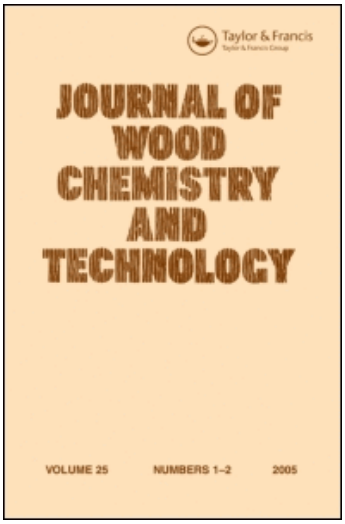

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Dimmel, Donald R. , Schuller, Lois F. and Apfeld, Patrick B.(1987) 'Electron Transfer Reactions in Pulping Systems (IV): An Example of a Large Reactivity Difference for Fragmentation of a β-ARYL Ether Bond by AHQ^{-2} and HS^{-}', Journal of Wood Chemistry and Technology, 7: 1, 97 — 113
To link to this Article: DOI: 10.1080/02773818708085255
URL: http://dx.doi.org/10.1080/02773818708085255

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(1), 97-113 (1987)

ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (IV): AN EXAMPLE OF A LARGE REACTIVITY DIFFERENCE FOR FRAGMENTATION OF A β-ARYL ETHER BOND BY AHQ^{-2} AND HS^-

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ABSTRACT

A lignin model (3E) with a propanol group on the β-carbon has been heated in alkali with no additives and with NaSH and anthrahydroquinone (AHQ) additives. The β-aryl ether bond of the model is efficiently fragmented by AHQ, but not by NaSH or simple NaOH. A competing cyclization of the propanol group with the quinonemethide of the model interferes with NaOH and NaSH fragmentation reactions. The data suggest that AHQ reacts by way of a mechanism different from that of NaSH - the AHQ by an electron transfer mechanism and the NaSH by an adduct mechanism. The reactions of β-allyl (3D) and β-propyl trityloxy (3F) models were also performed. The fragmentation efficiencies in these cases were: AHQ > NaSH > NaOH.

INTRODUCTION

The delignification of wood during alkaline (soda) pulping is aided by additives such as sodium hydrosulfide (NaSH, kraft pulping) and anthrahydroquinone (AHQ, anthraquinone pulping).[1] Primarily because of the structural complexities of lignin and lignin fragmentation products, delignification mechanisms are difficult to study directly. Models of lignin are often studied in order to help clarify possible pulping reaction mechanisms. Fragmentation of a model's β-aryl ether bond is considered to be indicative of wood delignification.[1] Generally the models are

capable of forming a key reactive lignin intermediate, a quinone-methide (QM), i.e., a structure similar to 1.

Model studies indicate that QM generation is the slow step in the additive-promoted delignification processes.[2,3] Because of this, kinetic studies often fail to provide useful mechanistic information about the nature of the additive-QM reactions.[3,4] Other complicating factors are that the additive reactions involve several steps (additions, deprotonations, eliminations, etc.) and compete with other reactions available to the QM, such as stilbene and vinyl ether formations.[3,5]

The study described herein purposely establishes a competing QM reaction in order to demonstrate the relative rates of additive-assisted delignification. The study employs model compounds which, in one respect, contain characteristic lignin groupings (α-hydroxy-β-aryl ether phenols), but, in another respect, contain atypical pentanol side chains.

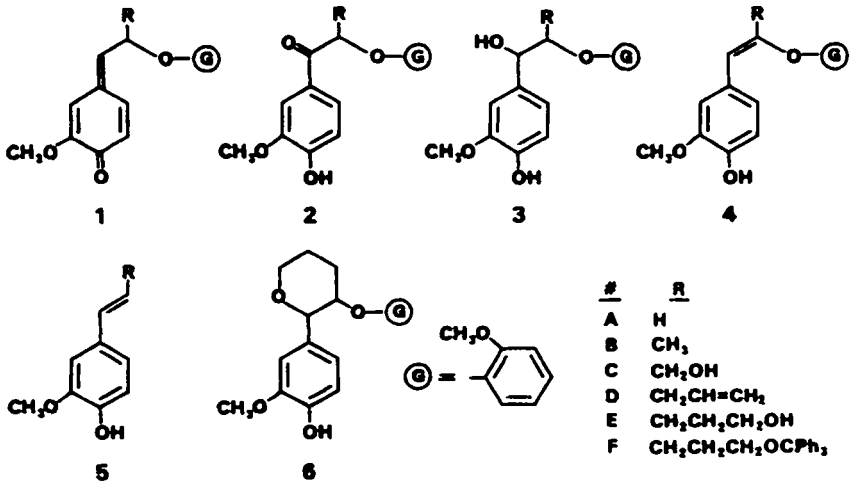
RESULTS

Model Compounds

Typical delignification (model fragmentation) studies use models such as 3A-C. These models can be readily prepared by reduction or alkylation-reduction of ketone 2A.[7] Similarly, alkylation of 2A with allyl bromide gives 2D, which when reduced by $NaBH_4$ affords model 3D. Hydroboration, followed by an aqueous alkaline hydrogen peroxide treatment, converts the "allyl" model 3D to the "propanol" model 3E. The latter, upon treatment with trityl chloride (Ph_3CCl or simply TrCl), affords the "propyl trityloxy" model 3F.

