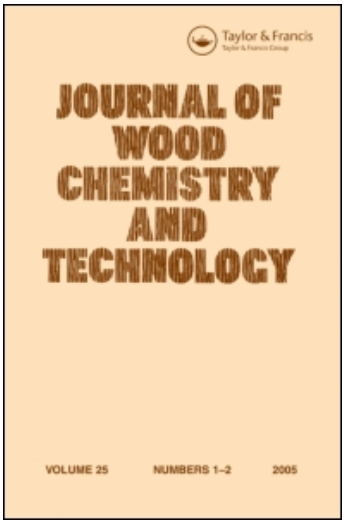

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Wallis, Adrian F. A. and Wearne, Ross H.(1987) 'Oxidation of Monohydric Alcohols with Anthraquinone and its Derivatives Under Soda Pulping Conditions', Journal of Wood Chemistry and Technology, 7: 4, 513 — 525
To link to this Article: DOI: 10.1080/02773818708085283
URL: http://dx.doi.org/10.1080/02773818708085283

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(4), 513-526 (1987)

OXIDATION OF MONOHYDRIC ALCOHOLS WITH ANTHRAQUINONE AND ITS DERIVATIVES UNDER SODA PULPING CONDITIONS

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ABSTRACT

Monohydric alcohols as models for cellulose were reacted with anthraquinone (AQ) and three of its alkali-soluble derivatives in 1M sodium hydroxide at 170°C. Cyclohexanol and cyclohexanemethanol were selected as soluble secondary and primary alcohols, respectively, and the steroidal alcohols, lithocholic acid and cholestan-3β-ol, as less soluble models. In every case the AQs oxidised the alcohols, although cyclohexanemethanol and the insoluble cholestanol were oxidised only to a minor extent with AQ after 6 h. The efficacy of oxidation by the quinones was in the order sodium AQ-2-sulfonate (AMS) > AQ-2-carboxylic acid > 2-hydroxy-AQ > AQ.

INTRODUCTION

The strengths of soda-anthraquinone (AQ) pulps are usually lower than those of kraft pulps, especially those from softwood samples (1). Recent studies have shown that the strength deficit of soda-AQ pulps, when compared to kraft pulps from *P. radiata*, is due to fibre damage (2) and may be caused by oxidative degradation of the cellulose by AQ (3), rather than to differences in bonding strength. In support of these findings, adding AQ to soda cooks of cotton cellulose has been found to reduce the viscosity of the residual cellulose (4). This viscosity reduction was considered to be due to random oxidation of some hydroxyl groups at C-2, C-3 or C-6 along the cellulose chain by AQ to carbonyl functions, rendering the glucosidic bonds more labile towards scission through a

β-elimination mechanism (4). To test the ease of such oxidations, studies on model compounds were carried out. Monohydric alcohols were chosen as cellulose models because their reaction product mixtures would be considerably simpler than those from carbohydrates.

The main reaction of AQ with polysaccharides under soda pulping conditions is oxidation of aldehyde end groups to aldonic acid groups (5), through an aldosulose intermediate (6). Sodium AQ-2-sulfonate (AMS) and AQ have also been found to oxidise lignin model benzyl and cinnamyl alcohols to carbonyl functions under alkaline conditions (7,8). However, no evidence for the reduction of AQ was noted after treating selected lignin and carbohydrate models in 1M sodium hydroxide with AQ in a flow-through reactor at 160°C for 45 min (9).

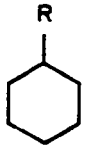
In the present work, cyclohexanol (Ia) and cyclohexanemethanol (Ib) were selected as models of soluble secondary and primary alcohols, respectively, and the steroidal alcohols, lithocholic acid (IIIa) and cholestan-3β-ol (IVa) as models of less-soluble alcohols. They were reacted under soda pulping conditions (1M sodium hydroxide at 170°C) with AQ and three of its alkali-soluble derivatives, AMS, 2-hydroxy-AQ and AQ-2-carboxylic acid.

