Reaction of *p*-Benzoquinone Monoimines with Benzoylacetanilides

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The kinetics of the reaction of 3-methylbenzoquinone 4-imine with *N*-benzoylacetyl-*m*-methoxycarbonylaniline in aqueous solutions has been investigated spectrophotometrically at 25 °C. The pH was varied from 7·5 to 10·0 and its effect assessed. A reaction scheme is suggested. The specific rate constants have been calculated for each step at different pH values by means of a computer. The calculated values agree with the reaction scheme. The pH-dependence of the specific rate constants shows that in a first step *N*-benzoylacetyl-*m*-methoxycarbonylaniline reacts with the monoimine in its undissociated form, and, secondly, with the product of the first step in a dissociated form.

IN the most important colour-photographic processes the dyes are formed by the coupling of an active methylene or methyne derivative (colour former) with a substituted *p*-benzoquinone di-imine which is the oxidation product of a *NN*-dialkyl-*p*-phenylenediamine, the oxidant being a silver halide.[1,2]

The *p*-benzoquinone di-imines, whose instability increases with increasing pH of the medium, can give rise to side reactions, such as their deamination to *p*-benzoquinone monoimines.[3] These products can react, for instance with benzoylacetanilides, finally giving dyes.[3,4]

The aim of the present paper is to investigate the reaction of 3-methylbenzoquinone 4-imine with *N*-benzoylacetyl-*m*-methoxycarbonylaniline in aqueous alkaline solution from pH 7·5 to 10·0.

EXPERIMENTAL

Quinone Monoimine (*QMI*).—The quinone monoimine investigated was the oxidation product of 4-amino-3-methylphenol. The same imine in the colour photographic process is formed by deamination of the di-imines obtained from three well known colour developers: 4-amino-*N*-ethyl-3-methyl-*N*-(2-methylsulphonylaminoethyl)aniline, 4-amino-*NN*-diethyl-3-methylaniline, and 4-amino-*N*-ethyl-*N*-(2-hydroxyethyl)-3-methylaniline.

The quinone monoimine was prepared directly in the reaction mixture by oxidation of 4-amino-3-methylphenol with potassium ferricyanide.[5]

In order to prevent oxidation by air, freshly crystallized 4-amino-3-methylphenol was dissolved immediately before use in a mixture of air-free water and acetone (3 : 1 v/v).

Colour Former (*CF*).—*N*-Benzoylacetyl-*m*-methoxycarbonyl aniline was prepared from ethyl benzoylacetate and methyl *m*-aminobenzoate in dry xylene[6] and crystallized from ethyl alcohol, and had m.p. 128—130 °C (Found: C, 68·85; H, 5·2; N, 4·7. Calc. for $C_{17}H_{15}NO_4$: C, 69·4; H, 5·05; N, 4·7%).

The solutions were prepared by dissolving colour former in a mixture of borate buffer and acetone (3 : 1 v/v), and were stable at least for a week at room temperature.

Buffer Solutions.—The buffer solutions were prepared by mixing reagent grade borax and HCl or NaOH solutions.[7]

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[1] C. E. K. Mees, 'The Theory of the Photographic Process,' Macmillan, New York, 1969, p. 382.

[2] P. W. Vittum and A. Weissberger, *J. Photographic. Sci.*, 1958, **6**, 157.

[3] L. K. J. Tong, *J. Phys. Chem.*, 1954, **58**, 1090.

[4] J. Eggers, *Mitt. Agfa*, 1958, **2**, 181; 1961, **3**, 72.

[5] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 207.

[6] C. J. Kibler and A. Weissberger, *Org. Synth.*, 1945, **25**, 7.

[7] L. Meites, 'Handbook of Analytical Chemistry,' McGraw-Hill, London, 1965, section 11-7.

The ionic strength of buffers was 0·06M. The pH of the reacting mixture was constant within 0·05 pH unit.

Oxidizing Agent (*OX*).—The oxidizing agent was potassium ferricyanide (reagent grade). The solutions were prepared immediately before use.

Apparatus.—The absorption spectra of the solutions were recorded on a Hitachi EPS 3T spectrophotometer.

