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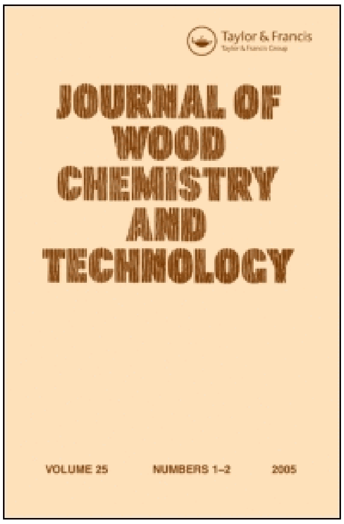

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(1), 57-71 (1982)

INFLUENCE OF HYDROPHILICITY ON THE DELIGNIFICATION EFFICIENCY OF ANTHRAQUINONE DERIVATIVES

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ABSTRACT

A series of substituted anthraquinones has been prepared to determine the influence of hydrophilic and hydrophobic substituents on the efficiency of delignification in soda pulping of Douglas fir. Regardless of redox potential and proximity to the ring system of the parent anthraquinone, carboxyl groups strongly diminish the activity of AQ. This effect is believed to be the result of increased hydrophilicity of the carboxyl derivatives relative to unsubstituted anthraquinone. Conversely, nonpolar hydrocarbon sidechains tend to increase the activity of anthraquinone in soda pulping. These effects suggest that adsorption phenomena may play a strong role in additive performance, and that hydrophobic substituents tend to concentrate the additive in the wood phase, while hydrophilic derivatives tend to remain in the liquid phase.

INTRODUCTION

For several years we have been interested in correlating the chemical features of anthraquinone derivatives with their relative performance as catalysts in alkaline delignification. At an early stage of this work we became intriqued with the observation made from some of Holton's data[1] that anthraquinones substituted with solubilizing groups, such as carboxylate and sulfonate, were much poorer catalysts of delignification than anthraquinone (AQ) itself and some of its alkyl derivatives. Though an explanation based on redox potentials was considered, the large and consistent difference in performance between relatively soluble AQs and AQs of relatively low solubility, as well as evidence for the same trends in the fluorenone series,[2] suggested that other factors may be at work. Moreover, our own results[2] and those of Bersier[3] now indicate that at least over a broad range of catalyst structures there is no correlation between redox potential and delignification efficiency. Thus, aside from possible differences in alkaline stability, the remaining most straightforward explanation focuses on the possibility that the performance of an additive will improve if it tends to concentrate within the wood chip due to adsorption effects.

Lindenfors,[4] though a proponent of the redox explanation of performance for some additives, was the first to suggest that highly soluble additives might give poor results due to a greater affinity for the liquid phase rather than the wood phase during pulping. However, he apparently viewed this as an extreme situation, appropriate only for very poor but highly soluble additives, such as anthraquinone-2, 7-disulfonate.

Recently, Werthemann[5] has expanded this view and has proposed that the relative delignification performance of such additives as anthraquinone-2-sulfonate (AMS), AQ, and 2-methylanthraquinone (2-Me-AQ) is mostly governed by their relative tendencies to partition between wood and cooking liquor. Thus, the poor performance of AMS is due to its hydrophilic preference for the liquid phase, rather than for the unreacted lignin in the wood phase. AQ gives better performance because it has a greater tendency to adsorb from solution onto the wood. The methyl group of 2-Me-AQ promotes even greater adsorption and therefore gives somewhat better results than AQ. Werthemann bases these conclusions on experiments which correlate liquor to wood ratio with a function of delignification efficiency defined by the Nernst adsorption isotherm. We have now arrived at similar conclusions regarding the influence of substituent hydrophilicity, though our experimental approach differs from that of Werthemann.

