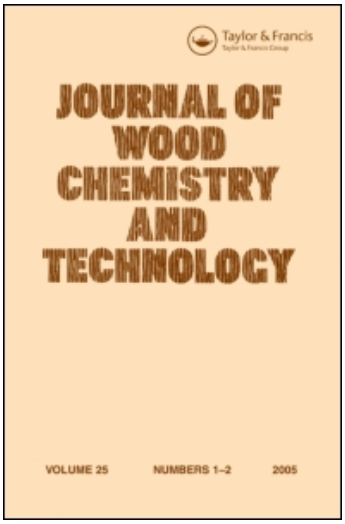

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Carola Storgard-envall[a]; Donald R. Dimmed[a]
[a] The Institute of Paper Chemistry, Appleton, Wisconsin

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DISSOLVING REACTIONS OF ANTHRAQUINONE AT HIGH TEMPERATURES

Carola Storgard-Envall[1] and Donald R. Dimmel[2]
The Institute of Paper Chemistry
P.O. Box 1039, Appleton, Wisconsin 54912

ABSTRACT

The conversion of anthraquinone (AQ) to anthrahydroquinone (AHQ) was determined by mixing AQ with typical pulping constituents (or models of) in a flow-through cell and filtering while hot. The very limited solubility of AQ in 1M NaOH at 160°C is increased significantly (by conversion to soluble AHQ^{-2}) with glucose, kraft lignin, or sodium sulfide. The flow-through filtering cell has also been used to estimate effective methods for reducing AQ and AQ-analogs to AHQ species and to attempt to recover AQ from pulping liquors.

INTRODUCTION

Even though the chemistry of AQ pulping systems has been extensively studied,[3] there are still simple aspects of the AQ story that are undefined. For example, how is AQ converted to AHQ^{-2} during the high temperature phase of pulping? Or, in other words, what species are capable of reducing AQ at 170°C in aqueous alkali? The study reported here is concerned with defining AQ-component reactions, establishing ways to effectively reduce AQ to AHQ^{-2}, and examining one possible method for recovering AQ from pulping liquors.

The small amount of AQ needed during pulping suggests that AQ is involved in a redox cycle process with AHQ, carbohydrates, and lignin (Fig. 1). Numerous experimental observations[3] lend support

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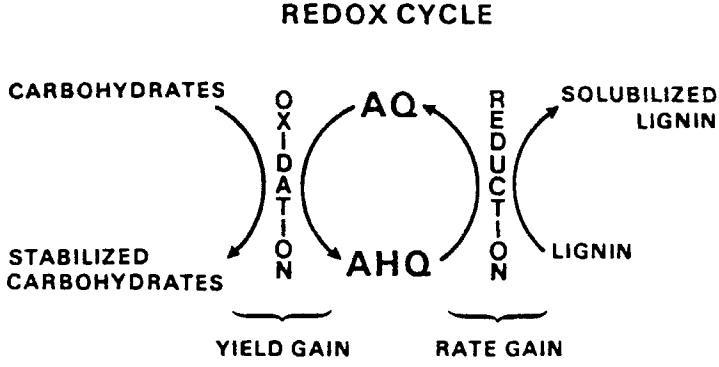


Figure 1. A redox cycle proposal for explaining the catalytic action of anthraquinone during pulping.

to the redox mechanism. The simple picture presented in Fig. 1 is not the whole story, however, since the concentration of "reactive" carbohydrates needed to reduce AQ molecules to AHQ^{-2} ions is low during the high temperature delignification phase of pulping.[4]

Besides oxidation of carbohydrates, AQ may also oxidize lignin structures.[5-7] Reduction of carbohydrates by AHQ also occurs to some extent.[6,8] It has been shown that participation of extractives in the redox cycle is very limited.[9,10] All of these studies involved analyzing structural changes of the non-AQ reactant.

This present study is aimed at looking at what happens to AQ when placed in contact with typical structures found in pulping liquor. The study was not intended to be all inclusive, however. The term "dissolved," as used here, means that the substrate went into solution as a result of disruption of its crystalline lattice and/or because of chemical conversion to a soluble substance.

RESULTS

Equipment and Procedures

The instrument used to study the reductive reactions of AQ in aqueous solutions, above the boiling point of water, was a