Model Reactions

Figures 1-3 give the guaiacol (2-methoxyphenol) yield data (i.e., % fragmentation) as a function of time when models 3D-F are



heated at 150°C under soda, kraft, and soda/AHQ conditions. The term "soda, kraft, and soda/AHQ" are used rather loosely here. Reagents and wood concentrations are much higher during the pulping of wood than the concentrations we have employed; for example, kraft pulping uses ~ 1M NaOH, while we used ~ 0.1M NaOH. Even though the reagent concentrations were low, the substrate concentrations were even lower. Our concentrations were designed to conserve expensive model compounds and ensure that reagents were not reaction limiting.

Gas chromatography-mass spectrometric (GC-MS) analysis of the product mixtures from the degradations of allyl model 3D showed fragmentation products, guaiacol and cis and trans styrenes 5D (which increased with increasing time when glucose, NaSH, and AHQ were present) and starting material (which decreased with increasing time). The level of vinyl ether by-product 4D, which was also observed, followed the order: no additive > glucose > NaSH > AHQ.

The vinyl ether and styrene products (4D-F and 5D-F) were not isolated or vigorously characterized. Their presence was indicated by GC retention time, by mass spectral analysis, and by inspection of NMR spectra of crude product mixtures. Accurate

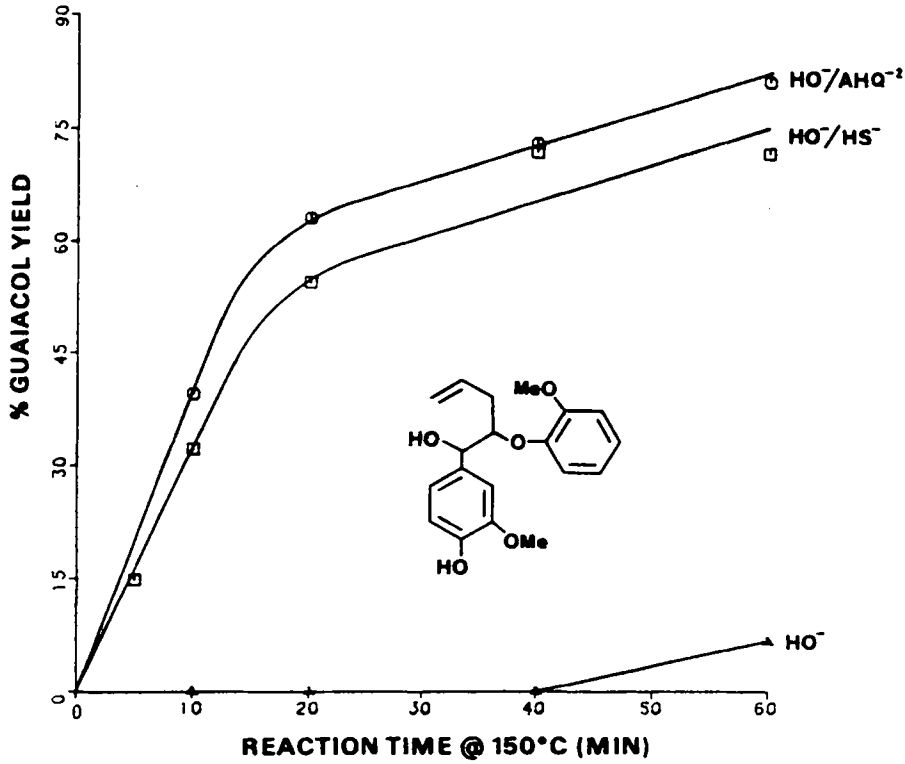


Figure 1. Guaiacol yield as a function of time for the degradation of model 3D at 150°C in water in the presence of 25 equiv. of NaOH, and 5 equiv. of NaSH, and 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

yield determinations of 4 and 5 type compounds were not attempted because (a) authentic samples were not available to get GC response factors relative to an internal standard and (b) secondary reactions, such as polymerizations and hydrolyses, are possible. Qualitative inspection of the GC data did, however, allow yield trends (relative to an internal standard) to be ascertained.

