# The Influence of Temperature on the Protolytic Equilibriums and Reaction-Rate Constants of Basic Triphenylmethane Dyes

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The protolytic reaction scheme that was earlier proposed for basic triphenylmethane dyes on the basis of measurements at 20°C in water solutions has now been examined for Methyl Green at 40°C and 60°C. The reaction scheme has proved to be valid at these higher temperatures as well. The dissociation, hydration, and reaction-rate constants have been determined at 20°, 40°, and 60°C. The apparent energies of activation for the slow reactions and the temperature coefficients of the dissociation and hydration constants have been calculated.

The measurements have been carried out spectrophotometrically in water solutions of constant composition and constant ionic strength (0.5 M).

As a continuation of our earlier investigations [1-3] of the protolytic reactions and reaction velocities in water solutions of basic triphenylmethane dyes, we have examined the temperature dependence of the dissociation, hydration, and reaction-rate constants.

The earlier investigations concerning the influence of the temperature on these dyes have only treated the temperature dependence of the reaction rates. They have above all been concerned with the reaction

$$\text{dye ion} + \text{OH}^- \rightleftharpoons \text{carbinol}$$

in alkaline solutions. Biddle and Porter [4], it is true, also examined the corresponding reactions in acid solutions, but they did not take into consideration the complicated protolytic scheme and therefore their rate-constants are complex constants for several simultaneous time-reactions. Furthermore, they were not able to take into account the fact that the temperature influences not only the complex rate-constants but the dissociation and hydration constants as well. A determination of all constants in the protolytic scheme was not published until 1956 by Cigén [1].

For Crystal Violet, Langvad [5] made an attempt in 1950 to determine from the Arrhenius equation the energy of activation for the formation of carbinol in alkaline solutions according to the reaction

$$\diagdown\!\!\underset{\diagup}{-}C^+ + OH^- \rightleftharpoons \diagdown\!\!\underset{\diagup}{-}COH$$
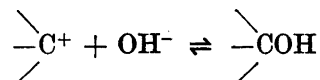
This led Turgeon and LaMer [6] to a careful reinvestigation of the carbinol formation of Crystal Violet as a complement to Hochberg and LaMer's [7] reaction-rate and equilibrium studies of the carbinol formation of triphenylmethane and sulfonphthalein dyes. In order to determine the true energies and entropies of activation Turgeon and LaMer carried out measurements in isocomposition and isodielectric solutions. Unfortunately specific solvent effects turned up in the measurements in isodielectric solutions (mixtures of water — ethanol and water — acetone) which explains why they were not able to verify the relations, deduced by LaMer and Amis [8], between the dielectric constants of solvents and the reaction rates.
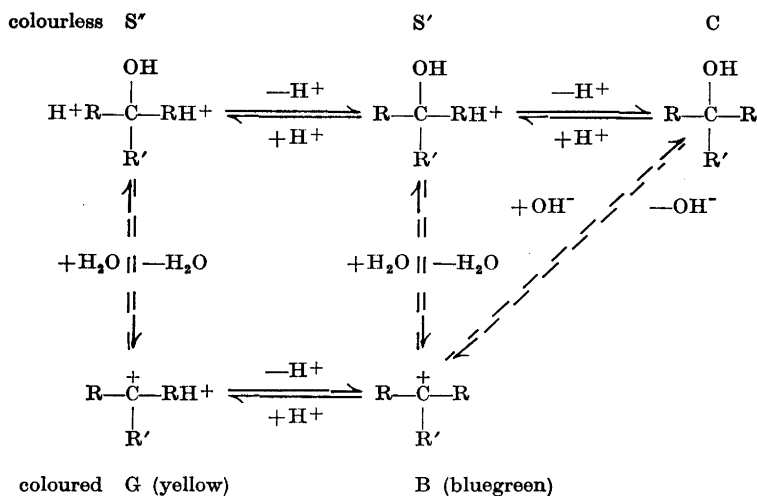
A theoretical treatment of the kinetics of solutions necessitates an extrapolation of the measurements to the ionic strength $\mu = 0$ and the dielectric constant $D = \infty$, as has been shown by Brönsted [9], Christiansen [10], Scatchard [11], LaMer [12] and others, if we want to determine the true energies and entropies of activation and the reaction-rate constants. This leads to experimental difficulties even for quite simple reactions, and for complicated reaction systems it seems at present impossible to determine true thermodynamic quantities in detail.

Owing to the above mentioned difficulties the present investigation has been carried out with solutions of constant composition. The ionic strength was kept constant (0.5 M) in order to keep the activity coefficients of the reacting ions and molecules as constant as possible.

*Methyl Green* $[[(CH_3)_2NC_6H_4]_2\overset{+}{C}C_6H_4\overset{+}{N}(CH_3)_3](ClO_4^-)_2$ was chosen as a representative of the types of dyes investigated. This dye was earlier investigated in detail at 20°C within the pH-range 0—9 [1]. Other investigations of dyes of the same type have led us to feel that Methyl Green could be investigated in detail also at 40° and 60°C even if the pH-range were extended to include the carbinol formation in strong alkaline solutions. If, for the sake of brevity, we write Methyl Green as $\overset{R}{\underset{R}{\diagdown}}\!\!\overset{+}{C}\!\!-R'$, where $R = (CH_3)_2NC_6H_4$ and $R' = (CH_3)_3\overset{+}{N}C_6H_4$, we can schematically indicate the reactions that take place when we change the pH of a solution of Methyl Green in the following manner (*cf.* Refs.[1-3]).

Whole arrows indicate that the reactions proceed with a non-measurable velocity — that is, instantaneously — whereas dashed arrows indicate that the reactions take place with a measurable velocity.

colourless  S″                          S′                          C

$$\text{H}^+\text{R}\underset{\text{R}'}{\overset{\text{OH}}{-\text{C}-}}\text{RH}^+ \underset{+\text{H}^+}{\overset{-\text{H}^+}{\rightleftharpoons}} \text{R}\underset{\text{R}'}{\overset{\text{OH}}{-\text{C}-}}\text{RH}^+ \underset{+\text{H}^+}{\overset{-\text{H}^+}{\rightleftharpoons}} \text{R}\underset{\text{R}'}{\overset{\text{OH}}{-\text{C}-}}\text{R}$$

