The Reactions of Lignin with Alkaline Hydrogen Peroxide.
Part III.* The Oxidation of Conjugated Carbonyl Structures

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The alkaline hydrogen peroxide oxidation of aryl-α-carbonyl structures and cinnamaldehyde structures related to lignin has been studied using a kinetic method. Aryl-α-carbonyl structures in phenolic units are quantitatively cleaved to form the corresponding hydroquinone derivatives with rates of reaction strongly dependent on the substitution pattern in the aromatic ring. The presence of heavy metal ions like Fe(III) or Mn(IV) accelerates the oxidation but decreases the yield of hydroquinone. In non-phenolic units the oxidation of aryl-α-carbonyl structures is dependent upon the structure of the side chain.

Cinnamaldehyde structures of the coniferaldehyde type are readily cleaved by alkaline hydrogen peroxide giving rise to the corresponding aromatic aldehyde. The reaction shows a first-order dependency on $[HO_2^-]$ whereas $[HO^-]$ has a negligible influence within the pH range studied.

The significance of these results for the bleaching of mechanical pulps with alkaline hydrogen peroxide is briefly discussed.

In the presence of sodium silicate and in the absence of heavy metal ions aqueous alkaline hydrogen peroxide is essentially stable.[1] Under such conditions hydrogen peroxide can be used as a lignin-preserving bleaching agent for mechanical pulps causing the elimination of coloured structures without any substantial dissolution of wood material.

Cinnamaldehyde structures and quinones are known to constitute the major coloured species present in lignin.[2,3] In addition, aryl-α-carbonyl structures may be present[4] or formed under oxidative conditions. In the present work, lignin model compounds of the coniferaldehyde and aryl-α-carbonyl types (Fig. 1) have been treated with aqueous alkaline hydrogen peroxide in the presence of sodium metasilicate and diethylenetriaminepentaacetic acid (DTPA). The kinetic behaviour of the models as well as the reaction products have been elucidated and the results interpreted with emphasis on the behaviour of mechanical pulps to hydrogen peroxide bleaching.

RESULTS

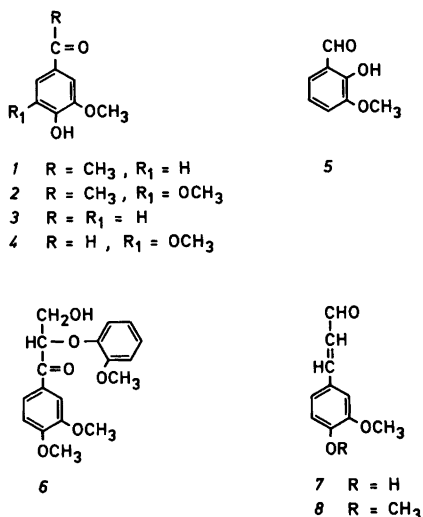*Oxidation of 4-hydroxy-3-methoxyacetophenone and related compounds (cf. Ref. 5). The oxidation*

*Fig. 1.* Model compounds.

* Part II. See Ref. 1.
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Table 1. First-order reaction rate constants k_{obs} for the oxidation of aryl-α-carbonyl structures with hydrogen peroxide (0.400 M) at pH = 10.5.

Compound	Temp./°C	Metal ion	$k_{obs}/10^{-3}$ min^{-1}
1	21.8		1.59
1	30.0		3.95
1	35.0		6.85
1	30.0	Fe(II)	4.23
1	30.0	Fe(III)	10.7
1	30.0	Mn(II)	5.29
1	30.0	Mn(IV)	10.5
2	30.0		50.0
3	30.0		7.00
4	30.0		127
5	30.0		25.9
6	30.0		12.3 [a]

[a] Reaction run in ethanol − water (1:1).

