Reactions of Sulphur During Sulphate Pulping

GÖSTA BRUNOW,[a] TAINA ILUS[a] and GERHARD E. MIKSCHE[b]

[a] *Department of Chemistry, University of Helsinki, E. Hesperiank. 4, SF-00100 Helsinki 10, Finland and* [b] *Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg 5, Sweden*

The elimination of sulphur from sulphur-containing intermediates formed from arylpropane-β-aryl ether structures in lignin during sulphate pulping has been studied with the aid of model compounds. Evidence has been found for a heterolytic reaction where the sulphur is lost in a zero-valent form. Sulphur(0) disproportionates in the alkaline liquor with the formation of sulphide ion.

It has been known for a long time that lignin takes up sulphur during the initial stages of a sulphate cook. Using relatively low temperatures and hydrosulphide as pulping agent, Enkvist and co-workers succeeded in isolating a product with a high content of sulphur, *ca.* 9 %. When this "thiolignin" was heated in alkaline solution at 160°, most of the sulphur was split off, and the product resembled an ordinary sulphate lignin with a sulphur content around 2 %.[1]

More recently, the mechanism of the sulphur uptake and subsequent depolymerization of lignin has been studied in detail. The most important depolymerization reaction was found to be the splitting of arylglycerol-β-aryl ether bonds.[2a] From a kraft cook of model compound *1*, conducted at a relatively low reaction temperature (100°), the dithiane *4* has been isolated in good yield; under the same conditions the proposed intermediates in the reaction sequence *1→2* (not shown in Fig. 1), and also the hydroxythiol *3*, gave the dimerization product *4*.[2a,b] On heating with white liquor at the maximum temperature of a technical sulphate cook (170°), the benzyl alcohol *1* as well as the dithiane *4* were transformed to amorphous products. It was noted, however, that the sulphur contents of the reaction products (7.2 %, *1*; 5.3 %, *4*) were considerably lower than the sulphur content of the dithiane *4* (17.6 %).[2a]

In an earlier paper,[3] a possible explanation of the elimination of sulphur from sulphur-containing intermediates in the degradation of arylglycerol-β-aryl ether structure was given. Kraft cooks of model compounds *6, 8,* and *9* (R = CH$_3$) as well as soda cooks of compounds *8* and *9* (R = CH$_3$) yielded *trans*-isoeugenol (*10*) as the common major product.[3] The heterolytic cleavage of the carbon-
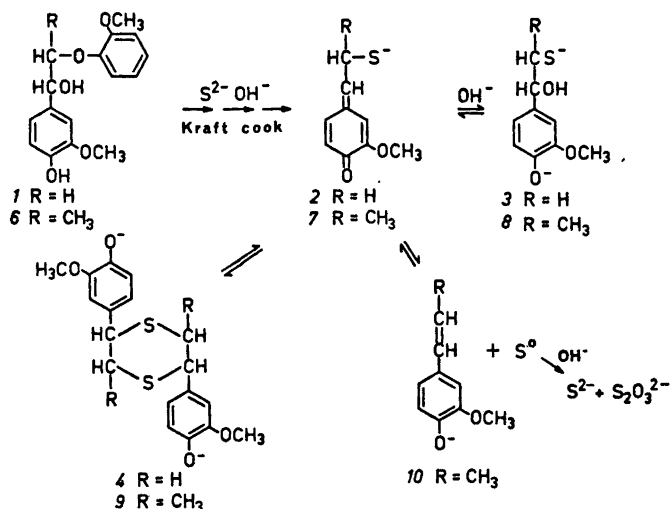
Fig. 1.

sulphur bond in the quinone methide intermediate *7* to give isoeugenol (*10*) implies an intramolecular electron transfer, the organic component being reduced and the sulphur being oxidized to an oxidation state corresponding to elemental sulphur (see Ref. 3). This type of C−S bond cleavage is favoured by the ease with which sulphur can release the binding electron pair and by resonance stabilization of the resulting organic anion.[4]

The transformation of the quinone methide *7* to isoeugenol *10* is reversible. This could be shown [5] by reacting *trans*-isoeugenol with sodium disulphide in excess alkali at 100°. A mixture of two stereoisomeric forms of the dithiane *9* was obtained in substantial yield. The nearly quantitative conversion of the dithiane *9* to isoeugenol at temperatures in the technical soda or kraft cook [3] is due to the disproportionation of sulphur in the presence of excess alkali at these temperatures (see below).