$+\text{OH}^-$   $-\text{OH}^-$

$+\text{H}_2\text{O} \parallel -\text{H}_2\text{O}$     $+\text{H}_2\text{O} \parallel -\text{H}_2\text{O}$

$$\text{R}\underset{\text{R}'}{\overset{+}{-\text{C}-}}\text{RH}^+ \underset{+\text{H}^+}{\overset{-\text{H}^+}{\rightleftharpoons}} \text{R}\underset{\text{R}'}{\overset{+}{-\text{C}-}}\text{R}$$

coloured  G (yellow)                    B (bluegreen)

The following constants are defined:

$$K_1 = \frac{[\text{G}]}{[\text{B}][\text{H}^+]}, \quad K_2 = \frac{[\text{S}'']_\infty}{[\text{G}]_\infty}, \quad K_3 = \frac{[\text{S}'][\text{H}^+]}{[\text{S}'']}, \quad K_4 = \frac{[\text{C}][\text{H}^+]}{[\text{S}']},$$

$$K_6 = \frac{[\text{B}]_\infty}{[\text{S}']_\infty}$$

$k_1$ = rate constant for the reaction $\text{G} + \text{H}_2\text{O} \rightarrow \text{S}''$
$k_2$ = » » » » » $\text{S}'' \rightarrow \text{H}_2\text{O} + \text{G}$
$k_3$ = » » » » » $\text{B} + \text{H}_2\text{O} \rightarrow \text{S}'$
$k_4$ = » » » » » $\text{S}' \rightarrow \text{B} + \text{H}_2\text{O}$
$k_5$ = » » » » » $\text{B} + \text{OH}^- \rightarrow \text{C}$
$k_6$ = » » » » » $\text{C} \rightarrow \text{B} + \text{OH}^-$

The investigations were carried out spectrophotometrically and therefore the concentrations of the dye are given in most cases in the form of specific extinctions. The following symbols are used:

$\varepsilon_\text{B}$, $\varepsilon_\text{G}$       = the molar extinction coefficient of B and G.
$e_0$, $e_t$, $e_\infty$     = the specific extinction of a solution at the times 0 and $t$ and at equilibrium (thickness of absorbing layer: $d = 1$ cm).
$E_0$, $E_t$, $E_\infty$   = the extinctions for $d \neq 1$ cm.
$e_\text{B}$, $e_\text{G}$       = the specific extinction of a solution containing only B resp. G.
$C_\text{M}$           = the total concentration of dyestuff.

We can derive the following equation for $K_1$ (cf. Refs.[1-2]):

$$K_1 = \frac{e_\text{B} - e_0}{(e_0 - e_\text{G})[\text{H}^+]} \tag{1}$$

which can be transformed to

$$\frac{[H^+]}{e_B - e_0} = [H^+]\frac{1}{e_B - e_G} + \frac{1}{K_1(e_B - e_G)} \tag{2}$$

A plot of $[H^+]/(e_B - e_0)$ against $[H^+]$ gives a straight line. The intercept, $y$, of this line on the $Y$-axis and its slope, $l$, give $e_B - e_G = 1/l$ and $K_1 = l/y$, respectively.

At equilibrium we get the extinction

$$e_\infty = \frac{e_B + K_1[H^+]\cdot e_G}{1 + 1/K_6 + K_4/K_6[H^+] + K_1[H^+](1 + K_2)} \tag{3}$$

For acid solutions, pH $\leq$ 2, (3) gives

$$K_2 = \frac{e_G}{e_\infty} + \frac{e_B - e_\infty(1 + K_1[H^+] + 1/K_6)}{e_\infty \cdot K_1[H^+]} \tag{4}$$

and for weakly alkaline solutions (3) can be written in the approximate form

$$\frac{[H^+]}{e_\infty} = [H^+]\cdot\frac{1 + K_6}{K_6 \cdot e_B} + \frac{K_4}{K_6 \cdot e_B} \tag{5}$$

We get $K_4/K_6$ from (5) and, under certain circumstances, $K_6$ as well if we plot $[H^+]/e_\infty$ against $[H^+]$.

We can derive an expression for $K_3K_4$ in the following way:

$$e_\infty = [B]_\infty \cdot \varepsilon_B + [G]_\infty \cdot \varepsilon_G = [B]_\infty(\varepsilon_B + K_1[H^+]\cdot\varepsilon_G) \tag{6}$$

$$C_M = [B]_\infty + [G]_\infty + [S'']_\infty + [S']_\infty + [C]_\infty$$

$$= [B]_\infty(1 + K_1[H^+] + 1/K_6 + [H^+]/K_3K_6 + K_4/K_6[H^+]) \tag{7}$$

From (6) and (7) we get

$$e_\infty = \frac{e_B + K_1[H^+]\cdot e_G}{1 + 1/K_6 + K_1[H]^+ + [H^+]/K_3K_6 + K_4/K_6[H^+]} \tag{8}$$

since $C_M \cdot \varepsilon_B = e_B$ and $C_M \cdot \varepsilon_G = e_G$. In very weakly acid solutions, pH $\sim$ 5, we can neglect $K_1[H^+]$ in the denominator and $K_1[H^+]\cdot e_G$ in the numerator if we carry out the measurements at a wavelength where $e_G \leq e_B$. After these approximations we differentiate $e_\infty$ with respect to $[H^+]$ and find that $e_\infty$ has a maximum when $[H^+] = \sqrt{K_3K_4}$.

We can deduce the following rate expression for the reactions if we assume that the individual rate constants $k_1$ to $k_4$ in the reaction scheme are independent of pH, which was the case for the dyestuffs investigated earlier. Since the total concentrations, $C_M$, of the dyestuff is very low as compared with the concentrations of the buffer solutions used during the measurements, the reactions are pseudo-unimolecular reactions.

$$k = \frac{1}{t} \ln \frac{e_0 - e_\infty}{e_t - e_\infty} =$$

$$= \frac{k_2[H^+]^2 + k_4 K_3[H^+] + k_6 K_3 K_4}{[H^+]^2 + K_3[H^+] + K_3 K_4} + \frac{k_1 K_1[H^+] + k_3 + k_5[OH^-]}{K_1[H^+] + 1} \qquad (9)$$

where $k$ is the rate constant of the total reactions.

In strong acid solutions, $pH \leq 1$, it is possible to approximate (9) to

$$k = \frac{1}{t} \ln \frac{e_0 - e_\infty}{e_t - e_\infty} = k_1 \cdot \frac{K_1[H^+]}{1 + K_1(H^+]} + k_2 \qquad (10)$$

In strong alkaline solutions we can aproximate (9) to

$$k = k_3 + k_6 + k_5[OH^-] \qquad (11)$$

Between these two extreme approximations we can make a smaller approximation of (9) in the pH-range 4—8.

$$k = \frac{k_4 K_3[H^+]}{[H^+]^2 + K_3[H^+] + K_3 K_4} + k_3 \qquad (12)$$

If we differentiate $k$ with respect to $[H^+]$, we find that $k$ has a maximum when $[H^+] = \sqrt{K_1 K_4}$ — that is, the same expression as was deduced above.

