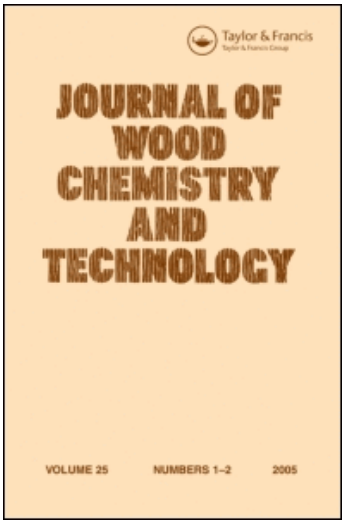


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Electron Transfer Reactions in Pulping Systems IX. Reactions of Syringyl Alcohol with Pulping Reagents

Dean A. Smith[a]; Donald R. Dimmel[a]
[a] Institute of Paper Science and Technology, Atlanta, Georgia

To cite this Article Smith, Dean A. and Dimmel, Donald R.(1994) 'Electron Transfer Reactions in Pulping Systems IX. Reactions of Syringyl Alcohol with Pulping Reagents', Journal of Wood Chemistry and Technology, 14: 2, 297 — 313
To link to this Article: DOI: 10.1080/02773819408003099
URL: http://dx.doi.org/10.1080/02773819408003099

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 14(2), 297-313 (1994)

ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (IX): REACTIONS OF SYRINGYL ALCOHOL WITH PULPING REAGENTS

Dean A. Smith and Donald R. Dimmel
Institute of Paper Science and Technology
500 10th Street, N.W., Atlanta, Georgia 30318

ABSTRACT

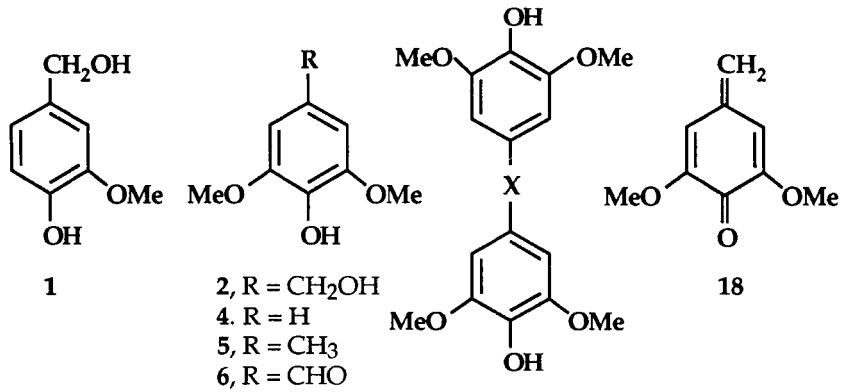
Syringyl alcohol was heated at 135°C in 1M NaOH in the presence of anthrahydroquinone, sodium hydrosulfide, and glucose. Dimerization of syringyl alcohol to disyringylmethane was suppressed by all three reagents. An analysis of the types and amounts of products formed at various times indicated (1) that the reagents reacted reversibly with intermediate quinone methides and (2) that electron transfer reactions occurred in the cases of anthrahydroquinone and glucose to give quinone methide radical anion intermediates. Sodium sulfide reacted as a nucleophile, rather than an electron transfer agent.

INTRODUCTION

Pulping to low lignin levels is the goal of several new pulping technologies. In part, the success of this approach depends on controlling the extent of condensation reactions which occur between dissolved lignin fragments. The chemistry of such reactions is reflected in the self-condensation reactions of vanillyl and syringyl alcohols (**1** and **2**).[1,2] Vanillyl alcohol produces a complex mixture of monomer, dimer, trimer, oligomer, and polymer components when heated in

alkali.[1] The corresponding syringyl alcohol condensation reaction gives a relatively simple product mixture for which component quantification is possible.[2]

Previous studies have shown that less vanillyl alcohol condensation reactions occur in the presence of anthrahydroquinone (AHQ) and sodium hydrosulfide (NaSH), the active agents in anthraquinone (AQ) and kraft pulping systems, respectively.[1] The intent of the study reported here is to determine how AHQ, NaSH, and a simple carbohydrate (glucose) affect the alkaline reactions of syringyl alcohol. The results provide mechanistic information about condensation reactions and the occurrence of electron transfer reactions in pulping reactions.



RESULTS AND DISCUSSION

Anthrahydroquinone

Anthrahydroquinone was selected for initial study because of its ability to: produce low lignin pulps;[4] inhibit vanillyl alcohol condensation reactions;[1] and promote electron transfer reactions.[5] Syringyl alcohol (2) was heated at 135°C in lM NaOH with different AHQ levels, and the concentrations of products and starting material were deter-

mined at numerous time intervals. The data for three time periods are given in Table 1; complete concentration-time profiles are available.[6] A comment on the nomenclature used in this report can be found in the previous paper,[2] reference 7.

