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Reactions of Thiosulphate with Vanillyl Alcohol *

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The kinetics of the reaction between vanillyl alcohol and thiosulphate has been studied. The mechanism of the reaction is discussed and compared with that of the bisulphite reaction of the alcohol.

During sulphite pulp cooking the thiosulphate present in the liquor is removed to varying extents by reaction with the benzyl alcohol and benzyl ether groups of lignin whereby benzyl sulphide groups are formed[1-3]. The mechanism of this type of reaction was indicated by a study of vanillyl alcohol (I)[4]. At pH 5 the alcohol reacts with thiosulphate according to first order kinetics and the rate constant has the same values as that found by Ivnäs and Lindberg[5] for the bisulphite sulphonation of vanillyl alcohol. The rate-controlling step of the thiosulphate reaction at pH 5 is then evidently the same as in the sulphonation, *viz.* the formation of the quinone methide (II) or the carbonium ion (III) from the alcohol[5,6]. The suggested path-ways for the two reactions are shown in Fig. 1.

To obtain further knowledge of the mechanism of the thiosulphate reaction, its pH dependency was studied. The first order rate constant, k_1, was determined as described in an earlier paper[4] from the first part of the reaction. The kinetics of the reaction could be followed in the pH-range 4.0 to 5.2. At lower pH, thiosulphate was not stable, while at higher pH, the reaction did not seem to follow simple kinetics. The results obtained showed that the rate did not changed much in the above-mentioned pH-range. At 80°C k_1 was 2.5, 2.0, and 2.3×10^{-3} min^{-1} for pH 4.0, 4.5, and 5.2, respectively. The slightly lower value at pH 4.5 may indicate the presence of a shallow rate minimum. Such a minimum is clearly shown in the sulphonation study, where the reaction was examined in a broader pH-range[5].

The Arrhenius activation energy for the thiosulphate reaction was 23 kcal/mole which is, within experimental limits, the same as that for the sulphonation, 24 kcal/mole[5]. The values were, however, determined at different

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* Part 4 of the reactions of thiosulphate during sulphite cooking. Part 3, Goliath, M. and Lindgren, B. O. *Acta Chem. Scand.* **16** (1962) 570.

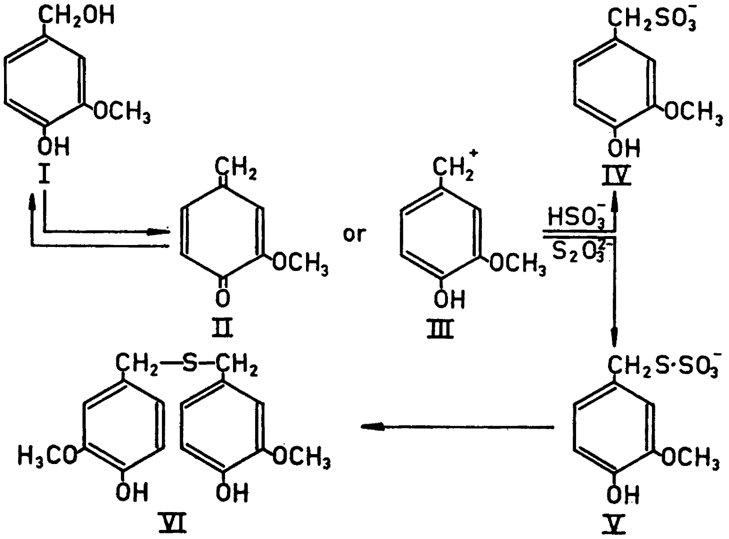

Fig. 1. The reactions of vanillyl alcohol with thiosulphate and bisulphite.

acidities, pH 5 for the thiosulphate reaction and pH 7 for the sulphonation.

A significant difference between the two reactions was found at pH values higher than 5. The sulphonation rate increased in this pH-range with rising pH and a combination of first and second order kinetics was obtained[5]. The rate of the thiosulphate reaction, on the other hand, decreased as is evident from Fig. 2. This indicates that at pH 7 the mechanisms of the two reactions may be of different types.

