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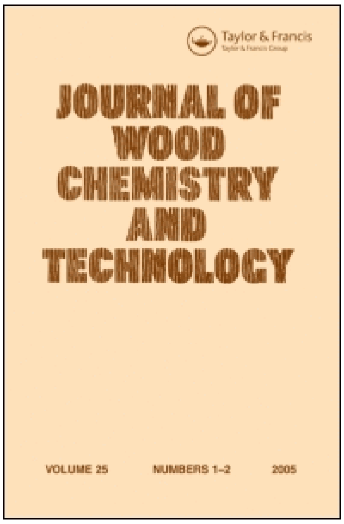

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ANTHRAQUINONE LOSSES DURING ALKALINE PULPING

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ABSTRACT

Extensive loss of anthraquinone (AQ) or the active catalyst anthrahydroquinone (AHQ) from the AQ — AHQ catalytic cycle has been explained in part by side reactions leading to the reaction product anthrone (anthracen-9-one), followed by subsequent formation of adducts with lignin quinone methides. Degradation of an adduct between anthrone and the quinone methide of guaiacylglycerol-β-guaiacyl ether, under soda pulping conditions, resulted in a complex mixture of products. The mixture included 3-guaiacylbenzanthrone, bianthronyl, bianthrone, guaiacol, AQ, trans-coniferyl alcohol, trans-coniferylaldehyde, cis- and trans-1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethene, vanillin, and 2-methoxy-4-vinylphenol. C-13 NMR studies of lignins isolated from soda/AQ spent liquors indicated the presence of residual anthrone adducts and a significant content of chemically attached AQ.

INTRODUCTION

Although it is well recognized that the anthraquinone (AQ)-anthrahydroquinone (AHQ) redox couple catalyzes alkaline delignification, some problems remain to be solved before full commercial exploitation can be realized. The most severe problem is the

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extensive loss of catalyst during pulping. This loss is especially serious in kraft/AQ pulping where careful control of cooking variables such as AQ charge is essential for favorable economics[3]. The extent of AQ losses was best illustrated by studies of soda digestions of wood in the presence of ^{14}C labeled AQ[4,5]. In these studies it was found that 50-60% of the label was chemically attached to the lignin isolated from the black liquor. About 15% was converted to soluble AQ-derived byproducts such as benzanthrone[6], 3-guaiacylbenzanthrone[4,7] 2-vanillylanthraquinone[6], 10-methyleneanthrone[8], anthrone[9], anthracene[9], and dihydroanthracene[9], all of which were isolated from soda/AQ black liquors during independent studies. Generally, 5-10% of the AQ charge was lost in the pulp and was essentially unextractable by aqueous or organic solvents[4,10]. Ultimately, a maximum of about 20% of the AQ charge was recovered unchanged[4].

Of all the AQ-derived byproducts isolated from black liquors, anthrone is of particular interest because it was shown that it reacts (as its alkali-stable form anthranol) with quinone methides in the same manner and more rapidly than the principal catalyst AHQ, giving analogous adducts[11-13]. Also, it was demonstrated that anthrone catalyzes delignification in alkaline systems even after careful exclusion of air to eliminate the possibility of its facile oxidation to AQ[14-16]. However, catalysis by anthrone was not as efficient as that by AQ.

It is expected that AHQ and anthranol react readily with quinone methides regardless of side chain as shown in Fig. 1. The lignin quinone methides are classified into two general types; the abundant β-O type, which represents about half of the inter-unit linkages, and the β-C type, such as β-Cl and phenylcoumaran structures, which together represent about 25% of the linkages[17]. Pathway A in Fig. 1 represents formation of a very unstable AHQ β-O adduct, which upon subsequent fragmentation results in the cleavage of a β-O linkage and regeneration of the catalyst. This pathway has been studied extensively and is thought to be the major route contributing to accelerated delignification[18-21]. There is