The GC-MS analysis of the product mixture from degradation of the propyl trityloxy model 3F was incomplete because of the low volatility of the tritylated compounds. A styrene fragmentation

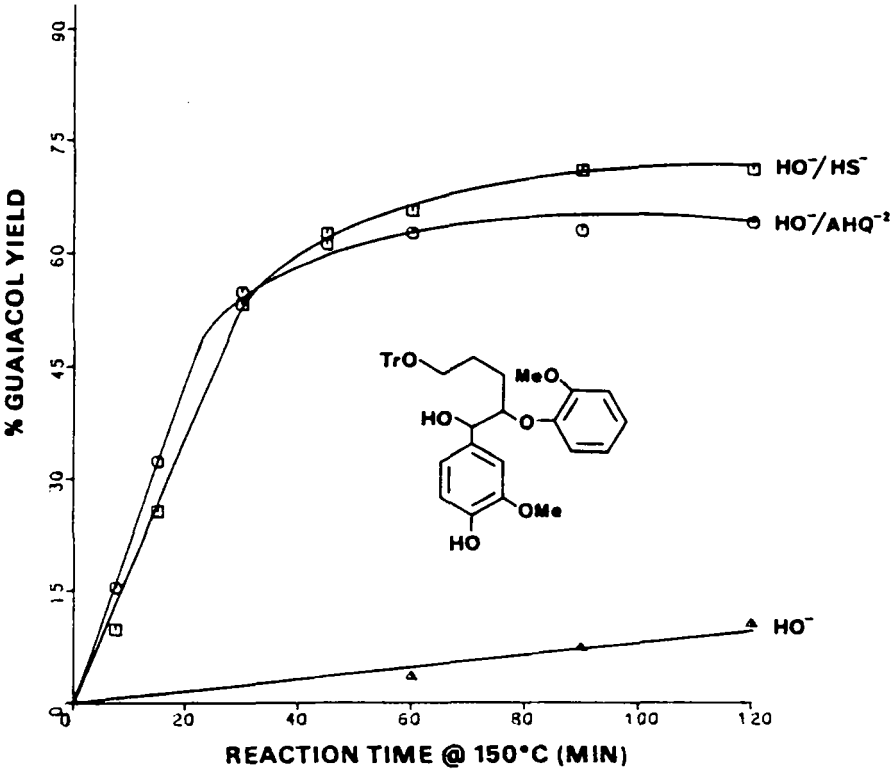


Figure 2. Guaiacol yield as a function of time for the degradation of model 3F at 150°C in 29% dioxane/water in the presence of 25 equiv. of NaOH, and 5 equiv. of NaSH, and 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

product 5F was, however, observed in significant amounts in additive degradation runs, but not in the simple NaOH run. Small amounts (ca. < 10%) of trityl alcohol and triphenylmethane were also observed in some of the product mixtures.

The degradation of the propyl trityloxy model 3F was conducted in 29% dioxane, a solvent medium in which 3F was soluble at room temperature. Dioxane, however, can adversely affect fragmentation yields;[8,9] for example, parallel degradations of models 3E, collecting data at six time intervals at 150°C and employing