If we measure the extinctions at the time $t = 0$ and at equilibrium and determine the total rate-constants for the slow reactions of a great number of solutions — obtained by mixing a dye stock solution with appropriate buffer solutions — we can determine the constants in the reaction scheme from the equations given above.

The above aproximations depend, of course, on the relative sizes of the constants; in some cases it may be necessary to carry out successive approximations.

## EXPERIMENTAL

*Chemicals und solutions.* A commercial preparations of *Methyl Green* ("Methylgrün" from Merck) was converted into the corresponding perchlorate, which was recrystallized in water to optical constancy; beautiful green needles with a metallic lustre were obtained. Stock solutions were prepared by weighing and dissolving the perchlorate in distilled water. In the stock solutions $C_M$ was $= 4 \times 10^{-5}$ M. Owing to the fact that the walls of glass vessels strongly adsorb the dyestuff, a stock solution should be stored for a week before use. The concentration of the dye in the stock solutions then becomes constant for a few months.

*Hydrochloric acid, sodium acetate, disodium hydrogen phosphate, potassium dihydrogen phosphate, boric acid,* and *sodium hydroxide,* all of analytical grade, were used in the buffer solutions. *Potassium chloride* of analytical grade was added to keep the ionic strength constant (0.5 M).

*Apparatus.* For the spectrophotometric measurements a modified Beckman DU spectrophotometer was used. It was furnished with double, heatisolated, thermostatic systems. The internal system contained the absorbtion cells and was kept at the experimental temperature by pumping water from a thermostat through its walls. The external system was kept at 30°C in the same way. The solutions for measurement were carried

from flasks in a thermostat to the absorption cells either with pipettes, furnished with double mantles through which water from a thermostat was pumped, or with special syringes. These syringes were furnished with mechanical stoppers, making it possible to regulate and reproduce the volume of the syringes to within 0.1 %. Furthermore the syringes were furnished with diverse, heat-isolating covers and were thermostated in a special air thermostat. Separate experiments were carried out to determine the loss of heat that might occur during the few seconds taken to carry the solutions for measurement from a thermostated flask to a thermostated absorption cell. The loss was compensated for by tempering the syringes used to a temperature somewhat above that of the actual investigation. All solutions were thermostated with an accuracy of ±0.01°C, and the temperature inside the absorption-cell house was held constant to within 0.05°C.

The determinations of [H$^+$] were carried out titrimetrically and potentiometrically. For the potentiometric measurements a reference solution (pH = 2) having the composition 0.01 M HCl + 0.49 M KCl was used. In the present paper pH always means -log[H$^+$] and not -log $a_{H^+}$. As electrodes chinhydron and platinum-plate were used for pH < 6 and platinum-black and hydrogen gas for pH>6. The electrolytically produced hydrogen gas was led through a wash-flask with 0.5 M KCl, which was held at the same temperature as the solutions for measurement.

## MEASUREMENTS AND RESULTS

In a water solution of Methyl Green the dye can only be present, for pH > 9, as a single component of those given in the protolytic scheme. At pH > 9 we only need to consider the almost insoluble carbinol. At lower pH-values we get mixtures of three or four components. This gives rise to some complications when we determine the constants as we can not determine $\varepsilon_B$, $\varepsilon_G$ or $e_B$, $e_G$ directly from the measured absorption curves.

We start with a very weakly buffered stock solution (pH ≈ 4.5) of the dye-stuff. In such a solution the concentration of the blue form, B, is 80—90 % of the total dye concentration. The remaining constitutents are distributed among S″, S′, and C. We can neglect [G] as compared with [B], [S′], and [S″]. In such a solution we denote the molar extinction coefficient by $\varepsilon'_B$ and the specific extinction by $e'_B$. From $e'_G/e_G = e'_B/e_B$ and eqn. (2) we can determine $K_1$ by replacing $e_B$ by $e'_B$ and $e_G$ by $e'_G$.

*Determination of $K_1$.* A series of solutions having the composition $x$ M HCl + (0.5 − $x$) M KCl were quickly mixed with an equivalent volume of a dye stock-solution containing 0.5 M KCl. In most cases the mixing was carried out by injecting the thermostated buffer directly into the thermostated absorption cell in the absorption-cell house. The equilibrium B + H$^+$ ⇌ G is reached instantaneously during the mixing, where upon the solution fades owing to the reaction G + H$_2$O ⇌ S″. By determining the fading rate and extrapolating the extinction to $t = 0$, $e_0$ was obtained. The measurements were carried out, as in the following, at the wavelength $\lambda$ = 633 m$\mu$, where the absorption curve for the blue component, B, has a sharp maximum and where G has very little extinction, $\varepsilon_G \ll \varepsilon_B$.

In Fig. 1 [H$^+$]/($e'_B$−$e_0$) is plotted against [H$^+$]. A linear relation is indicated, and from the slopes, $l$, and the intercepts, $y$, on the $y$-axis we can calculate $K_1$ according to eqn. (2). $e'_B$ was determined from measurements on the dye stock-solution. The following results were obtained ($C_M$ = 1 × 10$^{-5}$ M):

**Table 1.** Determination of $e_0$, $e_\infty$, $K_2$, $k$, and $k_1$ at 40° and 60°C in (HCl +KCl) solutions. $\lambda = 633$ m$\mu$.

| [H+] M | 40°C | | | | | 60°C | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $e_0$ | $e_\infty$ | $K_2$ | $k$ min$^{-1}$ | $k_1$ min$^{-1}$ | $e_0$ | $e_\infty$ | $K_2$ | $k$ min$^{-1}$ | $k_1$ min$^{-1}$ |
| 0.10 | 0.276 | 0.0081 | 66.8 | 0.394 | 0.624 | 0.308 | 0.0191 | 32.7 | 1.882 | 3.116 |
| 0.08 | 0.310 | 0.0101 | 66.6 | 0.364 | 0.629 | 0.344 | 0.0238 | 32.5 | 1.713 | 3.100 |
| 0.06 | 0.355 | 0.0134 | 66.3 | 0.322 | 0.629 | 0.391 | 0.0315 | 32.3 | 1.518 | 3.118 |
| 0.05 | 0.384 | 0.0159 | 66.5 | 0.297 | 0.636 | 0.418 | 0.0368 | 32.9 | 1.389 | 3.116 |
| 0.04 | 0.418 | 0.0198 | 66.6 | 0.272 | 0.647 | 0.453 | 0.0458 | 32.6 | 1.239 | 3.109 |
| Mean | | | 66.6 | | 0.633 | | | 32.6 | | 3.11 |

