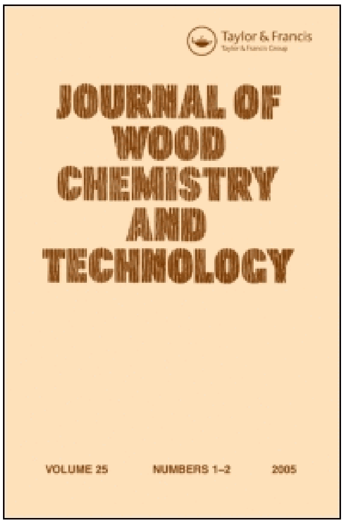

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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Donald Dimmel[a]; Sean Anderson[a]; Perla Izsak[a]
[a] Institute of Paper Science and Technology, Atlanta, Georgia, USA

To cite this Article Dimmel, Donald , Anderson, Sean and Izsak, Perla(2003) 'A Study Aimed at Understanding the AQ/Polysulfide Synergistic Effect in Alkaline Pulping', Journal of Wood Chemistry and Technology, 23: 2, 141 — 159
To link to this Article: DOI: 10.1081/WCT-120021922
URL: http://dx.doi.org/10.1081/WCT-120021922

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 23, No. 2, pp. 141–159, 2003

A Study Aimed at Understanding the AQ/Polysulfide Synergistic Effect in Alkaline Pulping

Donald Dimmel,* Sean Anderson, and Perla Izsak

Institute of Paper Science and Technology,
Atlanta, Georgia, USA

ABSTRACT

When polysulfide (PS) and anthraquinone (AQ) are employed together during alkaline pulping, the yield gain and the extent of delignification during pulping are more than expected based on simple additive effects. The reactions of two lignin model compounds were studied in an attempt to better understand the PS/AQ synergism chemistry. Diagnostic products were not observed with an "electron detector" compound; instead, it appears that PS preferentially oxidized the compound. Reactions of a "clock" compound indicated that PS could not reduce AQ to anthrahydroquinone (AHQ) at 140°C. However, the data indicated that β-aryl ether

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*Correspondence: Dr. Donald R. Dimmel, Institute of Paper Science and Technology, 500 10th St. NW, Atlanta, GA 30318, USA; E-mail: d_dimmel@hotmail.com.

DOI: 10.1081/WCT-120021922
0277-3813 (Print); 1532-2319 (Online)
www.dekker.com

fragmentation efficiencies for PS were better than sodium sulfide, the lignin active reagent in kraft pulping. In addition, AQ was observed to fragment the clock model by nonquinone methide chemistry.

Key Words: Polysulfide; Anthraquinone; Anthrahydroquinone; Pulping; Delignification mechanisms; Synergism.

INTRODUCTION

A synergism exists when using polysulfide (PS) and anthraquinone (AQ) together in alkaline pulping; the pulp yield and extent of delignification are more than expected based on simple additive effects.[1] The reasons for this are not well understood and led us to conduct the studies outlined herein.

The chemistry associated with delignification and yield gains with each individual reagent is fairly well understood. Anthrahydroquinone (AHQ) causes lignin to fragment and dissolve by an ionic addition or electron transfer mechanism.[2–6] Some recent studies suggest that polysulfide might aid delignification by destroying lignin vinyl ether structures,[7] normally a difficult unit to fragment during pulping.[8] The carbohydrate stabilization reactions likely involve transferring two electrons from an enediol to an oxidizing agent, either in one step or two one-electron steps (Fig. 1).[9] The oxidizing agent could be either polysulfide or AQ.

Anthraquinone and its reduced form, AHQ, participate in redox reactions that lead to carbohydrate oxidation and lignin reduction (fragmentation), as shown in Fig. 2.[2] Typically, the redox cycle is shown to involve only AQ and AHQ dianion. However, this simple picture has a serious flaw: to become reduced and soluble in the pulping liquor, AQ needs to react with *soluble* carbohydrate materials. Such reactions are of *no value* with respect to gains in pulp yield. It is only when AQ reacts with insoluble carbohydrates, such as cellulose, that yield gain will be realized. However, because AQ has very limited solubility in 1 M NaOH,[10] one would expect little or no reaction with insoluble, polymeric carbohydrates. A way around this discrepancy is to *first* have soluble carbohydrates reduce AQ to anthrahydroquinone ion radical, a water-soluble material; the ion radical could then oxidize insoluble carbohydrates. In this scenario, the redox cycle would consist of a shuttling back and forth between the partially reduced AHQ ion radical and fully reduced AHQ dianion; thus, AQ is bypassed. There is a large body of evidence that

