

## Studies on Benzaurin and Some of its Derivatives

### A. The Equilibria and Kinetics of 3,3'-Dimethylbenzaurin in Aqueous Solutions

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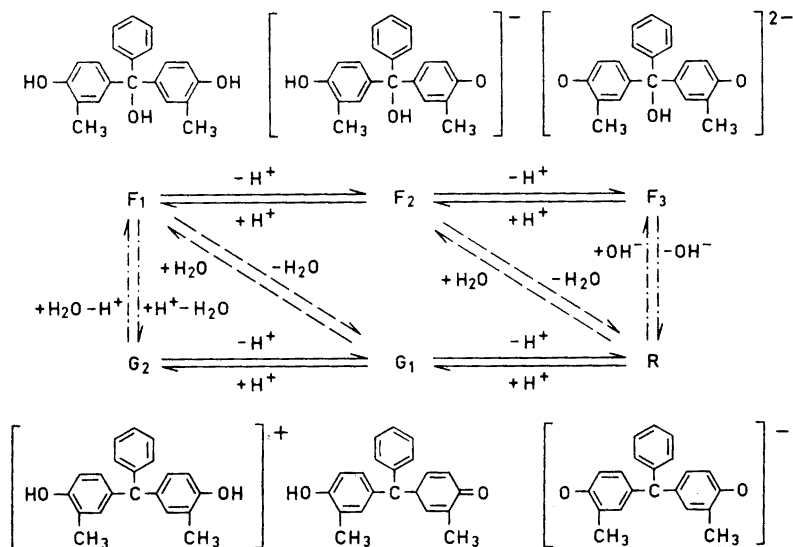
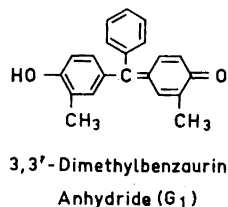
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In a series of papers <sup>1-7</sup> the six-member equilibrium system of benzaurin and five of its derivatives in aqueous solutions was described. Further the measurements leading to the determinations of the various equilibrium and velocity constants of the scheme were accounted for. The results of a corresponding investigation of 3,3'-dimethylbenzaurin, presented here, supplement the previous experiences and provide further support of the conclusions. Of the six members there are three coloured ones in pH-equilibrium, and three colourless ones also in pH-equilibrium. A colourless species can be formed by adding a water molecule to the corresponding coloured form. Such an addition is, like two other conversions, a time reaction. In the system there are four protolytic constants, two hydration constants and eight velocity constants. Apart from two velocity constants, which could not be calculated, the constants mentioned have been determined at 20°C, the ionic strength 0.50 M and in a solvent with the composition 98 % water + 2 % acetone. Some previously observed effects <sup>7</sup> of the various substituents on the magnitudes of the constants appear again. These phenomena are commented on in the discussion.

In a series of papers, previously published<sup>1</sup> (in German) under the common title of "Benzaurinstudien",<sup>1-6</sup> and a summarizing article,<sup>7</sup> the results of an investigation of benzaurin and five of its derivatives were discussed in detail. That investigation showed that dyestuffs of the benzaurin type in aqueous solutions form six different molecular species, three coloured anhydrous forms and three colourless carbinolic forms. The six species constitute an equilibrium system. The three anhydrous forms, R, G<sub>1</sub>, and G<sub>2</sub> (see the scheme), are in an instantaneously reached pH-equilibrium with each other. The same is true about the three carbinolic forms, F<sub>1</sub>, F<sub>2</sub>, and F<sub>3</sub>. Two of the anhydrous forms, G<sub>1</sub> and R, can take up water forming, by time reactions, the corresponding carbinolic forms, F<sub>1</sub> and F<sub>2</sub>, and after some time hydration equilibrium is reached between corresponding anhydrous and carbinolic forms.

Thus, starting with the anhydrous forms, the hydration reactions appear as a fading of the colour of the solution without changing the colour tone. The latter depends on the pH, which determines the relative amounts of the coloured forms R, G<sub>1</sub>, and G<sub>2</sub>. Apart from the hydrations mentioned above there are at least two other time reactions leading from an anhydrous to a carbinolic form or *vice versa* (see the scheme!). Within certain time limits all reactions are reversible.

