

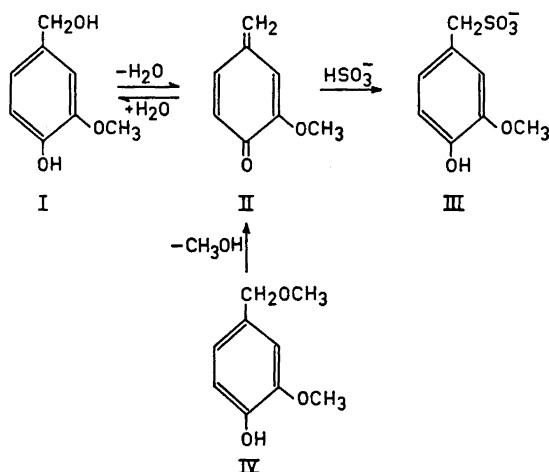
## Hydrolysis of Vanillyl Methyl Ether

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The hydrolysis of vanillyl methyl ether in the pH-region 3–10 at 80° has been studied. The ether was hydrolysed over the whole region, the reaction rate showing a minimum at about pH 5. At pH-values above 6 the kinetics were complicated by side reactions. The results indicate that the reaction proceeds *via* the methylene quinone, formed from the ether by elimination of methanol.

*p*-Hydroxybenzyl alcohols and ethers are easily transformed into *p*-hydroxybenzyl sulphonic acids on treatment with sulphite not only in acid but also in neutral or alkaline solutions and moreover show greater reactivity than the corresponding *p*-alkoxyderivatives in other reactions. It is believed that groups in lignin, showing similar reactivity, are also of the *p*-hydroxybenzyl alcohol or ether type<sup>1</sup>. In a previous paper from this department<sup>2</sup> dealing with the reaction between vanillyl alcohol (I) and sulphite it was concluded that the formation of the sulphonic acid (III) proceeded *via* the methylene quinone (II), the formation of which should be catalysed by both acids



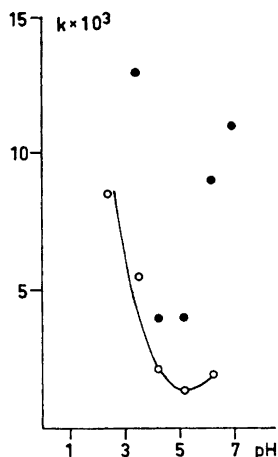
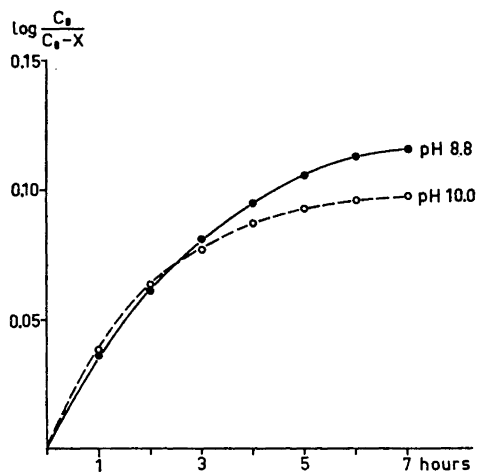
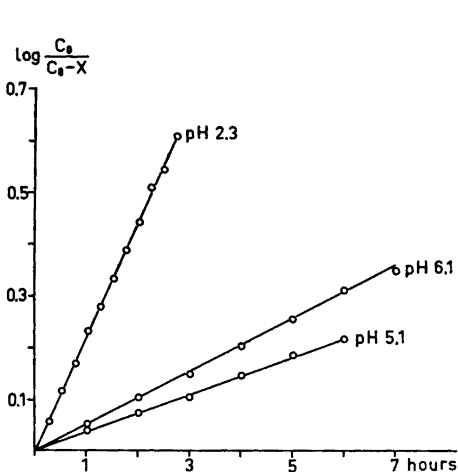


Fig. 1. First rate constant ( $\text{min}^{-1}$ ) for the hydrolysis, at  $80^\circ$ , of vanillyl methyl ether versus pH (full line and O). Approximate values for the first order rate constant for formation, at  $80^\circ$ , of the methylene quinone from vanillyl alcohol (●).

and bases. If *p*-hydroxybenzyl ethers, as vanillyl methyl ether (IV), react in an analogous way, then they should also be hydrolysed in acid as well as neutral and alkaline aqueous solutions. In order to test this, a study of the hydrolysis of vanillyl methyl ethers has been conducted.

Vanillyl methyl ether has not been described in the literature but has been prepared by Dr. B. Leopold and by Dr. J. Gierer by treating vanillyl alcohol with methanolic hydrogen chloride (private communications). It is a crystalline substance, m.p.  $34-35^\circ$ . The hydrolysis of the vanillyl methyl ether at  $80^\circ$



Figs. 2 and 3. Hydrolysis of vanillyl methyl ether at various pH-values.

$C_0$  = original concentration of starting material  
 $X$  = observed concentration of vanillyl alcohol.