Except when large levels of AHQ (and other additives) were present, the material balances were good (ca. 80-95%). Apparently, with 2 equiv. of AHQ, extensive formation of adduct structures occurs between AHQ and the quinone methide derived from syringyl alcohol. Analogous reactions between AHQ and other simple quinone methides are known.[7] The expected adducts would have low volatility and, therefore, would not be observable by typical gas chromatography (GC) analysis. Product characterization was aided by methylation of the mixture and then analysis by GC-mass spectroscopy (GC-MS).

The product mixture from reaction of syringyl alcohol with NaOH and 2 equiv. AHQ, after methylation, showed adducts **11**, **13**, **15**, **17**, and an unknown component having the same molecular weight as **17** (Scheme 1). Based on analogous reactions with structurally similar materials,[7,8] we believe that adduct **10** is the primary reaction product, and the other adducts are secondary products (Scheme 1). The quinone methide product **12** is simply a dehydration product of **10**, and the other secondary products, **14** and its enol isomer **16**, are reduction products of **10**.

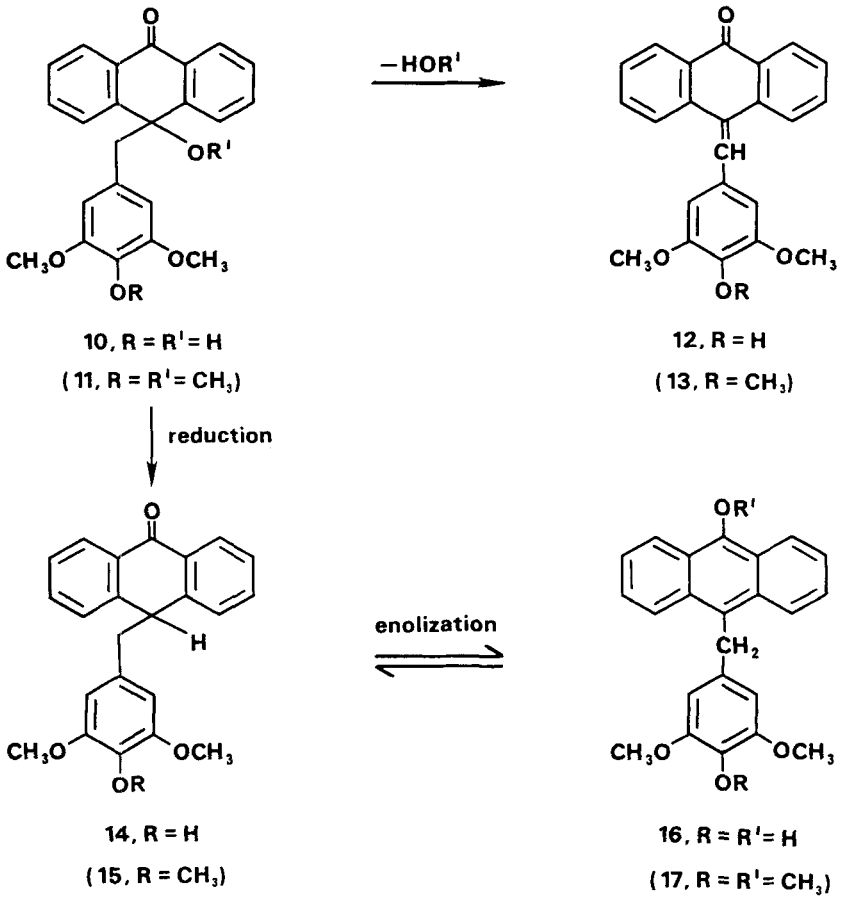
The data in Table 1 indicate that increasing the concentration of AHQ in the reaction mixture caused a more rapid loss in starting material, with a corresponding decrease in the production of disyringylmethane (**3**); also, there was an increased production of 4-methylsyringol (**5**), a suspected radical-derived product. The level of syringol (**4**) was fairly low in all runs and seemed not to be affected much by changes in AHQ levels. The production of syringaldehyde (**6**) was increased in the presence of AHQ and passed through a maximum at intermediate AHQ levels.

The different yield profiles for syringaldehyde can be explained by the set of reactions outlined in Eqs. 1-4. In alkali at 135°C, syringyl alcohol (as its phenolate) is in equilibrium with a quinone methide

Table 1. Component yields associated with heating syringyl alcohol (SA) at 135°C in 1M NaOH with different additives and different additive levels.

