

THE ELECTROCHEMICAL OXIDATION OF LIGNIN MODEL COMPOUNDS II.

OXIDATION OF 3,5-DIMETHOXY-4-HYDROXYACETOPHENONE

Wayne E. Britton and Cornelius Steelink

Chemistry Department, University of Arizona, Tucson, Arizona 85721

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We have recently reported on the electrochemical oxidation of the lignin model compound, 3,5-dimethoxy-4-hydroxy- α -methylbenzyl alcohol (1). The major product from that reaction in damp acetonitrile (AN) was 3,5-dimethoxy-*p*-benzoquinone, and was thought to arise via a mechanism involving fragmentative loss of acetaldehyde. Since this oxidation pathway was unavailable to 3,5-dimethoxy-4-hydroxyacetophenone $\underline{1}$, and because of our interest in understanding the oxidation chemistry of important hardwood lignin structural units, we undertook the electrochemical investigation of $\underline{1}$. Fig. 1 is a representative cyclic voltammogram of $\underline{1}$ at a platinum anode in AN containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The second oxidation wave was discussed briefly in the previous communication (1). The reduction wave at 0 volts is due to the reduction of protons formed in the oxidation process (2). Con-

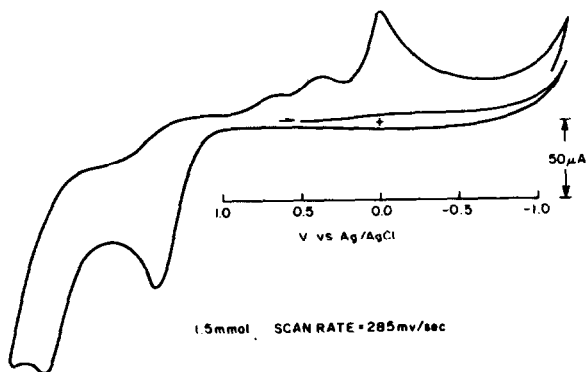


Fig. 1. Cyclic voltammogram of $\underline{1}$.

trolled potential electrolysis (3) of $\underline{1}$ at the first oxidation wave, and constant current electrolysis (4) (25 to 40 ma) afforded 3,4-dihydroxy-5-methoxyacetophenone ($\underline{2}$) as the major isolable product (20% isolated yield) along with an intractable tar. However, the yield of $\underline{2}$ may be somewhat larger than this, since the oxidation potential for the catechol $\underline{2}$ is about the same as starting material, $\underline{1}$ (Fig. 2), and products arising from oxidation of $\underline{2}$ give rise to at least some of the intractable tars. (5)

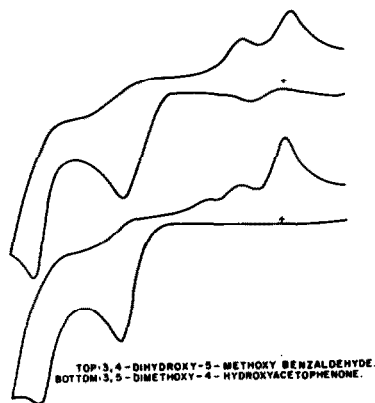
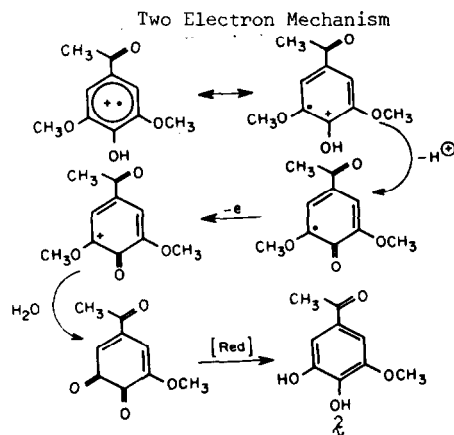
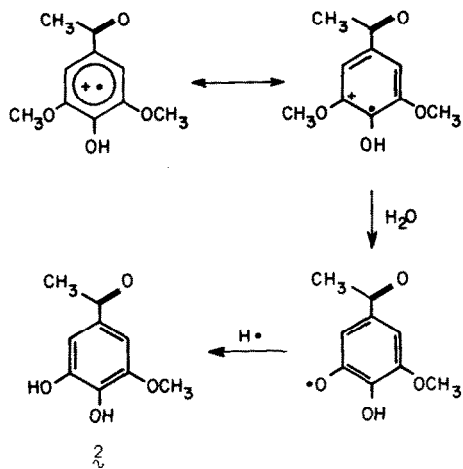


Fig. 2

Two reasonable mechanisms can be written for the formation of 2 and are presented in Scheme I.

Scheme I
One Electron Mechanism



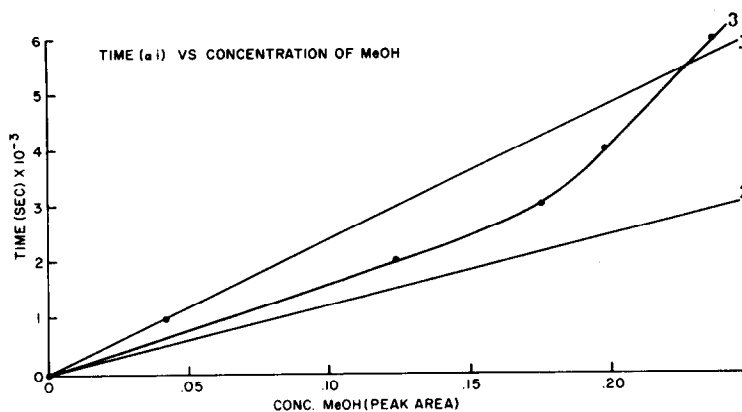


Fig. 3. Current versus Methanol concentration.

1. Theoretical Plot: Methanol per 2 electrons
2. Theoretical Plot: Methanol per 1 electron
3. Observed methanol/current plot

In both cases, methanol should be a product of the reaction; however in one case it is formed in a one electron oxidation, (6) while in the second case, it requires two electrons per molecule of methanol. When we monitored the electrolysis of k using thin layer chromatography (TLC), we observed the buildup of z at the expense of starting material. When 0.75 Faradays of current per mole of starting material had been passed, catechol z yield appeared to diminish and new TLC spots of low R_f value became significant. Semiquantitative estimates from TLC suggest that absolute yields may be as high as 30 to 40%. An analysis of the methanol formation as a function of the current was made using gas chromatography and constant current electrolysis, a plot of which is shown in Fig. 3. The top line of this plot represents the concentration of methanol-versus-time profile which would be observed if catechol and methanol were the only products formed by a two electron process. The bottom line represents the predicted one-electron process. The experimental points were found to fall inbetween these two extremes. Since one cannot have less than two electrons passed for a two electron oxidation, this data favors a one electron process; the additional current above the one electron profile is supplied by some side reaction which does not involve methanol evolution. Such a side reaction could involve oxidation of the catechol, vide supra. This information supports a one electron mechanism.

Additional support for the one electron mechanism can be obtained by carrying out the oxidation in the presence of 2,6-lutidine. In this case the oxidation substrate would be the phenoxide instead of the free phenol Ar-OH . Catechol formation from the phenoxide should not be affected for the two electron pathway, since the proton is lost during the course of the reaction anyway. However, the one electron mechanism requires that the phenol remain protonated. When the electrolysis of Ar-OH was carried out in the presence of excess lutidine, very little catechol Ar-OH_2 was formed. This result also supports the one electron mechanism.

We are continuing our investigations with the guaiacyl series (3-methoxy-4-hydroxy benzyl alcohols). These represent major structural components of softwood lignin .

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