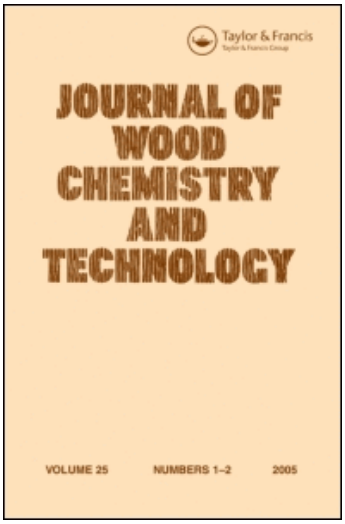

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ENHANCED CLEAVAGE OF ß-ARYL ETHER BONDS IN LIGNIN MODEL COMPOUNDS DURING SULPHITE-ANTHRAQUINONE PULPING

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ABSTRACT

Under sulphite-anthraquinone cooking conditions reduced anthraquinones, such as anthrahydroquinone (AHQ) or oxanthrone, promote cleavage of the ß-ether bond in the free phenolic ß-ether lignin model 1. This enhanced cleavage, and the products formed, can be rationalised by a mechanism involving formation of an adduct between the reduced quinone and the quinone methide 3. This adduct then fragments to afford the observed products.

Wood sugars are capable of reducing AQ to the catalytically active form during sulphite-AQ cooking. Consequently, AQ can catalyse the cleavage of free phenolic ß-aryl ether linkages in lignin when sugars are present. This finding explains why AQ is able to accelerate delignification during the initial phase of sulphite-AQ pulping. However, it does not provide the full story since it cannot explain why AQ catalyses delignification during the bulk phase of sulphite-AQ pulping.

Mixtures of low-molecular-weight sodium lignosulphonates, such as those produced during sulphite cooks of 1, can be readily analysed by ^1H nmr spectroscopy. This analytical method has two advantages over alternative methods; one it is simpler to carry out, and two, for the first time, approximate product ratios can be determined from model cooks.

INTRODUCTION

The addition of small quantities of anthraquinone (AQ), commonly 0.1% by weight of the oven-dried wood used, increases the rate and selectivity of delignification during sulphite pulping under neutral or alkaline conditions. The quinone, or its reduced forms, may be beneficially employed in sulphite pulping over a wide pH range, from 6.5 to 13.[1] Sulphite-AQ pulping may be used to prepare high-yield (80-90%) chemimechanical pulps, semichemical pulps, or low-yield (55-60%) full chemical pulps, and is particularly useful for pulping softwoods.[1] Besides increasing the rate of pulping, use of AQ leads to higher pulp yields and/or improvements in the properties of the resulting pulps. The advantages of adding AQ are such that it is now in regular use in a number of sulphite mills throughout the world, and is being investigated for use in several others.

It is frequently considered that two distinct processes are involved in sulphite-AQ pulping, i.e., neutral sulphite-AQ pulping, and alkaline sulphite-AQ pulping[2]. In the former the liquor consists of Na_2SO_3 plus Na_2CO_3, and the (cold) cooking pH starts at 11.5, dropping to around 7 to 8.5 during the cook. With alkaline sulphite-AQ pulping, the liquor consists of the above chemicals plus NaOH, and the pH of the cook ranges from 13 to 9.5. In practice, these distinctions are rather blurred and the terminology is frequently misused, so it is perhaps better to consider these processes simply as variants of one sulphite-AQ pulping process.

Very little work has been carried out to establish why AQ is such an effective catalyst during sulphite pulping.[3]

Anthraquinone is also very effective at promoting delignification under strongly alkaline conditions (pH 13-14) such as

those employed in the soda and kraft pulping processes.[4] Studies using lignin model compounds have provided evidence that AQ enhances the rate of alkaline pulping largely because reduced forms of AQ, such as anthrahydroquinone (AHQ), increase the rate of cleavage of free phenolic ß-aryl ether linkages in lignin.[5] Since AQ is readily reduced under alkaline conditions by wood carbohydrates[6], and regenerated during ß-ether cleavage, it is able to act as a catalyst for this reaction.

It cannot be assumed, however, that the same mechanism would operate under sulphite conditions, and indeed there are several reasons to suspect that a different mechanism might be involved. Firstly, the cooking liquors are different; that for soda-AQ pulping consists mainly of NaOH, whereas that for sulphite-AQ pulping consists mainly of Na_2SO_3, along with smaller amounts of Na_2CO_3 or NaOH to keep the cook alkaline.

Secondly the two processes operate in very different pH ranges: 13 to 14 during soda cooking as against 6.5 to 13 for sulphite-AQ pulping. This means, for example, that while phenols such as 1 or AHQ are completely dissolved (as their sodium salts) under soda conditions, under neutral sulphite conditions they are essentially insoluble at ambient temperature.

Both sulphite and pH influence AQ catalysis of delignification. Thus when Pinus radiata woodchips were pulped in the presence and absence of AQ in solutions containing mixtures of sodium hydroxide and sodium carbonate, the catalytic effectiveness of AQ dropped as the pH fell, so that at pH 13 it was without effect. However when sulphite was present AQ was shown to be still effective as a delignification catalyst at pH 7.

Furthermore, in the presence of AQ it is possible to produce full chemical pulps from softwoods under neutral sulphite

conditions, something it is very difficult to do with sulphite alone.

A study of the mechanism by which AQ promotes delignification under sulphite-AQ pulping conditions was therefore begun. Besides providing information on the fundamental chemistry of the process, the study was seen as having important practical implications. For example, the relative efficiencies of AQ and various alternative pulping catalysts under sulphite conditions may well be different from those determined under alkaline conditions (e.g., ref. 7). Consequently AQ may not be the best or most cost effective catalyst to use under sulphite conditions.

This paper describes reactions of the free phenolic ß-aryl ether lignin model 1 under neutral sulphite pulping conditions, in the presence and absence of AQ and its reduced forms. Although Gellerstedt and Gierer have also studied reactions of ß-aryl ether model compounds, including 1, under sulphite conditions[8-11], it is not known whether, as occurs under alkaline conditions, AQ catalyses cleavage of the ß-ether linkage in compound 1.