40°C: $e'_B = 0.650$, $y = 0.1092$ M, $l = 1.576$, $e_G = 0.015$, $K_1 = 14.43 \pm$ **0.15 M$^{-1}$.**

60°C: $e'_B = 0.665$, $y = 0.1273$ M, $l = 1.526$, $e_G = 0.010$, $K_1 = 11.99 \pm$ **0.10 M$^{-1}$.**

*Determination of* $K_2$. The dye stock-solution was mixed with suitable HCl + KCl buffers. The solutions were thermostated and the equilibrium extinction, $E_\infty$, was determined in 5 cm absorption cells. From eqn. (4) we can determine $K_2$ only if we know $e_B$ ($\varepsilon_B$). According to later measurements $\varepsilon_B$ was $7.75 \times 10^4$ at 40° and $7.80 \times 10^4$ at 60° in the stock solutions used. $C_M$ was $= 1 \times 10^{-5}$ M and this gives $e_B = 0.775$ at 40° (in this case $C_M$ was
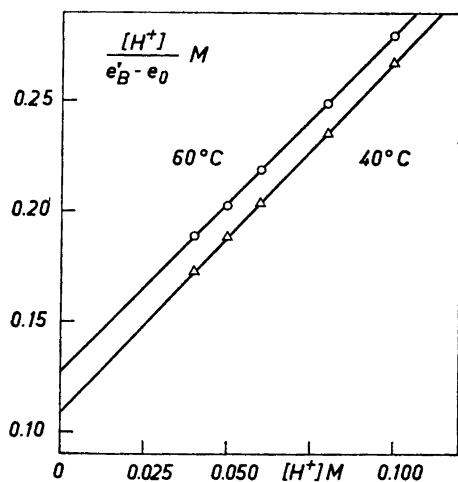


*Fig. 1.* [H+]/($e'_B - e_0$) as a function of [H+] for the determination of $K_1$ at 40° ($\triangle$) and 60° (O). $\lambda = 633$ m$\mu$, $C_M = 1 \times 10^{-5}$ M, $d = 1-2$ cm.
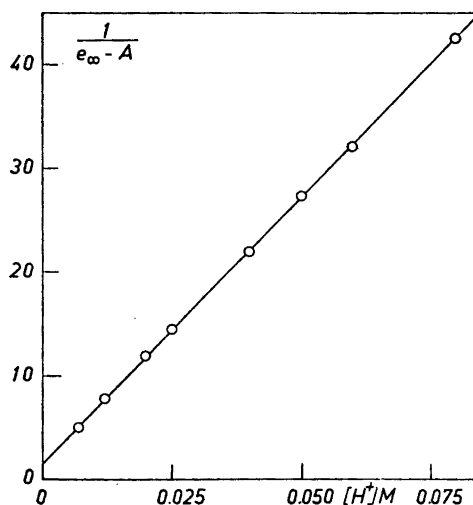
*Fig. 2.* $1/(e_\infty - A)$ as a function of [H+] for the determination of $K_1 + K_1 K_2$ at 60°. $\lambda = 633$ m$\mu$, $C_M = 1 \times 10^{-5}$ M, $d = 2-5$ cm.

$= 0.96 \times 10^{-5}$ M) and $e_{\mathrm{B}} = 0.780$ at 60°. Table 1 gives the $e_\infty$ obtained as well as the calculated $K_2$-values We get the following mean values: $K_2 = \mathbf{66.6} \pm \mathbf{0.6}$ at 40° and $K_2 = \mathbf{32.6} \pm \mathbf{0.3}$ at 60°C.

Because of the high reaction-rates at 60°C the value of $K_1$ may be uncertain For example, at this temperature the reaction $\mathrm{G} + \mathrm{H_2O} \rightleftharpoons \mathrm{S}''$ has a »half-life period» of 22 seconds when $[\mathrm{H^+}] = 0.1$ M. In order to get a further check on $K_1$ we have proceeded as follows. We can write eqn. (4) as

$$\frac{1}{e_\infty - A} = \frac{1 + 1/K_6}{e_{\mathrm{B}}} + [\mathrm{H^+}] \cdot \frac{K_1 + K_1 K_2}{e_{\mathrm{B}}} \qquad (13)$$

where $\quad A = \dfrac{K_1[\mathrm{H^+}] \cdot e_{\mathrm{G}}}{1 + 1/K_6 + [\mathrm{H^+}](K_1 + K_1 K_2)}$

In acid solutions with $[\mathrm{H^+}] \leq K_1$, $A$ is a correction term which at most reaches one per cent of $e_\infty$. In this correction term we can therefore use the values obtained for $K_1$ and $K_2$, even if $K_1$ is a bit uncertain. In Fig. 2 $1/(e_\infty - A)$ is plotted against $[\mathrm{H^+}]$ for $[\mathrm{H^+}] = 0.007 - 0.080$ M. A linear relation is indicated and the slope of the straight line, $l$, gives us $(K_1 + K_1 K_2)/e_{\mathrm{B}}$. From the figure we get $l = 514$ M$^{-1}$ and as $e_{\mathrm{B}} = 0.780$, we get $K_1 + K_1 K_2 = 402$ M$^{-1}$. The above determined $K$-values ($K_1 = 12.0$, $K_2 = 32.6$) give $K_1 + K_1 K_2 = 403$. $K_1 = 12.0$ is therefore correct.

*Determination of $K_4/(K_6 + 1)$.* A dye stock-solution was mixed with a series of phosphate buffers and the equilibrium extinctions were determined. In Fig. 3 $[\mathrm{H^+}]/e_\infty$ is plotted as a function of $[\mathrm{H^+}]$. According to eqn. (5)
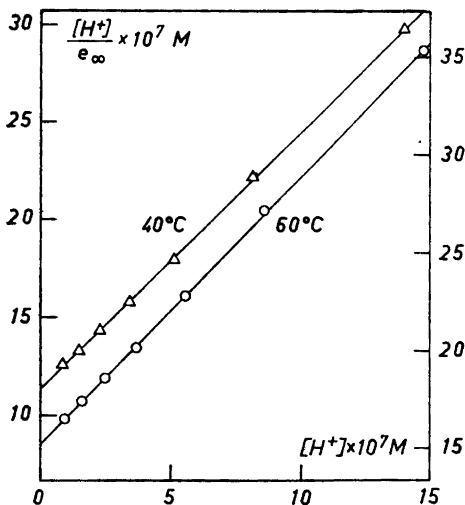


*Fig. 3.* $[\mathrm{H^+}]/e_\infty$ as a function of $[\mathrm{H^+}]$ for the determination of $K_4/(1 + K_6)$ at 40° ($\triangle$, ordinate left) and 60° ($\bigcirc$, ordinate right). $\lambda = 633$ m$\mu$, $C_{\mathrm{M}} = 1 \times 10^{-5}$ M, $d = 1$ cm.

