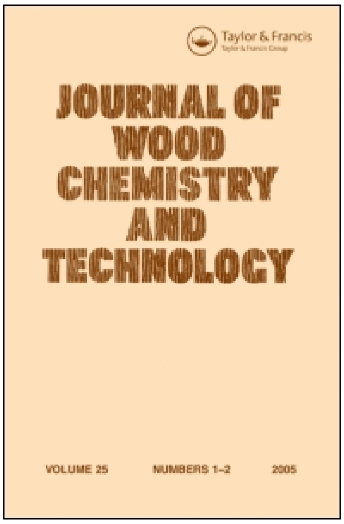

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Joncourt, M. J. , Froment, P. and Lachenal, D.(1998) 'Formation of Radical Species During ClO_2 Delignmcation', Journal of Wood Chemistry and Technology, 18: 2, 159 — 170
To link to this Article: DOI: 10.1080/02773819809349574
URL: http://dx.doi.org/10.1080/02773819809349574

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 18(2), 159-170 (1998)

FORMATION OF RADICAL SPECIES DURING ClO_2 DELIGNIFICATION

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ABSTRACT

Spin-trapping E.S.R. spectroscopy has been used to demonstrate that chlorine radicals (Cl°) were formed in conditions simulating chlorine dioxide (ClO_2) bleaching, in presence of iron cations. Chlorine radicals (Cl°) most probably originate from reaction of Fe^{2+}/Fe^{3+} with $HClO_2$ and with $Cl_2/ClOH$, equally produced when ClO_2 reacted with a phenolic unit. Adding Fe^{2+}/Fe^{3+} in a D bleaching stage of a softwood kraft pulp had a detrimental effect on both pulp viscosity and delignification. At the same time AOX and chlorate formation were increased. These effects were in accordance with the proposed mechanism for the formation of Cl° and showed that iron might be potentially harmful, if in a sufficient quantity in pulp or process water.

INTRODUCTION

The reaction of chlorine dioxide with lignin produces chlorite and hypochlorous acid.[1-5] The latter, which is in equilibrium with chlorine, is responsible for the formation of chlorinated organic compounds (AOX). It reacts also with chlorous acid with formation of chlorate and regeneration of chlorine dioxide. The mechanism and the kinetic of this reaction have been described in several papers.[6-9]

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It has been shown that iron could interfer with the mechanism in a way which has been studied by Schmitz and Rooze.[10-12] Their results can be summarized by the following set of reactions:

Initiation

$$ClO_2^- + Fe^{3+} \rightarrow ClO_2 + Fe^{2+} \tag{1}$$

$$HClO_2 + Fe^{2+} \rightarrow ClO^\circ + Fe^{3+} + OH^- \tag{2}$$

$$ClO_2^- + HClO_2 \rightarrow ClO_2 + ClO^\circ + OH^- \tag{3}$$

Propagation

$$HClO_2 + ClO^\circ \rightarrow ClO_3^- + Cl^\circ + H^+ \tag{4}$$

$$HClO_2 + Cl^\circ \rightarrow HClO + ClO^\circ \tag{5}$$

Termination

$$Cl^\circ + Fe^{2+} \rightarrow Cl^- + Fe^{3+} \tag{6}$$

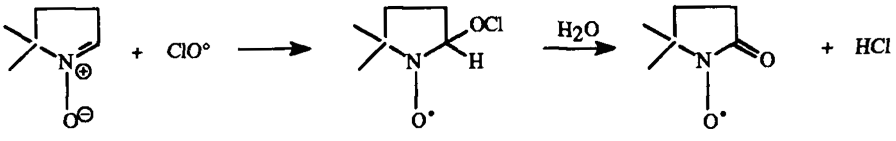
$$ClO^\circ + Fe^{2+} \rightarrow ClO^- + Fe^{3+} \tag{7}$$

According to the above scheme, iron can promote the regeneration of chlorine dioxide and favor the formation of radicals. However, it is not know if iron has any influence during the chlorine dioxide treatment. Thus, in the course of a study on the reduction of AOX during ClO_2 delignification[13], we investigated the effect of iron on delignification, viscosity of pulp and AOX formation.

