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The Reactions of Lignin during Sulphate Cooking

Part V.* Model Experiments on the Splitting of Aryl-alkyl Ether Linkages by 2 N Sodium Hydroxide and by White Liquor**

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The cleavage of arylether bonds in lignin by 2 N sodium hydroxide and by white liquor was studied with appropriate model compounds. β-Arylether linkages in phenolic units (type III) were found to be split by white liquor to a considerably greater extent than by 2 N sodium hydroxide (*cf.* also Ref.[11]). An attempt has been made to interpret this finding by suggesting a different course for the splitting reaction involved. The behaviour of β-arylether linkages in phenolic units may provide a possible explanation for the greater ease and rate of lignin dissolution during sulphate cooking compared with alkali cooking.

In previous communications of this series the structural requirements for, and the mechanisms of the degradation of lignin by alkali were investigated using appropriate model compounds[1] and "milled wood lignin".[2] It was shown that α-arylether bonds in phenolic phenylpropane units (A) and β-arylether bonds in non-phenolic phenylpropane units, containing a neighbouring hydroxyl group in the side chain (D), are split under the conditions of alkali cooking. The cleavage of type A was suggested to proceed *via* a corresponding intermediate of the quinone methide type, whereas type D was shown to be split *via* a corresponding epoxide intermediate. These two types of reactions were considered to constitute the main pathways of the alkaline cleavage of arylether linkages present in lignin.

The dissolution of lignin by the action of alkali is greatly enhanced if the alkaline cooking liquor contains sulphide ions as during sulphate cooking. Many theories have been put forward to interpret the greater ease and rate of lignin dissolution during sulphate cooking compared with alkali cooking.

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* Part IV, see Ref.[7]

** The term "white liquor" used throughout this work, refers to a solution of NaOH (3.5 g) and $Na_2S \cdot 9H_2O$ (3.1 g) in water (100 ml).

A widely held view suggests that sulphide ions present in the white liquor react with *p*-hydroxybenzylalcohol groups to yield first *p*-hydroxybenzylmercapto and then *p*-hydrobenzylsulphide groups. In this way, it is assumed that the most reactive sites in the lignin molecule are protected from undesirable condensation reactions. Whereas the formation of *p*-hydroxybenzylsulphide groups under mild conditions could be illustrated by numerous model experiments,[3] it seems rather doubtful whether this reaction may successfully compete with condensation reactions under the conditions of sulphate cooking. It was recently shown [4] that *p*-hydroxybenzylalcohols and *p*-hydroxybenzylsulphides, when subjected to these conditions, yielded similar condensation products (thin-layer chromatography).

Another view, advanced recently,[5] proposes that hydrogen sulphide, present in white liquors, splits hydroxy-diphenylmethane structures, thought to arise in lignin by alkaline condensation.[6,4] This view, however, could not be supported by model experiments. Four dihydroxy-diphenylmethanes were shown to be stable under the conditions of sulphate cooking.[7]

Thiolignin prepared from wood powder contains a larger proportion of phenolic hydroxyl groups per methoxyl group originally present than does alkali lignin prepared from the same source.[8] The same is true for the corresponding products prepared from "milled wood lignin".[8] The higher content of phenolic hydroxyl groups in thiolignins compared with alkali lignins is not accounted for by any of the theories mentioned above and a new hypothesis is therefore advanced.

In the present work it is presumed that the favourable effect of sulphide ions on the degradation and dissolution of lignin is at least partly due to a smoother and more extensive cleavage of arylether bonds. In order to find out whether some type(s) of arylether bonds are attacked more strongly by white liquor than by 2 N sodium hydroxide, appropriate model compounds were treated with both agents (heating at 170° for 2 h). The extent of cleavage of arylether linkages was determined by gas chromatographic methods. Differences in the behaviour of certain types of model compounds towards alkali and towards white liquor could be tentatively interpreted in terms of different reaction mechanisms.