RESULTS AND DISCUSSION

Cooks of 1 in the Presence of AQ or Reduced Anthraquinones

The study was begun by investigating whether AQ itself, or reduced forms of the quinone, promoted ß-ether cleavage of the lignin model 1 under conditions simulating those used in sulphite pulping. The procedure adopted consisted of heating the model 1 in the presence of 1.2 mole equivalents of the additive (e.g., AHQ) with a 4:1 mixture of 0.5 M Na_2SO_3 and dioxane in a glass tube at 140°C for 1 h (the initial pH and final pH were both between 10 and 10.5). The resulting mixture, after cooling, was partitioned between water and dichloromethane, and the

guaiacol 9 yield in the organic phase determined by gas liquid chromatography (glc). The yield of guaiacol provides a convenient measure of the extent of ß-ether cleavage in these reactions.

To check the stability of the guaiacol to the cooking conditions and the completeness of extraction, a solution of guaiacol was cooked, extracted and analysed as described above. The recovery of guaiacol was 94%.

The reproducibility of the guaiacol yield was good : the average guaiacol yield during sulphite cooks of 1, i.e. entry 1, Table 1, carried out on 9 separate occasions was 19.8% and the standard deviation 2%. This cook was performed as a control in all batches of cooks as a further check on the results obtained.

The results, presented in Table 1 and Fig. 1, clearly demonstrate that the quinones AQ (entry 2, Table 1) and sodium anthraquinone-2-sulphonate (entry 3), did not enhance the rate of ß-ether cleavage. However when stochiometric amounts of reduced anthraquinones such as anthrahydroquinone (AHQ), oxanthrone (10-hydroxyanthracen-9-one, the more stable keto tautomer of AHQ), or 1,4,4a,9a-tetrahydroanthraquinone (THAQ) were added to the cooks the rate of ß-ether cleavage was accelerated substantially with the guaiacol yields rising from 20% up to as high as 60% (entries 5-7). Anthrone (anthracen-9-one), a product known to be slowly formed from AQ under neutral sulphite conditions[3], was without effect (entry 4).

No starting model was detected in the organic extracts by thin layer chromatography (tlc) after any of the sulphite cooks of the free phenolic ß-ethers.

The Effect of Cosolvents

In contrast to the high solubility of the reagents under alkaline pulping conditions, neither the starting ß-ether 1 nor

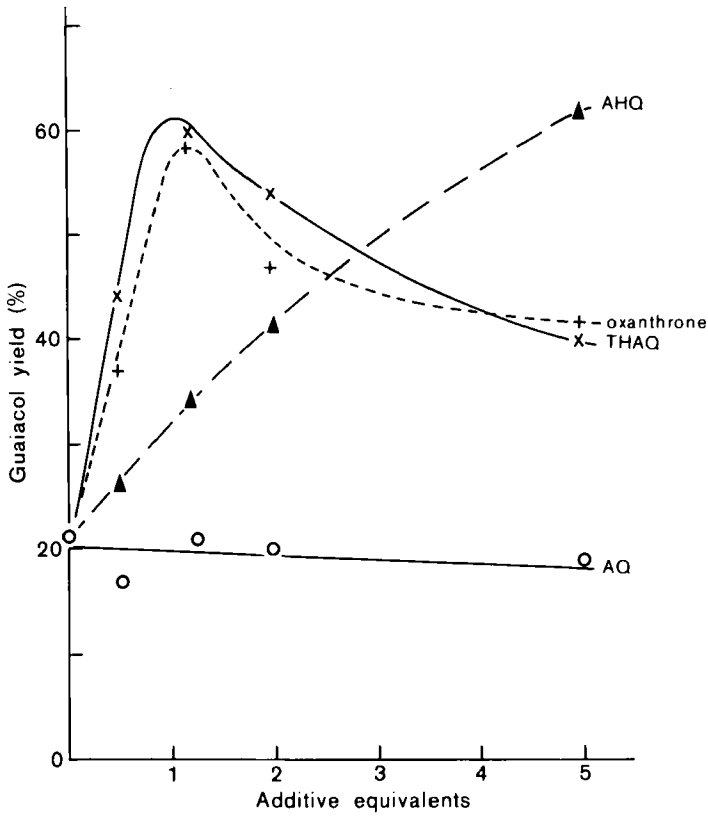


FIGURE 1 - Effect of additive concentration on the yield of guaiacol from sulphite cooks of 1

the reduced anthraquinones such as AHQ or oxanthrone are very soluble in cold sulphite liquor. To avoid problems associated with compound insolubility a homogeneous solution was desired. To this end the water-miscible organic cosolvent dioxane was added to sulphite cooks of 1 in the presence and absence of oxanthrone. From Table 2 it can be seen that there were very significant variations in the yield of guaiacol 9 depending on the amount of dioxane added.

TABLE 1

Yield of Guaiacol and Composition of Sodium Sulphonate Mixtures from Sulphite Cooks

Entry	Substrate	Additive*	Kraft pulp (mg)	Guaiacol yield (%)	Sulphonate Product Ratio 4 : 5 : 12		
1	1	-	-	21	87	13	0
2	1	AQ	-	21	86	12	2
3	1	AQ-2-sulphonate	-	25		-	
4	1	anthrone	-	21	80	16	4
5	1	AHQ	-	34	72	5	23
6	1	oxanthrone	-	52	46	6	48
7	1	THAQ	-	60	34	2	64
8	10	-	-	-	0	0	100
9	7	-	-	33	58	4	38
10	8	-	-	79		-	
11	2	-	-	1		-	
12	2	AQ	-	0		-	
13	2	oxanthrone	-	1		-	
14	4	-	-	8	94	6	0
15	4	oxanthrone	-	14	84	4	12
16	1	AQ	100	27	70	9	17
17	1	-	100	16	79	21	0
18	1	AQ + glucose, 50 mg	-	10		-	

* 1.2 mole equivalents

TABLE 2

The Effect of the Cosolvent on the Yield of Guaiacol (%) in Sulphite Cooks of 1

% cosolvent	1 + sulphite	1 + sulphite + oxanthrone
-	14	16
20% dioxane	21	52
20% isopropanol	21	58
40% dioxane	11	49
40% isopropanol	14	51

Examination of the hot tubes from cooks carried out without cosolvent showed that neither the ß-ether 1 nor the oxanthrone were completely soluble in the hot liquor; hence the low guaiacol yields and the ineffectiveness of the oxanthrone in these cooks. When cooks were carried out in 40% dioxane sodium sulphite precipitated out of solution, leading once again to a lowering of the guaiacol yield. In cooks with an intermediate amount of dioxane (20%) neither of these problems occurred and this proportion of cosolvent was employed for the remainder of the study.