of 4-hydroxy-3-methoxyacetophenone (acetoguaiacone, *1*) was performed at pH = 10.5 and 30 °C. By employing a large excess of hydrogen peroxide, running the reaction under nitrogen and having sodium metasilicate and DTPA present in the solution the pseudo first-order reaction rate constant could be determined (Table 1). First-order reaction plots of the concentration of starting material and formation of methoxyhydroquinone (determination based on GLC analysis) as a function of time both gave straight lines with identical slopes. Analysis of the consumption of hydrogen peroxide and alkali during the reaction indicates the mechanism outlined in Scheme 1 (*cf.* Ref. 6). The reaction, when performed at three different temperatures under otherwise identical conditions,
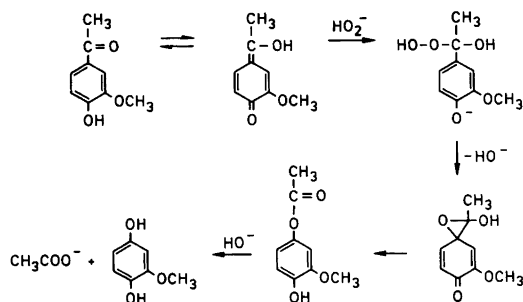
Scheme 1. Mechanism for the formation of methoxyhydroquinone from alkaline hydrogen peroxide oxidation of acetoguaiacone.

showed an activation energy of 83.3 kJ mol^{-1} for the oxidation of acetoguaiacone.

For comparison, several other phenolic aryl-α-carbonyl structures related to lignin (compounds *2−5*) were also oxidized with hydrogen peroxide at pH = 10.5 and 30 °C in the same manner. In all cases straight lines were obtained for the first-order reaction plots. As expected the reaction rate constants given in Table 1 show that an additional methoxyl group *ortho* to the phenolic hydroxyl group (compounds *2* and *4*) exerts a strongly positive influence on the rate of reaction (*cf.* Ref. 7). Furthermore, a compound (*5*) with the hydroxyl group *ortho* to the side chain is oxidized at a higher rate than the corresponding *para* isomer (*3*) which is in accordance with other observations.[8]

In the presence of heavy metal ions solutions of hydrogen peroxide rapidly decompose to give hydroxyl radicals, superoxide ions and oxygen.[9] The simultaneous presence of a chelating agent has, in a few cases, been demonstrated to lead to similar decomposition reactions.[9−11] In the present work the individual influence of manganese and iron ions on the rate of oxidation of *1* was evaluated. The complexes between DTPA and Fe(II), Fe(III), Mn(II) and Mn(IV), respectively, were separately prepared and added to the reaction mixtures (see Experimental). During each reaction the consumption of hydrogen peroxide and alkali was also measured. The results obtained revealed that the presence of DTPA/Fe(II) or DTPA/Mn(II) caused only slight increases in the rate of oxidation of *1* as well as in the consumption of hydrogen peroxide and alkali. This effect might have been due to the presence of small amounts of Fe(III) and Mn(IV) in the solutions. On the other hand, addition of either DTPA/Fe(III) or DTPA/Mn(IV) to the reaction mixtures increased the rate of oxidation almost three-fold. At the same time a four-fold increase in the consumption of hydrogen peroxide was observed. Thus, when present in higher valency states these heavy metal ions, even in their DTPA-complexed forms, induce the decomposition of hydrogen peroxide. The decomposition products formed are able to attack the phenolic ring in *1*[1] leading to an overall increase in the rate of oxidation and a decrease in the amount of methoxyhydroquinone formed.

It is clear that in order to use the alkaline hydrogen peroxide oxidation of phenolic aryl-α-carbonyl structures as a synthetic route to hydroquinone and catechol derivatives (the Dakin reaction)[12] *precau-*

tions must be taken to minimize the decomposition of hydrogen peroxide. This can be done by having sodium metasilicate and DTPA (or EDTA) present in the solution and performing the reaction under nitrogen.

The carbonyl group in non-phenolic aryl-α-carbonyl structures is not attacked by alkaline hydrogen peroxide. However, by using a lignin model containing a complete propanoid side chain (6) it could be demonstrated that under the conditions used in this work (pH = 10.5, 30 °C) alkali and hydrogen peroxide are able to attack and degrade "inner" lignin units containing an α-carbonyl group. In this reaction approximately 3 equivalents of hydrogen peroxide and 3.5 equivalents of alkali were consumed indicating a reaction mechanism similar to that proposed in Ref. 13.

