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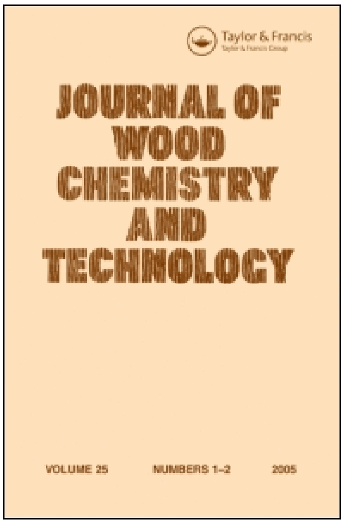

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(3), 261-283 (1996)

FUNDAMENTAL STUDY OF RELATIVE DELIGNIFICATION EFFICIENCIES (I): CONVENTIONAL PULPING SYSTEMS

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ABSTRACT

Reactions of a β-aryl ether model **1** [1-(4-guaiacyl)-2-(*O*-guaiacyl)-1,5-pentanediol] provide relative rates of pulping reactions that involve quinone methides (QMs). Model **1** was reacted under soda, kraft, soda/anthraquinone (AQ), and sulfite conditions. All alkaline conditions displayed the same lignin model disappearance rate, indicating a common rate determining step -- QM formation. The results indicate that reactions between pulping reagents and QM are reversible in most cases and that anthahydroquinone (AHQ) was the most effective reagent at facilitating β-aryl ether cleavage. Alkaline sulfite cooks of **1** gave a similar product distribution as a soda cooks of **1**; however, an α-sulfonate **11** [1-(4-guaiacyl)-2-(*O*-guaiacyl)-5-hydroxypentane-1-sulfonic acid] was the predominant product when **1** was reacted under neutral sulfite conditions. Model **11** reverted back to a QM at high pH values. All of the sulfite cooks of **1** showed only low levels of β-aryl ether cleavage. This paper is the first in a three-part study designed to examine β-aryl ether cleavage in multicomponent pulping systems (e.g., alkaline sulfite/AQ/methanol [ASAM]).

INTRODUCTION

Kraft and sulfite pulping are the two principal systems used to convert lignocellusosic materials into chemical pulps. Kraft has dominated for several reasons.[1] Chemical recovery of spent liquors has been a major drawback of sufite pulping; however, developments over the past decades may have resolved this issue.[2,3] Sulfite pulping yields strong pulps with higher yields than the kraft process.[2,4-6] In addition, the sulfite process produces easily bleached pulps[4-6] with less offensive odor.[2] These are important attributes in today's environmentally conscious society.

Studies in the past have investigated the fundamentals of sulfite pulping chemistry,[7-10] however, the current understanding of delignification reactions, such as β-aryl ether cleavage, is still vague. We sought to better understand the sulfite-lignin chemistry, especially in the newer systems that use anthaquinone (AQ)[11] and/or organic solvents.[12]

One of the difficulties in establishing the detailed chemistry of pulping systems is the dominance of the delignification rate by the first step in the process -- formation of a quinone methide (QM) intermediate. The rates of subsequent steps are difficult to determine; however, the rates of these steps are critical to the partitioning of the QMs toward fragmentation processes (β-aryl ether cleavage) as opposed to undesirable competing reactions (vinyl ether formation and condensation reactions).[13]

We have found that the fast QM reactions can be studied by employing a model that has a built-in "clock" reaction.[14] This model (**1**) has a β-aryl ether bond and a phenol unit capable of generating a QM (**2**) at high temperature in alkali (Fig. 1, path *a*). The long alcohol side chain in **1** is atypical of lignin, but is critical to our mechanistic studies. The terminal hydroxyl group, probably ionized at high pH, is capable of internally reacting with the QM intermediate to give a cyclic product **3** (Fig. 1, path *b*).

The rates of QM reactions can be "timed" relative to the cyclization event by determining the yields of different products in comparison to the yield of **3**. Besides cyclization, the model can react with pulping chemicals to give β-aryl ether cleavage (*via* paths *c* or *d*, Fig. 1), with pulping chemicals to yield new products (such as adducts, path *c*), or with base to give a vinyl ether **7** (path *e*). A high proportion of scission versus cyclization signifies a set of conditions corresponding to efficient delignification.

Our overall objective is to use the reactions of **1** to probe the proficiency of modified pulping systems, such as kraft/AQ,[15] organocell (soda/

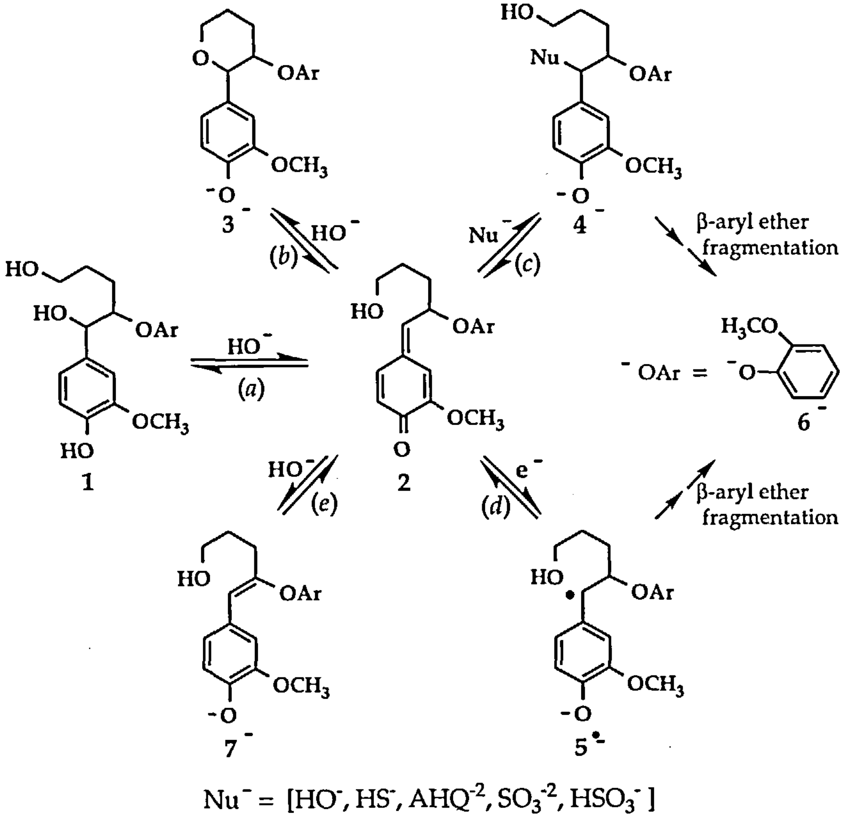


Figure 1. Potential reactions of model **1** and its corresponding quinone methide **2**.