Substitution of the chemically distinct solvent iso-propanol for dioxane produced very similar results (Table 2), demonstrating that the effect of these cosolvents in facilitating the reaction is due purely to increased reagent solubility.

The observed drop in guaiacol yield from cooks of 1 in the presence of greater than stochiometric amounts of THAQ or oxanthrone (see Fig. 1) may have been due to problems with reagent solubility since substantial amounts of both starting

material and additive remained undissolved in the hot liquor of these cooks.

Examination of the Sodium Lignosulphonates

Further insight into how reduced anthraquinonones promote ß-ether cleavage of 1 was obtained by examining the water soluble sodium lignosulphonates which are also formed during these reactions. Such mixtures of low-molecular-weight sodium lignosulphonates have in the past proved difficult to handle and analyse, mainly because the salts are water soluble. Consequently these compounds are difficult to separate from each other and also from any inorganic salts present, e.g., remaining Na_2SO_3.

To date the best method for determining the composition of such lignosulphonate mixtures has involved derivatising the salts by acetylating any free hydroxyls and then methylating the sulphonic acids.[8-13] The resulting acetylated methyl esters, which are soluble in organic solvents, can then be separated by column chromatography on silica, and the purified components identified by ^1H nmr and mass spectrometry. This approach was used by Gellerstedt and Gierer in their studies of the reactions of lignin models with sulphite.[8-11] Unfortunately, as well as being time consuming to prepare, the methyl sulphonates are unstable. Consequently the relative proportions of the various sulphonates present in reaction mixtures cannot be determined in this way.

We reasoned that it should be possible to directly analyse such mixtures of low-molecular-weight sodium lignosulphonates by ^1H nmr spectroscopy. In practice this technique proved to be successful. Initially, when the aqueous phase obtained after partitioning the sulphite cooks between water and dichloromethane was freeze dried and a portion of the resulting solid dissolved

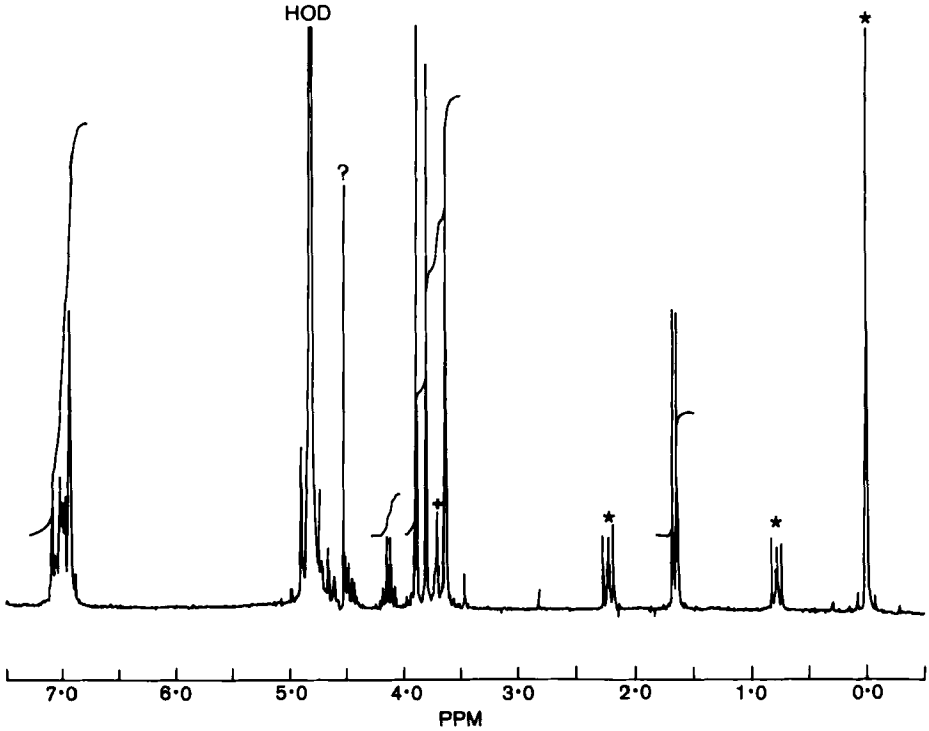


FIGURE 2 - ^1H nmr spectrum (D_2O) of the aqueous phase from sulphite cook of 1 in the presence of oxanthrone.

* Internal standard, sodium 3-(trimethylsily)propionate.
\+ Polyethylene glycol from the cooking bath.

in D_2O a reasonable proton spectrum could be obtained. However, better results were obtained when the amount of inorganic salts present in the preparations was reduced. This was conveniently accomplished by extracting the concentrated aqueous phase with 80% aqueous ethanol.[9] This extract was concentrated, taken up in water, and freeze dried to afford a solid containing only about 50% by weight of inorganic salts. A typical spectrum is shown in Figure 2.

To facilitate identification of the reaction products a number of reference sodium sulphonates were prepared using essentially literature methods and their ^{1}H nmr spectra were recorded.

An important advantage of this technique is that by integrating such ^{1}H nmr spectra it is possible to obtain, for the first time, reasonably accurate sodium sulphonate product ratios.