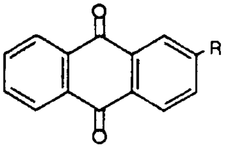
RESULTS AND DISCUSSION

In the present case we have chosen to examine the delignification efficiency of a closely related set of AQ derivatives in order to separate any redox effects from the expected influence of the substituent on the overall hydrophilicity of the compound. The group of compounds studied is shown in Table 1, along with their polarographic peak potentials, E_p, as determined in our standard alkaline system.[2] All of the substituents are placed in the 2 position of AQ and represent a wide range of hydrophilicity, as well as different arrangements of the carboxyl group with regard to the AQ parent.

Special mention should be made of compounds IV, VI and VII, which all derive from the synthetic scheme shown in Figure 1. This is a very simple avenue to a useful set of AQ derivatives for studies of substituent effects on and off the ring. Compound V, though not used directly in the present study, is the key intermediate for the production of a wide variety of AQ derivatives. The synthetic steps have not been optimized, but the yields are generally good and further improvements are likely.

The initial focus of this study was on anthraquinone-2-carboxylic acid (ACA), II, which is known to be a weaker catalyst of delignification than AQ. Of interest is whether this fact is due to the

TABLE 1. Polarographic Peak Potentials of Compounds Studied[a]



Compound, R =		Ep, V *vs* SCE
I	-H	-0.680
II	$-CO_2H$	-0.656
VI	$-CH_2-CH_2-CO_2H$	-0.720
VIII	$-CH=CH-CO_2H$	-0.627, -0.715
VII	$-CH_2-CH_2-CH_2OH$	-0.717
IV	$-CH_2-CH_2-CH=C-(CH_3)_2$	-0.725

[a] Potentials obtained in 0.5M NaOH, 0.1 M NaCl in 50% aqueous DMF.