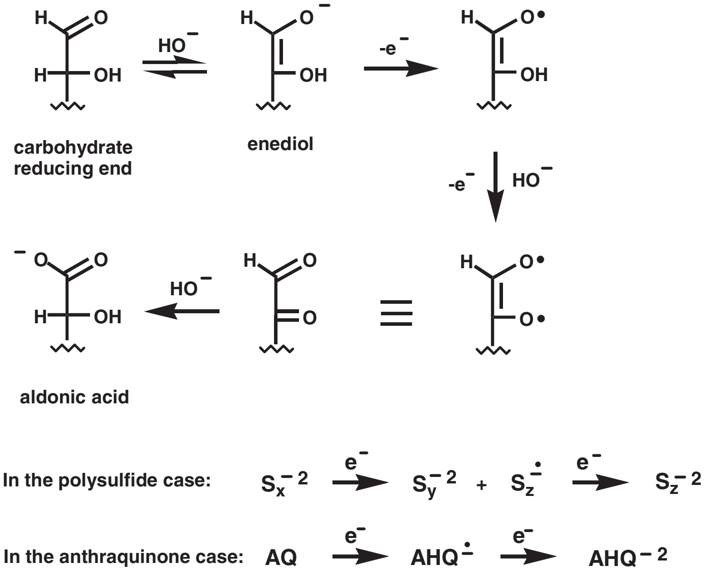


Figure 1. Proposed carbohydrate (enediol) oxidation reactions by AQ and PS.

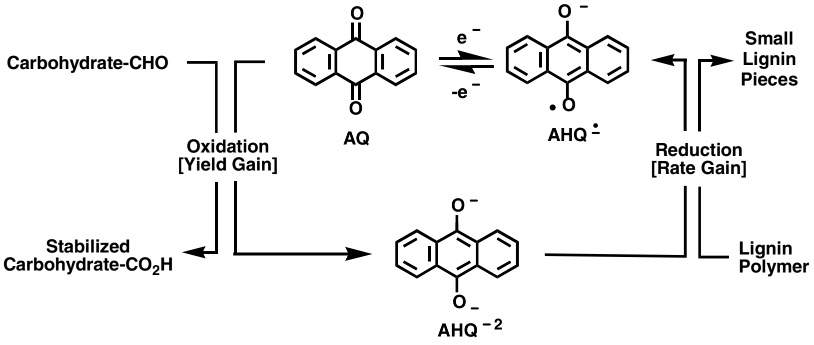


Figure 2. Redox reactions involving AQ, AHQ ion radicals, and dianions that result in carbohydrate stabilization and lignin fragmentation.

supports a single electron transfer reaction occurring between AHQ dianion and lignin that would result in the production of AHQ ion radical and fragmented lignin.[3–6]

So, how could a mixture of polysulfide and AQ enhance yields and pulping rates? The answer might lie in the ability of PS to reduce either

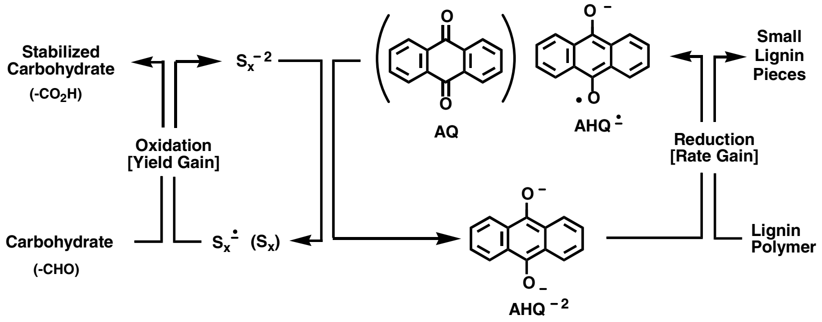


Figure 3. Proposed redox reactions involving polysulfide for carbohydrate stabilization and anthrahydroquinone for lignin fragmentation.

AQ or AHQ ion radical (Fig. 3). With proper oxidation/reduction potentials, the *soluble* polysulfide ion should be much more effective than *insoluble* polymeric carbohydrates at reducing *insoluble* AQ. A two-electron reduction of AQ would produce high levels of AHQ^{-2} that would assist lignin fragmentation. A one-electron reduction of AHQ ion radical would give the same result. The synergism between AQ and PS can be explained by this scheme if either elemental sulfur or polysulfide ion radical is more efficient at oxidizing carbohydrates than polysulfide dianion or AHQ ion radical. Because the oxidation (stabilization) involves electron transfer from the carbohydrate, we expect sulfur or PS ion radical would accept electrons better than PS dianion; it is more difficult to add charge to a species that is already extensively charged. Our research was aimed at establishing the validity of this hypothesis.

RESULTS

An easy test of whether polysulfide could reduce AQ to AHQ in NaOH solution is to just put the reagents together in an Erlenmeyer flask and heat to boiling, while bubbling nitrogen through the solution. With AQ/dithionite or AQ/glucose, you observe the production of the deep red AHQ dianion. A polysulfide solution, which is already orange before the addition of AQ, appeared to darken very little when heated in alkali. Thus, under these conditions, S_x^{-2} is not able to reduce AQ to AHQ^{-2}. The reaction requires that the oxidation potentials of polysulfide and AQ be close in value. Maybe this is not the case. However, such a reduction might be possible between S_x^{-2} and AHQ radical anion. Thus, the easy experiment did not provide the full answer, and other avenues were explored. We examined two approaches, both based on previous work in our laboratory.