AQ/methanol),[12] and alkaline sulfite/AQ/methanol (ASAM),[12] to promote β-aryl ether fragmentation. These modified systems could have reagent-reagent and reagent-solvent interactions that could facilitate β-aryl ether cleavage. Our approach to understanding the chemistry of multi-reagent systems has involved a three-part study: the reactions of model **1** with (a) individual reagents, (b) combinations of reagents, and (c) reagents in alcohol/water mixtures. The first area is described herein; the other areas are considered in the accompanying papers.[16,17]

RESULTS

Soda, Kraft, and Soda/AHQ Reactions of Model 1

Model 1 was heated in water in sealed reaction vessels at 150°C for various time periods in the presence of 25 equiv. of NaOH alone, or with 5 equiv. each of either NaSH or anthrahydroquinone (AHQ, the reduced form of AQ). Products were quantitatively analyzed by reverse phase liquid chromatography (LC). Previous studies of model 1 employed gas chromatography (GC) to quantify the amounts of liberated guaiacol (6) and cyclized compound (3) produced during reactions; the disappearance of the starting material was not quantified because model 1 undergoes varying degrees of dehydration during the GC analysis, leading to vinyl ether byproducts.[14] Dehydration is not a problem during LC analysis; thus, the whole product mixture can be easily quantified.

The rate of disappearance of model 1 is the same for the soda, soda/AHQ, and kraft cases (Fig. 2). This indicates a common slow step, namely QM formation. In terms of product differences, AHQ gave high levels of fragmentation and little cyclization; soda was just the reverse; and kraft conditions were in between (Fig. 3). The data agree with previous results: the fragmentation efficiency (delignification effectiveness) follows the order AHQ > kraft > soda.[14] The soda degradation of model 1 produced very small amounts (<10%) of vinyl ether 7 [14] that was not observed in the kraft and soda/AHQ cases.

Alkaline Sulfite Reactions of Model 1

There is a complex system of inorganic equilibria present during sulfite pulping.[18,19] The pH of a sulfite solution determines the predominant active ion in solution.[18] Equations (1)-(3) represent aqueous equilibria occurring between hydrated sulfur dioxide, bisulfite ion, and sulfite ion, respectively. The pK_a values listed are at standard conditions (25°C and 1 atm.)[18,19] and may differ from the actual constants during pulping since equilibria are thermodynamically controlled.

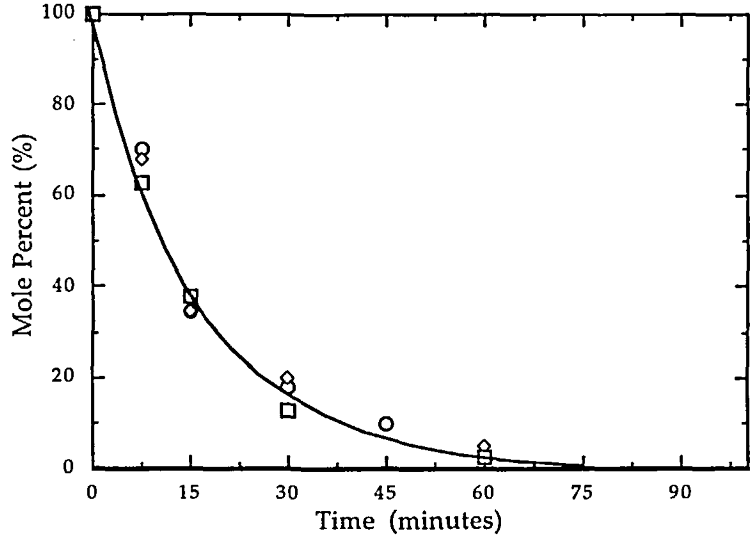


Figure 2. Disappearance of 1 as a function of time at 150°C for soda (□), kraft (◇) and soda/AHQ (○).

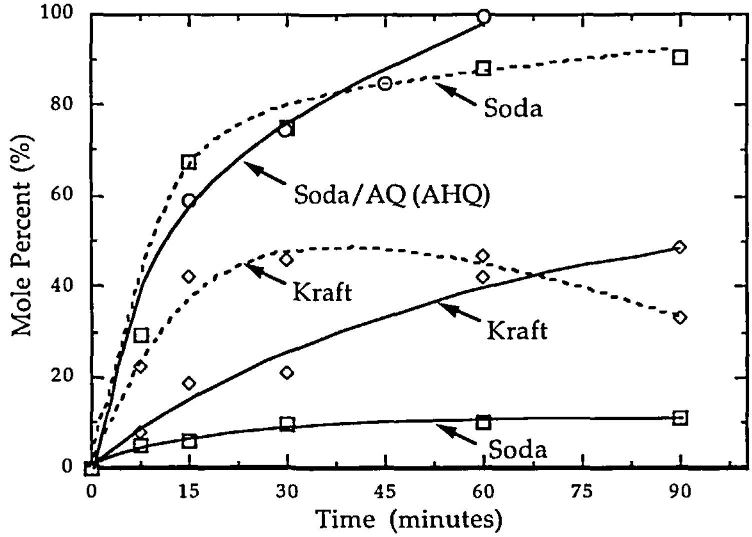


Figure 3. Yields of guaiacol 6 (—) and cyclized cpd. 3 (····) for soda (□) kraft (◇), and soda/AHQ (○) degradations of model cpd. 1 at 150°C.

Table 1. Yield comparisons for alkaline sulfite and control (soda) cooks with lignin models 1, 8, and 9, all with 25 equiv. of NaOH.

Substrate	Time (min.)	Temp (°C)	SO_3^{-2} (equiv.)	Product Composition - %		
				Substrate	Guaiacol	Other[b,c]
1	60	150	-	2	10	88
	60	150	5	8	9	65
	60	170	-	-[a]	15	77
	60	170	5	-[a]	11	72
8	40	150	5	38	10	54
	40	170	-	10	43	-[a]
	40	170	5	16	32	53
9	60	150	5	100	-[a]	▨
	60	170	5	100	-[a]	▨

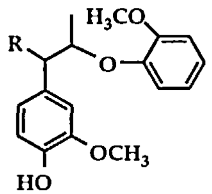
[a] nondetectable (HPLC/UV); [b] cpd. 3 for cpd. 1; [c] cpd. 10 for cpd. 8

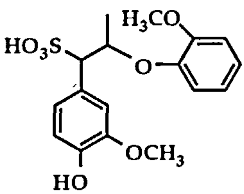
$$SO_2(g) + H_2O \rightleftharpoons SO_2{\bullet}H_2O\ (\text{"}H_2SO_3\text{"}) \qquad (1)$$

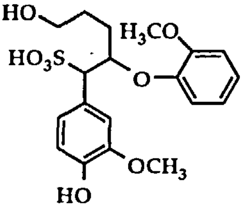
$$SO_2{\bullet}H_2O\ (\text{"}H_2SO_3\text{"}) \rightleftharpoons H^+ + HSO_3^- \qquad pK_a \approx 2 \qquad (2)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{-2} \qquad pK_a \approx 7 \qquad (3)$$

An alkaline sulfite cook of model 1 at 150°C with 25 equiv. of NaOH and 5 equiv. of Na_2SO_3 gave a product distribution as a function of time that was similar to a 25 equiv. NaOH (soda) cook. [The sulfite data is not shown in a figure; it similar to that given in Figure 1 for the soda case.] An additional set of degradations were done at 170°C, a temperature typically employed in commercial alkaline sulfite pulping.[8,9,18] The fragmentation of model 1 after 1 hour increased slightly with increased temperature for both an alkaline sulfite cook and a soda cook (Table 1). Sodium sulfite did not enhance fragmentation at either 150 or 170°C. [Most model degradations were conducted at 150°C to have direct comparison to previous studies[14] and have reaction rates that were easy to study.]