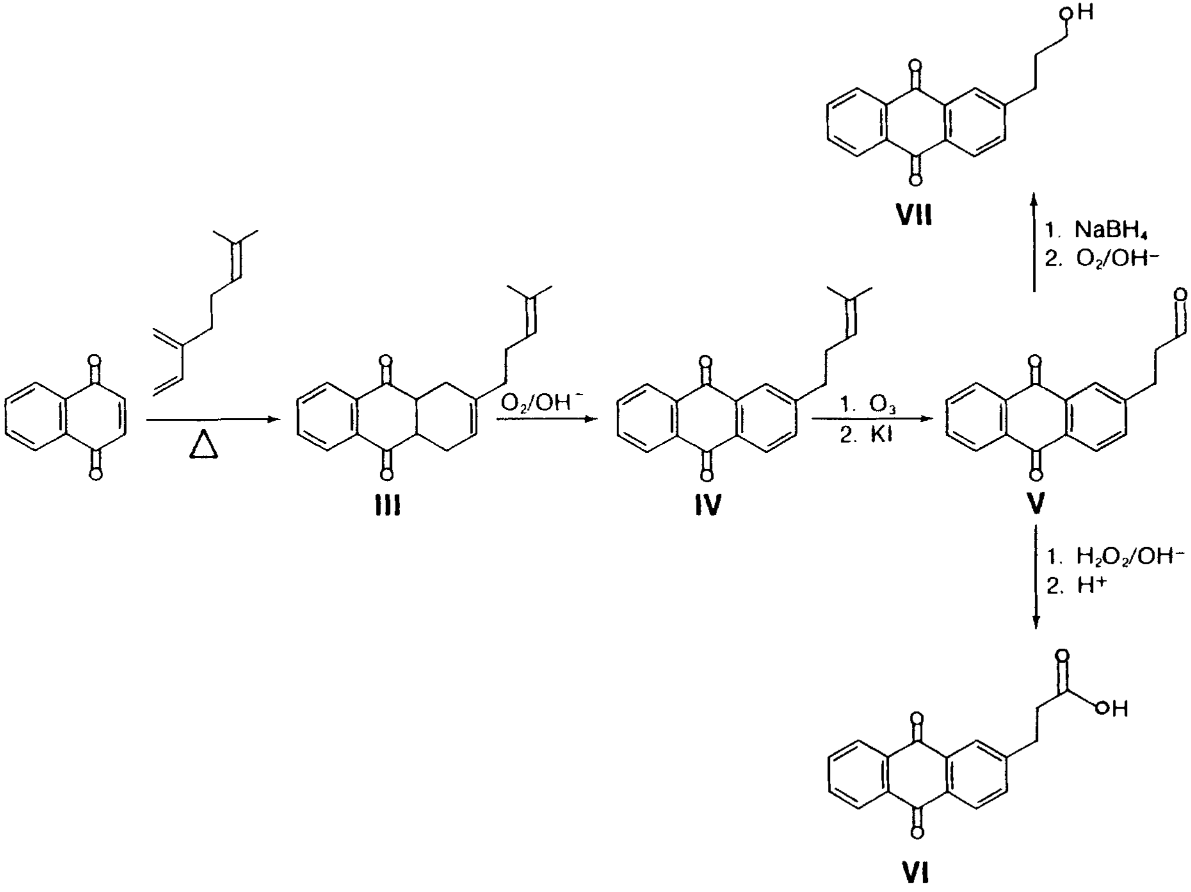


FIGURE 1 Synthesis of AQ Derivatives

influence of the carboxylate group on the polarographic peak potential of the parent AQ or whether it may be related to the additional hydrophilicity imparted upon the molecule by the carboxylate substituent. Therefore, its potential and pulping performance were compared with two other derivatives, VI and VIII, both of which separate the carboxyl group from the ring system, either by an alkane or alkene radical, respectively. As shown, the E_p value of ACA relative to AQ, I, is shifted to a more positive potential, while the propanoic acid, VI, is shifted to a more negative value. This latter shift is precisely what is expected for an alkyl group directly attached to the ring as, for instance, with 2-methylanthraquinone which has an E_p of -0.726 V in this same system. Except for the acrylic acid, VIII, the remaining compounds of Table I also have alkyl groups directly at the ring and also give E_p values between -0.717 and -0.725 V, as expected. Thus, the effect of a single alkyl unit attached to the ring is fairly consistent and results in a 37 mV to 46 mV cathodic shift relative to AQ, while direct attachment of a carboxyl group causes an anodic shift from AQ. The acrylic acid VIII is unusual in that we obtain two one-electron peaks in this aqueous-alkaline system. This may be a special influence of the conjugated double bond, which tends to obscure rigorous comparison of E_p values with those of the alkyl substituted AQs.

The delignification results for all the compounds of Table I except IV, vide infra, are shown in Figure 2 as plots of the reciprocal kappa number obtained from a standard soda cook of Douglas fir chips versus the square root of the additive charge, expressed as mmol of additive per 100 g OD wood. A molar basis is necessary here since some of the compounds differ significantly in molecular weight from AQ. The use of the square root plot in no way should suggest acquiescence to certain theories[9] on the reactions between AQ and lignin, but rather is a convenient device to present all of the data, including that for the soda control, in a linear plot.

The upper line in Figure 2 is for the AQ data, while the lower line is fitted to data for the carboxylic acids of Table I.