	Component yields (% of starting SA) as a function of time (min)																	
	2			3[c]			4			5			6			Total		
Additive (equiv.)	30	120	240	30	120	240	30	120	240	30	120	240	30	120	240	30	120	240
None[a]	64	27	12	22	47	58	1	2	3	1	2	2	2	5	12	89	83	87
AHQ (0.1)	60	22	7	23	44	53	2	3	4	2	6	8	8	14	16	95	89	88
AHQ (0.5)	60	3	0	17	26	29	2	3	4	5	11	12	11	31	36	95	74	81
AHQ (2)[a,b]	14	6	8	2	3	4	1	1	2	8	10	11	5	8	11	29	28	36
Glucose (2)[a]	34	10	4	9	18	23	1	1	2	4	7	10	0	1	1	48	37	40
Glucose (5)	0	0	0	2	3	3	1	1	1	4	5	5	1	1	1	8	10	10
NaSH (2)	39	27	24	9	27	43	1	1	2	0	1	1	0	1	2	49	57	72
NaSH (2)/glucose (2)	12	2	0	6	12	12	1	1	1	7	11	12	0	1	2	26	27	27
NaSH (1)/AHQ (1)	32	14	9	3	7	8	1	1	1	4	6	7	4	10	14	44	38	39

[a]Average of three runs.
[b]Bisyringyl (**7**) was observed at a level of 16 ± 2% from 7.5-240 min (Fig. 1); its presence in the other experiments was only at trace levels.
[c]2 Moles of SA are required to make 1 mole of **3**; yields are based accordingly.



Scheme 1

(QM **18**) and hydroxide ion (Eq. 1). The dianion of AHQ can transfer an electron to the quinone methide, giving rise to two radical anions, $\mathbf{18}^{\cdot-}$ and $AHQ^{\cdot-}$ (Eq. 2).[5,9,10] The $AHQ^{\cdot-}$ could also transfer electrons to **18** (Eq. 3). The benzylic alcohol group of syringyl alcohol can be oxidized by AQ to give syringaldehyde, **6** (Eq. 4).[11,12] When the beginning AHQ^{-2} concentration is low, the chemistry outlined in Eqs. 2 and 3 occurs; however, little AQ will be available to oxidize syringyl alcohol. With 0.5 equiv. of AHQ^{-2}, all will be converted to AQ via reduction reactions

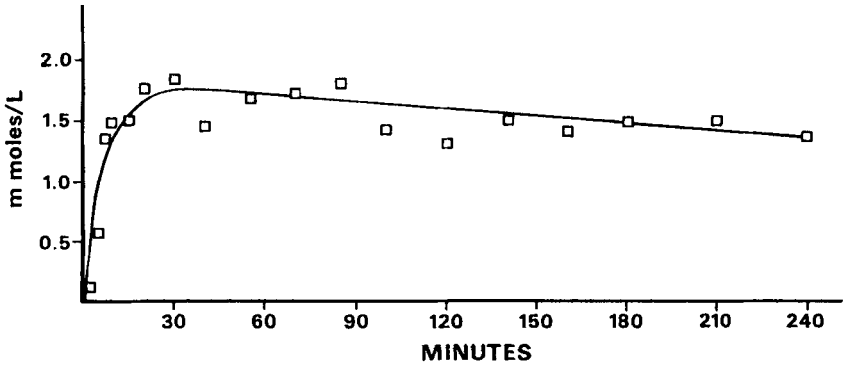


Figure 1. The concentration profile of bisyringyl upon heating syringyl alcohol (20 mmol/L) at 135°C with 1M NaOH and 2 equiv. of AHQ.

(Eqs. 2 + 3), and high levels of AQ will be available for syringyl alcohol oxidation (Eq. 4). At high concentrations of AHQ^{-2}, the chemistry outlined in Eq. 2 is expected to dominate over that indicated by Eq. 3, and there will be little AQ available to oxidize syringyl alcohol (Eq. 4). The syringaldehyde yield profile fits a chemistry where AQ, but not $AHQ^{\cdot-}$, is capable of oxidizing syringyl alcohol.

$$\mathbf{2}^{-} \rightleftharpoons \mathbf{18} + HO^{-} \quad (1)$$

$$QM\,\mathbf{18} + AHQ^{-2} \longrightarrow \mathbf{18}^{\cdot-} + AHQ^{\cdot-} \quad (2)$$

$$QM\,\mathbf{18} + AHQ^{\cdot-} \longrightarrow \mathbf{18}^{\cdot-} + AQ \quad (3)$$

$$\mathbf{2} + AQ + 2HO^{-} \longrightarrow \mathbf{6} + AHQ^{-2} + 2H_2O \quad (4)$$

With no or low levels of AHQ, only trace levels of bisyringyl (**7**) are formed. However, the bisyringyl yield increased substantially when 2 equiv. of AHQ was employed (Fig. 1). The yield rapidly reached 15-18% and then appeared to drop slightly after 30 min reaction time. This behavior suggests a radical dimerization process (to be discussed later) which gives rise to **7**, together with a slow secondary reaction which consumes **7** or a slow reversal of the dimerization reaction.

