The Reactions of Lignin with Alkaline Hydrogen Peroxide. Part II.*

Factors Influencing the Decomposition of Phenolic Structures

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The reaction between α-methylsyringyl alcohol, a model for the phenolic units in lignin, and aqueous hydrogen peroxide in the pH-range 10.0 − 12.5 has been studied using a kinetic method. It has been found that the reaction rate exhibits a strong maximum around pH = 11.5. Furthermore, the reaction rate at a constant pH value is accelerated by the presence of heavy metal ions or an inert salt such as sodium sulfate. An increase in temperature also results in a strongly enhanced rate of reaction. In the presence of sodium metasilicate, acting as a stabilizer for hydrogen peroxide, and under a nitrogen atmosphere, the phenol is stable against degradation indicating that the major reacting species are hydroxyl radicals, superoxide ions and oxygen formed in the decomposition of hydrogen peroxide.

Alkaline hydrogen peroxide is widely used as a bleaching agent in the pulp industry. In the presence of sodium silicate (acting as a buffer and a stabilizer for hydrogen peroxide), it can bleach lignin-rich pulps to rather high brightness levels without any substantial dissolution of lignin (lignin-retaining bleaching). Despite the presence of silicate, some hydrogen peroxide is nevertheless lost in non-bleaching reactions due to spontaneous decomposition of hydrogen peroxide and/or to decomposition caused by the action of trace amounts of heavy metal ions present in the pulps.

The brightening effect of hydrogen peroxide has been attributed to its ability to react with various coloured carbonyl structures present in lignin including quinones and cinnamaldehyde structures.[2,3] Solutions containing alkaline hydrogen peroxide have also been shown to attack phenols thus leading to an extensive degradation of unetherified phenolic units in lignin.[4,5] In these experiments no attempt was made to identify the actual reacting species. In a recent series of papers the reaction products and mechanisms for the oxidation of phenols related to lignin with oxygen as well as with hydrogen peroxide under strongly alkaline conditions have been extensively clarified.[6] From this work it was concluded that, under alkaline conditions, hydrogen peroxide is unable to attack phenols of the type present in lignin.

In recent years, interest in hydrogen peroxide as a non-polluting bleaching agent for pulps has increased and the possibility of using hydrogen peroxide not only for the lignin-retaining bleaching of high-yield pulps but also as a delignifying bleaching agent for chemical pulps has been discussed.[7,8] The present investigation was therefore undertaken in order to elucidate in detail the factors influencing the reactions between various lignin structures and hydrogen peroxide under conditions simulating bleaching processes.

In part I of this series,[1] it was shown that alkaline hydrogen peroxide decomposes to hydroxyl radicals and superoxide ions in the presence as well as in the absence of heavy metal ions. The radicals formed may react further either with themselves, with each other or with hydrogen peroxide giving rise to oxygen and water as the final reaction products. It was also shown that at least a part of the oxygen formed was present in the singlet ($^1\Delta g$) state.

* Part I, see Ref. 1.

The present work deals with the reactions between phenolic structures and hydrogen peroxide at pH values in the range $10-12$ and at moderately elevated temperatures. By maintaining constant reaction conditions the pseudo first-order reaction rate constant for the decomposition of the phenolic lignin model compound α-methylsyringyl alcohol 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanol has been calculated and the influence on the reaction rate of various additives as well as of pH and temperature elucidated.

RESULTS

In preliminary experiments [9] the lignin models 2-methoxy-4-methylphenol and 1-(4-hydroxy-3-methoxyphenyl)ethanol were oxidized at pH = 11.0 and 40 °C with a slight excess of hydrogen peroxide and the decrease in concentration of each phenol was followed by GLC. It could be demonstrated that in the presence of sodium metasilicate, acting as a stabilizer for hydrogen peroxide, and under a nitrogen atmosphere, these phenols were essentially stable towards hydrogen peroxide. In the absence of metasilicate, on the other hand, both compounds were rapidly degraded. This degradation was interpreted as being due to the action of singlet oxygen, formed by decomposition of hydrogen peroxide.