RESULTS AND DISCUSSION

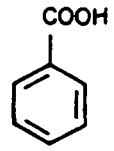
Treatment of AQ derivatives with alkali

The alkali-soluble AQ derivatives used in this study were tested for their stabilities in 1M sodium hydroxide at 170°C, and while AQ is stable under these conditions, AMS is known to hydrolyse to give the hydroxy derivative (10).

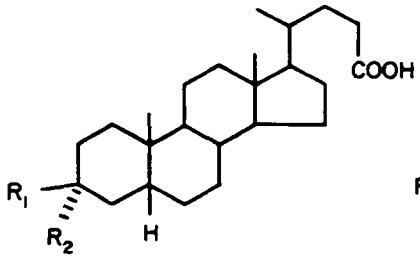
Reaction of AMS with alkali at 170°C gave 2-hydroxy-AQ as the sole product (gas chromatography (GC) analysis), and after 1 h the yield was 90% (Figure 1). The product had a deep red colour in alkaline solution, which is characteristic of hydroxy-AQ derivatives



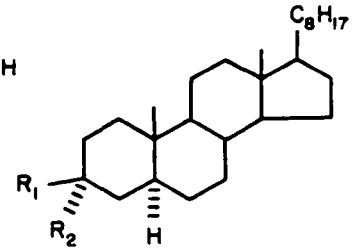
I a R = OH
b R = CH_2OH
c R = CHO
d R = CH (OH) OCH_3
e R = COOH



II



III a R_1 = H R_2 = OH
b R_1 = R_2 = O



IV a R_1 = OH R_2 = H
b R_1 = R_2 = O
c R_1 = OCH_3 R_2 = H

(11). AMS has often been used as a soluble AQ derivative in lignin and cellulose model compound studies at lower temperatures (6-8), conditions under which hydrolysis to 2-hydroxy-AQ presumably does not occur. However, numerous studies have been made on the effect of AMS as an additive in alkaline pulping, and during these experiments AMS would hydrolyse to 2-hydroxy-AQ. The formation of a red colour in alkaline solution of reduced species of AQ and its derivatives is often used as an indication that oxidation has taken place. This is clearly not valid for 2-hydroxy-AQ, nor for reactions of AMS in alkali at 170°C.

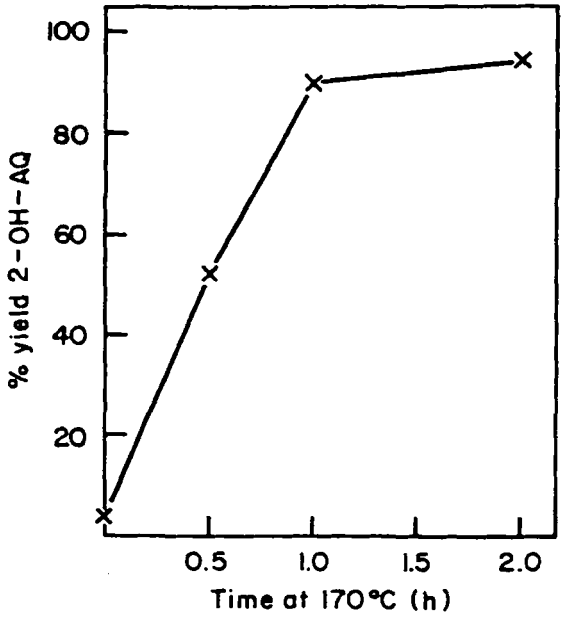


FIGURE 1. Formation of 2-hydroxy-AQ by reaction of AMS with 1M sodium hydroxide at 170°C.

Both 2-hydroxy-AQ and AQ-2-carboxylic acid were recovered unchanged after treatment with 1M sodium hydroxide at 170°C for 4 h.

Oxidation of cyclohexanol

The soluble secondary alcohol cyclohexanol (Ia) was stable under soda pulping conditions, and it was recovered quantitatively after 6 h at 170°C (Figure 2). In the presence of equivalent amounts of AQ and some of its alkali-soluble derivatives, cyclohexanol was oxidised to cyclohexanone. The combined yield of Ia and cyclohexanone in every case was > 75%.

