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# EFFECTS OF IRON, COPPER, AND CHROMATE IONS ON THE OXIDATIVE DEGRADATION OF CELLULOSE MODEL COMPOUNDS

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## ABSTRACT

Iron(II) and iron(III) ions promote the degradation of the cellulose model 1,5-anhydrocellobiitol by oxygen or hydrogen peroxide; copper and chromate ions have marked and different effects on the iron catalysis. With starch, iron promotes the hydrogen peroxide-induced reaction and copper and chromate ions further enhance the reaction rate. The tensile strength of paper board is reduced by the action of hydrogen peroxide and iron(II) salts, and mixtures of copper, chromate, and arsenate salts (CCA, a timber preservative) also promote degradation in the presence or absence of iron ions. The oxidation of 1,5-anhydrocellobiitol by oxygen in the presence of iron ions is strongly inhibited by CCA and by cetyltrimethylammonium chloride, and is accelerated by phenols and related compounds.

## INTRODUCTION

Rusting iron in contact with timber promotes its decomposition[1–3], the phenomenon being known — especially in the building industry which uses metal fasteners in timber constructions — as "nail sickness" or "iron rot". It has been shown that this chemical form of timber degradation follows the destruction of the cellulose component of the wood[2], and it is generally accepted that corroding metals promote oxidative degradation[1–4].

Radical-induced oxidation of cellulose is assumed to result from the following initial oxidative steps[5–7]:

$$RH + X^{\cdot} \rightarrow R^{\cdot} + HX,$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$$
$$RO_2^{\cdot} + YH \rightarrow ROOH + Y^{\cdot},$$

and, if the radicals and the hydroperoxides are formed at any of the hydroxylated carbon atoms of the β-D-glucopyranosyl residues, carbonyl products can be formed:

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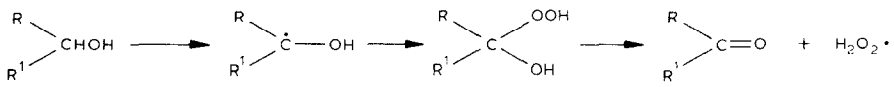


Scheme 1

Consequent upon this, $\beta$-elimination reactions, preceded by $\alpha$-hydroxycarbonyl isomerisation if necessary, lead to chain scission[8]. If, alternatively, radicals are produced at the inter-unit positions (C-1 or C-4), glycosidic cleavage can occur by facile hydrolysis[9,10].

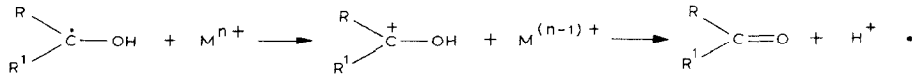
Metal ions (particularly iron ions) can promote these processes in several ways, in particular by inducing the formation of radical initiators[11]:

$$XH + M^{n+} \rightarrow X^{\cdot} + M^{(n-1)+} + H^{+},$$

and in wood this could conceivably occur most readily within the lignin component. Secondly, metal ions catalyse the decomposition of hydroperoxides and hydrogen peroxide to give further radicals — notably, with the latter, hydroxyl radicals which are powerful hydrogen abstractors[5-7,12]:

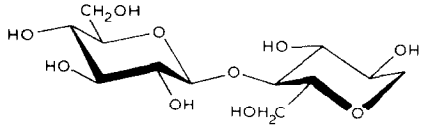
$$ROOH + M^{n+} \rightarrow RO^{\cdot} + M^{(n+1)+} + HO^{-},$$
$$ROOH + M^{(n+1)+} \rightarrow ROO^{\cdot} + M^{n+} + H^{+}.$$

Metal ions also promote the conversion of hydroxyalkyl radicals into carbonyl products[7,12]:



Scheme 2

This investigation examined the effects of added iron ions on the oxidation of 1,5-anhydrocellobiitol (**1**) and starch, which were selected as soluble cellulose models, and of paper board, which was regarded as a simple model timber. The individual components of the timber preservative "CCA"[13] (copper, chromate, and arsenate) have also been examined for their effects on the oxidative processes both independently and in conjunction with iron ions, and inhibitory influences of various compounds on the iron-promoted oxidations were tested.