In the present work α-methylsyringyl alcohol was chosen as the model compound and a large excess of hydrogen peroxide was used in order
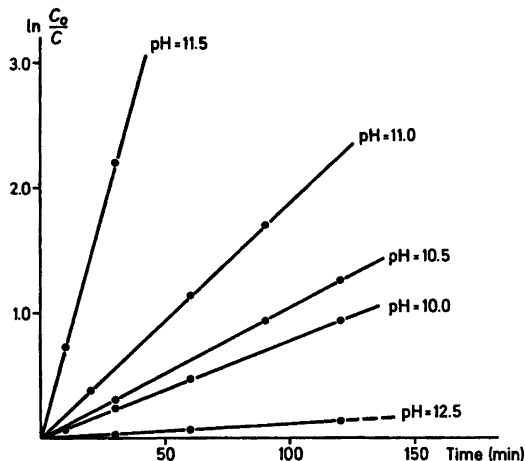

Fig. 1. Oxidation of α-methylsyringyl alcohol with hydrogen peroxide at 30 °C, at different pH levels.

to follow the kinetic behaviour of the phenol. The pH and temperature were kept constant in each experiment and the concentration of the phenol was determined by GLC at different intervals of time (see Experimental).

Influence of pH and temperature. Oxidation of α-methylsyringyl alcohol at 30 °C in the pH interval $10.0-12.5$ in each case gave linear relationships for the first-order reaction rate plots as illustrated in Fig. 1. The rate constants given in Table 1 show that when the pH during the reaction is equal to the pK_a-value of hydrogen peroxide ($pK_a = 11.6$) [10] a maximum

Table 1. First-order reaction rate constants, $k(\text{obs})$, for the decomposition of α-methylsyringyl alcohol.

pH	Temp./°C	$k(\text{obs})/10^{-3} \text{ min}^{-1}$
10.0	30	7.83
10.5	25	4.46
10.5	30	10.49
10.5 [a]	30	0.53
10.5	40	59.33
11.0	30	18.94
11.5	30	73.23
12.5	30	1.17

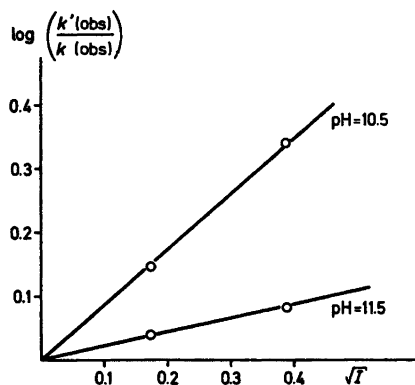[a] Addition of 2.2 mM DTPA and 0.072 M $Na_2SiO_3 \cdot 9H_2O$.

Fig. 2. Oxidation of α-methylsyringyl alcohol with hydrogen peroxide at 30 °C. Influence of ionic strength (I).

Table 2. First-order reaction rate constants, k_1(obs), for the decomposition of hydrogen peroxide.

pH	Temp./°C	k_1(obs)/10^{-3} min^{-1}
10.0	30	3.09
10.5	25	3.24
10.5	30	5.50
10.5 [a]	30	5.56
10.5	40	12.08
11.0	30	10.38
11.5	30	11.72
12.0	30	3.36
12.5	30	0.68

[a] Addition of 0.10 M Na₂SO₄.

Table 3. First-order reaction rate constants, k'(obs), for the decomposition of α-methyl-syringyl alcohol in the presence of Na₂SO₄ at 30 °C.

pH	Na₂SO₄ (M)	k(obs)/10^{-3} min^{-1}	k'(obs)/10^{-3} min^{-1}
10.5	—	10.49	
10.5	0.01		14.67
10.5	0.05		22.93
11.5	—	73.23	
11.5	0.01		80.30
11.5	0.05		88.60

Table 4. First-order reaction rate constants, k(obs), for the decomposition of α-methyl-syringyl alcohol in the presence of catalytic amounts of heavy metal ions (pH = 10.5, 30 °C).

Metal ion	Conc. (mM)	k(obs)/10^{-3} min^{-1}
Cu	0.285	25.85
Fe	0.285	19.34
Fe [a]	0.285	15.10
Mn	0.150	17.02
Mn	0.213	27.52
Mn [b]	0.213	3.70
Mn	0.285	39.97

[a] Addition of 1.4 mM DTPA. [b] Addition of 0.072 M Na₂SiO₃.9H₂O.

in the rate of decomposition of the phenol is obtained. Comparable experiments in the absence of α-methylsyringyl alcohol gave rate

constants for the decomposition of hydrogen peroxide as a function of pH. These values (Table 2) demonstrate a close relationship between the rate of oxidation of the phenol and the rate of decomposition of hydrogen peroxide.

From experiments run at 25, 30 and 40 °C (pH = 10.5) an activation energy of 133.6 kJ/mol^{-1} for the oxidation of α-methylsyringyl alcohol was found. The corresponding value for the decomposition of hydrogen peroxide was calculated to be 68.4 kJ/mol^{-1}.