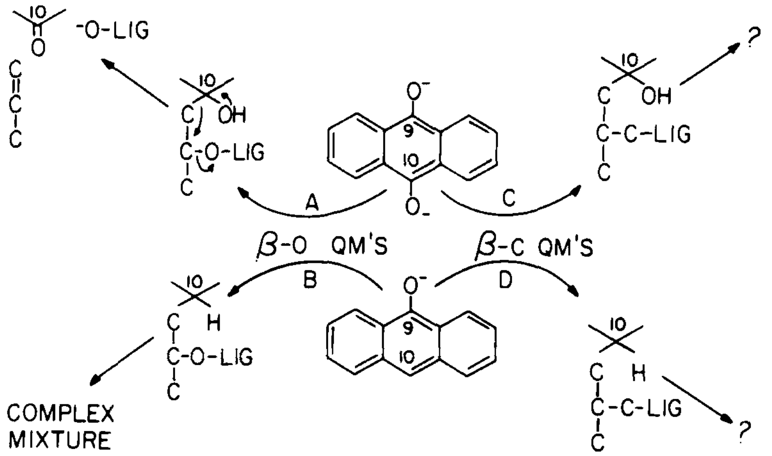

FIGURE 1. Reaction pathways during soda/AQ pulping. In the partial structures only C10 of the anthracene ring is shown.

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some evidence that a corresponding free radical pathway via anthrasemiquinone may contribute to some extent[22,23]. Pathway B, which is the formation and subsequent decomposition of anthranol β-O adducts, is not nearly as straightforward, and results in a variety of products. This pathway is the focus of the present study. Finally, corresponding reactions with β-C quinone methides represented by pathways C and D have not been studied, but are not expected to involve lignin interunit cleavages to any significant extent. However, pathways C and D may prove to be major causes of AQ losses during pulping.

To minimize AQ losses, a clearer understanding of the side reactions which the catalyst undergoes during pulping is essential. Although this study describes side reactions contributing to AQ losses which likely occur during soda/AQ pulping, the reaction mechanisms are also assumed to be operative under kraft conditions. This assumption is based upon numerous mechanistic studies[20,21,24–26] which have indicated that both AQ-promoted delignification and sulfide-promoted delignification operate via intermediate lignin quinone methides and are essentially parallel and competing reactions.

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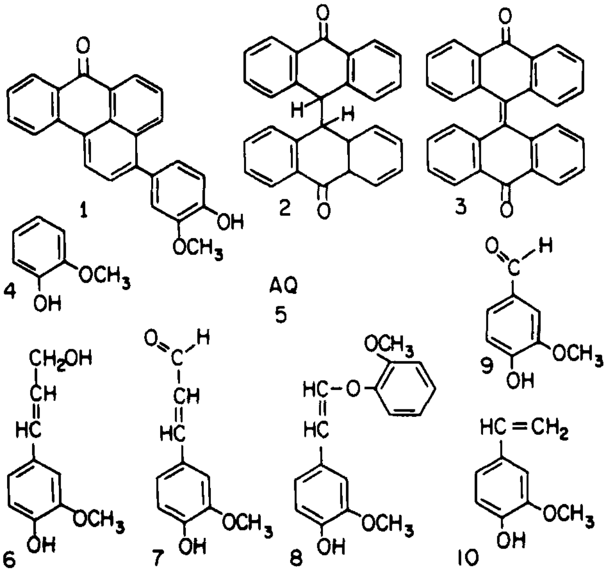

FIGURE 2. Degradation products of anthranol β-O adduct.

RESULTS AND DISCUSSION

Alkaline Degradation of Anthranol β-O-Adduct

Digestion of the adduct formed from anthranol and the quinone methide of guaiacylglycerol-β-guaiacyl ether[11] under soda pulping conditions resulted in a complex mixture. Ten of the products which together account for about 75% yield are illustrated in Fig. 2. The remainder included starting material and an unidentified polymeric substance. Quantitation of the acetylated mixture was partially successful by utilizing a combination of gel chromatography, thick-layer chromatography, and integration of ^1H NMR spectra of resulting two or three component mixtures. The substituted benzanthrone, 1, was the major component and was obtained in yields up to 25%. AQ was isolated in 15% yield even though air was excluded during workup, thus preventing facile oxidation of anthranol to AQ. The yields of all of the other products ranged between 3 and 10%, with compounds 2, 4, and 8 at the high end (7-10%). Surprisingly, no anthrone (or anthranol)

