

**MECHANISM OF HYDRATION AND ISOMERISATION OF  
4-ETHYLIDENE-2,6-DI-TERT-BUTYL-2,5-CYCLOHEXADIEN-1-ONE.  
KINETICS, ACID-BASE CATALYSIS AND SOLVENT  
DEUTERIUM ISOTOPE EFFECTS\***

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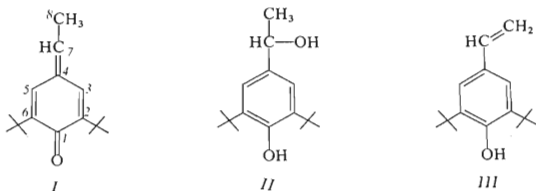
Competitive hydration and isomerisation of the quinone methide *I* at 25°C in an aqueous medium in the region of pH 2.4–13.0 was studied spectrophotometrically. The only reaction products in the studied range of pH are 4-hydroxybenzyl alcohol (*II*) and 4-hydroxystyrene (*III*). The form of the overall rate equation corresponds to a general acid-base catalysis. The mechanism of both reactions for three markedly separated pH regions is discussed on the basis of kinetic data and solvent deuterium effect.

Highly reactive *p*-quinone methides, formed in chemical delignification processes, represent a source of undesirable chromophore systems<sup>1</sup> which are relatively strongly bonded to cellulose. Therefore, considerable attention is paid recently to reactions, transforming *p*-quinone methides into colourless compounds<sup>2–4</sup>. However, most of the published studies are only of qualitative nature. Thus, *e.g.* for the addition of alcohols, phenols and acids to quinone methides, the reaction rate was shown to depend on the dissociation constant of the given hydroxy group<sup>5</sup> and further on the pH of the medium<sup>6</sup>. The exact values of rate constants are accessible only for the reactions of 2,6-disubstituted quinone methides with methanol<sup>3,7,8</sup> and hydroxyl ions<sup>9,10</sup> at high pH. Only for photolytically generated 7-vinylquinone methides the addition of water was studied in a wider pH interval<sup>11</sup>. The addition of nucleophilic species is usually accompanied by a concurrent isomerisation of 7-alkylquinone methides to substituted 4-vinylphenols. Similarly to the addition, also this reaction was studied mainly in non-aqueous solvents<sup>12,13</sup>. Except for strongly alkaline solutions<sup>9</sup>, the isomerisation in aqueous media, in which delignification processes<sup>14</sup> lead to lignin hydrolysis, has not been investigated.

Since the quinoid skeleton is of amphireactive nature (nucleophilic carbonyl oxygen and electrophilic methide carbon), we can expect a significant dependence of the

\* Part XIII in the series Quinone Methides and Fuchsones; Part XII: This Journal 41, 2919 (1976).

reaction rates on hydrogen ions concentration. The aim of this study is to investigate this dependence and to evaluate quantitatively the scope of the acid–base catalysis for the reaction of quinone methides in aqueous solutions. We have chosen 4-ethylidene-2,6-di-tert-butyl-2,5-cyclohexadien-1-one (*I*) as a suitable model which allows to follow both the reaction types simultaneously.



Generally, the observed rate constant ( $k_{\text{obs}}$ ) of an acid–base catalysed reaction is given by equation (*I*)

$$k_{\text{obs}} = k_0 + k_{\text{H}_3\text{O}^+}(a_{\text{H}_3\text{O}^+}/f) + k_{\text{OH}^-}(K_{\text{H}_2\text{O}}/a_{\text{H}_3\text{O}^+}f) + k_{\text{A}}[\text{A}] + k_{\text{B}}[\text{B}], \quad (I)$$

where  $k_0$  is the rate constant of the water reaction,  $a_{\text{H}_3\text{O}^+}$  and  $f$  are the activity and the mean activity coefficient, respectively, and  $k_{\text{A}}$  and  $k_{\text{B}}$  are rate constants corresponding to the acidic and basic components of the buffer. Evaluation of the single catalytic constants in equation (*I*) is based on following the change in  $k_{\text{obs}}$  in the series of buffers of the same buffer ratio  $r$  (ratio of concentration of the acid to that of its conjugated base) but with varying overall concentration at a constant ionic strength. The choice of the suitable series of buffers in this study was influenced not only by the substrate chosen but also by the experimental procedure. The series of acetate buffers with  $r = 1.11 - 9.14$  proved to be the best.