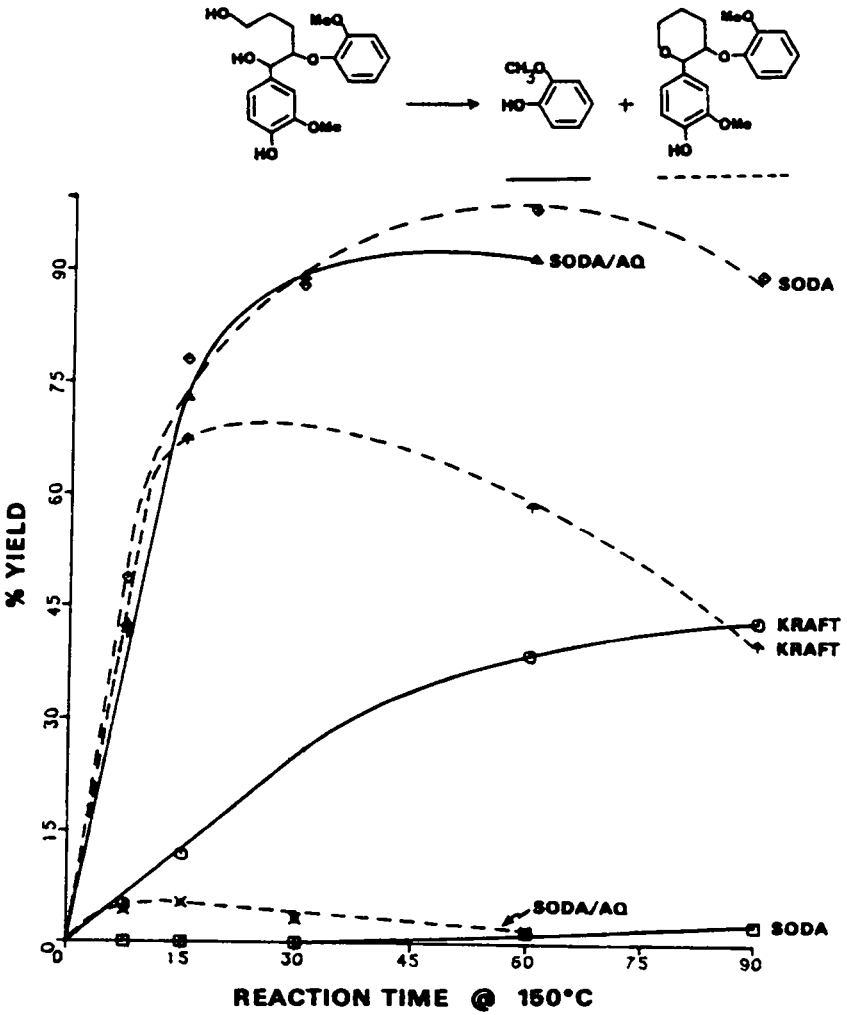


Figure 3. Yields of guaiacol (—) and cyclized compound 6 (— —) as a function of time in the soda, kraft and AHQ degradations of model 3E at 150°C.

either AHQ^{-2} or HS^- as additives, gave 70% less model fragmentation for the runs done in 29% dioxane versus runs done in pure water. On this basis the actual guaiacol yields observed with model 3F were quite high.

The levels of guaiacol produced (i.e., the degree of fragmentation) from the propanol model 3E followed the order AHQ^{-2} >> NaSH >> glucose = no additive (Fig. 3, solid lines). The GC-MS analyses of NaSH and AHQ product mixtures showed the usual loss of starting material and gain in fragmentation products, guaiacol and cis and trans styrenes 5E, with increasing time. The vinyl ether by-product 4E was not observed in any of the degradation runs of model 3E. Instead a side-chain cyclization product 6 was observed, increasing in the order: no additive = glucose > NaSH > AHQ (Fig. 3, dashed lines).

The cyclized product was present in high yields at long reaction times with the NaOH degradation of model 3E. It was isolated by chromatography of the soda reaction residue and characterized by spectral means (see Experimental Section for details).

Comparative degradations of the propanol model 3E and the cyclized compound 6 were done in aqueous alkali at both 150°C and 135°C with no additives, with AHQ and with NaSH. Fragmentation of 6 was not observed in the absence of the additives.

Figure 4, data collected at 135°C, shows that (a) AHQ^{-2} is quite superior to NaSH in fragmenting either model 3E or cyclized compound 6 and (b) fragmentation of the cyclized compound 6 occurs with both AHQ^{-2} and NaSH but at somewhat slower rates than fragmentation of model 3E. The same trends exist at 150°C, except that the relative differences between AHQ^{-2} and NaSH additives are less (see Fig. 3) and the guaiacol yields from fragmentation of the cyclized compound are higher, but still less than the yields obtained from direct fragmentation of propanol model 3E.

DISCUSSION

Model degradations typically show a fast fragmentation phase and a slow phase,[3,5] such as seen in Fig. 1. This behavior is

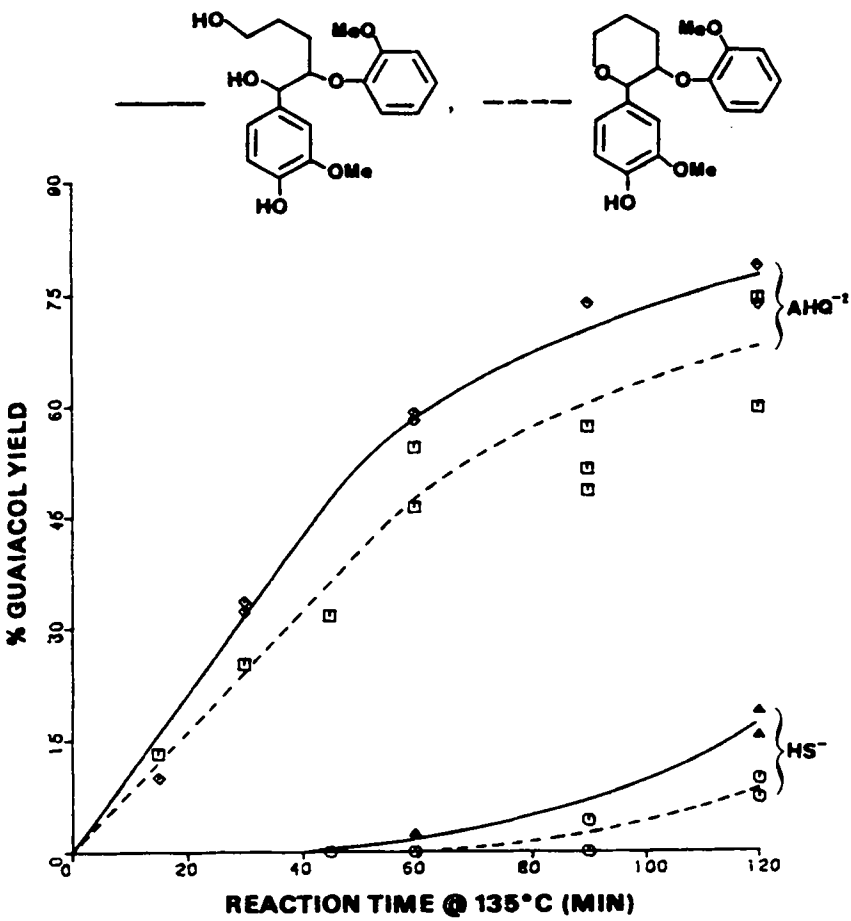
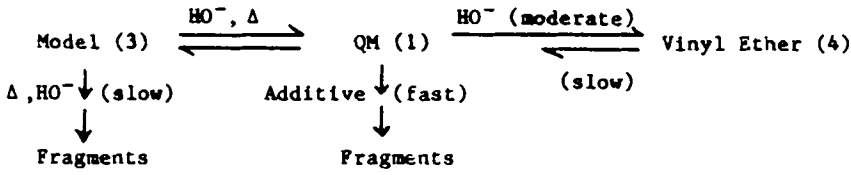