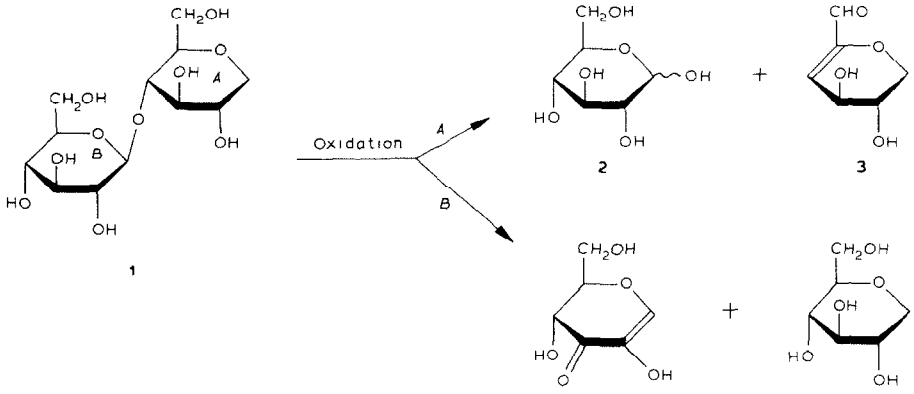


**1**

1,5-Anhydrocellobiitol (**1**) was selected as the main model compound, since it contains all of the functional and stereochemical features of the repeating unit of cellulose but does not have an aglycon, as does, for example, methyl β-cellobioside, which could lead to anomalous glycosidic bond cleavage[14]. To obtain adequate decomposition rates with oxygen as oxidant, reactions were carried out at 80°, and the reaction of the substrate was followed by gas chromatographic methods. Parallel room-temperature oxidations were carried out using hydrogen peroxide. With starch, the degradation by hydrogen peroxide in the presence of iron was conveniently monitored by viscometry. The much slower reaction with oxygen was, however, not amenable to this analytical method. Although the physical properties of starch are quite different from those of cellulose, the polymers contain closely related chemical functionality and might be expected to show correlatable chemical behaviour under the conditions of the experiments. This assumption is strengthened by the finding that maltose and cellobiose react similarly in analogous radical reactions[15]. Changes in the tensile strengths of paper board following soaking in water containing hydrogen peroxide and metal ions were also examined.

## RESULTS AND DISCUSSION

Studies of the metal-catalysed degradation of 1,5-anhydrocellobiitol (**1**) were carried out in buffer solutions at pH 6.0 and samples were investigated at intervals by g.l.c. examination of trimethylsilylated derivatives (internal *meso*-inositol). Trace amounts of compounds with retention times near those of the trimethylsilyl ether of **1** were detected; otherwise, three more-volatile compounds were detected which had the retention times of the trimethylsilyl ethers of α- and β-D-glucopyranose and 1,5-anhydro-D-glucitol. The combined amounts of the D-glucose ethers approximately equalled the amount of the anhydroglucitol ether, which suggests that initial hydrogen abstraction followed by inter-unit cleavage occurred approximately equally in each ring of the starting material. If oxidation occurred at C-6 of the deoxy moiety (*A*), D-glucose (**2**) would result together with the enal **3**, and an isomeric enone would be produced following oxidation at C-2 or C-3. Alternatively, oxidation at any secondary site of the D-glucose moiety (*B*) would, analogously, lead to the enone **4** and 1,5-anhydro-D-glucitol (**5**). Reaction at C-6 followed by β-elimination would give an enal which, being also a vinyl ether, would readily afford **5** together with a 1,5,6-tricarbonyl compound following hydrolysis. Finally, reaction at either the linking C-1 or C-4 positions and hydrolysis would give the observed products (**5** and **2**) and a lactone and a ketone. Since neither of these last carbonyl compounds nor the 1,5,6-tricarbonyl product nor the unsaturated compounds **3** or **4** were detected by g.l.c., it is assumed that they underwent further decomposition to relatively volatile products under the conditions of the experiment. Compounds **2** and **5** were isolated from the products of a preparative experiment and were characterised as their peracetates by $^{1}H$- and $^{13}C$-n.m.r. spectroscopy. The amounts isolated and those detected by g.l.c. represented only




Scheme 3

10–15% of the materials initially produced, which suggests that all first products had reacted further under the reaction conditions.