Reactions of the Electron Transfer Detector Compound

Our first approach involved studying the chemistry of **1**, a compound that we term the "electron transfer detector (ETD)" compound.[4,11] In base at 135°C, it is converted to a quinone methide (QM **2**); reagents that can transfer electrons to the QM lead to the reduction products **3** and **4**, highlighted in Fig. 4. Cyclization to a 5-membered ring (**4**) is evidence that radical intermediates were formed.

If less than one equivalent of AHQ is present, we expect incomplete reaction and less formation of reduced products. However, if polysulfide is present in excess amounts, the AHQ dianion might be regenerated. The reaction of 5 equivalents of polysulfide and 0.1 equivalent of AHQ may produce the high levels of reduced products that were observed when using 2 equivalent of AQ and 5 equivalent of glucose.[4]

When heated with polysulfide at 135°C, the ETD compound did not provide the expected products. Instead, we observed two principal

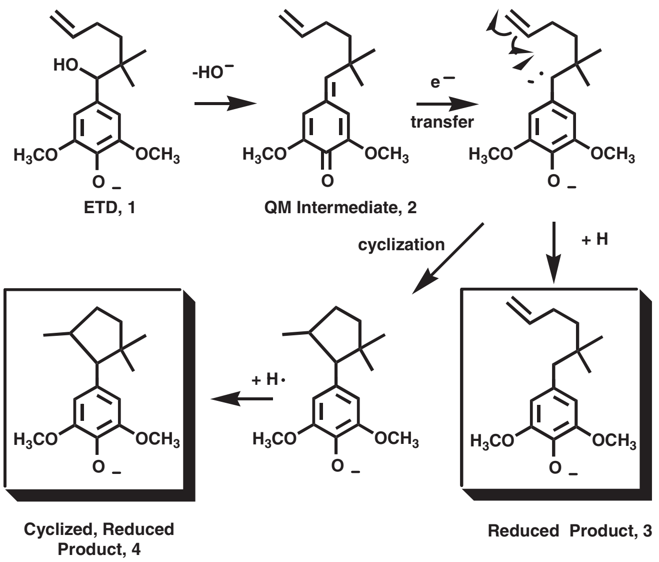
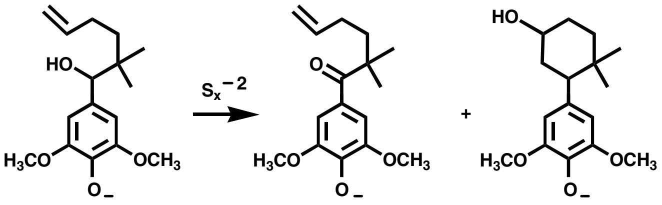


Figure 4. General reactions of the ETD compound with an electron transfer agent; diagnostic products are indicated with the boxes.

products, which were tentatively assigned structures based on GC/MS evidence and on our general knowledge of MS fragmentation patterns of similar compounds.[12] One of the products was obviously the ketone **5**, an expected oxidation product. The spectrum displayed a molecular ion two units less than the ETD compound and exhibited a strong acylium ion (ArC=O$^+$) signal. The spectrum of the other product indicates it was an isomer of the ETD compound, suggesting the 6-membered ring cyclic structure **6**. Such a product would be indicative of a carbocation being generated at the benzylic carbon.



1^- **5^-** **6^-**

(1)

Based on this discouraging result with PS, we did not pursue further experiments with AQ/PS/ETD compound mixtures. Instead, we examined an alternative approach to studying possible PS/AQ electron transfer chemistry.

Reactions of the Clock Compound

The "clock" compound, β-aryl ether model **7**, has previously been used to determine the relative efficiencies of reagents to induce β-aryl cleavage reactions.[13] Model **7** generates QM **8** at high temperature in alkali (Fig. 5, path a). The side chain terminal hydroxyl group, probably ionized at high pH, can internally react with the QM intermediate to give a cyclic product **9** (Fig. 5, path b). The rates of other QM reactions can be "clocked" relative to the cyclization event by determining the yields of different products in comparison with the yield of the cyclic product **9**. Besides cyclization, the model can react with pulping chemicals to give β-aryl ether cleavage (via path c, Fig. 5) or with base to give vinyl ether **10** (path d). A high proportion of scission vs. cyclization signifies conditions corresponding to efficient delignification.

