Hydrogen Sulfide Cookings of p-Oxybenzyl Alcohols. I.

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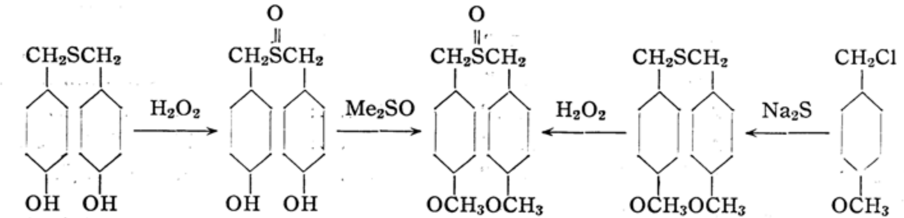
The first experiments on model compounds in connection with the mechanism of kraft cooking processes were made by Enkvist[1]. Among others[2] he obtained a very important result that vanillyl alcohol gives vanillyl disulfide on cooking with an aqueous solution of hydrogen sulfide of *pH* 7 during 72 hours at 100°C. He proposed a theory of mechanism of kraft cooking mainly from the behaviours of vanillyl disulfide against aqueous alkali and his opinion has been generally accepted by the chemists of this field[1][3].

In connection with the following paper, which deals with the hydrogen sulfide cookings of *p*-oxybenzyl ether, the reactivity of *p*-oxybenzyl alcohol was investigated at first. The expected product 4, 4′-dioxydibenzyl disulfide was not obtained but 4, 4′-dioxydibenzyl sulfide[1] was the only product obtainable when *p*-oxybenzyl alcohol was cooked during 6.5 hours or 70 hours. The yields of the monosulfide were 82 and 61% respectively for each cooking hours.

The structure of the monosulfide[1] was determined by the method shown in the scheme 1. As on methylation of the mono-



m.p. 141–2° (I)

m.p. 184.5–5.0° (II)

m.p. 171–2° (III)

(IV)

Scheme 1.
Determination of the constitution of 4, 4′–dioxydibenzyl sulfide

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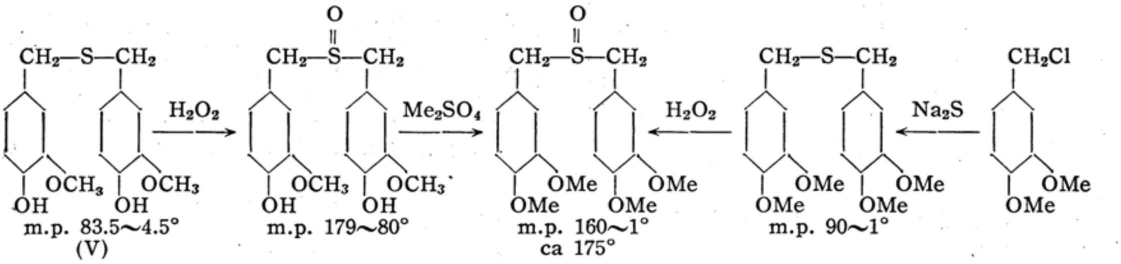
[1] Enkvist and Moilanen, *Svensk Papperstidn.*, **52**, 183 (1949).

[2] Enkvist and Hägglund, *festskrift tillägnad* J. Arvid Hedvall, **1948**, 149. Enkvist, *Svensk Papperstion.*, **51**, 225 (1948).

[3] Cf. Hägglund, " Chemistry of Wood ", Academic Press Publishers, Inc., New York, N.Y. 1951, p. 484.

sulfide (I) sulfur was split off (probably as dimethyl sulfide) and dianisyl sulfide (IV) was not obtained by this process, that was oxidized at first to sulfoxide (II) and then methylated to dianisyl sulfoxide (III). According to our experience, on methylation of thiolignin with dimethyl sulfate and alkali similar splitting off of sulfur occurs probably as dimethyl sulfide.

As *p*-oxybenzyl alcohol did not give the expected disulfide, vanillyl alcohol was also examined in the similar way. It gave again monosulfide (72%) (V) and a very small amount of divanillyl disulfide as the result of 8 hours cooking. The constitution of divanillyl sulfide was determined in the same way as in 4, 4′-dioxydibenzyl sulfide according to the scheme 2. Diveratryl sulfoxide has two melting points.



