Benzoquinone Imines. Part X.[1] The Mechanism and Kinetics of the Reactions of *p*-Benzoquinone Di-imine and *p*-Benzoquinone Monoimine with *C*-Methoxy-*m*-diamines and *p*-Methoxy- and *p*-Chloro-phenols

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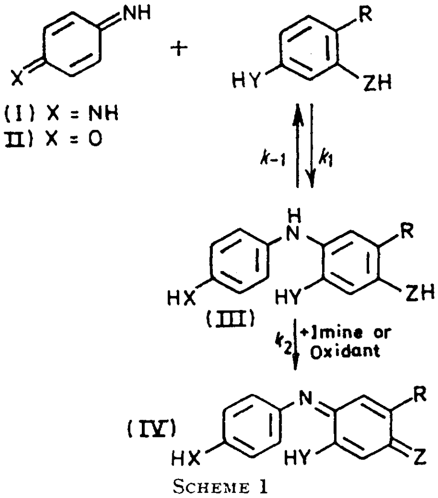
In its reaction with *p*-benzoquinone imines, 2,4-diaminoanisole behaves as a normal 4-equivalent coupler with the rate controlling coupling reaction occurring in the 5-position. The reaction of imines with 1,5-dimethoxybenzene-2,4-diamine or 5-methoxytoluene-2,4-diamine involves initial coupling at both the 1- and 5-positions, followed by elimination of methanol and/or dissociation of the adduct. With monoimine, the coupling step is rate controlling while with di-imine it is rate controlling at only high pH with the elimination step becoming rate controlling at low pH. The reactions of *p*-benzoquinone di-imine with *p*-methoxyphenol and with 4-chloro-2,5-xylenol involve initial, rate controlling, coupling at the 4-position followed by rapid elimination of methanol or hydrogen chloride respectively. The coupling steps have a similar pH dependence to that reported previously for the coupling of *p*-benzoquinone imines with simple *m*-diamine and phenolic couplers.

PREVIOUS parts of this series have dealt with the reactions of *p*-benzoquinone di-imine (I) and monoimine (II) with *m*-diamines,[2,3] phenols,[4,5] and *m*-aminophenols,[1] having at least one vacant position *para* to an electron donor. In each case the reaction follows a two-step mechanism in which the initial reaction of the imine with the coupler is rate controlling and is followed by rapid oxidation of the intermediate diphenylamine (III) by a second molecule of imine or by some other oxidant. This mechanism, shown in Scheme 1, is typical of 4-equivalent couplers.† In every case studied, the kinetics were consistent with the mechanism where $k_2 \gg k_1 \gg k_{-1}$.

Tong and Glesmann[6] have reported on the reaction of *N*-substituted di-imines with 4-methoxy-1-naphthols and phenols, in which dye formation involves elimination of methanol as a second step which is sometimes rate controlling. Since the rate of coupling of the parent imines exhibits a different pH dependence from that of the coupling of *N*-substituted imines it was thought that a study of their reactions with appropriately substituted 2-equivalent couplers † might reveal a change in the rate controlling process as the pH was changed.



SCHEME 1

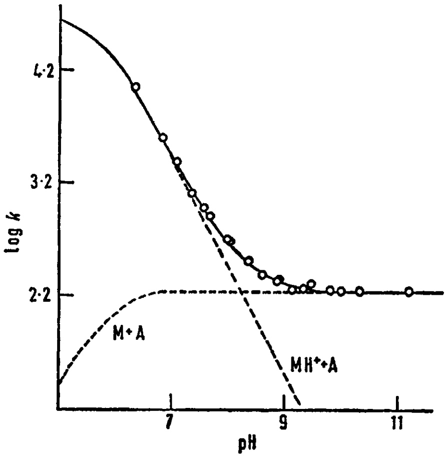


FIGURE 1 The effect of pH on the rate of reaction of *p*-benzoquinone monoimine with 2,4-diaminoanisole, at 30 °C. The full line represents the theoretical curve generated from equation (2) and the broken lines show the contribution of the reactions of the monoimine and of its conjugate acid with the neutral diamine. The open circles represent the experimental data