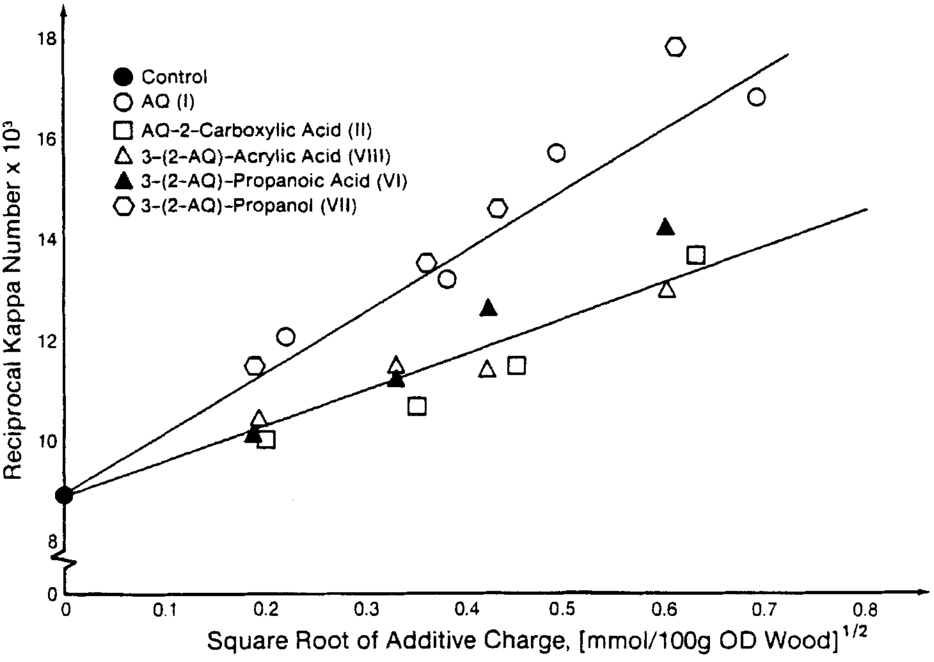


FIGURE 2 Influence of Hydrophilic Substituents on AQ Delignification Efficiency

Regardless of E_p value, the three acids are all significantly poorer catalysts than AQ and, in fact, behave very similarly to one another. This indicates that there is no correlation of delignification efficiency with redox potential, and distinctly shows the dominance of the very hydrophilic carboxyl group, no matter where its location in the molecule. The very similar catalytic ability of the three acids also suggests that their weakness is not due to alkali instability, since it is hardly likely that these three compounds would be degraded by a common mechanism. Recently, Carlson[6] has shown that anthraquinone-1-acetic acid (AMA) is also a poorer catalyst than AQ. The work also showed that after certain cooks, no residual AMA could be found in spent liquors, while AQ survived to the extent of 20% to 30% of its initial charge, suggesting that poor AMA performance may be due to instability of the catalyst. However, since these residual analyses were apparently made for soda cooks preceded by oxygen pretreatments, we tend to discount the value of these results for explaining performance differences in simple soda pulping experiments, such as our own.

Delignification data for the propanol, VII, is also shown in Figure 2. Its catalytic ability is very similar to that of AQ, suggesting that the hydroxyl group changes hydrophilicity very little. This may seem unlikely, since a hydroxyl group should improve the interaction of the molecule with the aqueous solvent, and therefore the catalytic efficiency should be intermediate between AQ and the group of carboxylic acids. However, the hydroxyl group is added along with a three-carbon hydrophobic alkyl group, and the two moieties may cancel each other.[7]

The remaining compound in Table I, the six-carbon alkene, IV, was not originally part of this pulping study and was only used as a synthetic means to obtain some of the other compounds. However, after reflecting on the initial results, it was decided to include this compound to demonstrate just how much a very hydrophobic substituent can enhance the activity of the AQ parent. A second round of cooks on a new batch of Douglas fir chips was made using AQ again and the previously neglected alkene. Cooking conditions were identical to those used for the other compounds in Table I.

The delignification results for the alkene IV and AQ are shown in Figure 3. The plot is again on a molar basis. It is evident that the very hydrophobic alkene substituent causes a major improvement in the delignification efficiency of the parent compound. Substantial improvement remains even when the compounds are compared on a straight weight-to-weight basis. This, then, is an exaggeration of the basic enhancements which have been observed with both 2-Me-AQ and 2-Ethyl-AQ[1]. In our view, the major effect of these alkyl substituents is to increase the hydrophobicity of the ionic species of the hydroanthraquinone parent molecule. This effect, in turn, helps to increase the concentration of the reduced quinone in the wood phase or, more specifically, in the unreacted lignin gel.