Such sodium lignosulphonates can also be analysed by ^{13}C nmr and reverse phase high performance liquid chromatography. The results of such analyses will be reported separately.

The Fate of the Additives

To establish what happens to the reduced anthraquinones after sulphite cooks with the ß-ether 1, the organic phase was concentrated and examined by ^{1}H nmr and thin layer chromatography. In all cases the major additive-derived product isolated was anthraquinone itself. Anthrone was also found in the organic extract of these cooks, the amount varying from a trace only (e.g., entry 5, Table 1) to as much as 28% of the mixture when THAQ was the 'catalyst' (entry 7). These two compounds, AQ and anthrone, were accompanied by small amounts of several other unidentified products.

The formation of some anthrone in these experiments was expected. Australian workers have established that under neutral sulphite conditions AQ is slowly reduced to anthrone (7% conversion after 1 h at 180°C) and that THAQ is efficiently (70%) converted to anthrone under the same conditions.[3]

No reduced anthraquinones, e.g., AHQ, oxanthrone or THAQ, could be detected after any of the reactions carried out as

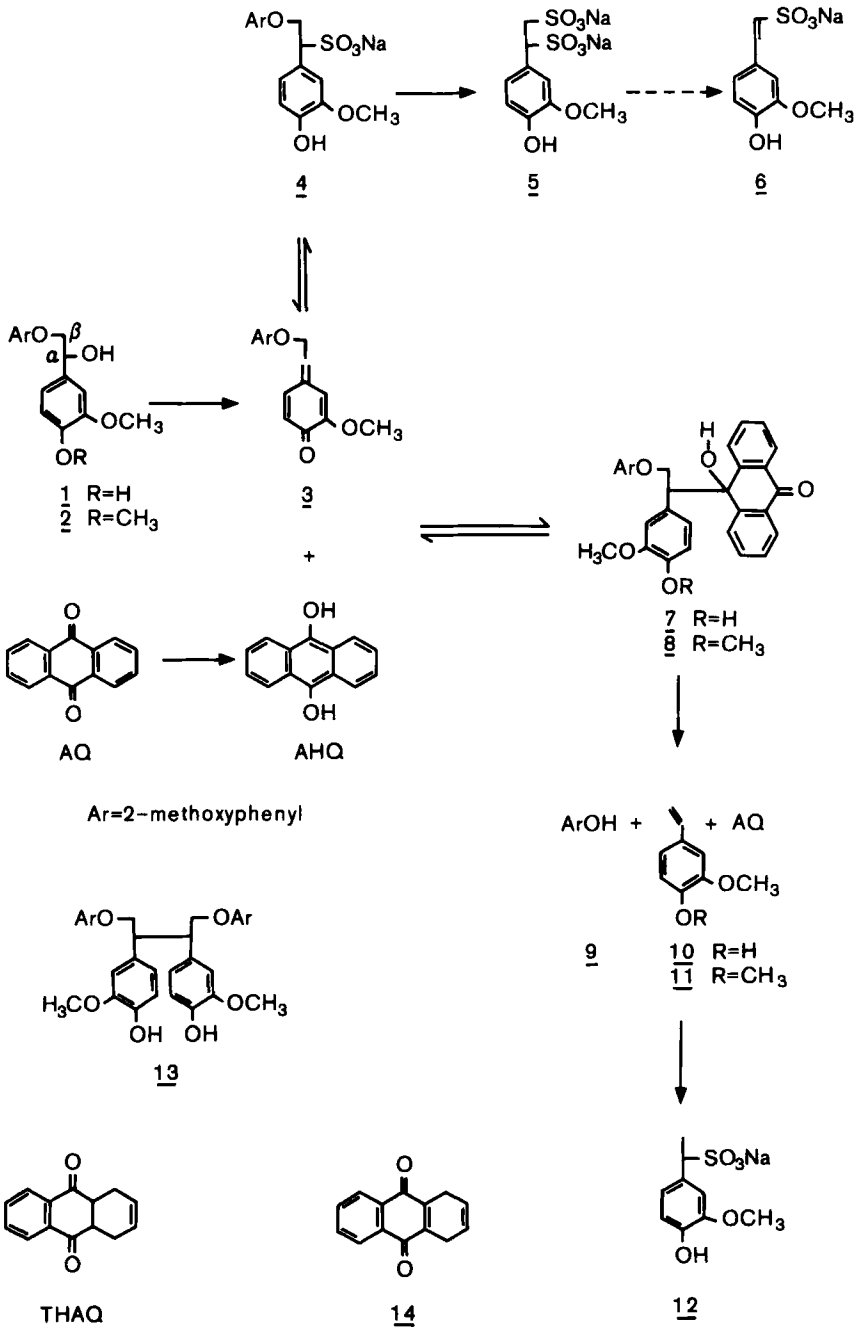
described above, except during cooks in the presence of THAQ (entry 7) where 1,4-dihydroanthraquinone 14 was tentatively identified in the reaction mixture (ca. 26%) by tlc and ^{1}H nmr.

Identification of the Sulphonated Reaction Products

In their study of the reactions of the ß-ether 1 with sulphite Gellerstedt and Gierer[8] isolated the vinyl sulphonate 6 (in the form of its acetylated methyl ester) as the major water-soluble reaction product. However when the same model 1 was cooked under the milder conditions employed in this study, two major sodium sulphonates, the α-sulphonated ß-ether 4 and the disulphonate 5, were present in the aqueous phase in the ratio of 87:13 (entry 1, Table 1). No evidence was seen by ^{1}H nmr spectroscopy for the formation of the vinyl sulphonate 6 in this work. Since the postulated route to the vinyl sulphonate 6[9] proceeds, as shown in the Scheme, via the intermediacy of the α-sulphonate 4 and the disulphonate 5, results of the above experiments are consistent.

