The Reactions of Lignin with Alkaline Hydrogen Peroxide.
Part IV.* Products from the Oxidation of Quinone Model Compounds

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Simple para- and ortho-quinoid structures related to lignin have been oxidized with hydrogen peroxide under mild alkaline conditions. Most of the reaction products, i.e. carboxylic acids formed by oxidative cleavage of the quinoid ring together with acids formed by more extensive degradation of the starting materials, were identified after conversion into esters. In addition, small amounts of hydroxylated quinones were found. Mechanisms for the formation of these products are suggested and the significance of the results for the bleaching of mechanical pulps with hydrogen peroxide is briefly discussed.

Cinnamaldehyde structures and quinones constitute the major coloured systems present in lignin and their removal is thus essential for the successful bleaching of mechanical pulps with hydrogen peroxide. In part III of this series, the alkaline hydrogen peroxide oxidation of lignin structures of the cinnamaldehyde and aryl-α-carbonyl types was described. These reactions were shown to proceed through nucleophilic attack by hydroperoxy ions on electron deficient carbon atoms giving rise to epoxide intermediates which in turn were cleaved to yield the end products, i.e. aromatic aldehydes and hydroquinones, respectively.

In the present work, simple para- and ortho-quinoid structures related to lignin have been oxidized with alkaline hydrogen peroxide under mild alkaline conditions and the major reaction products identified.

Fig. 1. Model compounds.

RESULTS

Oxidation of p-quinones. The oxidation of 1 and 2 (Fig. 1) was performed at a constant pH = 9 and 25 °C by adding the quinone to an aqueous solution containing sodium metasilicate, diethylenetriaminepentaacetic acid (DTPA) (both of which act as stabilizers for hydrogen peroxide) and a five-fold excess of hydrogen peroxide (based on quinone). After 60 min the consumption of alkali ceased and the reaction mixtures were separated into neutral and acidic fractions. The neutral fraction in both cases contained small amounts of material, mostly starting material and the corresponding hydroquinone. The latter is probably formed through the reduction of starting material by some hydroquinoid intermediate in the reaction mixture. Employing the working-up procedure described (see Experimental), small amounts of the corresponding hydroxylated quinones were also obtained in the neutral fractions. These quinones are assumed to be formed through elimination of water after attack by hydroperoxy ions on the 3- or 5-position of the starting materials.

* Part III. See Ref. 2.
Scheme 1. Major reaction between alkaline hydrogen peroxide and the para-quinones 1, 2 and 3.

Scheme 2. Suggested reaction sequence for the formation of 6 from alkaline hydrogen peroxide oxidation of 2.

The carboxylic acids contained in the acidic fractions were converted into the corresponding ethyl esters and separated by GLC and preparative column chromatography. From the quinones 1 and 2 the corresponding substituted maleic acid derivatives were obtained as the strongly predominant products together with acetic acid. The formation of these acids (Scheme 1) is consistent with a reaction between the quinones and hydrogen peroxide proceeding via the addition of a hydroperoxy ion to the carbon atom adjacent to the methoxyl group. A subsequent nucleophilic attack by the resulting hydroperoxide on the carbonyl group gives a dioxetane structure which is cleaved to form a dicarboxylic acid (after hydrolysis of methanol). Intramolecular lactonization, followed by cleavage of the carbon—carbon bond adjacent to the lactone bond, affords acetic acid and an acid anhydride which is immediately hydrolyzed to the corresponding acid. In the oxidation of 2, the acid 6 was also isolated. The reaction sequence for the formation of this acid, outlined in Scheme 2, is assumed to involve a decarboxylation step probably taking place during the working-up procedure.

A number of carboxylic acids formed by a more severe fragmentation of the starting material 1 could also be identified, viz. formic acid, oxalic acid, glycolic acid, malonic acid and methoxy-acetic acid (cf. Ref. 3).

The oxidation of the quinone 3 was carried out at pH = 10, and 40 °C, using a ten-fold excess of hydrogen peroxide. The corresponding phenyl-substituted maleic acid derivative (Scheme 1) constituted ~75 % of the acidic fraction whereas methoxy-maleic acid was found in trace amounts only. The presence of five other acids in small amounts could also be detected by GLC of the ester mixture. Two of these were identified as benzoic acid and phenylacetic acid.

