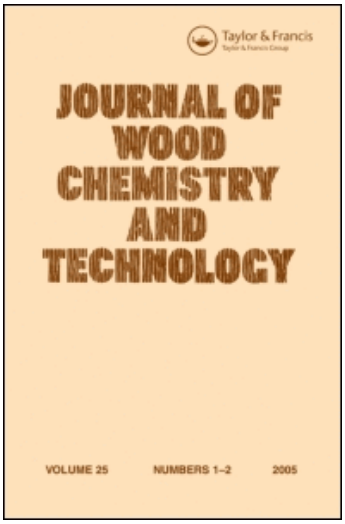


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

AQ Pulping - A Mechanism for 3-Guaiacylbenz-Anthrone Formation

Jacqueline A. Hemmingson[a]
[a] DSIR, Chemistry Division, Petone, New Zealand

To cite this Article Hemmingson, Jacqueline A.(1982) 'AQ Pulping - A Mechanism for 3-Guaiacylbenz-Anthrone Formation', Journal of Wood Chemistry and Technology, 2: 4, 417 — 430
To link to this Article: DOI: 10.1080/02773818208085143
URL: http://dx.doi.org/10.1080/02773818208085143

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(4), 417-430 (1982)

AQ PULPING - A MECHANISM FOR 3-GUAIACYLBENZANTHRONE FORMATION

Jacqueline A Hemmingson, DSIR, Chemistry Division, Private Bag, Petone, New Zealand

ABSTRACT

A mechanism previously proposed for the formation of 3-guaiacylbenzanthrone in anthraquinone pulping cooks is investigated and discussed. Some implications for AQ loss and recoverability are also briefly discussed.

INTRODUCTION

A substantial amount of the anthraquinone (AQ) added to pulping cooks is lost through incorporation into products which are stable under pulping conditions, or into intermediates which do not regenerate AQ when they break down.[1] This adversely affects the economics and effectiveness of AQ usage. 3-Guaiacylbenzanthrone is one stable, monomeric product which has been isolated from pulping liquors in significant amounts and thus contributes to this loss.[2,3] An understanding of the mechanism of formation of this compound would therefore help in the search for ways to prevent or reduce the occurrence of reactions which consume the catalyst.

A former publication,[4] reported a study of model systems in which the product of addition of anthrone to the extended quinone methide formed from coniferyl alcohol was shown to be a possible intermediate in 3-guaiacylbenzanthrone formation in pulping cooks. A mechanism was proposed for the cyclization/aromatization

reactions necessary for the transformation. This paper explores that mechanism in some detail.

RESULTS AND DISCUSSION

The mechanism proposed for the formation of 3-guaiacylbenzanthrone (5ii) during AQ pulping is shown in Fig. 1. It was based on a study of the reactions of anthrone and anthrahydroquinone in basic solution, with the 2,6-dimethyl analogue (1i), of the extended quinone methide formed from coniferyl alcohol (1ii).[4]

Step 1.

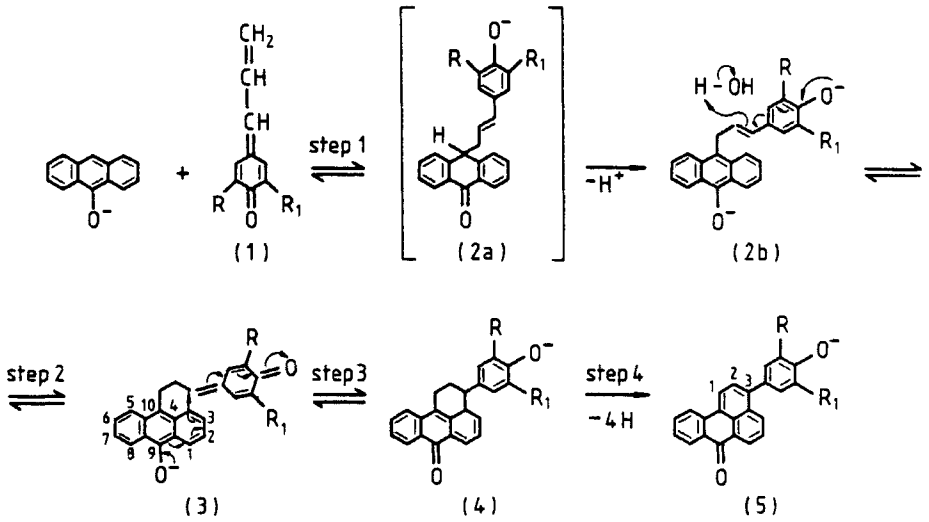
The product of step 1 was isolated as an isomeric mixture of the 10-substituted anthrone (2a) and the 10-substituted anthranol (2b), as a result of protonation of the anthracene moiety at C_{10} and oxygen, respectively. These compounds gave the benzanthrone (5i) in about 10% yield, when refluxed in basic solution for 24 hr.[4]