Figure 4. Guaiacol yield as a function of time for the degradation of models 3E (—) and 6 (— —) at 150°C in water in the presence of 25 equiv. of NaOH and 5 equiv. of NaSH, or 5 equiv. of AHQ (prepared from 5 equiv. each of AQ and glucose).

SCHEME 1
Typical Model Reaction Pathways



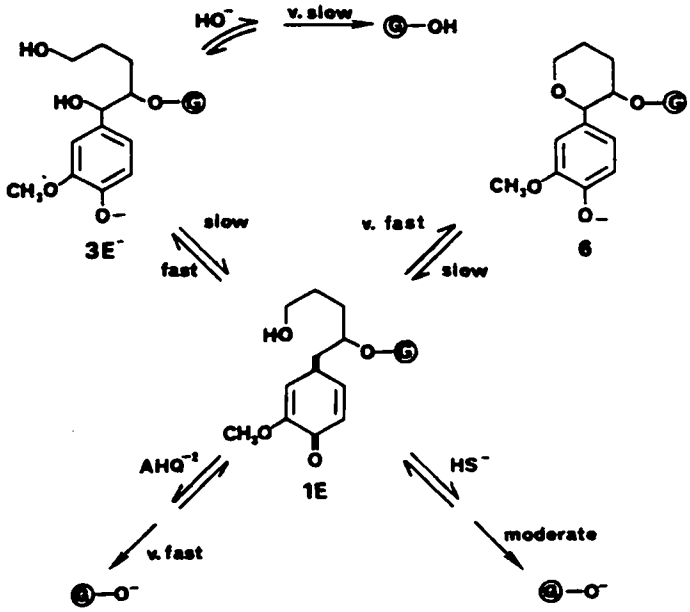
indicative of competing reactions of the type shown in Scheme 1.[3,5] Initially the model is converted to fragments and vinyl ether products. The fast fragmentation process decreases when the supply of QMs diminishes. After a while, the only supply of QMs is from the slow reversal of the vinyl ether formation reaction.[10]

Both the allyl and propyl trityloxy models, 3D and 3F, appear to display this type of behavior. Also, each gave small, but real, amounts of fragmentation under soda conditions and similar, relatively high fragmentation yields with NaSH and AHQ. The observation here (especially at early reaction times) that AHQ gives somewhat higher fragmentation yields than NaSH agrees with earlier findings and has been interpreted to mean that AHQ is more effective at diverting QM intermediates toward fragmentation and away from nonproductive side reactions.[3] The fact that the sterically hindered model 3F fragmented to a high level in the presence of either HS^- or AHQ^{-2} indicates further that C_β-steric effects do not play a role in the rate determining step.[4]

Scheme 2 summarizes, in a qualitative manner, the degradation results with the propanol model 3E. In the absence of additives the model is efficiently converted to cyclized product 6 and fragmentation is not observed. This means that the direct fragmentation of the model is slow relative to QM formation and that intramolecular cyclization of the QM is quite fast, superceding other competing reactions such as vinyl ether formation.