Scheme 2.
Determination of the constitution of divanillyl sulfide

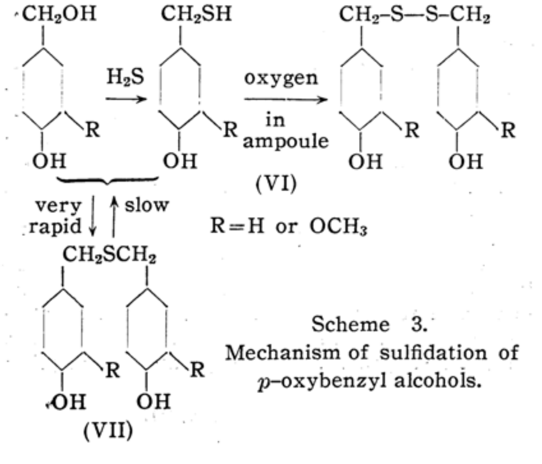
The reactivities of 4, 4′-dioxydibenzyl sulfide (I) and divanillyl sulfide (V) with aqueous alkali were also tested in the same manner as the procedure used by Enkvist in the case of divanillyl disulfide[1]. Monosulfides also split off sulfur as hydrogen sulfide, as is shown in the following table.

TABLE I. DESULFIDATION OF MONOSULFIDE (I) AND (V) WITH AQUEOUS ALKALI. (5% NaOH, 100°)

	hrs.	splitted.
4, 4′-dioxydibenzyl Sulfide (I)	3	10.8%
	5	88.0%
Divanillyl sulfide (V)	3	19.7%

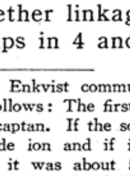
1) On the Mechanism of Sulfidation of *p*-Oxybenzyl Alcohols.

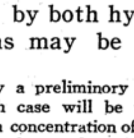
The following mechanism (scheme 3) is assumed to be most probable. At the beginning, hydrogen sulfide reacts with *p*-oxybenzyl alcohol so as to give *p*-oxybenzyl mercaptan (VI), which condenses rather rapidly with the remaining alcohol. The primary reaction product is thus monosulfide (VII). Monosulfide is, however, not completely stable; there it is in equilibrium with the alcohol and mercaptan.



Scheme 3.
Mechanism of sulfidation of *p*-oxybenzyl alcohols.

This assumption is not unreasonable, because, as will be shown in the next paper, benzyl ether linkage is very susceptible of being hydrolysed when it is activated by the phenolic hydroxyl group in its paraposition


(VIII)


(IX)

(e.g. VIII and IX) and, therefore, the benzyl thioether linkage activated by both hydroxyl groups in 4 and 4′ positions may be surely

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4) Enkvist communicated privately a preliminory opinion as follows: The first product in each case will be vanillyl mercaptan. If the solution has a high concentration of hydrosulfide ion and if its *p*H is slightly lower than 7—in his case it was about 5 after the digestions, as he reported proviously (cf. (1))—the substance will remain as vanillyl mercaptan until the opening of the tube. Then, the outer air will oxidize it during crystallization to vanillyl disulfide. If the concentration of hydrogen sulfide is slightly less and the *p*H is 7 or slightly higher as in our case, the vanillyl mercaptane will find occasion to react with vanillyl alcohol or sodium vanillyl mercaptide under the formation of vanillyl monosulfide.

hydrolyzable. Molecular oxygen in the air space of glass ampoule will oxidize the mercaptan, which exists in equilibrium with the monosulfide although its concentration is very low. Thus, monosulfide and disulfide are expected in our experiment, as the oxygen in the ampoule is rather limited. The reaction product obtained by Enkvist consisted mainly of disulfide, but this is not explainable by the above mechanism, as according to his private communication the ampoule used by him was not large enougn to supply the necessary amount of oxygen. It is therefore possible that some other unknown factors are determining the course of the reaction; in one case mainly monosulfide and in the other mainly disulfide is obtained as reaction product[4].

2) On the Mechanism of the Kraft Cooking Process.