Step 2.

This type of proton transfer has been discussed by Aminoff, Brunow, Miksche and co-workers and is thought to be involved in the dimerization of coniferyl alcohol in alkaline solution.[5,6]

Step 3.

The isomeric products of Step 1 (2a and 2b) were catalytically hydrogenated to the corresponding dihydrocompounds (6a) and (6b) (Fig. 2). These compounds were oxidised in dichloromethane solution, by aqueous potassium ferricyanide, to compounds assigned structures (3a) and (3b) on the basis of the following properties: (a) their u.v. absorption spectra, $\lambda_{max}(CH_2Cl_2)$ 307-309 nm were consistent with the presence of a simple quinone methide moiety.[7,8] (b) In acidic or basic solution (e.g. ethanol), absorbance at 307-309 nm decayed readily and was replaced by absorbance with a maximum at 268-270



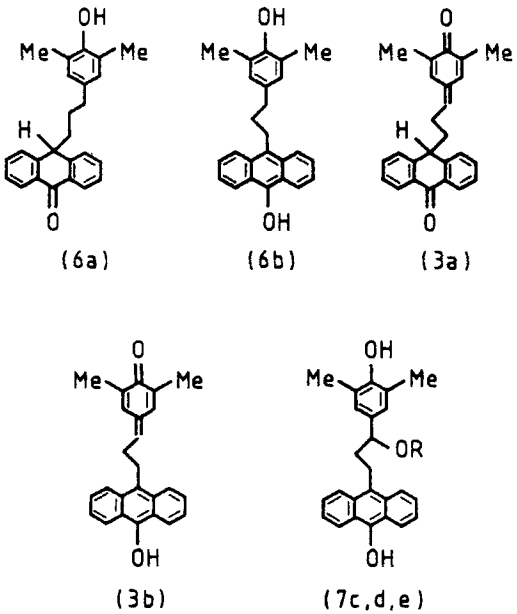
(i) R = R_1 = Me (2,6-dimethyl analogue), (ii) R = OMe, R_1 = H (guaiacyl moiety)

FIGURE 1. Mechanism for formation of 3-guaiacylbenzanthrone.

nm, in neutral solution, similar to that of the parent compounds (270-272 nm). (c) Reaction with t-butanol containing a trace of acid or base, or with methanol gave the ether product expected to result from addition of the alcohol to a quinone methide moiety ((7c,d), Fig. 2).

A solution of quinone methide (3a) in dichloromethane, when it was added to a nitrogen-purged aqueous solution of sodium hydroxide and refluxed for 48 hr gave (5i), the 2,6-dimethylanalogue of 3-guaiacylbenzanthrone (5ii), in 40% yield.

Further support for the participation of this type of quinone methide in the cyclization reaction mechanism was obtained by refluxing the t-butyl ether (7c) in basic solution, which also gave (5i) in high yield (48%). Under these conditions, p-hydroxybenzylether moieties are thought to undergo displacement of the ether



(7c) R = t-Bu, (7d) R = Me, (7e) R = H

FIGURE 2. Synthesized intermediates.

substituent via formation of a quinone methide intermediate, i.e. (3i) would be generated from (7c).[9,10]

The 25% yield of (5i) obtained by refluxing (2a) or (2b) in basic solution is considerably lower than that obtained from (3a) or (7c). This suggests that the proposed cyclization of step 3, via addition of the deprotonated anthranol moiety (reacting as a carbanion with charge localized at C_4) to the quinone methide moiety, competes effectively with reversal of step 2, i.e. base-catalysed removal of a proton from the β-carbon atom of the propanoid side chain.