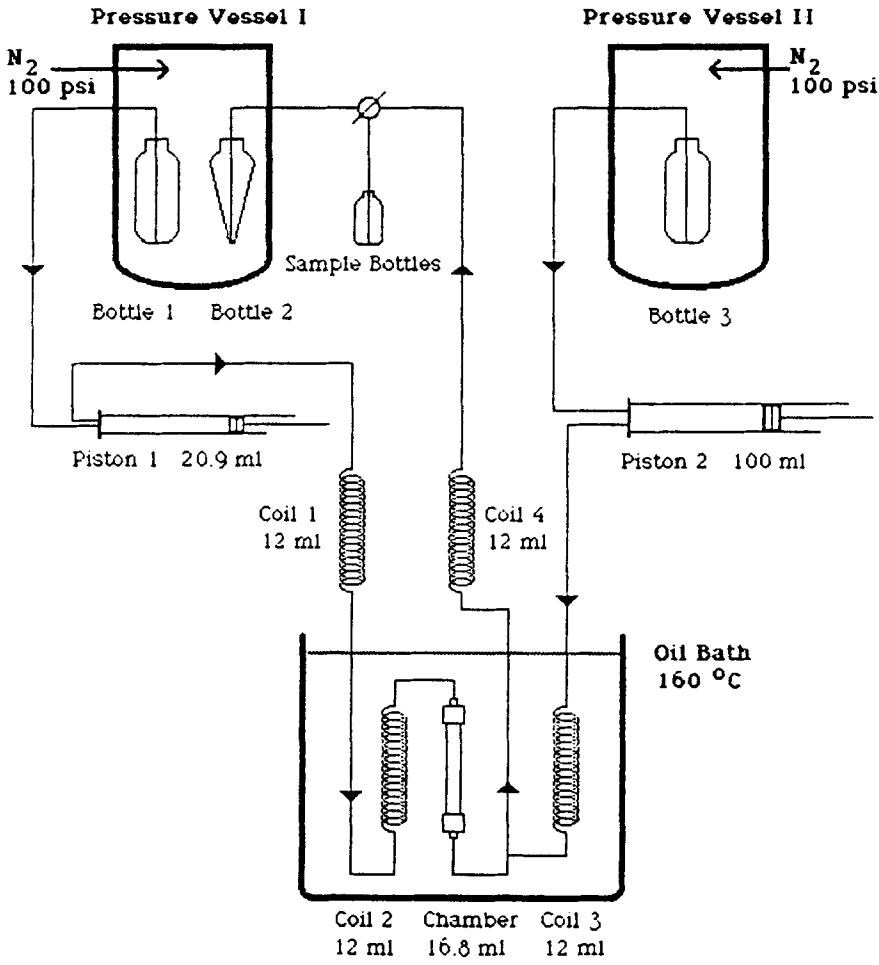


Figure 2. The system used for determining AQ solubilities in aqueous solutions at 160°C.

modified fast-flow reactor[11] as shown in Fig. 2. The system, which is explained in detail in the Experimental Section, allows a "reactant" solution in bottle 1 to be pumped (under nitrogen) through a heated reaction chamber containing AQ. The chamber (Fig. 3) has porous metal filter plates and gaskets on each end.

To establish that the system functioned well we placed benzoic acid in the chamber with some water, flushed the chamber

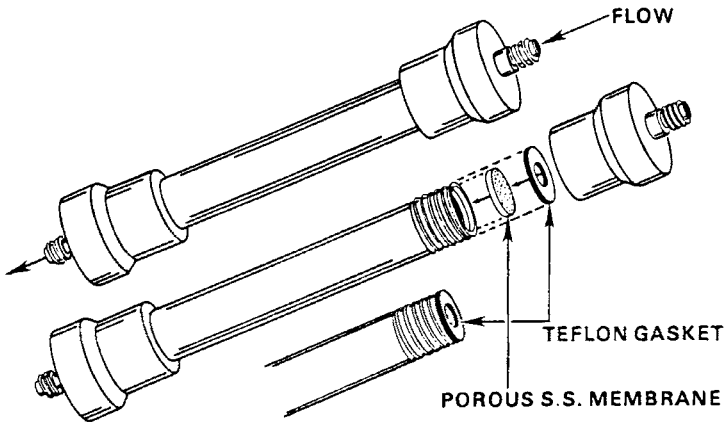


Figure 3. Reaction chamber design.

(heated at 75°C) with fresh water, and collected dissolved benzoic acid in the sample bottle. The solubility value we obtained was within 2% of the reported value[12] at 75°C.

Briefly, the general procedure for determining the extent to which AQ reacts with different substrates consisted of pumping approximately 50 mL of reactant solution through the chamber, which contained 0.1 g of AQ, at room temperature and then 450 mL of solution in increments over about 45 min at 160°C. Generally, six samples consisting of four rapid flushes of the chamber were collected at 160° and analyzed for AQ content. If the substance in the reactant solution reduced AQ to AHQ^{-2}, the collected samples were red in color. A temperature of 160°, rather than 170°, was chosen for safety reasons.

High Temperature Reactions of AQ by Different Substrates

The amounts of AQ that passed through the chamber's filter for several different reactant solutions are listed in Table 1, expressed as percentages of the original amount. The amount recovered from the chamber and the total recovery is also presented.

The substrates examined are listed in increasing order of effectiveness for dissolving AQ; some doubts, however, exist for those substances that were used in limited amounts and where the procedure was varied. The red color of AHQ^{-2} (or $AHQ^{\cdot -}$) was apparent only for the last four entries in the table, meaning that these were the only compounds which "apparently" reacted with AQ.

