Quinones in alkaline pulping

Characterization of an anthrahydroquinone – quinone methide intermediate

ABSTRACT
Cyclic voltammetric examination of the anthraquinone redox system indicated that the predominant species in aqueous alkali is anthrahydroquinone (AHQ), and the corresponding semiquinone has only transient existence at best. Reaction of AHQ with the quinone methide (QM) derived from guaiacylglycol-β-guaiacyl ether (1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol) resulted in the formation of an intermediate AHQ/QM adduct, 1-(3-methoxy-4-hydroxyphenyl)-10-hydroxyanthracen-9-one-10-yl)-2-(2-methoxyphenoxy)ethane. 1H NMR spectroscopy of the adduct and its derivatives is consistent with the proposed structure. Further confirmation was provided by an independent synthesis of a derivative of the adduct. Treatment of the adduct with alkali at elevated temperature gave the same cleavage fragments (guaiacol and 2-methoxy-4-vinylphenol) which were formed upon digestion of I in soda-AHQ pulping liquor.

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It has been recently shown (1) that upon digestion of the lignin model guaiacylglycol-β-guaiacyl ether (I) in soda pulping liquor with a reduced form of anthraquinone (AQ) or 1-H-benz[f]indazole-4, 9-dione (NQ), the major products were the cleavage fragments guaiacol (III) and 2-methoxy-4-vinylphenol (IV), presumably via reaction pathway A in Fig. 1. In the absence of additives, pathway B predominated to give the vinyl ether V, as has also previously been reported (2). It is significant that under soda pulping conditions, and in the presence of the oxidized forms of the quinones (AQ or NQ), much smaller increases in guaiacol yield resulted, and pathway B was still a major factor in the overall reaction.

1. Reaction products upon alkaline digestion of guaiacylglycol-β-guaiacyl ether (I).
On the basis of the product distributions from the model reactions, and upon analysis of isolated lignins, it was proposed that the accelerated delignification in soda-AQ wood cooks results from enhanced \( \beta \)-ether cleavage of free phenolic units (\( I \)). These units would include both the initial free phenolic \( \beta \)-ethers in wood plus those formed during pulping as a result of the cleavage of \( \beta \)-ether bonds.

A recently completed kinetic study of the veratryl analog of 1 showed that AHQ had no effect on the alkaline cleavage of blocked phenolic \( \beta \)-ether units (3). As a result of an earlier investigation, it had been postulated (\( I \)) that a reduced form of the quinone reacts directly with the transient quinone methide (\( II \), Fig. 1), thus competing effectively with the formation of vinyl ether.

The subject of the present investigation is the characterization of the reduced form of AQ responsible for accelerated delignification and its reaction with quinone methides.

Results and discussion

Reduced form of AQ

It has been postulated on the basis of polarographic measurements in aqueous solution that AQ undergoes a reversible one-electron reduction at a potential of -0.77 to -0.83 V vs. a saturated calomel electrode (SCE) (4). However, this is only the case in organic solvents such as dimethylformamide (DMF) or dimethylsulfoxide (DMSO). When a methylene chloride solution of AQ was examined by means of cyclic voltammetry (5), two sets of peaks were observed, one centered at -0.80 V and one at 1.26 V vs. SCE (as shown in Fig. 2). The separation between the anodic and cathodic peaks within both sets is approximately 70 mV and did not vary with scan rate, indicating two reversible one-electron changes. This behavior is consistent with earlier polarographic studies of AQ in DMF (6, 7). The first cathodic wave corresponds to the reduction of AQ to anthrasemiquinone (ASQ), and the second cathodic wave indicates further reduction to anthrahydroquinone (AHQ) (Fig. 3).

The well-separated couples in the cyclic voltammogram indicate that the ASQ is relatively stable toward disproportionation. When water or sodium hydroxide solution was gradually added to the DMSO solution, the second set of waves shifted toward more positive potential, indicating increasing instability of the ASQ. Ultimately, in aqueous solution the ASQ rapidly disproportionated to AQ and AHQ and the cyclic voltammogram exhibited only one set of waves, centered at about -0.8 V, corresponding to a two-electron redox process.

As a result of cyclic voltammetry studies of AQ in aqueous alkali, it is clear that the predominant species in solution is AHQ. Although this observation indicates that the AHQ is the active reductant under soda-AQ pulping conditions, the possibility of semiquinone involvement cannot be discounted.