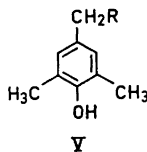
in aqueous buffers between pH 3 and 10 was studied. The ionic strength was the same, 0.3, in all experiments. The reaction was followed by determining the vanillyl alcohol formed by the colour reaction with 2,6-dibromo-benzoquinone-4-chloroimine<sup>3</sup>, which gives a blue indophenol with the alcohol but not with the ether. Good first order rate constants were observed up to pH 6 (Fig. 1).

At higher pH-values the significance of the results was obscured by side reactions. The solutions turned dark and a precipitate was formed. This is not unexpected as methylene quinones are known to be extremely labile in alkaline solutions, giving dimers and polymers<sup>4</sup>. The solutions gave the colour reaction with 2,6-dibromo-benzoquinone-4-chloroimine, which indicates the formation of vanillyl alcohol also at these pH-values. The formation of colour went through a maximum, which is expected as the vanillyl alcohol formed should also react further in analogous reactions, proceeding over the methylene quinone. The presence of vanillyl alcohol in the reaction product was demonstrated by thin layer chromatography, which also revealed the presence of products other than vanillyl alcohol and the starting material.

In our previous communication<sup>2</sup> were included approximate values for the rate of formation of the methylene quinone from vanillyl alcohol determined at 80° and various pH-values. The values obtained are plotted in Fig. 1 together with values for the hydrolysis of vanillyl methyl ether under the same conditions. The two sets of values are of the same order of magnitude and show the same pH-dependence, with a minimum around pH 5.

Vanillyl methyl ether is thus hydrolysed at all the pH-values studied. Further the rate of hydrolysis and the analogous rate of formation of the methylene quinone from vanillyl alcohol are of similar orders of magnitude and show the same pH-dependency. The similar high reactivity of *p*-hydroxybenzyl alcohols and *p*-hydroxybenzyl ethers towards sulphite, sulphides, methanolic hydrogen chloride and other reagents, as well as the reactivity of the corresponding groups in the lignin molecule towards the same reagents, are readily understood if it is assumed that they proceed over a methylene quinone intermediate, formed by elimination of water or alcohol from the *p*-hydroxybenzyl derivative.

In a recent paper Filar and Winstein<sup>5</sup> have stated that all nucleophilic substitutions of substances of the type V, including the alkaline hydrolysis of



the acetate (R = OAc), proceed over the corresponding methylene quinone. This lends further support to the conclusions reached in the present study.

The hydrolysis of vanillyl methyl ether at pH 5.1 and 70° and 90° was also studied. From the values of the rate constants obtained, the apparent activation energy could be determined to be 26 kcal/mole.

## EXPERIMENTAL

*Vanillyl methyl ether.* Vanillyl alcohol (2 g) was dissolved in 0.5 % methanolic hydrogen chloride (100 ml) and kept at room temperature overnight. The solution was neutralised with silver carbonate, filtered, concentrated to dryness and the residue distilled under reduced pressure. The crystalline product was recrystallised several times from ethyl ether-light petroleum, yielding the pure substance (0.8 g), m.p. 34–35°. (Found: OCH<sub>3</sub>, 37.4. Calc. for C<sub>9</sub>H<sub>12</sub> O<sub>3</sub>: OCH<sub>3</sub> 36.9).

*Kinetic determinations.* The buffers used, all about 0.2 M, were acetate-hydrochloric acid (pH 2.3), citrate (pH 3.4), acetate (pH 4.1 and 5.1), phosphate (pH 6.1, 6.9, 7.2 and 7.5) and borate (pH 7.9, 8.8 and 10.0). Sodium chloride was added to the buffers to an ionic strength of 1.0. For each pH-value known amounts of vanillyl alcohol were dissolved in buffer-water (3:7). To one ml of the solution 14 ml of 0.043 N aqueous sodium hydroxide and 0.2 ml of 0.5 % 2,6-dibromo-benzoquinone-4-chloroimine in ethanol were added. After exactly 10 min at room temperature the extinction was determined at 640 m $\mu$ . Linear calibration curves, differing only slightly for the different pH-values, were obtained.

Buffer and a 0.0015 M solution of vanillyl methyl ether in the proportions 3:7 were mixed and kept at 80°  $\pm$  0.1 in a thermostatically controlled polyethylene glycol bath. 1 ml samples were withdrawn at regular intervals, and poured into 0.043 N aqueous sodium hydroxide (14 ml), after which the vanillyl alcohol in the sample was determined as above. Some typical diagrams, showing the first order kinetics observed at lower pH-values and the undefinable kinetics found at higher pH-values are given in Figs. 2 and 3.

*Thin layer chromatography.* The reaction products were investigated by thin layer chromatography on silica gel G, using as solvent chloroform. The fast moving starting material and the slower vanillyl alcohol were observed at all pH-values, while at the higher values unidentified spots with lower mobilities than vanillyl alcohol were also observed.

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