The purpose of this investigation was to establish the fate of the sulphur formed in the decomposition of the quinone methide *7*. To this end, the alkaline cooking of the thiol *8* was reexamined.

The determination of sulphide and thiol concentrations. The changes in thiol and sulphide concentrations during the desulphurization reaction were measured using an ion selective membrane electrode. An electrode of this type has recently been introduced [6-10] for the determination of sulphide ion in aqueous solutions. It seems of potential value in the study of the chemistry of the sulphate cook.[10]

The electrode contains a crystalline silver sulphide membrane and responds to changes in silver ion activity. It can be used either for direct potentiometry or as an end point indicator in titrations with silver nitrate. In the present investigation, titration with silver nitrate was found to be the most convenient method. Fig. 2 shows titration curves obtained with sodium sulphide, ethane-1,2-dithiol, and thiol *8*.
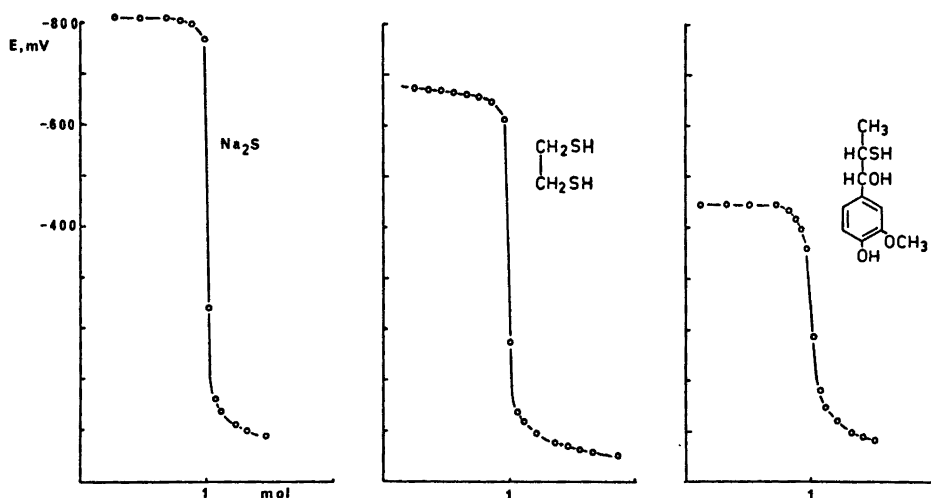
Fig. 2. Potentiometric titration of sodium sulphide, ethane-1,2-dithiol, and thiol *8* with 0.100 M AgNO₃.

The thiols give a smaller voltage drop at the end point than the inorganic sulphide ion. This might be due to the different solubilities of the silver salts of the thiols and silver sulphide.

The sensing element of the electrode allows silver ions to pass between the sample solution and an internal reference solution which is kept at a fixed silver ion level. The distribution of silver ions between the two solutions develops a potential which depends on the silver ion activity in the sample solution.[7]

$$E = E_a + (2.3RT/nF) \log A_{Ag^+}$$

The silver ion activity in the sample solution depends on the sulphide ion activity in the sample solution and can be calculated from the solubility of the silver salt. Thus the different solubilities of the silver salts of the thiols will lead to different voltage drops during titration with silver nitrate.

It has been reported [10] that direct titration with silver nitrate gives only the inorganic sulphide ion content, whereas argentimetric back titration (addition of excess silver nitrate and back titration with potassium iodide) gives the sum of organic and inorganic bivalent sulphur. In the case of the thiols studied in this work, forward and back titrations gave identical results. Therefore, only direct titration with silver nitrate was used.

RESULTS AND DISCUSSION

When compound *8* was heated in 1 M sodium hydroxide at 140° or 170° for 2 h under nitrogen, thin layer chromatography showed that the starting material had disappeared. The major organic product was isoeugenol (*10*, quantitative determination by GLC gave 65 − 70 % almost pure *trans*-isomer).