The velocity and equilibrium constants of the system can thus be calculated from measurements of the light extinction (*E*) during the fading reactions and at equilibrium over a sufficient pH-range. As expected the same equilibrium scheme has proved valid for 3,3'-dimethylbenzaurin, the investigation of which is presented in this paper. The scheme follows below.\*



The equilibrium constants are defined in agreement with those in the previous papers<sup>1-7</sup> as follows:

Protolytic constants

$$K_1 = \frac{[G_1]}{[H^+][R]}, \quad K_7 = \frac{[H^+][G_1]}{[G_2]}, \quad K_3 = \frac{[H^+][F_2]}{[F_1]}, \quad K_4 = \frac{[H^+][F_3]}{[F_2]},$$

Hydration constants

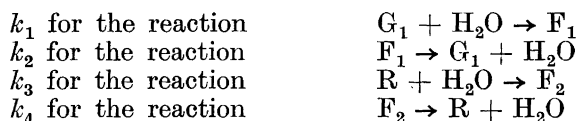
$$K_2 = \frac{[F_1]_\infty}{[G_1]_\infty}, \quad K_6 = \frac{[R]_\infty}{[F_2]_\infty}, \quad ([H_2O] \text{ is constant}).$$

\* In the scheme the arrows  $\longrightarrow$  indicate instantaneous reactions (proton transfers), the arrows  $\dashrightarrow$  hydration reactions and the arrows  $\cdots\cdots\rightarrow$  other reactions from (to) coloured to (from) colourless forms, the two latter types being time reactions.

It follows that  $K_1 \cdot K_2 \cdot K_3 \cdot K_6 = 1$

Further we have  $K_w = [\text{H}^+][\text{OH}^-]$

In the previous investigation<sup>1-6</sup> it was at first assumed that the only conversions from (to) coloured to (from) colourless forms were the two hydrations  $\text{G}_1 + \text{H}_2\text{O} \rightleftharpoons \text{F}_1$  and  $\text{R} + \text{H}_2\text{O} \rightleftharpoons \text{F}_2$  and in accordance with this assumption the following velocity constants were defined



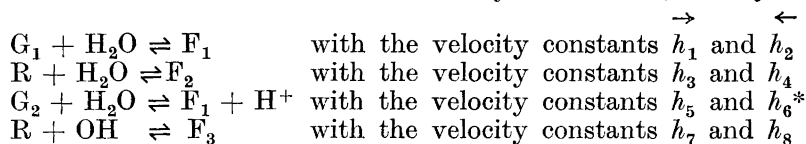
It follows that  $k_2 = k_1/K_2$  and  $k_4 = k_3 \cdot K_6$ ;  $k_1$  and  $k_3$  include  $[\text{H}_2\text{O}]$ .

That this assumption could not be the whole truth was strikingly demonstrated by the measurements. The determination of the velocity "constants" showed that these in fact are linear functions of  $[\text{H}^+]$  and  $[\text{OH}^-]$ , respectively, according to the expressions

$$\begin{aligned} k_1 &= k_1^\circ + k_1' \cdot [\text{H}^+] & k_3 &= k_3^\circ + k_3' \cdot [\text{OH}^-] \\ k_2 &= k_2^\circ + k_2' \cdot [\text{H}^+] & k_4 &= k_4^\circ + k_4' \cdot [\text{OH}^-] \end{aligned}$$

The fact that  $k_1$  and  $k_2$  are linear functions of  $[\text{H}^+]$ , and  $k_3$  and  $k_4$  of  $[\text{OH}^-]$ , can be explained by assuming two further conversions between coloured and colourless forms *i.e.*  $\text{G}_2 + \text{H}_2\text{O} \rightleftharpoons \text{F}_1 + \text{H}^+$  and  $\text{R} + \text{OH}^- \rightleftharpoons \text{F}_3$ .