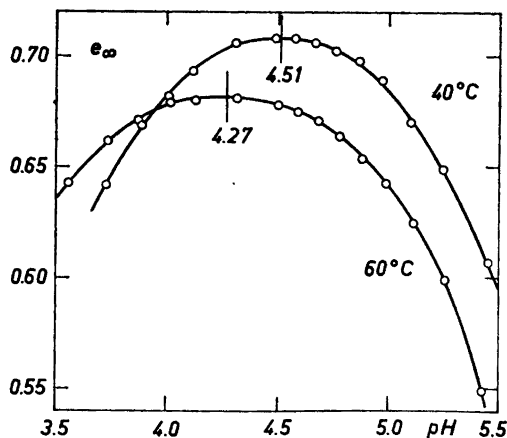*Fig. 4.* $e_\infty$ as a function of pH for the determination of $K_3 K_4$ at 40° (upper curve) and 60°. $\lambda = 633$ m$\mu$, $C_{\mathrm{M}} = 1 \times 10^{-5}$ M, $d = 1$ cm.

*Fig. 5.* $k$ as a function of [OH⁻] for the determination of $k_5$ and $k_3 + k_6$ at 40°. Borate buffers. $\lambda = 633$ m$\mu$, $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm.

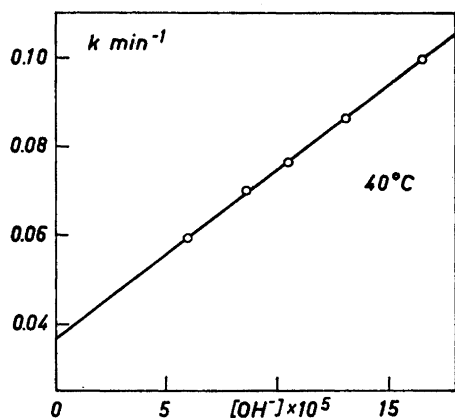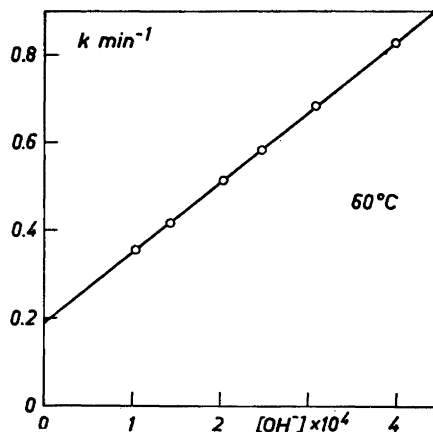*Fig. 6.* $k$ as a function of [OH⁻] for the determination of $k_5$ and $k_3 + k_6$ at 60°. Borate buffers. $\lambda = 633$ m$\mu$. $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm.

we get linear relations; the slopes, $l$, and intercepts, $y$, on the $y$-axis give $K_4/(K_6 + 1) = y/l$ or $K_4/K_6 = y \cdot e_B$. From Fig. 3 we obtain at 40°:

$$y = 1.130 \times 10^{-6} \text{ M}, \quad l = 1.314 \text{ and at } 60°: \quad y = 1.517 \times 10^{-6} \text{ M}, \quad l = 1.367.$$

We can determine $K_4/K_6$ only when we know $e_B$ or $K_6$. We get $K_4/(K_6 + 1) = $ **8.60 $\times$ 10⁻⁷ M** at 40° and **1.110 $\times$ 10⁻⁶ M** at 60°C. In these cases the dye socksolutions used gave, according to later determinations, $e_B = 0.809$ at 40° and $e_B = 0.759$ at 60°C.

*Determination of $K_3K_4$.* The equilibrium extinctions were measured for a series of solutions with Methyl Green in acetate buffers. In Fig. 4 $e_\infty$ is plotted as a function of pH. The maxima of the curve in this figure can bee determined (*cf.* p. 982) and we have

$$e_{\infty\text{max}} \text{ for } [H^+] = \sqrt{K_3 K_4} \tag{14}$$

From Fig. 4 we obtain $e_{\infty\text{max}}$ for pH $= 4.51$, $K_3K_4 = $ **9.55 $\times$ 10⁻¹⁰ M²** at 40° and pH $= 4.27$, $K_3K_4 = $ **2.88 $\times$ 10⁻⁹ M²** at 60°.

The remaining constants in the protolytic scheme can be determined by means of kinetic measurements and eqn. (9).

*Determination of $k_3$, $k_5$, and $k_6$.* In alkaline solutions eqn. (9) is approximated as $k = k_3 + k_6 + k_5[OH^-]$ (11). The fading rate of Methyl Green in borate buffers was determined for different pH-values and in Figs. 5 and 6 $k$ is plotted against [OH⁻]. We get linear relations that, according to eqn. (11), give at 40°C (Fig. 5): $k_5 = $ **382 $\pm$ 3 min⁻¹ M⁻¹**, $k_3 + k_6 = 0.0367 \pm 0.0003$ min⁻¹ and at 60°C (Fig. 6): $k_5 = $ **1 500 $\pm$ 10 min⁻¹ M⁻¹**, $k_3 + k_6 = 0.189 \pm 0.002$ min⁻¹. A check on $k_5$ at 40°C was carried out by kinetic measurement in 0.005
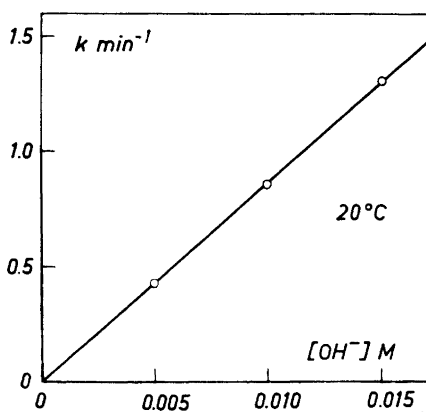
Fig. 7. *k* as a function of [OH⁻] for the determination of $k_5$ at 20° in NaOH + KCl. $\lambda = 633$ m$\mu$, $C_M = 2 \times 10^{-6}$ M, $d = 5$ cm.
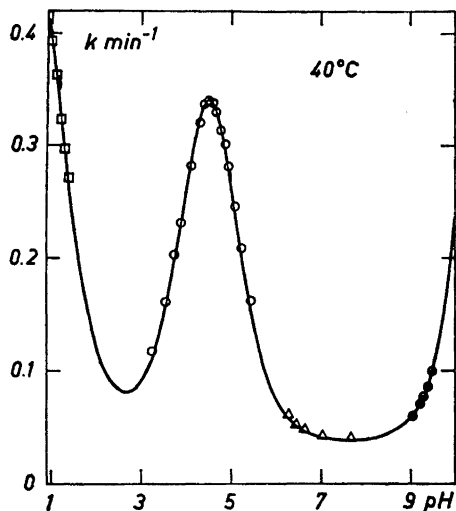
Fig. 8. *k* as a function of pH at 40°. The solid curve has been calculated from eqn (9). The symbols have been determined experimentally by kinetic measurements in HCl+KCl (□), acetate buffers, (O), phosphate buffers (△), and borate buffers (◑).