A small amount of a white precipitate (2 – 5 % by weight) was identified as a dithiane (9) by comparison of its IR-spectrum with that of material synthesized according to Ref. 2b. Titration of the reaction mixture with silver nitrate revealed that sulphide ion had been formed and that its amount was exactly half the initial amount of thiol sulphur (after correction for the small amount of dithiane present).
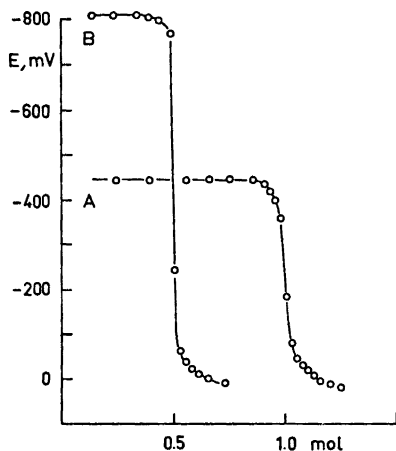

Fig. 3. Potentiometric titration of thiol *8* before (A) and after (B) heating in sodium hydroxide solution.

The fact that half the thiol sulphur initially present was found in the form of sulphide ion although the thiol had been consumed completely, suggests that the thiol sulphur has been split off as sulphur(0). The latter can be expected to disproportionate in the presence of excess sodium hydroxide in the following manner:[10,11]

$$4 \ S_0 + 6 \ OH^- \rightarrow 2 \ S^{2-} + S_2O_3{}^{2-} + 3 \ H_2O \tag{1}$$
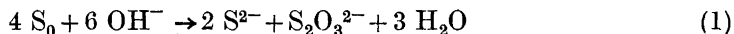
To study the stoichiometry of this reaction under the conditions used in this work, elemental sulphur was treated with 1 M aqueous sodium hydroxide in the same way as the thiol. The amount of sulphide found indicated that a disproportionation according to eqn. (1) had taken place; Table 1.

Table 1. Titrimetric determination of sulphide.

Substance	Temp. °C	Time h	Starting material (mol)	Mol S^{-2} formed
8	140	2	0.10	0.050 ± 0.001
8	170	2	0.10	0.050
Sulphur	140	2	0.10	0.050

CONCLUSIONS

The ion-selective sulphide electrode permits determination of thiols and of sulphide ion. Reproducible results are obtained by direct potentiometric titration with silver nitrate.

Heating thiol *8* in aqueous sodium hydroxide causes an oxido-reduction where the organic component is reduced to isoeugenol and the thiol sulphur is oxidized to the oxidation state of elemental sulphur. Under the employed reaction conditions, the sulphur disproportionates with the formation of sulphide ion.

Isoeugenol is also obtained in high yields by heating *β*-aryl ether *1* (R = CH₃) in "white liquor",[3] *i.e.* an aqueous solution of NaOH and Na₂S. The formation of isoeugenol from both *1* and *8* suggests that the quinone methide *7* is a common intermediate in the degradation of these compounds.

In lignin, arylpropane-*β*-aryl ether bonds are structural elements of high frequency and the splitting of such bonds during the sulphate cook will lead to sulphur-containing quinone methides of type *7*. These will lose their sulphur in the way outlined above at the high temperature and alkalinity of the sulphate cook. The regeneration of sulphide ion is thus due to disproportionation of zerovalent sulphur rather than the hydrolysis of episulphides as suggested earlier.[12,13]

EXPERIMENTAL

NMR-spectra were recorded in $CDCl_3$ with TMS as internal reference on a Varian A-60 spectrometer and IR-spectra on a Perkin-Elmer Model 237 instrument.

Sulphide ion measurements were made with an Orion Model 407 Specific Ion Meter. The electrodes used were: a silver sulphide membrane electrode model 94 − 16 A and a double junction reference electrode model 90 − 02, both from Orion Research Inc.

All aqueous solutions were made in freshly boiled distilled water and kept under nitrogen.

Elemental analyses were performed by Messrs. Dornis and Kolbe, Mülheim, Federal German Republic.

Alkaline cooks. All cooks were performed in stainless steel cylinders under nitrogen. In a typical run 500 mg of thiol was dissolved in 20 ml of M NaOH. The solution was divided into two 10 ml portions and the cookings and titrations were done in duplicate. An aliquot of each thiol solution was titrated with $AgNO_3$ before cooking to determine the exact amount of thiol in the solution. After heating, 2 ml of the solution was added to 2 ml of 25 % ($d = 0.91$) aqueous NH_3 and 26 ml of M NaOH and titrated with 0.100 M $AgNO_3$.