In aqueous solutions and in an atmosphere of oxygen, 1,5-anhydrocellobiitol reacted very slowly at room temperature even in the presence of iron(II) or iron(III) ions; after 7 and 20 weeks, 85 and 60%, respectively, of the compound remained unoxidised. At 80° under oxygen and in the presence of iron salts, 70% reaction occurred in ~28 days (Fig. 1B). The reaction rate was negligible in the

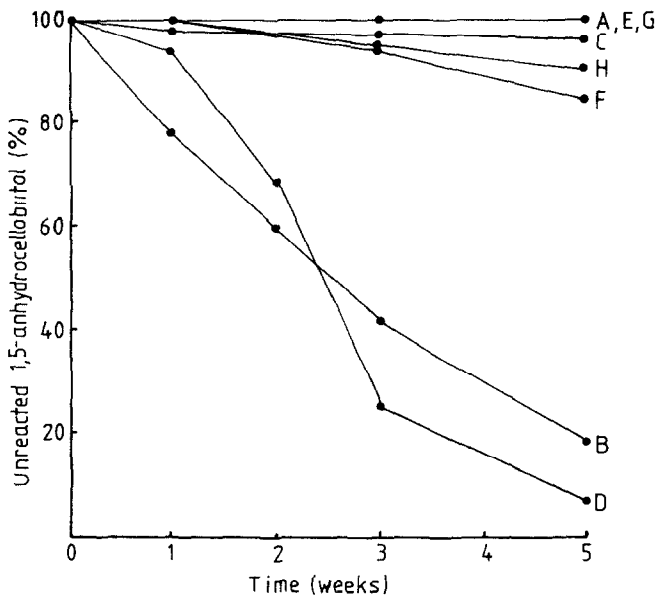



Fig. 1. Degradation of 1,5-anhydrocellobiitol by oxygen in aqueous solution at pH 6.0 and 80° in the presence of metal ions as follows (see Experimental for details): A, none; B, iron(II); C, copper(II); D, iron(II) and copper(II); E, chromate; F, iron(II) and chromate; G, copper(II), chromate and arsenate (CCA); H, iron(II) and CCA.

TABLE I

PERCENTAGE OF 1,5-ANHYDROCELLOBIITOL (15.4mM) REMAINING AFTER 2 WEEKS AT 80° IN THE PRESENCE OF IRON(II) IONS (mM), OXYGEN, AND ADDITIVES (8mM)

| *Inhibitor* | *Percentage remaining* | *Promoter* | *Percentage remaining* |
|---|---|---|---|
| None | 60 | None | 60 |
| Copper, chromate, arsenate (CCA) | >95 | *p*-Aminophenol | <35 |
| Cetyltrimethylammonium chloride | >95 | Hydroquinone | <35 |
| Sodium thiocyanate | 85–95 | Sodium bisulphite | <35 |
| Sodium nitrite | 85–95 | Sodium dithionite | 35–45 |
| Hexylamine | 85–95 | 2,4,6-Trimethylphenol | 35–45 |
| Potassium iodide | 75–85 | Ethylenediamine | 35–45 |
| Thiourea | 75–85 | 8-Hydroxyquinoline | 35–45 |
| Bis(tributyltin) oxide | 65–75 | Phenol | 45–55 |
| Benzyltriethylammonium chloride | 65–75 | Sodium borate | 45–55 |
| EDTA | 65–75 | Urea | 45–55 |
| Pentachlorophenol | 60–65 | Sodium fluoride | 45–55 |
| Diethylenetriamine | 60–65 | *o*-Phenylenediamine | 55–60 |
| Sodium thiosulphate | 60–65 | Diphenylamine | 55–60 |
| Sodium formate | 60–65 | Magnesium sulphate | 55–60 |

absence of either metal ions (Fig. 1A) or oxygen and therefore, as anticipated, iron ions [and iron(II) and iron(III) species had the same effect] were shown to promote the oxidation reaction. This observation indicated that the selected test system was appropriate for examination of phenomena associated with "nail sickness".