The proton transfer of step 2 has been reported by Brunow and Miksche to be the least favoured of three possible types of reaction of coniferyl alcohol in

basic solution.[5] Reaction as the β-carbanion in nucleophilic addition reactions and elimination of water to generate the extended quinone methide (lii), which then reacts with the above carbanion, are both more favoured reactions. This could account for the increased yield of (5i) when the synthesis is started from the product of step 2.

No formation of the methyl ether of (5i), 3-(3,5-dimethyl-4-methoxyphenyl)benzanthrone was detected, when the monomethyl ether of(2b) was refluxed in basic solution. As this compound cannot generate a quinone methide, this observation also supports the hypothesis that a simple quinone methide moiety is formed before cyclization can take place.

The participation of radical reactions in benzanthrone formation does not appear to be significant. Oxidation of (2b) with potassium ferricyanide resulted in extensive polymer formation and the u.v. spectral behaviour of these solutions indicated the presence of simple quinone methide moieties ($\lambda_{max}(CH_2Cl_2)$ 303), most probably formed by β-O coupling of phenoxy radicals. Refluxing the oxidation products in basic solution gave a low yield (ca. 10%) of (5i). Benzanthrone formation could result either from alkaline cleavage of polymeric material with regeneration of (2b), or from cyclization within the polymer, followed by expulsion of the β-ether substituent on aromatization.

Step 4.

No receptor of the hydrogen atoms lost during aromatization was detected among the other products (discussed below) of the reaction yielding (5i). However, oxidative transformations during the work-up and separation of these products could be the reason for this.

Isolation of a Cyclized Intermediate. (Step 3).

Two reaction procedures aimed at forming and isolating (4i), the proposed product of step 3, were devised. These were based on the supposition that formation of (4i) should take place at a much lower temperature than dehydrogenation to the benzanthrone, i.e. step 4.

Procedure 1.

This involved reacting the hydrogen chloride addition product of (3a) or (3b) with t-butoxide ion in t-butanol. Use of the p-hydroxybenzylchloride derivative was designed to protect the quinone methide moiety from nucleophilic attack until deprotonation of the anthrone or anthranol moiety had taken place. Facile regeneration of the quinone methide was expected to occur, followed hopefully by cyclization.

A mixture of products was obtained, which gave (5i) in 21% yield when refluxed for 27 hr in basic solution. The mixture was separated by p.l.c. into groups of compounds of similar Rf, which were tested for benzanthrone formation by the above procedure. One group of compounds corresponding to about 25% of the original reaction mixture gave (5i) in 25-30% yield and was further separated into two compounds, both of which gave significant yields of (5i) (ca. 13% and 21% respectively) on basic reflux. The former (henceforth called (4i)) had the following mass spectrum: m/e (%) 354(10) (M^+), 207(47), 194(7), 162(34), 148(100), 135(23), which could arise from structure (4), while the latter appeared to be compound (2b). The yield of each compound was low (ca. 3%). Each p.l.c. separation gave polymer and AQ, which indicated that some product breakdown had taken place.

By analogy with the formation of substituted oxanthrones and disubstituted anthrones, which is readily

reversible in basic solution,[4,11] the formation of (4i) should also be reversible, thus allowing, in the absence of the conditions necessary for stabilization by aromatization, diversion into other more stable compounds. The formation of some (2b), via proton loss from regenerated (3i) is therefore not surprising. The irreversibility of monosubstituted anthrone formation is no doubt due to the removal of the second C_{10} proton.