Influence of ionic strength. Oxidation experiments carried out at 30 °C and pH = 10.5 in the presence of 0.01 and 0.05 M sodium sulfate gave a linear relationship between the logarithm for the rate constant and the square root of the ionic strength (Fig. 2 and Table 3). The slope was calculated to be 0.87 ± 0.03 indicating that the major part of the reaction between α-methyl-syringyl alcohol and hydrogen peroxide proceeds with the participation of charged species at this pH. At pH = 11.5 the influence of the ionic strength was much less (slope = 0.22 ± 0.04) and a reaction involving oxygen in the ground state and/or in the excited singlet state is indicated. The rate of decomposition of hydrogen peroxide was shown to be independent of the ionic strength.

Influence of heavy metal ions (cf. Refs. 11–14). The presence of a catalytic amount of copper(II), iron(III) or manganese(IV) in the oxidation of α-methylsyringyl alcohol (pH = 10.5, 30 °C) gave in each case an increased rate of reaction of the model compound. An increased rate was also observed when the reaction was carried out in the presence of iron(III) chelated with DTPA [11] (molar ratio DTPA/Fe(III) = 5:1) (Table 4). Experiments run at different concentrations of manganese(IV) gave a linear relationship between the rate constant and the concentration of manganese(IV) with a slope of 1.33 ± 0.01 (Table 4 and Fig. 3).

The rate of oxidation of α-methylsyringyl alcohol with hydrogen peroxide was strongly retarded when sodium metasilicate and DTPA were present in the solution (Table 1) and when the reaction was carried out under nitrogen no reaction took place at all under the conditions used. The presence of manganese(IV) together with metasilicate gave a slight increase
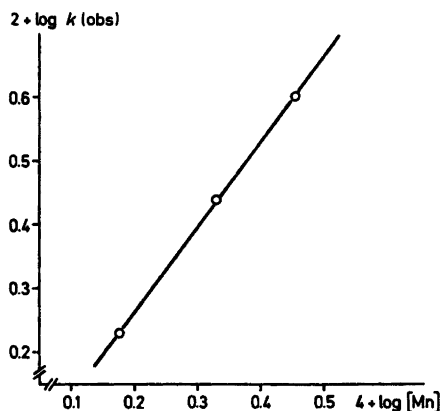
Fig. 3. Oxidation of α-methylsyringyl alcohol with hydrogen peroxide at 30 °C and pH = 10.5. Influence of the concentration of manganese.
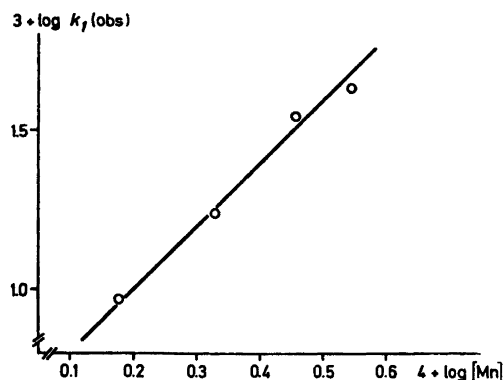

Fig. 4. Decomposition of hydrogen peroxide at 30 °C and pH = 10.5. Influence of the concentration of manganese.

in the rate of reaction but the rate was still much lower than in the absence of metasilicate (Table 4).

Comparable experiments run in the absence of α-methylsyringyl alcohol gave rate constants for the decomposition of hydrogen peroxide (Table 5). These values show that an increased rate of decomposition of hydrogen peroxide generally leads to an increased rate of oxidation of α-methylsyringyl alcohol. In the presence of metal ions a direct interaction between metal ion and the phenol is, however, also possible (*cf.* Ref. 15) since copper(II) as well as iron(III), which are weak catalysts for the decomposition

Table 5. First-order reaction rate constants, $k_1(\text{obs})$, for the decomposition of hydrogen peroxide in the presence of catalytic amounts of heavy metal ions (pH = 10.5, 30 °C).
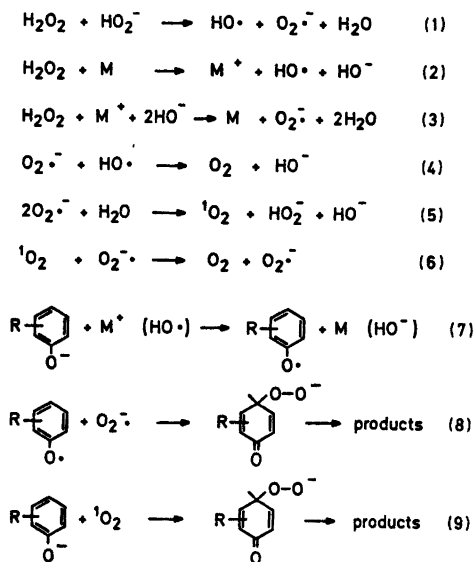
Metal ion	Conc. (mM)	$k_1(\text{obs})/10^{-3} \text{min}^{-1}$
Cu	0.285	6.00
Fe	0.285	8.57
Fe [a]	0.285	14.80
Mn	0.150	9.33
Mn	0.213	17.33
Mn [b]	0.213	1.60
Mn [a]	0.213	0.34
Mn	0.285	34.83
Mn	0.349	42.57