Glucose

Carbohydrates are a component of pulping liquors and, consequently, their effects on lignin condensation reactions were of interest. The consumption rate of syringyl alcohol was increased from the control by the addition of 2 equiv. of glucose; the production of methane was cut in half (Table 1). The observed overall decreased yields of syringyl-related monomers and dimers were probably due to a preferential reaction between glucose (or glucose fragments) with the quinone methide (**18**) derived from syringyl alcohol, giving rise to adducts (represented generically as structure **19**). Analogous QM-carbohydrate adducts are known.[13]

The addition of five equivalents of glucose led to a very rapid consumption of syringyl alcohol, with the formation of a large quantity of unanalyzable adducts. As for the typically observed products, only 4-methylsyringol (**5**) showed an increase in yield as compared to the control reaction. The production of 4-methylsyringol, a suspected radical-derived product, was greater with 2 equivalents of glucose than with 5 equivalents; the yield was almost double that of the control.

Sodium Hydrosulfide

The kraft pulping system employs sodium sulfide (Na_2S) to achieve effective delignification in short reaction times. Under the conditions of pulping (and those used here), the Na_2S is effectively hydrolyzed to NaSH and NaOH.[14-18] Heating syringyl alcohol in an aqueous solution of 1M NaOH and 2 equiv. of NaSH led to an initial rapid consumption, followed by a moderate consumption, of starting material. As can be seen in Table 1, the initial consumption was not accompanied by an increased production of disyringylmethane. Instead, disyringylmethane production was depressed throughout the reaction. But unlike the control reaction, the rate of production of disyringylmethane was still significant after four hours.

Addition of NaSH also decreased the production of the other products; for example, the yield of 4-methylsyringol was less than a

fourth of that produced in the control reaction. The reaction solution, however, contained two unique sulfide addition products: 3,5-dimethoxy-4-hydroxybenzylthiol (**8**) and di-(3,5-dimethoxy-4-hydroxybenzyl)-sulfide (**9**). Previous studies with vanillyl alcohol and NaSH at temperatures of 75-95°C provided the analogous di-(3-methoxy-4-hydroxybenzyl)sulfide as the major product.[19]

The production of the sulfur adducts was high initially but decreased thereafter (Fig. 2). Crude calculations indicate that the missing material in the NaSH experiment (Table 1) can be accounted for by the sulfur adducts.[5] The sulfide reactions can be explained by the reactions shown in Scheme 2. Adducts **8** and **9** effectively lower the concentration of QM **18**, which means there is less opportunity for **18** to be diverted to products **3-6**. However, the typical dimerization can still occur if the adducts are in equilibrium with QM **18**, which is in equilibrium with syringyl alcohol. The adducts provide a steady source of syringyl alcohol, such that the amount of syringyl alcohol after 4 hours in the sulfide run is greater than that of the control run by almost a factor of two. Because syringyl alcohol is being regenerated from the adducts, disyringylmethane production starts out slow but builds to respectable levels after 4 hours. Gierer and Lindeburg,[20] in studies with coniferyl alcohol, also conclude that "sulfidation constitutes only a temporary protection against condensation and degradation."

Additive Combinations

Pulping liquors often contain a combination of additives; therefore, additive combinations were examined with syringyl alcohol. With 2 equiv. each of sodium hydrosulfide and glucose, the syringyl alcohol was quickly consumed, and the levels of disyringylmethane (**3**), syringol (**4**), and syringaldehyde (**6**) were significantly reduced relative to the control (Table 1). However, the formation of 4-methylsyringol (**5**) was high, roughly the same as that observed with 2 equiv. of AHQ. The level of **5** was greater than that observed for glucose or sodium hydrosulfide alone.