8 R = (HO-)
9 R = (O=)


10a Erythro
10b Threo


11a Erythro
11b Threo

Alkaline Sulfite Reactions of Models 8 and 9

An alkaline sulfite cook of model 8 [1-(4-guaiacyl)-2-(*O*-guaiacyl)-1-propanol] was also performed. The purpose was to learn (a) if β-aryl cleavage would occur in the absence of a competing cyclization reaction and (b) if the reaction between SO_3^{-2} and the intermediate QM is reversible. The alkaline sulfite degradation of 8 (Fig. 4) showed only a slightly higher amount of β-aryl ether scission than that observed with 1 (13.5% vs. 9% at 60 min. and 150°C). An alkaline sulfite cook of model 8, performed at 170°C, gave 32% guaiacol after 40 min.; however, the guaiacol produced was less than a control (soda) cook at 170°C (Table 1).

The principal products of the alkaline sulfite reactions of model 8 were a mixture of erythro/threo α-sulfonated compounds **10a/b** [1-(4-guaiacyl)-2-(*O*-guaiacyl)-propane-1-sulfonic acid] which co-eluted during the LC analysis. The structures of **10a** and **10b** were assigned based on several pieces of evidence. First, the compounds eluted early, indicating that they are polar, preferring the mobile polar solvent phase to adsorption onto the organic C-18 stationary phase. The UV spectrum of the compounds lacked absorptions above 280 nm that are indicative of a styrene structure.[20,21b,21c] Compounds **10a/b** were synthesized by subjecting model 8 to neutral sulfite conditions. The resulting product eluted at the same time and had the same UV spectrum as the alkaline sulfite compound. The residue was characterized by NMR specroscopy through selective decoupling experiments and cross correlations of ^1H and ^{13}C-signals. Detailed structural assignments are given in the Experimental Section. The product distribution over the reaction time for model 8 sug-

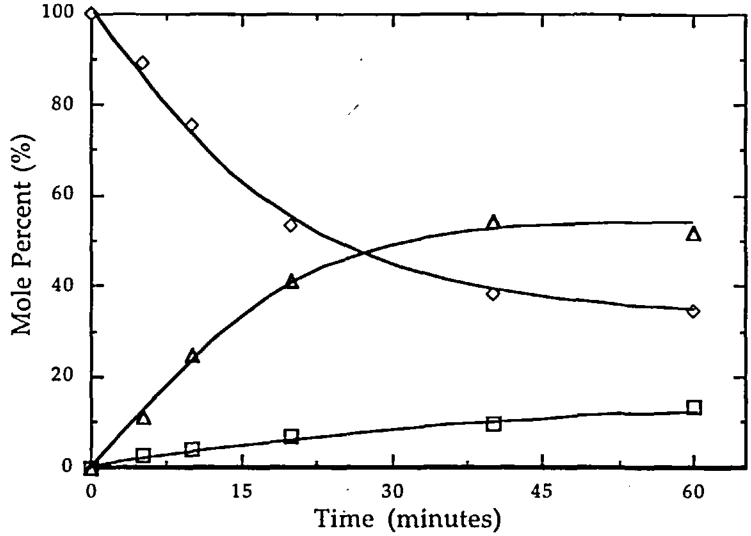


Figure 4. Yields of guaiacol **6** (□) and α-sulfonate **10a/b** (Δ) for the alkaline sulfite degradation of model cpd. **8** (◇) at 150°C.

gests that α-sulfonation is reversible, since the level of α-sulfonated product **10a/b** and the disappearance of starting material levels off after 30 min. (Fig. 4).

Alkaline sulfite cooks were also performed with the α-ketone **9** [1-(4-guaiacyl)-2-(*O*-guaiacyl)-1-propanone]. The purpose was to see if β-aryl fragmentation would occur when an electron withdrawing substituent was present to activate the C_β for S_N2 displacement by an SO_3^{-2} ion.[8,13] Model **9** showed no signs of fragmentation or substitution after 60 min. at either 150 or 170°C (Table 1).

Neutral Sulfite Reactions of Model 1

A neutral sulfite cook of model **1**, employing 5 equiv. of Na_2SO_3 and no added NaOH, gave only a small amount of cyclized product **3** and no fragmentation (Fig. 5). The major product (~90% after 90 min.) was a

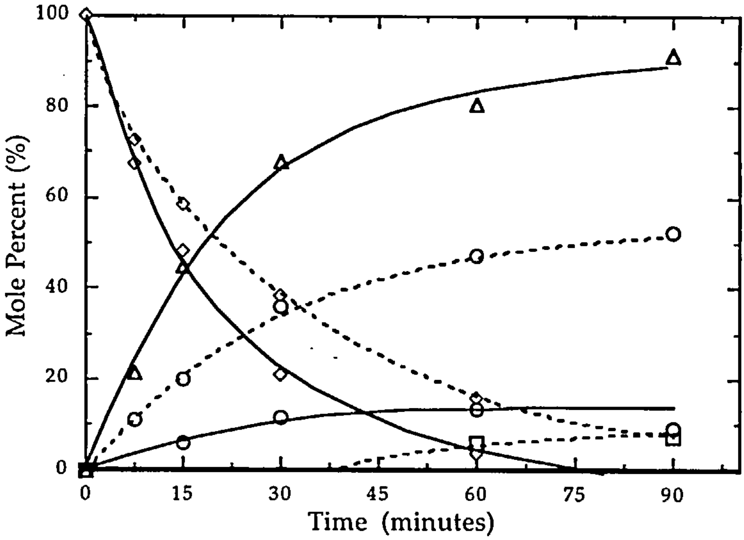


Figure 5. Yields of guaiacol 6 (□), α-sulfonate **11a/b** (△), and cyclized cpd. 3 (○) for neutral sulfite (—) and control (····) [starting pH ~ 8.5] degradations of model cpd. 1 (◇) at 150°C.