The monosulfide group of thiolignin had been assumed to be stable to aqueous alkali, but the present results indicate that this group is not stable just as disulfide group, at least when this is activated by both phenolic hydroxyl groups in 4 and 4′ positions. It seems, therefore, to be possible to explain the mechanism of sulfidation of lignin and desulfidation of thiolignin without considering the formation of the disulfide group. The mechanism may be explained more reasonably if the formation of both mono- and di-sulfide groups are taken in consideration. Because the side chain of lignin contains oxygen atoms of various oxidation stages, the formation of the disulfide group by self-oxidation will be easier in the case of lignin than in the model compounds. However, quantitatively speaking, the main part of the sulfur atoms, split off by alkali in the kraft cooking process may exist as a form of monosulfide.

As Mikawa et al. observed[5], X group of lignin was sulfidated with hydrogen sulfide quite rapidly and this reaction was completed after about 5 hours. The velocities of sulfidation of *p*-oxybenzyl alcohol and vanillyl alcohol are not yet clear. But the fact that they are sulfidated to a considerable extent during less than 10 hours cooking will support the opinion that X group of lignin is a benzyl alcoholic hydroxyl group with a phenolic hydroxyl in its para-position.

Experimental Part

1. Hydrogen Sulfide Cooking of *p*-Oxybenzyl Alcohol.

3.7 g. of *p*-oxybenzyl alcohol was added to a solution (final *p*H was adjusted to just 7) of $Na_2S \cdot 9H_2O$ (7.2 g.) in 300 cc. of Clark-Lubs buffer solution (108 g. of KH_2PO_4 and 15 g. of NaOH in 1000 cc. of water). The mixture was heated at 100° for 6.5 hours in a stainless autoclave of just 550 cc. capacity. On cooling, crystals of almost pure 4, 4′-dioxydibenzyl sulfide separated (3.29 g., 82%), which were recrystallized from toluens containing a little dioxane, m.p. 141–2°. Found: S, 12.9%, Calculated for $C_{14}H_{14}O_2S$: S, 13.0%.

The same reaction was performed during 70 hours in a rotating glass ampoule of 150 cc. capacity (*p*-oxybenzyl alcohol 2.0 g., $Na_2S \cdot 9H_2O$ 3 g., buffered hydrogen sulfide water of *p*H 7, 100 cc.). The yield of melting point pure 4, 4′-dioxydibenzyl sulfide was 1.2 g. (61%). 4, 4′-dioxydibenzyl disulfide was not obtained from the reaction mixture.

2. Hydrogen Sulfide Cooking of Vanillyl Alcohol.

The reaction was performed mainly as in the experiment 1 (vanillyl alcohol 2.5 g., $Na_2S \cdot 9H_2O$ 3 g., hydrogen sulfide water 100 cc., 8 hours at 100°, capacity of autoclave just 150 cc.). The separated crystals were filtered off, dissolved in alcohol, passed through a layer of active Al_2O_3, the alcohol was evaporated and the residue was recrystallized from toluene. Yield 1.8 g. (72%), m.p. 83.5–4.5°. This is divanillyl sulfide. Found: S, 10.5; MeO, 19.8, Calculated for $C_{16}H_{18}O_4S$: S, 10.4 MeO, 20.3%.

The mother liquor of this crystal separates after about a week, forming a mixture of large crystals of monosulfide and fine crystals of disulfide, from which the former were separated with a pincette and the latter were dissolved in acetone and purified by reprecipitation by water (50 mg.). It melted at 128–9° and does not show any m.p. depression in admixture with the authentic sample of divanillyl disulfide, which was synthesized according to the method of Manchot and Zahn[6].

3. Syntheses of 4, 4′-Dioxydibenzyl Sulfoxide and Divanillyl Sulfoxide.

4, 4′-Dioxydibenzyl sulfide (100 mg.) was dissolved in 4 cc. of glacial acetic acid, 0.3 cc. of 30% H_2O_2 was added and the solution was set aside over night at the ordinary temperature[7]. The reaction mixture was diluted with water and neutralized with $NaHCO_3$. The separated crystals were filtered, washed with water, dissolved in alcohol and reprecipitated with water, yield 70 mg., m.p. 184.5–5.0°. The analysis agrees with the compound, 4, 4′-dioxydibenzyl sulfoxide. Found: S, 11.8, Calculated for $C_{14}H_{14}O_3S$: S, 12.2%.

Divanillyl sulfoxide was also synthesized similarly from divanillyl sulfide (100 mg.). Yield 50 mg. Found: S, 9.7, Calculated for $C_{16}H_{18}O_5S$: S, 9,95%.