[a] Addition of 1.4 mM DTPA. [b] Addition of 0.072 M $Na_2SiO_3.9H_2O$.

of hydrogen peroxide, both gave enhanced rates of oxidation of α-methylsyringyl alcohol. The Fe(III)/DTPA-complex on the other hand, although a good catalyst for the decomposition of hydrogen peroxide, decreases the rate of oxidation of α-methylsyringyl alcohol compared with the rate with iron(III) alone indicating that the complex does not interact directly with the phenol. From the values in Table 5 the influence of various amounts of manganese(IV) on the decomposition of hydrogen peroxide was shown to follow the relation $k_1(\text{obs}) = k[\text{Mn}]^2$ with $k = 3.98 \times 10^5 \text{ min}^{-1} \text{ mol}^{-2}$ (Fig. 4).

As shown in Table 5 both sodium metasilicate and DTPA stabilize hydrogen peroxide against decomposition in the presence of manganese (IV). In the absence of heavy metal ions either of these additives gives an almost complete stabilization of hydrogen peroxide, suggesting that the decomposition of hydrogen peroxide not only in the presence but also in the absence of heavy metal ions proceeds *via* a radical chain mechanism.

DISCUSSION

The results presented above show that the decomposition products of hydrogen peroxide *viz.* hydroxyl radicals, superoxide ions and oxygen (formed according to Scheme 1, reactions 1 − 6 [12,13,16−18]) but not hydrogen peroxide itself can attack phenols of the type present

$$H_2O_2 + HO_2^- \longrightarrow HO\cdot + O_2^{-}\cdot + H_2O \qquad (1)$$

$$H_2O_2 + M \longrightarrow M^+ + HO\cdot + HO^- \qquad (2)$$

$$H_2O_2 + M^+ + 2HO^- \longrightarrow M + O_2^{-}\cdot + 2H_2O \qquad (3)$$

$$O_2^{-}\cdot + HO\cdot \longrightarrow O_2 + HO^- \qquad (4)$$

$$2O_2^{-}\cdot + H_2O \longrightarrow {}^1O_2 + HO_2^- + HO^- \qquad (5)$$

$${}^1O_2 + O_2^{-}\cdot \longrightarrow O_2 + O_2^{-}\cdot \qquad (6)$$

$$R-\text{C}_6H_3(O^-) + M^+ (HO\cdot) \longrightarrow R-\text{C}_6H_3(O\cdot) + M (HO^-) \qquad (7)$$

$$R-\text{C}_6H_3(O\cdot) + O_2^{-}\cdot \longrightarrow R-\text{(O-O}^-\text{)(O)} \longrightarrow \text{products} \qquad (8)$$

$$R-\text{C}_6H_3(O^-) + {}^1O_2 \longrightarrow R-\text{(O-O}^-\text{)(O)} \longrightarrow \text{products} \qquad (9)$$

Scheme 1. Formation of decomposition products from hydrogen peroxide and their reactions with phenols.

in lignin.* The participation of charged species in the reaction and the formation of a dimer from 4-*tert*-butylguaiacol (*cf.* Ref. 15) when this compound was treated with aqueous alkaline hydrogen peroxide (see Experimental) indicate that the reaction proceeds *via* formation of a phenoxy radical as shown in Scheme 1 (reaction 7). In the presence of heavy metal ions the formation of phenoxy radicals is brought about not only by hydroxyl radicals but also by the metal ions.** Superoxide ions may also react with phenols but under the conditions used the phenol is totally ionized and this possibility is ruled out since it has been shown that superoxide ions do not react with phenolate ions.[20] Superoxide ions can, however, react with the intermediately formed

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* The possibility of formation of a methylene-quinone from α-methylsyringyl alcohol (*cf.* Ref. 19), which could subsequently be attacked by hydrogen peroxide in a nucleophilic reaction, was ruled out by treating α-methylsyringyl alcohol with alkali and sulfite under the conditions employed in this work. No degradation of the starting material could be detected after 2 h of reaction.