35/65 mixture of erythro/threo α-sulfonated products (**11a/b**). [The % observed was estimated based on assumed LC response factors.] The α-sulfonated products were characterized by LC retention times, UV spectra, and NMR (see Experimental Section for details). Other studies of model lignin compounds under neutral sulfite conditions also show a predominant α-sulfonated product.[7-9] The disappearance of 1 during the neutral sulfite cooks was approximately the same as the other alkaline cooks of 1 (Fig. 6).

A control experiment was also performed to see the effect of pH on the degradation of model 1. The model was heated at 150°C at pH 8.5 in the absence of sulfite. There was an initial fast loss of model 1, followed by a more gradual loss after ~10 min. (Fig. 5). The pH was also observed to drop to ~7. The product mixture was dominated by cyclized compound 3; some fragmentation also occurred at longer reaction times. There was ~30% unaccountable products after 90 min. The fact that the neutral sulfite

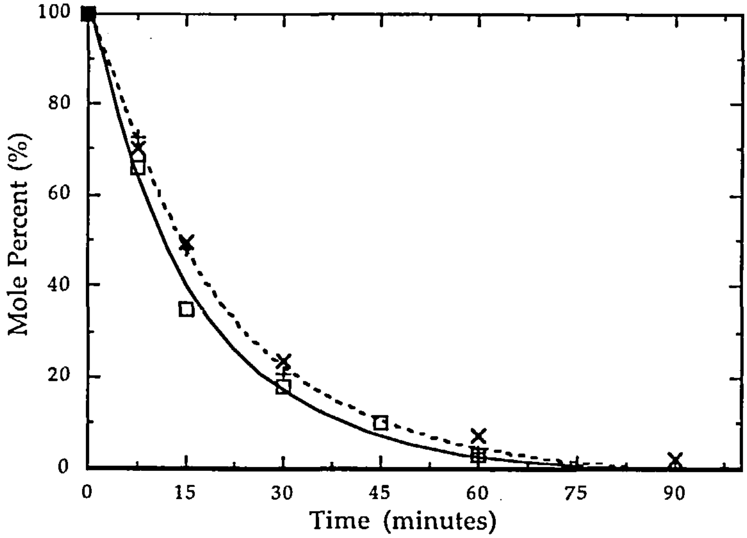


Figure 6. Disappearance of **1** as a function of time at 150°C for sulfite [alkaline (X) and neutral (+)], and soda, kraft, and soda/AHQ cooks [averages (□)].

run, also starting at pH 8.5, displayed a more rapid loss of starting material and no unaccountable products suggests that there was a sulfite/bisulfite buffering action that helped maintain a constant pH during the 90-min. reaction period.

Alkali Reactions of Model **11**

Experiments were performed to learn more about the reversibility of sulfite addition reactions. Samples of **11a/b** were synthesized by subjecting **1** to neutral sulfite conditions at 150°C for 45-min. The resulting product mixture was quenched to 25°C and NaOH was added (~25 equiv.). The samples were reheated at 150°C for various times (Fig. 7). Analysis of the product mixtures showed the disappearance of α-sulfonate **11a/b** and appearance of cyclized product **3**. Obviously, the α-SO_3^- group was released from **11a/b** during the second heating period. The resulting QM **2** reacted with the terminal hydroxyl group to form **3**.

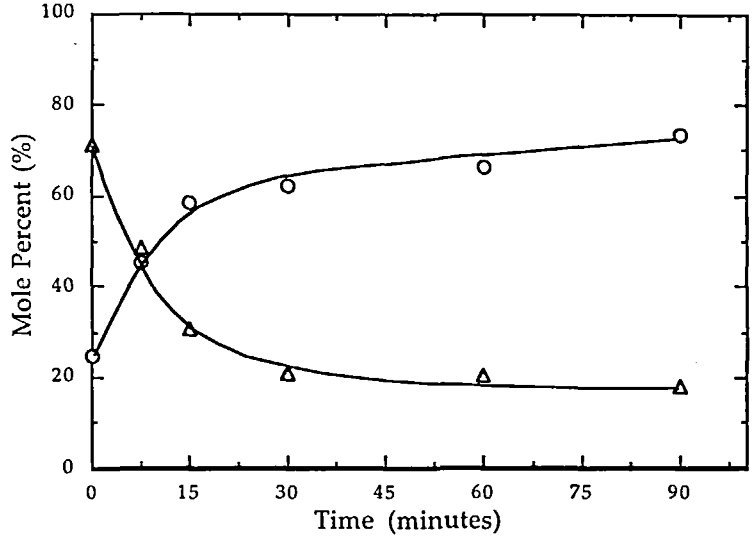


Figure 7. Disappearance of 11a/b (Δ) and appearance of cyclized cpd. 3 (O) as a function of time at 150°C.

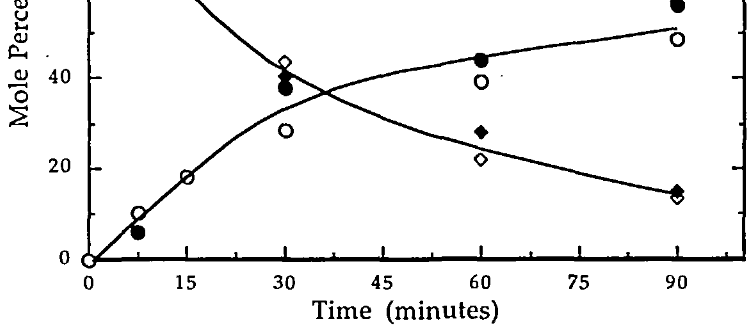


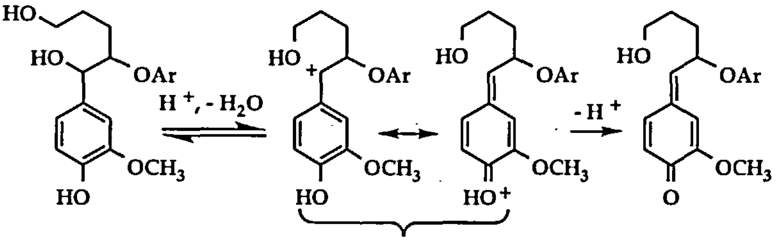
Figure 8. Yields of cyclized cpd. 3 (O;●) for acid bisulfite (●;◆) and control (O;◇) [pH ~4.5] degradation of model 1 (◇;◆) at 150°C. [Production of guaiacol 6 and 11a/b omitted for simplicity.]