RESULTS AND DISCUSSION

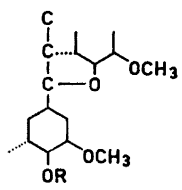
Gas chromatographic methods were found to give more reliable and reproducible results than isolation and weighing of the alkaline cleavage products. The values for the degree of splitting by alkali reported earlier [1] should therefore be revised, and where necessary, replaced by those given in Table 1, left column. The right column of Table 1 contains the values for the degree of splitting of the same model compounds by white liquor.

α-Arylether bonds in phenolic units (type A) were found to be split both by 2 N sodium hydroxide and by white liquor (XVIII [1], XIX [9]). In contrast, *α*-arylether bonds in non-phenolic units (type B) proved to be essentially stable towards both agents. The small proportion of phenolic hydroxyl groups liberated from XX by white liquor (9 %) may arise partly by slow demethylation of the 3,4-dimethoxyphenyl moiety (*cf.* also Ref.[10]) and partly by cleavage of the resulting *p*-hydroxybenzyl-arylether XVIII. Liberation of phenolic

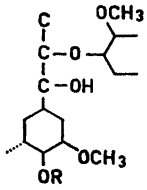
Table 1. Splitting of model compounds by 2 N NaOH and by white liquor at 170° C (2 h)

Compound	Treatment with			
	2 N NaOH		White liquor	
	%Guaiacol split off	Remarks	%Guaiacol split off	Remarks
Type C (phenolic β-arylethers)				
I	34	XII isolated as Na-salt	97.5	XII formed only in traces (thin-layer chrom.)
II	52	XIII isolated as Na-salt	80	XIII formed only in traces (thinlayer-chrom.)
III	33	XII isolated as Na-salt	83.5	XII formed in a small amount (thin-layer chrom.)
IV	46.5	XII isolated as Na-salt	94.5	XII formed in traces (thin-layer chrom.)
XII	17	starting material recovered	14.5	starting material recovered
Type D (non-phenolic β-arylethers)				
V	91		81	
VI	73		68	
VII	89		77	
VIII	nil	97 % of the starting material recovered [4]	8	
IX	16.5	80 % of the starting material recovered [4]	16	
X	82.5		80	
XI	75		73	
XVI	93		99	
XVII	85		67	
Types A and B (α-arylethers)	Guaiacol groups liberated		Guaiacol groups liberated	
XVIII	not determined	stilbene derivative isolated [1]	not determined	stilbene derivative isolated [4]
XX	nil	starting material recovered [1]	9	
XXI	nil	starting material recovered [1]	13	

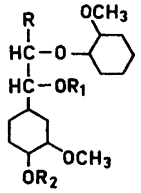
hydroxyl groups solely due to demethylation was observed when compound XXI was treated with white liquor. The guaiacol groups formed and methanol split off corresponded with each other (gas chromatography).

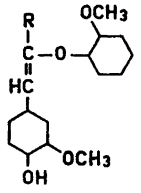


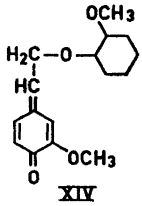
A R = H
B R = next side-chain



C R = H
D R = next side-chain



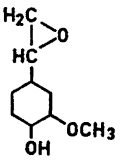




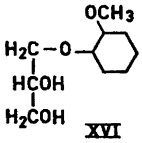
XIV

I R = R_1=R_2=H
II R = CH_3, R_1 = R_2=H
III R = CH_2OH, R_1=R_2=H
IV R = H, R_1=CH_3, R_2=H
V R = R_1=H, R_2=CH_3
VI R = CH_3, R_1=H, R_2=CH_3
VII R = CH_2OH, R_1=H, R_2=CH_3
VIII R = H, R_1=R_2=CH_3
IX R = CH_2OH, R_1=R_2=CH_3
X as V but CO instead of CHOH
XI as VII but CO instead of CHOH