Anthraquinone did not dissolve to any appreciable extent in any of the reactant solutions **at room temperature.** Its solubility in 1M NaOH at 160°C was only about 8 mg/450 mL or 0.02 g/L. The solubility of AQ appeared to be slightly depressed by most of the simple phenol substrates tested.

The only substance tested which appeared to enhance the solubility of AQ without significantly reacting with AQ was wood rosin. This was probably due to a "soap" effect. An earlier study had established that there is a small amount of reaction between AQ and abietic acid, a major constituent of wood rosin.[9] Linoleic acid, which can also form soaps in alkaline solutions, showed little effect, however.

A somewhat surprising result was the small degree (if any) of dissolution of AQ by vanillin, the benzyl alcohol compounds, and coniferyl alcohol. We expected that these compounds would reduce AQ to AHQ^{-2} and thus the AQ would dissolve. Earlier, we had observed red color in the reaction of anthraquinone monosulfonate (AMS) with α-methyl-benzyl alcohol;[7] working with model compounds, Gratzl and coworkers observed the following relative ease of oxidation of functional groups by AMS: carbohydrate reducing end groups > coniferyl alcohol >> phenolic benzyl alcohols > non-phenolic benzyl alcohols.[5,6]

How do we rationalize these differences? The obvious answer is that if AQ were soluble, like AMS, it probably would have oxidized many of the compounds tested. If the rate of reduction of AQ were somewhat slow, however, alkali promoted reactions of the substrates, such as condensation reactions *via* quinonemethides in the cases of vanillyl and coniferyl alcohols, may dominate. An altered substrate structure may be relatively poor at reducing AQ.

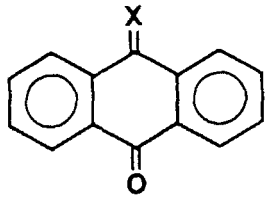
TABLE 1

Dissolution of AQ in 1M NaOH with Various Reagents

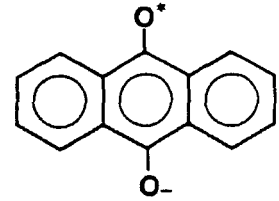
Reactant[a]	Dissolved AQ (%),[b] sample number								AQ (%) in Chamber[c]	AQ (%) Recovered
	0	1	2	3	4	5	6	Total		
Creosol	0.0	0.7	0.4	0.3	0.5	0.4	0.8	3.1	85.3	88.4
Resorcinol	0.0	0.8	0.9	0.8	0.6	1.0	--	4.1	88.3	92.4
Na_2SO_3[d]	0.0	0.7	0.8	0.7	0.8	0.7	0.9	4.6	86.7	91.3
Guaiacol	0.0	0.8	1.1	0.6	0.7	0.7	0.7	4.6	90.0	94.6
Coniferyl alcohol[e,f]	--	1.0	0.6	0.7	0.8	0.5	1.0	4.6	84.1	88.7
Vanillin	0.1	1.2	0.6	1.2	0.9	2.0	--	6.0	85.6	91.6
Vanillyl alcohol	0.1	1.8	0.7	0.6	0.7	0.6	1.6	6.1	89.1	95.2
Acetovanillone	0.1	1.9	1.3	1.1	1.2	0.7	1.2	7.5	85.2	92.7
Linoleic acid[g,h]	0.1	2.0	1.5	1.1	0.7	2.4	--	7.8	55.0	62.8
--	0.2	1.6	1.7	1.0	1.1	1.4	1.1	8.1	78.0	86.1
Methyl-α-D-glucopyranoside	0.1	1.4	1.5	1.7	1.6	3.5	2.2	12.0	86.8	98.8
3-Hydroxybenzyl alcohol	0.0	2.1	1.7	1.7	2.9	3.9	3.5	15.8	76.1	91.9

α-Methyl vanillyl alcohol[e,i]	0.1	1.8	2.9	--	--	--	--	4.8	84.1	88.9
Wood rosin[h,j]	0.1	4.0	5.9	9.3	13.4	7.6	18.6	58.9	29.6	88.5
Kraft lignin[e,k]	--	0.6	4.7	5.8	7.8	24.3	--	43.4	48.2	91.6
Na_2S	0.5	12.5	7.1	7.2	7.8	8.4	9.1	52.6	36.9	89.5
$Na_2S_2O_4$[l]	1.8	59.4	22.2	4	0.1	0.2	0.1	87.8	0.4	88.2
Glucose[l]	0.1	55.8	28.4	8	2.4	1.0	0.5	96.0	1.0	97.0