Acid Bisulfite Reactions of Model 1

A portion of the experimental results of a pH ~4.5 acid bisulfite cook of **1** and a pH ~4.5 control cook without bisulfite is shown in Figure 8. Both cooks displayed a similar loss of **1** and appearance of **3**. A 90-min. bisulfite cook gave 56% cyclized product **3**, 17% α-sulfonated product **11a/b**, 15% starting material **1**, and 6% guaiacol; the corresponding control cook gave 49% cyclized product **3**, 14% starting material, and 5% guaiacol. The amount of fragmentation observed was attributed completely to the pH of the medium. The control cook had a considerable amount of unaccountable material compared to the bisulfite cook (67% vs. 94% material balance at 90 min., respectively).

DISCUSSION

The rate of disappearance of model **1** was the same for all alkaline reactions studied. This indicates a common slow step: QM formation from a phenolate ion. The disappearance was slower in the acidic bisulfite reaction and at pH < 8.5. A QM could have been formed here; the sequence of steps would involve α-OH protonation, loss of water to generate a benzyl cation, and loss of a phenolic proton (Eq. 4). The reduced rate of reaction of **1** in acid probably reflects a higher energy of activation needed to produce the quinone methide -- such observations have been reported before.[8]



1 2^+ **2** (4)

Based on the criteria that high levels of fragmentation (guaiacol production), accompanied by low levels of cyclization for model **1** signifies an effective delignification condition, we can conclude that the order of reactivity for additives in the system is AHQ > NaSH > NaOH = sulfite/bisulfite. The low reactivity of the sulfite ion at high alkalinity could be because (a) the sulfite ion reacts more slowly than the internal side chain OH group or (b) there exists a fast reversible addition of sulfite ion to the quinone methide, but that the resulting α-sulfonated product does not readily fragment. We suspect that the latter explanation is more likely.

Support for a rapid addition/elimination of sulfite ions to quinone methides comes from several observations. First, the loss of SO_3^{-2} from α-sulfonated **11a/b** was shown to be rapid in ~0.1M NaOH at 150°C; if **11a/b** had formed during the alkaline sulfite reaction of **1**, little would have survived the reaction conditions -- none was detected. Second, the reactions of the simple γ-methyl model **8** indicated both α-sulfonation and loss of the α-SO_3^- group under highly alkaline conditions; the latter is shown by the equilbrium developing between **8** and **10a/b** at longer reaction times (leveling concentration of **8** and **10a/b** after 30 min., Fig. 4).

Third, vinyl ether production occurred in minute amounts during the soda reaction of **1**,[21b,21c] but not in the alkaline sulfite, AHQ, and kraft reactions of **1**. The lack of vinyl ethers in the latter cases indicates that the QM reacts efficiently with the nucleophile in the system to give α-adducts (or ion radicals) rather than undergoing a high energy enolization reaction.[14,21-23] Fourth, α-sulfonation of **1** was a fast reaction under neutral sulfite conditions; the reaction should be equally fast at higher pH. Finally, sulfonation kinetic studies with wood have observed higher lignin sulfonation levels at pH 8.0 than at pH > 9.5.[24]

Under neutral sulfite conditions, the pH is relatively low (~8.5). This pH is sufficient for phenol OH deprotonation of model **1**, and subsequent QM generation. [The pK_a of a simple lignin-like phenol is ~8.5.[25]] However, once a sulfite ion adds to the α-carbon, the phenolate ion of the resulting adducts **11a/b**$^{-2}$ will likely be protonated to give **11a/b**$^{-}$. In other words, the pK_a of the α-SO_3^- phenol will rise because the molecule is already ionized. At pH 8.5, the phenolic OH group of adduct **11a/b** will be unionized, meaning there is no good mechanism to generate a QM; the adduct is a stable end product. At high pH, **11a/b** will be completely deprotonated, facilitating QM generation. Since α-SO_3^- groups are probably excellent leaving groups in such a reaction,[7-10,13] the α-SO_3^- adduct will have a very short lifetime at high pH.

Alkaline sulfite reactions with models **1**, **8**, and **9** indicate that the sulfite ion is relatively ineffective in promoting β-aryl ether cleavage in comparison to sulfide and AHQ. The observed guaiacol formation could be accounted for by the hydroxide in the system. The electron withdrawing α-ketone on model **9** and the α-SO_3^- on **10a/b** did not sufficently activate the C_β for S_N2 displacement by other sulfite ions.

The alkaline reactions of **1** can be best understood by the energy diagram shown in Figure 9. The proposed energy differences are not accurately known, but our work supports the relative differences shown. The energies required for fragmentation and vinyl ether formation in the soda case (Fig. 1, paths *c* and *e*) are similar and higher than cyclization (path *b*); consequently, cyclization dominates. In the sulfite case, we propose a low energy adduct formation step (path *c*), but a high energy fragmentation step. For kraft, cyclization is faster than fragmentation, but the energies are somewhat similar. For AHQ, the lowest energy pathway is fragmentation. The positions of the energy levels of the cyclized product, vinyl ether, and α-sulfonated product are shown to depict our belief of the relative ease of each to reverse back to the QM.[14,21-23]

The rate of cyclization (i.e., the "clock" reaction) will likely change with the pH. At high pH, some of the side chain OH groups will be ionized; the alkoxide ion should be a good internal nucleophile for attack on the QM (Fig. 1).[26] At moderate and low pH, the internal nucleophile will be an unionized OH group, a much poorer nucleophile for attacking the C_α of the QM. The pK_a values for most primary alcohols are ~16 at room temperature.[25] The ratio of ionized primary alcohol appendages to nonionized appendages at pH ~13 is 1:1 x 10^3. At pH 8.5, as in the neutral sulfite case, the ratio drops to about 1:3 x 10^7.

At low pH, the QM might have benzyl cation characteristics (Eq. 4), and thus, the α-carbon should be attractive to both an internal OH group and an external nucleophile. Comparing the amount of cyclized product **3** during alkaline, neutral, and acidic sulfonations could, therefore, be misleading. For example, the lower relative amount of cyclized pro-