The fact that cyclized compound 6 gives significant levels of fragmentation (guaiacol) upon treatment with AHQ^{-2} or NaSH at

SCHEME 2
Reactions of the β-Propanol Model 3E



150°C indicates that the cyclization step is reversible. The additives can act upon the QM formed by ring opening of 6 to cause fragmentation; direct attack of additives on the cyclized material 6 to give guaiacol would be unlikely.[1,11,12]

Once formed, the QM has several reaction options, all of which regenerate an aromatic system. It is apparent from our data that the option of reacting with AHQ to give fragments is of low energy and quite favorable. The AHQ fragmentation option competes favorably with the fast side-chain QM cyclization reaction (Fig. 3). On a relative basis, capture of the QM by HS^- and subsequent fragmentation is slow compared to cyclization of the QM (Fig. 3).

The qualitative interpretation presented in Scheme 2 can also be expressed by an energy diagram, Fig. 5. Fragmentation by OH^- is a high energy process.[5] The slow step for fragmentation by an additive (HS^- or AHQ^{-2}) is initially QM formation from the simple

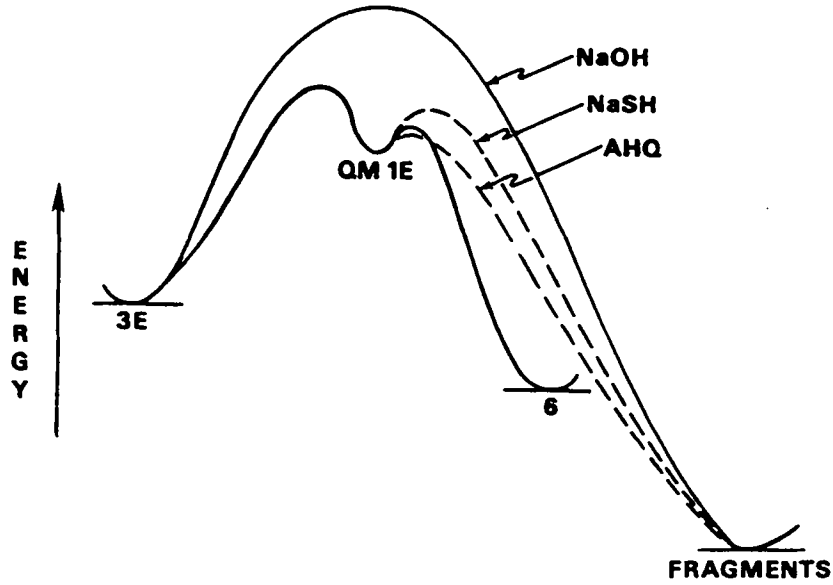
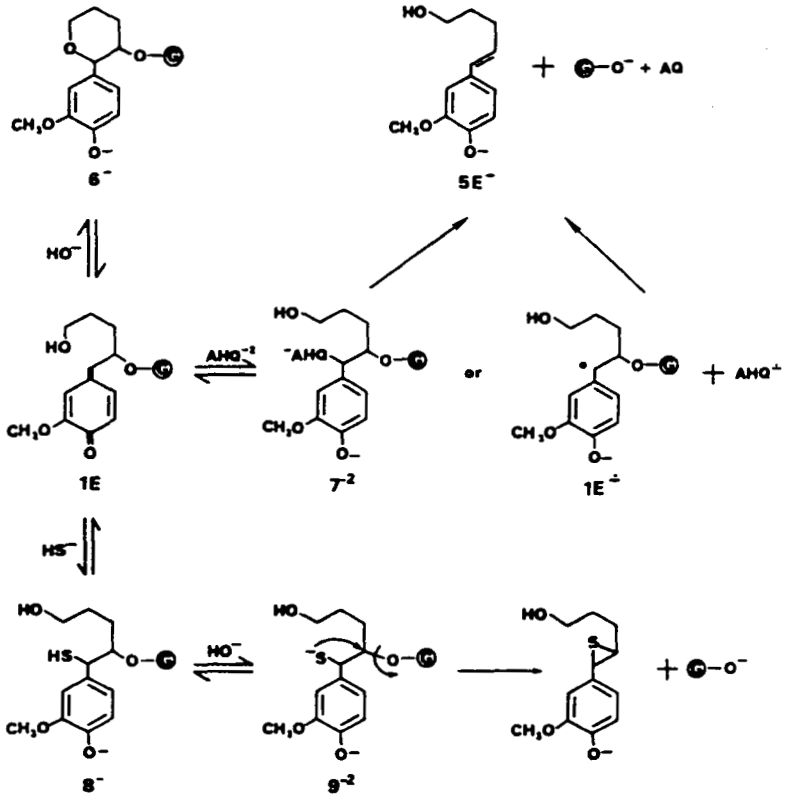


Figure 5. Proposed energetics for the reactions associated with model 3E. For simplicity, the multiple steps associated with the NaOH, NaSH and AHQ fragmentation processes have been omitted and the fragmentation products are considered to have the same energies from all processes.

model 3E.[3] After the reactions proceed for a while and 3E has essentially been fragmented or converted to cyclized product 6, the slow step appears to be QM generation from 6. Consequently, the rates of the forward and backward steps in the cyclization process have a major impact on the extent of fragmentation possible with slower competing processes, such as the OH^- and SH^- reactions.