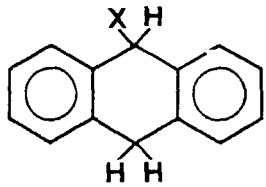
[a]Dissolved in the 1M NaOH flush solution.
[b]Amount of AQ that was removed from the chamber by flushing with reactant solution: expressed as a % of the original, 0 - two flushes at room temperature, 1-5 - four flushes each at 160°C, 6 - two flushes.
[c]Amount of AQ recovered from the chamber by $CHCl_3$ extraction with benzophenone IS and GC analysis.
[d]Flushing solution was 0.77M sodium sulfite and 0.19M sodium carbonate - a simulation of a neutral sulfite cook.
[e]Only a limited amount of reactant was available.
[f]Single flushes of 12-18 mL were used.
[g]Low recovery due to extraction emulsion problems.
[h]0.3M NaOH used instead of 1M NaOH, since the substrate was not soluble in the latter. Samples were not noticeably red.
[i]Placed here in the table based on the first two flushes.
[j]Some interfering signals in the GC analysis.
[k]The amount of AQ and the number of flushes were halved. All samples were dark brown, but the last also appeared to be red.
[l]Coil 2 (Fig. 2) was omitted.



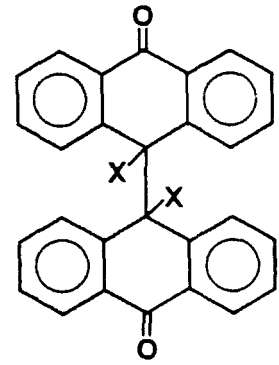
AQ X = O
thiol AQ X = S
anthrone X = H,H



$AHQ^{\cdot}$ * = ·
AHQ^{-2} * = $:^{-}$



dihydroanthracene X = H
anthranol X = OH



bianthrone X = H
bi(hydroxyanthrone) X = OH

Figure 4. Anthraquinone, some of its reduction products, and a possible sulfur analog.

Of perhaps more interest are the compounds that obviously reacted with AQ; these compounds are kraft lignin, sodium sulfide, sodium dithionite, and glucose (the last four entries in Table 1). If these compounds had reduced AQ, several derivatives are possible, including $AHQ^{\cdot}$, AHQ^{-2}, anthrone, anthranol, anthracene, dihydroanthracene, and bianthrones (Figure 4). Many of these reduction products have been observed in AQ pulping liquors[12] and most

TABLE 2

AQ Recovery from a Static Na_2S Experiment

Sample No.	Time from Start (min)	Sample Color	AQ (%) Recovered
1	30	red	3.4
2	35	red	10.1
3	40	yellow	4.7
4	45	clear	1.4
5	50	orange	2.6
6	60	red	6.5
7	70	red	8.8
8	80	red	6.4
9	90	red	6.5
10	100	red	5.5
11	110	red	4.5
12	120	red	4.9
13	130	red	3.1
14	140	red	4.3
Chamber			14.4
			87.1

should be soluble in (hot) alkali. The major reduction products expected are of the anthrahydroquinone type,[13] but our method of analysis (involving an oxidative work-up) would not distinguish AHQ ions from the other possible reduction products.

Dissolution of AQ by kraft lignin showed trends which were quite different from the other "reactive" substrates. The level of AQ removed from the chamber progressively increased with each new flush solution. The last sample collected was a combination of a kraft lignin flush, followed by a 1M NaOH flush; this sample was particularly high in AQ/AHQ^{-2}. An explanation of the observed behavior is not obvious. It is possible that some of the AQ is being dispersed by the soluble lignin and being carried from the chamber as colloidal particles.[14]

The experiment with Na_2S indicated that SH^- is capable of slowly reducing AQ to AHQ^{-2}; the presumed sulfur by-product is polysulfide ion S_xH^-. There is, however, more to these reactions than appears on the surface. In another experiment, 440 mg (12 equiv.) of Na_2S was placed in the reactor with 100 mg of AQ, and the chamber (heated at 160°C) was flushed 14 times (ca. 30-35 mL each time) with 1M NaOH over a period of roughly 2 1/2 hours. The AQ analysis data for the experiment are given in Table 2.

Anthrahydroquinone was continually produced long after the NaSH had been flushed from the chamber. This result suggests a reaction between AQ and SH^- that produces an AQ derivative which can reform AQ at later times. Such a derivative could be monothiol AQ.[15] This material might form via SH^- addition to one of AQ carbonyl groups to give a thiol hemiacetal, which would then lose water. The reverse of these steps at later times would give AQ, in the presence of SH^-; reduction of AQ to a soluble AHQ species by SH^- could then occur. The relative instability of thiol ketones[14] casts doubt, however, on this suggestion.

Another explanation of this "memory effect" is that AQ is reduced by SH^- to anthrone or some type of bianthrone.[14] The latter could presumably be formed by the coupling of two ion radicals and, upon standing in the chamber, break down to soluble ion radicals again. Bianthrone has been observed in the reactions of a lignin model compound and anthrone.[16] If formed, anthrone may slowly dissolve from the chamber as anthranol ion.

Regardless of the exact nature of these reactions, hydrosulfide ion did reduce AQ to AHQ^{-2}. Also, benzyl mercaptans readily reduce AMS.[7] Consequently, there appear to be several ways for the sulfur species in a kraft-type pulping process to keep AQ in the AHQ^{-2} form; this could help improve delignification efficiencies.