An attempt to stabilize (4i) by acetylating it, in admixture with (2b), immediately following the p.l.c. separation of these two compounds from the other reaction products caused partial breakdown and acetylated (4i) and (2b) were isolated in only 10% and 8% yield respectively. The p.m.r. and m.s. spectral data for these compounds, which are given in Table 1 showed similarities and differences consistent with an isomeric relationship between them. The identity of (2b) was confirmed and each compound was shown to contain one acetate group located on the dimethylhydroxyphenyl moiety. The p.m.r. spectrum of acetylated (4i), i.e. (A4i), also showed two singlets each equivalent to one proton, at 6.64 and 6.84 ppm respectively, for the aromatic protons of the phenolic moiety. Neither resonance was significantly affected by either decoupling irradiation or by heating the compound in nitrobenzene from 30-122°C. However, significant changes in δ and $\Delta\delta$ occurred on transferring the compounds from deuterochloroform to deuteroacetone or nitrobenzene (δ = 6.78, 7.11 in acetone-d_6, 7.00, 7.25 in nitrobenzene-d_5 and 6.64, 6.84 in $CDCl_3$). Formation of a 1:1 mixture of cis and trans isomers on cyclization is one possible explanation for these observations, while hindered rotation of the phenolic moiety remains a possibility. Repetitive tlc or HPLC gave only the one major compound.

TABLE 1

Spectral Data for (A4i) and (A2b)

(A4i) High resolution m.s. M^+ 396.1709.$C_{27}H_{24}O_3$ requires 396.1724.
M.s. (250°) m/e (%) 396 (M^+) (6), 394(4), 392(3), 354(3), 352(8), 350(15), 207(100), 194(36), 193(33), 165(26), 161(64), 151(87), 148(47), 135(55).
P.m.r. δ($CDCl_3$), 1.65-2.60(6, m, methylene and methine protons), 2.15 (6,s,Me), 2.33 (3,s,OAc), 6.64 (1,s,ArH of phenolic moiety), 6.84 (1,s, ArH of phenolic moiety), 7.15-7.80 (5,m,ArH of anthrone moiety), 8.16 (2,dd, J = 7.0 Hz, 1.3Hz, C_1 and C_8 of anthrone moiety).
KBr $\nu_{C=O}$ 1755 cm^{-1} (OAc), 1670 cm^{-1} (anthrone moiety)
EtOH λ_{max} 268.

(A2b) M.s. (250°) m/e (%) 396(M^+)(9), 354(3), 352(8), 231(20), 207(50), 203(61), 194, 193, (31), 165(39), 161(100).
P.m.r. δ($CDCl_3$) 1.98 (6, s, Me), 2.25 (3, s, OAc) 3.12 (2, d, J = 7.2 Hz, CH_2), 5.08-5.86 (1, m, vinyl CH), 5.25 (1, br.s, OH), 5.96 (1, d, J = 15.9 Hz, vinyl CH), 6.60 (2, s, ArH), 7.25-7.80 (6, m, ArH), 8.35 (2, d, J = 7.4 Hz, ArH).

(A4i) gave (5i) in 17% yield when refluxed in basic solution for 46 hr, while (A2b) gave a 7% yield under the same conditions.

The above results show (A4i) to be a precursor for formation of benzanthrone (5i) and the spectral data shown in Table 1 suggest that it very probably has the structure proposed. No evidence for (A4i) having an isomeric structure of lower energy was found.

Procedure 2.

This involved dropwise addition of a dichoromethane solution of (3b) to a basic, 50% aqueous tetrahydrofuran reaction medium. However, owing to miscibility problems with this medium, unreacted quinone methide was present at work-up and was reacted with hydrogen chloride in aprotic solution during isolation of the reaction products. The product mixture gave precursors of (5i) in about 36% yield and these were separated by p.l.c. into three fractions whose mass and n.m.r. spectra suggested that one was crude (4i), one crude (7e), (the water addition product of (3b)), and one a mixture of these two compounds and the hydrogen chloride addition product of (3b). The yields were 11%, 8% and 17% respectively. The fragments m/e 135, 148, 151, 161, 194, 207, 352, 354 and in the case of (7e), 372 were prominent in the mass spectra of these fractions. Both (4i) and (7e) gave (5i), in about 21% and 38% yield respectively, when refluxed in basic solution, in support of the above assignments.