## EXPERIMENTAL

The quinone methide *I* (m.p. 90–91°C), the 4-hydroxybenzyl alcohol *II* (m.p. 102–103°C) and the 4-vinylphenol *III* (m.p. 43–44°C) were prepared according to the literature<sup>13,15</sup>; their melting points agreed with the published ones.

**Buffers.** For spectral measurements in the region pH 2.4–13.0 we used the universal buffer according to Davies<sup>16</sup>; the ionic strength ( $I$ ) was adjusted to  $I = 0.3$  by the addition of calculated amount of KCl. The buffer solutions were prepared from the purest commercial chemicals, the water was deionised and twice glass-distilled. The  $r$  and pH values of the buffers employed are summarised in Table I.

*Values of pH and pD.* The data, read from the pH-meter (Radiometer Copenhagen), were corrected for the mean activity coefficients ( $f$ ) using equations (2) and (3) where  $Z$  is the ion charge. The pD values were calculated using the relationship<sup>17</sup>  $pD = pH + 0.41$ .

$$pH = -\log ([H_3O^+] f) \quad (2)$$

$$\log f = (-0.51Z^2I^{0.5})/(1 + 1.5I^{0.5}) \quad (3)$$

*Kinetic measurements.* The decrease in concentration of the quinone methide *I* was followed spectrophotometrically at 305 nm (on a Specord UV VIS instrument). The quartz cells (width 1 cm, volume 2 ml) which served as the reaction vessels, were thermostated, the temperature variation being  $\pm 0.1^\circ\text{C}$ . A calculated amount of the stock solution of the quinone methide *I* in anhydrous acetonitrile<sup>18</sup> was added under stirring to a buffer solution (1.5 ml) in the thermostated ( $25^\circ\text{C}$ ) cell by means of a calibrated Hamilton syringe. In all experiments the pseudo-first-order reaction was followed to 80–90% conversion. The rate constants were determined by the weighed least squares linear regression method using the Margerison procedure<sup>19</sup>. Only runs with index of determination greater than 0.99 were considered. The rate coefficients are the mean values of duplicated experiments and were tested for homogeneity. Some of the slower reactions were followed to only 4–5 half-lives and  $k_{\text{obs}}$  were calculated by the Guggenheim method<sup>20</sup>. Concentration of the compound *II* was followed by measuring the extinction of the band at 550 nm due to the indophenol, formed from the alcohol *II* by the action of 2,6-dibromo-1,4-benzoquinone-4-chloroimide<sup>21</sup>. The accuracy of this method was  $\pm 5\%$ . The concentration changes of the product *III* were determined from the material balance. The accuracy of this method, which combines the errors of the other concentration determinations, is smaller than that of the direct spectrophotometric determination of concentrations of the compounds *I* and *II*. Therefore, in the calculation, the obtained concentrations of *III* were regarded as having a lower statistical weight. The rate constants in the suggested reaction schemes were calculated from the known dependence of the concentration of the reaction mixture components on time, using a programme which combined the Rosenbrock optimisation method with the integration procedure. All calculations were performed on a Hewlett-Packard calculator (Model 9830A).

*Product analysis.* A solution of the quinone methide *I* (0.232 g; 1 mmol) in acetonitrile (10 ml) was added to the buffer (200 ml; pH 4.0,  $I = 0.3$ ) at  $25^\circ\text{C}$ . After 1 h the mixture was extracted with chloroform ( $6 \times 50$  ml), the organic layer washed with water ( $3 \times 50$  ml), dried over magnesium sulfate and evaporated *in vacuo*. The crude product consisted of two compounds which were separated by preparative thin-layer chromatography on silica gel. The alcohol *II* (200 mg; 0.8 mmol) was crystallised from ether–light petroleum; m.p.  $101\text{--}102^\circ\text{C}$ . The vinylphenol derivative *III* (25 mg; 0.11 mmol) on crystallization from hexane melted at  $43^\circ\text{C}$ . When the reac-

TABLE I  
Dependence of pH Values of Acetate Buffers on  $r$  ( $I$  0.1)

$r^a$	1.11	1.82	3.00	4.00	5.71	7.14	9.14
pH	4.71	4.51	4.27	4.14	4.00	3.90	3.80

<sup>a</sup> For all values of  $r$ , the acetate ion concentrations were 0.025, 0.05, 0.07 and 0.10 mol dm<sup>-3</sup>.

tion time was prolonged to 3 days, (other reaction conditions and the work-up procedure being the same as above) only small amount of the alcohol *II* was detected, the vinyl phenol *III* being the principal product (210 mg; 0.92 mmol). With the same reaction time (3 days) and at pH 8.2 we obtained 149 mg (0.59 mmol) of the alcohol *II* and 85 mg (0.37 mmol) of the vinyl phenol *III*; both with correct melting points.