When sulphite cooks of the ß-ether 1 were carried out in the presence of 1.2 mole equivalents of the reduced quinones, AHQ, oxanthrone or THAQ, a further sodium sulphonate, the apocynol sulphonate 12, became a major reaction product (entries 5 to 7, Table 1). No sulphonate 12 could be detected by ^{1}H nmr in the aqueous phases of cooks of 1 in the presence of sulphite alone (entry 1), and only trace quantities (ca. 2%) were detected during sulphite cooks in the presence of AQ.

This apocynol sulphonate 12 is, like compound 5, a product resulting from cleavage of the ß-ether bond in the starting material. In fact there is a reasonable correlation between the guaiacol yield and the amounts of apocynol and disulphonate formed during the reactions.



Proposed Mechanism

In their study of the reactions of coniferaldehyde with sulphite, Gellerstedt, Gierer and Pettersson[13] isolated the apocynol sulphonate 12 as one of the major reaction products. They postulated that the sulphonate 12 was formed via formal addition of 'HSO_3^-' to vinyl guaiacol 10, which in turn had been formed by degradation of the coniferaldehyde.

It is suggested therefore that the reduced forms of AQ promote ß-ether cleavage of 1 via a mechanism similar to that believed to operate under the highly alkaline soda or kraft pulping conditions[14,15], i.e., involving formation of an adduct 7 between AHQ and the quinone methide 3, decomposition of this adduct to vinyl guaiacol 10, guaiacol 9 and AQ, and finally reaction of the vinyl guaiacol with sulphite to give the observed sodium sulphonate 12. Further evidence for this proposal is presented below.

Sulphite Cooks of Vinyl Guaiacol 10

When vinyl guaiacol 10[16] was cooked under sulphite conditions the sodium apocynol sulphonate 12 was the only significant organic product formed, thus confirming Gellerstedt and Gierer's proposal.[13]

Sulphite Cooks of the Adduct 7

When the adduct 7[14], postulated to be an intermediate in the formation of 12, was cooked under neutral sulphite conditions it reacted to give anthraquinone, guaiacol (33%), and in the aqueous phase a mixture of the three sulphonates 4, 5 and 12 in the approximate ratio of 58:4:38 (entry 9, Table 1). This experiment shows that the adduct 7 can decompose, at least in part, to guaiacol 9, AQ, and the apocynol sulphonate 12 as proposed, but that it also reverts back to AHQ and the quinone

methide 3. This quinone methide then reacts further with sulphite, as occurs in the absence of reduced quinones, to afford 4 and the disulphonate 5.

To establish whether fragmentation of the adduct 7 to AQ, guaiacol and the apocynol sulphonate 12 under sulphite conditions could proceed directly without reversion to the quinone methide 3 and AHQ, the reactivity of the methylated adduct 8[15] was investigated. When 8 was cooked under neutral sulphite conditions, AQ, methylated vinyl guaiacol 11, and guaiacol (79%), plus a little recovered starting material were isolated. Only traces of sulphonated material were detected. Since methylation of the phenol blocks reversion of the adduct to AHQ and the quinone methide 3, this experiment establishes that the Grob-like fragmentation of 8 can occur under the mildly alkaline conditions of sulphite-AQ pulping. Hence fragmentation of the adduct 7 directly to AQ, guaiacol, and vinyl guaiacol, as shown in the Scheme, is possible under sulphite conditions.

Formation of the Adduct 7

Anthrahydroquinone-quinone methide adducts such as 7 are normally prepared under strongly alkaline conditions by adding a solution of the appropriate quinone methide to an aqueous solution of the anthrahydroquinone dianion.[15,18]. It was not clear, however, that such adducts would be formed under the less basic conditions used in sulphite-AQ pulping, particularly since in the pH range used AHQ would be largely in unionised form.

To investigate this, a dichloromethane solution of the quinone methide 3[18] was added slowly to an excess of freshly prepared AHQ in the same solvent. Proton nmr examination of the concentrated reaction mixture showed that a mixture of the adduct 7 and the two possible isomers of the dimer 13 ((±)- and *meso*-forms) were formed in the ratio of 56:23:20, along with

some AQ and AHQ. It proved impossible to chromatographically separate this mixture on silica using a variety of solvents. However, a small sample of one of the isomers of 13 could be isolated and the ^{1}H and ^{13}C nmr and mass spectral data were consistent with the assigned structure. The dimers 13 presumably arise via radical coupling of the quinone methide 3.

We have thus established that strongly alkaline conditions are not required to form adducts between AHQ and quinone methides such as 3. Since it is known that quinone methides can be formed during sulphite cooking of 1 (e.g., compound 4 and 5 are known to be formed via the intermediacy of the quinone methide 3[9]), adducts like 7 could well be formed during neutral sulphite pulping.

Quinone Methide Involvement

When the methylated ß-ether model 2 was cooked with sulphite, either in the presence or absence of AQ or oxanthrone, it was recovered largely intact (runs 11-13). Since methylation blocks the formation of the quinone methide 3 these experiments strongly suggest that, as occurs under alkaline conditions[5], or when sulphite alone is present[9], reduced anthraquinones promote ß-ether cleavage of 1 via the intermediacy of the quinone methide 3.

Cooks of the α-Sulphonate 4

As discussed earlier, in the absence of reduced anthraquinones the ß-ether 1 is believed to react with sulphite, initially via the quinone methide 3, to afford the α-sulphonate 4, which then can react further to afford the disulphonate 5 or the vinyl sulphonate 6.[8,9] Is the α-sulphonate 4 also an intermediate in the formation of the apocynol sulphonate 12 when reduced quinones are present?

To answer the above question the α-sulphonate 4 was prepared independently and then cooked with sulphite in the presence and absence of oxanthrone. The guaiacol yields obtained in these cooks, 8 and 14% respectively (entries 14 and 15, Table 1), clearly show that 4 is not an intermediate in the formation of the apocynol sulphonate 12 from 1. For 4 to be an intermediate, the yield of guaiacol 9 and apocynol sulphonate 12 should be at least as high for sulphite cooks of 4 as for cooks of the ß-ether 1. The much lower yields actually obtained suggest that the addition of AHQ to the quinone methide 3 (leading via the adduct 7 to the apocynol sulphonate 12) and addition of sulphite to the same intermediate 3 (leading to the α-sulphonate 4) are two parallel and competing reactions.