A compound, which had the following mass spectrum, consistent with it being (4i) was isolated by HPLC from the mixture fraction: m/e (%) 354(12)(M^+), 207(83), 194(48), 161(88), 148(100), 135(62). This compound, after acetylation co-chromatographed with (A4i), both by HPLC and t.l.c. It appears therefore, that (4i) is a common product of both procedure 1 and procedure 2, which provides further support for step 3.

Polymerization and Breakdown of (2i) Accompanying Formation of Benzanthrone (5i)

Products other than (5i) isolated from solutions of (2i) after basic reflux were primarily polymer (ca. 50% yield), AQ, anthrone and 3,5-dimethyl-4-hydroxybenzaldehyde. Small amounts of bianthronyl, bianthrone and the highly insoluble compound naphthodianthrone were

also found. The p.m.r. spectrum of the polymeric material showed broad methyl and aromatic resonances and thus the presence of both anthrone and 3,5-dimethyl-4-hydroxyphenyl moieties. The susceptibility of (2a), (2b) and anthranol to oxidative breakdown during work-up makes the amounts of some of these compounds actually formed during the reaction uncertain, but these observations do indicate other possible sources of AQ loss during pulping and are in accordance with reports of AQ being found incorporated into a wide molecular weight range of material in pulping liquors.[12,13]

Implications for AQ Pulping

Model system studies have shown one possible pathway for AQ loss during pulping to be via the formation of an addition product between anthrone and the extended quinone methide derived from coniferyl alcohol, both of which may be formed during a cook. The most easily detected end product of this process is the substituted benzanthrone (5ii), but the above work indicates that a considerable proportion could be diverted into higher molecular weight material. This is probably due to the propensity of the addition product to react as a carbanion via the β-carbon atom of the propanoid side chain, or via the C_{10} position of the anthrone moiety, rather than via the proton transfer leading to formation of (5ii). One possible way of blocking both benzanthrone formation and further reaction through the C_{10} position could be to use a 1,4,5,8-tetrasubstituted AQ, e.g. the tetramethyl derivative, to prevent aromatization to (5ii) and to sterically hinder the C_{10} carbanion reaction. This could however direct the intermediate into further condensation with lignin fragments via the β-carbon atom, which may not be beneficial to the delignification process. The irreversibility of monosubstituted anthrone formation in basic solution presents problems

for the regeneration of AQ, but the potential exists for reversible reactions and oxidative cleavage in treated pulping liquors.

EXPERIMENTAL

The preparation of compounds (2a) and (2b) and the formation of (5i) from them has been described previously.[4]

Hydrogenation of (2a,b): 50-100 mg of the compound was dissolved in 25-30 ml of ethanol and reacted with H_2 at atmospheric pressure, in the presence of PtO_2 catalyst, for 1 hr. The PtO_2 was removed by filtration and the solution was concentrated to dryness. The crude products were purified by p.l.c. (ether:hexane 3:2, 7:3) and (6a,b) were obtained as yellow gums.

(6a): M.s. (110°) m/e (%) 356 (M^+) (19), 207(30), 194(100), 165(45), 163(100), 135(85). P.m.r. δ($CDCl_3$), 1.57-2.63 (6,m,CH_2), 2.15 (6,s,Me), 4.31 (1,t, J = 5.6 Hz, $C_{10}H$), 5.17 (1,br.s,OH), 6.49 (2,s,ArH), 7.47 (6,m,ArH), 8.19-8.37 (2,m,ArH).

(6b): M.s. (110°C) m/e (%) 356 (M^+)(37), 355(27), 233(11), 207(42), 194(27), 193(30), 165(11), 161(27), 149(42), 135(100) P.m.r. δ($CDCl_3$) 1.68-2.42 (6,m,CH_2), 2.12 (6,s,Me), 4.66 (2,br. s.,OH), 6.42 (2,s,ArH of phenolic ring), 7.50 (6,m,ArH), 8.35 (2,br.d, J ≐ 7.4 Hz, ArH).

Preparation of (3a,b): A solution of the compound in dichloromethane (e.g. 50 mg in 150 ml) was shaken for ca. 30 sec. with 25 ml of 0.1M alkaline $K_3Fe(CN)_6$ solution and its u.v. spectrum was examined for quinone methide formation. The dichloromethane solution was then concentrated to ca. 20 ml for use as a reactant.