The rate of the thiosulphate reaction was also determined in acetate buffer solutions (pH 5) containing varying amounts of sodium chloride. It was found to be independent of the ionic strength. The rate constant k_1 was 2.2, 2.4, and 2.2×10^{-3} min^{-1} for the ionic strengths 1.24, 0.90, and 0.57, respectively. On the other hand, it decreased considerably if the reaction was carried out in dioxane-water instead of water. k_1 was 2.2, 0.9, and 0.3×10^{-3} min^{-1} for water, dioxane-water 1:3, and dioxane-water 1:1 v/v, respectively. The pH of all three solutions was 5.1. The results are not easily interpreted especially as the salt and solvent effects of S_N1 reactions of alcohols have not been so elaborately studied as those of halogenides.

Recently Schöön[7] studied the destruction of thiosulphate during sulphite pulp cooking at varying acidity. He found that it decreased with increasing pH and stopped completely at pH 4—5. The reason for this cannot be that lignin is lacking in reactivity as, according to Enkvist[8], it reacts with thiosulphate in neutral solutions. This is also evident from Fig. 3, which shows the uptake of sulphur by wood powder during heating with a thiosulphate solution buffered to pH 5. As also shown this uptake is inhibited if the wood is first heated with a sulphite solution of pH 5. In this case the reactive groups of lignin have been blocked by sulphonation.

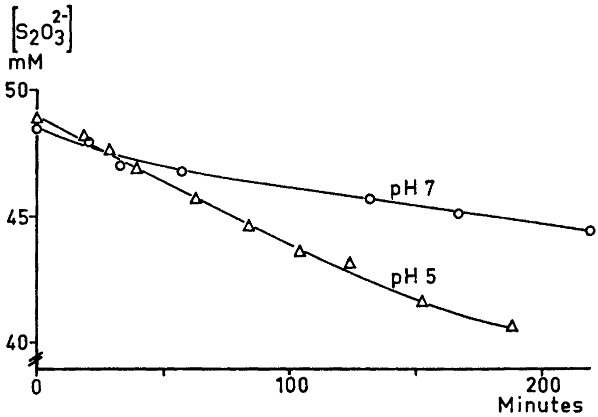

Fig. 2. The thiosulphate-vanillyl alcohol reaction. The thiosulphate concentration *versus* the reaction time at pH 5 and 7. Reaction temperature was 80°C and vanillyl alcohol concentration, 50 mM.

From this it follows that at lower acidity the reactive groups of lignin probably react faster with sulphite than they do with thiosulphate. To illustrate the pH dependency of the lignin-thiosulphate reaction vanillyl alcohol was heated with sulphite solutions of varying acidity. The solutions contained small amounts of thiosulphate. As also described earlier[3] the thiosulphate was consumed in the more acidic solutions. At pH 2.5 and higher it did not react, however, as is shown in Table 1. From an experiment carried out with an equimolar solution of thiosulphate and bisulphite buffered to pH 5 the sulphonic acid (IV) was the preponderant reaction product. In addition only a small amount of vanillyl sulphide was obtained. The low yield of the sulphide could not be due to its sulphonation by bisulphite[9] as it was found to be stable under the relatively mild conditions chosen.

It therefore seems probable that bisulphite reacts much faster with the common intermediate (II or III) than thiosulphate does. However, the possi-

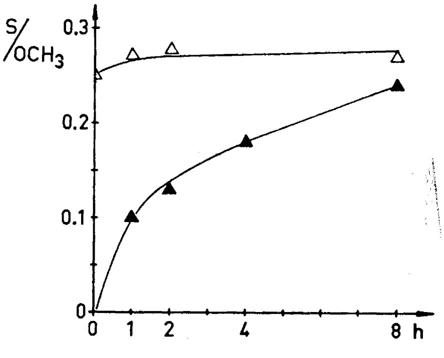

Fig. 3. The uptake of sulphur during heating of spruce wood powder (▲) and sulphite-pretreated wood powder (△) with thiosulphate at pH 5, 120°C. The pretreatment consisted of heating of the wood powder at 135°C with a sulphite-bisulphite solution (pH 6.0) for 16 h.

Table 1. The change in thiosulphate content when heating sulphite solutions which contained vanillyl alcohol (32.5 mM) and sodium thiosulphate (13.8 mM) and had varying pH.

pH	1	1.5	2.4			5.8		
Heating time at 110°, h	1	2	1	2	4	1	2	4
$S_2O_3^{2-}$, mM	6.6	8.2	14.0	13.6	15.6	14.0	14.4	14.6

bility that the sulphonic acid was formed by a reaction between vanillyl thiosulphate (V) and bisulphite cannot be excluded. An experiment showed that this reaction occured under the conditions used.