Reaction of quinone methide with AHQ

When a methylene chloride solution of \( II \) was slowly added to an alkaline solution of AHQ at 45°C, an adduct was obtained in nearly quantitative yield. When the adduct was heated in aqueous alkali at 80°C the products were \( III, IV \), and AQ (Fig. 1). Treatment of \( I \) with AHQ under the same conditions led only to quantitative recovery of starting material, which was expected since the reaction temperature was not high enough for the generation of \( II \) (8).

An infrared spectrum of the adduct revealed a strong carbonyl absorption at 1677 cm\(^{-1} \), and the \( ^1 \)H NMR spectrum exhibited two different deuterium-exchangeable protons. On the basis of spectra interpretation, structure \( VI \) was postulated (Fig. 4). Formation of the adduct is probably a concerted nucleophilic addition to the \( \alpha \)-carbon of II. The electron shifts which occur in the AHQ dianion are analogous to those which take place in the transannular tautomeration demonstrated in the well-known anthrone–anthranol equilibrium (9). Also, the mode of addition of AHQ to the quinone methide parallels one reported previously in which 2,6-dimethylphenol is added in a transannular fashion to \( II \) (10). When \( VI \) was heated at 80°C in aqueous alkali, the same cleavage fragments (AQ, III, and IV) were obtained as those which formed upon digestion of 1 in soda-AHQ pulping liquor (1). A plausible decomposition mechanism is illustrated in Fig. 4.

An adduct of a quinone methide and AHQ was recently proposed (11) which was postulated to be linked by a carbon–oxygen bond rather than a carbon–carbon bond. However, the results obtained in this study are clearly inconsistent with such a carbon–oxygen linkage.

The \( ^1 \)H NMR spectrum of \( VI \) is shown in Fig. 5 along with the assigned locations of the two deuterium-exchangeable protons, \( H_a \) and \( H_b \). Methylation of \( VI \) with diazomethane resulted in the disappearance of the \( H_b \) resonance and the appearance of a new methoxyl resonance at 3.7 \( \delta \) (VII, Fig. 5). The unusual lowfield position of the aliphatic hydroxyl proton \( H_a \) may be explained by its hydrogen bonding with a phenoxo oxygen atom as shown in

![Diagram](image_url)

4. Formation and decomposition of the AHO-quinone methide adduct VI.
5. $^1H$ NMR spectra of adduct VI and derivatives.

Fig. 6 (12). This stereochemical arrangement also allows explanation of the upfield displacement of the three aromatic protons $H_a$, $H_d$, and $H_e$ (δ = 6.4, 5.5, and 5.4, respectively) and the methoxyl protons in ring A (δ = 3.4); rotation of this ring about the alkyl-aryl bond brings all of these protons well within the shielding regions of rings C and D. The ring-B methoxyl protons are situated well outside these shielding regions, resulting in a more typical resonance at δ = 4.0 (Fig. 5).

Acetylation of VII gave VIII, which exhibited a paramagnetic shift of the methine proton $H_f$ (from ~3.6 to 4.7 δ) as shown in Fig. 5. This shift can readily be explained by long-range deshielding by the acetate carbonyl group (13). The simultaneous diamagnetic shift of the ring-B methoxyl protons (from 4.0 to 3.7 δ) can likewise be explained by the structure in Fig. 6 since a Fieser model of VIII indicates that the methoxyl group is forced into a shielding cone of the acetate carbonyl group (14).

As an additional confirmation of structure VI, the methylated adduct VII was reduced with lithium aluminum hydride to give IX, as shown in Fig. 7. Subsequent dehydration with glacial acetic acid gave XI via the unstable enol X. By an independent route compound XII was synthesized by the addition of anthranol anion XIII (generated from anthrone XIV) to the quinone methide II. Finally, methylation of XII with diazomethane gave a compound shown by $^1H$ NMR to be identical to XI derived from VI. $^{13}C$ NMR analyses of both VI and XI provided further proof of the proposed structures.

Since the presentation of this paper the structure of VI has been verified (15). A more detailed $^1H$ NMR investigation of derivatives of VI along with those of similar adducts is the subject of current research.