## RESULTS

The overall pH-rate profile of the reaction of the quinone methide *I* with water exhibits three markedly separated regions (Fig. 1). The first corresponds to an acid catalysis (pH 2.4–5.1) with the slope  $-1.00$  (correlation coefficient 0.998). The second, flat, region between pH about 5.1 and 9.5 indicates a pronounced sensitivity to the water reaction. In the third region between pH 10.0–13.0, the hydroxyl ion catalysis proves to be the dominant factor, determining the overall rate. The slope of this part of profile is 0.99 (correlation coefficient 0.995).

The fact, that at constant pH and ionic strength  $k_{\text{obs}}$  values change with changing buffer concentration (Fig. 2) is typical for reactions subjected to general acid-base catalysis. For reactions in acetate buffers, the equation (1) is transformed to the form

$$k_{\text{obs}} = k_0 + rk_{\text{H}_3\text{O}^+} K_{\text{AcOH}} + k_{\text{OH}^-} K_{\text{H}_2\text{O}} / rK_{\text{AcOH}} + (k_{\text{AcO}^-} + rk_{\text{AcOH}}) [\text{AcO}^-] \quad (4)$$

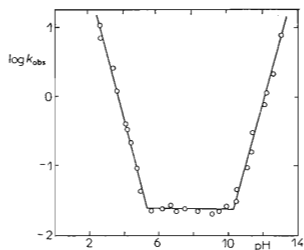


FIG. 1

Plot of Logarithm of Pseudo-First-Order Rate Constants (in  $\text{min}^{-1}$ , extrapolated to zero buffer concentration) against pH (25°C, ionic strength 0.30) for the Reaction of Quinone Methide *I* with Water

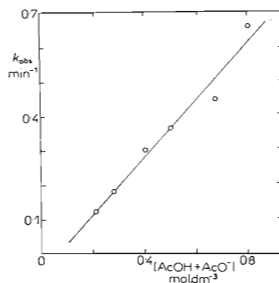


FIG. 2

Dependence of  $k_{\text{obs}}$  on Total Buffer Concentration (25°C, ionic strength 0.10)

and for a given  $r$ , the plot of  $k_{\text{obs}}$  against the acetate ion concentration (Fig. 3) is linear with the slope

$$S_r = k_{\text{AcO}^-} + rk_{\text{AcOH}} \quad (5)$$

and the intercept

$$I_r = k_0 + rk_{\text{H}_3\text{O}^+} + K_{\text{AcOH}} + k_{\text{OH}^-} - K_{\text{H}_2\text{O}}/rK_{\text{AcOH}} \quad (6)$$

From the graphical representation of the functions  $S_r = f(r)$  and  $I_r = f([\text{H}_3\text{O}^+])$  we can obtain the values of the catalytic constants  $k_{\text{AcOH}}$ ,  $k_{\text{AcO}^-}$ ,  $k_{\text{H}_3\text{O}^+}$  and  $k_0$ . A case, corresponding to equation (5), is depicted in Fig. 4. The catalytic constant  $k_{\text{OH}^-}$  was determined independently from the function  $k_{\text{obs}} = f([\text{OH}^-])$ . As expected<sup>22</sup>, the catalytic constant for the water reaction,  $k_0$ , is the same on extrapolation to zero concentration of the hydroxyl as well as hydronium ions and its value corresponds well to the value of the rate constant for an unbuffered reaction of the quinone methide *I* with water. The numerical values of thus-determined coefficients in the equation (4), together with those read from the pH-rate profile are summarised in Table II.