The efficacy of oxidation by the quinones was in the order AMS > AQ-2-carboxylic acid > 2-hydroxy-AQ > AQ (Figure 2). The slower oxidising action of AQ could be due to its insolubility in the

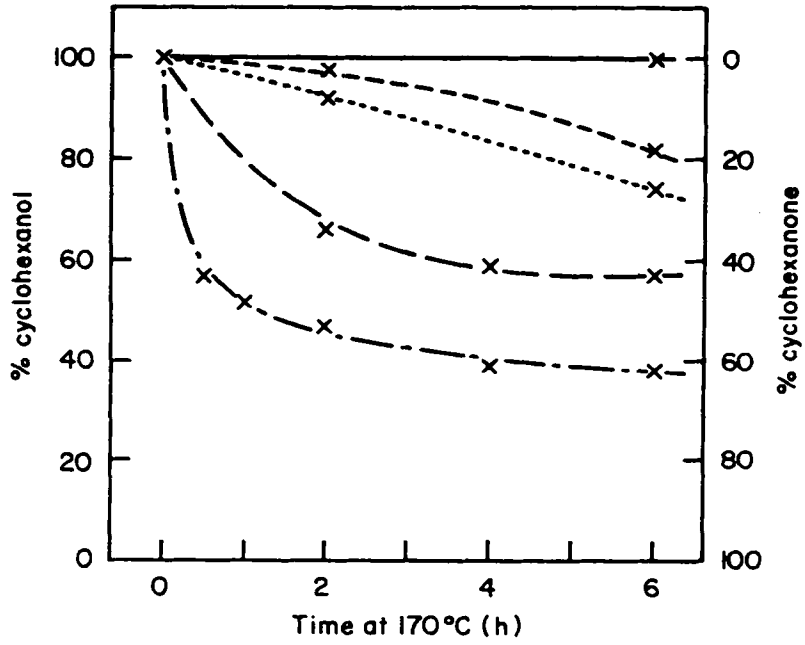


FIGURE 2. Oxidation of cyclohexanol at 170°C with quinones in soda liquors; no quinone ——, AQ – – – –, 2-OH-AQ ·····, AQ-2-COOH — —, AMS —·—.

aqueous medium. The observation that the apparent oxidation rate of Ia with AMS fell rapidly after 1 h was probably because of its conversion to 2-hydroxy-AQ, which is a weaker oxidant than AMS. In spite of the competing hydrolysis reaction, AMS was still the most effective oxidant of the three derivatives, and was thus used as the soluble AQ derivative in subsequent experiments.

Oxidation of cyclohexanemethanol

Cyclohexanemethanol (Ib) was used as a water-soluble model for the primary alcohol group at C-6 in cellulose. It was stable under soda pulping conditions and was recovered unchanged after 4 h at 170°C.

TABLE 1

Reactions of Cyclohexane Derivatives Ib, Ic and Ie

Cook	Time at 170°C (h)	% Yield			
		Ib	Ic	Ie	II
Ib/soda	4.0	100.4	0.6	-	-
Ib/soda-AQ	2.0	100.0	0.9	-	-
	4.0	100.8	0.9	-	-
	6.0	99.3	1.7	tr.	-
Ib/soda-AMS	0.5	95.5	1.7	4.5	3.2
	1.0	93.0	2.6	4.6	3.2
	2.0	62.1	0.9	7.7	6.4
	4.0	54.1	0.9	10.6	11.1
Ic/soda	2.0	19.2	13.0	27.7	-
Ic/soda-AMS	0.5	0.9	0.9	35.2	4.3
	1.0	0.9	0.5	38.3	7.0
	2.0	3.9	1.6	33.1	3.6
Ie/soda-AQ	6.0	-	-	84.4	-
Ie/soda-AMS	4.0	-	-	99.0	-

When the alcohol Ib was oxidised with 2.4 equivalents of AQ under soda pulping conditions for 2–6 h, the reaction solutions became light red in colour, and after 6 h, only small amounts of the aldehyde Ic and trace amounts of the acid Ie were formed (Table 1). Thus AQ oxidises the primary alcohol Ib slower than the secondary alcohol Ia.