Both sodium dithionite and glucose convert AQ to AHQ^{-2} at 160°C with high efficiency, 88 and 96%, respectively. The pattern of AQ conversion followed a regular course of a high degree of conver-

TABLE 3

AQ Recovery from a Prewarmed Glucose Experiment at 160°C[a]

Sample No.	Time from Start (min)	Sample Color	AQ (%) Recovered
0[b]	0	Yellow	0.1
1	10	Dark brown	56.1
2	15	Dark brown	9.2
3	20	Dark brown	2.0
4	25	Dark brown	2.4
5	30	Dark brown	2.5
6	35	Dark brown	0.7
Chamber			22.0
			95.0

[a]See text for details.
[b]Room temperature flush of the chamber.

sion initially, followed by lesser degrees as the AQ reservoir in the chamber was depleted (Table 1). On this basis, these reagents appear to be suitable compounds to use for in situ production of AHQ^{-2} during model studies.

Several temperature and system changes were examined with the glucose and dithionite/AQ reactions. The high degrees of conversion of AQ to AHQ^{-2} reported in Table 1 were accomplished by not prewarming the glucose and dithionite solutions prior to flushing the reaction chamber (coil 2 was omitted). Both glucose and $Na_2S_2O_4$ are unstable in 1M NaOH at 160°C; the former undergoes a series of reactions which destroy its aldehyde group. The aldehyde groups and/or their degradation products are apparently necessary for reduction of AQ, since methyl-α-D-glucopyranoside (a protected aldehyde sugar) gave very little reduction of AQ (Table 1).

An experiment in which the glucose was prewarmed to 160° (coil 2 was in place) prior to passage through the chamber produced the

data shown in Table 3. The first flush of the chamber produced the same level of AHQ^{-2} as before (see Table 1), since the glucose solution in the chamber was cold at the start. Subsequent flushes of the chamber, however, gave much less AHQ^{-2} than previously observed.

A similar experimental arrangement employing glucose at different temperatures produced the following AQ (%) dissolutions: room temperature, 0.2% (light yellow); 70°C, 43% (red); 160°, 22% (dark brown); chamber, 25%; total recovery of 90%. Conclusions which can be drawn from these studies are that (1) alkali degraded glucose appears to be relatively ineffective at reducing AQ to AHQ^{-2} and (2) warming a mixture of AQ and glucose from room temperature to ca. 160° will result in reasonably high conversions to AHQ^{-2}.

With the prewarming coil in place, $Na_2S_2O_4$ at 75°C gave (with 8 multiple flushes) a 67% conversion of AQ to AHQ^{-2}. The same % conversion was observed when the $Na_2S_2O_4$ solution was held in contact with AQ for 30 min at 75°C, warmed to 160°C, and then flushed with 1M NaOH solution (not containing $Na_2S_2O_4$). In this latter experiment 12 samples were collected over about 2 hours. Each sample consisted of several chamber flushes. While the majority of AQ (as AHQ^2) was obtained in the first three samples (41%), subsequent samples were initially red in color. The original dithionite solution should have been completely removed with the first sample; therefore, there must be some sort of "memory effect" similar to what was found in the Na_2S cases.

Finally, a few experiments were performed to see how well AHQ-diacetate hydrolyzed to AHQ^{-2} and sodium acetate in alkali at 150°C. Only a few percent dissolved AQ (presumably AHQ^{-2}) was obtained by treating AHQ-diacetate with either 0.2 or 1.0M NaOH at 60 and 150°C for 15-30 min. Much of the original AHQ-diacetate was found unchanged in the reaction chamber. Experiments with small, sealed pressure vessels gave similar results; some red color was observed, but analysis showed that only small amounts of hydrolysis had occurred.

It is interesting to note that lignin model degradations employing AHQ-diacetate hydrolysis for *in situ* generation of AHQ^{-2} give results very similar to degradations employing AQ-glucose.[17] Since these two methods appear to be very different in their capabilities for generating AHQ^{-2}, it is likely that the excess AHQ^{-2}, generally employed in these studies may be unwarranted. In support of this contention, Poppius has found that AHQ^{-2} "catalytically" cleaves β-aryl ether bonds of lignin model compounds.[18] Model degradations done in the presence of AHQ-diacetate and alkali generally are bright red in color.[17] Based on these observations, we suspect that hydrolysis of the highly water insoluble AHQ-diacetate is slow in simple 1M NaOH but occurs to an appreciable extent when its product, AHQ^{-2}, is needed for reaction.

Dissolution Studies of AQ Analogs

The reactions of 2,3 and 1,4-dimethyl AQ with glucose and dithionite have also been examined. Efficient methods were needed to reduce these methylated AQs *in situ* for some related lignin model studies.[17]

Glucose treatment of 2,3-dimethyl AQ at 160°, without preheating, led to significant reduction to 2,3-dimethyl AHQ^{-2} (initial samples were dark red-brown in color). The conversion (65%) was less than that found with AQ (96%). After 500 mL of glucose flushes, 22% of the 2,3-dimethyl AQ was left in the chamber; another 2% was recovered from the rinse lines to provide an 89% total recovery.