RESULTS AND DISCUSSION

Preliminary experiments were carried out to observe the influence of iron on chlorite disproportionation. In acidic medium (pH 1.5) chlorine dioxide is readily formed when Fe^{2+} or Fe^{3+} is added to a chlorite solution. Actually, Fe^{3+} concentration is always above Fe^{2+} concentration since it is determined by the redox potential of the medium. At a pH higher than 4 iron forms hydroxide and no chlorine dioxide formation was observed.

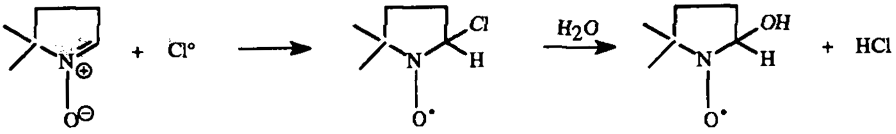
ESR spectroscopy was used to ascertain the formation of radicals. Chlorine dioxide has its own spectrum consisting of four lines with equal intensity and a hyperfine splitting of 18.5 G.[14] For the others radicals we carried out spin trapping experiments with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as spin trap. The reaction of ClO° with DMPO forms an adduct which gives 5,5 dimethyl-2-pyrrolidone-n-oxyl (DMPO.Ox) by hydrolysis according to the reaction:[15]



DMPO DMPO-Ox

The spectrum of DMPO-Ox ($a_N = 7.2$ G, $a_{H\gamma} = 4.1$ G) shown on Figure 1 was obtained by mixing $NaClO_2$ and DMPO at pH 1.5. The same spectrum is obtained by oxidation of DMPO with a variety of agents including chlorine dioxide and hypochlorous acid. Thus the observation of this spectrum was not a proof of the presence of ClO°.

The reaction of Cl° with DMPO[16] gives the same adduct as the reaction of the hydroxyl radical (HO°) with DMPO: the 5,5-dimethyl-2-hydroxypyrrolidine-N-oxyl (DMPO-OH)



DMPO DMPO-OH

ESR spectrum of DMPO-OH with its charateristic four lines ($a_N = a_H = 14.9$ G) is shown on Figure 2. The ambiguity between Cl° and HO° is easy to rule out. One only has to add ethanol or dimethylsulfoxide to the mixture. If HO° is present it reacts with these compounds to give carbon centered radicals and the corresponding spectrum would contain 6 more lines.[17]

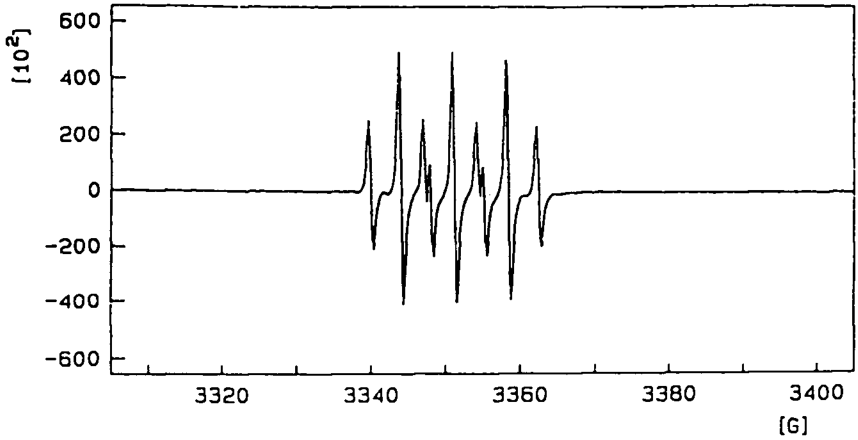


FIGURE 1: ESR spectrum of DMPO-Ox.