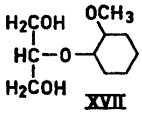
XII R = H
XIII R = CH_3



XV



XVI

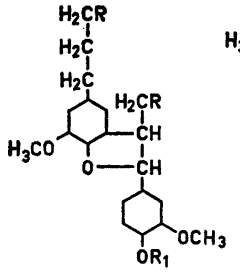


XVII

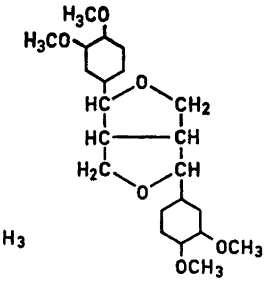
β-Arylether bonds in non-phenolic units containing a neighbouring hydroxyl group (type D) were cleaved by both agents to comparable degrees. The somewhat greater extent of splitting of compounds V, VI, VII, IX, X, XI, and XVII by the action of sodium hydroxide may be due to the stronger alkalinity of this agent rather than to differences in the reaction mechanisms involved. Thus, the splitting of α-arylether linkages in phenolic units (type A) and of β-arylether linkages in non-phenolic units containing a neighbouring hydroxyl group (type D) by white liquor may be assumed to proceed essentially *via* the same intermediates (quinone methide- and epoxide structures, respectively) as were proposed for the cleavage of these linkages by sodium hydroxide.[1]

β-Arylether linkages in phenolic units (type C) were previously reported to be stable towards 2 N sodium hydroxide at 170°.[1] A reinvestigation of the behaviour of compounds I, II, III, and IV under the conditions mentioned, using a modified working-up procedure and a gas chromatographic method for the determination of guaiacol revealed, however, that they were split to a considerable extent (see Table 1).

The cleavage of β-arylether linkages in phenolic units (type C) by 2 N sodium hydroxide was studied in more detail using compound I as a model.



XVIII R = R_1 = H
XIX R = OH, R_1 = H
XX R = H, R_1 = CH_3



XXI

Two possible pathways for the splitting of guaiacol from I have to be considered: it may be liberated either by alkaline cleavage *via* the corresponding epoxide (XV) or by alkaline hydrolysis of the corresponding quinone methide (XIV).

In general, the former (epoxide) route of arylether cleavage can be blocked by methylation of the neighbouring hydroxyl group (*cf.* Refs.[1,12]). Methylation of the benzylalcoholic hydroxyl group in I, however, yields the *p*-hydroxybenzyl-methylether IV, which on treatment with alkali may be reconverted *via* the quinone methide (XIV) into the benzylalcohol I.[13] About the same amount of guaiacol should therefore be expected from IV as was split off from I. The amount of guaiacol actually obtained from IV was somewhat greater than that from I. This result indicates that the elimination of the elements of methanol from IV proceeds with at least the same ease as the elimination of the elements of water from I, and furthermore, that the rate of formation of the quinone methide XIV is greater than that of the formation of the epoxide XV. Once formed, the quinone methide XIV may be expected to undergo splitting of the guaiacylether bond or stabilisation by proton elimination (see below). The dissociation of the phenolic hydroxyl group ($pK \approx 10$) and the supply of π-electrons from the resulting phenolate ion *via* the ring to the α-carbon atom greatly facilitates the elimination of the hydroxyl- and methoxyl ions from the α-position in I and IV, respectively. These processes apparently compete successfully with the dissociation of the alcoholic hydroxyl group ($pK \approx 18$) and the subsequent nucleophilic attack of the resulting alcoholate ion. Preference is therefore given to a formulation of the alkaline splitting of β-arylether bonds in phenolic units *via* the corresponding quinone methide intermediates (see scheme 1).

After treatment of compound I with sodium hydroxide, the enolether XII can be isolated from the reaction mixture as the sodium salt.[1] Compound XII may either be regarded as a stabilised product of the quinone methide XIV, formed by proton elimination, or less likely, as a primary reaction product of I, formed by elimination of the elements of water. When subjected to the same alkali treatment, compound XII yields only a small amount (17 %) of guaiacol. This cleavage of XII may contribute to the overall splitting reaction of compound I to a certain extent.