In order to decide whether the observed rate constant depends on the termolecular rate term<sup>23</sup>  $k_{(\text{AcOH})(\text{AcO}^-)} [\text{AcOH}] [\text{AcO}^-]$  we extended the equation (4) by this term and rewrote it in the form

$$(k_{\text{obs}} - I_r)/[\text{AcO}^-] = rk_{\text{AcOH}} + k_{\text{AcO}^-} + k_{(\text{AcOH})(\text{AcO}^-)} [\text{AcOH}] [\text{AcO}^-] \quad (7)$$

Plotting the left side of the equation (7) against the concentration of acetic acid led to straight lines of zero slopes. Further, we followed the dependence of the expression

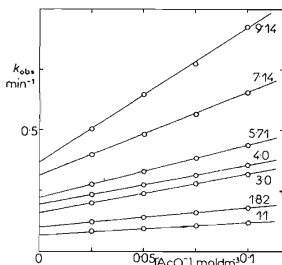


FIG. 3

Effect of Acetate Concentration and pH on  $k_{\text{obs}}$  for the Reaction of Quinone Methide *I* with Water (25°C, ionic strength 0.10)

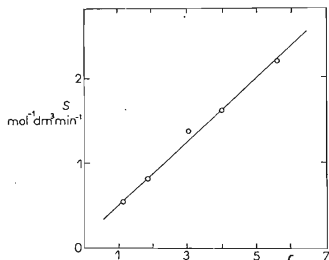


FIG. 4

Determination of Catalytic Rate Coefficients  $k_{\text{AcOH}}$  and  $k_{\text{AcO}^-}$ . Dependence of the Slopes of Lines in Fig. 3 on the Buffer Ratio

$k_{\text{obs}} - I_r$  on the acetate ion concentration. It is graphically represented by a series of straight lines with correlation coefficients greater than 0.99. This proved<sup>24</sup> that in the equation (4) the termolecular term does not operate under the reaction conditions employed.

As shown by product analysis, throughout all the three pH profile regions, the reaction of the quinone methide *I* with water affords the alcohol *II* and the vinyl phenol *III* as the sole products. A reversible reaction  $III \rightleftharpoons I$  or  $III \rightleftharpoons II$  was not observed under the reaction conditions employed.\*

The solvent deuterium isotope effects,  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ , for the individual catalytic regions are given in Table III.

## DISCUSSION

*Reaction mechanism at low pH.* In the region of pH 2.4–5.1 the observed rate constant,  $k_{\text{obs}}$ , depends linearly on pH with a slope of unity which indicates that the empirical formula of the transition state contains one proton more than that of the

TABLE II  
Catalytic Constants of the Equation (4) for the Quinone Methide *I*

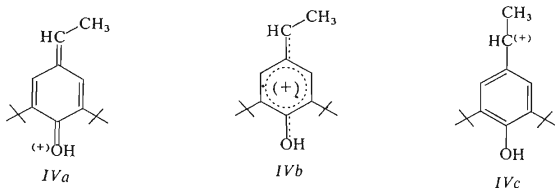
Constant	Bell-Darwent	Other method
$10^2 k_0^a$	$4.32 \pm 0.26$	$4.14 \pm 0.24^c$
$10^{-3} k_{\text{H}_3\text{O}^+}^b$	$2.02 \pm 0.21$	$2.06 \pm 0.14^d$
$10^{-1} k_{\text{OH}^-}^b$		$4.48 \pm 0.35^d$
$10 k_{\text{AcO}^-}^b$	$1.92 \pm 0.21$	$4.32 \pm 0.28^e$
$10 k_{\text{AcOH}}^b$	$3.50 \pm 0.11$	

<sup>a</sup>  $\text{min}^{-1}$ ; <sup>b</sup>  $\text{mol}^{-1} \text{dm}^3 \text{min}^{-1}$ ; <sup>c</sup> determined from the reaction of the quinone methide *I* with water; <sup>d</sup> values from the pH-rate profile; <sup>e</sup> slope of the function  $k_{\text{obs}} = f([\text{OH}^-])$ .

TABLE III  
Rate Constants for the Partial Steps in Scheme 1(A) at pH 4

Constant	$k_1$	$k_{-1}$	$k_2$	$k_{-2}$	$k_3$
$\text{min}^{-1}$	0.3753	0.0016	4.4280	0.0891	0.3842