To summarize, in the competition between thiosulphate and bisulphite for reaction with vanillyl alcohol, thiosulphate reacts preferentially at low pH and bisulphite at pH 5. Thus the alcohol reacts in this respect as lignin does.

This competition is reminiscent of that between a reactive phenol, such as pinosylvine, and bisulphite for reaction with benzyl alcohols[10]. In both cases the sulphonation dominates at higher pH but at lower pH the main reaction products are benzyl sulphides or diphenyl methanes, respectively. A common explanation is therefore probable and the following is suggested.

At pH below 1.8 the sulphite is mainly present as SO_2 and at higher pH, up to 5.3, as HSO_3^-. Because HSO_3^- has a negative charge and is a stronger base than SO_2 it is undoubtedly a stronger nucleophilic reagent than SO_2. Such a comparison can be made because the nucleophiles have the same type of attacking atom, a four-valenced sulphur atom. SO_2 may even function as an electrophilic reagent, for example in its complexes with phenols, phenol ethers and thiosulphate. If it is assumed that the nucleophilicities of thiosulphate and pinosylvine are between those of SO_2 and HSO_3^- it is understandable why sulphonation dominates at higher pH and the other reactions at lower. The increase of the sulphonation rate with the acidity, in spite of the dominance in acid solution of the less reactive form, is very likely to be caused by hydrogen ion catalysis.

EXPERIMENTAL

Kinetics of the vanillyl alcohol-thiosulphate reaction. The first order rate constant was determined as described in Ref.[4] In all runs the starting concentration of vanillyl alcohol was 65.0 mM and that of thiosulphate, 80.0 mM. Acetate buffer solutions were used. The ionic strength was 0.57 and the temperature 80.2°C if not otherwise stated. The Arrhenius activation energy was determined from runs at 69.6°, 79.2°, and 84.8°C, which gave $k_1 = (0.96 \pm 0.10)$, (2.20 ± 0.09) and $(3.93 \pm 0.07) \times 10^{-3}$ min^{-1}, respectively. From these the activation energy was found to be 23 kcal/mole.

Competition between thiosulphate and bisulphite for vanillyl alcohol. (a) Varying acidity. Solutions containing vanillyl alcohol (32.5 mM), sodium thiosulphate (13.8 mM), sulphur dioxide (702 mM), and sodium hydroxide (0, 330, 680 and 850 mM, respectively) were heated at 110°C for varying times in steel autoclaves. The thiosulphate contents of the resultant solutions (Table 1) were determined by iodimetric titration in the presence of formalin.

(b) At pH 5. Vanillyl alcohol (1 g) dissolved in an acetate buffer solution (50 ml, pH 5) which contained 0.25 moles of both sodium thiosulphate and sodium bisulphite per liter was heated at 80°C for 24 h. The solution obtained was extracted with chloroform. The chloroform solution was dried and evaporated to dryness, giving a residue of 10.6 mg. It gave a spot corresponding to vanillyl sulphide when examined by thin layer chromatography.

From the aqueous solution the pyridinium salt of guaiacyl-methane sulphonic acid (IV) was obtained as described earlier [10]. The yield was almost quantitative. M.p. 174—190°C (decomp.). (Found: S 10.8; OCH_3 10.6. Calc. for $C_{13}H_{15}O_5SN$: S 10.8 ;OCH_3 10.4).

Treatment of sodium vanillyl thiosulphate with bisulphite. A solution of sodium vanillyl thiosulphate was obtained by heating vanillyl alcohol (1 g) dissolved in 0.25 M sodium thiosulphate solution buffered to pH 5 (acetate buffer, 50 ml) for 4 h at 80°C [4]. Unreacted vanillyl alcohol (0.32 g) was removed by extraction with ethylene chloride.

Sodium bisulphite was added to the vanillyl thiosulphate solution. Its concentration was the same as that of the thiosulphate, 0.25 M. The solution was then heated at 80°C for 24 h. The solution obtained was extracted with ethylene chloride. Evaporation of the organic solvent phase yielded 4 mg of residue.

From the aqueous phase the pyridinium salt of guaiacyl-methane sulphonic acid was obtained as described above.

Treatment of vanillyl sulphide with bisulphite. Vanillyl sulphide (0.5 g) was heated with an acetate buffer solution (pH 5, 50 ml) containing sodium bisulphite (0.25 M) at 80°C for 24 h. The sulphide was recovered almost quantitatively.

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