M NaOH + 0.495 M KCl. The experimental value for *k* (1.97 min⁻¹) is in good agreement with the calculated value (1.95 min⁻¹).

In previous investigations on Methyl Green (Ref.[1]) all constants in the protolytic scheme except $k_5$ and $k_6$ were determined at 20°C. Those measurements have now been completed with kinetic measurements in NaOH + KCl at 20°C. In Fig. 7, *k* is plotted against [OH⁻] and we get $k_5 = \mathbf{86.8 \pm 0.8}$ min⁻¹ M⁻¹ at 20°C. We can not determine $k_3 + k_6$ from the diagram as the straight line passes almost through the origin. However, $k_3$ has previously been determined to be 0.00621 min⁻¹ (in Ref.[1], $k_3 = 0.00270$ since it was calculated by using ¹⁰log). $k_6$ can be calculated in the following way. At equilibrium we have

$$k_5[\text{OH}^-][\text{B}]_\infty = k_6[\text{C}]_\infty \tag{15}$$

But $[\text{H}^+][\text{C}]_\infty = K_4[\text{S}']_\infty$ and $K_6[\text{S}']_\infty = [\text{B}]_\infty$ and therefore

$$k_6 = k_5 K_w K_6 / K_4 \tag{16}$$

From Ref.[1] we have $K_w = 1.24 \times 10^{-14}$ M² and $K_6/K_4 = 1.43 \times 10^6$ M⁻¹ at 20°C and from (16) we get $k_6 = \mathbf{(1.54 \pm 0.06) \times 10^{-6}}$ min⁻¹. Thus $k_6 \ll k_5$ at 20° and the same is true also at 40° and 60°C. Therefore from Fig. 5 we get $k_3 = \mathbf{0.0367 \pm 0.0003}$ min⁻¹ at 40° and from Fig. 6, $k_3 = \mathbf{0.189 \pm 0.002}$ min⁻¹ at 60°C.

*Determination of* $K_3$, $K_4$, $K_6$ *and* $k_4$. These constants can be calculated from eqn. (12), which may be written in the form

$$k = \left( \frac{K_3 K_6 [H^+]}{[H^+]^2 + K_3[H^+] + K_3 K_4} + 1 \right) \cdot k_3 \qquad (17)$$

as $k_3[B]_\infty = k_4[S']_\infty$ and $[B]_\infty = K_6[S']_\infty$, giving $k_4 = k_3 K_6$. We already know $K_3 K_4$, $k_3$, and $K_4/(K_6 + 1)$. From kinetic measurements in acetate buffers we can determine $k$ for a series of different pH-values.

A stock solution of Methyl Green was almost decoloured by dissolving the dyestuff in 0.01 M HCl + 0.49 M KCl. The greater part of the dye was then transformed into colourless S″ owing to the reactions B + H$^+$ + H$_2$O ⇌ G + H$_2$O ⇌ S″. This partially decoloured solution was quickly mixed with suitable acetate buffers and the rate, $k$, was determined. $k$ is the rate at which the blue colour is restored owing to the reactions S″ ⇌ S′ + H$^+$ ⇌ B + H$^+$ + H$_2$O. $k$ was plotted against pH, and then different values of $K_6$ were tried in eqn. (17).

If we fix $K_6$ we can determine $K_3$ and $K_4$. For every value of $K_6$ we get a curve from eqn. (17). The value of $K_6$ was chosen so that the curve calculated from eqn. (17) coincides best with the experimentally found $k$-values.

In Fig. 8 the $k$-values, obtained from measurements in acetate buffers at 40°C (circles), are plotted against pH. The solid curve was calculated from eqn. (9). By magnification of the central part of Fig. 8 we find that a curve drawn through the experimental points has a maximum at pH = 4.51, where $[H^+] = \sqrt{K_3 K_4}$. Thus we get the same value of $K_3 K_4$ from the kinetic measurements as from the extinction equilibrium measurements (Fig. 4). The same agreement was also obtained at 60°C. The results were:

at 40°C: $k_{max} = 0.340$ min$^{-1}$ for pH = 4.51, $K_6 = 16.0 \pm 0.2$, $K_3 = (6.54 \pm 0.10) \times 10^{-5}$ M, $K_4 = (1.46 \pm 0.02) \times 10^{-5}$ M, $k_4 = 0.587 + 0.015$ min$^{-1}$.
at 60°C: $k_{max} = 1.118$ min$^{-1}$ for pH = 4.27, $K_6 = 27.5 \pm 0.3$, $K_3 = (9.13 \pm 0.15) \times 10^{-5}$ M, $K_4 = (3.16 \pm 0.05) \times 10^{-5}$ M, $k_4 = 5.20 \pm 0.10$ min$^{-1}$.

*Determination of* $k_6$. The ionic product of water, $K_w$, was determined by measurements with a platinum-hydrogen gas electrode in solutions of the type $x$ M NaOH + $(0.5 - x)$ M KCl, where $x = 0.01$ and 0.02. $K_w$ was found to be $5.21 \times 10^{-14}$ M$^2$ at 40° and $1.83 \times 10^{-13}$ M$^2$ at 60°C. Then $k_6$ was obtained from $k_6 = k_5 K_w K_6/K_4$. $k_6 = (2.18 \pm 0.06) \times 10^{-5}$ min$^{-1}$ at 40° and $k_6 = (2.39 \pm 0.06) \times 10^{-4}$ min$^{-1}$ at 60°C.