Procedure.—The reagents were mixed by successive addition of colour former, 4-amino-3-methylphenol, and ferricyanide to the buffer solution. 4-Amino-3-methyl phenol was oxidized in the presence of colour former, so that deamination of quinone monoimine started simultaneously with the coupling reaction. The experiments were carried out at 25 ± 1 °C. The mixing was made rapidly under red light in order to minimize side reactions due to the action of light.

Data from a typical experiments are in Table 1. They show that the reacting mixture did not contain more than 1% acetone.

TABLE 1

Data for a typical experiment

	$10^3 \times$ Concn. (M)	ml
1 Buffer		47·0
2 Colour former	2·0	1·00
3 4-Amino-3-methylphenol	2·0	1·00
4 Oxidant	8·0	1·00

RESULTS

On mixing quinone monoimine and colour former in stoicheiometric amounts at pH 8·0 the solution becomes red, with an absorption maximum at 500 nm (preliminary experiments showed that without addition of colour former this absorption did not appear).

The optical density (o.d.) at 500 nm (at full development of the colour) increases on increasing the ratio of equivalents of oxidant per mol of 4-amino-3-methylphenol and assumes a constant value when the value of the ratio is >4 (see Figure 1). By considering that the complete oxidation to quinone monoimine requires 2 equiv. of oxidant per mol of 4-amino-3-methylphenol,[5] it seems reasonable to assume the intermediate formation of a leuco by reaction of quinone monoimine with colour former. The reaction of the leuco with 2 equiv. of oxidant gives rise to a dye (R) which is responsible for the absorption at 500 nm. A similar scheme occurs in the reaction of *p*-benzoquinone diimines with colour formers.[8]

The formation rate of the dye R increases by adding an excess of one of the reagents (quinone monoimine or colour former) as shown in Figure 2. Figure 3 shows a series of absorption spectra of a solution containing an excess of quinone monoimine; they were taken at different times from the start of the reaction. The o.d. at 500 nm reaches a maximum and then decreases later. The spectra show an isosbestic point at 418 nm. This suggests that the dye R is transformed into a product whose absorption is displaced toward shorter wavelengths: we will indicate this product as U.

By carrying out the reaction with a ratio [QMI] : [CF] < 1 the absorption spectrum of the solution changes with time as shown in Figure 4. The o.d. at 500 nm increases at first, then decreases with a simultaneous slower increase in the

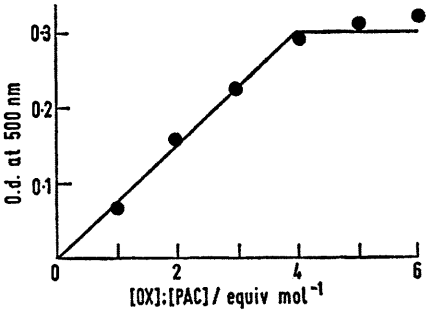

FIGURE 1 Maximum values of o.d. at 500 nm as a function of equivalents of oxidant per mol of 4-amino-3-methylphenol; pH 8·0 $[PAC]_0 = 4{\cdot}0 \times 10^{-5}$M; $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M; 25 °C

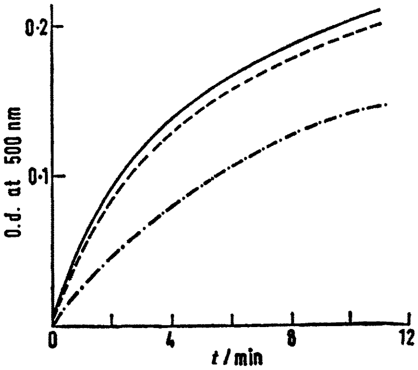

FIGURE 2 Effect of reactant concentrations on formation rate of R at 25 °C; — · — · — $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M, $[PAC]_0 = 4{\cdot}0 \times 10^{-5}$M, $[OX]_0 = 1{\cdot}6 \times 10^{-4}$M; - - - - $[CF]_0 = 1{\cdot}6 \times 10^{-4}$M, $[PAC]_0 = 4{\cdot}0 \times 10^{-5}$M, $[OX]_0 = 1{\cdot}6 \times 10^{-4}$M; —— $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M, $[PAC]_0 = 1{\cdot}6 \times 10^{-4}$M, $[OX]_0 = 4{\cdot}0 \times 10^{-4}$M