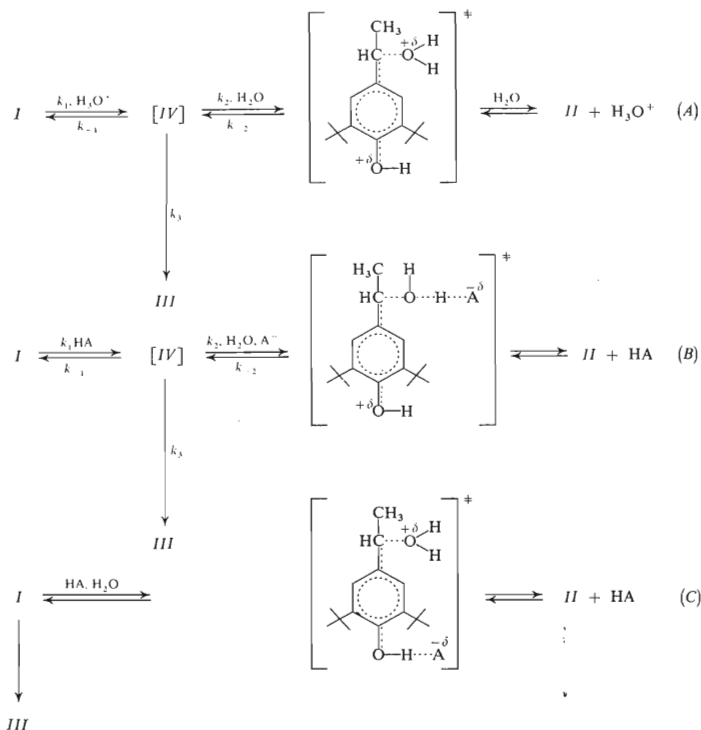
ground state. The protonation must take place at an atom with the highest electron density, *i.e.* at the carbonyl oxygen (formula *IVa*). Although the quinone methide is optimally represented by the "carboxonium" structure *IVb* with a delocalised charge, the proper reactive species is undoubtedly the carbocation *IVc*. The operation of these species in acid-catalysed reactions of quinone methides has moreover been proved spectroscopically<sup>25,26</sup>.



In the next step the protonated species reacts under formation of either the vinylphenol *III* by a mechanism analogous to that of the formation of styrene from the corresponding benzylic cation<sup>27,28</sup> or with water to give the alcohol *II*. It is obvious that this reaction does not proceed by the previously suggested mechanism:  $\text{R}^+ + \text{H}_2\text{O} \rightleftharpoons \text{ROH}_2^+ \rightleftharpoons \text{ROH} + \text{H}^+$ , where the second equilibrium is acid-base catalysed, but by a one-step mechanism<sup>26,29</sup> without any participation of the intermediate  $\text{ROH}_2^+$ .

On the basis of the proved general acid catalysis and of the finding<sup>26</sup> that the equilibrium between the quinone methide and the carbinol must necessarily involve the carbocation intermediate we may describe the acid-catalysed reaction of the quinone methide *I* with water by three alternative equations shown in Scheme 1. Decisive for the operation of the mechanism (A) or (B) is the concentration of hydronium ions in the reaction medium. Both these mechanisms assume participation of a strongly developed carbocation. The mechanism (A) (specific hydronium ion catalysis) will predominate in the region of low pH values, the mechanism (B) is supported by the proof of the general acid-base catalysis. The assumption of these two mechanisms is supported also by the good accord of the experimental and computer-generated curves of the concentration dependences at pH 4.0, where both the mechanisms participate, the contribution of (A) being far larger than that of (B). The rate constants corresponding to the solution of the differential equations describing the system (A) are given in Table III. Also the deuterium solvent isotope effect,

\* Equilibrium of the type  $\text{III} \rightleftharpoons \text{I}$  was used<sup>11</sup> in explanation of the low polymerisation reactivity of 4-isopropenyl-2,6-di-tert-butylphenol in a non-aqueous medium with sulfuric acid as catalyst.