Oxidation of Ib with 2.4 equivalents AMS under soda conditions gave, besides the expected aldehyde and acid products Ic and Ie, benzoic acid (II) as an additional oxidation product. After 4 h, 46% of the starting material had reacted and acids Ie and II were each obtained in 11% yield (Table 1).

A check on the stability of the aldehyde Ic under soda conditions revealed that Ic underwent the Cannizarro reaction to give the alcohol Ib and acid Ie. The aldehyde Ic on treatment with soda-AMS yielded the cyclohexane acid Ie as the major product with smaller amounts of the alcohol Ib (from the Cannizarro reaction) and benzoic acid. Because of the approximately equal amounts of Ie and II produced by oxidation of Ib with AMS, it is probable that the aldehyde Ic is not an intermediate in the formation of both acids. Because the material balances for reactions of the aldehyde Ic with soda and soda-AMS liquors were poor (Table 1), it is probable that a competing reaction would be aldol condensation of Ic, and the product would not be expected to appear on the GC trace.

Soda-AQ and soda-AMS cooks of the cyclohexane acid (Ie) gave no products and Ie was recovered in 84 and 99% yield respectively. Thus Ie is not a precursor of benzoic acid, and the acid probably arises by direct oxidation of cyclohexanemethanol. There appears to be no precedence for the direct oxidation of cyclohexanemethanol to benzoic acid. The possible involvement of dissolved glass in the reaction was ruled out, as identical products and yields were obtained from reactions of Ib with AMS in teflon-lined vessels.

Oxidation of sterols IIIa and IVa

The above results show that AQ and its alkali-soluble derivatives oxidise soluble alcohols under soda pulping conditions. The sterols lithocholic acid (IIIa) and cholestan-3β-ol (IVa) were selected as cellulose models due to their low solubilities in aqueous media. Lithocholic acid would be expected to be partially soluble in alkali because of its carboxyl group, although the cholestanol IVa would be very insoluble.

The acid IIIa followed a similar pattern to that of cyclohexanol - it was stable in soda liquor at 170°C and was recovered unchanged after 6 h. The acid was oxidised to the ketone IIIb by AQ and AMS, more so by the latter (Figure 3).

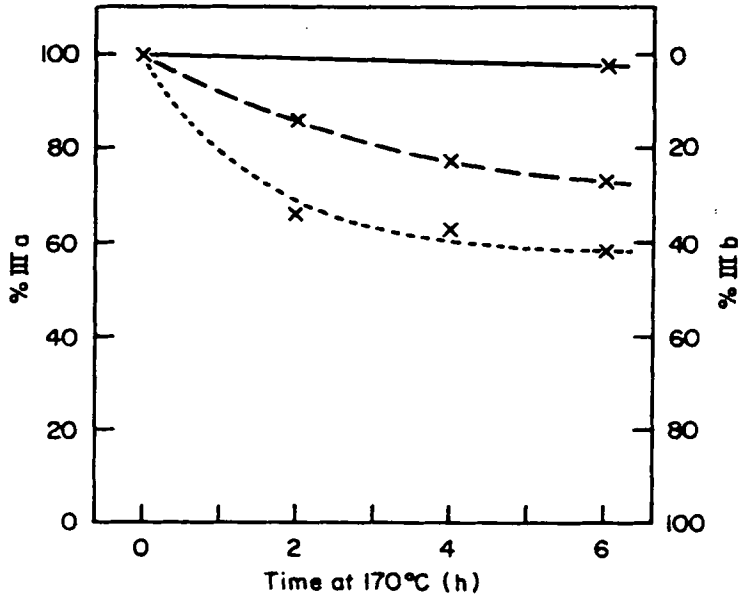


FIGURE 3. Oxidation of lithocholic acid (IIIa) at 170°C with quinones in soda liquors; no quinone ——, AQ ----, AMS ------ .