**Summary**

Studies of the reduced form of AQ in aqueous alkali by cyclic voltammetry indicated that the predominant species is anthrahydroquinone (AHQ). An adduct formed from AHQ and the quinone methide of guaiacylglycol-$eta$-guaiacyl ether (I) was isolated and
characterized both by 1H NMR spectroscopy and by an independent synthetic method. Upon mild heating (80°C) with alkali the adduct gave the same cleavage products as did I upon digestion in soda pulping liquor at 160°C in the presence of AHQ.

The present model study suggests a possible mechanism of quinone-induced β-ether cleavage in lignin which leads to an increased delignification rate in alkaline pulping. The presence of an intermediate adduct between lignin quinone methides and AHQ would be very difficult to detect under pulping conditions because of its extremely transient nature. However, alignment of a quinone methide moiety with the AHQ molecule (such as a charge-transfer complex) followed by a rapid concerted formation and decomposition may be all that is needed to explain an increased delignification rate according to the present mechanistic study. Investigations aimed at detecting adduct formation in isolated lignins are currently in progress.

Experimental

Analytical methods

1H NMR spectra were determined in CDC13 solutions on a Varian T-60 spectrometer with tetramethylsilane as internal reference (δ = 0 ppm). 13C NMR spectra were determined on a JEOL FX60 (15.00 MHz) spectrometer as totally proton decoupled, and with single-frequency, off-resonance decoupling (SFORD) to determine peak multiplicities. The mass spectrum was determined on a Finnigan 4021-T GC/MS. Infrared spectra of samples in KBr disks were determined on a Beckman IR-12 spectrometer. Melting points were determined on a calibrated Thomas-Hoover capillary mp apparatus. Unless noted otherwise, the adduct VI and derivatives exhibited only one spot upon thin-layer chromatography (on silica gel with 30-50% ethyl acetate/petroleum ether as developer).

Electrochemical methods

Cyclic voltammograms were determined with a Princeton Applied Research (PAR) Model 174A polarographic analyzer, in conjunction with a PAR Model 175 Universal Programmer and Houston Instruments Omniphonic, Series 2000, X-Y recorder. A three-electrode system was used which consisted of a PAR hanging mercury drop working electrode, a platinum wire counter electrode, and a saturated calomel electrode separated from the sample solution by a bridge filled with a 1:1 mixture of water and 0.1 M tetrabutylammonium fluoroborate (TBAF) in DMSO.

The AQ solutions (10⁻³ M in 0.1 M TBAF/DMSO) were purged with nitrogen for at least 5 min prior to analysis. Scan rates of 20 to 500 mV/s were used.

Preparation of AHQ - quinone methide adduct

A methylene chloride solution of the quinone methide II was prepared from I (1.00 g, 3.45 mmoles) by a method similar to that reported previously (16). An AHQ solution was prepared by stirring a mixture of AQ (0.62 g, 3.00 mmoles), sodium dithionite dihydrate (1.26 g, 6.00 mmoles), and 1 M NaOH (50 ml) under nitrogen at 50°C for 1 hr. The cold (60°C) solution of II was then added dropwise, over a 30-min period, to the AHQ solution through an open neck of the reaction flask so that the solvent was able to flash off. The N₂ flow was continued throughout the addition during which a temperature of 45°C ± 2°C was maintained. The resulting red suspension was cooled to room temperature and filtered. The solid was suspended in water (50 ml) and the suspension neutralized with acetic acid, then extracted with chloroform (4 x 25 ml). The organic layer was dried over MgSO₄ and evaporated under vacuum, leaving a pale-yellow amorphous solid (1.35 g, 2.74 mmoles, 91%), mp 166-173°C dec.; γ<sub>α</sub> = 1677s cm⁻¹. The 1H NMR spectrum is illustrated in Fig. 5. 13C NMR (acetone-d₆): δ 55.8, 56.4 (methoxyls), 60.3 (C-1), 71.0 (C-2), 76.6 (C-10), 182.3 (C-9), 183.2 (C-9). 13C NMR (CDCl₃): δ 85.7, 56.0 (methoxyls), 59.0 (C-1), 71.0 (C-2), 10 lost under CDCl₃, peaks, 111.9 to 149.6 (aromatics), 182.6 (s, C-9).