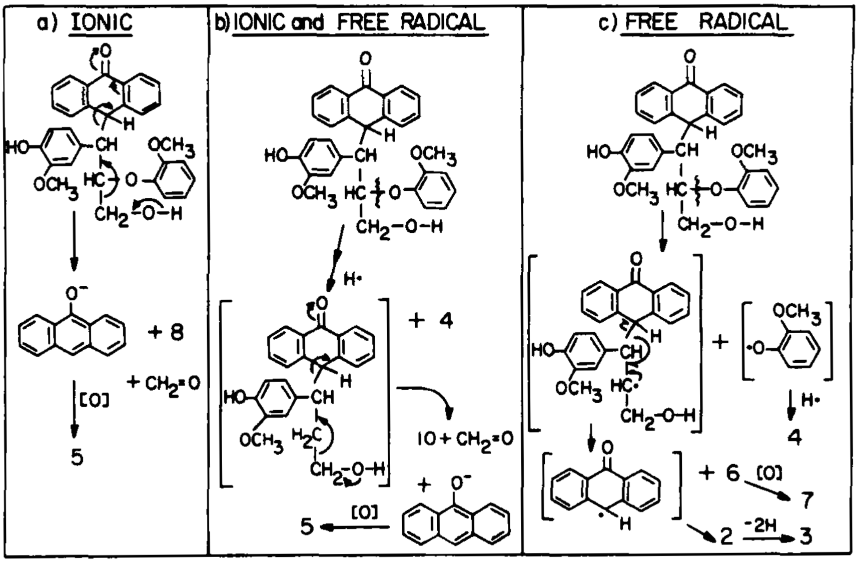

FIGURE 3. Proposed fragmentation pathways of anthranol β-0 adduct.

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was detected in the mixtures, perhaps because of facile dimerization to 2 or oxidation to AQ under the reaction conditions.

Anthranol undoubtedly causes β-ether cleavage as is shown by more than half of the isolated decomposition products. Both ionic and free radical pathways are likely during decomposition of the adduct. Possible routes which account for most of the observed products are illustrated in Fig. 3. Formation of the vinyl ether 8 may be explained by an ionic mechanism (Fig. 3a) which resembles a reverse aldol reaction. Formation of vinyl ethers by similar mechanisms have been described[24]. A strictly free radical mechanism (Fig. 3c), initiated by homolytic cleavage of the C_β-0 linkage, would presumably lead to the initial products 2, 4, and 6. Alternatively, an analogous mechanism initiated by cleavage of the C_α-C_{10} linkage (not shown) would lead to the same products. Subsequent reactions would then give 3 and 7. The presumption that homolytic cleavage of either of the two linkages lead to 2, 4, and 6 is consistent with the fact that these were the only three degradation products obtained upon refluxing the anthranol adduct in xylene. Under these conditions, in the absence of both acid and alkali, thermal homolytic cleavage is the predictable degradation pathway. Finally, a mixture of ionic and radical pathways (Fig. 3b) could explain the formation of the vinyl phenol, 10. Possible mechanisms for the formation of the major product, 1, have been described elsewhere[12,27,28].

Adduct Formation in Lignin-
^{13}C NMR Studies

In a previous study[12], adduct formation in lignin was accomplished by allowing 9,10-^{13}C enriched (50%) AHQ or the corresponding anthranol to react with acetylated milled loblolly pine lignin under alkaline conditions at 10° and 30°C, respectively. Acetylation was necessary to induce formation of quinone methides under these mild conditions[18]. It does not necessarily follow that analogous reactions occur under pulping conditions. Therefore, to obtain further insight to the nature of AQ species following a pulping reaction, lignins precipitated from spent liquors from soda, soda/AQ, and soda/9,10-^{13}C enriched AQ cooks of loblolly pine were acetylated and examined by ^{13}C NMR spectroscopy.