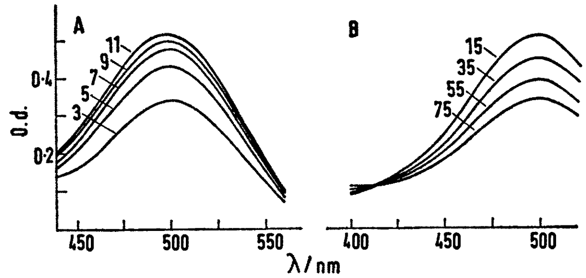

FIGURE 3 Spectra of a reaction mixture at pH 8·0 and 25 °C; $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M, $[PAC]_0 = 3{\cdot}2 \times 10^{-4}$M, $[OX]_0 = 7{\cdot}2 \times 10^{-4}$M, at several times, shown in minutes on the curves

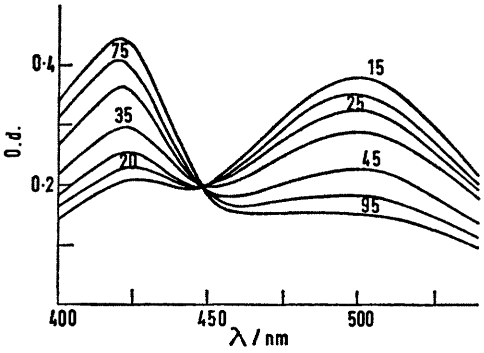

FIGURE 4 Spectra of reaction mixture at pH 8·0 and 25 °C; $[CF]_0 = 3{\cdot}2 \times 10^{-4}$M, $[PAC]_0 = 4{\cdot}0 \times 10^{-5}$M, $[OX]_0 = 1{\cdot}6 \times 10^{-4}$M; spectra were taken after the maximum value of o.d. at 500 nm had been reached; times are shown in minutes on the curves

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[8] L. K. J. Tong and C. Glessman, *J. Amer. Chem. Soc.*, 1957, **79**, 583.

o.d. at 420 nm. There is in the spectra an isosbestic point at 448 nm.

A yellow dye is formed from the red one. We suppose that Y could be formed by reaction (1) of colour former with R. Such an interpretation is in agreement with the

$$\mathrm{R} + \mathrm{CF} \longrightarrow \mathrm{Y} \qquad (1)$$

fact that the formation of Y is slower than that of R (see Figure 4) and that Y is not formed when the ratio quinone monoimine to colour former is greater than 1 in the reacting mixture. This assumption is further supported by the sequence of spectra obtained when quinone monoimine and colour former are in stoicheiometric proportions. Initially there is an increase both in the o.d. due to R as well as to Y; in fact the unchanged colour former can combine both with quinone monoimine and with R. When colour former has reacted completely, the o.d. due to Y assumes a constant value. The concentration of R after the initial increase reaches a constant value when the rate of its formation is equal to the rate of disappearance (owing to the formation of Y and U); then R decreases, because of further formation of U and the exhaustion of colour former.

In another experiment, the addition of an excess of colour former to a reacting mixture having a ratio [QMI] : [CF] > 1, made when the o.d. at 500 nm of the reacting solution reached the maximum (after about 31 min), produces a further increase of the R concentration (owing to excess of quinone monoimine now reacting with the added excess colour former), followed by the formation of Y, not obtained before with [QMI] : [CF] > 1.

Attempts to ascertain by spectrophotometric titration if the formation of Y requires exactly 2 mol of colour former per mol of quinone monoimine failed, because the side reaction gives U. The o.d. at 420 nm increases when the ratio equiv. of oxidizing agent to mol of 4-amino-3-methylphenol increases, becoming constant when the ratio is larger than 6 (see Figure 5). This suggests that the reaction of colour former with R gives another leuco that by oxidation forms a yellow dye. In the following experiments with excess of colour former, 6 equiv. of oxidant per mol of 4-amino-3-methylphenol were used.