Reaction of (3a) with Base.

A 0.7M solution of sodium hydroxide in 30% t-butanol-water was purged with nitrogen for 2 hr at 20°C. The solution of (3a) in dichloromethane was added dropwise to the stirred base and stirring was continued for 10 min after addition was complete. The reaction mixture was then brought to reflux and residual dichloromethane was allowed to distil off, after which reflux was continued for 48 hr. Work-up was as described previously, i.e. after cooling to ambient temperature, the mixture was neutralised with ammonium chloride and extracted twice with chloroform.[4] The benzanthrone (5i) in the crude product mixture was isolated by p.l.c. and the yield was determined spectrophotometrically in ethanol solution (ε = 4000 at 422 nm).[4]

Procedure 1. Preparation of the Hydrogen Chloride Addition Product of (3a,b) and Reaction with Basic t-Butanol.

Compound (3a) or (3b) (80-100 mg) in dichloromethane (25 ml) was added to 0.1 M hydrogen chloride in hexane (25 ml) and reacted for 30 min. The mixture was then concentrated to dryness and the products were redissolved in dichloromethane. U.v., t.l.c., and n.m.r. analysis indicated that the chloride was formed in good yield. The reactant solution was then added dropwise to a nitrogen purged solution (50 ml) of potassium butoxide in t-butanol (0.025 M) and stirred for 2 hr. at 25°C protected from light. The reaction mixture was worked up by adding 100 ml of ice-cold, 0.2 M aqueous ammonium chloride and extracting with dichloromethane (200 ml). After concentration to dryness at 25-30°C the products were separated by p.l.c. (ether:hexane 2:1) and obtained as pale yellow gums. Acetylation was carried out under nitrogen with acetic

anhydride:pyridine (2:1) and the products were separated as above.

Procedure 2. Reaction of (3b) with Dilute Base and Isolation of (4i)

The procedure was analogous to that described above, except that the reaction medium was 0.025 M sodium hydroxide in 50% tetrahydrofuran-water (200 ml) and (3b) was not derivatised before use. After 5 hr reaction time at 15-20°C the reaction mixture was extracted with chloroform. The chloroform extract was treated with hydrogen chloride in hexane to remove unreacted (3b) and then concentrated to dryness. The product mixture was separated by p.l.c. (ether:hexane 3:1) and the compounds suspected to be precursors were isolated as yellow gums.

ACKNOWLEDGEMENTS

The author is grateful to Dr H. Wong of Chemistry Division, DSIR for FT-80A n.m.r. spectra and to Professor R. Hodges of Massey University, Palmerston North for the high resolution mass spectrum.

REFERENCES

1. B.I. Fleming, G.J. Kubes, J.M. MacLeod and H.I. Bolker, Tappi 62 55 (1979).

2. T.J. Fullerton and B.I. Fleming, Sven. Papperstidn., 83 396 (1980).

3. D.W. Cameron and E.L. Samuel, Tetrahedron Letters, 3035 (1979).

4. T.J. Fullerton, J.A. Hemmingson, G.J. Leary and L.J. Wright, J. Wood Chem. and Technol, 2 97 (1982).

5. G. Brunow and G.E. Miksche, Applied Polymer Symp., No. 28 1155 (1976).

6. H. Aminoff, G. Brunow, K. Falck and G.E. Miksche, Acta Chem. Scand., B28 373 (1974).

7. J.A. Hemmingson, Tetrahedron Letters, 2967 (1977).

8. L.J. Filar and S. Winstein, Tetrahedron Letters, 9 (1960).

9. J.A. Hemmingson, Aust. J. Chem., 32 225 (1979).

10. L. Ivnäs and B. Lindberg, Acta Chem. Scand., 15 1081 (1961).

11. D.R. Dimmel and D. Shepard, J. Org. Chem., 47 (1) (1982), in the press.

12. W.H. Algar, A. Farrington, B. Jessup, P.F. Nelson and N. Vanderhoek, Appita, 33 33 (1979).

13. R.F. Cassidy, L.E. Falk and C.W. Dence, Sven. Papperstidn., 84 R94 (1981).