p-Benzoquinone monoimines have been shown to react with *m*-phenylenediamines to give indo-dyes having the structure (III; Y = Z = NH, X = O).[3] When a mixture of *p*-aminophenol and 2,4-diaminoanisole is oxidized with potassium ferricyanide a dye is formed having a pH-dependent spectrum (Figure 1) similar to, but distinguishable from, that of the dye formed from a similar reaction with *m*-phenylenediamine.[3] This, together with the stoicheiometry of the reaction (Table 1) indicated that reaction occurs at

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† Reactions of benzoquinone imines with couplers are normally carried out by oxidizing a mixture of the corresponding *p*-phenylenediamine or *p*-aminophenol and the coupler. Oxidation of the diamine or aminophenol requires two equivalents of oxidant per mole. Couplers bearing hydrogen at the reactive site react to give a leuco-base which requires a further two equivalents of oxidant for conversion into the dye; such couplers are referred to as 4-equivalent couplers. Couplers bearing a suitable leaving group X give leuco-bases which are converted into the dye by elimination of HX; these are designated 2-equivalent couplers.

[1] Part IX, J. F. Corbett, *J.C.S. Perkin II*, 1972, 539.

[2] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 827.

[3] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 823.

[4] J. F. Corbett, *J. Chem. Soc.* (*B*), 1970, 1418.

[5] J. F. Corbett, *J. Chem. Soc.* (*B*), 1970, 1502.

[6] L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, 1968, **90**, 5164.

the 5-position to give the dye (IV; Y = Z = NH, X = O, R = MeO), in which the methoxy-group is retained. This was confirmed by unequivocal synthesis of the dye by the condensation of 5-chloro-2,4-dinitroanisole with *p*-aminophenol and reduction of the product to 2,4-diamino-4′-hydroxy-5-methoxydiphenylamine. Oxidation of the latter gave a dye which was chromatographically and spectroscopically identical with that obtained above.

TABLE 1

The stoicheiometry of the reaction of *p*-benzoquinone monoimine with 2,4-diaminoanisole at pH 10·0

p-Aminophenol	Pot. ferricyanide	2,4-Diaminoanisole	Final O.D.$_{610}$ (4 cm)	Dye concn. (10^5M)
2·5	5·0	2·5	0·87	1·25
2·5	5·0	5·0	0·87	1·25
5·0	10·0	5·0	1·74	2·5
5·0	10·0	2·5	1·73	2·5
5·0	10·0	2·0	1·38	2·0

Stoicheiometry: [*p*-Aminophenol] : [Ferricyanide] : [Diamine] = 2 : 4 : 1, *i.e.* 2,4-diaminoanisole is a 4-equivalent coupler.

A kinetic study of the reaction was made using either pure *p*-benzoquinone monoimine [7] or *in situ* generation of the monoimine from *p*-aminophenol and potassium ferricyanide. The latter reaction [equation (1)] has previously been shown [8] to give an almost instantaneous and quantitative formation of the monoimine at pH > 7. Owing to the instability of 2,4-diaminoanisole in the presence of ferricyanide, the reaction mixtures were prepared using stoicheiometric amounts of reactants

$$p\text{-Aminophenol} + 2[\mathrm{Fe(CN)_6}]^{3-} \longrightarrow \text{Monoimine} + 2[\mathrm{Fe(CN)_6}]^{4-} \quad (1)$$

(Table 1). Measurements were made over the pH range 6—11·5 and the rate of dye formation was found to follow second-order kinetics throughout this range. This, as before,[3] indicates that coupling of the monoimine with the *m*-diamine is the rate controlling process and is followed by the rapid oxidation of the resulting leuco-dye by a second molecule of the monoimine.