4. Methylation of Sulfoxides.

4, 4′-Dioxydibenzyl sulfoxide or divanillyl sulfoxide (80 mg.) was dissolved in 10 cc. of sodium hydroxide solution (NaOH 0.8 g.). 0.8 cc. of dimethyl sulfate was added and the whole shaken until it disappeared. The separated dianisyl or

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[5] Mikawa, Sato, Takasaki and Okada, *J. Soc. Chem. Ind. Japan*, **54**, 299 (1951); TAPPI in the press.
Mikawa, *J. Soc. Chem. Ind. Japan*, **54**, 651; 762 (1951).

[6] Manchot and Zahn, *Ann.*, **345**, 320 (1906).

[7] Hinsberg, *Ber.*, **41**, 2838 (1908).

diveratryl sulfoxide (yields were very good) was filtered, washed and purified by reprecipitation from its acetone solution with water. Their melting points were not depressed in admixture with the authentic samples synthesized according to the experiments 5 and 6.

5. Syntheses of 4, 4'-Dimethoxydibenzyl Sulfide and Sulfoxide.

$Na_2S\cdot 9H_2O$ (2.40 g.) was dissolved as far as possible in alcohol (40 cc.), anisyl chloride (1.56 g.) was added and the whole refluxed for about 30 min.[8]. Water was added to the mixture, extracted with ether, washed with water, the ether was evaporated and the residue (1.5 g.) was distilled at 0.005 mmHg (bath temp. 150°). The residue (0.7 g.) was dissolved in several grams of glacials acetic acid. 0.8 cc. of 30% H_2O_2 was added (during which some heat was evolved), and after about 4 hours poured into water. The precipitated crystals were filtered, washed with water, dried and recrystallized twice from ethyl alcohol containing a little water, m.p. 172–3°. Found: MeO, 20.4; S, 11.3, Calculated for $C_{16}H_{18}O_3S$: MeO, 21.4; S, 11.0%.

6. Syntheses of Diveratryl Sulfide and Sulfoxide.

Veratryl alcohol (3 g.) was converted to chloride according to the method of Freudenberg[9]. The somewhat crude veratryl chloride obtained was subjected to reaction with 2.5 g. of $Na_2S\cdot 9H_2O$ in 80 cc. of alcohol. NaCl was filtered and the filtrate was concentrated in vacuo, water was added and the neutral reaction product extracted with benzene, the benzene extract was dried with Na_2SO_4, the solvent was evaporated and the residue was crystallized from its ether solution by petroleum ether. Recrystallisation from the mixture of benzene and petroleum ether yielded a product (1.0 g.), which melted at 90–1°. The analysis agrees with the theory that the compound is diveratryl sulfide. Found: S, 10.8, Calculated for $C_{18}H_{22}O_4S$: S, 9.6%.

Diveratryl sulfide (100 mg.) and H_2O_2 (30%, 0.4 cc.) was dissolved in 4 c.c. of glacial acetic acid and set aside overnight at the room temperature. Water was added to the solution, neutralized with $NaHCO_3$ and the separated crystals were filtered, dissolved in acetone and reprecipitated with water (70 mg.), which melted at 169.5–70.5° when heated rapidly and at ca. 175° when heated slowly. The analysis agrees with the theory that the compound is diveratryl sulphoxide. Found: S, 9.0, Calculated for $C_{18}H_{22}O_5S$: S, 9.14%.

7. Reactions of 4, 4'-Dioxydibenzyl Sulfide (1) and Divanillyl Sulfide (2) with Aqueous Solution of Alkali.

100 mg. of (1) or (2) was heated at 100° with 5% (cf. reference (1)) aqueous solution of NaOH in a micro-methoxyl apparatus due to Zeisel in the atmosphere of hydrogen. The solution was cooled and acidified with glacial acetic acid and the liberated hydrogen sulfide was swept with hydrogen into dilute NaOH in wash trap and receiver. The combined sodium hydroxidesolution was oxidized with bromine water and SO_4'' was determined as usual. Results obtained are shown in the table.

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[8] Märker, *Ann.*, **136**, 88 (1965).

[9] Freudenberg, Carrara and Cohn, *Ann.*, **446**, 87 (1925).