Thus the conversions between coloured anhydrous forms and colourless carbinolic forms can occur in at least four ways of reaction, namely:



The formulas previously used<sup>1-7</sup> have originally been based on the assumption of four velocity constants,  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ . They are, however, valid also for the extended scheme, since  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  in the latter are not real constants but the linear functions of  $[\text{H}^+]$  and  $[\text{OH}^-]$ , respectively, as stated above. As can easily be shown, the eight constants in these functions correspond to the eight velocity constants  $h_1, h_2, \dots, h_8$  as follows

$$\begin{aligned} h_1 &= k_1^\circ, \quad h_2 = k_2^\circ, \quad h_3 = k_3^\circ, \quad h_4 = k_4^\circ \\ h_5 &= k_1' \cdot K_7, \quad h_6 = k_2', \quad h_7 = k_3', \quad h_8 = k_4' \cdot K_w/K_4 \end{aligned}$$

The equilibrium and velocity constants of 3,3'-dimethylbenzaurin do not differ very much from those of 4"-chloro-3,3'-dimethylbenzaurin.<sup>6</sup> Thus the conversions are relatively slow, and in alkaline solutions it is impossible to obtain stable and reproducible equilibrium values of the light extinction. This effect, previously observed, is probably due to an irreversible breaking down of the dyestuff caused by oxidation. As a result of this some constants in the alkaline region could not be determined with a normal degree of accuracy.

\*  $h_5$  is identical with the previously<sup>7</sup> used  $k_5$ .

## EXPERIMENTAL

The investigation was carried out in the same manner as before.<sup>1-7</sup> The stock solutions of the dyestuff were prepared by dissolving a weighed amount of the G<sub>2</sub>-perchlorate in absolute acetone. Such a solution does not contain any of the colourless carbinolic forms. The concentration of the dyestuff was  $(0.7-3.5) \times 10^{-4}$  M. In order to make the stock solutions less sensitive to traces of water (the risk of fading by hydration), small amounts of triethylamine were added<sup>8</sup>; the concentration of the amine was  $1.0 \times 10^{-2}$  M. The addition of the amine, which has no undesired effects, makes the solutions alkaline, which results in the coloured forms predominating. The solutions for the measurements were prepared by mixing 49.0 ml of the buffer in question with 1.0 ml (exactly 1.062 ml) of the acetone stock solution of the dyestuff. The latter was added to the buffer from a hypodermic syringe, the volume of which had been accurately determined by weighing. As time proceeds, the light extinction,  $E$ , of a solution so obtained decreases on account of the conversion reactions. From measurements of  $E$  as a function of time,  $t$ , the velocity constants are calculated. The equilibrium constants are calculated from the equilibrium values of the light extinction,  $E_{\infty}$ , and from the initial values,  $E_0$ , obtained by extrapolation. The measurements have been performed for solutions over the pH-range 0.7–12.1. The values of  $[H^+]$  were either defined by the addition of exactly known amounts of HCl or NaOH, respectively, or measured potentiometrically. The measurements of  $[H^+]$  were performed with quinhydrone and a platinum-plate electrode or with hydrogen gas and a platinum-plate electrode covered with platinum-black. The reference solution had the composition 0.02 M HCl + 0.48 M NaCl. By the addition of NaCl to the buffer solutions, the ionic strength of the measurement solutions was kept constant at 0.50 M. As the stock solutions of the dyestuff were made up in acetone, the results are throughout referred to a solvent with the composition 98 % water + 2 % acetone.

The measurements of the light extinctions were performed with a Beckman Quartz Spectrophotometer, Model DU.

All the measurements were performed at 20°C. Before and between the measurements the solutions were kept in a thermostat at this temperature. Under the conditions stated above the value of  $K_w$  has previously been determined<sup>2</sup> to  $1.22 \times 10^{-14}$ , which value is used here, too.

## MEASUREMENTS AND RESULTS

*The substance.* The preparation of the dyestuff investigated has been briefly commented on in a previous paper.<sup>1</sup> The G<sub>2</sub>-perchlorate C<sub>21</sub>H<sub>19</sub>O<sub>6</sub>Cl, the analysis of which was given there, has been used throughout the investigation. In addition it should be noted that the perchlorate had been recrystallised to a constant light absorption. Other chemicals used were of the best qualities obtainable from Baker, Merck etc.