From the data in Table 2, it can be seen that the rate is pH independent in the pH range 9·4—11·2, but increases with decreasing pH in the range 6—9. This is characteristic of a reaction between the neutral monoimine (M) and the neutral *m*-diamine (C) at high pH, and the conjugate acid of the monoimine (MH$^+$) with the neutral *m*-diamine at lower pH. For such a scheme, the effect of pH on the rate is given by equation (2), where k is the observed rate constant, k_a is the specific second-order rate constant for reaction between the neutral species, and k_b that for the reaction of the

$$k = k_a\alpha_M\alpha_C + k_b\alpha_{MH^+}\alpha_C \quad (2)$$

conjugate acid and the *m*-diamine, and α_M, α_{MH^+}, and α_C are the fractions of the reactants existing as the designated species at the pH to which k pertains. Using pK_a values of 3·7 for the monoimine [8] and 5·72 for the *m*-diamine, the best values for k_a and k_b for the data in Table 2 were calculated as $k_a = 1{\cdot}90 \times 10^2$ l mol^{-1} s^{-1} and $k_b = 6{\cdot}3 \times 10^6$ l mol^{-1} s^{-1}. Using these values in equation (2) there is an excellent agreement between the calculated and experimental values (Figure 1) which supports the reaction mechanism proposed in Scheme 1.

TABLE 2

Rate data for the reaction of *p*-benzoquinone monoimine with 2,4-diaminoanisole at 30 °C

pH	10^5[Monoimine] *	k (l mol^{-1} s^{-1})
6·35	5·0 †	$9{\cdot}17 \times 10^3$
6·85	5·0 †	$3{\cdot}25 \times 10^3$
7·08	5·0	$2{\cdot}50 \times 10^3$
7·36	5·0	$1{\cdot}33 \times 10^3$
7·57	5·0	$1{\cdot}00 \times 10^3$
7·70	5·0 †	$8{\cdot}52 \times 10^2$
7·97	5·0	$5{\cdot}45 \times 10^2$
8·05	5·0 †	$5{\cdot}40 \times 10^2$
8·33	5·0	$3{\cdot}33 \times 10^2$
8·58	5·0	$2{\cdot}57 \times 10^2$
8·86	20·0	$2{\cdot}22 \times 10^2$
8·90	5·0	$2{\cdot}22 \times 10^2$
9·11	10·0	$1{\cdot}90 \times 10^2$
9·35	5·0	$1{\cdot}93 \times 10^2$
9·81	20·0	$1{\cdot}87 \times 10^2$
9·98	5·0	$1{\cdot}83 \times 10^2$
10·32	5·0	$1{\cdot}90 \times 10^2$
11·20	5·0	$1{\cdot}93 \times 10^2$

* [Monoimine] = 2[2,4-diaminosole]. † Using pure monoimine, others using *p*-aminophenol and 2 molar proportions of ferricyanide.

The reaction of *p*-benzoquinone monoimine with 2,4-diamino-1,5-dimethoxybenzene was found to yield *N*′-(*p*-hydroxyphenyl)-2-amino-5-methoxy-*p*-benzoquinone di-imine (VI), *i.e.* the same product as that produced by the reaction of the monoimine with 2,4-diaminoanisole. The former reaction thus involves the displacement of a methoxy-group, and the elimination of methanol becomes the second step of the reaction, instead of oxidation. This is supported by the results of a study of the stoicheiometry (Table 3) which indicate that the diamine is a 2-equivalent coupler—equations (3) and (4).

$$\text{Monoimine} + m\text{-Diamine} \xrightarrow{-\mathrm{MeOH}} \text{Indo-dye} \quad (3)$$

$$p\text{-Aminophenol} + m\text{-Diamine} + 2[\mathrm{Fe(CN)_6}]^{3-} \xrightarrow{-\mathrm{MeOH}} \text{Indo-dye} + 2[\mathrm{Fe(CN)_6}]^{4-} \quad (4)$$