TABLE 2

Reactions of Cholestan-3β-ol (IVa)

Cook	Time at 170°C (h)	% Yield	
		IVa	IVb
Soda	4.0	98.0	2.0
Soda-AQ	4.0	96.0	4.0
	6.0	94.7	5.3
Soda-AMS	4.0	97.9	2.1
	6.0	98.4	1.6

The insoluble alcohol, cholestanol (IVa), was stable in soda liquor at 170°C, and the ketone IVb shown in 2% yield after 4 h (Table 2) was present at a similar level in the starting material. The reaction mixtures obtained on treating IVa with AQ under soda pulping conditions for 4 or 6 h were light red in colour, which was indicative of oxidation by AQ. The ketone was formed in 4-5% yield. Surprisingly, oxidation of IVa with AMS for 4 and 6 h did not give a greater amount of ketone IVb than the soda control (Table 2). Thus the insoluble alcohol IVa was slowly oxidised by the insoluble AQ, and not by the soluble AMS.

Concluding remarks

The results show that monohydric alcohols which are either soluble or insoluble in water are oxidised by AQ under soda pulping conditions, and contrast the results of a recent study of similar reactions at 160°C, in which no evidence for AQ reduction was obtained (9). Although the reactions are very slow compared to oxidation of reducing end groups of sugars, they do indicate that oxidation of hydroxyl groups along the cellulose chains is possible. The model reactions are probably only an indication of the AQ reactions which occur in the wood cell wall during soda-AQ pulping, and factors such as proximity of the AQ to the cellulose after penetration into the cell wall could aid the reactions on cellulose hydroxyls. Oxidation of only a few cellulose hydroxyls could lead to cleavage of some glucosidic bonds which in turn could give a significant drop in DP of the cellulose.

EXPERIMENTAL

Analytical grade chemicals were used. Purity of starting materials and identity of products were determined by GC and GC-mass spectrometry (GC-MS).

GC and GC-MS data were obtained with Hewlett-Packard 5830A and 5995A instruments respectively, with BP1, BP10 and BP20 bonded phase vitreous silica capillary columns (12 m x 0.2 mm ID) (Scientific Glass Engineering, Melbourne) and flame ionisation detection for the

5830A instrument. Split ratio: 100:1, carrier gas: helium, injector and detector temperatures: 250°C.

General reaction conditions

Monohydric alcohols and/or quinones were added to 4 mL 1M sodium hydroxide in 10 mL glass tubes which were then sealed under nitrogen and placed with ca. 3 mL water in 20 mL sealed steel vessels. The vessels were heated, four at a time, in a rocking air bath to 170°C during 30 min. At the end of the reaction the vessels were rapidly cooled in water, the reaction mixtures acidified to pH 2 with 10M hydrochloric acid, extracted, and the products analysed by GC.

Alkaline hydrolysis of AMS

Sodium AQ-2-sulfonate (10 mg) and 1M sodium hydroxide (4 mL) were heated at 170°C for 0-2 h. The colour of the reaction mixtures varied from light pink after attaining 170°C, to dark red after 2 h. To the acidified reaction mixtures, 1,8-dimethoxy-AQ (4 mg) in dichloromethane (1 mL) was added as the internal standard, and the resulting solutions were extracted with ethyl acetate (3 x 20 mL). The combined extracts were dried and the solvent was evaporated. The residue was silylated with Sylon BTZ (Supelco Inc., 0.3 mL) and pyridine (1 mL) for 2 h at 60°C, and then analysed by GC with a BP1 column at 200°C. Retention times: 2-hydroxy-AQ TMS ether, 4.6 min; 1,8-dimethoxy-AQ, 6.5 min. The only product peak observed in the chromatograms was that of 2-hydroxy-AQ TMS ether; no peak for 1-hydroxy-AQ TMS ether (retention time 3.5 min) appeared in the chromatograms.

Alkaline treatment of AQ derivatives

2-Hydroxy-AQ (10 mg) or AQ-2-carboxylic acid (10 mg) and 1M sodium hydroxide were heated at 170°C for 1-6 h. The mixtures were isolated and derivatised as above for AMS and were analysed by GC with a BP1 column at 200°C. Retention times: 2-hydroxy-AQ TMS ether, 4.6 min; 1,8-dimethoxy-AQ, 6.5 min; AQ-2-carboxylic acid

TMS ester, 8.1 min. The chromatograms showed no additional product peaks.