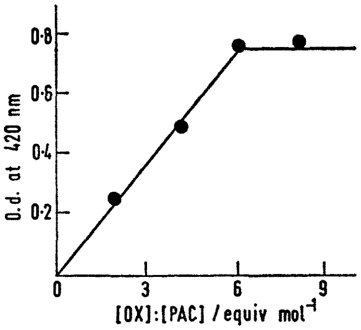


FIGURE 5 Maximum values of o.d. at 420 nm as a function of equiv. of oxidant per mol of 4-amino-3-methylphenol at pH 8·0 and 25 °C; $[\mathrm{CF}]_0 = 3{\cdot}2 \times 10^{-4}$M, $[\mathrm{PAC}]_0 = 4{\cdot}0 \times 10^{-5}$M

Effect of pH.—As shown in Figure 6, the rate of formation of R decreases by increasing pH. The experiments carried out with [QMI] : [CF] > 1 showed that the rate of the reaction R ⟶ U increases with increasing pH.

The spectra of the reacting mixtures at pH > 10·0 did not show a maximum at 500 nm. There was only an increase of the o.d. at 420 nm with time. This suggest that, by increasing the pH of the medium, R becomes more and more unstable because of the increase of the formation rates of Y and U.

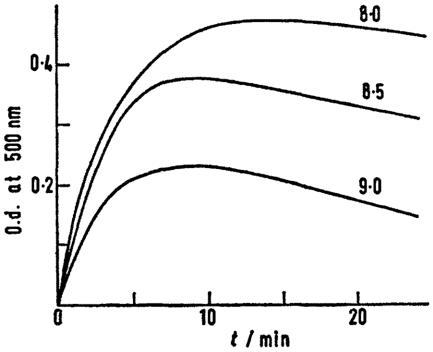


FIGURE 6 The pH effect on formation rate of R. All the experiments were carried out with $[\mathrm{CF}]_0 = 4{\cdot}0 \times 10^{-5}$M, $[\mathrm{PAC}]_0 = 3{\cdot}2 \times 10^{-4}$M, $[\mathrm{OX}]_0 = 7{\cdot}2 \times 10^{-4}$M, at the pH values indicated in figure at 25 °C

The experimental data seem to be consistent with Scheme 1, where Q is the deamination product of the quinone monoimine.

$$\begin{tikzcd}
\mathrm{QMI} + \mathrm{CF} \arrow[r] \arrow[d] & (\mathrm{Leuco})_{\mathrm{R}} \arrow[r, "\mathrm{OX}", "\mathrm{fast}"'] & \mathrm{R} \arrow[r, "\mathrm{CF}"] \arrow[d] & (\mathrm{Leuco})_{\mathrm{Y}} \arrow[r, "\mathrm{OX}", "\mathrm{fast}"'] & \mathrm{Y} \\
\mathrm{Q} & & \mathrm{U} & &
\end{tikzcd}$$

SCHEME 1

The validity of Scheme 1 must be tested quantitatively by computer calculation of the kinetic constant of each step by comparison with the experimental data.

In order to determine the kinetic constant of each step and to test the consistency of the model suggested, one must first calculate the concentration C^t_{ij} of each species i at time t_j according to the suggested model; secondly one must minimize the difference between calculated and experimental data.

Calculation of C^t_{ij}.—An approximate procedure was followed for the resolution of the system of differential equations derived from the kinetic model. The kinetic scheme was separated into a few groups of reactions and it was assumed that, in a short time Δt, each group contributes independently to the variation of the concentration of a single species. Obviously the approximation introduced by this assumption will be better, the lower the number of groups of reactions and the smaller Δt.

After each Δt the initial concentrations of the single species are corrected by adding or subtracting all the variations occurred during Δt, because of the different groups of reactions.

The calculated o.d. are compared with the experimental ones and the unknown parameters (kinetic constants, molar absorptivities) are optimized by successive iterations. These calculations were made with a IBM 360/44 computer.

Evaluations of the Approximate Kinetic Constants and the Molar Absorptivities.—In order to reduce the calculation time, a rough estimation for the kinetic constant of each step as well as the molar absorptivities of R at $\lambda = 500$ nm (ε_R) and Y at $\lambda = 420$ nm (ε_Y) was made. Data on k_Q are available in the literature.[3]

This constant, and all the others, depends on the pH of the solutions. Therefore we will indicate them as $(k_i)_{[H^+]}$. $(k_1)_{[H^+]}$ was evaluated from kinetic experiment on reaction mixtures with [QMI] : [CF] > 1 (in order to minimize the formation of Y). Besides, in order to reduce the effect of the decomposition of R to U, only data from the first few minutes from start of the reaction were used for calculation. Second-order kinetics is assumed and accordingly the function (2) was plotted as function of time,

$$\frac{1}{[QMI]_0 - [CF]_0} \ln \frac{[CF]_0([QMI]_0 - [R])}{[QMI]_0([CF]_0 - [R])} \qquad (2)$$

$$[R] = \frac{\text{o.d.}_{\lambda = 500\ \text{nm}}}{\varepsilon_R} \qquad (3)$$

where [R] is given by equation (3) and ε_R is calculated as below. The linear behaviour showed that (in the experimental conditions) the concentration of R is not appreciably affected by the reaction $R \longrightarrow U$.