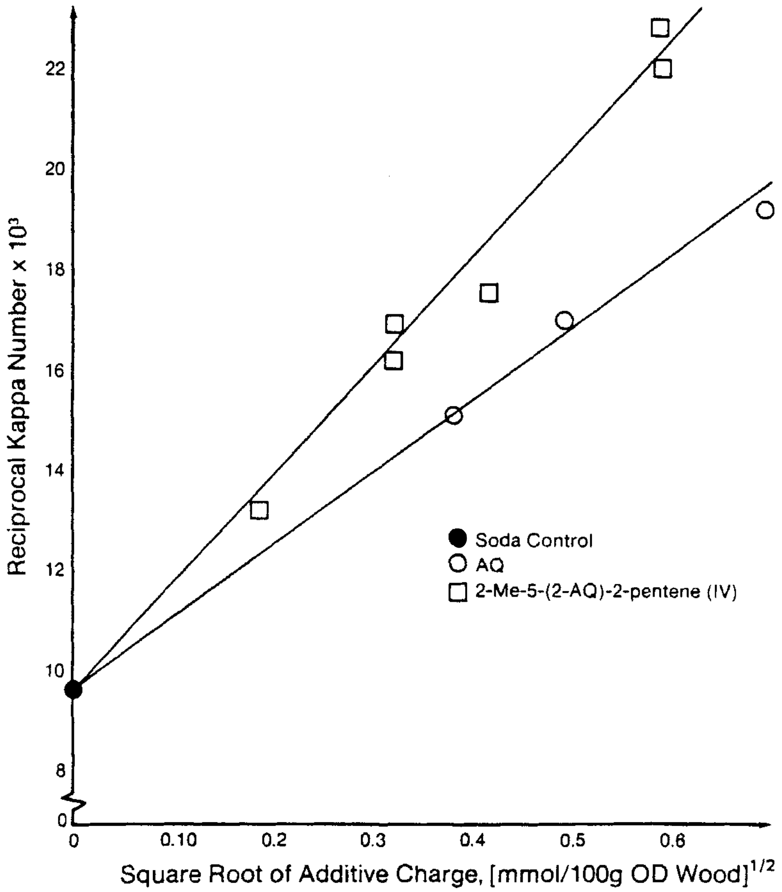


FIGURE 3 Influence of a Hydrophobic Substituent on AQ Delignification Efficiency

This phenomenon may provide a further explanation, in addition to that of the redox cycle, as to why such major increases in delignification are obtained from such small additions of AQ. Adsorption effects may tend to magnify the working concentration of an additive many fold beyond its calculated concentration in the bulk liquid.

Finally, it should be noted that the hydrophilicity/xylophilicity (HX) balance, as Werthemann has called it, should not be confused with solubility. In our view, the HX balance is specifically concerned with the reduced form of the quinone which, since it is ionized in the aqueous alkaline system, will almost never have solubility limitations in the sense of being released from or returned to its bulk solid phase. Nevertheless, and despite its solubility, the hydroquinone dianion is subject to adsorption effects at the solid wood or gel surfaces. These adsorption effects can be attenuated by the nature of a substituent and thus arises the effect many substituents have on the efficiency of an AQ additive.

Solubility per se is primarily of interest for the oxidized or quinone form, since it is this form which is most likely to have a solubility limitation in an aqueous system. Furthermore, solubility of this form can become critical and drastically influence delignification results if it imposes a limit on the extent or rate at which the quinone can be reduced and thereby enter or return to the pulping system as the lignin-active hydroquinone. Examples of this limitation have been shown by Werthemann[8] and will be given in a subsequent paper.