A comparison of the spectra in Fig. 4 shows some notable differences. The most pronounced is the presence of the predominant cluster of peaks at 182-186 ppm (A) in only the labeled AQ lignin which is consistent with ^{13}C enriched carbonyls in AHQ and anthranol adducts[12]. The only other difference between the AQ lignins is the small, but significant cluster at 43-47 ppm (C) in the labeled AQ lignin which corresponds to the enriched aliphatic C10 of anthranol adducts[12]. Corresponding aliphatic C10 peaks of AHQ adducts at 70-85 ppm would not be expected, following a soda cook, considering the instability of the C10-lignin linkage in AHQ adducts as noted in previous studies[11,12]. Although this region is partially obscured by the solvent peaks, examination of expanded spectra revealed no significant difference between that of the labeled and unlabeled soda/AQ lignins. The greater intensity in the 125-140 ppm region (B) in both of the soda/AQ lignins, as

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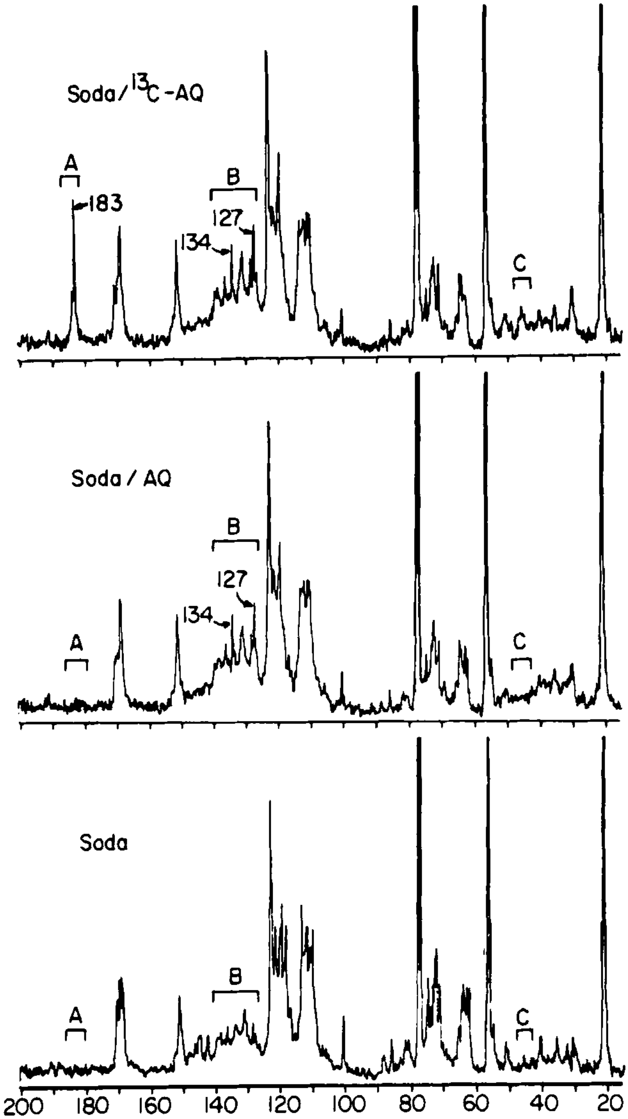

FIGURE 4. ^{13}C NMR spectra of acetylated lignins ($CDCl_3$) isolated from loblolly pine spent liquors.

