# The Reaction between Vanillyl Alcohol and Sulphite

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A kinetic study of the reaction between vanillyl alcohol and sulphite in aqueous solutions of various pH values has been made. The results indicate that the formation of sulphonic acid proceeds *via* the methylenequinone formed from vanillyl alcohol by elimination of one molecule of water. This hypothetical intermediate also explains the high reactivity of *p*-hydroxybenzyl alcohols compared to that of analogous *p*-alkoxybenzylalcohols.

The suggestion that benzyl alcohol and benzyl ether groupings in the lignin are responsible for several of the latter's characteristic reactions (*e.g.* sulphonation on the reaction with sulphite) was originally made by Berg and Holmberg [1]. Further studies on the reactions of lignin and model substances have corroborated this hypothesis; it is also in agreement with the conception of the lignin molecule obtained from biogenetic studies. (*cf.* Ref.[2]).
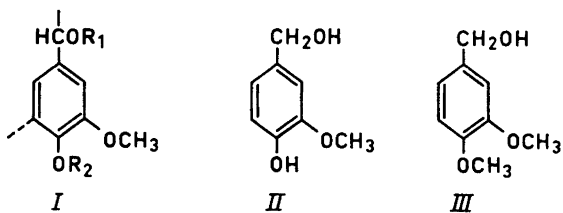
a. $R_1 = R_2 = H$
b. $R_1 = alkyl$, $R_2 = OH$
c. $R_1 = H$, $R_2 = alkyl$
d. $R_1 = R_2 = alkyl$

The generalised structure for a benzyl alcohol or ether grouping in coniferous lignin (I) can be divided into four alternative structures (a, b, c and d). Model substances, representative of these types, show differences in reactivity which are especially pronounced in models which carry a hydroxyl group (a and b) and an alkoxyl group (c and d) in a *p*-position to the benzyl group. It is belie-

ved that important lignin reactions, such as sulphonation, and etherification with methanolic hydrogen chloride, can be rationalised, at least to a considerable degree, as being due to the presence of these four structural elements.

Lindgren [3] made a qualitative study of the reaction of some model substances, among them vanillyl alcohol (II) and veratryl alcohol (III), in sulphite solutions of different pH at 135°. He found that vanillyl alcohol was sulphonated rapidly in both alkaline and acid solutions. Veratryl alcohol, however, was rapidly sulphonated only in acid solutions; in neutral or alkaline solutions, the reaction was slow. Groupings which show analogous reactivities are also present in lignin. Migita et al. [4] made a kinetic study of the reaction between vanillyl alcohol and sulphite and found that the velocity was rather independent of pH in the pH range studied.

Results from the present study have shown that vanillyl alcohol reacts with sulphite at 80° and pH 6.9 about 1 000 times faster than veratryl alcohol does at the same pH and 135°. The difference in σ-values [5] in Hammet's equation for p-OH (-0.357) and p-OCH$_3$ (-0.268) can not possibly account for this disparity and it must be assumed that the reactions proceed according to different mechanisms. In the present paper a kinetic study of the reaction between vanillyl alcohol and sulphite is reported. Most of the reactions were performed at 80° but some were conducted at 50° in order to obtain an approximation of the activation energy. The solutions were buffered at pH 3.4, 4.1, 5.1, 6.1, and 6.9; the ionic strength was about 1.0 in all experiments. The initial concentration of vanillyl alcohol was about 0.02 M and three runs were made at each pH with the initial concentrations of sulphite equal to 0.04, 0.02, and 0.01 M. The reactions were followed by iodometric titration of the sulphite.

The values were analysed assuming a first and a second order reaction, according to eqns. 1 and 2.

$$\frac{d[VS]}{dt} = k_I [V] \qquad (1) \qquad\qquad \frac{d[VS]}{dt} = k_{II}[V][S] \qquad (2)$$

VS = vanillyl sulphonic acid
V = vanillyl alcohol
S = total sulphite

The sulphite is present as SO$_3^=$, HSO$_3^-$ and H$_2$SO$_3$, but as the solutions were strongly buffered, the relative concentrations of these three species at each pH were constant throughout the reaction. It is justified, therefore, to consider the total sulphite concentration only in eqns. 1 and 2. The results of these calculations are summarised in Table 1. At pH 4.1 and 5.1 the reaction is approximately first order, but at higher and lower pH-values the deviations from this order are considerable. On the other hand, the deviations from the second order at the highest and the lowest pH-values studied (3.4 and 6.9) are smaller.