Oxidation of cinnamaldehyde structures (cf. Ref. 5). On oxidation with alkaline hydrogen peroxide (pH = 10.5, 30 °C) in the presence of sodium metasilicate and DTPA the model compounds coniferaldehyde (4-hydroxy-3-methoxycinnamaldehyde, 7) and coniferaldehyde methyl ether (8) both yielded the corresponding aromatic aldehydes in rapid and quantitative reactions. In the oxidation of 7, vanillin is formed which is able to react further with hydrogen peroxide to form methoxyhydroquinone (see above). The side chain of the model

compounds is simultaneously oxidized to formic acid indicating the intermediate formation of glyoxal. During the oxidation of 7 and 8 approximately 3 equivalents of hydrogen peroxide and 2 equivalents of alkali were consumed. These results indicate the oxidation mechanism outlined in Scheme 2. The reaction was further investigated at 0 °C using 8 as a model compound. By measuring the disappearance of 8, as well as the formation of veratric aldehyde, the influence on the reaction of
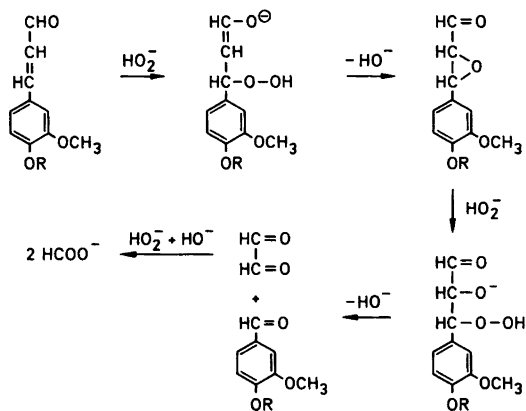
Scheme 2. Mechanism for the cleavage of cinnamaldehyde structures by alkaline hydrogen peroxide.

Table 2. First-order reaction rate constants k_{obs} for the oxidation of cinnamaldehyde structures.

pH	Temp./°C	Total [H$_2$O$_2$]/M	[HO$_2^-$]/mM[a]	k_{obs}/10^{-3} min^{-1}
Compound 7				
10.5	30.0	0.400	33	52.4
Compound 8				
9.0	0	0.400	0.28	47.6, 2.32[b]
9.5	0	0.400	0.89	49.1
9.5	21.8	0.400	2.4	189
9.5	30.0	0.400	3.5	296
10.0	0	1.265	8.9	63.0
10.5	0	0.200	4.4	34.1
10.5	0	0.400	8.8	67.3
10.5	0	0.400	8.8	67.3[c]
10.5	0	0.400	8.8	68.4[d]
10.5	0	0.690	15	116
11.0	0	–	–	1.43
11.0	0	0.127	8.4	80.0
11.0	0	0.400	26	189

[a] pK_a-values (extrapolated) for H$_2$O$_2$ taken from Ref. 14. [b] Based on veratric aldehyde formed. [c] Presence of 0.1 M Na$_2$SO$_4$. [d] Presence of 0.254 mM Fe(III).
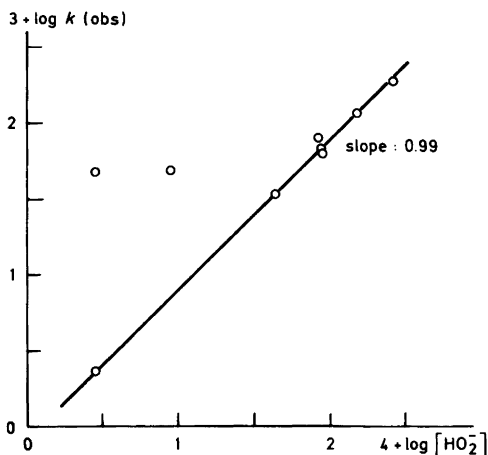
Fig. 2. Order in $[HO_2^-]$ in the alkaline hydrogen peroxide oxidation of coniferaldehyde methyl ether (values taken from Table 2, based on consumed starting material and/or veratric aldehyde formed).