Solubility data for the quinone form should be used cautiously in predicting the HX balance with regard to the reduced form. For instance, relative solubilities for the alkene IV and AQ were measured by polarography at room temperature in alkaline 1:1, water-DMF. The alkene is actually slightly more soluble than AQ. Assuming this solubility is synonymous with the HX balance of the hydroquinone would lead to the conclusion that, all things being equal, there should be little difference between AQ and the alkene in their effects on delignification, which, of course, is wrong. Despite the solubility of the quinone form, the hydrocarbon group of IV does exert a hydrophobic effect in the hydroquinone which, in our view, leads to greater adsorption and enhanced delignification relative to AQ. This may be a case where solubility of the quinone IV was higher than expected because of relatively low lattice energy (mp of IV is 86° to 88°C, compared to 285° to 286°C for AQ). But as Werthemann has noted, lattice energy does not influence the partitioning of a species between two phases.[5] As a result, IV has solubility equal to AQ in their quinone forms, but IV behaves much more hydrophobically in their hydroquinone forms.

EXPERIMENTAL

Mass spectra were taken using a Finnigan 4023 gas chromatograph/mass spectrometer equipped with a solid probe. Probe temperature typically was programmed from 80° to 350°C at 50°/min heating rate; the spectrometer was operated at 70 eV. A Varian CFT-20 spectrometer, observing ^{13}C at 20 MHz, was employed to acquire ^{13}C NMR spectra in $CDCl_3$, DMSO-d_6 or acetone-d_6 solution; assignments were listed in Table 2. Infrared spectra were recorded with a Perkin-Elmer Model 283 spectrophotometer on samples dispersed in KBr pellets. A Carlo Erba Model 1104 CHNO analyzer gave elemental compositions. Reduction potentials in aqueous alkaline DMF were measured with a PARC Model 174 polarograph.

Pulping experiments were made with Douglas fir chips using a multiple digester assembly consisting of six bombs of 1 L capacity, each fitted into a rotating rack within an electrically heated oven. To each bomb 100-g OD of screened chips (retained between 28.5 and 3.1-mm slots) were charged. All cooks were made under the following conditions: 22% caustic on OD wood, 4:1 liquor-to-wood ratio, 90 min rise to a maximum temperature of 170°C, and 90-min retention at this temperature. Additive charge was variable. Cooked chips were defibered, washed, and tested for kappa number, as reported earlier.[2]

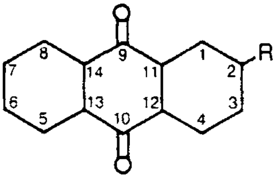
Anthraquinone Derivatives

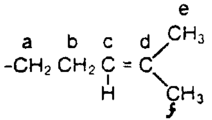
Anthraquinone and anthraquinone-2-carboxylic acid (II) were obtained from commercial sources. A sample of 3-(2-anthraquinone)-acrylic acid (VIII) was generously provided by Dr. Amar Neogi. The remaining compounds in this study were obtained by the general scheme in Figure 1 and were prepared as follows.

2-Methyl-5-(2-Anthraquinone)-2-Pentene (IV)

Both technical grade 1,4-naphthoquinone and tech. myrcene (Aldrich) were used without further purification. The Diels-Alder adduct III was formed by adding 43.2 g of myrcene to 27.5 g of naphthoquinone in 200 mL of toluene and heating this solution at