Decomposition of VI in alkali

A mixture of VI (200 mg, 0.41 mmole) in 1 M NaOH (25 ml) was heated at 80°C for 4 hr under an N₂ atmosphere while stirring magnetically. The resulting red suspension was then stirred in air at room temperature for several hours during which time the red color disappeared and a yellow suspension resulted. Extraction of the suspension with chloroform yielded AQ (83 mg, 0.400 mmole, 98%). Neutralization of the aqueous layer with acetic acid and reextraction with chloroform yielded a yellow oil (79 mg). A 1H NMR spectrum of the oil indicated a mixture of roughly equal molar amounts of III and IV.

Preparation of VII by methylation of VI

The adduct VI (100 mg, 0.21 mmole) in methanol (10 ml) was treated with a solution of diazomethane (large excess) in diethyl ether at room temperature for 2 hr. Evaporation of the solvent left a yellow solid (VII, 100 mg: 0.2 mmole, 97%), mp 134-141°C, γ<sub>α</sub> = 1670s cm⁻¹. The 1H NMR spectrum is illustrated in Fig. 5.

Preparation of VIII by acetylation of VII

The adduct VII was refluxed with 1:1 pyridine:acetic anhydride for 5 hr and then worked up in a typical manner, giving VIII as a yellow oil; γ<sub>α</sub> = 1677s, 1752s cm⁻¹. The 1H NMR spectrum is illustrated in Fig. 5.

Preparation of IX by reduction of VII

A solution of VII (86 mg, 0.17 mmole) and LiAlH₄ (2.4 mmole) in tetrahydrofuran (8 ml) was refluxed for 1 hr. Typical workup yielded a crude yellow oil (87 mg), which was purified on a thick-layer silica gel plate developed with 25% ethyl acetate-petroleum ether. The expected product IX was obtained from the predominate band (R<sub>f</sub> = 0.1) as a pale yellow oil (59 mg, 0.12 mmole, 70%). The 1H NMR spectrum is consistent with the expected product.

Preparation of X by dehydration of IX

A solution of IX (59 mg, 0.12 mmole) in glacial acetic acid (5 ml) was refluxed for 14 hr. The cooled solution was then poured into water (25 ml) and the resulting suspension extracted with chloroform (3 x 10 ml). The extract was washed with water (10 ml), dried over MgSO₄, and evaporated, leaving a pale yellow oil (39 mg). Purification by thick-layer chromatography as described previously (R<sub>f</sub> = 0.2) yielded a colorless oil (16 mg, 0.033 mmole, 28%). 1H NMR (CDCl₃): δ 2.38 (s, 3H, methoxyl), respectively, in phenylmethane ring (ring A), 3.97 (s, methoxyl in guaiacyl ring (ring B), 3.4 to 4.5 (m, C-1 methine and C-2 methylene), 5.13 (d, C-1 methine, J = 4 Hz), 5.48 (d, H-2 in ring A, J<sub>2,6</sub> = 2.5), 5.57 (dd, H-6 in ring A, J<sub>5,6</sub> = 8, J<sub>2,6</sub> = 2.5), 6.20 (57), 6.38 (5), 7.2 to 7.7 (m, H-2, 3, 4, 5, 6, 7 in antherone moieties), 7.9 to 8.2 (m, H-1, 8 in antherone moieties). 13C NMR (CDCl₃): δ 44.4 (d, C-10), 55.0 (d, C-1), 55.6. 56.1 (methoxyls), 69.6 (t, C-2), 111.9 to 150.3 (aromatics), 183.6 (s, C-9). Mass spectrum m/e (%): 480 (M⁺, 9), 356 (3), 301 (7), 287 (43), 286 (23), 193 (40), 165 (30), 164 (100), 163 (57), 149 (67), 148 (33), 123 (28).

Independent synthesis of XI

A solution of anthranol XIII was prepared by heating a mixture of anthrone (XIV, 0.58 g, 3.00 mmoles) and 1 M NaOH (50 ml) at 100°C for 30 min under a N₂ atmosphere. The resulting orange solution was then treated with a solution of II in an analogous fashion as that described for preparation of VI. The same workup yielded a cream-colored amorphous solid (1.17 g, 84%); mp 135-140°C. The 1H NMR spectrum is consistent with structure XII. Methylation of XII (0.68 g,
1.46 mmoles) with an excess of diazomethane gave a cream-colored solid (0.66 g, 1.38 mmoles, 94%); mp 137-141°C. The 1H NMR spectrum confirmed its equivalence with XI obtained from the previous experiment.

Literature cited

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