Very little cyclization occurs when 5 equivalent of AHQ is reacted with **7**.[13] In NaOH alone, the major product is cyclic product **9**. A

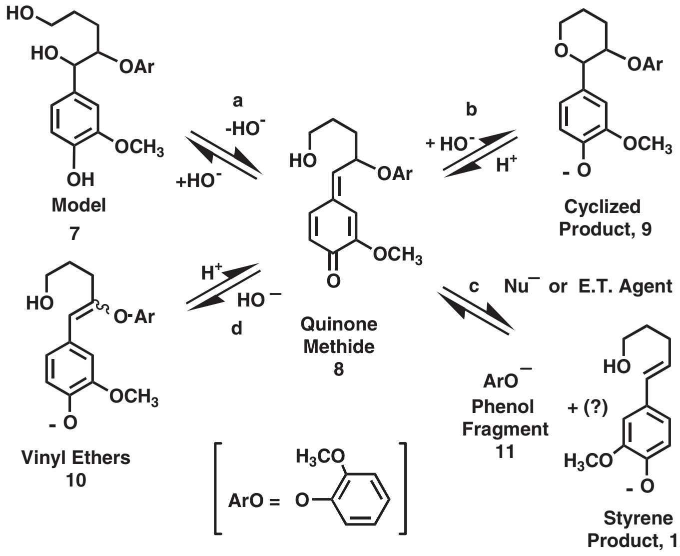


Figure 5. Potential reactions of the quinone methide (**8**) derived from model **7**.[8]

mixture of NaOH and NaSH (kraft conditions) gives roughly an equal mixture of fragmentation and cyclization. If only 2 equivalents of AHQ are used in the model **7** degradations, the efficiency of fragmentation falls off by ~50%. However, the efficiency can be restored to 100% by adding 50% methanol to the 2 equivalent AHQ reaction. The addition of 50% methanol to soda or kraft reactions of **1** had no positive benefits. To summarize our previous model **7** studies, we have seen a large synergism for AHQ/methanol and small synergism in the case AHQ/Na_2SO_3.[13] The system looked to be an attractive one in which to observe possible synergism between AQ and PS.

Preliminary Reactions of Model 7 with AHQ

We examined three ways to generate AHQ; each employed deoxygenated aqueous NaOH. The first way involved forming, isolating, and adding AHQ to a reaction vessel containing model **7**.[13] However, achieving anaerobic conditions during all these steps, with the crude glove box at our disposal, proved difficult.

Alkaline hydrolysis of AHQ-diacetate gives AHQ^{-2}; however, the hydrolysis reaction is very slow because of the very low water solubility of the diacetate. Fearing that hydrolysis would be slower than quinone methide generation, we first heated AHQ-diacetate with aqueous NaOH for an hour at 150°C in a sealed pressure vessel under anaerobic conditions in the absence of **7**. The reaction vessel was cooled, opened in a glove box in a nitrogen atmosphere, compound **7** added, resealed, and heated again.

The third way was to generate AHQ by reducing AQ with sodium dithionite in an aqueous NaOH solution containing **7**. Appropriate controls demonstrated that dithionite did not interfere with model **7** reactions. We principally used this last method. The dithionite reduction consumes 4 equivalents of NaOH. All reactions were conducted with 45 equivalents of NaOH/equivalent of **7**. For example, when 2 equivalent each of AQ and dithionite were used, 53 equivalent of NaOH were employed to give 45 equivalent of NaOH after the reduction reaction.

Unlike our previous study,[13] the reaction solutions were not acidified prior to HPLC analysis and a different internal standard, vanillyl alcohol, was employed. Constituent elution times changed somewhat; our previous internal standard no longer had a unique elution time. The high sample pH of the injected sample is nullified by dilution during the HPLC processing. These small changes allowed us to see a styrene product not previously seen, which helped explain the chemistry of PS pulping; more will be said about this later.

A series of 140°C reactions of **7** with different levels of AHQ (AQ/dithionite) produced the data shown in Fig. 6. There is no basic

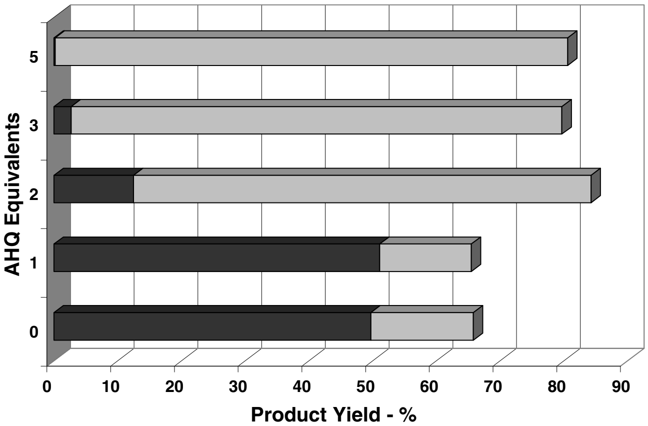


Figure 6. Reactions of **7** at 140°C for 1 h with different levels of AHQ; black area = cyclized product **9**; gray area = fragmentation product **11**.

difference in the yields of **9** (cyclization) and **11** (fragmentation) when using 1 equivalent or no AHQ. However, as the AHQ relative concentration was increased, fragmentation took on greater importance; at 5 equivalent of AHQ, **11** was observed in only 0.2% yield. While we strived for anaerobic conditions, it appears that our deoxygenated water still contained $\sim 1^+$ equivalent of O_2, enough to convert some AHQ back to AQ. Anthraquinone has much less effect on **7** in NaOH than AHQ; more will be said about this later. A preliminary 150°C run, involving different levels of AHQ-diacetate and NaOH, gave results similar to those shown in Fig. 6.

