

Oxidation of *p*-Hydroxystyrenes by Aqueous Sodium Polysulfide.*

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p-Hydroxystyrenes are formed as reactive intermediates in lignin degradation under kraft pulping conditions (heating of wood with aqueous sodium hydroxide—sodium sulfide; polysulfide formed during the cook). The reaction of *p*-hydroxystyrenes with polysulfide was investigated by heating appropriate model compounds with polysulfide liquor. They yield aromatic ketones and aldehydes, presumably by disproportionation of intermediate alkyl-hydropolysulfides. These results provide an explanation of the reaction of S⁰ with lignin in kraft and polysulfide pulping of wood.

p-Hydroxyarylglycerol- β -aryl ether structures are the most important site of lignin degradation in kraft pulping (heating of wood with aqueous sodium sulfide—sodium hydroxide to about 170 °C). They fragment to *p*-hydroxycinnamyl alcohols and phenols with formation of S⁰ in the form of polysulfide.¹ As only small amounts of elemental sulfur are liberated on acidification of black liquors (the alkaline solution containing carbohydrates, lignin and salts which is produced in a kraft cook), the polysulfide ions must have undergone further transformations.

Because of the formation of S⁰ a kraft cook is in fact a polysulfide cook with a low content of elemental sulfur. In aqueous solution, sodium oligosulfides ("sodium polysulfide") are known to disproportionate to thiosulfate and sulfide, the rate of reaction being dependent on hydroxide ion concentration.² Under technical cook conditions, reactions with carbohydrates and lignin compete with disproportionation.²

* Part V of the series "Degradation of Lignin by Kraft Cooking"; Part IV, Ref. Id.

Carbohydrates are oxidized by aqueous polysulfide.² From model experiments and IR-data it has been concluded that lignin reacts with polysulfide by oxidation of its benzylic hydroxyl groups to carbonyl groups.³ These studies were, however, carried out with model compounds which do not sufficiently reflect the reaction modes of the *p*-hydroxyarylglycerol- β -aryl ether structures of lignin. We therefore decided to re-investigate the reaction of aqueous polysulfide with lignin.

In alkaline media, the ionized phenolic hydroxyl group is the functional entity of lignins that normally will most easily undergo oxidation. This is, however, not the case in polysulfide reactions as is shown by the quantitative recovery of 4-propylguaiaicol from a sodium polysulfide—sodium hydroxide cook at 120 °C ("sodium polysulfide cook", although the sulfur content corresponds to a sodium disulfide cook; cf. Experimental).

p-Hydroxystyrenes which are formed as reactive intermediates in the reaction of lignin with aqueous sodium sulfide were considered to be another substrate that possibly could be oxidized by polysulfide. We have found that *trans*-isoeugenol (*1*) in a sodium polysulfide cook yields 60 % of 4-hydroxy-3-methoxy-propio-phenone (*5*). This reaction (Fig. 1) possibly proceeds *via* the quinone methide *2*, a ketonization product of the anion of *1*. Under the same conditions *5* was also formed from 1-(4-hydroxy-3-methoxyphenyl)-1-propanol, but 1-(3,4-dimethoxyphenyl)-1-propanol was not affected. The formation of vanillin and 4-hydroxy-3-methoxy-acetophenone in polysulfide cooks of

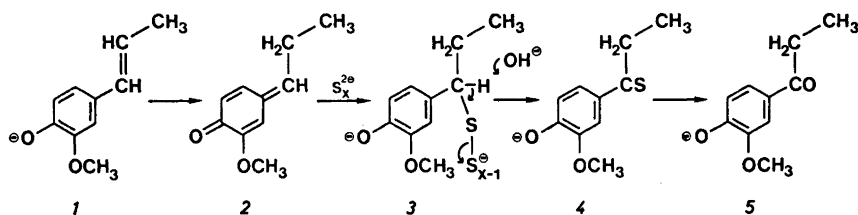


Fig. 1. Compounds 1, 3, 4 and 5 are depicted as anions.

vanillyl alcohol and 1-(4-hydroxy-3-methoxyphenyl)-1-ethanol, respectively, has been reported.³ 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2,2-dimethyl-1-propanol, which cannot be dehydrated to a *p*-hydroxystyrene, similarly yields 1-(4-hydroxy-3,5-dimethoxyphenyl)-2,2-dimethyl-1-propanone as the main product.