Furthermore, since some apocynol sulphonate is produced during sulphite cooks of 4 in the presence of oxanthrone (entry 15), the addition of sulphite to the quinone methide 3 must, like addition of AHQ to the same species, be at least partially reversible. That is, under sulphite cooking conditions, the α-sulphonate 4, can revert, in part, to $SO_3^{=}$ and the quinone methide 3.

Adduct Formation vs. Electron Transfer

Although catalysis of ß-ether cleavage of 1 by reduced anthraquinones can be rationalised in terms of the adduct-type of mechanism[14,15] shown in the Scheme, none of the experiments reported above rule out the involvement of an electron transfer mechanism.[19] This alternative mechanism, which has been suggested to operate during soda-AQ pulping[19], predicts the same final products as does the adduct mechanism, but does not invoke the intermediacy of an adduct such as 7.[19]

The results of the present study demonstrate that during sulphite-AQ pulping (i) the postulated intermediate adduct 7 can

be formed at the relatively low pH used, (ii) such adducts do decompose as predicted to guaiacol, AQ and the apocynol sulphonate 12, and (iii) the decomposition of 7 does not necessarily require reversion to AHQ and the quinone methide 3 since the methylated adduct 8, which cannot revert to the quinone methide, also fragments. However, we cannot rule out decomposition of the adduct 7 proceeding via the quinone methide 3 as required in the electron transfer mechanism, because the formation of the α-sulphonate 4 during cooks of the adduct 7 shows that reversion of 7 to the quinone methide does in fact occur. Further work would be required to distinguish between these two possibilities.

Cooks in the Presence of Sugars

Under soda or kraft pulping conditions wood sugars readily reduce AQ to the anthrahydroquinone dianion.[6] To determine whether AQ is also reduced by wood sugars under neutral sulphite conditions the ß-ether was cooked with sulphite in the presence of 1.2 mole equivalents of AQ and 100 mg of bleached Pinus radiata kraft pulp. A modest increase in the yield of guaiacol 9 from 21 to 27% was observed when the pulp was added and some of the sodium apocynol sulphonate 12 was produced (entry 16). Addition of kraft pulp in the absence of AQ did not lead to any enhancement of the rate of ß-ether cleavage, nor lead to the formation of 12 (entry 17).

Cameron et al have reported that AQ is slowly reduced to anthrone under pine sulphite-AQ pulping conditions.[3] This observation provides additional evidence for the reduction of AQ under sulphite-AQ pulping conditions since anthrone is formally at the oxidation level of THAQ i.e. reduced further than AHQ or oxanthrone. We have also looked at the reaction of AQ with sulphite liquor at somewhat higher temperatures than used in this study (170°C) and found that greater amounts of reduced AQ-derived products (principally a sulphonated anthrone) were

formed when kraft pulp was also added to the cook. This work will be reported separately.[20]

These experiments demonstrate that, as occurs under alkaline conditions[6], wood sugars are capable of reducing AQ to the active form (presumably AHQ) under neutral sulphite pulping conditions. The lower yields of guaiacol and apocynol sulphonate 12 found during sulphite cooks of 1 in the presence of AQ and kraft pulp, compared, say, with those when oxanthrone was present (entry 16 vs. 6), can be readily explained by postulating that the reduction of AQ by the pulp is slower than the rate of formation of the quinone methide 3 from 1 and its subsequent reaction with sulphite.

From a more practical viewpoint it should be noted that when similar experiments were carried out using glucose as the reducing sugar the guaiacol yield was less than that obtained in cooks of 1 with sulphite alone (entry 18). The decreased guaiacol yield when glucose was present was presumably due to degradation of the glucose in the sulphite liquor leading to some lowering of the pH (the pH after cooking was 9) and/or reactions leading to sulphite consumption.

Significance of the Results to Sulphite-AQ Pulping

We have established here that AQ is reduced by wood sugars to the catalytically active reduced form during sulphite-AQ pulping, and that reduced forms of AQ promote the cleavage of free phenolic ß-ether linkages during sulphite-AQ pulping. In this regard we have also shown that reduced forms of AQ promote the fragmentation of the 3C ß-ether model guaiacylglycerol-ß-guaiacyl ether and that this model breaks down to afford products consistent with the adduct-type of mechanism proposed above.[21]

The above mechanism can thus explain why AQ catalyzes delignification during the initial phase of sulphite-AQ pulping where there are free phenolic ß-aryl ether linkages present to allow quinone methide formation. It should also be noted that sulphite plays no role in this process except possibly to make the degradation products water soluble.

However during sulphite-AQ pulping anthraquinone also promotes delignification during the bulk phase of cooking. In this phase of pulping it is considered that cleavage of non-phenolic interunit bonds of lignin is required along with sulfonation prior to lignin dissolution.[22,23] Neither the mechanism described above, nor the reactions of sulphite with the lignin in the absence of AQ[11] can explain how AQ could catalyze delignification during the bulk phase of sulphite-AQ pulping. The above proposal also fails to explain why AQ promotes delignification at pHs as low as 7 only when sulphite is present. It is difficult to explain this latter observation purely on the basis of the solubilizing effect of sulphite on the lignin at the lower cooking pHs.

We therefore speculate that there may be a further reaction involving both AQ and sulphite which can lead to cleavage of non-phenolic interunit linkages in lignin, and thus expose further free phenolic ß-ether linkages. Such a reaction would perform a similar function to the cleavage of non-phenolic ß-ethers via the intermediacy of an epoxide during soda-AQ and kraft pulping[24] and serve to break the lignin chain and generate new free phenolic endgroups which are then cleaved by the mechanism described in this article. Further experiments aimed at testing this proposal are in progress.

It should be noted that a similar conclusion was reached by Eagle and McDonough in their study of the kinetics of sulphite-AQ delignification of loblolly pine.[23] These authors found that

the activation energy for sulphite-AQ pulping was higher than that for both neutral sulphite pulping of hardwoods and for kraft pulping. They therefore concluded for the bulk phase that "the action of AQ in the sulphite system is not that of a catalyst for sulphite reactions, but enables reaction with lignin species that are relatively inert in the absence of AQ".