TABLE 3

The stoicheiometry of the reaction of *p*-benzoquinone monoimine with 4,6-dimethoxybenzene-1,3-diamine

Reactant concentrations (10^5M)			Final	
p-Aminophenol	Pot. ferricyanide	*m*-Diamine	O.D.$_{610}$ (4 cm)	Dye concn. (10^5M)
2·5	5·0	2·5	1·74	2·5
2·5	5·0	5·0	1·75	2·5
5·0	10·0	5·0	3·5	5·0
2·5	5·0	1·25	0·87	1·25

Stoicheiometry: [*p*-Aminophenol] : [Ferricyanide] : [Diamine] = 1 : 2 : 1, *i.e.* the diamine is a 2-equivalent coupler.

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[7] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 213.

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

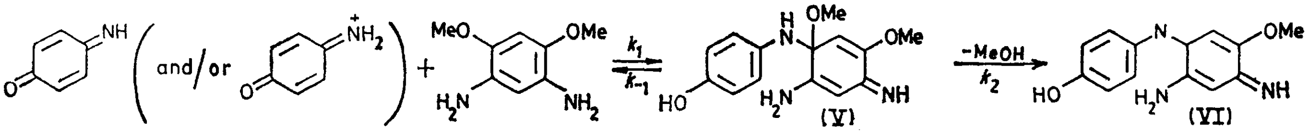
Kinetic experiments, over the pH range 6·5—12·5, using stoicheiometric amounts of reactants, showed that dye formation follows second-order kinetics. This indicates that the elimination of methanol from the intermediate is fast compared with the rate of coupling over the whole of this pH range. However, examination of the effect of pH on the rate of dye formation (Table 4) shows that it does not follow the simple form observed for the reaction of monoimine with 2,4-diaminoanisole. Thus, while at pH > 11·2, the rate is independent of pH, the rate then decreases with decreasing pH, passing through a minimum at pH *ca.* 9 and then increases with decreasing pH in the pH range 5·5—9·5.

TABLE 4

Rate data for the reaction of *p*-benzoquinone monoimine with 4,6-dimethoxybenzene-1,3-diamine at 30 °C

pH	10^5[Monoimine] *	k_0 (l mol^{-1} s^{-1})
12·50	5·0	$3{\cdot}63 \times 10^3$
11·30	2·5	$3{\cdot}63 \times 10^3$
11·12	5·0	$3{\cdot}18 \times 10^3$
10·14	2·5	$2{\cdot}28 \times 10^3$
10·00	2·5	$1{\cdot}70 \times 10^3$
9·50	2·5	$1{\cdot}43 \times 10^3$
9·35	2·5	$1{\cdot}45 \times 10^3$
9·16	2·5	$1{\cdot}38 \times 10^3$
8·95	2·5	$1{\cdot}70 \times 10^3$
8·82	2·5	$1{\cdot}82 \times 10^3$
8·26	2·5	$2{\cdot}67 \times 10^3$
7·73	2·5	$3{\cdot}07 \times 10^3$
7·30	2·5 †	$5{\cdot}35 \times 10^3$
6·80	2·5 †	$1{\cdot}45 \times 10^3$
5·50	2·5 †	$>5 \times 10^4$

* [Monoimine] = [*m*-Diamine]. † Using pure monoimine. Others used *p*-aminophenol with 2 molar proportions of ferricyanide.