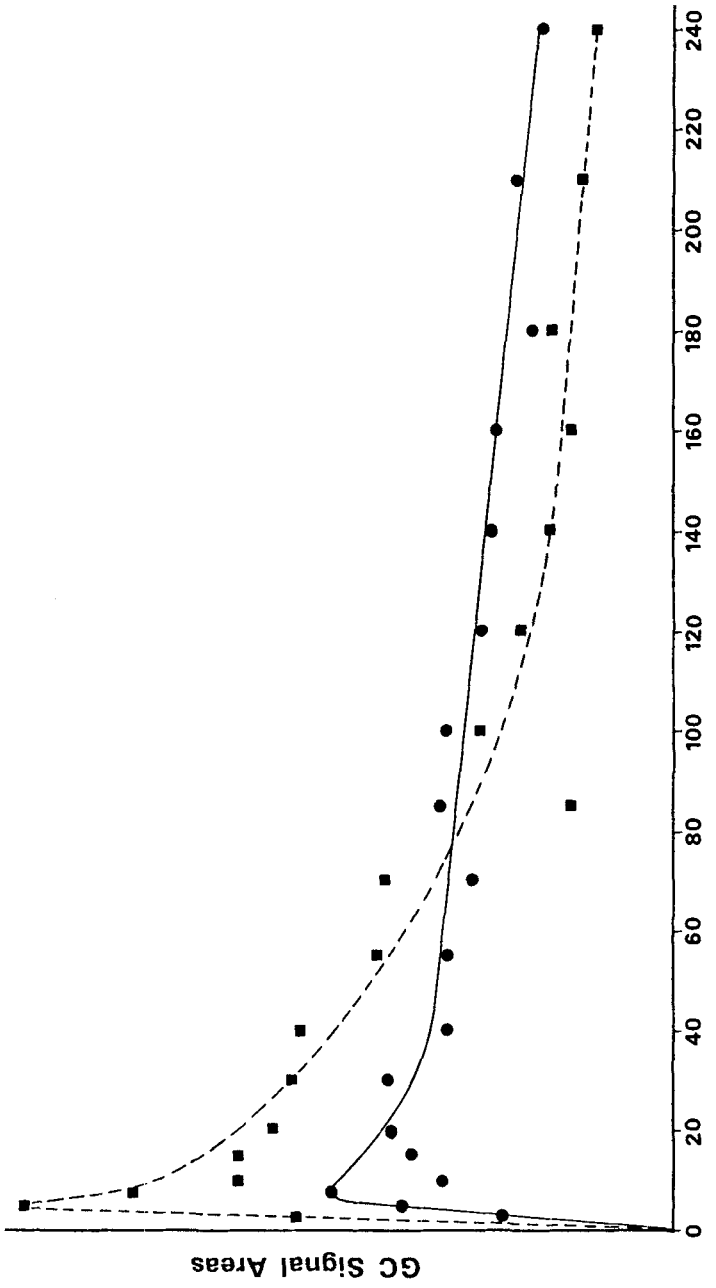
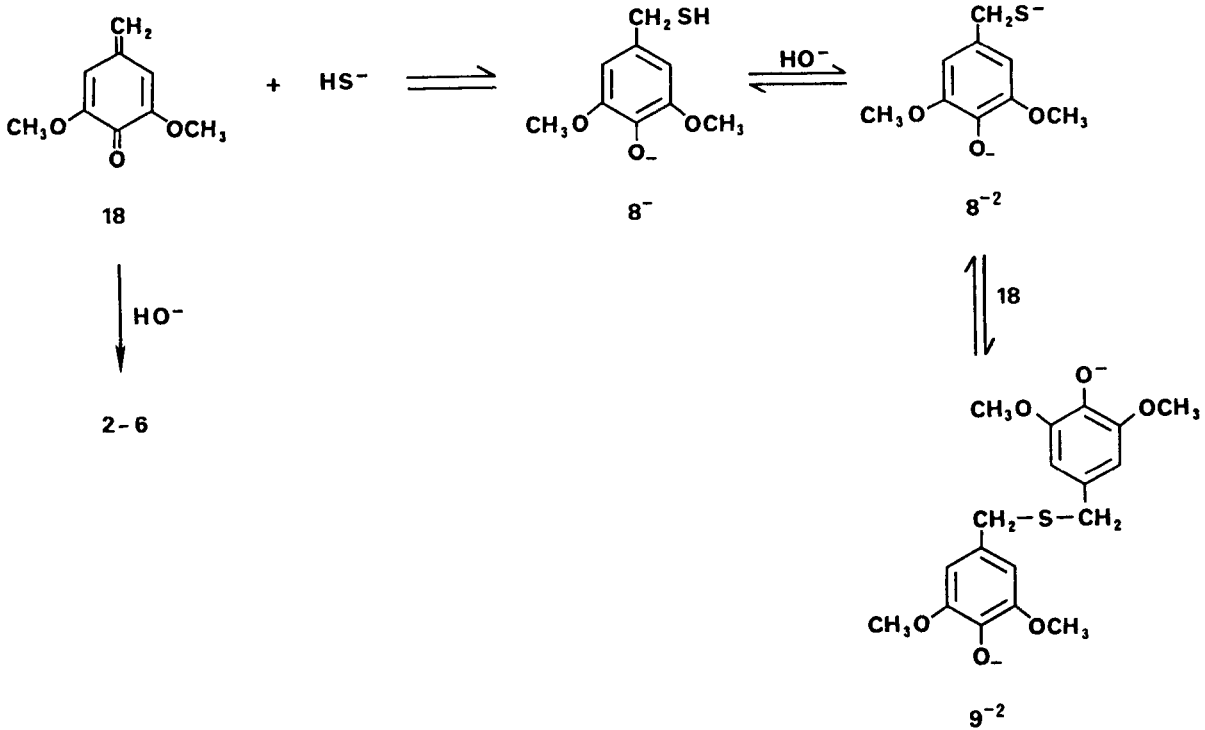


Figure 2. Relative GC signal areas (arbirary units) for 3,5-dimethoxy-4-hydroxybenzylthiol (8), , vs syringaldehyde-d_2 standard and for di-(3,5-dimethoxy-4-hydroxybenzyl)sulfide (9), ■● vs disyringylmethane-d_2.