Oxidation of the α-quinone 4. Oxidation of 4 at pH = 9 and 25 °C gave rise to the appearance of small amounts of 4-tert-butylcatechol and 5 in the neutral fraction together with three major components in the acidic fraction. After separation, these latter components which amounted to ~ 80 % of the total acidic products, were identified as 7, 8 and 9. The mechanisms for the formation of these products are outlined in Scheme 3 and involve epoxidation of one or both of the double bonds followed by oxidative cleavage between the carbonyl groups. The resulting mono-epoxide dicarboxylic acids are subsequently converted, by intramolecular nucleophilic attack, to the corresponding lactonic acids (cf. Refs. 4, 5).
Oxidation of the p-quinone 5. After the separate oxidation of 1, 2 and 4, small amounts of the corresponding hydroxylated quinones could be detected in the reaction mixtures thus indicating that such structures are more resistant to oxidation by hydrogen peroxide than the corresponding non-hydroxylated analogues. This observation was confirmed by oxidizing 5 and, in this case, it was necessary to carry out the reaction at pH = 11 and 40 °C in order to obtain a complete degradation in 60 min. Four major products were obtained amounting to approximately 80% of the total product mixture. After separation these were identified as I0, II, I2a and I2b which suggested the modes of formation as outlined in Scheme 4. The formation of these products indicates that the quinoid ring has to be epoxidized and/or hydroxylated prior to ring opening (cf. Ref. 6), i.e. reactions which are rendered difficult due to the negative charge already present in the molecule.

DISCUSSION

Simple quinoid structures related to those assumed to be present in lignin are rapidly degraded to carboxylic acids by the action of alkaline hydrogen peroxide. The reaction starts through nucleophilic attack by hydroperoxy anions on one of the electron deficient carbon atoms in the quinoid ring followed by either elimination of water (formation of a hydroxyquinone), elimination of a hydroxyl ion (formation of an epoxide) or ring closure to a dioxetane structure (cf. Ref. 5). These intermediates are then further attacked by hydroperoxy and hydroxyl ions in one or several steps to yield the final products. The hydroxyquinoid structures formed are comparatively stable and may survive further oxidation thus indicating that mechanical pulps bleached with hydrogen peroxide may contain such structures. Since these are strongly coloured, in particular when present in ionized form (pKa ~ 5), even the presence of small amounts can contribute substantially to the residual colour in bleached mechanical pulps.

EXPERIMENTAL

Model compounds. The model compounds I—5 were prepared according to Refs. 8—11.

Oxidation procedure. Sodium metasilicate (Na2SiO3·9H2O) (4.4 g) and DTPA (150 mg) were dissolved in 300 ml of water. 50 mmol of hydrogen peroxide was added and the pH-value adjusted (see
below) by addition of acid (or base). Oxygen-free nitrogen was bubbled through the solution. After 15 min, the addition of nitrogen was interrupted and the solution (10 mmol, 5 mmol of 3) added to the solution in one portion. During the oxidation the pH was kept constant by means of an autoburette (1 N NaOH) connected to a pH-meter. When the consumption of alkali had ceased the reaction mixture was neutralized to pH ~6 with Dowex 50 W—X8 cation exchange resin in the hydrogen form and platinum black was added to decompose excess hydrogen peroxide. Neutral components were obtained by extraction with ethyl acetate. The aqueous solution was further acidified to pH ~1 by addition of cation exchange resin. After filtration, the solution was neutralized to pH = 7 with tetrabutylammonium hydroxide and evaporated. The residue was dissolved in methylene chloride and refluxed for 2 h in the presence of ethyl iodide. After evaporation, the residue was dissolved in diethyl ether and filtered. The solution containing carboxylic acid ethyl esters was analyzed by GLC (3% SE-30 on Chromosorb G. 80—250 °C, 5 °C min⁻¹) and the esters preparatively separated on a silica gel column (Merck, silica gel 60).

Analyses. ¹H NMR and ¹³C NMR spectra were run in CDCl₃ at 60 and 80 MHz, respectively. MS were recorded at 70 eV IP and are presented with m/e-values and % rel. int. Elemental analyses were run on C, H and O. Analytical data was given as a percentage based on starting material.