ionic strength, Fe(III) ions, pH, temperature and hydrogen peroxide concentration was studied over the pH interval 9−11. The first-order reaction rate constants given in Table 2 reveal that neither the ionic strength nor the presence of DTPA-bound ferric ions affects the rate of oxidation of 8. At pH = 9.5 the influence of temperature is weak giving an activation energy at this pH of 41.2 kJ mol⁻¹, i.e. a value very close to that previously observed in the bleaching of mechanical pulps with hydrogen peroxide.[15] At a constant pH value (pH = 10.5) the reaction was shown to be first-order with respect to $[H_2O_2]$. However, a more informative result was obtained by plotting the rate constant for reactions run at different pH values against $[HO_2^-]$ (Fig. 2). In this case too a first-order dependency was obtained demonstrating that $[HO_2^-]$ determines the rate of reaction whereas $[HO^-]$ has an almost negligible influence at least in the pH range studied. In a separate experiment it was shown that the reaction between 8 and alkali alone is very slow at pH = 11 (Table 2).

At pH values below 10 the consumption of 8 was found to be faster than the formation of 3,4-dimethoxybenzaldehyde (veratric aldehyde) thus indicating some other reaction(s) competing with that depicted in Scheme 2. A preparative scale oxidation at pH = 8.5 revealed the formation of a new major reaction product; it was tentatively assigned structure 9 (see Experimental). The formation of 9 is

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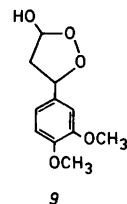
consistent with a reaction between 8 and hydrogen peroxide leading initially to the same hydroperoxide as depicted in Scheme 2 the keto form of which cyclized to the 1,2-dioxolane structure (cf. Ref. 16).

By analyzing the amount of veratric aldehyde formed from the oxidation of 8 at pH = 9 it could be demonstrated that the first-order dependency on $[HO_2^-]$ for the reaction presented in Scheme 2 is also valid at this pH (see Fig. 2).

DISCUSSION

The results presented above demonstrate that coloured lignin structures of the cinnamaldehyde type are highly reactive towards hydrogen peroxide. The reaction gives rise to the formation of aryl-α-carbonyl structures. These structures present in phenolic units, as well as those originally present in lignin, are degraded by hydrogen peroxide to give hydroquinones. Non-phenolic phenylpropane units containing an α-carbonyl group may also be degraded in the presence of alkali and hydrogen peroxide. The observation that $[HO_2^-]$ to a large extent determines the rate of oxidation of cinnamaldehyde structures implies the possibility of bleaching mechanical pulps at a lower pH than normal provided that $[HO_2^-]$ can be maintained at a high level. This conclusion has been confirmed both in the laboratory bleaching of mechanical pulps[17] and in a recently published procedure for the lignin-retaining bleaching of mechanical pulps with hydrogen peroxide.[18] Furthermore, the formation of hydroquinoid structures in lignin may be expected to make the pulps prone to colour reversion due to the facile conversion of hydroquinones to quinones on exposure to oxygen (cf. Ref. 19).

During bleaching of mechanical pulps heavy metal ions in their high valency states, even when chelated with DTPA, catalyze the decomposition of hydrogen peroxide. The decomposition products are able to attack phenolic units in lignin[1] leading to the formation of quinones[13] which in turn are oxidized by hydrogen peroxide thus giving rise to a

further consumption of hydrogen peroxide. It is well-known that in order to obtain a high brightness and to save bleaching chemicals it is necessary to remove as far as possible the metal ions in mechanical pulps prior to bleaching.

EXPERIMENTAL

Model compounds. The compounds *6*, *7* and *8* were prepared according to Refs. 20 − 22. Compounds *1* − *5* were commercially available.