As seen in Fig. 6, when fragmentation is high, cyclization is low. However, there was not always a perfect correlation between the two. To get better accuracy, we focused on the cyclization product (**9**) yield, because its HPLC signal was always Guassian; the guaiacol signal was not always Guassian, suggesting the presence of an occasional interfering signal.

Reactions of 7 with Na_2S_x, NaSH, and Combinations with AHQ

Because polysulfide decomposes at high temperatures in alkali,[14] we conducted the PS/model **7** reactions at 140°C. Figure 7 highlights the results of several 140°C cooks of **7** with different reagents and

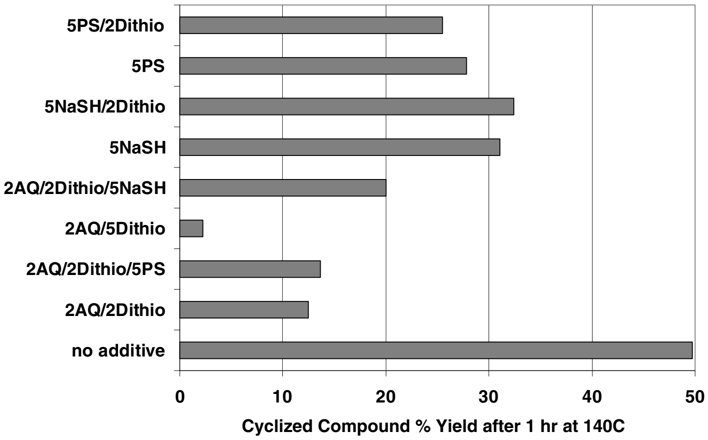


Figure 7. Amount of compound **9** formed when reacting **7** at 140°C for 1 h with different reagent combinations.

combinations of reagents, all performed under anaerobic conditions for 1 h. The low level of cyclization product **9** in the case of 2 equivalents of AQ and 5 equivalents of dithionite signifies highly efficient fragmentation. Both residual oxygen in the solution and reaction with QM **8** consume the initial AHQ^{-2} in the solution; however, the excess available dithionite converts AQ (or AHQ ion radical) back to AHQ^{-2}, thereby effectively raising the concentration of AHQ^{-2} to ~5 equivalents for reaction with QM **8**. Note that 2AQ/2dithio/5PS and 2AQ/2dithio have about the same effectiveness, meaning that *PS is not reducing AHQ ion radical or AQ*.

Product distributions when reacting **7** at 140°C for different time periods with 2AQ/2dithio/5PS are shown in Fig. 8. The purpose of doing a time study (several were done) was to verify reaction trends, rather than relying totally on the data of one time to draw conclusions. The trend observed in this case models what we have previously seen with only modestly effective fragmentation conditions.[13] The cyclized compound can reverse back to the QM **8** and be lost with time.

Dithionite causes no increase in fragmentation of **7**; this is apparent from the similar efficiencies of 5PS/2dithio to that of 5PS and of 5NaSH/2dithio to that of 5NaSH. It is also apparent that 2AQ/2dithio is better at fragmenting the model than 5NaSH, even considering that some of the AHQ is consumed by O_2-reactions. The fact that AHQ $\gg$ NaSH has been noted before.[13] You might think that 5NaSH/2AQ/2dithio would be as good as, or even better than 2AQ/2dithio, because NaSH positively effects fragmentation. The data below appear to contradict this conclu-

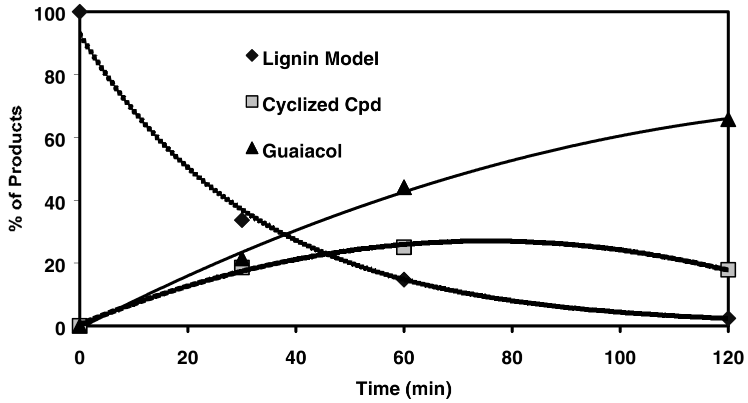


Figure 8. Product distribution when reacting **7** at 140°C for different time periods with 2AQ/2dithio/5PS.

sion; however, it is likely that the degassed NaSH solution may have contained some dissolved oxygen that effectively hurt the level of AHQ^{-2} in solution.

