

Free Radical Formation in the Neutral Sulphitation of Wood at High Temperature

In a previous report¹, it was shown that, when wood and cellulose, pretreated with sodium hydroxide and afterwards freeze-dried, were rapidly heated in the cavity of an electron spin resonance (ESR) spectrometer to a temperature between 180° and 190° C, rapid formation of free radicals (radical centres) was recorded, and it was found that within a relatively short time free-radical decay took place, following approximately an exponential function. After cooling, a limited number of free radicals remained in the specimens; these free radicals were quite stable over a considerable period of time and were considered to be trapped by a 'cage effect' of the polymers.

A question of interest was whether similar phenomena take place when wood, holocellulose and cellulose are treated in the same way but impregnated with water-free Na₂SO₃ instead of NaOH. Such knowledge might contribute towards a better understanding of high-temperature neutral-sulphite pulping of wood.

The following materials were used: (a) black spruce sawdust (the fraction which passed the 40-mesh sieve but was retained by the 60-mesh sieve); (b) chlorite holocellulose prepared from the same black spruce sawdust by a series of mild chloriting stages similar to the procedure of Wise *et al.*²; (c) commercial, acetate grade, high alpha-cellulose (96 per cent) pulp.

These materials were subjected to 30 min impregnation at 83° C in a 10 per cent Na₂SO₃ solution (pH about 8.6) in a ratio of 1 : 20. At the end of the impregnation period, the materials were separated from the liquor on a sintered glass crucible and then pressed to remove the remaining liquor excess. Later, they were freeze-dried to remove water; finally, they contained about 25 per cent Na₂SO₃. Weighed specimens were introduced into quartz capillaries; after evacuation and filling the capillaries with nitrogen at atmospheric pressure, the capillaries were sealed.

The filled capillaries were rapidly heated to 190° C in the cavity of a Varian Associates model 'V-4500' electron spin resonance spectrometer by a stream of hot nitrogen. Single line signals (first derivatives) were found and recorded (modulation 630, gain 630, range 16) with increasing time of heating. For comparison, the changes of the signal area (sq. cm) of the three specimens, calculated free of inorganics, and based on the same initial wood weight are presented in Fig. 1. The holocellulose yield

was about 71 per cent and that of the high-alpha-cellulose pulp about 40 per cent. Thus, the curves show how holocellulose and the high alpha-cellulose pulp obtained in these ratios from the same wood weight compare with the initial wood.

It can be seen that free radicals were formed with each material investigated, and that the concentration of the radicals trapped in the polymeric substances increased with increase of the heating time. However, after a definite reaction time (wood, about 25 min; holocellulose, about 20 min; high alpha-cellulose pulp, about 15 min) a levelling-off was observed. Probably, as polymer degradation progressed, the 'cage effect' of the degraded material approached a distinct limit value. In contrast to the alkaline pulping experiments¹, no immediate formation of free radicals in very high concentrations at the very start of reaction, followed by free-radical decay according to an approximate first-order pattern, was observed. This seems to indicate that the mechanisms of alkaline delignification and high-temperature sulphitation of the wood are distinct phenomena.

As shown in Fig. 1, for equal reaction times, the ESR signal area as a measure of the free radical concentration decreased in the order: wood, holocellulose, high alpha-cellulose pulp. Remarkably, the holocellulose values were relatively high when compared with those of the wood; even if correction was made for the alpha-cellulose portions of the holocellulose, these values still accounted for about half those of the wood. This appears to constitute evidence that during reaction, besides thermal degradation and sulphonation of the lignin, considerable changes of the hemicellulose portions also took place, both resulting in free radical formation.

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² Wise, L. E., Murphy, N., and D'Addieco, A. A., *Tappi*, **29**, 210 (1946).

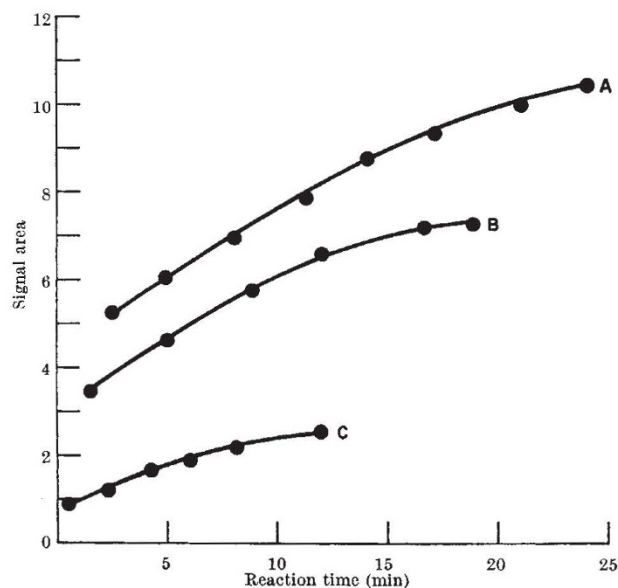


Fig. 1. Signal areas in relation to reaction time. A, Wood (0.015 g); B, holocellulose (0.01065 g); C, high-alpha-cellulose pulp (0.006 g)

Synthesis of Tris-(hexafluoroacetylacetonato)-Chromium (III)

REDUCTION of Cr(VI) in the presence of chelating ligands offers a promising approach to synthesis of Cr(III) chelates in high yield. This principle was used by Aikens and Reilly¹ to devise a rapid chelometric method for determination of chromate. Reduction of chromate with bisulphite in a buffered solution of ethylenediaminetetraacetic acid (EDTA) gave quantitative formation of Cr(III)-EDTA. The quantitative yield of Cr(III) EDTA suggested that this might be the basis of a general method for synthesis of Cr(III) complexes. We have now applied this principle to synthesis of Cr(III) chelates of much lower stability as exemplified by *tris*-(hexafluoroacetylacetonato)-Cr(III).

Efforts to synthesize *tris*-(hexafluoroacetylacetonato)-Cr(III) in aqueous solution in a manner similar to the synthesis of Cr(III) EDTA were unsuccessful. Attempted synthesis in hydroxylic non-aqueous solvents, such as methanol with paraldehyde as the reductant, also failed. A successful synthesis was based on the heterogeneous reaction of hexafluoroacetylacetonone with potassium dichromate. This reaction is interesting because evidently the ligand acts as the reductant.

0.5 g (0.0017 mole) of finely powdered potassium dichromate was placed in a 100-ml. round-bottom flask and covered with 4.16 g (0.020 mole) of the ligand. The flask was fitted with a water-cooled condenser and the