Adler and co-workers recently found [11] that white liquor splits β-arylether bonds in phenolic units (type C) to a considerable extent. For the sake of comparison this cleavage reaction in structures of type C was now investigated, using the same compound (I) as in the study of the splitting with 2 N sodium hydroxide. Whereas the latter agent gave a 34 % yield of guaiacol (see above), white liquor brought about an almost quantitative cleavage under the same reaction conditions (see Fig. 1). Similar differences in the behaviour towards

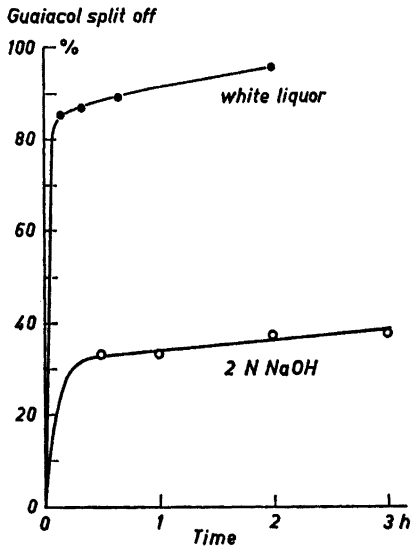
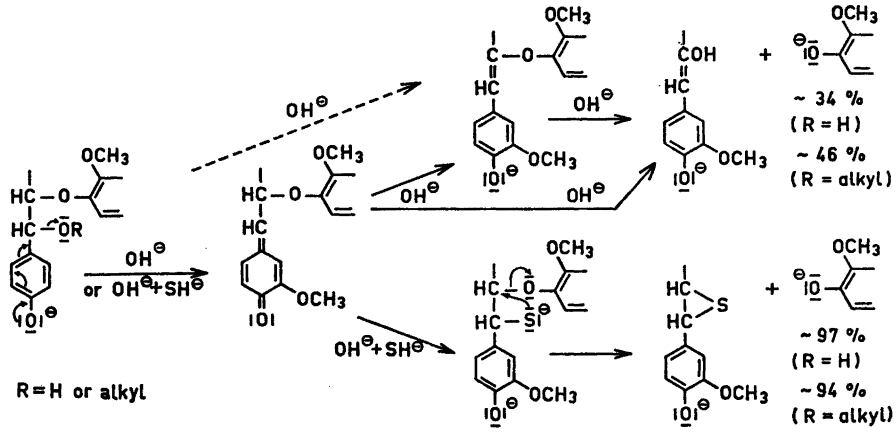


Fig. 1. Cleavage of the β-guaiacylether bond in α-(3-methoxy-4-hydroxyphenyl)-ethyleneglycol-β-guaiacylether by 2 N NaOH and by white liquor at 170°C (2 h).

2 N sodium hydroxide and white liquor were also observed with compounds II, III, and IV (see Table 1). These differences cannot be explained in terms of the different alkalinities of the two splitting agents, since the white liquor used corresponded only to about 1 N sodium hydroxide with respect to its content in effective alkali. The high proportion of guaiacol split off, *e.g.* from compound I, by the action of white liquor indicates therefore that the reaction follows a course essentially different from the cleavage with 2 N sodium hydroxide. This view is supported by the fact that the enolether XII, suggested to be a main product in the reaction of I with sodium hydroxide,[1] was only detected in trace amounts after the more extensive cleavage of this compound by white liquor (thin-layer chromatography, see Table 1). When the enolether XII was treated with white liquor, about the same amount of guaiacol (14 %) was obtained as on treatment with 2 N sodium hydroxide.

Methylation of the benzylalcoholic hydroxyl group (I → IV) did not impair the splitting by white liquor to any noticeable degree. This result is consistent with the assumption of a common intermediate (quinone methide XIV, see below) in the reaction of these compounds with white liquor, just as in the reaction with sodium hydroxide.

We therefore propose that the cleavages of β-arylether linkages in phenolic units (type C) by alkali and by white liquor follow the different pathways depicted in Scheme 1.



Scheme 1. Splitting of β-arylether linkages in phenolic units by alkali and by white liquor.