Comparison of Model 7 Fragmentation Efficiencies for Na_2S_x and NaSH

The Fig. 7 data suggest that PS may be a somewhat better reagent than NaSH in fragmenting model **7** at 140°C. Additional experiments were conducted to establish this fact. The product distribution when reacting **7** at 140°C for 1 h with different levels of PS (Fig. 9) indicates a good correlation of PS concentration and fragmentation efficiency. At 10 equivalents of PS the yield of guaiacol was 70% and cyclic compound < 10%.

Table 1 gives data that compare the product distribution for reacting **7** for 1 h at 140°C with either 5 equivalents of PS or NaSH.

The data clearly demonstrate that polysulfide is more effective than sodium sulfide in fragmenting model **7**.

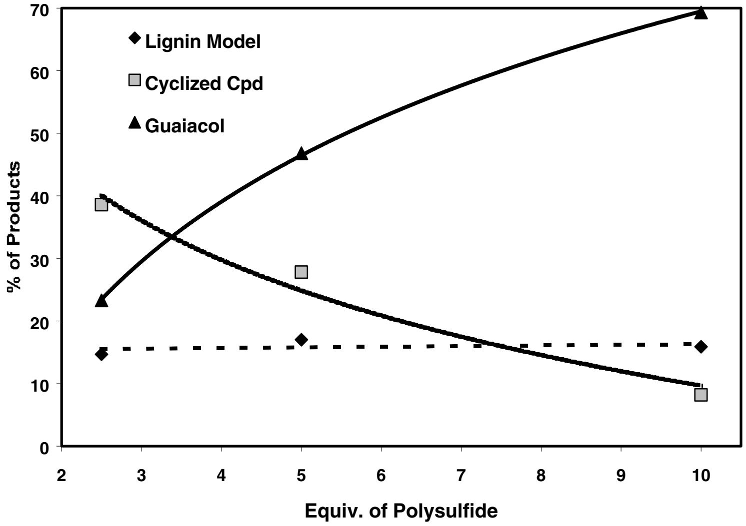


Figure 9. Product distribution when reacting **7** at 140°C for 1 h with different levels of PS.

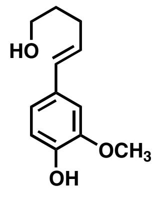
Table 1. Product distribution for three 1-h 140°C reactions of **7** with either 5 equivalents of PS or NaSH.

Additive	% Cycl. Cpd. (**9**)	% **9** Av.	% Guaiacol (**11**)	% **11** Av.
PS	27.8, 25.5, 25.0	25.8	46.8, 45.0, 44.1	45.3
NaSH	31.1, 32.4, 31.9	31.8	32.1, 32.9, 33.4	32.8

Model 7 Reaction Products

In general, the yields of **7**, **9**, and **11** totaled 80–100%. Reactions involving AHQ and PS displayed an HPLC signal that we assigned to styrene structure **12**. Complete ultraviolet spectra for eluting HPLC signals were occasionally recorded. Compounds **7**, **9**, and **11** had similar UV spectra, while the styrene component **12** had a spectrum closely matching that of coniferyl alcohol.[15] The fact that the levels of **11** and **12** were closely related (discussed later) argued for the structural assignment of **12**. The only other major signals observed were fast eluting ones in the cases of NaSH and Na_2S_x cooks, which were assigned to UV-absorbing inorganic sulfur compounds; such signals were present in PS solutions containing no model. An example chromatograph is provided in the Experimental section.

Other possible products include: polysufide adduct **13** and ketone **14** (or its hemiacetal **15**). The relatively high material balance and clean product distribution indicate that these components are probably not present. The UV evidence indicates that these are not coeluting with other components; it is unlikely that they have very long retention times (outside our 25-min HPLC run time).



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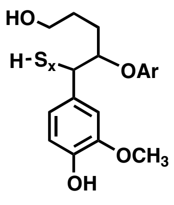

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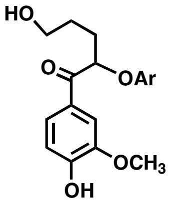

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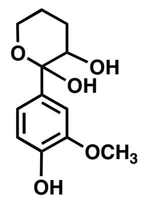

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There was a good correlation between fragmentation and formation of styrene **12** when either AHQ or polysulfide was employed (Fig. 10). The absolute yield values for **12** are not really known; we had to assume

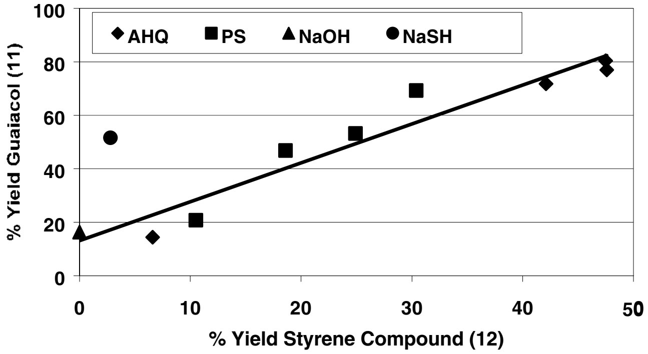

Figure 10. Correlation of the levels of styrene **12** and guaiacol (**11**) when treating model **7** at 140°C for 1 h with different additives.