*Buffer substances* were Na<sub>2</sub>HPO<sub>4</sub>–NaOH, H<sub>3</sub>BO<sub>3</sub>–NaOH, NaH<sub>2</sub>PO<sub>4</sub>–Na<sub>2</sub>HPO<sub>4</sub> in the following approximate pH-ranges  $9.9 < \text{pH} < 11.1$ ,  $7.8 < \text{pH} < 9.7$ ,  $5.7 < \text{pH} < 7.8$ . In the acid solutions with  $\text{pH} < 1.5$   $[H^+]$  was defined by the addition of an exactly known amount of HCl. Correspondingly, in the alkaline solutions with  $\text{pH} > 11.6$ ,  $[OH^-]$  was defined by the addition of an exactly known amount of NaOH and  $[H^+]$  calculated from the relation  $[H^+] \cdot [OH^-] = 1.22 \times 10^{-14}$ .

*Designations.*  $C$  = the total concentration of the dyestuff,

$d$  = the (optical) pathlength (= the thickness of the absorbing layer),

$E$  = the light extinction ( $E_0$  at zero time,  $E_{\infty}$  at equilibrium)

$E_R$  ( $E_{G_1}$ ,  $E_{G_2}$ ) = the light extinction at constant  $d$  of a solution in which  $C = [R]$  ( $[G_1]$ ,  $[G_2]$ ),

$\lambda$  = the wave length,

$t$  = the time.

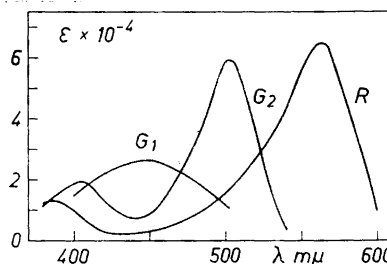


Fig. 1. Light extinction curves. The molecular extinction coefficient,  $\epsilon$ , as a function of the wave length,  $\lambda$ , in  $m\mu$ .

*Light extinction curves.* In Fig. 1 are drawn the curves for the different coloured forms of the substance, *i.e.* for the positive ion  $G_2$  (red-yellow), the molecule  $G_1$  (yellow) and the negative ion R (blue-red). The curves show the molecular extinction coefficient,  $\epsilon$ , as a function of the wave length,  $\lambda$ , in  $m\mu$ .

The curve of R was taken up in a solution with  $\text{pH} = 10.053$  and  $C = 7.52 \times 10^{-6}$  M, and  $E$  was measured immediately after the addition of the dyestuff at  $d = 2$  cm. As the fading reaction is very slow at this pH, it can be ignored during the time used for the measurements (less than 30 min). Thus  $\epsilon_R$  was calculated from the equation

$$E = \epsilon_R \times 2 \times 7.52 \times 10^{-6}$$

The curve of  $G_1$  was taken up at  $\text{pH} = 5.867$  and  $C = 1.502 \times 10^{-6}$  M. At every wave length chosen,  $E$  was measured at  $d = 10$  cm as a function of  $t$ , and  $E_0$  obtained by extrapolation. The values of  $E_0$  obtained were corrected for the small amount of R present, to give  $E_{G_1}$ . The values of  $\epsilon_{G_1}$  were calculated from the equation

$$E_{G_1} = \epsilon_{G_1} \times 10 \times 1.502 \times 10^{-6}$$

The curve of  $G_2$  was taken up in a solution with  $[\text{H}^+] = 0.211$  M and  $C = 1.502 \times 10^{-6}$  M, and  $E_{G_2}$  calculated from the formula

$$E = \frac{K_7 \cdot E_{G_1} + [\text{H}^+] \cdot E_{G_2}}{K_7 \cdot (1 + K_2) + [\text{H}^+]}$$

where  $E$  is the measured extinction of the solution at  $d = 10$  cm.\*

It was found that

$(\epsilon_R)_{\text{max}} = 6.5 \times 10^4$	at	$\lambda \approx 564$ $m\mu$
$(\epsilon_{G_1})_{\text{max}} = 2.6(2) \times 10^4$	at	$\lambda \approx 450$ $m\mu$
$(\epsilon_{G_2})_{\text{max}} = 1.9(4) \times 10^4$	at	$\lambda \approx 405$ $m\mu$
$(\epsilon_{G_1})_{\text{max}} = 5.8 \times 10^4$	at	$\lambda \approx 500$ $m\mu$

### Equilibrium constants

*Determination of  $K_1$ .* For six solutions in the range  $7.6 < \text{pH} < 8.4$   $E$  was measured at  $\lambda = 564$   $m\mu$  as a function of  $t$ , and  $E_0$  obtained by extrapolation.