Kinetic runs. The experimental equipment described in Ref. 1 was used. Hydrogen peroxide was analyzed by iodometric titration. An aqueous solution (200 ml; in the oxidation of *6* a mixture of 100 ml of ethanol and 100 ml of water) containing 1.27 mM DTPA, 0.05 M Na$_2$SiO$_3$.9H$_2$O and hydrogen peroxide (see Tables 1 and 2) was prepared and its pH adjusted to the desired value. Oxygen-free nitrogen was bubbled through the solution. After 30 min 1.0 mmol of the model compound dissolved in 5 ml of dioxane was added. At different intervals of time samples were withdrawn, silylated (compounds containing hydroxyl groups) and analyzed by GLC (3 % SE-30 on Chromosorb HP 80 − 100 mesh, 3 mm o.d. × 2 m stainless steel, 15 ml min^{-1} N$_2$) following the procedure described in Ref. 1. (Model compound, internal standard, column temperature/°C: *1*, heptadecane, 145; *2*, nonadecane, 165; *3*, hexadecane, 150; *4* octadecane, 165; *5*, hexadecane, 150; *6*, docosane, 240; *7*, tetracosane, 260; *8*, nonadecane, 165; methoxyhydroquinone, hexadecane, 150; veratric aldehyde, hexadecane, 145, 2 °C min^{-1} after 2 min.) The oxidation of *1* and *8* was also followed by measuring the formation of methoxyhydroquinone and veratric aldehyde, respectively.

Addition of heavy metal ions. In oxidation experiments carried out in the presence of heavy metal ions, a solution of DTPA in 50 ml of water was neutralized (pH = 6.5) and MnSO$_4$.H$_2$O, FeSO$_4$.7-H$_2$O or FeCl$_3$ (0,254 mM) was added. The Mn(IV) complex was prepared by oxidizing the Mn(II) complex with oxygen for 30 min at pH = 10.5 and room temperature during which time a red colour developed (*cf.* Refs. 10, 11) but no attempt was made to identify the actual species obtained. The resulting solutions were added to 150 ml of water containing sodium metasilicate and hydrogen peroxide and pH adjusted as described above.

Identification of formic acid from 7 and 8. Formic acid was isolated from the reaction mixtures by ion-pair extraction using tetrabutylammonium ion followed by esterification with benzyl bromide.[23] The resulting benzyl ester was identified by comparison with an authentic sample (GLC/MS). No other acidic products were found.

Identification of 9. Compound *8* (1 mmol) was oxidized with hydrogen peroxide as described above at pH = 8.5 and 0 °C for 180 min. Extraction with ethyl acetate afforded one major component (TLC) (giving a positive peroxide test), which on standing rapidly decomposed to veratric aldehyde, 3,4-dimethoxyphenyloxirane, 3,4-dimethoxyacetophenone (*cf.* Ref. 24) and *8* (GLC/MS). Two further components in trace amounts could also be detected by GLC/MS. These were assigned the structures 3-(3,4-dimethoxyphenyl)-3H-1,2-dioxole [MS: 208 (M, 34 %), 180(54), 165(51), 151(77), 137(16), 119(29), 107(33), 91(75), 77(45), 65(34), 32(100)] and 3-hydroxy-5-(3,4-dimethoxyphenyl)-1,2-dioxolane (*9*) [MS: 226 (M, 0 %), 225(34), 210(11), 207(3), 191(54), 182(8), 163(21), 147(46), 119(38), 103(30), 91(34), 77(50), 65(18), 44(39), 32(100)].

A part of the ethyl acetate extract was carefully evaporated with nitrogen at low temperature and the residue reduced with LiAlH$_4$ in diethyl ether. The resulting products were acetylated and subjected to analysis by GLC/MS. 1-(3,4-dimethoxyphenyl)-1,3-diacetoxypropane expected to be formed from *9* was identified by its MS [296 (M, 1 %), 236(18), 194(15), 193(17), 177(23), 165(16), 151(100), 138(22)]. In addition, the acetates from 3,4-dimethoxybenzyl alcohol, 3,4-dimethoxyphenylethane-1,2-diol, 1-(3,4-dimethoxyphenyl)ethanol and 3,4-dimethoxycinnamyl alcohol were found and identified by comparison (MS) with authentic samples.

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