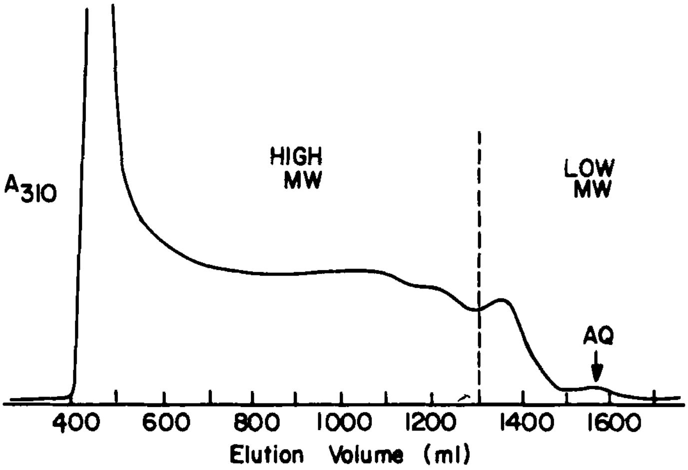

FIGURE 5. Typical molecular weight profile of lignin from soda-AQ spent liquor.

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compared with the soda lignin, is consistent with aromatic tertiary carbons of anthracenyl structures. The spectra in Fig. 4 represent the total precipitate, which includes excess AQ and low molecular weight byproducts. For example, the three sharp peaks at 127, 134, and 183 ppm in the soda/^{13}C AQ lignins are assigned to free AQ. The peaks at 127 and 134 ppm each represent four identical tertiary carbons, and the peak at 183 ppm is assigned to the carbonyl carbons. The natural abundance AQ carbonyls are not seen in the soda/AQ lignin because of their long relaxation time. This is also true of the aromatic quaternary carbons which are not observed in either of the AQ lignins.

Molecular weight (MW) profiles of the acetylated lignins were obtained by gel chromatography on styrene-divinylbenzene copolymer beads. Since the chromatograms did not differ significantly (except for the absence of an AQ peak in the soda lignin), they can be represented by that in Fig. 5. The lignins were divided into high and low MW fractions which represent approximately 90% and 10% by weight, respectively. The last peak in the low MW por-

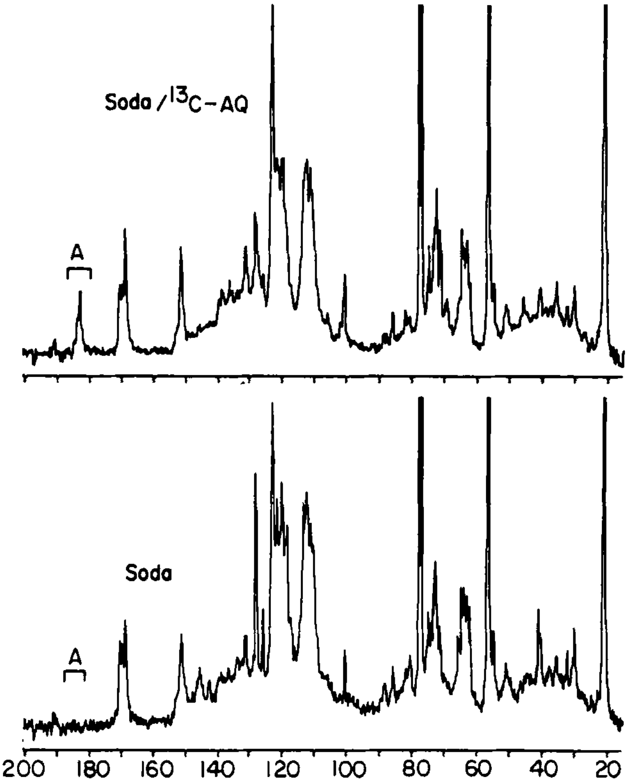

FIGURE 6. ^{13}C NMR spectra of high molecular weight portions of acetylated lignins.

tion in the two AQ lignins represents a 16-18% isolated recovery of the initial AQ charge. The other substances in the low MW fraction have not been identified. The ^{13}C NMR spectra of the high MW portions of both the soda/^{13}C AQ lignin and the soda control are shown in Fig. 6. Clearly, a significant portion of the ^{13}C label is still present as shown by the ^{13}C enriched carbonyls at 182-186 ppm (A) in the soda/AQ cook. This is direct evidence of anthracenyl moieties chemically attached to the lignin. Examination of narrower MW fractions of the recovered lignins is in progress and is expected to provide further insight into the nature of these anthracenyl-lignin adducts.