An estimate of $(k_2)_{[H^+]}$ was made from o.d. data at 500 nm of reaction mixtures with [QMI] : [CF] > 1 in order to minimize the formation of Y. The o.d. was measured after it has reached its maximum and after it has already started to decrease. The experimental data are in agreement with pseudo first-order kinetics.

In order to estimate the value of $(k_3)_{[H^+]}$ the o.d. data at 420 nm of reaction mixtures with [QMI] : [CF] < 1 were measured. The assumption was made that Y is formed after the R concentration has reached its maximum (this is practically true at lower pH values). Bearing in mind that the reaction $R \longrightarrow U$ is competitive with the reaction $R \longrightarrow Y$, we obtain expression (4) and this was plotted as

$$\log \frac{[R]_0([CF]_0 - [Y])}{[CF]_0([R]_0 - m[Y])} \left(\text{where } m = 1 + \frac{k_2}{k_3[CF]_0}\right) \qquad (4)$$

function of time.[8] ε_R Was evaluated by extrapolating the o.d. data at 500 nm on reaction mixtures with increasing ratios [QMI] : [CF] (at pH 7·5). In these conditions the reaction $R \longrightarrow U$ is slow enough to allow an evaluation of ε_R.

ε_Y Was evaluated at 420 nm by extrapolating the experimental data at pH 9·0 from reaction mixtures containing decreasing ratios [QMI] : [CF]. (Corrections for ferricyanide absorptions at 420 nm were made.) Table 2 collects the estimated values of the molar absorptivities and of the kinetic constants at pH 8·0.

TABLE 2

Estimated values of molar absorptivities and kinetic constants at pH 8·0 and 25 °C

ε_R/l mol^{-1} cm^{-1}	$1{\cdot}4 \times 10^4$ at 500 nm
ε_Y/l mol^{-1} cm^{-1}	$2{\cdot}0 \times 10^4$ at 420 nm
$(k_1)_{[H^+]}$/l mol^{-1} s^{-1}	14
$(k_2)_{[H^+]}$/s^{-1}	$1{\cdot}1 \times 10^{-3}$
$(k_3)_{[H^+]}$/l mol^{-1} s^{-1}	1·0

Optimization of Data.—The problem was to determine the values of the parameters ε_R, ε_Y, k_1, k_2, and k_3 which minimize the function (5), where C^t_{ij} and C^s_{ij} are respectively the calculated and the experimental concentrations of the component i at time j, N is the number of species in the kinetic scheme, their concentration being measured and calculated at times from zero to t_M.

$$S = \sum_{i=1}^{N} \sum_{j=0}^{M} [C^s_{ij} - C^t_{ij}(\varepsilon_R, \varepsilon_Y, k_1, k_2, k_3)]^2 \qquad (5)$$

At first the experimental data and the assumed values of the parameters to be optimized are fed into the computer. The assumed values of the parameters should be correct enough for the optimization procedure, otherwise the optimization procedure could stop at a relative minimum having no physical meaning.

For reaction mixtures with [QMI] : [CF] > 1 Scheme 2 was used.

$$Q \xleftarrow{k_Q} QMI \xrightarrow[+CF]{(k_1)_{[H^+]}} (\text{Leuco})_R \xrightarrow{\text{fast}} R \xrightarrow{(k_2)_{[H^+]}} U$$

SCHEME 2

Three variables had to be calculated, namely ε_R, $(k_1)_{[H^+]}$, and $(k_2)_{[H^+]}$; o.d. data at 500 nm corresponding to runs at different initial concentrations of the quinone monoimine at pH 8·0 were fed into the computer. Figure 7 shows the plot of the experimental curves and the calculated curves at pH 8·0 at three different initial concentrations of quinone monoimine.