\* As equilibrium is reached instantaneously,  $E_{\infty} = E_0$ .

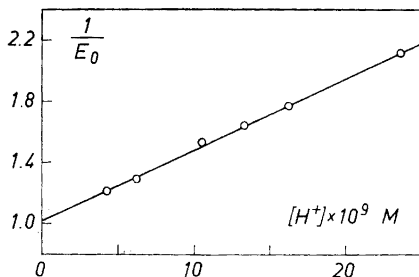


Fig. 2.  $1/E_0$  as a function of  $[H^+]$  at  $\lambda = 564 \text{ m}\mu$  for the determination of  $K_1$  (and  $E_R$ ).  $C = 3.00 \times 10^{-6} \text{ M}$  and  $d = 5 \text{ cm}$ .

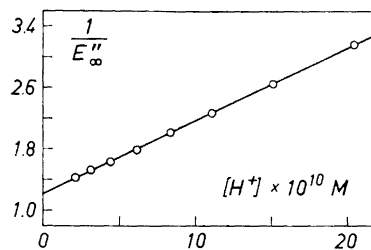


Fig. 3.  $1/E_\infty''$  as a function of  $[H^+]$  at  $\lambda = 564 \text{ m}\mu$  for the determination of  $K_3 \cdot K_6$  and  $K_6$ .  $C = 7.51 \times 10^{-6} \text{ M}$  and  $d = 2 \text{ cm}$ .

The measurements were performed at  $C = 3.00 \times 10^{-6} \text{ M}$  and with  $d = 5 \text{ cm}$ . The measured quantities are represented graphically according to formula (1)<sup>7</sup>

$$\frac{1}{E_0} = \frac{1}{E_R} + \frac{K_1 \cdot [H^+]}{E_R}$$

A straight line is obtained from which  $K_1$  and  $E_R$  are calculated; see Fig. 2.

$$1/K_1 = 2.1(9) \times 10^{-8}, \quad E_R = 0.982$$

*Determination of  $K_3 \cdot K_6$  and  $K_6$ .* For a series of solutions in the range  $8.5 < \text{pH} < 9.7$   $E_\infty$  was measured at  $\lambda = 564 \text{ m}\mu$ ,  $C$  was  $7.51 \times 10^{-6} \text{ M}$  and  $d = 2 \text{ cm}$ . For some solutions  $E$  was measured as a function of  $t$  and  $E_0$  obtained by extrapolation.  $E_R$  was calculated from the  $E_0$ -values by correcting for the small amounts of  $G_1$  present. Thus  $E_R$  was determined to be 0.97(4), which well agrees with the value above. The measured  $E_\infty$ -values were corrected<sup>2</sup> for the small amounts of  $G_1$  and  $F_3$  present, and the corrected quantities ( $E_\infty''$ ) represented graphically according to formula (4).<sup>7</sup>

$$\frac{1}{E_\infty''} = \frac{1 + 1/K_6}{E_R} + \frac{[H^+]}{E_R \cdot K_3 \cdot K_6}$$

A straight line is obtained, from which the following values are determined; see Fig. 3.

$$K_3 \cdot K_6 = 1.08 \times 10^{-9}, \quad K_6 = 5.(3), \quad K_3 = 2.0(3) \times 10^{-10}$$

*Determination of  $K_4$  by means of formula (5)<sup>7</sup>*

$$\frac{[H^+]}{E_\infty} = \frac{K_4}{E_R \cdot K_6} + \frac{1 + 1/K_6}{E_R} \cdot [H^+]$$

could not be performed as before by separate determinations of  $K_4/E_R \cdot K_6$  and  $(1 + 1/K_6)/E_R$  from a straight line representing the measurements in the proper pH-range. The waiting-times for reaching equilibrium are long and the reproducibility of the  $E_\infty$ -values unsatisfactory. By making the measurements in a still more alkaline region, where the fading reactions run considerably faster, however, it was possible to determine  $E_\infty$  with some degree of

accuracy. As the value of  $[H^+]$  is known,  $K_4/E_R \cdot K_6$  was calculated as the difference  $[H^+]/E_\infty - (1 + 1/K_6) \cdot [H^+]/E_R$ , where the last term in this alkaline region has the character of a correction term. The measurements of  $E_\infty$  were performed at  $11.8 < \text{pH} < 12.1$  with  $d = 2$  cm for solutions with  $C = 7.52 \times 10^{-6}$  M.