Quinone methide structures are assumed to be intermediate structures in both reactions. On treatment with alkali these intermediates are partly hydrolysed, yielding phenolic hydroxyl groups, and partly converted into enolether structures, which in their turn are hydrolysed to a small extent. On treatment with white liquor, however, sulphide ions add to the quinone methide structures to yield benzylmercaptide ions, which immediately displace the neighbouring aroxyl substituents by a nucleophilic attack with formation of episulphide structures (as intermediates) and new phenolic hydroxyl groups.[14] Hence, the different courses of the splitting reactions of β-arylether structures in phenolic units (type C) with alkali and with white liquor may ultimately be due to (*a*) a stronger tendency of sulphhydryl ions to coordinate their valence electrons with the α-carbon atom of the quinone methide structures, (*b*) a more complete dissociation of the benzylmercapto groups under the conditions used, and (*c*) a greater nucleophilicity of the resulting mercaptide ions, these three properties of sulphur containing intermediates being compared with those of their oxygen containing analogues.

Attempts to illustrate these different pathways of the alkaline splitting of compound I have been made by treating the suggested common intermediate (quinone methide XIV) both with 2 N sodium hydroxide and with white liquor. The results obtained[15] were essentially in agreement with the proposed mechanisms.

EXPERIMENTAL

Model compounds. The model compounds used were prepared as described earlier.[1,12] Compound IV[1] was now obtained crystalline as small needles, and recrystallised from benzene-hexane, m.p. 68.5–69.0°. (Found: C 67.13; H 6.74; O 26.08; OCH_3 28.64. Calc. for $C_{17}H_{20}O_5$: C 67.11; H 6.58; O 26.32; OCH_3 30.58).

The enolether XII was prepared by treating compound I with 2 N NaOH at 170°. It was isolated and used as the sodium salt.[1]

Cooking liquors. Sodium hydroxide (2 N) and "white liquor", containing NaOH (3.5 g) and $Na_2S \cdot 9H_2O$ (3.1 g) in water (100 ml) were used as cooking liquors. Non-phenolic model compounds, which exhibited low solubility in both liquors, were treated with solutions prepared by mixing double strength aqueous liquors with an equal volume of absolute ethanol. All model compounds were completely dissolved under the cooking conditions.

Cooking procedure. The compound (about 100 mg) was dissolved in the cooking liquor (10 ml) and the solution placed into a reaction vessel of stainless steel. The air in the reaction vessel was replaced by nitrogen and the sample rotated in a polyglycol bath. The warming up period from room temperature to 170° was 2.5 h and the reaction time at 170° 2 h. The sample was then cooled to room temperature, neutralised by addition of an excess of dry ice, and extracted with chloroform (4 × 3 ml). In all tests the completeness of the extraction was controlled by slightly acidifying the water phase with dilute HCl and repeating the extraction with chloroform. The combined chloroform extracts containing guaiacol and/or other phenolic substances were dried (Na_2SO_4) and analysed. Most of the cooks were repeated three or more times and the average values determined.

Gas chromatographic procedure. A quantitative gas-liquid chromatographic procedure was used to estimate the guaiacol present in the chloroform solutions (see above), with *p*-cresol as an internal standard. After addition of the internal standard to the chloroform solutions, aliquots (0.2—1.0 ml) were withdrawn and injected into the gas chromatograph. For each solution at least three determinations were made and the average value calculated.

A Perkin-Elmer 800 dual column gas chromatograph with ionisation detector was used throughout the investigation. Columns 6 mm × 2 m, packed with 20 % Carbowax 20 M stationary phase on Chromosorb W with a nitrogen flow rate of 30 ml/min gave a complete separation of the components. A programmed temperature schedule with an initial isothermal period was followed. The injection temperature of 130° was maintained for 3 min in order to flash off solvent and subsequently raised at approximately 40°/min. to 180° in order to elute the higher boiling components.

When the cleavage resulted in the formation of phenolic substances other than guaiacol, the extent of splitting was determined by evaporating the chloroform extract, oxidising the residue with periodate and then determining the liberated methanol by gas chromatography. The gas chromatographic procedure described previously [2] was essentially followed, except that acetonitrile was used as an internal standard instead of benzene and a Perkin-Elmer W column instead of Triton on Chromosorb.

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