SCHEME 2

The observations can be explained by considering the mechanism shown in Scheme 2. Thus, at high pH (>9), while coupling of the neutral monoimine with the neutral *m*-diamine, to give the pseudo quinone-imine (V), is the major rate-controlling factor, a further factor is superimposed by the effect of pH on the rate of dissociation of (V) and/or the rate of elimination of methanol, *i.e.* on the ratio k_2/k_{-1}. If we consider the general form shown in equation (5), and assume a steady state for [C], we get equation (6) and, since d[D]/d*t* =

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow{k_2} D \qquad (5)$$

$$d[C]/dt = k_1[A][B] - (k_{-1} + k_2)[C] = 0 \qquad (6)$$

whence

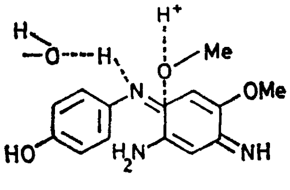
$$[C] = \{k_1/(k_{-1} + k_2)\}[A][B]$$

$$d[D]/dt = \{k_1k_2/(k_{-1} + k_2)\}[A][B] \qquad (7)$$

k_2[C] we get equation (7). Thus, the observed rate constant k_0 is given by equation (8). By analogy with

$$k_0 = k_1k_2/(k_{-1} + k_2) \qquad (8)$$

the reaction of monoimine with other *m*-diamines,[3] we would expect k_1 to be independent of pH over the pH range 9—12·5. Thus, the observed decrease in k_0 must be due to an increase in k_{-1} and/or a decrease in k_2 with decreasing pH. Tong and Glesmann[6] found that the elimination step in the reaction of certain quinone di-imines with a complex naphthol derivative was pH independent, and postulated a concerted mechanism for this elimination which, in the present case would be represented by the transition state (VII). Thus, we are left with k_{-1} as the only pH dependent term on the right hand side of equation (8). This relates to the dissociation of the adduct (V) which would be expected to be stabilized in the anionic form. In this case, k_{-1} would change with pH in accordance with the ionic concentration of (VIII), and will become pH independent below the pH which is two units below the pK_a of (V). Since the adduct (V) is phenolic, it would be expected to have a pK_a of *ca.* 9·5 and, since below a pH of 8 reaction between the conjugate acid of the monoimine and the neutral *m*-diamine would become significant, k_2 and thus k_0 would be expected to undergo the observed increase with decreasing pH.



(VII)

Since neither k_{-1} nor k_2 could be measured experimentally, a model system was devised in which the pK_a of (V) was given the value 9·5, k_2 was assigned a value of $1{\cdot}67 \times 10^4$ s^{-1}, so that $k_2/k_1 > 10^{-3}$ over the whole pH range,‡ and k_{-1} was assigned a value $4{\cdot}67 \times 10^4$ s^{-1}, so that k_0 would have the experimental minimum value of $\sim 1{\cdot}3 \times 10^3$ l mol^{-1} s^{-1} at pH = 9. The value

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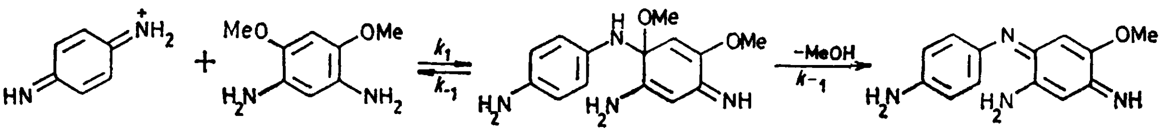
‡ It can be shown (J. F. Corbett, *J. Chem. Educ.*, in the press) that for the rate of product formation from a bi-uni reaction with stoicheiometric reactant concentrations to exhibit second-order kinetics, the ratio k_2/k_1 must be greater than 70*a*, where *a* is the initial reactant concentration. For the present case, where *a* *ca.* $2{\cdot}5 \times 10^{-5}$M we get $k_2/k_1 > 10^{-3}$. Furthermore, it can be shown that such reactions exhibit second-order kinetics, over the range 40—80% reaction provided that $k_2/k_1 > 10^{-4}$. Similarly, for such reactions to exhibit first-order kinetics throughout, k_2/k_1 must be less than $3{\cdot}5 \times 10^{-7}$ and for them to exhibit first-order kinetics over the range 40—80%, k_2/k_1 must be less than 10^{-6}.

of k_1 was calculated from equation (2) using the experimental value $k_a = 3{\cdot}67 \times 10^3$ l mol s^{-1}, and a value $k_b = 1{\cdot}0 \times 10^8$ l mol^{-1} s^{-1}, to give the best fit at lower pH values while giving a ratio k_b/k_a of the same order of magnitude as that for the reaction with 2,4-diaminoanisole. The pK_a of the diamine is 5·80. The derived values of k_0 are shown in Table 5 and can be seen, from Figure 2, to exhibit a similar pH dependence to that observed experimentally. Thus supporting the mechanism shown in Scheme 2.