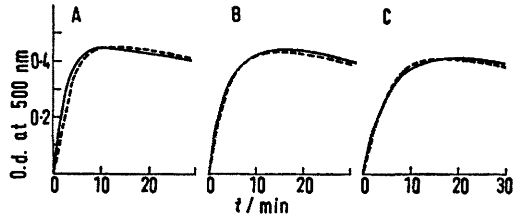
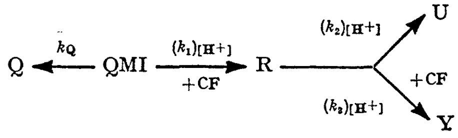


FIGURE 7 Experimental (– – – –) and calculated (——) curves for runs at pH 8·0 and 25 °C; A, $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M, $[PAC]_0 = 3{\cdot}2 \times 10^{-4}$M, $[OX]_0 = 7{\cdot}2 \times 10^{-4}$M; B, $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M, $[PAC]_0 = 2{\cdot}4 \times 10^{-4}$M, $[OX]_0 = 5{\cdot}6 \times 10^{-4}$M; C, $[CF]_0 = 4{\cdot}0 \times 10^{-5}$M, $[PAC]_0 = 1{\cdot}6 \times 10^{-4}$M, $[OX]_0 = 4{\cdot}0 \times 10^{-4}$M

For pH 7·5, 8·5, and 9·0 the calculations were made by assuming the value of ε_R found at pH 8·0 as a constant. For reaction mixtures with [QMI] : [CF] < 1 Scheme 3 was used, and the calculation was made for the o.d. data at 500 nm (account being taken of the absorption of Y) and at 420 nm (account being taken of the absorptions of R and ferricyanide). The only variable parameters were ε_R and $(k_3)_{[H^+]}$ whereas the values of $(k_1)_{[H^+]}$, $(k_2)_{[H^+]}$, and ε_R found in the previous calculations were left constant.



SCHEME 3

The same procedure was followed for the data corresponding to reaction mixtures at pH 7·5, 8·5, and 9·0. But in these cases the only adjustable parameter was $(k_3)_{[H^+]}$, ε_Y being constant (the value was found in the experiment at pH 8·0).

Also the values of $(k_1)_{[H^+]}$ and $(k_3)_{[H^+]}$ at pH 10·0 were calculated from o.d. data at 420 nm.

The other adjustable parameters were fixed. $(k_2)_{[H^+]}$ At this pH was obtained by extrapolation from a plot of log $(k_2)_{[H^+]}$ as a function of pH (see below). The agreement between experimental data and calculated curves can be considered as satisfactory.

DISCUSSION

The values of ε_R, ε_Y, and $(k_i)_{[H^+]}$ found after optimization are given in Table 3. The values of k_Q were taken from the literature.[3]

TABLE 3

Values of $(k_i)_{[H^+]}$ at 25 °C and molar absorptivities found by means of optimization

pH	7·5	8·0	8·5	9·0	10·0
$(k_1)_{[H^+]}$/l mol^{-1} s^{-1}	14·0	15·5	12·2	7·2	2·8
$10^3(k_2)_{[H^+]}$/s^{-1}	0·05	0·15	0·48	1·35	15 *
$(k_3)_{[H^+]}$/l mol^{-1} s^{-1}	0·5	1·9	4·8	9·2	18·8
$10^3(k_Q)_{[H^+]}$/s^{-1}	0·30	0·16	0·14	0·12	0·08
ε_R/l mol^{-1} s^{-1}	1·4 × 10^4 at 500 nm				
ε_Y/l mol^{-1} s^{-1}	2·4 × 10^4 at 420 nm				

* Extrapolated value.

The effect of pH on $(k_i)_{[H^+]}$ can be explained as follows. $(k_1)_{[H^+]}$ decreases with increasing pH. This suggests that the reaction occurs between quinone monoimine and undissociated colour former. A similar behaviour has been found in the coupling reaction of unsubstituted *p*-phenylenediamine with colour formers. From this assumption we obtain equation (6). By

$$k_1 = (k_1)_{[H^+]}(1 + K_{CF}/[H^+]) \qquad (6)$$

measuring the o.d. of colour former (320 nm) at different pH, pK_{CF} was estimated to be 9·14. The best value of k_1 was 15·5 l mol^{-1} s^{-1} (see Figure 8).