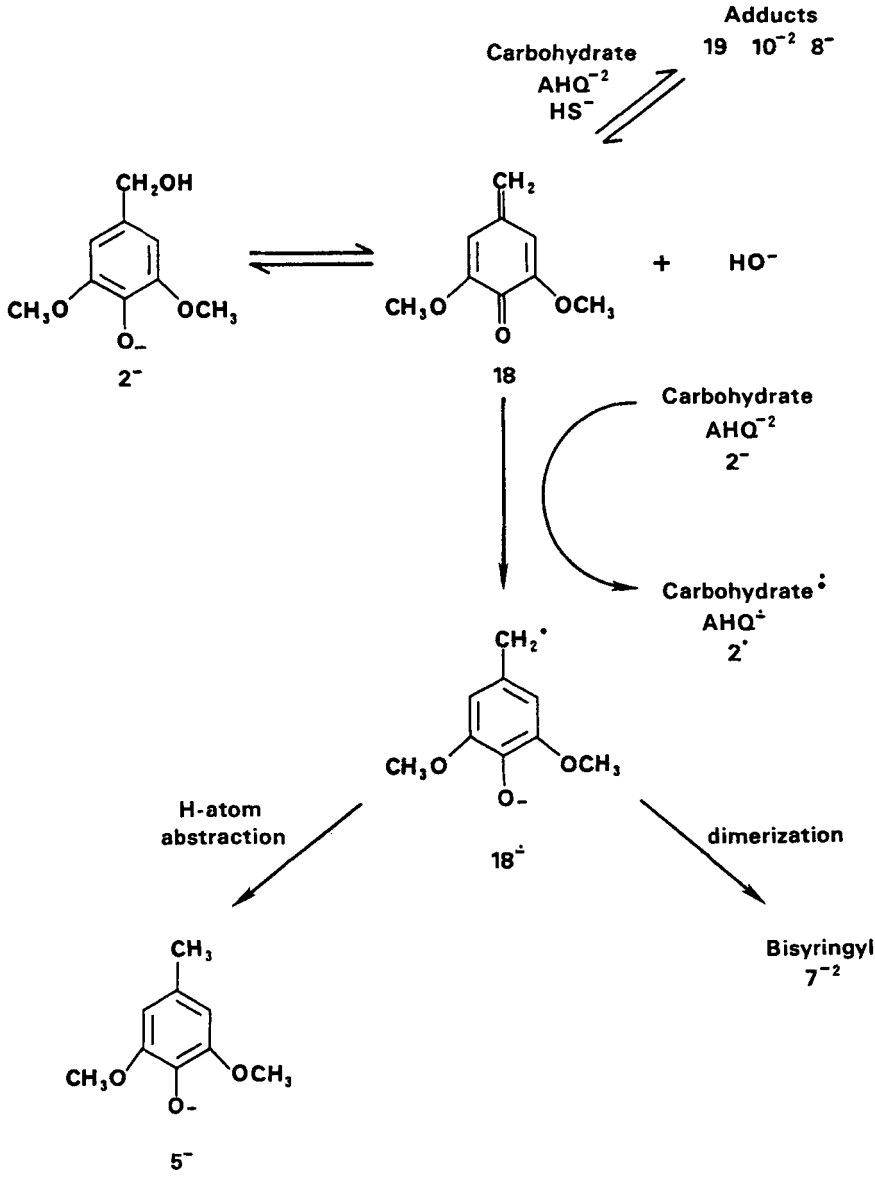
Scheme 2

With 1 equiv. each of NaSH and AHQ, the syringyl alcohol concentration dropped at a rate intermediate between that expected for the individual additives (Table 1). Consequently, the two additives must be competing with each other in reactions with the intermediate quinone methide. The low level of observed disyringylmethane (**3**) and high levels of 4-methylsyringol (**5**) and syringaldehyde (**6**) indicate that AHQ/AQ reactions eventually dominate. This may be because the adduct formation reactions are reversible, providing a constant source of QM which AHQ can divert to other products; however, NaSH can only add back to give more adduct. There was obviously adduct formation, based on poor material balance.

CONCLUSIONS

Our results can best be explained by the sets of reactions shown in Scheme 3. In lM NaOH at 135°C, syringyl alcohol is ionized and the phenolate ion is in equilibrium with a quinone methide (**18**). It is apparent from the material balance for components **2-7**, and extended product analyses, that the QM **18** can be captured by carbohydrates, AHQ^{-2}, and HS^- to give adducts. Since glucose is unstable in alkali at 135°C,[21] it is not certain whether glucose or a glucose-derived product is reacting with the QM. Based on product composition data as a function of time, we believe that the adduct formation reactions are reversible, at least in the cases of AHQ and NaSH.

The sequence of events which appears to occur in the AHQ-syringyl alcohol case is as follows: (a) QMs are formed from syringyl alcohol rapidly at 135°C; (b) AHQ^{-2} efficiently converts many of these QMs to $QMs^{\cdot-}$, coproducing $AHQ^{\cdot-}$; (c) coupling of a $QM^{\cdot-}$ with $AHQ^{\cdot-}$ within a solvent cage[22,23] may be a major pathway for adduct generation; (d) with large levels of AHQ^{-2} present, a good concentration of $QMs^{\cdot-}$ is produced simultaneously at early reaction times; (e) some of the $QMs^{\cdot-}$ escape the solvent cage and either (f) couple with another $QM^{\cdot-}$ or QM to give bisyringyl[2] or (g) are reduced by hydrogen atom transfer to give 4-methylsyringol. Later into the reaction, QMs are



Scheme 3

formed by breakdown of the QM-AHQ adduct structures and are converted to $QMs^{\cdot-}$ by electron transfer from AHQ^{-2}; the concentration of $QMs^{\cdot-}$ and available QMs is low at this point so that the probability of coupling is low, and hydrogen atom abstraction thus dominates.