CONCLUSIONS

Under sulphite-AQ cooking conditions, reduced anthraquinones such as oxanthrone, present in stochiometric amounts, promote the fragmentation of the ß-ether bond in free phenolic ß-ether models such as 1. In this process the ß-ether is decomposed to guaiacol and the sodium apocynol sulphonate 12, and the oxanthrone is oxidised to AQ.

The effectiveness of reduced anthraquinones in promoting ß-ether cleavage can be rationalised via the mechanism presented in the Scheme. This involves the formation of an adduct between AHQ and the quinone methide 3, and its subsequent decomposition to AQ, guaiacol 9 and the sulphonate 12. Experiments carried out to test this mechanism have verified that all steps in the proposed sequence could in fact occur under sulphite conditions.

It was further established that, as occurs under highly alkaline soda pulping conditions, wood sugars are capable of reducing AQ to give a species, presumably AHQ, which promotes ß-ether cleavage in 1 under sulphite-AQ cooking conditions.

Consequently AQ is capable of cataylsing the cleavage of free phenolic ß-aryl ether linkages in lignin. This observation explains, in particular, why AQ is effective at accelerating delignification during the initial phase of sulphite-AQ pulping, since delignification during this early stage of cooking is attributed largely to reactions of free phenolic phenylpropane units.[22, 23]

However the results obtained here cannot explain why AQ also promotes delignification during the bulk phase of sulphite-AQ pulping or why AQ is only an effective delignification catalyst at low pHs when sulphite is present. Work aimed at rationalizing these observations is under way.

EXPERIMENTAL

General

^{1}H nmr spectra were recorded at 200 MHz on a Bruker AC 200 instrument in either deuterochloroform (organic-soluble compounds) or deuterium oxide (water-soluble compounds). ^{13}C nmr spectra were recorded on the same instrument at 50 MHz. The mass spectrum was obtained as a probe on a Hewlett Packard 5985 GC/MS operating under electron impact conditions. Thin layer chromatography (tlc) was carried out on commercial precoated silica gel 60 plates (Merck No. 5554) with ethyl acetate-hexanes (1:1) as the developing solvent.

Starting Materials and Reference Compounds

The substrates were prepared via literature methods: guaiacylglycol-ß-guaiacyl ether 1[25]; veratrylglycol-ß-guaiacyl ether 2 via methylation of 1; vinyl guaiacol 10[16]; oxanthrone (10-hydroxyanthracen-9-one)[26]; anthrahydroquinone (AHQ)[17]; dichloromethane solutions of the quinone methide 3[18]; the anthrahydroquinone-quinone methide adduct 7 via the procedure in ref. 14 and purified via flash chromatography on acetic acid and ethanol-deactivated silica gel[17] eluting with ethyl acetate-hexanes (1:1); the methylated adduct 8[14]; and the disulphonate 5.[9] The α-sulphonated ß-ether 4 was prepared by shaking a solution of the quinone methide 3 in dichloromethane[18] with aqueous sodium sulphite.[9] The aqueous phase was separated, extracted with dichloromethane, concentrated and extracted with aqueous ethanol as described in the cooking procedure below. The

resulting ethanolic extract was concentrated, redissolved in water, and acidified by passage through a short column of Dowex 50W X8 ion exchange resin in the H^+ form. The sulphonic acid solution was freeze dried, redissolved in water, adjusted to pH 7 with 1 M sodium hydroxide and then freeze dried again to afford 4 as a colourless powder free of most of the inorganic salts. The apocynol sulphonate 12 was prepared from apocynol [1-(4-hydroxy-3-methoxyphenyl)-ethanol][27] by shaking a solution of the corresponding quinone methide with aqueous sodium sulphite and isolating the resulting sodium sulphonate as described for the preparation of 4.

Anthraquinone (AQ) anthrone and tetrahydroanthraquinone were recrystallised before use; AQ once from acetic acid, anthrone twice from benzene-light petroleum (3:1), and tetrahydroanthraquinone (Kawasaki Kasei) twice from ethanol.

Commercial bleached Pinus radiata kraft pulp was employed for cooks with wood pulp.

Sulphite Cooking Liquor

The sulphite cooking liquor used was a 0.5 M solution of sodium sulphite (analytical grade) in water (pH 10.5) and was freshly prepared for each batch of cooks.

General Cooking Procedure

The substrate (e.g., 1, 20-25 mg), dioxane (1 ml, freed of peroxides by passage through a column of neutral activity I alumina), and sulphite liquor (4 ml) were placed in a teflon-capped glass reaction vessel and purged with nitrogen. The additive (1.2 mole equivalents) was then added if required. The vessel was sealed, and placed in a polyethylene glycol bath maintained at 140°C for 1 h, allowing 2 min for the vessel to heat up. The bomb was removed, cooled to room temperature,

opened, and the contents transferred into distilled water (100 ml).

The resultant mixture was extracted with dichloromethane (3 x 15 ml). The combined extracts were dried by filtration through anhydrous sodium sulphate, and the filtrate and washings made up to 50 ml. The guaiacol yield was then determined by glc as described below. If required this extract could be concentrated and analysed by tlc and/or nmr spectroscopy.

The extracted aqueous phase was concentrated to dryness under reduced pressure. The resulting solid was extracted in three portions with a total of 30 ml of 80% aqueous ethanol[9] and the filtered extract concentrated. This solid was dissolved in water (5 ml), the solution was filtered (to remove small amounts of catalyst-derived products) and freeze dried to afford a solid (30-90 mg) containing the sodium sulphonates plus inorganic material. The approximate composition of the sulphonate mixture was determined by ^{1}H nmr spectroscopy.