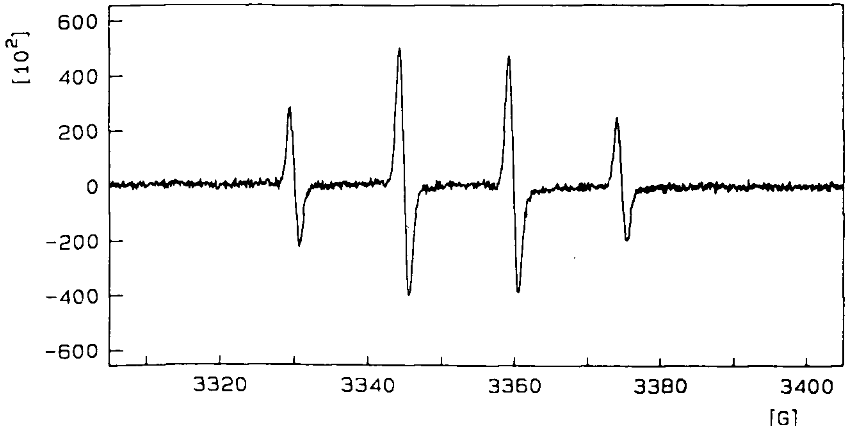


FIGURE 2: ESR spectrum of DMPO-OH.

Then a mixture of $HClO_2$ and iron, in presence of DMPO, should give a complicated spectrum, which would be a superimposition of ClO_2 (which results from the chlorite disproportionation), DMPO-Ox and DMPO-OH spectra. Therefore it is necessary to limit the number of constituents in the mixture. ClO_2 can be captured by adding vanillin, which reacts rapidly with ClO_2 even in acidic medium. This method has the advantage to produce in situ $HClO_2$ and HClO which are the precursors of the radicals to be trapped.

Several experiments were performed. In the first experiment a solution was prepared by mixing DMPO , $HClO_2$, and vanillin at pH 1.5. The characteristic spectrum of DMPO-Ox was obtained. Therefore, DMPO has been oxidized by chlorous acid.

The same experiment was carried out with chlorine dioxide instead of chlorous acid. A low resolution, low intensity spectrum indicated that small quantities of radicals were formed. Adding iron cations to the constituents of this mixture gave a well resolved DMPO-OH spectrum. Fe^{2+} and Fe^{3+} had the same effect.

In the next experiment DMSO was added as a further constituent. A pure DMPO-OH spectrum was observed but its intensity was lower and decreasing with time (FIGURE 3). No interference from any $CH_3°$-based radical was seen which would indicate that Cl° and not HO° was at the origine of the DMPO-OH product. Moreover DMSO is known to capture hypochlorous acid or chlorine as soon as they are generated.[18] Such generation occured here by reaction of ClO_2 with vanillin. The fact that the intensity of the spectrum decreased with time would be consistent with the formation of at least some Cl° from Cl_2 or ClOH according to reactions (8):[19]

$$Cl_2 + Fe^{2+} \rightarrow Cl° + Cl^- + Fe^{3+} \quad (8)$$

$$HClO + Fe^{2+} \rightarrow Cl° + OH^- + Fe^{3+} \quad (8')$$

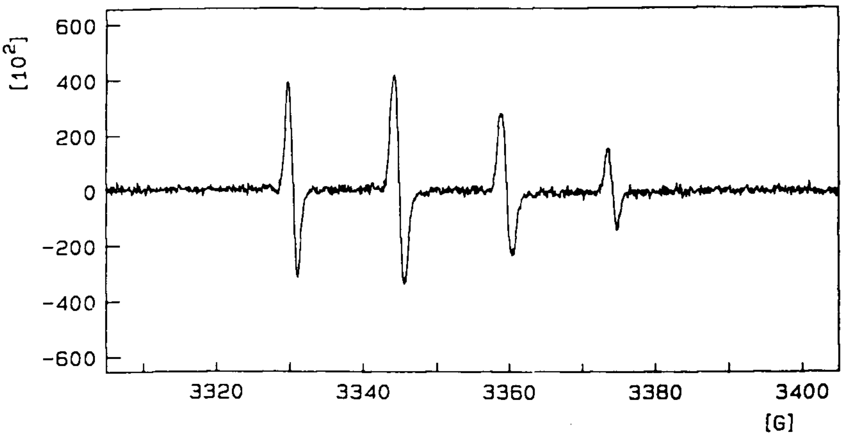


FIGURE 3: ESR spectrum of DMPO-OH featuring a decreasing intensity with time (case of DMSO addition).