an HPLC response that could be inaccurate, because its UV spectrum is quite different from the other components. This type of product is significant in AQ pulping and AHQ lignin model reactions, but produced in only low (or no) yields in soda or kraft conditions.[16] The same trend is apparent in Fig. 10. In general, styrene products are not very stable and are rarely seen in levels comparable to guaiacol (**11**), its coproduct.

Reactions of Model 7 with AQ

Finally, the data in Table 2 indicate that AQ can cause model fragmentation. The process is not as efficient as AHQ-induced fragmentation via a quinone methide intermediate. While there is some simultaneous NaOH-induced fragmentation, the AQ reaction appears to operate outside of QM chemistry, possibly by an α-oxidation mechanism. Prior research indicates that such chemistry is possible with lignin models and presumably with lignin during pulping.[17] There were no new signals in the AQ reaction HPLC chromatogram indicative of oxidation products.

The AQ-induced fragmentation reaction mixture showed $<2\%$ styrene product. The level of reacted starting material **7** with >3 equivalents of AQ was much lower than normally observed after a 1-h reaction. All reactions, except these AQ reactions, typically result in 15–18% **7** remaining after 1 h, presumably because these reactions are going through a rate-determining slow quinone methide generation. The AQ reaction adds a new way of fragmentation.

Table 2. Product distribution for alkaline 140°C reactions of **7** with different levels of AQ.

AQ equiv.	**7**%	**9**%	**12**%	**11**%
0	16	49	0	16
1	11	41	2	24
3	7	29	1	41
5	7	29	2	38

CONCLUSIONS

Our studies show that polysulfide is apparently incapable of reducing (transferring electrons) anthraquinone or anthrahydroquinone radical anion. If it had, a mixture of 2AQ/5$Na_2S_2O_4$ and 2AQ/5Na_2S_x would have given similar product distributions with model **7**. The former was much better at inducing **7** to fragment, rather than cyclize. Even so, Na_2S_x was better than NaSH at causing **7** to fragment.

The relative model fragmentation efficiencies were AHQ > PS > NaSH. Because the former is believed to operate by electron transfer to a QM and the latter by way of a QM adduct, PS must be a poorer electron transfer reagent than AHQ^{-2}, but better than NaSH at causing adduct fragmentation. The product distribution, especially the generation of styrene **12**, resembled that of AHQ/**7**, the electron transfer case. Our data do no support α-oxidation of **7** by PS, which might also provide fragmentation. A reaction scheme supporting our observations is shown in Fig. 11.

In the case of heating the ETD compound **1** in alkali in the presence of PS, quinone methide **2** (and possibly a PS/QM adduct) was reversibly produced. However, there is no β-aryl ether unit in the structure, so fragmentation is not an option. Any electron transfer reactions between QM **2** and PS would have given products **3** and **4**. Because these products were not observed, the relative rate of electron transfer must be slow in comparison to benzylic oxidation and possible cation cyclization. Such observation might indicate that electron transfer is not the mechanism by which PS causes model **7** to fragment.

EXPERIMENTAL

A more detailed description of the experimental protocol and HPLC analysis can be found in an earlier publication.[13] The HPLC analysis was slightly modified; the column was a Spheri ODS-2 (250 × 4.6 mm,

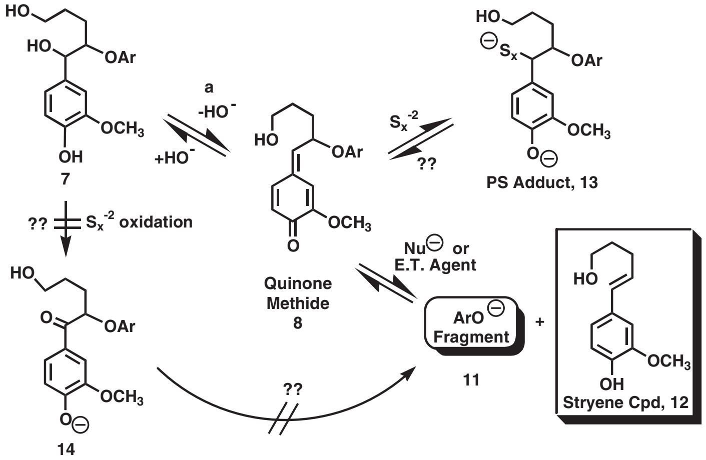

Figure 11. Proposed reactions of model **7** in the presence of polysulfide.

packing size = 5 μm) column and the flow rate was 1.0 mL/min. A UV diode array detector, set at 230 nm, was used.