(VIII)

SCHEME 3

TABLE 5

Rate/pH profile for the model system of equation (5)

pH	$10^{-3}k_1$ *	$10^{-4}k_2$	$10^{-4}k_{-1}$ †	$10^{-3}k_0$ ‡
12	3·67	1·67		3·67
11	3·67	1·67		3·67
10	3·67	1·67	1·17	2·17
9	4·17	1·67	3·50	1·33
8	8·67	1·67	4·50	2·33
7	48·3	1·67	4·67	12·7
6	250·0	1·67	4·67	65·0
5	470·0	1·67	4·67	123·0

* $k_1 = k_a\alpha_A\alpha_B + k_b\alpha_{AH^+}\alpha_B$, where $k_a = 3{\cdot}67 \times 10^{-3}$ l mol^{-1} s^{-1}, $k_b = 1{\cdot}0 \times 10^8$ l mol^{-1} s^{-1}, p$K_{AH^+} = 3{\cdot}7$, and p$K_{BH^+} = 5{\cdot}8$. † $k_{-1} = k'_{-1}\alpha_{CH}$ where $k'_{-1} = 4{\cdot}67 \times 10^4$ s^{-1} and p$K_{CH} = 9{\cdot}5$. ‡ Calculated according to equation (8).

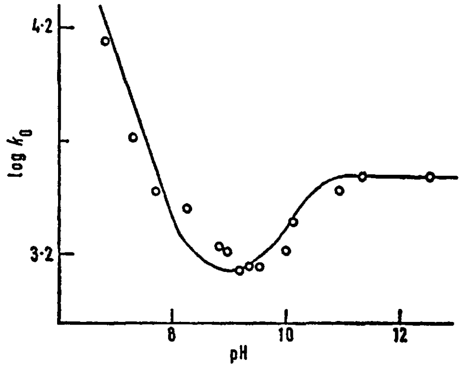


FIGURE 2 Comparison of the experimentally determined rate data (open circles) and the theoretically generated curve from Table 5, for the reaction of p-benzoquinone monoimine with 4,6-dimethoxybenzene-1,3-diamine at 30 °C

It has been shown previously that p-benzoquinone di-imines react with m-diamines to give the aminoindamine dyes.[2] This has now been shown to be true for 2,4-diaminoanisole, which reacts with p-benzoquinone di-imine to give 2-amino-5-methoxyindamine (Table 6), behaving as a normal 4-equivalent coupler (Scheme 1, where X = Y = Z = NH, and R = OMe). The structure of the dye was proved by unequivocal synthesis from 5-methoxy-2,4-dinitrochlorobenzene and p-phenylenediamine.

Kinetic studies showed the rate of reaction between the di-imine and 2,4-diaminoanisole to be first order with respect to both reactants, with the rate of formation of product following the second order rate law. The pH dependence is indicative of the rate-controlling step involving electrophilic attack of the conjugate acid of the di-imine (DH^+) on the neutral m-diamine (C) (Table 7). From this it follows that the observed rate constant, k_0, is given by equation (9) where k_a is the specific second-order rate constant for the reaction

TABLE 6

The stoicheiometry of the reaction of p-benzoquinone di-imine with 2,4-diaminoanisole (A) and 4,6-dimethoxybenzene-1,3-diamine (B) at pH 8

Reactant concentrations (10^5M)		Final dye concn. (10^5M) from	
Di-imine	m-Diamine	A	B
10·0	10·0	5·0	10·0
10·0	5·0	5·0	5·0
5·0	10·0	2·5	5·0