In the glucose case, where electron transfer to QMs is known[5] to be much slower than AHQ^{-2}, the first step appears to be ionic adduct formation. Reversal of the adduct formation gives a low steady-state concentration of QMs and, by electron transfer, QMs^{-}; coupling will be rare, but reduction to 4-methylsyringol could occur.

In the hydrosulfide ion case, there appears to be an efficient, reversible production of sulfur adducts, probably via a simple ionic Michael addition of a sulfur ion to C_α of the QM.[24] Reversal of the reaction provides a steady concentration of QM which, in the absence of electron transfer reagents, undergoes a normal[2,24] dimerization to disyringylmethane (**3**). In the presence of electron transfer reagents, such as in the mixed additive experiments with NaSH and AHQ or glucose, the QM released from sulfur adducts can be diverted via radical reactions to give some 4-methylsyringol (**5**).

The observation of relatively large levels of 4-methylsyringol (**5**) in the presence of AHQ and glucose and low levels in the presence of NaSH and no additives (other than 1M NaOH) parallels observations made with regard to the abilities of these reagents to transfer electrons to quinone methides.[5] The $QM^{\cdot-}$, produced by electron transfer from AHQ^{-2} or glucose to QM **18**, can give rise to 4-methylsyringol by abstraction of a hydrogen atom from a monoprotonated AHQ (i.e., $AHQ\text{-}H^{-}$), a carbohydrate fragment, a starting syringyl alcohol molecule, or other organic products in the mixture. Previous studies have established that the benzylic hydrogens of syringyl alcohol are the source of hydrogen atoms in a simple NaOH system[2] and that AHQ systems are better able to supply hydrogen atoms than glucose systems.[5] Hydrogen atom abstraction from syringyl alcohol may account for part of the observed syringaldehyde.[2]

EXPERIMENTAL

The equipment, procedures, and most of the compound characterization are described in the previous paper.[2] The gas chromatography analysis employed a Hewlett-Packard 5890 with a flame ionization detector and a six-foot OV-17 column with 30 mL/min of helium (carrier gas) and a temperature program of 110-300°C at 15°/min, with holds at 185°C (4 min) and at 275°C (2 min).

Syringyl Alcohol Additive Reactions. The additive reactions were run in a manner similar to the NaOH control case.[2] Some additives, such as sodium sulfide (0.47 g, 2 equiv.) and anthrahydroquinone (various levels), were placed in the reaction vessel with the NaOH before warming. Glucose, because of its limited stability in alkali,[19] was added to the hot reaction vessel simultaneously with the syringyl alcohol; the quantities used were 1.08 g (2 equiv.) in 5.0 g of water or 2.70 g (5 equiv.) in 12.5 g of water. Additive combinations were performed in a similar way.

Anthrahydroquinone was prepared in a nitrogen atmosphere (glove bag) by the reduction of anthraquinone by dithionite. To a 250 mL Erlenmeyer flask was added 150 mL of oxygen-free water, enough 30% ultrapure NaOH to make at least a 1M NaOH solution, the preweighed anthraquinone (1.25 g, 2 equiv.; 0.31 g, 0.5 equiv.; or 0.06 g, 0.1 equiv.), and a three-fold excess of $Na_2S_2O_4$. The solution was stirred for at least an hour after which 2M H_2SO_4 was added until precipitation occurred. The solid was collected by filtration, washed twice with oxygen-free water, and placed in the reaction vessel.

Bisyringyl (7) Analysis. The concentration of syringyl alcohol (**2**) and reaction products **3-6** was determined by GC/MS selective ion monitoring (SIM) using deuterated analogs as internal standards.[2] A deuterated analog of **7** was not available for use. Only trace levels of **7** were observed in all the experiments except the reaction of syringyl alcohol with 2 equiv. of AHQ. The quantity of bisyringyl present in the latter case was estimated by comparing the GC signal area of **7** to the GC signal area of **2**/**2**-d_2, which elute simultaneously; the response factors

for **7** and **2**/**2**-d_2 were assumed to be similar, since they have similar molecular structures and weights.