An approximate value of  $K_4/E_R \cdot K_6$  was calculated from the  $E_\infty$ -values of three solutions

$$K_4/E_R \cdot K_6 \approx 0.75 \times 10^{-11}$$

Inserting  $K_6 = 5.3$  and  $E_R = 0.966$ , obtained by extrapolation, one obtains

$$K_4 \approx 3.9 \times 10^{-11}$$

*Determination of  $K_2$*  was performed at  $7.6 < \text{pH} < 8.4$ . The solutions were identical with those used for the determination of  $K_1$ . The values of  $E_\infty$  at  $\lambda = 564$  m $\mu$  were measured at  $d = 5$  cm and  $K_2$  calculated from formula (7) <sup>7</sup>

$$K_2 = \frac{E_R - E_\infty \cdot (1 + K_1 \cdot [H^+] + 1/K_6)}{E_\infty \cdot K_1 \cdot [H^+]}$$

$K_2 = 19.4 \pm 0.5$  (average value from six solutions).

The definitions require that  $K_1 \cdot K_2 \cdot K_3 \cdot K_6 = 1$ . In good agreement with this the experimentally determined values give  $K_1 \cdot K_2 \cdot K_3 \cdot K_6 = 0.96$ .

*The determination of  $K_7$*  was performed at  $\text{pH} < 1.5$ . The equilibrium between  $F_1$ ,  $G_1$ , and  $G_2$  was reached instantaneously. For seven solutions the  $E$ -values were measured at  $\lambda = 500$  m $\mu$ ,  $d = 10$  cm and  $C = 1.502 \times 10^{-6}$  M.\* The measured quantities are represented graphically according to formula (9).<sup>7</sup> ( $E_{G_1}/(1 + K_2) = 0.013$  was determined by measuring  $E$  in an acetate buffer with  $\text{pH} = 4.311$ ).

$$\frac{[H^+]}{E - E_{G_1}/(1 + K_2)} = \frac{K_7 \cdot (1 + K_2)}{E_{G_2} - E_{G_1}/(1 + K_2)} + \frac{[H^+]}{E_{G_2} - E_{G_1}/(1 + K_2)}$$

A straight line is obtained; see Fig. 4. The following values are calculated

$$K_7 \cdot (1 + K_2) = 0.222, \quad K_7 = 1.08(5) \times 10^{-2}, \quad E_{G_2} = 0.853$$

### Velocity constants

The velocity constant  $k$  of the fading reaction is determined by measuring  $E$  as a function of time,  $t$ , for a number of solutions with different, suitably chosen  $\text{pH}$ -values; see Fig. 5. The calculation of  $k$  is made by means of formula (11)<sup>7</sup>

$$k = \frac{1}{t} \cdot \ln \frac{E_0 - E_\infty}{E - E_\infty}$$

\* Cf. footnote p. 2159.

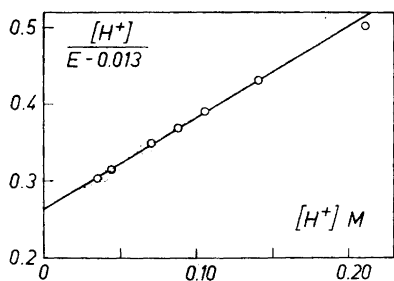


Fig. 4.  $\frac{[H^+]}{E - E_{G_1}/1 + K_2}$  as a function of  $[H^+]$  at  $\lambda = 500 \text{ m}\mu$  for the determination of  $K_7$ .  $C = 1.052 \times 10^{-6} \text{ M}$  and  $d = 10 \text{ cm}$ .