A similar glucose treatment of 1,4-dimethyl AQ left only 2% in the chamber and only a 78% total recovery. The material which was collected (76%) was found in several parts of the system: pressure vessel bottle 2, the rinse lines and a clogged sample rinse line. The lines were rinsed with $CHCl_3$ to recover the 1,4-dimethyl AQ. It appears that 1,4-dimethyl AHQ^{-2} was produced in fairly high yield, but precipitated in the lines as the solutions cooled somewhat. Cleaning the lines was difficult and apparently not thorough, since small amounts of 1,4-dimethyl AQ showed up in the

analyses of the next three experiments (which did not have 1,4-dimethyl AQ as a substrate).

Dithionite experiments with the methylated AQs, in which $Na_2S_2O_4$ was placed in the chamber with the AQs and flushed with 1M NaOH at 160°C, gave for 2,3-dimethyl AQ: 9% collected in the samples and 88% remained in the chamber, providing a 97% recovery. For 1,4-dimethyl AQ, 21% was collected in pressure vessel bottle no. 2, 1% remained in the chamber, and the rest presumably coated the rinse lines (although the line precipitate was not analyzed in this case). Under similar conditions, 41% of AQ was reduced to AHQ^{-2}.

Based on the above results, it is apparent that glucose is more effective than dithionite in reductively dissolving the methylated anthraquinones. Even with glucose, the % reduction of the methylated AQ appears less than that with simple AQ.

Effluent Analyses

Several of the collected AQ and methylated AQ samples were analyzed by GC-MS. The samples examined were the neutral, $CHCl_3$ soluble portions obtained by extracting of the aqueous alkaline flush solutions. The phenolic starting materials and products would remain in the aqueous portion. In general, all that was observed was AQ (and methylated AQs) and the benzophenone internal standard (IS).

All the runs with glucose, however, contained one or two small GC signals in addition to the IS and the kind of AQ used. The new signals were 14 units higher in molecular weight, indicating that the AQ substrate was methylated by glucose; such reactions have been observed previously.[19] Because two GC signals were observed (one minor, one trace), methylation must occur on at least two different sites on the AQ substrates.

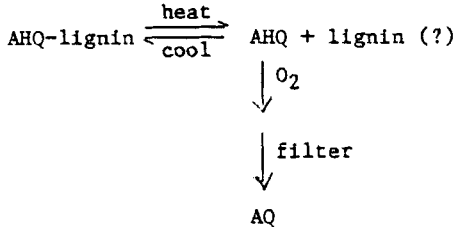
Recovery of AQ from a Soda-AQ Pulping Liquor

Anthrahydroquinone reacts at room temperature with simple quinonemethides (QMs) to form QM-AHQ adducts.[3] Upon warming to

ca. 100°C, simple QM-AHQ adducts are converted to QM-anthrone adducts; further warming to 170°C causes the QM-anthrone adducts to break down to several products, including AQ.[20] Of the compounds that we have studied here, vanillyl and α-methylvanillyl alcohols should form QMs at 160° and then possibly adducts;[21] yet, high recoveries of AQ were observed with these substrates. Consequently, the formation and breakdown of QM-AHQ adducts is a very temperature dependent process.

During soda/AQ pulping of wood, much of the "free" AQ becomes "lignin-bound" AQ. This conclusion is based on a study in which the location of ^{14}C-labeled AQ was determined for pulp and cooled liquor samples taken during the course of a pulping experiment.[22] Based on the discussion above, one has to wonder whether the lignin-bound AQ structures are lignin QM-AHQ adducts which formed upon cooling (but are not present at 170°) or are mainly benzanthrone and similar structures[23] which would be stable at 170°C.

If a large portion of "lignin-bound" AQ is formed only when cooling occurs, then exposure of hot liquor samples to oxygen would convert "unbound" AHQ^{-2} to AQ and free the latter for recovery (Scheme II). Commercially, this could possibly be done with black liquor samples prior to the chemical recovery furnace. Efficient recovery of AQ would greatly improve the economics of soda/AQ and kraft/AQ pulping systems.



Scheme II. Hypothetical pulp liquor reactions and AQ recovery.