Syringyl Alcohol-AHQ Adducts. Duplicate syringyl alcohol experiments, employing 135°C, 1M NaOH, and 2 equiv. AHQ, were conducted; nine samples were collected over a 4-hour reaction time. Each sample (~3 mL) was methylated by adding, with stirring, 1 mL of dimethylsulfate. After 15 min, the excess dimethylsulfate was quenched with 4.5 mL of concentrated NH_4OH, and the methylated sample was then extracted with chloroform. The samples were qualitatively analyzed by GC, and the adducts were identified by GC/MS.[25] The components, in increasing elution order, gave the following *m/e* (%) values (the assignments for **17** and the unknown, **?**, may be reversed):

11: 404 (M^+, 1), 223 (13), 181 (100).
15: 374 (M^+, 1), 193 (3), 181 (100).
17: 388 (M^+, 100), 373 (46), 345 (30), 221 (17), 202 (39), 101 (35).
13: 372 (M^+, 100), 357 (30), 297 (31), 213 (20), 171 (26).
? : 388 (M^+, 100), 373 (56), 311 (10), 255 (10), 221 (10), 215 (12), 207 (12), 178 (24), 163 (18), 122 (12), 119 (11), 133 (16).

Sulfur Compounds. The qualitative concentration analysis of the sulfur products formed from the addition of 2 equiv. of sodium sulfide to an alkaline reaction of syringyl alcohol was accomplished by obtaining GC chromatograms for 18 reaction samples. As with the analysis of bisyringyl, the assumption was made that syringaldehyde and disyringylmethane and their deuterium-enriched analogs had the same response factors. This assumption allowed for the subtraction of the nondeuterated portion of the GC peaks; the amount of syringaldehyde and disyringylmethane in each sample was determined by SIMS. Thus, the GC areas of **8** and **9** were compared to the GC areas of deuterated syringaldehyde and deuterated disyringylmethane, respectively. This GC area ratio was then divided by the moles of deuterated compound contained in the sample and the volume of the sample. The mass spectra of the sulfur compounds gave the following *m/e* (%) values:

8: 200 (M^+, 26), 167 (100), 148 (34), 136 (21).

9: 366 (M^+, 11), 332 (2), 200 (6), 168 (38), 167 (100), 148 (20), 136 (13).

ACKNOWLEDGMENTS

Portions of this work were used by D. A. Smith as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry (now the Institute of Paper Science and Technology). We would like to thank Dr. Leland Schroeder for helpful suggestions.

REFERENCES

1. Dimmel, D. R., Shepard, D., and Brown, T. A., J. Wood Chem. Technol., 1, 123 (1981).

2. Smith, D. A. and Dimmel, D. R., J. Wood Chem. Technol., preceding paper.

3. Kondo, R. and McCarthy, J. L., J. Wood Chem. Technol., 5, 37 (1985).

4. McDonough, T. J. and Van Drunen, V. J., Tappi, 63(11), 83 (1980).

5. Smith, D. A. and Dimmel, D. R., J. Org. Chem., 47, 5428 (1988).

6. Smith, D. A., Ph.D. Thesis, The Institute of Paper Chemistry, Appleton, Wisconsin.

7. Dimmel, D. R. and Shepard, D., J. Org. Chem., 47, 22 (1982).

8. Dimmel, D. R. and Shepard, D., J. Wood Chem. Technol., 2, 73 (1982).

9. Dimmel, D. R., J. Wood Chem. Technol., 5, 1 (1985).

10. Dimmel, D. R., Perry, L. F., Palasz, P. D., and Chum, H. L., J. Wood Chem. Technol., 5, 15 (1985).

11. Apfeld, P. B. and Dimmel, D. R., J. Wood Chem. Technol., 2, 269 (1982).

12. Wallis, A. F. A. and Wearne, R. H., J. Wood Chem. Technol., 7, 513 (1987).

13. Fullerton, T. J. and Wilkins, A. L., J. Wood Chem. Technol., 5, 189 (1985).

14. Samuelson, O. and Wennerblom, A., Svensk Papperstid., 57, 827 (1954).

15. Regnfors, L. and Stockman, L., Svensk Papperstid., 59, 507 (1956).

16. Teder, A. and Tormund, D., Svensk Papperstid., 76, 607 (1973).

17. Smith, D. A. and Dimmel, D. R., J. Wood Chem. Technol., 4, 75 (1984).

18. Blythe, D. A. and Schroeder, L. R., J. Wood Chem. Technol., 5 (3), 313 (1985).

19. Enkvist, T., Ashorn, T., and Hastbacka, K., Paperi Puu, 44, 395 (1962).

20. Gierer, J. and Lindeberg, O., Acta Chem. Scand., B32, 577 (1978).

21. Green, J. W., Pearl, I. A., Hardacker, K. W., Andrews, B. D., and Haigh, F. C., Tappi, 60(10), 120 (1977).

22. Lowry, T. H. and Richardson, K. S., Mechanism and Theory in Organic Chemistry, 2nd Edition, Harper and Row Publishers, Inc., New York, 1971, pp. 700-702.

23. Ashby, E. C., Buhler, J. D.; Lopp, I. G., Wiesemann, T. L., Bowers, J. S., Jr., and Laemmle, J. T., J. Am. Chem. Soc., 98, 6561, (1976).

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