Thus, it is obvious that the reaction is no simple first or second order reaction but must follow a more complicated course. As will be demonstrated below, the assumption that the reaction proceeds via the unstable methylene-

Table 1. Values for the velocity constants obtained when the reaction between vanillyl alcohol and sulphite is treated as a first and second order reaction. $t = 80.7°$, $[V_o] = 0.02M$. Time in min.

pH	$[S_o] : [V_o]$	$10^3 \times k_I$	$10 \times k_{II}$
3.4	2	7.2 ± 0.5	2.1 ± 0.4
3.4	1	$5.3 \to 3.6$	$2.8 \to 3.5$
3.4	0.5	$2.6 \to 1.5$	$2.9 \to 3.6$
4.1	2	3.2 ± 0.3	$0.5 \to 1.0$
4.1	1	3.4 ± 0.2	$1.7 \to 2.3$
4.1	0.5	2.6 ± 0.3	$2.9 \to 5.5$
5.1	2	3.1 ± 0.4	0.95 ± 0.15
5.1	1	2.7 ± 0.3	$1.0 \to 2.2$
5.1	0.5	2.7 ± 0.2	$1.8 \to 8.7$
6.1	1.7	5.3 ± 0.2	1.8 ± 0.2
6.1	0.6	3.6 ± 0.1	$3.3 \to 6.2$
6.1	0.3	2.5 ± 0.2	$5.5 \to 9.8$
6.9	2	9.5 ± 2.0	2.9 ± 0.6
6.9	1	5.7 ± 0.7	$3.3 \to 4.4$
6.9	0.5	3.8 ± 0.6	$6.3 \to 9.1$

quinone (IV) intermediate is in agreement with the observed results. This possibility was also discussed by Migita *et al.*[4]
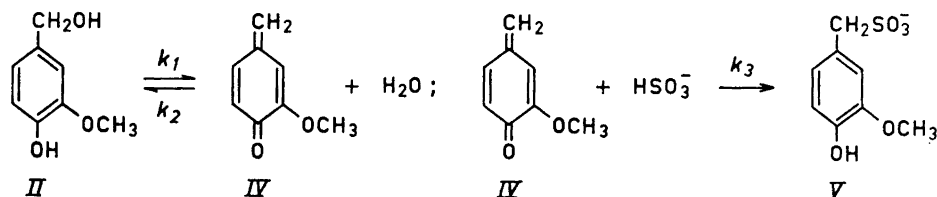
Using the method of the unstable intermediate, the velocity is expressed by eqn. 3.

$$-\frac{d[VS]}{dt} = \frac{k_1 \cdot k_3}{k_2 + k_3[S]} [V][S] \tag{3}$$

p-Methylenequinones are easily formed by the reaction of *p*-hydroxybenzyl halogenides with alkali. A similar reaction of *p*-hydroxybenzyl alcohols does not seem improbable, nor does the fact that the latter react with acids to give methylenequinones and not carbonium ions. Methylenequinones are also known to be highly reactive,[6] easily adding the elements of water.

The reversible transformation of vanillyl alcohol into methylenequinone is catalysed both by acids and bases. This is possibly an example of general acid-base catalysis which is also dependent upon the components and their concentrations in the buffering system. At high and low pH-values, k_2 may be expected to be high compared to k_3 [S] and eqn. 3 then approaches that of a

second order reaction. On the other hand, k_2 may be much smaller than k_3 [S] at some intermediate pH-values, and then the reaction approaches a first order reaction, as happens at pH 4.1 and 5.1 in the concentration range studied. The assumption of a methylenequinone derivative as intermediate also accounts for the great difference in reactivity between vanillyl alcohol and veratryl alcohol in neutral and alkaline solutions, as only the former substance can give this reactive intermediate. At lower pH-values, veratryl alcohol probably reacts *via* the carbonium ion (VI), while vanillyl alcohol (as discussed above) may also form the methylenequinone in this pH-region.

$$k_1 = \frac{k_2}{k_3} \cdot k_{II} + k_I \qquad (4)$$

VI
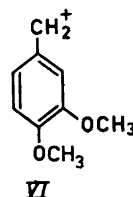
Integration of eqn. 3 gives eqn. 4, in which k_I and k_{II} are variables; the latter values can be calculated from eqns. 1 and 2. k_1 and k_2/k_3 were calculated from eqn. 4. The values obtained, which must be regarded only as approximate, are given in Table 2.

As is evident from Figs. 1 and 2, the experimentally observed values lie reasonably close to the theoretical concentration *versus* time curves constructured from the values of k_1 and k_2/k_3 in Table 2.

Some experiments were performed at 50° and pH 6.9 and the same concentrations used at 80°. From these experiments the apparent energy of activation was determined to be 24 kcal · mole^{-1}.

A similar reaction, the formation of sulphonate from epinephrin (VII) and sulphite, has recently been studied by Higuchi and Schroeter [7].