The reactions of the propanol model 3E, together with its competing cyclization reaction, demonstrate that AHQ^{-2} is a much more effective additive than HS^- at promoting model fragmentation. Why? Both AHQ and NaSH could be acting <u>via</u> "adduct" mechanisms,[1,13] with the QM-AHQ adduct (7^{-2}) being either easier to form or more prone to fragment than the QM-SH adduct (9^{-2}), Scheme 3.

SCHEME 3
Possible Cleavage Mechanisms of the β-Propanol Model QM 1E



Alternatively, AHQ^{-2} could be acting <u>via</u> a chemistry which has significantly lower energy requirements than the standard (NaSH) adduct chemistry. This unique chemistry could be electron transfer[13] between AHQ^{-2} and QM 3E, leading to radical ion intermediates $AHQ^{\cdot-}$ and $1E^{\cdot-}$ and subsequent fragmentation of the latter (Scheme 3). Reactions of this type have been demonstrated under idealized conditions.[14]

CONCLUSIONS

The propanol model 3E has a built-in cyclization reaction possible when its quinonemethide (1E) is formed in aqueous alkali. The superior ability of AHQ^{-2} to fragment this model indicates that there is a chemistry available, probably electron transfer chemistry, which can effectively compete with the cyclization reaction. The poor effectiveness of NaSH to induce fragmentation of 3E suggests that its adduct mechanism does not compete well with cyclization.

With the other models, 3D and 3F, vinyl ether generation competes with model fragmentation. Both AHQ and NaSH-induced fragmentation appear to be of lower energy than vinyl ether generation. The fact that AHQ^{-2} fragmentation efficiencies are higher than that of NaSH suggests that the energy of AHQ-fragmentation is lower than that of NaSH-fragmentation and, thus, competing reactions will be less for the AHQ case. The slow step in the additive reactions and vinyl ether generation is still quinonemethide generation. If it were not for competing reactions, the fragmentation efficiencies of AHQ^{-2} and HS^- would be the same.

EXPERIMENTAL SECTION

The equipment,[15] guaiacol analysis by methylation and GC analysis with *p*-isopropylphenol as an internal standard,[5] model degradation procedures,[3,5] and model/reagent amounts[3,5] have been previously described. Some specific details are given in the figure captions. The synthesis of the models will appear in a separate publication.[16] The model names are: 2-(2-methoxyphenoxy)-1-(3-methoxy-4-hydroxyphenyl)-4-penten-1-ol (3D), 2-(2-methoxyphenoxy)-1-(3methoxy-4-hydroxyphenyl)-1,5-pentadiol (3E), and 2-(2-methoxyphenoxy)-1-(3methoxy-4-hydroxyphenyl)-5-triphenylmethoxy-1-pentanol(3F).

Analysis of the methylated product mixtures by GC-MS led to the tentative identification of several compounds. The identifications were based on GC elution times relative to known components

of the mixtures and an interpretation of the mass spectra. The compounds tentatively identified by this procedure are listed below.

1-(3,4-Dimethoxyphenyl)-1,4-pentadiene (methylated 5D) and isomers

Two isomers of apparent molecular weight of 204 were observed in the methylated reaction mixtures from the AHQ and NaSH degradations of model 3D; the two were assumed to be cis/trans isomers of the 1,4-pentadiene type, but could be other position isomers such as 1,3 or 2,4 (conjugated) pentadienes. The two eluted at times intermediate between methylated guaiacol and dimer 3D and had nearly identical spectra: m/e (%), 204 (100, $M^{\cdot+}$), 189 (74, M-CH_3), 174 (35, M-CH_2O), 173 (64, M-OCH_3), 158 (57, M-CH_3, OCH_3), 131 (26), 129 (44), 128 (24), 115 (32), and 91 (20).

The products from several small scale 150°C reactions of 3D with AQ/glucose/NaOH were combined, exposed to air, filtered to remove AQ, acidified, and $CHCl_3$ extracted. The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evaporated; the resulting residue was dissolved in $CDCl_3$ and a ^1H-NMR spectrum recorded. Based on the intensities of the signals in the 1.8 δ (=C-CH_3), 2.9 δ (=C-CH_2-C=), 4.9-5.2 δ (=CH_2) and 5.5-6.6 δ (=CH-) regions, the sample appears to have substantially more conjugated diene components (ArCH=CH-CH=$CHCH_3$) than nonconjugated diene components (ArCH=CH-CH_2-CH=CH_2).