Oxidation of 1. Oxidation conditions: pH = 9.0, 25 °C, 60 min. 3.3 equivalents of NaOH consumed. Neutral fraction: 150 mg, containing 1, 2,6-dimethoxy-hydroquinone and 2,6-dimethoxy-3-hydroxy-p-benzoquinone identified by comparison with authentic samples (TLC and UV-VIS spectroscopy). Acidic fraction: 2.23 g. Column chromatography in methylene chloride—aceton 20:1 gave one major component in 66% yield identified as methoxy-maleic acid diethyl ester [¹H NMR: 1.36 (6H, t), 3.70 (3H, s), 4.33 (4H, q), 5.16 (1H, s). MS: 202 (8, M), 173 (72), 157 (63), 145 (13), 129 (100), 127 (35), 115 (35), 101 (56). Anal. C₉H₁₈O₄]. By comparison of the MS-fragmentation patterns with authentic samples the following compounds were also identified: Oxalic acid diethyl ester, malonic acid diethyl ester and glycolic acid ethyl ester. The benzylic esters of formic acid, acetic acid (strongly dominant) and methoxy-acetic acid were identified (comparison with authentic samples) after esterification of a small portion of the carboxylic acid mixture with benzylic bromide.

Oxidation of 2. Oxidation conditions: pH = 9.0, 25 °C, 60 min. 3.1 equivalents of NaOH consumed. Neutral fraction: 230 mg containing 2, 2-methoxy-6-methylhydroquinone, 2-methoxy-3(or 5)-hydroxy-6-methyl-p-benzoquinone (TLC and UV-VIS spectroscopy). Acidic fraction: 1.5 g. Preparative separation in light petroleum—acetone (9:1—4:1) afforded methyl-maleic acid diethyl ester as the major product [¹H NMR: 1.24 (3H, t), 1.31 (3H, t), 2.02 (3H, d, J = 1.4 Hz), 4.13 (2H, q), 4.26 (2H, q), 5.80 (1H, q, J = 1.4 Hz). MS: 186 (1, M), 171 (43), 141 (28), 140 (22), 113 (100), 112 (39). Anal. C₉H₁₆O₄]. Furthermore, a moderate yield of z-methyl-z-epoxy-γ-hydroxybutyric acid ethyl ester (ethyl ester of 6) was obtained [¹H NMR: 1.27 (3H, t), 2.18 (3H, s), 2.88 (2H, d, J = 5.3 Hz), 4.19 (2H, q), 4.37 (1H, t, J = 5.3 Hz). MS: 160 (2, M), 131 (2), 127 (6), 117 (5), 114 (3), 101 (3), 87 (100)]. Methoxy-maleic acid diethyl ester was also identified by comparison of the MS fragmentation pattern with an authentic sample.

Oxidation of 3. Oxidation conditions: pH = 10.0, 40 °C, 60 min. 4.1 equivalents of NaOH consumed. Neutral fraction: 100 mg, mostly 3. Acidic fraction: 1.15 g. Preparative separation in light petroleum—acetone (20:1—4:1). The major component was obtained in 69% yield and identified as phenylmaleic acid diethyl ester [¹H NMR: 1.29 (3H, t), 1.35 (3H, t), 4.21 (2H, q), 4.39 (2H, q), 6.25 (1H, s), 7.37 (5H, braid s). MS: 248 (28, M), 219 (14), 203 (24), 191 (11), 175 (91), 147 (92), 131 (37), 103 (72), 102 (100). Anal. C₁₅H₁₄O₄]. Ethyl benzoate, phenylacetic acid ethyl ester (each obtained in 6% yield) and methoxy-maleic acid diethyl ester (traces) were identified by comparison with authentic samples.