Oxidation of cyclohexanol

Solutions of cyclohexanol (10 mg, 0.1 mmol) in 1M sodium hydroxide (4 mL) were reacted with various quinones; AQ (25 mg, 0.12 mmol), AMS (37 mg, 0.12 mmol), 2-hydroxy-AQ (27 mg, 0.12 mmol) and AQ-2-carboxylic acid (30 mg, 0.12 mmol). The reaction mixtures were acidified and anisole (5 mg) in dichloromethane (1 mL) was added as the internal standard. The resulting mixtures were extracted with dichloromethane (2 x 2 mL) and the extracts were dried and analysed by GC with a BP20 column at 90°C. Retention times: cyclohexanone, 2.6 min; anisole, 3.3 min; cyclohexanol, 4.3 min. No additional product peaks were apparent in the chromatograms.

Oxidation of cyclohexanemethanol

Solutions of cyclohexanemethanol (11.5 mg, 0.1 mmol), or cyclohexanecarboxaldehyde (11.5 mg, 0.1 mmol) or cyclohexanecarboxylic acid (13.0 mg, 0.1 mmol) in 1M sodium hydroxide (4 ml) were reacted with AQ (50 mg, 0.24 mmol) or AMS (74 mg, 0.24 mmol). The reaction mixtures were acidified and veratrole (5 mg) in dichloromethane (1 mL) was added as the internal standard. The resulting mixtures were extracted with dichloromethane (2 x 2 mL). The solvent was removed from the combined extracts under a stream of nitrogen and the residues were reacted with boron trifluoride–methanol (1 mL) for 90 min at 60°C. After adding water (10 mL) to the mixtures, the products were extracted with dichloromethane (2 x 5 mL), and the extracts were dried, concentrated and analysed by GC on a BP20 column. The column temperature was 90°C for 5 min, then 5°C/min to 200°C. Retention times: cyclohexanecarboxaldehyde, 2.0 min; compound Id, 2.8 min; methyl cyclohexanecarboxylate, 3.3 min; cyclohexanemethanol, 7.2 min; methyl benzoate, 8.8 min; veratrole, 11.5 min. The aldehyde

(Ic) was analysed before derivatisation, due to partial conversion to its hemiacetal (Id) with the BF_3-methanol complex.

Oxidation of lithocholic acid

A suspension of lithocholic acid (10 mg, 0.026 mmol) in 1M sodium hydroxide (4 mL) was reacted with AQ (10 mg, 0.048 mmol) or AMS (37 mg, 0.12 mmol). The reaction mixture was acidified, 3β-methoxycholestane (IVc) (5 mg) in dichloromethane (1 mL) was added as the internal standard and the resulting mixture was extracted with dichloromethane (2 x 10 mL). The combined extracts were dried and the residue obtained after evaporation of the solvent was treated with 0.1M methanolic hydrochloric acid (2 mL) for 4 h at 60°C. After evaporation, the residue was reacted with 1:1 pyridine:acetic anhydride (1 mL) for 18 h at 20°C, and the excess reagents were removed, after adding toluene, by rotary evaporation. Analysis of the mixture was by GC with a BP1 column at 250°C. Retention times: 3β-methoxycholestane, 5.6 min; methyl 3-oxocholanate, 7.0 min; methyl 3α-acetoxycholanate, 8.7 min.

Oxidation of cholestan-3β-ol

A suspension of cholestan-3β-ol (10 mg, 0.026 mmol) in 1M sodium hydroxide (4 mL) was reacted with AQ (10 mg, 0.048 mmol) or AMS (15 mg, 0.048 mmol). The reaction mixture was acidified, 3β-methoxycholestane (IVc) (5 mg) in dichloromethane (1 mL) was added as the internal standard and the resulting mixture was extracted with dichloromethane (25 mL). The extract was evaporated and the residue silylated with BSTFA (200 μL) for 18 h at 100°C. After removal of the excess BSTFA with nitrogen, the residue was dissolved in 1 mL dichloromethane and analysed by GC with a BP10 column at 250°C. Retention times: 2-hydroxy-AQ TMS ether, 2.2 min; 3β-methoxycholestane, 7.9 min; cholestan-3β-ol TMS ether, 8.9 min; cholestan-3-one, 12.4 min.

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