** The exact nature of the various metal ion species present is not known but it is denoted as M and M$^+$ in Scheme 1 to represent the reduced and oxidized states, respectively.

phenoxy radicals[21] giving rise to a hydro-peroxide (reaction 8) which is subsequently degraded to low molecular weight compounds. The phenoxy radicals are also able to react with oxygen,[6] formed by quenching of singlet oxygen (reaction 6) and/or by the reaction between hydroxyl radicals and superoxide ions (reaction 4). The possibility of phenolate ions reacting directly with singlet oxygen (reaction 9) may also be envisaged since the high reactivity of phenols towards singlet oxygen [9,22] (*cf.* Ref. 23) means that such a reaction might compete with the quenching of singlet oxygen by superoxide ions.

The high reactivity of α-methylsyringyl alcohol towards the decomposition products from hydrogen peroxide suggests that phenolic lignin units may be efficiently degraded by hydrogen peroxide in the absence of stabilizing agents such as sodium silicate. Thus the lignin-degrading bleaching of chemical pulps should be possible particularly if the pH during bleaching can be maintained close to the pK_a-value for hydrogen peroxide. The presence of heavy metal ions, in particular manganese, should promote the lignin-degrading reactions due to the high catalytic power of this metal.

Under lignin-retaining bleaching conditions, the presence of trace amounts of heavy metal ions in the pulp may give rise to some decomposition of hydrogen peroxide leading to a minor degradation of lignin. This degradation yields quinones, which are highly reactive towards hydrogen peroxide, as primary reaction products from phenolic structures.[6] Such reactions may thus explain the fairly large consumption of hydrogen peroxide which is observed in practice during lignin-retaining bleaching.

EXPERIMENTAL

Model compounds. α-Methylsyringyl alcohol was prepared by reducing 4-hydroxy-3,5-dimethoxyacetophenone with sodium bis(2-methoxyethoxy)aluminium hydride. M.p. 95.0 – 95.5 °C (lit.[24] M.p. 95.5 – 96.6 °C). 4-*tert*-Butylguaiacol (2-methoxy-4-*tert*-butylphenol) was prepared according to Ref. 25.

Kinetic runs. Oxygen-free nitrogen was bubbled through 200 ml of an alkaline water solution placed in a thermostated bath (deviation ± 0.1 °C). The pH was kept constant by means of an automatic titration equipment

(Radiometer, Copenhagen). After 30 min, 80.0 mmol of hydrogen peroxide were added. Heavy metal ions, when present, were added as concentrated solutions of $CuSO_4.5H_2O$, $FeSO_4.7H_2O$ or $MnSO_4.H_2O$, respectively. The decomposition of hydrogen peroxide was followed by iodometric titration. In experiments with α-methylsyringyl alcohol, 198 mg (1.0 mmol) of the phenol dissolved in 5 ml dioxane were added 10 min after the addition of hydrogene peroxide. At the same time, the flow of nitrogen was interrupted. (In order to maintain a high ratio hydrogen peroxide/model compound, calculated amounts of concentrated hydrogen peroxide were added at intervals during the oxidation. The error caused by dilution was neglected). After different intervals of time, samples (3 × 1.00 ml) were withdrawn. Each sample was neutralized with 2 ml of a buffer solution (phosphate buffer, pH = 6.5) and treated with 1 ml 1 M $NaHSO_3$ in order to decompose peroxides. After extraction with ethyl acetate (3 × 3 ml) and evaporation, the residue was treated with 200 μl CH_3CN, 100 μl pyridine, 300 μl N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and 20 μl hexadecane (internal standard) for 4 h at room temperature. After evaporation the residue was dissolved in 200 μl CH_3CN and analyzed by gas-chromatography. Column: 10 % SE-30 on chromosorb W HP 80-100 mesh (3 mm o.d. × 1 m, stainless steel). Carrier gas: N_2, 15 ml min⁻¹. Injector temp. 200 °C. Detector temp. 220 °C. Column temp. 145 °C. The peaks from hexadecane and the silyl ether of α-methylsyringyl alcohol were integrated and compared with a corresponding standard curve giving the amount of α-methylsyringyl alcohol at each time as the mean value of three analyses.

Oxidation of 4-tert-butylguaiacol. 4-tert-Butylguaiacol (180 mg, 1 mmol) dissolved in dioxane (5 ml) was added to 80 mmol of hydrogen peroxide in 200 ml water at pH = 10.5 and 30 °C. After 4.5 h the solution was acidified to pH ~ 6, treated with sodium sulfite and extracted with ethyl acetate. The extract was analysed by TLC in two different solvents using 4-tert-butylguaiacol and 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-di-tert-butylguaiacol (prepared according to Ref. 26) as reference substances. Both these compounds were found in the reaction mixture together with smaller amounts of unidentified material.

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