Oxidation of 4. Oxidation conditions: pH = 9.0, 25 °C, 60 min. 1.9 equivalents of NaOH consumed. Neutral fraction: 700 mg containing 4-tert-butylicetohexol and 5 (TLC and UV-VIS spectroscopy). Acidic fraction: 1.57 g. Repeated separations in light petroleum—acetone (9:1) afforded three major components: 2-oxo-5-tert-butylyl-5-(1′-hydroxy-2′-ethoxycarbonyl)-2,5-dihydrofuran (ethyl ester of 7. M.p. 73.5—74.0 °C. Yield 26%). [¹H NMR: 1.10 (9H, s), 1.27 (3H, t), 3.10 (1H, d, disappears on addition of CD₃COOD), 4.18 (2H, q), 4.68 (1H, d, singlet on addition of CD₃COOD). 6.09 (1H, d, J = 5.8 Hz), 7.53 (1H, d, J = 5.8 Hz). ¹³C NMR (off resonance spectrum): 13.96 (q), 25.87 (q), 38.08 (s), 62.84 (t), 72.98 (d), 93.62 (s), 123.30 (d), 155.44 (d), 171.75 (s), 172.50 (s). MS: 242 (0, M), 224 (4), 186 (7), 182 (8), 181 (7), 169 (4), 168 (11), 167 (12), 153 (7), 140 (43), 139 (51), 125 (72), 113 (74), 111 (49), 57 (100). IR (KBBr): 1725, 3400 cm⁻¹. Anal. C₁₃H₁₄O₃]. α,γ-diepoxy-γ-tert-butylylhexanedioic acid diethyl ester (ethyl ester of 8, yield 8%). [¹H NMR: 1.10 (9H, s), 1.31 (6H, t), 3.42 (1H, s), 3.4—3.6 (2H, dd), 4.20 (4H, q). MS: 286 (0, M), 271 (3), 229 (1), 213 (5), 169 (8), 157 (7), 127 (10), 111 (37), 57 (100). Anal. C₁₄H₁₆O₄]. 2-oxo-4-tert-butylyl-5-(1′-hydroxy-2′-ethoxycarbonyl)-2,5-dihydrofuran (ethyl ester of 9. M.p. 71.5—72.0 °C, Acta Chem. Scand. B 34 (1980) No. 9.
yield 15% \[^{1}H \text{NMR: 1.28 (9H, s), 1.34 (3H, t), 2.95}\]
(1H, d, disappears on addition of CD\(_2\)COOD), 4.34 (2H, q), 4.52 (1H, d on addition of CD\(_2\)COOD, J = 1.6 Hz), 5.31 (1H, dd, J = 1.6, 1.4 Hz), 5.87 (1H, d, J = 1.4 Hz). \[^{13}C \text{NMR (off resonance spectrum): 14.16 (q), 29.50 (q), 33.55 (s), 62.96 (t), 69.31 (d), 82.99 (d), 117.26 (d), 171.00 (s), 172.36 (s), 176.75 (s). MS: 242 (0, M), 224 (t), 169 (13), 153 (3), 151 (3), 140 (100), 139 (22), 125 (81), 111 (55). IR (KBr): 1735, 1760, 3350 cm\(^{-1}\). Anal. C\(_{12}\)H\(_{18}\)O\(_{4}\).\] Small amounts of five further components were detected but these were not identified.

Oxidation of S. Oxidation conditions: pH 11.0, 40 °C, 60 min. Acidic fraction: 2.63 g. Preparative separations in light petroleum – diethyl ether (9:1) and light petroleum – ethyl acetate (18:1→4:1) afforded four major components: 2,3-exoxy-3-tert-butyl-4-oxy-pentanoic acid ethyl ester (ethyl ester of 10), yield 17%. \[^{1}H \text{NMR: 1.02 (9H, s), 1.23 (3H, t), 2.29 (3H, s), 3.48 (1H, s), 4.13 (2H, q). MS: 214 (4, M), 171 (4), 169 (4), 157 (5), 141 (5), 115 (100), 99 (16), 87 (92). Anal. C\(_{12}\)H\(_{18}\)O\(_{4}\).\] tert-butylmalonic acid diethyl ester (diethyl ester of 11), yield 53%. \[^{1}H \text{NMR: 1.06 (9H, s), 1.29 (6H, t), 3.52 (1H, s), 4.20 (4H, q). MS: 216 (0, 1, M), 201 (0.3), 171 (24), 143 (7), 125 (13), 115 (54), 87 (58), 57 (100).\] α-tert-butyl-β-hydroxy-succinic acid diethyl ester (first form, diethyl ester of 12a, yield 6%). \[^{1}H \text{NMR: 1.04 (9H, s), 1.32 (6H, t), 2.99 (1H, d, J = 8.6 Hz), 3.97 (1H, s), 4.30 (2H, q), 4.36 (2H, q), 4.96 (1H, d, J = 8.6 Hz). MS: 246 (0, M), 229 (0.01), 202 (1), 173 (8), 156 (24), 145 (9), 128 (30), 127 (12), 111 (7), 57 (100).\] α-tert-butyl-β-hydroxy-succinic acid diethyl ester (second form, diethyl ester of 12b, yield 18%). \[^{1}H \text{NMR: 1.00 (9H, s), 1.34 (6H, t), 2.89 (1H, d, J = 10.6 Hz), 4.22 (4H, q), 4.82 (1H, d, J = 10.6 Hz). MS: 246 (0, M), 229 (0.02), 202 (2), 201 (1), 173 (7), 156 (32), 145 (9), 128 (43), 127 (12), 111 (5), 57 (100).\] Small amounts of six further components were detected by GLC but these were not identified.

REFERENCES


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