The addition of polysulfide ion then should give 1-(4-hydroxy-3-methoxyphenyl)-1-propyl hydropolysulfide (3). The mechanism of the disproportionation of 3 to sulfide and 5 has not been ascertained. As outlined in Fig. 1, the fragmentation of the sulfur-sulfur linkage could be induced by base abstraction of a benzylic hydrogen or possibly by transformation to a sulfenic acid. The resulting thiopropiophenone 4 should then be rapidly transformed to 5. This disproportionation mechanism would be analogous to the decomposition of a number

of hydroperoxides,⁴ peroxides,⁵ and disulfides⁶ by base.

trans-Coniferyl alcohol (6) yields vanillin (12) and 4-hydroxy-3-methoxyacetophenone (9) as dominant mononuclear degradation products in a polysulfide cook. These two compounds, together with guaiacol, also constitute the major mononuclear degradation products from a cook of *erythro*-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (guaiacylglycerol- β -guaiacyl ether). A reasonable explanation for their formation is given in Fig. 2.

The *retro*-aldol reactions of coniferaldehyde (11) giving vanillin and acetaldehyde, and of 1-(4-hydroxy-3-methoxyphenyl)-3-hydroxy-1-propane (8) are known.^{7,8} An alternative route leading to 9 (not depicted in Fig. 2) is the elimination of formaldehyde from the quinone methide 7 to give 4-vinyl-guaiacol which is

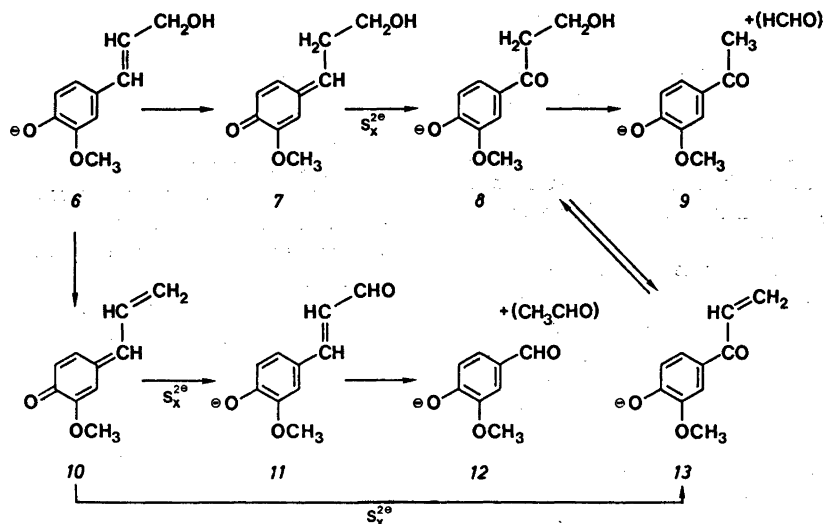


Fig. 2. Compounds 6, 8, 9, 11, 12 and 13 are depicted as anions.

oxidized by polysulfide *via* its tautomeric quinone methide. Intermediates *11* and *13* presumably react to a considerable extent with carbanions by Michael-addition, giving rise to condensation products of higher molecular weight. Similar reactions should also occur in pulping, and will partially counterbalance lignin degradation. A quantitative assessment of the contributions of the two major routes of transformation of *6* – by formation of the vinylogous quinone methide *10* and by protonation to *7* – is not possible since precise knowledge of the rate processes involved is lacking.

If *trans*-coniferyl alcohol (*6*) is heated with aqueous sodium hydropolysulfide rather than with polysulfide, the main product is 4-hydroxy-3-methoxy-acetophenone, vanillin being formed at best in trace amounts. Two other compounds, 4-hydroxy-3-methoxy-propiofenone (*5*) and 1-(4-hydroxy-3-methoxyphenyl)-2-propanone, were encountered in minor amounts. *5* is possibly formed *via* addition of HS_x^- to 1-(4-hydroxy-3-methoxyphenyl)-2-propen-1-one (*13*), the resulting alkyl hydropolysulfide then disproportionating to *5* and S^0 . This side reaction seems to be suppressed by hydroxide ion as no *5* was detected among the products of a polysulfide cook of *6*. The reaction leading to 1-(4-hydroxy-3-methoxyphenyl)-2-propanone may be initiated by nucleophilic substitution of hydropolysulfide by the anion of *6* (reaction in β -position).

The results of the hydrosulfide cook of *6* give an explanation of the results of Ashorn⁸ obtained on hydrosulfide cooking of spruce wood and of guaiacylglycerol- β -guaiacyl ether. Ashorn observed the formation of *5* and *9*, as well as of small amounts of *11*, and suggested the ketol *8* as an intermediate.