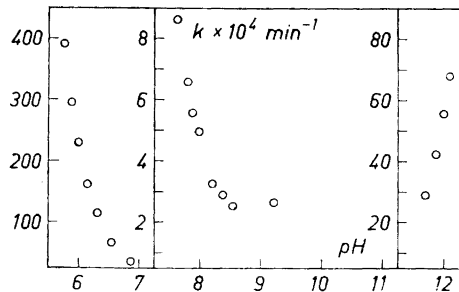


Fig. 5. The velocity "constant"  $k$  as a function of the pH-value of the solution.

In this expression  $k$  is a complex velocity constant according to formula (12)<sup>7</sup>

$$k = \frac{k_2 \cdot [H^+]^2 + k_4 \cdot K_3 \cdot [H^+]}{[H^+]^2 + K_3 \cdot [H^+] + K_3 \cdot K_4} + \frac{k_1 \cdot K_1 \cdot [H^+] + k_3}{1 + K_1 \cdot [H^+]}$$

*Determination of  $k_1$  and  $k_2$ .* In a sufficiently acid region formula (12) may be simplified to formula (13)<sup>7</sup>

$$k = k_1 \cdot \frac{K_1 \cdot [H^+]}{1 + K_1 \cdot [H^+]} + k_2$$

In such a region  $k$  was determined at different  $[H^+]$ -values and the corresponding value of  $k_1$  calculated from the formula where  $k_2 = k_1/K_2$ . The measurements were performed at  $5.7 < \text{pH} < 6.8$ ,  $d = 10 \text{ cm}$ ,  $C = 1.502 \times 10^{-6} \text{ M}$  and  $\lambda = 450 \text{ m}\mu$ .

The  $k_1$ -values obtained obey formula (14)<sup>7</sup>

$$k_1 = k_1^\circ + k_1' \cdot [H^+]$$

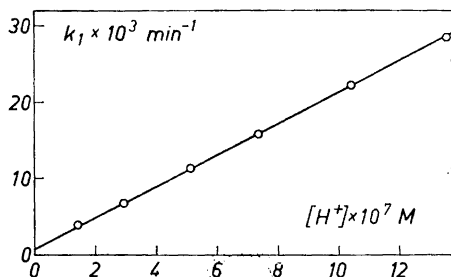


Fig. 6. The velocity "constant"  $k_1$  as a function of  $[H^+]$ .

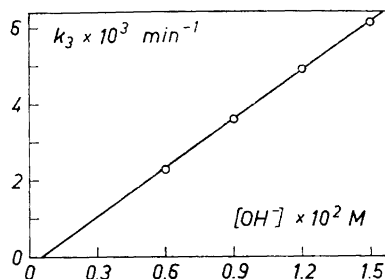


Fig. 7. The velocity "constant"  $k_3$  as a function of  $[OH^-]$ .



which gives a straight line; see Fig. 6. The following values are obtained \*

$$k_1^\circ = 7.5 \times 10^{-4}, k_1' = 2.06 \times 10^4$$

$$k_1 = 7.5 \times 10^{-4} + 2.06 \times 10^4 \cdot [\text{H}^+] \text{ min}^{-1}$$

and as  $k_2 = k_1/K_2$

$$k_2^\circ = 3.8(5) \times 10^{-5}, k_2' = 1.06 \times 10^3$$

$$k_2 = 3.8(5) \times 10^{-5} + 1.06 \times 10^3 \cdot [\text{H}^+] \text{ min}^{-1}$$

*Determination of  $k_3$  and  $k_4$ .* In a sufficiently alkaline region formula (12) may be simplified to formula (15) <sup>7</sup>

$$k = k_4 \cdot \frac{[\text{H}^+]}{[\text{H}^+] + K_4} + k_3$$

From the values of  $k$ , determined in four solutions at  $11.6 < \text{pH} < 12.1$  from measurements of  $E$  at  $\lambda = 564 \text{ m}\mu$ ,  $d = 2 \text{ cm}$  and  $C = 7.52 \times 10^{-6} \text{ M}$ , the corresponding  $k_3$ -values were calculated from the above formula, inserting  $k_4 = k_3 \cdot K_6$  and the approximate value of  $K_4$  determined above. According to formula (16) <sup>7</sup>  $k_3$  is found to be a linear function of  $[\text{OH}^-]$ ; see Fig. 7.