Syntheses

α-Thioacetoxy-4-acetoxy-3-methoxy-propiophenone. α-Bromo-4-acetoxy-3-methoxy-pro-piophenone [14] (3.0 g) was dissolved in 15 ml of dry 1,2-dimethoxyethane. Solid potassium thioacetate (1.1 g) was added and the mixture shaken at room temperature for 1 h. The precipitate was filtered off and the filtrate evaporated to dryness. The residue (2.7 g) was a colourless oil which was purified by column chromatography (silicic acid Mallinckrodt, eluent ethyl acetate-cyclohexane 1:1). The purified oil was chromatographically homogeneous. (Found: C 56.78; H 5.40; S 10.90. Calc. for $C_{14}H_{16}O_5S$ (296.28): C 56.75; H 5.44; S 10.82.) NMR δ-values: 1.52 (2) d, $C-CH_3$; 2.29 (3) s, $SCOCH_3$ or $OCOCH_3$; 2.32 (3) s, $SCOCH_3$ or $OCOCH_3$; 3.87 (3) s, OCH_3; 5.26 (1) q, $C-CH-C$; 7.0−7.7 (3) m, H_{ar}; $J_{\alpha\beta} = 7.0$ cps.

1-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanethiol (8). Lithium aluminium hydride (390 mg) was dissolved in 40 ml dry ether and cooled to 0°. α-Thioacetoxy-4-

acetoxy-3-methoxypropiophenone (3.4 g) in 40 ml ether was added with cooling and the mixture kept for 24 h at room temperature. Excess LiAlH$_4$ was destroyed with moist ether and water. Acidification with Dry-Ice and extraction with ether gave 1.5 g (61 %) of a colourless oil. Small amounts of by-products were removed by preparative thin layer chromatography (Kieselgel Merck PF$_{254}$ 1.5 mm, eluent cyclohexane-ethyl acetate 1:1). This purification was performed immediately before the cooking experiments; the substance is not stable in contact with air at room temperature. The thiol was analysed as the triacetate (a chromatographically homogeneous oil). (Found: C 56.36; H 5.99; S 9.28. Calc. for C$_{16}$H$_{20}$O$_6$S (340.32): C 56.46; H 5.92; S 9.42.) NMR δ-values: 1.25 (3) d, C$-$CH$_3$; 2.08 (3) s, OCOCH$_3$; 2.29 (6) s, ArOCOCH$_3$ and SCOCH$_3$; 3.87 (3) s, OCH$_3$; 4.0 (1) m, Ar$-$C$-$CH; 5.83 (1) d, Ar$-$CH; *ca.* 6.96 (3) m, ArH. $J_{\alpha\beta} =$ 7.0 cps.

REFERENCES

1. Enkvist, T. *Tappi* **37** (1954) 350.
2. (a) Gierer, J. and Smedman, L. Å. *Acta Chem. Scand.* **19** (1965) 1103;
   (b) Gierer, J. and Smedman, L. Å. *Acta Chem. Scand.* **20** (1966) 1769.
3. Brunow, G. and Miksche, G. E. *Acta Chem. Scand.* **23** (1969) 1444.
4. Mayer, R. *Quart. Rep. Sulfur Chem.* **5** (1970) 125.
5. Brunow, G. and Miksche, G. E. *To be published.*
6. (a) Hseu, T. M. and Rechnitz, G. A. *Anal. Chem.* **40** (1968) 1054;
   (b) Rechnitz, G. A. *Accounts Chem. Res.* **3** (1970) 69.
7. *Instruction Manual, Sulfide Ion Electrode*, Model 94 − 16 A, Orion Research Inc. Cambridge, Mass., U.S.A.
8. Bock, R. and Puff, H.-J. *Z. anal. Chem.* **240** (1968) 381.
9. Light, T. S. and Swartz, J. L. *Anal. Lett.* **1** (1968) 825.
10. Swartz, J. L. and Light, T. S. *Tappi* **53** (1970) 90.
11. Tartar, H. V. and Draves, C. Z. *J. Am. Chem. Soc.* **46** (1924) 574; Gustafsson, L. and Teder, A. *Svensk Papperstid.* **72** (1969) 249.
12. Rydholm, S. A. *Pulping Processes*, Interscience, New York 1965, p. 594.
13. Jensen, W. Ed. *Puukemia*, Suomen Paperi-insin. Yhd. 1967. B 5 18.
14. Riegel, B. and Wittcoff, J. *J. Am. Chem. Soc.* **68** (1946) 1913.