A last experiment was performed to confirm that Cl° could indeed originate from reactions (8) under the conditions used during D bleaching. Cl_2 was prepared as described by Cady[20] and mixed with DMPO at pH 1.5 in presence of Fe^{2+}. The DMPO-OH spectrum was obtained. Nothing was changed when Fe^{3+} was put in place of Fe^{2+}. The same experiment was carried out at pH 4.5. At this pH Fe^{3+} concentration was limited by the $Fe(OH)_3$ solubility product and Fe^{2+} concentration was very low. A much lower intensity spectrum was observed.

These experiments clearly showed that Cl° was formed when ClO_2 reacted with a lignin model compound (vanillin) in the presence of iron. However since both Cl_2 and $HClO_2$ were present in the reaction mixture it is not possible to conclude whether Cl° was only formed from Cl_2 or also from $HClO_2$ via the ClO° intermediate, as shown by the chlorite decomposition mechanism.

TABLE 1

ClO_2 Bleaching of a Softwood Kraft Pulp in Presence of Fe^{2+}

Fe^{2+} % on pulp	Kappa D	Viscosity D mPas	Chlorate % Cl	Kappa E	Viscosity E mPas	AOX DE kg/t
0	12.7	26.2	4.5	6.2	25.1	1.40
0	*12.9*	*27,8*	*4.5*	*7.5*	*27,0*	*1.30*
0.14	17.1	21.4	7.9	11.2	20.8	1.55
0.28	19.1	21.7	7.9	11.2	20.5	1.75

D chlorine dioxide bleaching stage, E alkaline extraction stage
AOX chlorinated organic compounds
Italic numbers refer to the pulp pretreated by EDTA (see experimental).

The effect of adding Fe^{2+} in ClO_2 bleaching of a softwood kraft pulp was investigated (TABLE 1).

The results showed that delignification was less when Fe^{2+} was added in the D stage. Ferrous ions (Fe^{2+}) consume chlorine dioxide and Fe^{3+} formed should react with chlorous acid to produce chlorine dioxide. It is difficult to ascertain if the two effects would compensate. At the same time cellulose degradation was substantially increased and more AOX and chlorate were formed. Cellulose depolymerization was consistent with the formation of Cl°. Degradation of cellulose by Cl° was put forward to explain pulp degradation during drastic chlorination stages.[21] The increase in AOX formation may be due to the catalytic effect of iron on chlorination reactions described by Fredricks *et al.*[22] Another explanation would be that in the absence of iron half the HClO produced by reaction between ClO_2 and lignin reacts with all the $HClO_2$ according to (9):

$$ClO_2H + 1/2\,HClO \rightarrow ClO_2 + 1/2\,HCl + 1/2\,H_2O \qquad (9)$$

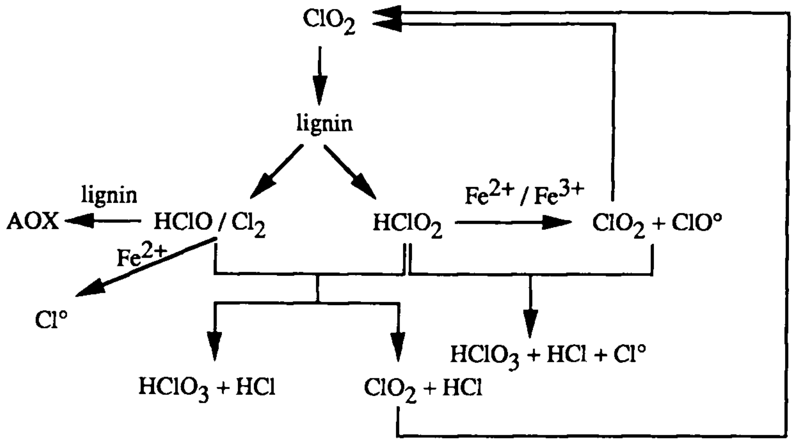


FIGURE 4: ClO_2 reaction scheme during delignification in presence of iron.

the other half reacting with lignin. When iron is added part of the ClO_2H disappears by reaction (3) and more HClO is left to react with lignin. The presence of a higher quantity of chlorate would agree with the formation of ClO° (see reactions 3 and 4). Consequently one can conclude that at least part of the Cl° detected by ESR spectroscopy came from ClO° (reaction 4) and not only from reaction (8) (or 8'). The weaker delignification indicated that less ClO_2 had actually reacted with the pulp. One likely explanation is that the disproportionation of $HClO_2$ according to reaction (3) leads to one mole of ClO_2 from two moles of $HClO_2$ whereas all the $HClO_2$ is converted into ClO_2 by reaction (9), in the absence of iron.