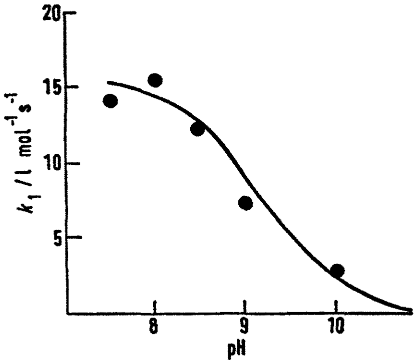


FIGURE 8 Second-order rate constant $(k_1)_{[H^+]}$/l mol^{-1} s^{-1} as a function of pH at 25 °C. The solid curve is calculated from equation (6) and the points are experimental

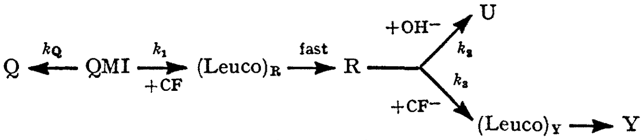
The calculated values log $(k_2)_{[H^+]}$ are a linear function of pH indicating that k_2 is a pseudo-first-order rate constant $k_2 = (k_2)_{[H^+]}/[OH^-]$. Its value is accordingly 1·46 × 10^{-2} l mol^{-1} s^{-1}.

The dependence of the values of $(k_3)_{[H^+]}$ on pH suggests that the reaction R + CF $\longrightarrow$ Y involves the participation of the dissociated form of colour former.

The experimental data support the above assumption giving equation (7). The final scheme of reaction is accordingly as in Scheme 4.

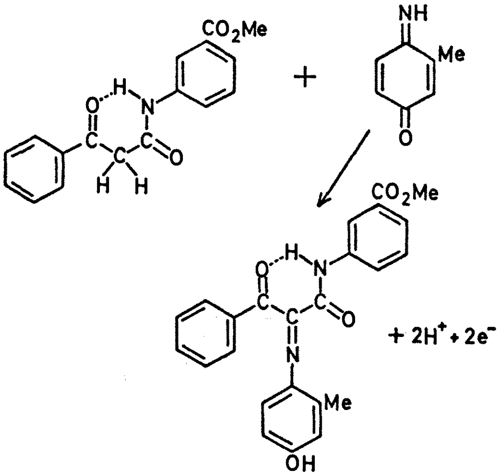
$$k_3 = (k_3)_{[H^+]}(1 + [H^+]/K_{CF}) = 22{\cdot}0 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (7)$$

Taking into account Scheme 4 and the mechanisms suggested in the literature for reactions of this type we

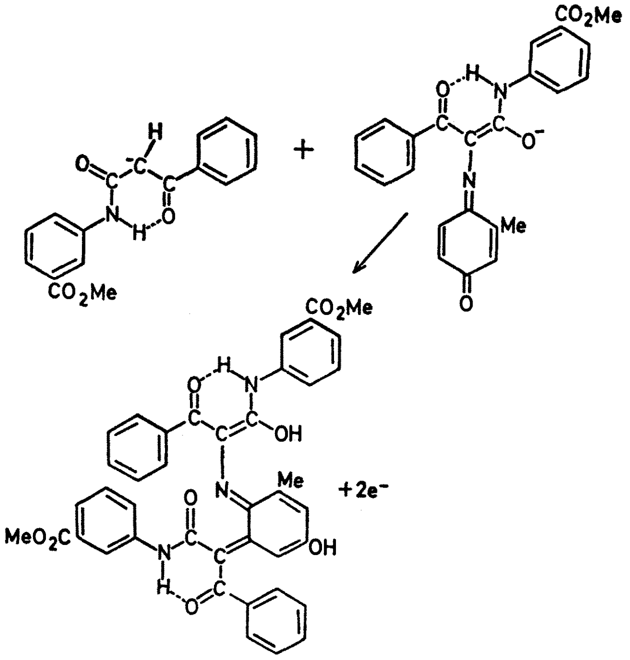


SCHEME 4

can tentatively suggest Scheme 5 for the reaction of formation of R, and Scheme 6 for the formation of Y.



SCHEME 5



SCHEME 6

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