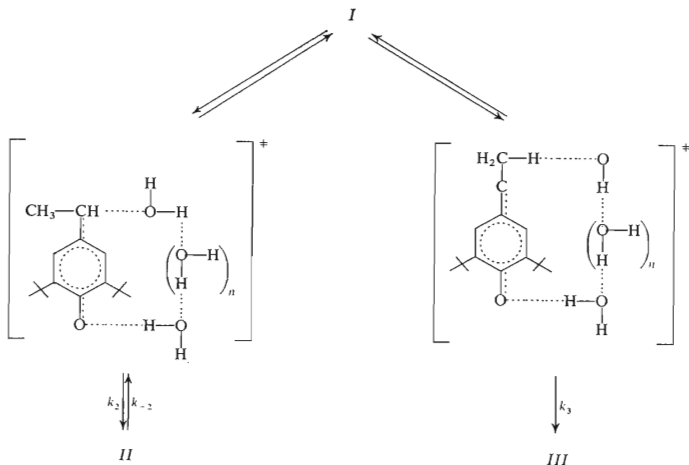
SCHEME 1

$k_{H_3O^+}/k_{D_3O^+} > 1$  (Table IV) represents another support (Table IV) for the discussed mechanism. We may thus assume a proton transfer to the substrate in the rate-determining step<sup>30</sup>. We exclude the mechanism (C) because according to this pathway, the vinyl phenol III would arise by a direct isomerisation of the quinone methide I and consequently the rate of its formation should be approximately the same in acidic as well as in neutral regions which contradicts the observed facts.

**Mechanism in the region of the "water reaction".** This region is determined by two breaks in the pH-rate profile curve at pH 5.1 and 9.5. Here no carbocation is



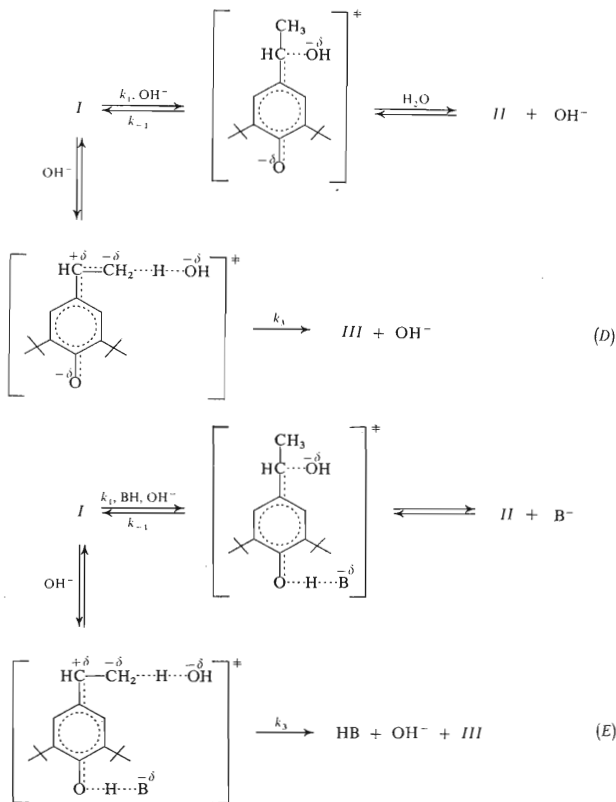
formed and the rate of formation of products (which are the same as in the acid catalysis region) is influenced only by the catalytic effect of water. Our value of the deuterium solvent isotope effect for the attack of water on the quinone methide *I* agrees well with the reported values<sup>30,31</sup> for the proton transfer between oxygen and a general basic catalyst ( $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} \sim 2.3$ ). We can therefore assume that the reaction proceeds by a generally base-catalysed attack of a water molecule, the second molecule of water acting as a basic catalyst. We cannot exclude that the transition state (Scheme 2) is stabilised by a concerted catalysis at the basic and acidic centers of the



SCHEME 2

TABLE IV  
Solvent Deuterium Isotope Effects,  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$

Catalytic system	$k_{\text{H}}/k_{\text{D}}$
$\text{H}_2\text{O} - \text{D}_2\text{O}$	2.56
$\text{OH}^- - \text{OD}^-$	0.92
$\text{H}_2\text{O}^+ - \text{D}_3\text{O}^+$	1.20



SCHEME 3

molecule by a quasi-cyclic mechanism<sup>32,33</sup>. Quinone methides which are relatively polar compounds (dipole moment of 4-isopropylidene-2,6-di-tert-butyl-2,5-cyclohexadien-1-one<sup>34</sup> is 4.55 D) facilitate this mechanism. The rate constants for the system  $\text{II} \rightleftharpoons \text{I} \rightarrow \text{III}$  (Scheme 2;  $k_2 = 1.68 \cdot 10^{-2} \text{ min}^{-1}$ ,  $k_{-2} = 0.204 \cdot 10^{-2} \text{ min}^{-1}$  and  $k_3 = 0.605 \cdot 10^{-2} \text{ min}^{-1}$ ) shows that the rate of the reaction of the quinone methide I

with water is by about two orders of magnitude larger in this region than in the region of acid catalysis.