Copper(II) salts had little effect on promoting the oxygen-induced reaction of 1,5-anhydrocellobiitol (Fig. 1C), but they modified the influence of iron ions, initially inhibiting, but eventually accelerating, degradation (Fig. 1D). Chromate ions also had little effect by themselves (Fig. 1E) but, conversely, they showed a marked inhibitory influence on the action of iron ions (Fig. 1F); arsenate was inactive by itself and did not modify the action of iron, and zinc, aluminium, and chromium(III) ions were similarly inactive. Combined copper, chromate, and arsenate had no effect (Fig. 1G) but, in the presence of iron, the effect of chromate dominated and the action of iron in promoting oxidation was markedly impeded (Fig. 1H).

To test the effects of various compounds, especially antioxidants, on the iron-catalysed reaction of 1,5-anhydrocellobiitol in oxygen, reactions were run for two weeks in the presence of 0.5 molar equivalent of additives; the results are given in Table I. Most effective were CCA (by virtue of the influence of the chromate component, see above) and cetyltrimethylammonium chloride (tetra-alkylammonium chlorides are used as wood preservatives)[16], but other compounds, including some antioxidants, also had a marked effect. Several aromatic antioxidants, alternatively, which act by breaking radical chain-reactions[5,6], were not just non-inhibitors but strongly promoted the reaction.

In order to study comparable oxidations at room temperature, the above-

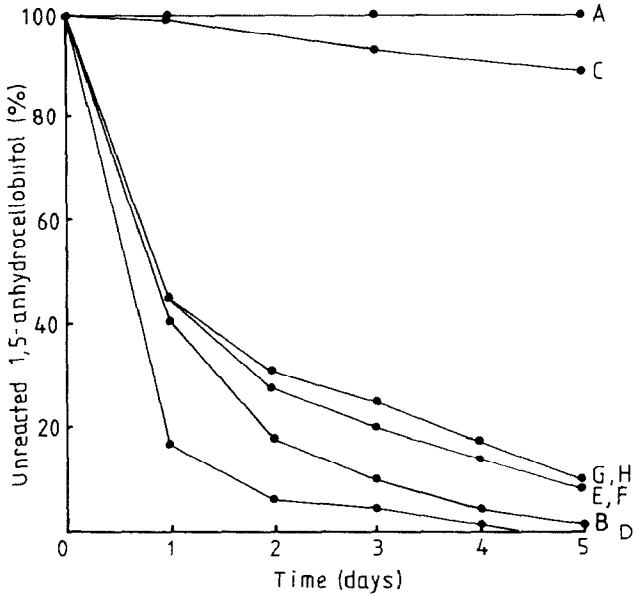



Fig. 2. Degradation of 1,5-anhydrocellobiitol by hydrogen peroxide in aqueous solution at pH 6.0 and 20° in the presence of metal ions. For coding, see caption to Fig. 1; for details, see Experimental.

mentioned reactions were carried out in the presence of added hydrogen peroxide, which is involved to some degree as an intermediate in the oxygen-dependent processes. Under the selected conditions, 1,5-anhydrocellobiitol reacted to completion with hydrogen peroxide in the presence of iron(II) or iron(III) salts at 20° in ~5 days (Fig. 2B); without metal ions, there was no detectable reaction (Fig. 2A). As in the case of the oxygen-induced reaction, copper ions enhanced the influence of iron although, in this case, no initial rate inhibition occurred (Fig. 2D); it is known that copper ions markedly accelerate the oxidation of organic compounds by Fenton's reagent[17]. A change occurred with chromate, however, which independently promoted the degradation efficiently (Fig. 2E), but with iron it again annulled the action of the latter (Fig. 2F). In the presence of copper and arsenate (Fig. 2G), and copper, arsenate, and iron (Fig. 2H), chromate again acted as the dominant ion. This influence, it is concluded, follows from the presence of some reactive species derived by the action of hydrogen peroxide with chromate (which is known to give unstable peroxy chromium complexes[18]) and which initiates oxidation of 1,5-anhydrocellobiitol.