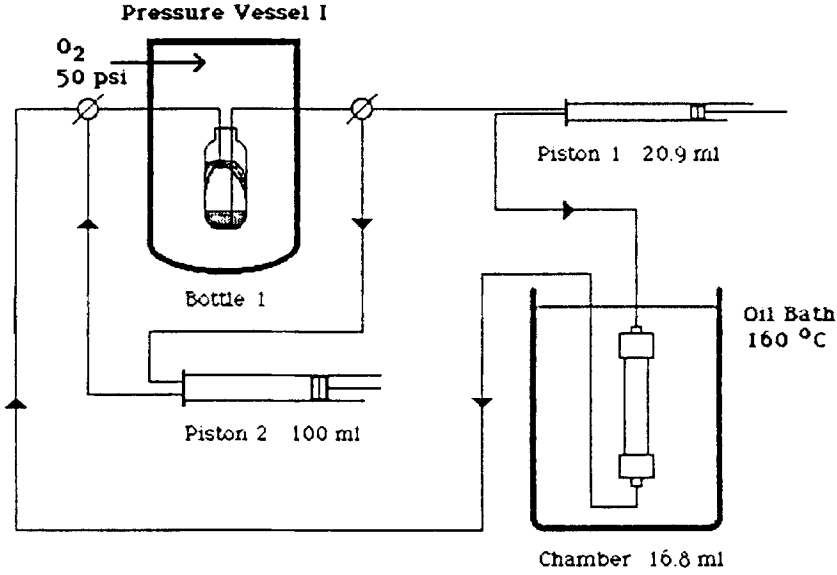


Figure 5. The system used in attempting to recover AQ from pulp liquor samples.

The experimental setup shown in Fig. 5 was employed in an attempt to recover AQ from a southern pine soda/0.1% AQ pulping liquor. The liquor was pumped through the hot chamber which had only one filter in place, the bottom end (away from the flow). The liquor was saturated with oxygen by spraying the liquor at a high speed (with piston 2) into bottle 1 in pressure vessel 1, which had an oxygen atmosphere. The procedure of alternate filtering through the chamber and spraying in the pressure vessel was repeated several times. The liquor outside of the chamber was hot, but not as hot as the 160°C chamber. The experiment was concluded by removing the oil bath, rinsing the chamber with 1M NaOH, and extracting the chamber contents with $CHCl_3$.

Only a small amount of AQ was collected in the chamber. The amount represented only about 10% of the originally charged AQ. Consequently, it would appear that strong lignin-AQ bonds are

present at high temperatures and that the described technique will not allow an efficient recovery of AQ from pulping liquors.

CONCLUSIONS

A method has been developed which provides information on the extent of dissolution of anthraquinone in aqueous solutions at temperatures above the boiling point of water. The method demonstrated that AQ has only a very limited solubility (~ 20 mg/L) in 1M NaOH at 160°C, which is not appreciably affected by the addition of simple phenolics, benzyl alcohols, aromatic aldehyde and ketone compounds, or sodium sulfite. The lack of oxidation of these substrates by AQ, which would have caused AQ to dissolve, was probably related to the heterogeneous nature of these reactions. An analogous water soluble derivative, AMS, reportedly oxidizes several of the tested substrates.[5-7]

Kraft lignin, sodium sulfide, sodium dithionite and glucose cause a significant amount of AQ to dissolve by presumably generating alkali soluble reduction products. The sulfur substrates also appeared to produce an AQ derivative which, with continued heating and solvent changes, afforded a steady amount of a soluble version of AQ. The structure of this "AQ derivative" was not investigated.

The most efficient way to dissolve (reduce) AQ appears to be a reaction with glucose in alkali at temperatures at or above 60°C. This is especially true for two tested methylated analogs of AQ. Dithionite reduction is also effective. The generation of AHQ^{-2} by alkaline hydrolysis of AHQ-diacetate is poor in the absence of a reactant for the AHQ^{-2}.

An attempt to recover AQ by oxidizing and filtering a hot soda/AQ pulping liquor was unsuccessful.

EXPERIMENTAL

All the compounds used were commercially available except for α-methylvanillyl alcohol (prepared by the method of Bailey and

Dence),[24] methyl-α-D-glucopyranoside,[25] kraft lignin[26] (analysis showed 84% Klason lignin and a maximum of 2.4% carbohydrates), and wood rosin.[27]

AQ Dissolution Procedure. The system (Fig. 2) contained two pressure vessels which were filled with 100 psi nitrogen during a run; the nitrogen pressure was needed to prevent the hot aqueous solutions from boiling out of the reaction chamber and coils, and to avoid air contact, which would oxidize AHQ^{-2} back to AQ. Also for this latter reason, deoxygenated water and chamber loading in a nitrogen glove bag were employed.

Solutions were moved through the system by hydraulic pistons (large metal syringes) and a series of on/off valves (most of which are not shown in Fig. 2). The solution lines and coils were constructed of 1/8-inch diameter, type 316 stainless steel tubing. The filters in the 16.8-mL capacity reaction chamber (Fig. 3) were stainless steel with a mean pore size of 0.5 μm. The holding and receiving bottles were made of polypropylene.

The various coils served several purposes. Coils 2 and 3 provided preheated solutions for rinsing the chamber and lines. Coils 1 and 4 were needed for mixing solutions in the chamber. By partially retracting and advancing piston 1 (with the proper valve manipulation), the reactant solutions were periodically moved back and forth through the chamber. Coil 1 provided a safeguard between the hot solutions and piston 1; coil 4 provided 1M NaOH and a reservoir for N_2 during piston retraction. Coil 4 also helped to partially cool the solutions during sample collection and, thus, helped to extend the lifetime of the exit valve.