The vinyl phenol *III* (Scheme 2) arises from the quinone methide *I* by a 1,7-prototropic shift<sup>13</sup> under simultaneous participation of base and its conjugated acid. In the acid catalysis region the vinyl phenol is formed much faster by the reaction  $IV \rightarrow III$  than by the reaction  $I \rightarrow III$  and therefore in Scheme 1 the latter reaction can be neglected; on the contrary, in Scheme 2 the direct reaction  $I \rightarrow III$  is the only possible explanation of the formation of this vinyl phenol.

*Reaction mechanism at high pH.* In this region the reaction rate is directly proportional to the concentration of the hydroxyl ions. Consequently, the empirical formula of the transition state must contain one proton less than that of the ground state plus or minus any number of water molecules. As an analogy to the acid-catalysed reaction we assume (Scheme 3) a hydroxyl ion catalysis (mechanism *D*) as well as a general base catalysis in the equilibrium  $H_2O + B^- \rightleftharpoons HB + OH^-$  (mechanism *E*). The formation of the vinyl phenol *III* in both these mechanisms is conditioned by sufficient acidity of the protons of the terminal methyl group; however, compared with the "water" region, the splitting off of the proton is facilitated by both hydroxyl ion and the base. The kinetic scheme  $III \leftarrow I \rightleftharpoons II$ , corresponding to the path *D* with the rate constants  $k_1 = 1.264 \text{ min}^{-1}$ ,  $k_{-1} = 0.141 \text{ min}^{-1}$ , and  $k_2 = 0.018 \text{ min}^{-1}$  at pH 12.3 was described by us already previously<sup>9</sup>.

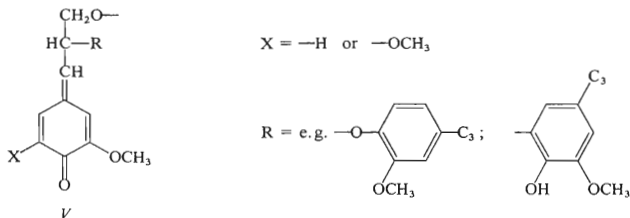
The observed value 0.92 for the ratio  $k_{OH^-}/k_{OD^-}$  (Table IV) is in an interval expected for a solvent deuterium isotope effect under assumption that in the transition state the proton transfer between water and carbonyl oxygen is not well developed.

We can conclude that for all regions of the pH-rate profile both the product analysis and the kinetic data proved the existence of the equilibrium  $I \rightleftharpoons II$  and the irreversible step  $I(IV) \rightarrow III$ . This finding indicates that the alcohol *II* arises in a kinetically controlled step whereas the formation of the vinylphenol *III* is thermodynamically controlled. This fact is expressed quantitatively by the relative rate constants  $k_2/k_3$  given in Table V. From this Table it follows further that the formation of the alcohol *II* is preferred throughout the whole studied region of pH, predominantly, however, in the base-catalysis region. This is in accord with our assumption that the vinyl phenol *III* arises more easily from the carbocation *IV* (at low pH values) than directly from the quinone methide *I*.

TABLE V  
Rates of Formation of *II* and *III* at Various pH

pH	4.0	8.2	12.3
$k_2/k_3$	11.5	2.8	70.2

The applicability of these results to the chemistry of delignification processes is conditioned by the similarity between the structure of the quinone methide *I* and the classical structure of a simple lignin model *V*.



It is most probable that substitution of the OCH<sub>3</sub> groups (or X) for the tert-butyl groups (model *I*), as well as the substitution at the C<sub>(8)</sub> atom by an R group (model *V*), will result only in a change of the overall reaction rate. Nevertheless, the mechanism of hydration and isomerisation of the basic structural unit (quinone methide, substituted at C<sub>(7)</sub>) with an alkyl group) will be the same for both the compounds *I* and *V*.

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*Note added in proof:* After completion of our work there appeared a kinetic study of the reaction of quinone methides with alcohols, phenols, carboxylic acids and water in tert-butyl alcohol (Leary G., Miller I. J., Thomas W., Woolhouse A. D.: *J. Chem. Soc., Perkin Trans. 2*, 1977, 1737). The interesting assumption of a ternary complex between two acid molecules and one molecule of the quinone methide loses somewhat its value due to the fact that the authors completely disregard the protonation equilibria between tert-butyl alcohol and the acid.