TABLE 2. ^{13}C NMR Assignments*



CARBON No.	COMPOUND				
	 a b c d e f $-CH_2CH_2C(H){=}C(CH_3)_2$		a b c $-CH_2CH_2CHO$	a b c $-CH_2CH_2CO_2H$	a b c $-CH_2CH_2CH_2OH$
	III	IV	V	VI	VII
a	37.5	36.3	28.1	30.3	31.7
b	27.7	29.3	44.4	34.2	33.5
c	124.0	122.8	200.4	173.4	59.7
d	131.7	131.5	—	—	—
e	17.7	17.7	—	—	—
f	25.7	25.6	—	—	—
1	26.3	127.3	127.7	126.8	126.9
2	135.6	149.5	147.6	148.2	149.6
3	118.3	134.3	134.3	132.7	132.8
4	24.9	126.9	126.7	126.1	126.1
5, 8	126.9	127.1	127.2	126.5	126.5
6, 7	134.2	133.8	134.1, 134.2	134.3	134.3, 134.4
9	198.1	182.8	182.8	181.9	182.0
10	198.2	183.2	183.1	182.2	182.4
11	46.7	133.6	133.6	na	na
12	47.2	na	131.8	130.9	130.8
13, 14	na	133.0	133.5	na	na
solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	DMSO-d_6	DMSO-d_6

* δ_C in ppm *vs* internal TMS; "na" indicates no assignment.

reflux for 12 hours. The toluene was then removed under vacuum to leave a grey to black oil which solidified after standing overnight in the hood. A small sample of this solid was recrystallized several times from hexane to give pale white crystals of mp 58°-59°C. MS m/e (%): 294 ($M^{+\bullet}$, 8), 207 (22), 133 (23), 77 (25), 69 (89), 41 (100). IR (KBr): 1700 cm^{-1}, carbonyl. ^{13}C NMR ($CDCl_3$): See III in Table 2.

The remainder of adduct III was dehydrogenated with oxygen and alkali to obtain IV. The above black solid was pulverized and added to 1400 mL of methanol containing 45 g of KOH. This mixture was stirred and heated to boiling while oxygen was bubbled through the solution. Heating was stopped after 15 min at boiling, while stirring and oxygenation were continued for an additional 45 min. From this cooled solution precipitated a yellow solid which was removed by filtration and washed with a little methanol. This solid was then dissolved in 800 mL of boiling hexane. A black, oily layer separated which contained most of the impurities from the technical grade naphthoquinone and residual methanol. The yellow hexane layer was decanted and filtered through a jacketed sintered glass filter, heated with hot tap water to prevent cooling and crystallization of the product during filtration. Upon cooling the filtrate in an ice bath, yellow crystals of IV, 15.0 g, were deposited and removed. After some evaporation of the filtrate, a second batch, 12.2 g, of IV was obtained. Both batches gave mp 86°-88°C and were then combined for further analysis and pulping work. MS m/e (%): 290 ($M^{+\bullet}$,11), 222 (48), 165 (12), 69 (100), 41 (68). IR (KBr): 1682 cm^{-1} carbonyl. ^{13}C NMR ($CDCl_3$): See IV in Table 2.

3-(2-Anthraquinone)-Propanal (V)

This compound was prepared in several batches by ozonolysis of compound IV. Typically, 2.90 g (0.01 mol) of IV was dissolved in 500 mL of hot methanol contained in a gas washing bottle fitted with a sparge tube and stir bar. The canary yellow solution was cooled with stirring in an acetone/dry ice bath to give a fine suspension of IV. Into this suspension was bubbled an excess of ozone (1.8 g over 30 min). During this time the yellow color faded to white. After terminating the ozone flow, the suspension was allowed to stand 30 min, then removed from the cold bath and treated with 4 g of potassium iodide in 30 mL of glacial acetic acid. The material dissolved upon returning to room temperature.

After standing overnight, enough 0.1 N thiosulfate solution was added to discharge the iodine color and about half the methanol was removed under vacuum at 40°-50°C. The title compound began to precipitate at this point and was fully forced from solution by dilution with 1 to 2 L of water and some thiosulfate solution, if required. The precipitate was filtered (very slowly), washed with water, and dried. After recrystallization from ethanol, the yield was 66% of compound V with mp 118°-120°C. MS m/e (%): 264 ($M^{\ddagger}$, 25), 235 (100), 222 (19), 193 (22), 178 (27), 165 (31), 152 (20), 76 (20). IR (KBr): 1720 cm^{-1}, aliphatic carbonyl; 1675 cm^{-1}, quinone carbonyl. ^{13}C NMR ($CDCl_3$): See V in Table 2. Elemental Analysis:

	Theory	Found
% C	77.3	75.6
% H	4.6	4.9

3-(2-Anthraquinone)-Propanoic Acid (VI)

Several combined batches of crude aldehyde V were used without recrystallization. Thus, 5 g of aldehyde was dissolved in 25 mL of hot ethanol and added dropwise over 15 min to a 60°C solution of ethanol (25 mL), 1N NaOH (50 mL) and 5 mL of 30% hydrogen peroxide. The reaction was continued for another 60 min, cooled and acidified with 4N sulfuric acid. A precipitate was obtained and collected on a filter, suspended in distilled water, and stirred 1 h, and refiltered. The product was dried in a vacuum oven at 50°C overnight and then recrystallized once from toluene. This material was shown by NMR to be a nearly 1:1 mix of the desired VI and anthraquinone-2-carboxylic acid. The latter apparently is due to overoxidation and its formation was found in subsequent work to be very difficult to avoid. Pure VI was obtained by two or three recrystallizations of the crude mixtures from ethyl acetate; however, the overall yields of VI were only 35%-40%. Pure VI had mp 216°-219°C. MS m/e (%): 280 ($M^{\ddagger}$, 28) 235 (100), 193 (30), 178 (32), 165 (31), 151 (24), 76 (41). IR (KBr): 1710 cm^{-1}, carboxyl; 1677 cm^{-1}, quinone carbonyl. ^{13}C NMR (DMSO-d_6): See VI in Table 2.

Elemental Analysis:

	Theory	Found
% C	72.9	73.6
% H	4.3	4.4

2-(2-Anthraquinone)-Propanol (VII)

The alcohol was prepared directly from crude aldehyde, V. A 250 mL flask was charged with 100 mL of ethanol and 400 mg of sodium borohydride. This mixture was cooled in ice water and stirred magnetically. To a second flask 75 mL of ethanol and 2.0 g of V were added and heated to dissolve. The warm solution was slowly added to the borohydride solution over 10 min. The resulting red-brown solution was stirred another 2 h, then the reaction was stopped by sparging with air until the red-brown color discharged. The solution was quickly acidifed and poured into 800 mL of water to precipitate the product. The material was filtered, suspended in water, stirred overnight, refiltered, and dried.

This material was found to be contaminated with 5%-10% of the acid, VI (originally an impurity in the crude aldehyde). Therefore the product was dissolved in warm chloroform, cooled, and extracted twice with 100-mL portions of 1% NaOH, followed by washing with 100 mL of water. The chloroform solution was dried over sodium sulfate, evaporated, and the residue recrystallized from methanol to give 0.96 g of VII with mp 114°-116°C. MS m/e (%): 266 ($M^{\dot{+}}$, 100), 235 (68), 222 (48), 165 (66). IR (KBr): 1679 cm^{-1}, quinone carbonyl. ^{13}C NMR (acetone-d_6): See VII in Table 2.

	Theory	Found
% C	76.7	75.5
% H	5.3	5.3

ACKNOWLEDGMENTS

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7. Another rationalization for the behavior of the propanol versus the carboxylic acids would suggest that only ionizable functionalities interfere with delignification. Thus, the approach of the AQ parent to reactive sites in an alkali-swollen, negatively charged lignin gel is retarded by charge-repulsion effects from an ionized pendant group such as carboxylate or sulfonate. The aliphatic alcohol group of VII is much less prone to ionization and, therefore, regardless of its hydrophilicity versus AQ, it is not hampered in its approach to reaction sites any more than AQ is. As palatable as this simple explanation is, we tend to reject it at present, since it only explains the poor result from ionizable substituents and offers nothing to rationalize the superior results of alkylated AQs. The hydophilicity theory encompasses both.

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