$$k_3 = k_3^\circ + k_3' \cdot [\text{OH}^-]$$

One obtains  $k_3' = 0.42(3)$  from the line. However,  $k_3^\circ$  cannot be determined. As is seen from the figure, various errors cooperate to give a negative value to  $k_3^\circ$ , which is not surprising considering the great uncertainty of the  $K_4$ -value. Thus one obtains

$$k_3 \approx k_3^\circ + 0.42(3) \cdot [\text{OH}^-], \quad k_4 \approx k_4^\circ + 2.2(6) \cdot [\text{OH}^-] \text{ min}^{-1}$$

## RESULTS

### Equilibrium constants

$$K_7 = 1.08 \times 10^{-2}, 1/K_1 = 2.1(9) \times 10^{-8}, K_3 = 2.0 \times 10^{-10}, K_4 \approx 3.9 \times 10^{-11}$$

$$K_2 = 19.(4), \quad K_6 = 5.(3)$$

$$K_1 \cdot K_2 \cdot K_3 \cdot K_6 = 0.96$$

### Velocity constants

Reaction	min <sup>-1</sup>	
	→	←
$\text{G}_1 + \text{H}_2\text{O} \rightleftharpoons \text{F}_1$	$h_1 = 7.5 \times 10^{-4}$	$h_2 = 3.8(5) \times 10^{-5}$
$\text{R} + \text{H}_2\text{O} \rightleftharpoons \text{F}_2$	$h_3$ not calc.	$h_4$ not calc.
$\text{G}_2 + \text{H}_2\text{O} \rightleftharpoons \text{F}_1 + \text{H}^+$	$h_5 = 0.223 \times 10^3$	$h_6 = 1.06 \times 10^3$
$\text{R} + \text{OH}^- \rightleftharpoons \text{F}_3$	$h_7 = 0.42(3)$	$h_8 = 7.1 \times 10^{-4}$

The velocity constants are calculated by means of logarithms with 10 as basis.

\* The values of  $k_1^\circ$  and  $k_2^\circ$  are uncertain; see Fig. 6.

## DISCUSSION

The numerical values of the constants determined show no unexpected effects, but confirm the results of the earlier investigation<sup>7</sup>. From this it is evident that the introduction of a *p*-Cl-atom into the third benzene nucleus has only a slight effect; benzaurin and 4''-chlorobenzaurin differ but little in their constants. A corresponding slight effect can now be seen again by comparing the constants of 3,3'-dimethylbenzaurin with those of 4''-chloro-3,3'-dimethylbenzaurin previously investigated<sup>(6),7</sup>. In both cases the effect of the substitution is strongest as regards  $K_7$ , which is increased by the factors 2.8 and 2.1, respectively.

At the same time the great effects of the methyl groups are again strikingly demonstrated by comparing the results with those of the previous investigation.<sup>7</sup> The introduction of these groups favours the formation of the coloured anhydrous forms in the hydration equilibria. Thus the constant  $K_2$  is decreased by the factors 5.1 and 4.7 when the two methyl groups are introduced into benzaurin and 4''-chlorobenzaurin, respectively, and in the former case  $K_6$  is correspondingly increased by the factor 5.7.\*

The previously mentioned tendency<sup>7</sup> of the methyl groups to increase the electron density of the central carbon atom and to cause a corresponding decrease of the velocity constants of the additions of H<sub>2</sub>O and OH<sup>-</sup>, respectively, is further illustrated by the results. Introducing the methyl groups into benzaurin  $h_1 = k_1^\circ$  is decreased by the factor 7,  $h_5 = k_1 \cdot K_7$  by the factor 6 and  $h_7 = k_3'$  by the factor 4.8; from a corresponding calculation for the 4''-chloro-derivatives the factors 10 and 7.5 are obtained for  $h_1$  and  $h_5$ , respectively.

No doubt, the regularities of the substitution effects make the reactions suggested in the scheme (p. 2156) probable.

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\* In the latter case  $K_6$  is not calculated for 4''-chloro-3,3'-dimethylbenzaurin.