Analysis of the Aqueous Phases

The freeze-dried organic phases were dissolved in deuterium oxide and analysed by ^{1}H nmr using sodium 3-(trimethylsilyl)-propionate as the internal standard. ^{1}H nmr data are given below for the sodium sulphonates:

4 δ : 3.64, 3.80 (s, s, 3H each); 4.4-4.9 (m, 3H); 6.8-7.2 (m, 7H).

5 δ : 3.5-3.8 (m, 2H); 3.90 (s, 3H); 4.37 (d of d, 1H, J = 10, 4 Hz); 6.8-7.1 (m, 3H).

12 δ : 1.65 (d, 3H, J = 7.1 Hz); 3.88 (s, 3H); 4.13 (q, 1H, J = 7.1 Hz); 6.8-7.1 (m, 3H).

Guaiacol Analysis

To an aliquot of the dichloromethane extract (200 μl) in a sealed vial containing the internal standard, *p*-cresol, was added bis(trimethylsilyl)trifluroacetamide (50 μl) and the resulting solution stood for 1 h before glc analysis. The glc analysis was carried out on a 12 m x 0.3 mm OV1 capillary column using helium, flowing at 1.5 ml/min, as the carrier gas and employing the purged splitless injection technique with the purge beginning after 20 s. The oven temperature was programmed from 35 to 60°C at 20°C/min and then from 60 to 100°C at 4°C/min. The detector temperature was 250°C and the injector temperature 225°C.

Guaiacol Recovery Tests

A solution of guaiacol (6.90 mg) in dioxane (1 ml) and sulphite liquor (4 ml) was prepared, cooked, and analysed as described above. The recovery of guaiacol was 94%. The results presented in Tables 1 and 2 and Fig. 1 are not corrected for guaiacol loss.

The Effect of Cosolvents

Cooks of the ß-ether 1 were carried out as described above with 4 ml of sulphite liquor and 1 ml of either water, dioxane or isopropanol and also with 3 ml of sulphite liquor and 2 ml of either dioxane or isopropanol and the guaiacol yields determined. The results are presented in Table 2.

Investigation of the Organic Phases

Analysis by tlc indicated that no starting ß-ether 1 was recovered from cooks of this model with sulphite either in the presence or absence of additives (entries 1-7, 16, 17, Table 1). The methylated ß-ether 2 was cleanly recovered after similar cooks (entries 11-13).

With two exceptions (entries 3 and 17), cooks of 1 in the presence of additives gave organic phases which contained, in addition to guaiacol 9, mainly AQ, plus varying amounts of anthrone [trace (entries 2, 16) to 28% (entries 4, 7)] and small amounts of unidentified components. No reduced anthraquinones, e.g., AHQ, oxanthrone, THAQ, were detected in the organic phases after cooking, with the exception of cooks with THAQ (entry 7) where the quinone 14 was tentatively identified. This compound exhibited: ^{1}H nmr ($CDCl_3$) δ : 3.23 (d, 4H, J = 1.0 Hz, C-1 and C-4 protons); 5.86 (s, 2H, C-2 and C-3 protons); 7.71 (m, 2H, C-6 and C-7 protons); 8.08 (m, 2H, C-5 and C-8 protons).

When the adduct 7 was cooked with sulphite the organic phase contained guaiacol (33% by glc), and AQ and anthrone in the approximate ratio of 6:1. No starting material 7 was detected.

Compounds identified from the organic phases of cooks of the methylated adduct 8 were guaiacol, a small amount of recovered starting material, anthraquinone and methylated vinyl guaiacol 11, ^{1}H nmr ($CDCl_3$) δ : 3.88, 3.91 (s, s, 3H each $-OCH_3$); 5.15 (d, 1H, J = 10.9 Hz, C-ß proton); 5.51 (d, 1H, J = 17.5 Hz, C-ß proton); 6.65 (d x d, 1H, J = 17.5, 10.9 Hz, C-α proton); 6.85 (m, 3H, aromatic protons).

Reaction of AHQ with the Quinone Methide 3

A cold (-78°C) solution of the quinone methide 3 in dichloromethane (10 ml, 0.344 mmol, prepared from 100 mg of the ß-ether 1[18]) was added dropwise over 50 min, under nitrogen, to a stirred solution of freshly prepared anthrahydroquinone (200 mg, 0.95 mmol)[17] in dry dichloromethane (20 ml) at room temperature. The yellow solution was stirred at room temperature for a further 30 min then concentrated. Examination of this solid by ^{1}H nmr spectroscopy indicated that, in addition to AQ and AHQ, three components were formed: the adduct 7 δ ($-OCH_3$) : 3.41, 4.01

(14); and the two possible isomers ((±)- and *meso*-) of 13 δ (-OC$\underline{H}_3$) : 3.71, 3.77 and δ (-OC$\underline{H}_3$) : 3.54, 3.83 in the approximate ratio of 56 : 23 : 20. While it proved impossible to chromatographically separate out the adduct 7 and the two isomers of 13 by tlc on silica using a variety of solvent systems, a small amount of one of the isomers of 13 could be separated from the mixture by flash chromatography on silica gel (deactivated with a 1% solution of acetic acid in ethanol), eluting with 7% ethyl acetate in dichloromethane. The isomer of 13 was crystallised as fine needles from ether and exhibited: ^{1}H nmr δ : 3.55 (br s, 2H); 3.72, 3.77 (s, s, 6H each,); 3.75-4.10 (m, 4H,); 5.52 (br s, 2H,); 6.40-7.06 (m, 14H). ^{13}C nmr δ : 47.8; 55.6; 56.1; 70.9; 111.7; 112.3; 114.0; 120.8; 121.0; 121.4; 133.3; 134.1; 144.3; 146.3; 148.8; 149.6. Mass spectrum (EI, 70 eV) m/z: 546 (3), 299 (19), 273 (46, 1/2 M^+), 149 (100).

Cooks in the Presence of Pulp

For cooks in the presence of bleached kraft pulp, the air-dry pulp (100 mg) was added just prior to closure of the bomb and was removed by filtration of the aqueous phase after extraction with dichloromethane. Ninety four milligrams of dry pulp was recovered.

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