As a second soluble test-system starch was used, and the assumption was made that viscosity changes reflected glycosidic bond cleavages at central parts of the polymer chains. Whereas the solutions were slightly unstable over three days at pH 6 and room temperature in the presence of hydrogen peroxide (Fig. 3A), the addition of iron(II) salts caused a marked enhancement of degradation rate (Fig. 3B). As with 1,5-anhydrocellobiitol and hydrogen peroxide, copper ions enhanced

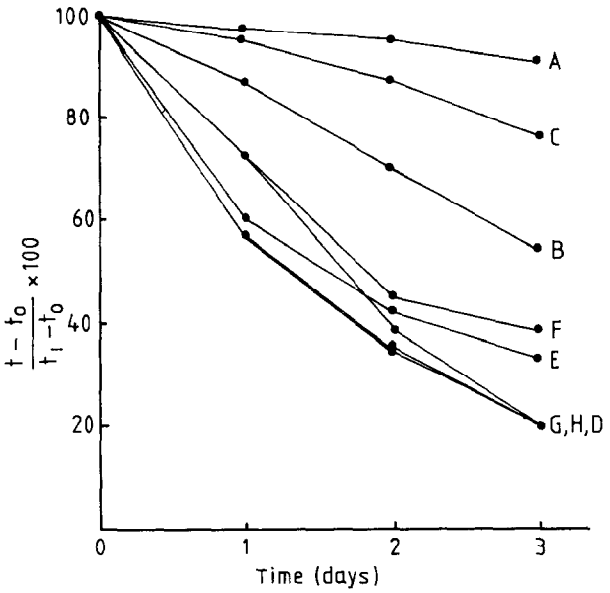



Fig. 3. Viscosity of starch solutions by hydrogen peroxide at pH 6.0 and 20° in the presence of metal ions. For coding, see caption to Fig. 1; for details, see Experimental; t = flow time of sample; $t_i$ = initial flow time of sample; $t_o$ = flowtime of solvent containing the appropriate metal salts.

TABLE II

TENSILE STRENGTHS OF PAPER BOARD AFTER TREATMENT AT pH 6.0 AND 20° WITH HYDROGEN PEROXIDE AND ADDED SALTS[a]

| *Reagents* | | | *Time (weeks)* | *Tensile strength[b] (Newtons)* | *Standard deviation* |
|---|---|---|---|---|---|
| $H_2O_2$ | $Fe^{2+}$ | *CCA* | | | |
| – | – | – | 2 | 281 | 14 |
| – | – | – | 5 | 276 | 21 |
| + | – | – | 2 | 282 | 19 |
| + | – | – | 5 | 294 | 24 |
| – | + | – | 2 | 248 | 20 |
| – | + | – | 5 | 261 | 16 |
| – | + | + | 2 | 265 | 10 |
| – | + | + | 5 | 271 | 22 |
| + | + | – | 2 | 173 | 11 |
| + | + | – | 5 | 119 | 17 |
| + | – | + | 2 | 145[c] | 26 |
| + | – | + | 5 | 76 | 22 |
| + | + | + | 2 | 137 | 20 |
| + | + | + | 5 | 58[d] | 26 |

[a]See Experimental for details. [b]Average values for 10 samples, except when otherwise stated. [c]Average for 9 samples. [d]Average for 3 samples.

the effect of iron(II) ions (Fig. 3D) without themselves causing a major effect (Fig. 3C), whereas chromate ions caused marked degradation (Fig. 3E). Again, the influences of mixtures of chromate with other salts (Figs. 3FGH) were similar to the effects of chromate alone (Fig. 3E), and copper enhanced rather than diminished its activity (Figs. 3GH).

In a brief extension of the work into a heterogeneous system, strips of bleached paper-board were soaked in buffer solution containing hydrogen peroxide and added salts for two or five weeks. They were then washed, dried at constant humidity, and tested for tensile strength. The results (Table II) are consistent with those obtained above for the hydrogen peroxide experiments; marked degradation occurred in the presence of iron ions, and CCA also had a strong degrading influence.

In summary, the results indicate that iron ions have a general accelerating effect on oxidations by either oxygen or hydrogen peroxide; while it is notable that chromate ions can diminish this effect, copper ions have an enhancing influence.