An EDTA pretreatment was performed on the unbleached pulp containing 30 ppm Fe (TABLE 1). No substantial effect on D was observed, which indicated that the minimum level of iron needed to affect ClO_2 bleaching significantly was higher than that usually present in unbleached pulps. However the efforts made to reduce the volume of water and to burn some of the bleaching effluent may modify the average amount of metal ions on or around the fibers.

According to what was found out in the present study a new reaction scheme for bleaching was proposed (FIGURE 4).

CONCLUSION

Spin-trapping E.S.R. studies have demonstrated the presence of Cl° under the conditions simulating chlorine dioxide bleaching when iron cations were present. The source of these radicals may be either $HClO_2$ or Cl_2 (HClO) or most probably both. Reactions taking place during chlorine dioxide bleaching have been revisited accordingly.

Addition of iron in chlorine dioxide bleaching of a softwood kraft pulp had a negative effect on delignification and caused a viscosity loss. These effects could be explained by the previous reactions and indicated that iron might be potentially harmful when present in sufficient quantity in pulp or process water.

EXPERIMENTAL

DMPO was obtained from Aldrich. Other chemicals were the best commercial grade available. Solutions were prepared with deionized water. Electron spin resonance (ESR) spectra were obtained at ambient temperature on a Bruker instrument (center field 3355 G, sweep width 100 G, microwave frequency 9.4 G)

ESR spectrum were obtained at pH 1.5 with following concentrations:

- DMPO ($2{,}5.10^{-4}$ M), $HClO_2$ ($5{,}5.10^{-3}$ M), vanillin (3.10^{-2} M)
- DMPO (0,26 M), ClO_2 (0,011 M), vanillin (0,028 M)
- DMPO (2.10^{-4} M), ClO_2 (9.10^{-3} M), vanillin (2.10^{-2} M), Fe^{2+} (2.10^{-4} M)
- DMPO (2.10^{-4} M), ClO_2 (0,02 M), vanillin (0,012 M), Fe^{2+} (5.10^{-4} M), DMSO ($3{,}5.10^{-3}$ M)
- DMPO (4.10^{-4} M), Cl_2 (9.10^{-3} M), Fe^{2+} ($9{,}5.10^{-4}$ M)

A softwood kraft pulp of initial kappa 39.5 - viscosity 28.2 mPas was bleached under the following conditions:

ClO_2 stage: 5% consistency - 70 °C - 60 min. - pH 1.5

chlorine multiple 0.2 for the D stage if not specified
E stage: 3.95% NaOH - 5% consistency - 70 °C - 60 min.
EDTA stage: 1% EDTA - 10% consistency - 90 °C - 60 min.
Chlorate concentration was determined by capillary electrophoresis. AOX DE was the sum of AOX in D and AOX in E measured separately with a Dohrmann analyzer.

Preparation of HClO: Chlorine monoxide Cl_2O was prepared by reaction of Cl_2 in CCl_4 with mercuric oxide under anhydrous conditions as described by Cady.[20] The preparation of Cl_2O in CCl_4 was stored at - 6 °C and kept protected from light. Pure HOCl was obtained by extracting Cl_2O with water. The concentration of HOCl in the aqueous layer was determined iodometrically.

The content in transition metals ions was determined at the Service Central d'Analyse du CNRS - Vernaison (France) (TABLE 2):

TABLE 2

Cationic Metals Ions in the Pulp

	Fe (ppm)	Cu (ppm)	Mn (ppm)
initial pulp	30	< 1	30
EDTA pretreated pulp	10	< 1	< 1
water washed pulp	24	< 1	23

When no EDTA pretrearment was performed the pulp was previously washed with distilled water applying the same conditions as the EDTA pretreatment (10% consistency - 90 °C - 60 min.).

ACKNOWLEDGEMENTS

The authors gratefully acknowledge A. JEUNET (Joseph Fourier University - Grenoble) for his assistance in ESR spectroscopy.

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