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SUMMARY

AQ losses during alkaline pulping were attributed in part to the formation of anthranol, a reduction byproduct of AQ, which forms adducts with quinone methides which are analogous to AHQ adducts. The anthranol adducts fragment, giving a complex variety of products, most of which are catalytically inactive, and only a very low yield of AQ and no anthranol. ^{13}C NMR studies of lignins isolated from soda/AQ cooks provided evidence of the presence of a significant anthracenyl content which is chemically attached to the lignin. A small amount of these anthracenyl structures were shown to be C10-linked anthranol adducts.

EXPERIMENTAL

Alkaline degradation of anthranol adduct, threo-1-(3-methoxy-4-hydroxyphenyl)-1-(9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy) propan-3-ol. This adduct was prepared as described previously[11]. A typical degradation was as follows: The adduct (120 mg) was digested in 0.5M NaOH (10 ml) in the presence of glucose (50 mg, reducing agent) under nitrogen in a stainless steel bomb at 170°C for 20 min. At the end of the digestion the bomb contents were cooled to room temperature and poured into 0.5M HCl (12 ml). The resulting suspension was extracted with $CHCl_3$ (5 x 5 ml) and the bright yellow extract was dried over $MgSO_4$ and evaporated, leaving an orange oil. Acetylation of the oil with 1/1 acetic anhydride/ pyridine gave a brown solid (132 mg) which was applied on a 210 x 3.2 cm column of BIO-RAD Bio-Beads S-X8. Gravity elution with $CHCl_3$ gave 11-12 overlapping peaks which were further resolved on silica gel thick-layer plates. Compound 1 illustrated in Fig. 2 was identified by comparison of its ^{1}H and ^{13}C NMR chemical shifts with those previously reported[6]. Compounds 2 through 10 were identified by comparison with authentic compounds.

Wood Cooks and Lignin Preparation

Air-dried loblolly pine wood meal (40 mesh, 3.7 g ovendry basis) was digested in 1.2M NaOH solution (60 ml, 78% NaOH on wood)

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at 170°C for 90 min (110 min to temperature) in slowly tumbling stainless steel bombs. AQ cooks contained 24 mg (0.7% on wood) of unlabeled or 9,10-^{13}C enriched (50%) AQ (prepared as described in reference 12). At the end of the cooks the pulps were filtered and washed with water (2 x 25 ml) and dioxane (2 x 25 ml). The pulp yields/kappa numbers for the soda, soda/AQ, and soda/^{13}C AQ pulps were 50/56, 47/17, 48/18, respectively. The pulp washings were added to their respective filtrates and the pH was adjusted to 7.0 with glacial acetic acid. The resulting suspensions were concentrated to 30-40 ml (50°/25 mm), then filtered through a Millipore Pellicon PT series membrane (nom. mol. wt. cutoff = 100,000). The retentate was washed with water (3 x 40 ml) and freeze dried. Lignin yields for the soda, soda/AQ, and soda/^{13}C AQ cooks were 0.59 g, 0.75 g, and 0.72 g, respectively. The lignins were acetylated with 1/1 acetic anhydride/pyridine for 18 hr at room temperature prior to ^{13}C NMR examination. Separation of the acetylated lignins into high and low MW portions was accomplished by applying the samples (400 mg) on a 93 x 5 cm column of BIO-RAD Bio-Beads S-X1, followed by gravity elution with $CHCl_3$. The eluant was monitored at 310 mµ with an ISCO UA-5 absorbance monitor.

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^{13}C NMR Spectra

Proton decoupled ^{13}C spectra were determined at a frequency of 62.9 MHz with a Bruker WM-250 FT spectrometer equipped with a 5 mm broadband probe. The acetylated lignin samples (60-80 mg) were dissolved in $CDCl_3$ (0.3 ml). Spectra were obtained at 30°C from approximately 40,000 transients with 8K data points and zero-filling to 16K. A pulse angle of 75° and a relaxation delay of 0.5 sec were used.

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