Polysulfide was generated by adding elemental sulfur to a 30% sodium sulfide solution. The PS concentration was determined by the difference between two potentiometric titrations with $HgCl_2$, which measured the NaSH concentration in each case. The first titration was of the prepared PS solution. The second was after treating the prepared PS solution with sodium–mercury amalgam, which reduced the sodium polysulfide present to NaSH. The procedure is TAPPI Method T694-om90, which was withdrawn in 1997.

The nanopure water, which was degassed by boiling in the presence of a fast-flowing stream of nitrogen, was used in the reactions and for making up solutions of 0.1 M NaOH and 0.1 M $NaOH/Na_2S_2O_4$. Polysulfide and NaSH solutions were similarly degassed. Reagents were weighed and solutions prepared inside a glove box flushed with ultrahigh-purity nitrogen. Weighed AQ and solutions of 0.1 M NaOH, alkaline $Na_2S_2O_4$, NaSH, Na_2S_x, and water were added by a pipette to 4.5-mL pressure vessels (bombs). The amount of NaOH solution and water added were done in such a way to provide 3.5 mL of solution, having a residual of 45 equivalents of NaOH after AQ reduction. The bombs were sealed inside the glove box and then heated in a hot fluidized sand bath at 70°C for 30 min to insure complete reduction of AQ to AHQ^{-2} by sodium dithionite; this temperature is well below that needed for quinone methide generation.[18]

The bombs were removed from the bath and the bath temperature increased to 140°C before the bombs were replaced in the sand bath. The bombs were removed after specific time periods, cooled quickly with cold water, and opened in the air. The bomb contents were filtered through an HPLC Acrodisc syringe filter (0.45-micron pore size, 0.25-mm diameter) into an 8-mL vial. The bomb was rinsed with a 1.0-mL aliquot of 0.1 M NaOH, which was added to the vial. Then 0.50-mL of a 0.00075 M solution of vanillyl alcohol internal standard was added and the vial was sealed, shaken, and a small aliquot removed for HPLC analysis.

Component response factors were determined by injecting solutions of known ratios of compound and internal standard onto the HPLC column; response factors for compounds **7** and **9** were 2.07 and for **11** the value was 0.55. The response factor for styrene compound **12**, which was not available to be tested, was assumed to be the same as compound **7**. The large difference in response factors for **7/9** vs. guaiacol (**11**) was also observed previously[13]; this means that the signal intensity of **11** will be small in comparison with the other components. An example chromatogram is provided in Fig. 12. The elution times of the key components were: vanillyl alcohol at 3.2 min, guaiacol (**11**) at 5.7 min, model **7** at

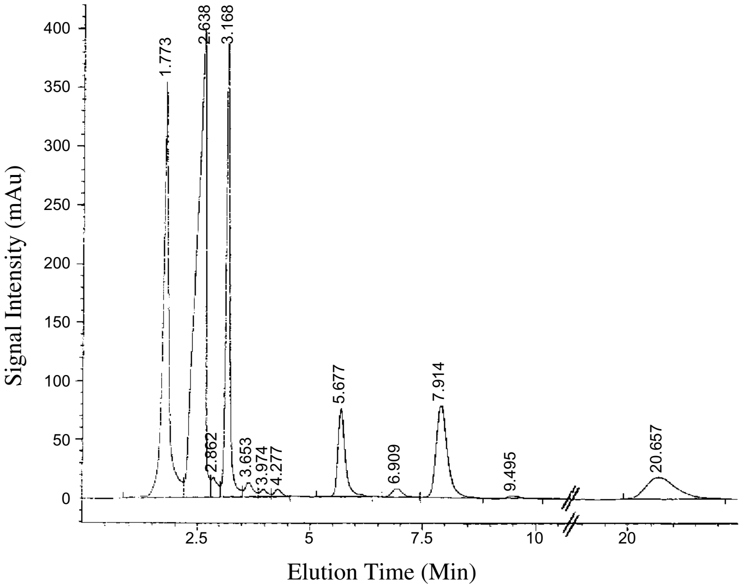

Figure 12. HPLC chromatogram of the product mixture of a 2-h 140°C reaction of model **7** with 2AQ/2dithio/5PS.

6.9 min, styrene compound **12** at 8.0 min, and cyclic compound **9** at 20.5 min. Note: Figure 12 is of a 2-h run, in which the residual starting material amount is low. Except for **12** and the fast eluting inorganic sulfur species, all the other components displayed similar UV spectra, namely a strong signal <210 and weak signals at 220–230 and 270–280 nm. Styrene **12** displayed strong signals at 213 and 268, together with a modest signal at 300 nm. The 1.7 and 2.6-min retention time components were also seen in a reaction blank (PS/NaOH, but no lignin model). The 2.6-min component had strong absorbance maximum <200 and at 210 nm. The 1.7-min component, which was seen in variable amounts with nearly all injections, even those with no sulfur species present, was considered to be solvent related; it had strong broad absorbance band at ~210 nm.

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