*Determination of* $k_1$ *and* $k_2$. The fading rates of the solutions were measured in the experiments giving the $K_1$-values. In Figs. 9 and 10, $2 + \log(e_t - e_\infty)$ is plotted against the time $t$. From the intercepts on the ordinate axes the $e_0$-values were calculated. The $e_0$-values are tabulated in Table 1, which also contains the complex rate-constants, $k$, and the $k_1$-values calculated from eqn. (9). $k_2$ is obtained from the equations $k_1[G]_\infty = k_2[S'']_\infty$ and $K_2[G]_\infty = [S'']_\infty$, which give $k_2 = k_1/K_2$. The following $k$-values were obtained: $k_1 = 0.633 \pm 0.010$ min$^{-1}$, $k_2 = 0.00950 \pm 0.00020$ min$^{-1}$ at 40° and $k_1 = 3.11 \pm 0.02$ min$^{-1}$, $k_2 = 0.0954 \pm 0.0015$ min$^{-1}$ at 60°C.
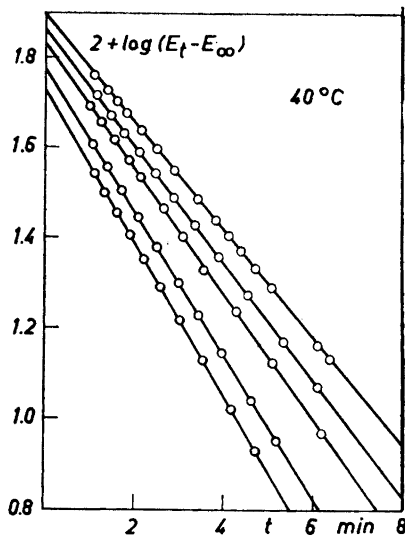
*Fig. 9.* $2 + \log(E_t - E_\infty)$ as a function of $t$ for the determination of $e_0$, $k_1$, and $k_2$ at 40°. From above [H+] = 0.10, 0.08, 0.06, 0.05, and 0.04 M. $\lambda = 633$ m$\mu$, $C_M = 1 \times 10^{-5}$ M, $d = 2$ cm.

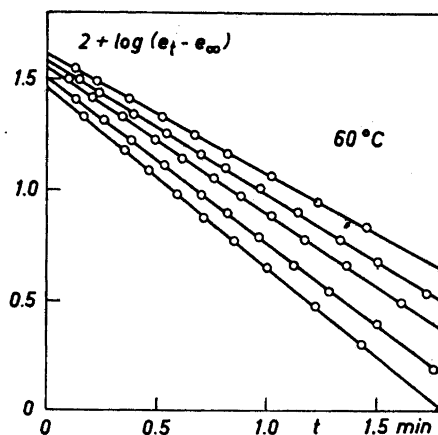*Fig. 10.* $2 + \log(e_t - e_\infty)$ as a function of $t$ for the determination of $e_0$, $k_1$, and $k_2$ at 60°. From above [H+] = 0.10, 0.08, 0.06, 0.05, and 0.04 M. $\lambda = 633$ m$\mu$. $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm.

From Fig. 10 we see that it is possible to carry out careful kinetic measurements by means of a manual recording of the extinctions and times even when the "half-life periods" of the reactions are as short as 20 seconds.

In Fig. 8 the experimentally obtained $k$-values at 40°C are plotted against pH in the pH-interval 1—10. The solid curve was calculated from eqn. (9) by using the values of the constants given above.

Thus all of the constants in the protolytic scheme have been determined. As a check we can use the relation $K_1K_2K_3K_6 = 1$ (by definition). Experimentally we get $K_1K_2K_3K_6 = 0.98$ at 40° and $K_1K_2K_3K_6 = 1.00$ at 60°C. The previous measurements at 20°C gave $K_1K_2K_3K_6 = 1.06$, but the measuring methods and precision have been improved since that time.

At higher temperatures we do not have the same difficulties with the adsorption on the walls of flasks and absorption cells or the precipitation of the almost insoluble carbinol as at 20°C. The most exact measurements were probably carried out at 60°C as the precautions to keep the solutions at the correct temperature in all operations were most rigorous. The reproducibility was very good at 60°C and the greatest uncertainly probably lies in the absolute determination of the temperature inside the absorption-cell house.

A strict, objective error calculation can hardly be performed on such complicated systems as those of the present investigation. The error limits given are therefore based partly on the writer's subjective view gained through many years of work with the same apparatus. The reproducibility of a single

*Table 2.* The temperature influence on the dissociation and hydration constants. $A_K$ = mean temp.coeff./degree.

| Temp. | $K_1$ | $A_{K_1}$ | $K_2$ | $A_{K_2}$ | $K_3 \times 10^5$ | $A_{K_3}$ | $K_4 \times 10^6$ | $A_{K_4}$ | $K_6$ | $A_{K_6}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 20°C | 16.7 | | 132 | | 5.2 | | 6.5 | | 9.3 | |
| 40°C | 14.4 | 0.992 | 66.6 | 0.965 | 6.5 | 1.014 | 14.6 | 1.040 | 16.0 | 1.027 |
| 60°C | 12.0 | | 32.6 | | 9.1 | | 31.6 | | 27.5 | |

*Table 3.* Reaction-rate constants at 20°, 40°, and 60°C and "apparent" energies of activation.

| | | 20°C | 40°C | 60°C | $\triangle E_{40°\text{-}20°}$ kcal | $\triangle E_{60°\text{-}40°}$ kcal |
|---|---|---|---|---|---|---|
| $k_1$ | min$^{-1}$ | 0.124 | 0.633 | 3.11 | 14.9 | 16.5 |
| $k_2 \times 10^3$ | min$^{-1}$ | 0.943 | 9.50 | 95.4 | 21.1 | 23.9 |
| $k_3 \times 10^2$ | min$^{-1}$ | 0.621 | 3.67 | 18.9 | 16.2 | 17.0 |
| $k_4 \times 10^1$ | min$^{-1}$ | 0.575 | 5.87 | 52.0 | 21.2 | 22.6 |
| $k_5$ M$^{-1}$ | min$^{-1}$ | 86.8 | 382 | 1 500 | 13.5 | 14.2 |
| $k_6 \times 10^5$ | min$^{-1}$ | 0.154 | 2.18 | 23.9 | 24.2 | 24.8 |

measurement is in certain cases greater than the absolute accuracy we can obtain through a whole series of measurements.