VII
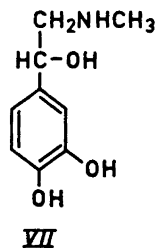
At pH values above 5 the reaction was of second order and at pH 4 it approached first order, being independent of the sulphite concentration. The authors suggest that the reaction is of the *SN* 2 type, in competition with a *SN* 1 reaction with a carbonium ion intermediate. The first order reaction accounts for the fact that an optically inactive sulphonic acid is obtained from optically active epinephrin; the latter substance is also racemised at a comparable rate at pH 4.0 in the absence of sulphite. At higher pH-values when the reaction

Table 2. k_1 and k_2/k_3 calculated from the observed values, using eqn. 4.

pH	$k_1 \times 10^{-3}\,min^{-1}$	$k_2/k_3 \times 10^3$ moles
3.4	13	30
4.1	4	—
5.1	4	—
6.1	9	13
6.9	11	9

is of second order, optically inactive sulphonic acid is also obtained and the authors assume that the initially-formed, optically active sulphonic acid is rapidly racemised. Alternatively, the results of Higuchi and Schroeter may be explained by the assumption of a methylenequinone intermediate. Epinephrin occurs as an ammonium ion in the pH-range studied, 4—7. It seems reasonable to assume that by an inductive effect the base catalysed formation of methylenequinone is facilitated and the acid catalysed is hindered. Consequently, the apparent order should be second at higher pH values and first at
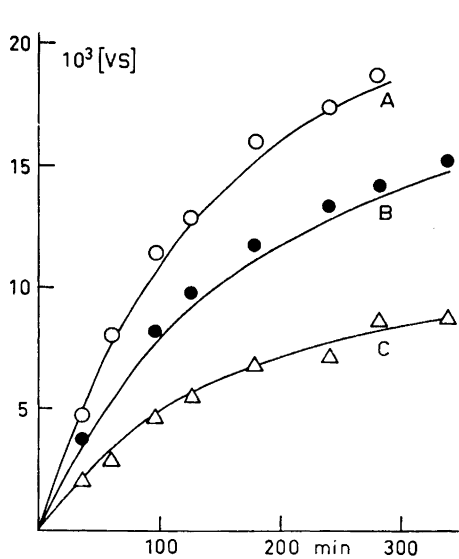

Fig. 1. Concentration of reaction product *versus* time at pH 3.4. The curves are calculated from the initial concentrations and the values of k_1 and k_2/k_3 given in Table 2. The symbols represent the observed values.

Curve A, O $[V_o]$ = 0.0219, $[S_o]$ = 0.0416
Curve B, ● $[V_o]$ = 0.0219, $[S_o]$ = 0.0209
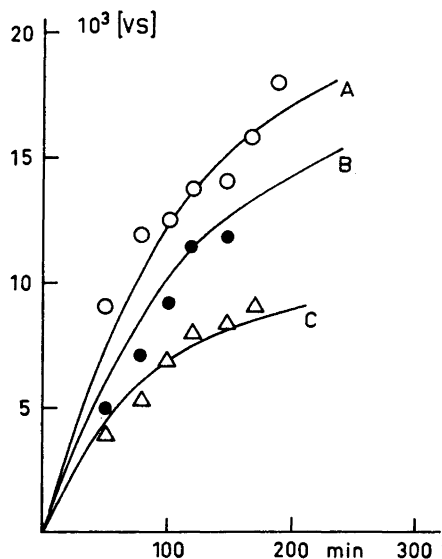Curve C, △ $[V_o]$ = 0.0219, $[S_o]$ = 0.0102

Fig. 2. Concentration of reaction product *versus* time at pH 6.9. The curves are calculated from the initial concentrations and the values of k_1 and k_2/k_3 given in Table 2. The symbols represent the observed values.

Curve A, O $[V_o]$ = 0.0213, $[S_o]$ = 0.0409
Curve B, ● $[V_o]$ = 0.0213, $[S_o]$ = 0.0197
Curve C, △ $[V_o]$ = 0.0213, $[S_o]$ = 0.0095

lower ones. With the uncharged vanillyl alcohol, however, it seems reasonable to find a second order reaction both at high and low pH-values and first order at intermediate levels.

The hypothesis of methylenequinones as intermediates in the reactions of *p*-hydroxybenzyl alcohols is not restricted to the reaction with sulphite. It seems possible that several other reactions which proceed with great ease, such as the etherification on treatment with alcohol and acid and the reactions with various thiols, also proceed *via* this intermediate.

EXPERIMENTAL

Solutions Vanillyl alcohol, 0.085 M, in water

Sodium sulphite, 0.17 — 0.042 M, in water
M Citrate buffer, pH 3.4
M Acetate buffer, pH 4.1
M Acetate buffer, pH 5.1
0.2 M Phosphate buffer, pH 6.1
0.2 M Phosphate buffer, pH 6.9

Sodium chloride was added to the buffers to an ionic strength of 2.0. The solutions were flushed with and stored under nitrogen.

Kinetic experiments. The solutions of vanillyl alcohol (1 part), sulphite (1 part) and buffer (2 parts) were added to test tubes which were flushed with nitrogen and sealed. The test tubes, 10 in each run, were placed in a water bath maintained at 80.7°. The variation was about 0.1°. At intervals tubes were removed, cooled in icewater, opened under water and the amount of sulphite determined iodometrically. Three blanks without vanillyl alcohol were run simultaneously.

The three series at pH 5.1 were repeated. The average values for k_I were 2.6 and $2.8 \cdot 10^{-3}$ in the two runs.

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