2-(2-Methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,4-pentadiene (methylated 4D)

This compound was most prominent in the soda degradation of 3D and eluted just prior to methylated 3D: m/e (%) 326 (100, $M^{\cdot+}$), 300 (23, M-HC≡CH), 257 (30, M-HC≡CCH_2), 226 (21), 225 (21), 202 (34, M-$HOPhOCH_3$), 188 (23), 178 (29), 172 (29), 151 (33, $diOMePhCH_2^+$), and 115 (23).

5-(3,4-Dimethoxy phenyl)-4-penten-1-ol (5E)

This compound was observed in the methylated product mixtures

from the reaction of model 3E with AQ/glucose; it eluted just prior to AQ in the GC: m/e (%) 222 (100, $M^{+\cdot}$), 221 (34), 191 (72), 166 (48), 165 (65) and 151 (35). Several reactant solutions were combined and column chromatographed. NMR spectra of chromatography fractions did not, however, verify the presence of 5E. The compound, which is of the styrene type, may have polymerized sometime during the isolation procedure. Its identification should be considered tentative.

1-(3,4-Dimethoxyphenyl)-5-triphenylmethoxy-1-pentene (methylated 5F)

This compound was observed in the AHQ and NaSH degradations of 3F at 25.7 min (6 ft glass column packed with 3% OV-1 on 100-120 mesh gas chrom WHP, temperature programmed at 65° for 2 min, 2°/min to 80°, 30°/min to 285° and then hold at 285°C); m/e (%) 464 (3, M^{+}), 243 (100, Ph_3C^{+}), 221 (45, M-CPh_3), 177 (48, diOMePhCH=$CHCH_2^{+}$), 165 (53, PhCHPh), 151 (15, diOMePhCH_2^{+}), and 105 (26, PhC≡O^{+}). As with 5E, chromatography isolation and NMR characterization was not successful; the structure of 5F should be considered tentative.

1-(3-Methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy) tetrahydropyran (6)

This compound was observed in product mixtures from high temperature alkaline degradation reactions of 3E. Methylated 6 displayed the following mass spectrum: m/e (%) 344 (55, M^{+}), 221 (100, M-C_2 substituent), 220 (24, M-C_2 subst. and H), 165 (27, 3,4-diOMePhC≡O^{+}) and 151 (41, 3,4-diOMePhCH_2^{+}). The compound (underivatized) was also isolated from 3E degradations as described below.

Into each of 26 small pressure vessels (bombs)[5] was placed 40 mg of 3E and 3.5 mL of 1M NaOH, prepared from deoxygenated distilled water; the filling and sealing of the bombs was done in

a glove bag under a nitrogen atmosphere. The bombs were rotated in a 135°C oil bath for 3 hrs, cooled, opened, and added collectively (along with 1M NaOH rinses of the bombs) to a separatory funnel. The solution was acidified with dilute HCl and extracted three times with $CHCl_3$. The combined $CHCl_3$ extracts were dried (Na_2SO_4) and evaporated.

The viscous liquid residue was dissolved in a small volume of CH_2Cl_2 and applied to the top of a CH_2Cl_2 slurry packed silica gel-60 column (1.5 x 60 cm). The column was eluted with 50 mL of CH_2Cl_2, 100 mL of 2.5% EtOAc/CH_2Cl_2, 200 mL of 5% EtOAc/CH_2Cl_2, and 300 mL of 10% EtOAc/CH_2Cl_2; roughly 70-10 mL fractions were collected. Analysis by GC showed that fractions 13-20 (550 mg, 53%) were pure compound 6: m/e (%) 330 (38, M^+), 207 (100, M-R), 206 (34, M-RH), 151 (38, $RC{\equiv}O^+$), 137 (57, RCH_2^+), 124 (10, RH^+), 109 (13) and 77 (14), where R is a 3-methoxy-4-hydroxyphenyl or 2-methoxyphenoxy group; ; ^{1}H-NMR ($CDCl_3$) δ 1.81 (m, 3, C_4-protons and one of the C_3-protons), 2.40 (m, 1, one of C_3-protons), 3.5-3.8 (m, 1, C_2H), 3.71 and 3.80 (s, 3 and 3, OCH_3), 4.05 (m, 2, C_5-protons), 4.34 (d, J = 9.0 Hz, 1, C_1H), 5.52 (s, 1, OH) and 6.5-7.0 (m, 7, ArH) - the assignments were aided by specific proton decoupling experiments; ^{13}C-NMR ($CDCl_3$) δ 25.5 and 30.2 (t, C_3 and C_4 methylene carbons), 55.7 and 55.8 (q, OCH_3 groups), 68.1 (t, C_5), 79.2 (d, C_2), 82.8 (d, C_1), 110.1, 112.3, 113.7, 117.2, 120.4, 120.5, and 121.8 (d, protonated aryl carbons), 131.6, 144.9, 145.8, 147.0 and 150.3 (s, nonprotonated aryl carbons).

ACKNOWLEDGMENTS

Portions of this work were used by P. B. Apfeld as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry.

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