## DISCUSSION

The protolytic scheme that was previously formulated for basic triphenylmethane dyes on the basis of measurements at 20°C thus proves to be valid even if the temperature is raised up to 60°C. Raising the temperature has the effect of displacing the equilibriums towards the coloured, dehydrated forms. Consequently the values of the rate constants $k_2$, $k_4$, and $k_6$ increase with the temperature considerably more than $k_1$, $k_3$, and $k_5$. The dissociation constants increase with the temperature if they are defined as acid constants — that is, as $K_3$, $K_4$, and $1/K_1$.

In Tables 2 and 3 are given all of the constants obtained at 20°, 40°, and 60°C. We can not calculate true reaction heats, nor can we say how specific solvent effects influence the different constants. The dielectric constant, viscosity, and association of water change with temperature and influence the activity factors in a way that is difficult to calculate for undiluted solutions. We may note that the effect of the temperature on the acid dissociation constants $K_3$ and $1/K_1$ is small — that is, on the average, 0.8 % and 1.4 % per degree, respectively, and somewhat greater for $K_4$, namely 4.0 % per degree, on the average. For the hydration constants $K_2$ and $K_6$ the temperature coefficients are, on the average, 3.6 % and 2 % per degree, respectively, in the interval 20°—60°C. The temperature coefficients $A$ in Table 2 are calculated from $K_{60°} = K_{20°} \cdot A^{40}$. The accuracy of the constants determined hardly permits

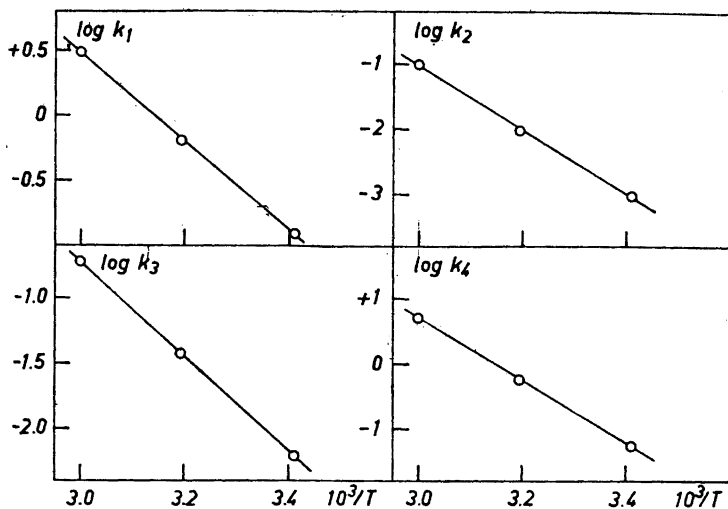Fig. 11. log $k_1$, log $k_2$, log $k_3$, and log $k_4$ plotted against $1/T$.

us to decide whether the temperature coefficients are constant or not within the temperature interval investigated.

The rate constants for 20°, 40°, and 60°C are given in Table 3. We can not determine, in the present investigation, the different contributions to the energy of activation and thereby the true energies and entropies of activation. Therefore, the ''apparent'' energy of activation, $\Delta E$, was only calculated from the Arrhenius equation
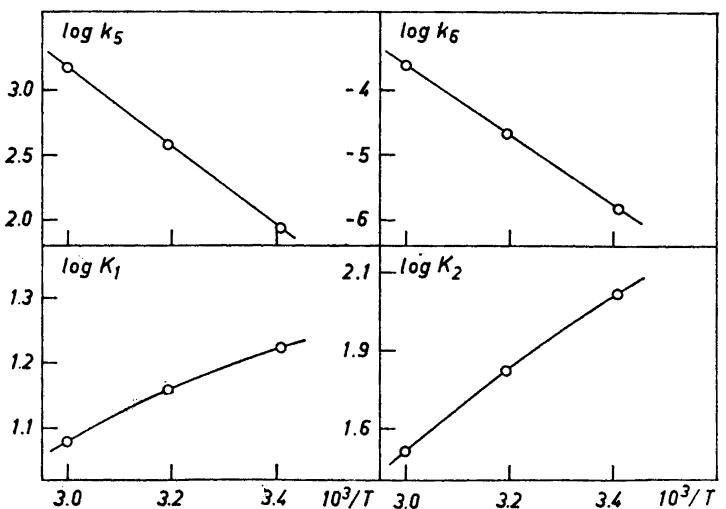


Fig. 12. log $k_5$, log $k_6$, log $K_1$, and log $K_2$ plotted against $1/T$.

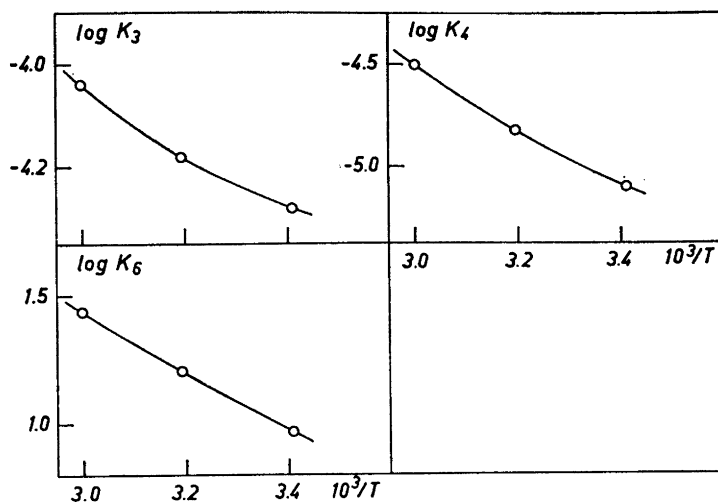*Fig. 13.* log $K_3$, log $K_4$, and log $K_6$ plotted against $1/T$.

$$\ln \frac{k_{T''}}{k_{T'}} = \frac{\Delta E}{R} \left( \frac{T'' - T'}{T'T''} \right)$$

$\Delta E$ is not constant in the interval 20°—60°C. Table 3 contains the $\Delta E$ obtained for the intervals 20°—40°C and 40°—60°C, if it is assumed that $\Delta E$ is constant within each of these intervals.

From the table we see that $\Delta E$ is 0.7—2.7 kcal higher at 50°C than at 30°C.

In Figs. 11—13 log $K$; or log $k$; are plotted against $1/T$. For the rate constants $k_1$ to $k_6$ we get almost straight lines, but in each of the small diagrams the middle point lies somewhat below the indicated straight line. This also shows the difference in $\Delta E$ at 50° and 30°C. For the remaining constants the small diagrams show curved lines.

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