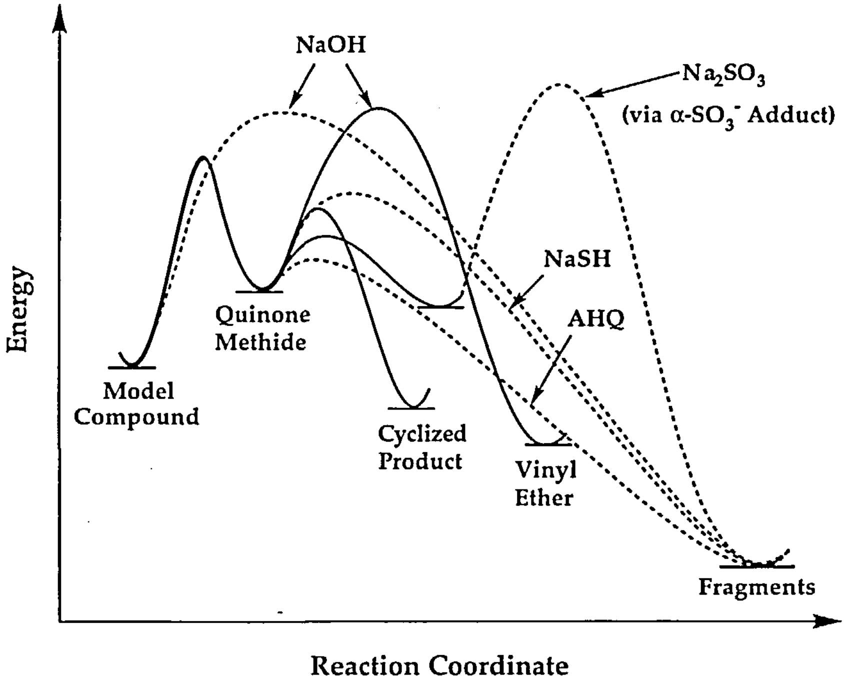


Figure 9. Proposed energy diagram for the reactions of **1**; β-aryl cleavage reactions are noted by (---) and unproductive reactions are noted by (—). Except in the case of sulfite, intermediate steps for fragmentation processes have been omitted for simplicity.

duct **3** under neutral sulfite conditions probably reflects a slower "clock" reaction of **1** rather than a faster adduct formation reaction.

The rate of adduct formation was fast enough during neutral sulfite reactions to effectively compete with regeneration of the starting material; a reaction that would slow the rate of disappearance of **1** -- something not observed. The low amount of fragmentation of model **1** under neutral sulfite conditions agrees with the findings of Suckling who studied the neutral sulfite reactions of a simple lignin model dimer at 140°C.[7] The low amount of guaiacol observed during bisulfite cooks and control cooks (at pH ~4.5) of **1** can be attributed to dehydration to a vinyl ether which is then hydrolyzed.[13,27]

CONCLUSIONS

Our results suggest that reactions of the pulping reagents with quinone methides are generally reversible and that AHQ is the most effective reagent for promoting fragmentation reactions. Since sulfite adducts were not observed with **1** at high pH conditions, our experiments did not allow us to rank the relative effectiveness of sulfite ions in capturing quinone methides. We suspect that a sulfite ion rapidly adds reversibly to QM **2**, but at high pH, the α-sulfonated adduct is short lived, and cyclization of the quinone methide dominates. The cyliza-tion reaction is probably less reversible than SO_3^{-2} addition/elimination since an α-alkoxide is a poorer leaving group than an α-SO_3^- group. Alkaline sulfite reactions with lignin models **8** and **9** suggest that sulfite ion is ineffective at promoting β-aryl ether fragmentation at 170°C. Neutral and acidic sulfite conditions led to an α-sulfonated product.

EXPERIMENTAL

General Analytical Procedures

The synthesis and characterization of 1-(4-guaiacyl)-2-(*O*-guaiacyl)-1, 5-pentanediol (**1**),[14,28] 1-(4-guaiacyl)-2-(*O*-guaiacyl)-tetrahydropyran (**3**),[14] 1-(4-guaiacyl)-2-(*O*-guaiacyl)-1-propanol (**8**),[29] and 1-(4-guaiacyl)-2-(*O*-guaiacyl)-1-propanone (**9**)[29] have been previously reported (guaiacyl = 2-methoxyphenol). The synthesis and charaterization of 5-(4-guaiacyl)-4-(*O*-guaiacyl)-4-penten-1-ol (**7**) will appear in a seperate pubication.[21b,21c]

Reverse phase liquid chromatography analyses (LC) were performed on a Hewlett Packard HP 1090 Liquid Chromatograph. The analyses were done at room temperature with a Spheri 5 R-18 (100 x 4.6 mm, packing size = 5 mm) column, a solvent system of 50% (v/v) aq. methanol, flowing at 0.450 mL/min., an injection volume of 4.2 mL, and a diode array detector operating at 230 nm.

Quantitative LC work used β-(*O*-guaiacyl)-α-(4-guaiacyl)-ethanol,[29] a lignin dimer, as an internal standard. Response factors were determined by subjecting solutions of known ratios of compound and internal stan-

Table 2. LC retention times and response factors.

Compound	Retention Time (min.)	Response Factor
Model **1**	6.2	1.00
Cyclized compound **3**	16.8	1.00
Guaiacol **6**	4.9	4.03
Internal standard	10.3	1.00
α-Sulfonate **11a/b**	1.8	1.00*
γ-Methyl model dimer **8**	9.9	1.00*
α-Ketone model dimer **9**	8.6	1.00*
α-Sulfonate **10a/b**	1.8	1.00*

*estimated

dard to the same work-up procedure as a reaction sample. Response factors for compounds **8**-**11** were assumed to be the same as compounds **1**, **3**, and the internal standard since all had nearly identical UV spectra. The retention times and response factors are given in Table 2.

^{1}H-NMR and ^{13}C-NMR spectra of selected model compounds were recorded with a Varian 300 MHz or Bruker DMX 400 MHz NMR spectrometer at ambient temperatures.

Reagents and Compounds

Anthrahydroquinone. Anthrahydroquinone was prepared by heating AQ with glucose *in situ* or in advance of a planned reaction. If prepared in advance, 1 g of AQ was heated at 75°C for ~3 hr with 5 g of glucose in 500 mL of nanopure water containing 4 g of NaOH; this and all other steps were carried out under a nitrogen atmosphere (often inside a glove bag). The hot, dark red solution of AHQ^{-2} was filtered to remove any unreacted AQ, cooled, neutralized with acid to give a greenish-yellow precipitate of AHQ, and filtered. The collected solid was rinsed three times with deoxygenated water. The moist solid was stored in a glass vial, kept in a glove bag, and used within a week after preparation.

Solutions of AHQ were made by dissolving a portion of the moist solid in 0.100 M NaOH solution inside the glove bag. Concentrations of AHQ were determined by dispensing a fixed volume of the solution into a tared vial, evaporating in a 105°C oven, cooling in a desiccator, and weighing. The amount of AHQ was determined by subtracting the weight of the NaOH associated with the solution. The above procedure was repeated two additional times and the mean of three measurements recorded. Solutions of AHQ were used within a day after preparation.