Direct oxidation by aqueous polysulfide of the quinone methides formed from *p*-hydroxybenzyl alcohol substructures (primarily *p*-hydroxyarylglycerol- β -aryl ether structures) in lignin has also to be considered. This reaction mode, originally proposed by Nakano *et al.*,³ is however ruled out by the result of a polysulfide cook of *erythro*-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-1-propanol. The main products are *1*, *5* and guaiacol, only small amounts of by-products being formed. Under the same conditions 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-1-propanone

gave guaiacol, but neither *1* nor *5*. These experiments demonstrate that the quinone methides formed from *p*-hydroxyarylglycerol- β -aryl ether substructures by the rate determining loss of water⁹ are not oxidized by aqueous polysulfide, but are cleaved in the same way as under the conditions of a kraft cook.

The oxidation of the aldehyde groups of reducing carbohydrates by sodium polysulfide may proceed in a way analogous to the oxidation depicted above. The addition of S_x^{2-} to the carbonyl groups should be followed by β -elimination of $\text{HS}_{(x-1)}^-$ from the intermediate hydroxyalkyl hydropolysulfide.

The reactions of aqueous polysulfide with the *p*-hydroxystyrenes *1* and *6* outlined in this paper provide an explanation of the reactions of S^0 with lignin in kraft and polysulfide pulping of wood.

EXPERIMENTAL

References to model and reference compounds. (4-Hydroxy-3-methoxyphenyl)-*Gu*-; *8*;¹⁰ *11*;¹¹ 1-*Gu*-2-propanone;¹² *erythro*-1-*Gu*-2-(2-methoxyphenoxy)-1-propanol;¹³ 1-*Gu*-2-(2-methoxyphenoxy)-1-propanone;¹³ *erythro*-1-*Gu*-2-(2-methoxy-phenoxy)-1,3-propanediol;¹⁴ 1-*Gu*-1-propanol;¹⁵ 1-(3,4-dimethoxy)-1-propanol;¹⁵ 1-(4-hydroxy-3,5-dimethoxyphenyl)-2,2-dimethyl-1-propanol;¹⁶ 1-(4-hydroxy-3,5-dimethoxyphenyl)-2,2-dimethyl-1-propanone.¹⁶

Sodium polysulfide cooks. The model compound (0.5 mmol) in 0.2 M NaOH (3 ml) containing Na_2S (1 mol/liter) and elemental sulfur (1 mol/liter) was heated in a teflon-clad autoclave (120 °C, 6 h, N_2). The solution was then acidified to pH 5, extracted twice with ether, and the evaporation residue of the extract was dissolved in 80 % ethanol, elemental sulfur being removed by filtration. After addition of water the product was isolated by extraction with methylene chloride. After a preliminary investigation by TLC (silica gel, acetone-hexane 1:3), the product was derivatized by reaction with trimethylsilyl-trifluoroacetamide in pyridine and analyzed in a gas chromatograph-mass spectrometer (single focussing instrument with electron impact source, electron energy 70 eV, Becker-Ryhage separator at 275 °C). The components were identified by comparison of spectra with those of the trimethylsilyl derivatives of synthesized reference compounds. For GLC conditions, see below.

In the case of 1-(3,4-dimethoxyphenyl)-1-propanol, the reaction was carried out in a rotating autoclave. A preparative experiment with model *1* (0.3 g in 10 ml of cooking liquor, 120 °C, 18 h) yielded 198 mg of *5*, isolated by

preparative TLC (silica gel, acetone-hexane 1:2), m.p. 56–59 °C (aqueous ethanol), Lit.¹⁷ m.p. 61–62 °C.

Sodium hydropolysulfide cooks. Carried out as described for the sodium polysulfide cook, except that the cooking liquor was adjusted to pH 8.5–9 by addition of KH_2PO_4 . Precipitated sulfur was removed by filtration.

In the case of model 6, the gas chromatographic separation was preceded by preparative thin layer chromatography (as described above). This allowed the separation of 5 from vanillin and 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (not resolved). These fractions were also analyzed by GLC as acetates. *GLC.* 1.75 m stainless steel column (o.d. 6 mm) with 1.5 % OV 17 on acid-washed, HDMS-treated Chromosorb G. *T* = 180 °C, 25 ml N_2 per min. *Retention times* (acetates, min): 5, 7.1; 9, 5.0; 1-(4-hydroxy-3-methoxyphenyl)-2-propanone, 6.8.

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