A typical procedure used was the following. Bottles 1 and 3 (Fig. 2) were filled with 1M NaOH deoxygenated water solutions, the oil bath and the reaction chamber were removed, and the chamber was replaced with tube fittings. By means of the pistons, 1M NaOH was pumped through the entire system under a N_2 atmosphere, at standard pressure. The chamber, containing 0.1 g of AQ in a nitrogen atmosphere, was then rapidly put in place and flushed with

1M NaOH from bottle 1 (via piston 1) until filled. The flushed solutions were removed from bottle 2; analysis showed no AQ was present in these solutions.

The NaOH solution in bottle 1 was replaced with "reactant" solution. The latter contained a substrate at a concentration such that the ratio of substrate/AQ in the 16.8 mL reaction chamber would be 1:1 to 4:1. The chamber was flushed twice (20.9 mL) with reactant solution; the exit lines and coil 4 were rinsed with 1M NaOH solution contained in bottle 3 via piston 2. The two flushes and rinse were collected in bottle 2 and then transferred to a sample bottle (labeled the zero sample). The purpose of these flushes was to completely fill the chamber with reactant solution at room temperature. Generally, little AQ was found in the zero sample.

The next steps involved bringing the system up to 100 psi nitrogen pressure, checking for leaks, putting the prewarmed oil bath in place, as shown in Fig. 2, and starting a timer. Samples were collected at regular time intervals by filling piston 1 with solution from bottle 1, changing some valve positions, and forcing the 20.9 mL solution in the piston through the coils and chamber into bottle 2. This process was repeated three more times for samples 1-5 and one more time for sample 6 as quickly as possible to ensure that all the AHQ^{-2} produced in the chamber was swept out. The exit line from the bath was rinsed with 1M NaOH solution from bottle 3 via piston 2 and heated coil 3. The sample solution (and rinses) in bottle 2 were emptied into a sample bottle by means of a valve manipulation and the pressure difference that existed between vessel I (100 psi) and the sample bottle (atmospheric).

The solutions in the sample bottles were cooled and exposed to oxygen, allowing any AHQ^{-2} to be converted back to AQ. The solutions were then extracted several times with chloroform (the first extract of which contained benzophenone internal standard). The extracts were analyzed by gas chromatography (GC). The GC conditions consisted of a 6 foot glass column packed with 3% OV17 on

100-120 mesh chromosorb W HP; helium flow rate of 20 mL/min; oven temperature of 175°C (1 min) and then 30°/min to 250° (3 min); injector temp. 250°; detector temp. 300°; Hewlett Packard 5890 GC; Perkin-Elmer Sigma 10 Integrator with a 1 min analysis delay. Response factors were determined by examining standard solutions of AQ and benzophenone.

If signals other than AQ and IS appeared in the GC analysis, the samples were analyzed by GC/MS using a 5985B Hewlett Packard GC/MS spectrometer, a 3 foot glass column containing 3% OV17 on 230-270 mesh Gas Chrom Q (Ultrapack), programmed from 150° at 10°/min to 300°C (15 min).

Modifications of this generalized procedure are explained in the text and tables. For example, some of the glucose reactant solutions were not prewarmed prior to being introduced to the chamber. Similar procedures were used for the 1,4 and 2,3-dimethyl AQ solubility studies.

Black Liquor Filtration. Soda/AQ black liquor (100 mL, containing theoretically 25 mg of free and/or bound AQ) was obtained from a cook of 80 g of southern pine wood using 0.1% AQ based on wood, a 3.2/1 liquor to wood ratio, 19% effective alkali, 125° (15 min), then 45 min to 174°, and 174° (18 min) to give pulp of kappa no. 93.

A brief description of the procedure is given in the text; only specific details will be given here. Bottle 1 in pressure vessel I (Fig. 5) was loaded with the 100 mL liquor sample and the system pressurized with oxygen gas to 50 psi. After checking for leaks, the chamber (with a filter on only one end) was immersed into the preheated oil bath (160°C). Four portions (20.9 mL each) were pumped through the heated chamber via piston 1 and back to bottle 1. After a change of valve positions, the liquor in bottle 1 was recirculated four times with the aid of piston 2 (100 mL capacity); the rate of liquor movement during recycle was fast to ensure good exposure of the liquor to O_2 and therefore complete conversion of AHQ^{-2} to AQ. The line feeding bottle 1 had a

stainless steel cap with horizontal holes which sprayed the liquor to the sides of the bottle.

After four flush/recycle procedures, the chamber was cooled, rinsed with 1M NaOH, and extracted with $CHCl_3$. Analysis of the $CHCl_3$ extract by GC using a benzophenone IS gave 2.3 mg one time and 1.8 mg in a second experiment.

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