1-(4-Guaiacyl)-2-(O-guaiacyl)-5-hydroxypentane-1-sulfonicacid (11a/b). To five 4.5 mL pressure vessels (bombs) was added 1 mL of 0.075 M Na_2SO_3, 1 mL of 0.015 M **1**,[14,28] and 1.5 mL of deoxygenated water. The bombs were sealed, agitated in a 150°C fluidized sand bath for 1.5 hr, removed, quenched in ice water, and emptied. The combined solutions were acidified to a pH 2 with concentrated sulfuric acid and freeze dried. The solid residue was rinsed once with 1 mL of $CHCl_3$ and three times with 1 mL samples of methanol. The methanol washings were combined and evaporated to give a white solid consisting of an erythro and threo mixture of **11a/b**: ^{1}H-NMR (CD_3OD) δ 1.68 (m, $C\underline{H}_2CH_2OH$), 1.91 (m, $C\underline{H}_2CH_2CH_2OH$), 3.53 (t, J = 6.6 Hz, $C\underline{H}_2OH$), 3.71 and 3.81 (2 s, $ArOC\underline{H}_3$, threo), 3.83 and 3.85 (2 s, $ArOC\underline{H}_3$, erythro), 4.15 (d, J = 6 Hz, $C\underline{H}_\alpha$, threo), 4.42 (d, J = 4.5 Hz, $C\underline{H}_\alpha$, erythro), 5.2 (m, $C\underline{H}_\beta$), and 6.7 - 7.4 (m, aryl); ^{13}C-NMR ($CDCl_3$) ppm 29.3 and 30.5 ($\underline{C}H_2\underline{C}H_2$), 56.0 and 56.4 (threo $ArO\underline{C}H_3$), 62.8 ($\underline{C}H_2OH$), 66.0 (erythro $\underline{C}_\alpha$), 70.1 (threo $\underline{C}_\alpha$) 80.0 ($\underline{C}_\beta$), 114-127 (aryl $\underline{C}$), and 147-152 (aryl $\underline{C}$-O).

The integrated areas for the ^{1}H-NMR signals correlated well with the proposed structure and for a 35/65 ratio of erythro/threo isomers. The assignment of erythro and threo was based on the expectation that the threo isomer will have the larger C_α-C_β coupling constant.[30] The ^{1}H-NMR assignments for H_α, H_β, and H_γ were verified with homonuclear decoupling experiments; irradiation at δ 5.2 caused the $C_\alpha\underline{H}$ signals to collapse to singlets and the $C_{\gamma}\underline{H}$ to go from a multiplet to a triplet. The signals in ^{13}C-NMR spectrum were weak because of low solubility of the sample in methanol; some signals were obviously missing. An inverse $^{1}H/^{13}C$ correlation, HMQC (heteronuclear multiple quantum coherence) experiment helped to provide the exact ^{13}C assignments.

1-(4-Guaiacyl)-2-(*O*-guaiacyl)-propane-1-sulfonic acid (10a/b). An experiment similar to the one above was performed on model **8** [29] to give a purple solid consisting of an erythro and threo mixture of **10a/b**: ^{1}H-NMR (CD_3OD) δ 1.30 and 1.40 (d, J = 7 Hz, $C\underline{H}_3$, erythro and threo), 3.68 and 3.80 (2 s, $ArOC\underline{H}_3$, threo), 3.82 and 3.86 (2 s, $ArOC\underline{H}_3$, erythro), 4.10 (d, J = 7 Hz, $C\underline{H}_{\alpha}$, threo), 4.41 (d, J = 4 Hz, $C\underline{H}_{\alpha}$, erythro), 5.20 (m, $C\underline{H}_{\beta}$, threo), 5.27 (m, $C\underline{H}_{\beta}$, erythro), and 6.7-7.4 (m, aryl); ^{13}C-NMR ($CDCl_3$) ppm 17.4 ($\underline{C}H_3$, threo), 19.7 ($\underline{C}H_3$, erythro), 56.3-56.7 ($ArO\underline{C}H_3$), 69.0 (erythro $\underline{C}_{\alpha}$), 72.5 (threo $\underline{C}_{\alpha}$), 76.0 (erythro $\underline{C}_{\beta}$), 77.0 (threo $\underline{C}_{\beta}$), 114-128 (aryl $\underline{C}$), 147-151 (aryl $\underline{C}$-O).

The integrated areas for the ^{1}H-NMR signals correlated well with the proposed structure and showed a ~35/65 ratio of erythro/threo isomers. The assignment of erythro and threo were based on the expectation that the threo isomer will have the larger C_{α}-C_{β} coupling constant.[30] The ^{1}H-NMR assignments for H_{α}, H_{β}, and H_{γ} were verified with homonuclear decoupling experiments; irradiation at δ 5.2 caused the $C_{\alpha}\underline{H}$ and $C_{\gamma}\underline{H}$ signals to collapse to singlets. An inverse $^{1}H/^{13}C$ HMQC experiment aided in the ^{13}C assignments.

Kinetic Procedures

Reaction System and Procedure. Degradation experiments were carried out in 4.5-mL pressure vessels (bombs). A bomb had a steel cap screwed to a steel vial, with a Teflon sealing ring. The bombs were attached to a metal plate by screwing a threaded rod soddered on the vial portion into one of 16 threaded holes on the metal plate. The plate was attached to a rocker arm and suspended in a hot fluidized sand bath. The bath was heated 3°C above the reaction temperature to allow for the temperature drop associated with the initial heating of the bombs. The bath temperature was readjusted to the correct temperature once the bombs were lowered into the sand bath. The plate containing the attached bombs was vibrated vigorously during the reaction period.

Appropriate amounts of dry reactants (e.g., AQ) were weighed into the bombs in air. The reactants, solutions, bombs, and equipment needed to dispense liquid solutions were placed inside of a glove bag and sealed. The air inside the glove bag was displaced with high purity grade nitrogen. Bombs were filled with appropriate reactants to a 3.5-mL level. Standard solutions of reactants were made in deoxygenated water (Na_2S, Na_2SO_3) or NaOH solution (premade AHQ) and pipetted into the bombs. When all additions were complete, each bomb contained 0.0015 mM (= 1 equiv.) of **1**, and 5 equiv. of AHQ, NaSH or Na_2SO_3.

For highly alkaline reactions, model **1** was dissolved in 0.3 M NaOH in a volumetric flask and added to the bombs with a pipette; additional 0.3 M NaOH solution was added to the bomb to give 25 equiv. of NaOH. When making AHQ *in situ*, we used a 1:1 ratio of glucose to AQ. For neutral and acidic reactions, model **1** was placed in deoxygenated water in a partially filled volumetric flask, warmed to dissolve **1**, cooled, diluted to a standard volume, and added to the bombs with a pipette. Neutral and acidic sulfite solutions used no NaOH, 5 equiv. of sodium sulfite and, in the case of acidic sulfite reactions, conc. HCl to adjust the pH to ~4.2.

Once filled, the bombs were sealed, removed from the glove bag, and placed into a water bath preheated at 60°C for 30 min. to (a) allow for the conversion of AQ to AHQ^{-2} for bombs containing AQ and glucose, and (b) decrease the associated temperature drop when the bombs were placed (after drying) in the sand bath.

