1957).
- 5) Ref. 3, Ch. 8.
- 6) M. Sainsbury and R. F. Schinezi, J. Chem. Soc., Chem. Comm., 718 (1972).
- 7) N. S. Moe, Acts. Chem. Scand., **21**, 1389 (1967).
- 8) See V. D. Parker and R. N. Adams, Tetrahedron Lett., 1721, (1969) for mechanistic evidence supporting the loss of a benzylic proton through an ECE process.