## EXPERIMENTAL

1,5-Anhydrocellobiitol hepta-acetate[19] was prepared from β-cellobiose octa-acetate[20] and hepta-*O*-acetyl-α-cellobiosyl bromide[21], the latter being dehalogenated by use of tributyltin hydride[22] in toluene at 80–90° under nitrogen. Deacetylation was effected with sodium methoxide in methanol and gave 1,5-anhydrocellobiitol, m.p. 174–175°, $[\alpha]_D$ +29° (water); lit.[19] m.p. 172°, $[\alpha]_D$ +29° (water).

*Oxidation of 1,5-anhydrocellobiitol in the presence of oxygen.* — Substrate solutions were 0.5% (15.4mM) in citric acid–phosphate buffer (pH 6.0) (prepared according to ref. 23 and diluted five-fold). All inorganic salts were used at mM. Experimental solutions (5 mL) were saturated with oxygen at 80 ±2°, sealed in tubes with rubber septa, and kept at this temperature in an oil bath. All solutions to be compared with each other were stored concurrently in the same bath. Samples (0.2 mL) were withdrawn at intervals by micropipette, *meso*-inositol (0.16 mg, in water) was added as internal standard, and the ions were removed by mixed cation–anion exchange resins. Water was removed at 50° under reduced pressure and the residues were trimethylsilylated using trimethylsilyl chloride–hexamethyldisilazane in pyridine[24]. G.l.c. was carried out on a Pye Unicam PU 4500 instrument, using a glass column packed with 3% of SE-52 on Chromosorb WAW DMCS 100/120 and temperature programming (injector temperature, 270°; detector temperature, 270°; initial column temperature, 200° for 6 min; final column temperature, 264°; heating rate, 16°/min). Under these conditions, the retention times of the trimethylsilyl ethers of 1,5-anhydrocellobiitol, *meso*-inositol, β- and α-D-glucopyranose, and 1,5-anhydro-D-glucitol were 13.0, 5.7, 3.9, 3.0, and 2.7 min, respectively.

For the isolation of reaction products, 1,5-anhydrocellobiitol (400 mg) was treated as described in the presence of iron(II) sulphate for four weeks. Water was removed under reduced pressure and the residue was treated in pyridine (100 mL)

with acetic anhydride (50 mL) for 48 h. The solution was poured into water, and the acetates were extracted into chloroform. Drying and removal of the chloroform left a dark syrup which was purified on a column of silica gel, to give a colourless oil (65 mg) which was shown by $^{1}H$- and, especially, $^{13}C$-n.m.r. spectroscopy to consist of the peracetates of $\alpha$- and $\beta$-D-glucopyranose and of 1,5-anhydroglucitol in the ratio ~1:1. In addition, 1,5-anhydrocellobiitol hepta-acetate was isolated (20%).

Tests of inhibitory powers (Table I) were carried out under normal conditions for 14 days in the presence of 0.5 molar equivalent of test substances.

*Oxidations of 1,5-anhydrocellobiitol in the presence of hydrogen peroxide.* — 1,5-Anhydrocellobiitol and salt solutions were used as described above and, at the beginning of the experiments, hydrogen peroxide was added to give an initial concentration of 25mM. Samples were kept at room temperature and the same amounts of additional hydrogen peroxide were added at 24-h intervals.

*Oxidation of starch.* — Viscosities were measured at 23 ±0.1° with a simple capillary viscometer[25], using 10-mL samples of 1% solutions of soluble starch in citrate–phosphate buffer of pH 6.0; a thin layer of toluene was added to prevent microbiological degradation. Iron(II) sulphate was used at 0.5mM and other salts at mM; hydrogen peroxide was added to 10mM, and the same amounts of the reagent were then added every 12 h. Corrections were made to flow times to account for the small dilution factor involved.

*Oxidation of paper board.* — Bleached paper-board supplied by the Forestry Research Institute of New Zealand (Rotorua) was cut into strips (300 × 30 mm) and immersed in the citrate–phosphate buffer containing added salts at mM for two or five weeks during which hydrogen peroxide was added daily to give a concentration of 4mM. Samples were withdrawn, rinsed with water, air-dried, and conditioned at 20 ±2° and 65 ±5% relative humidity for two weeks. Their tensile breaking strengths were then tested as specified for the standard test method ASTM D 828-60 at the Building Research Association of New Zealand.

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