The bombs were lowered into the heated sand bath and agitation commenced. The initial time (time zero) started 30 seconds later - the estimated time to warm the bombs to 150°C. The bombs were removed periodically from the sand bath by lifting the metal plate with attached bombs out of the sand bath and quickly detaching one or more of the bombs. Once removed from the sand bath, the bombs were immediately quenched in ice water. Contact with the ice water was defined as the end of the reaction. The bombs were then dried, opened, and the contents quantitatively transferred to a 10-mL screw cap sample vial.

Sample Work-up. For LC analysis, a 1.00-mL aliquot was taken from the sample vial to an 8-mL vial. To this vial was added 0.33 mL of a 0.0129 M solution of internal standard in 0.30 M NaOH. The pH was then adjusted to approximately 7 by adding 1.25 mL of 0.30 M HCl and 0.41 mL of nanopure water to the vial for alkaline reactions (~13 pH) and 0.31 mL of 0.30 M HCl and 1.35 mL of nanopure water for neutral (pH 6-8) and acidic reactions (pH < 5). The prepared vial was sealed, shaken, opened, and a small aliquot (0.3-0.6 mL) transferred to an LC vial for analysis.

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REFERENCES

1. T. M. Grace, E. W. Malcolm and M. J. Kocurek, Pulp and Paper Manufacture, Vol. 5, Alkaline Pulping, Chapt. 1 - Overview, The Joint Textbook Committee of the Paper Industry, Atlanta, 1989.

2. O. V. Ingruber, M. J. Kocurek and A. Wong, Pulp and Paper Manufacture, Vol. 4, Sulfite Science & Technol., Historical Develop. & Chap. 9, The Joint Textbook Committee of the Paper Industry, Atlanta, 1985.

3. A. W. Krotscheck, W. Künstner and W. Peter, TAPPI Pulping Conf. Proceed., Atlanta, GA, p. 237 (1993).

4. N. Nimmerfroh, H. U. Suss and J. D. Kronis, TAPPI Pulping Conf. Proceed., Boston, MA, p. 791 (1992).

5. O. V. Ingruber, M. J. Kocurek and A. Wong, Pulp and Paper Manufacture, Vol. 4, Sulfite Science & Technol., Chap. 2 - Sulfite Pulp Quality, The Joint Textbook Committee of the Paper Industry, Atlanta, 1985.

6. A. Teder and K. Sjöström, Int'l Pulp Bleaching Conf. - Posters Session Proceed., Vancouver, BC, p. 137 (1994).

7. I. D. Suckling, J. Wood Chem. Technol., 8, 43 (1988).

8. G. Gellerstedt, Svensk Paperstid., 79, 537 (1976).

9. G. Gellerstedt and J. Gierer, Acta Chem. Scand., B29, 561 (1975).

10. G. Gellerstedt and J. Gierer, Acta Chem. Scand., 22, 2510 (1968); G. Gellerstedt and J. Gierer, *ibid.*, 24, 1645 (1970).

11. T. J. McDonough, V. Van Drunen and T. W. Paulson, Pulp. Paper Sci. 11, 167 (1985); A. J. Eagle and T. J. McDonough, Appita 41, 141 (1988).

12. H. L. Hergert and E. K. Pye, Proceed. TAPPI Solvent Pulping Symp., Boston, MA, p. 9 (1992); A. Glasner and H.-L Schubert, Proceed.; TAPPI Pulping Conf. Proceed., San Diego, CA, pp. 155, 289 (1994).

13. J. Gierer, Wood Sci. Technol., 19, 289 (1985).

14. D. R. Dimmel, L. F. Schuller and P. B. Apfeld, J. Wood Chem. Technol., 7, 97 (1987).

15. P. A. Watson, R. R. Gustafson, W. T. McKean and E. K. Andrews, TAPPI Pulping Conf. Proceed., Boston, MA, p. 847 (1992); H. H. Holton and F. L. Chapman, Tappi, 60(11), 121 (1977); J. M. MacLeod, B. I. Fleming, G. J. Kubes and H. I. Bolker, Tappi, 63(1), 57 (1980).

16. B. N. Brogdon and D. R. Dimmel, J. Wood Chem. Technol., following article (part II); B. N. Brogdon and D. R. Dimmel, TAPPI Pulping Conf. Proceed., San Diego, CA, p. 1209 (1994).

17. B. N. Brogdon and D. R. Dimmel, J. Wood Chem. Technol., following article (part III).

18. O. V. Ingruber, M. J. Kocurek and A. Wong, Pulp and Paper Manufacture, Vol. 4, Sulfite Science & Technol., Chaps. 1 & 2, The Joint Textbook Committee of the Paper Industry, Atlanta, 1985.

19. A. Senning, Sulfur in Organic and Inorganic Chemistry, Vol. 2, Chap. 14, Marcel Dekker, Inc., New York, 1972.

20. R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectrometric Identification of Organic Compounds, 5th Ed., John Wiley & Sons, Inc., NY, 1991, p. 309-310.

21. (a) D. R. Dimmel, L. F. Bovee and B. N. Brogdon, J. Wood Chem. Technol., 14, 1 (1994); (b) B. N. Brogdon and D. R. Dimmel, "Competing Reactions Affecting Delignification in Pulping Systems," *ibid.*, following article; (c) B. N. Brogdon, M.S. Thesis, Institute of Paper Science and Technology, Atlanta, GA, 1994.

22. D. R. Dimmel and L. F. Schuller, J. Wood Chem. Technol., 6, 535, 565 (1986).

23. D. R. Dimmel and L. F. Bovee, J. Wood Chem. Technol., 13, 583 (1993).

24. P. Engstrand, L.-Å. Hammar and M. Htun, Int'l Symp. Wood and Pulping Chem. Proceed., Vancouver, B.C., p. 275 (1985); S. Wennerås, I.P.C. Abstracts, 38, No. 9155 (1968).

25. J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, p. 221, 2nd ed., McGraw-Hill, New York, 1977.

26. G. A. Reed, D. R. Dimmel and E. W. Malcolm, J. Org. Chem., 58, 6364 (1993).

27. K. Sakai, H. Takeuti, S.-P. Mun and H. Imamura, J. Wood Chem. Technol., 8, 29 (1988); K. Sakai, T. Takagi and H. Imamura, J. Japan Wood Res. Soc., 36, 553 (1990).

28. P. A. Apfeld and D. R. Dimmel, J. Wood Chem. Technol., 8, 461 (1988).

29. D. R. Dimmel and D. Shepard, J. Org. Chem., 47, 4799 (1982); D. R. Dimmel and D. Shepard, J. Wood Chem. Technol., 2, 297 (1982).

30. R. M. Ede, J. Ralph and A. L. Wilkins, Holzforschung, 41, 239 (1987); J. Ralph and A. L. Wilkins, *ibid.*, 39, 341 (1985); J. Ralph and R. A. Young, *ibid.*, 35, 39 (1981).