TABLE 7

Rate data for the reaction of p-benzoquinone di-imine with 2,4-diaminoanisole * at 30 °C

pH (±0·01)	10^5[Di-imine] † (M)	k_0 (l mol^{-1} s^{-1})	10^6k_a ($k_0/10^8\alpha_{DH^+}$)
10·00	10·0	$2{\cdot}78 \times 10^2$	4·95
8·99	10·0	$2{\cdot}87 \times 10^3$	5·00
8·99	5·0	$2{\cdot}80 \times 10^3$	4·87
8·74	5·0	$4{\cdot}43 \times 10^3$	4·40
8·51	5·0	$1{\cdot}00 \times 10^4$	5·77
8·02	2·5	$2{\cdot}67 \times 10^4$	5·00

* [2,4-Diaminoanisole] = 2[Di-imine]. † Generated *in situ* from p-phenylenediamine and 2 molar proportions of ferricyanide.

$$k_0 = k_a\alpha_{DH^+}\alpha_C \qquad (9)$$

of DH^+ with C, and the α values are the fraction of the reactants existing as the designated ionic species at the pH to which k_0 pertains. Using the data in Table 7 and pK_a values for the di-imine[8] and 2,4-diaminoanisole of 5·75 and 5·72, respectively, k_a was found to have the value $5{\cdot}0 \times 10^6$ l mol^{-1} s^{-1}.

Studies of the reaction of p-benzoquinone di-imine with 2,4-diamino-1,5-dimethoxybenzene showed the latter to behave as a 2-equivalent coupler (Table 6) in forming 2-amino-5-methoxyindamine (IX). Thus, the reaction involves displacement of a methoxy-group, presumably in the second step.

Kinetic studies of the reaction (Table 8) show that while at pH > 9·5 the formation of dye follows a second-order kinetic law, at pH < 8·5 it follows first-order kinetics. From the pH dependence of the rate, in the pH range 9·5—11·0, it is evident that the rate-controlling step (Scheme 3) involves reaction of the conjugate acid of the di-imine with the neutral *m*-diamine. Thus, the observed rate constant is given by equation (9) where $k_a = 1{\cdot}58 \times 10^8$ l mol^{-1} s^{-1}. At the lower pH range, the coupling reaction will be very rapid—from equation (9) we get $t_{\frac{1}{2}} < 0{\cdot}02$ s at pH $< 8{\cdot}5$—and it is evident that the elimination of methanol from the intermediate (VIII) is the rate-controlling step. Furthermore, it can be seen from Table 8 that this step is pH independent, at least over the pH range 7·7—8·3. The fact that the rate data, over the pH range 9·5—11, fits equation (9) suggests that, in this case, $k_2 \gg k_{-1}$ and thus that k_0 is the true second-order rate constant for the coupling reaction, *i.e.* $k_0 = k_1$.

TABLE 8

Rate data for the reaction of *p*-benzoquinone di-imine with 4,6-dimethoxybenzene-1,3-diamine at 30 °C

pH (±0·01)	Reactant Concn.* (10^5M)	Reaction times (s) 50%	75%	87·5%	k_2 (s^{-1})	k_1 (l mol^{-1} s^{-1})
10·96	10·0	10	30·5	71		$1{\cdot}0 \times 10^3$
10·72	10·0	5·6	17	40		$1{\cdot}8 \times 10^3$
9·92	2·5	4·2	12·2	27		$1{\cdot}0 \times 10^4$
9·62	10·0		1·5	3·4		$2{\cdot}0 \times 10^4$
9·42	2·5	1·0	2·6	4·8		
8·90	2·5	0·6	1·5	3·0		
8·24	2·5	0·9	1·9	2·8	0·760	
7·74	2·5	0·9	1·8	2·8	0·760	

* $[\text{Di-imine}]_0 = [m\text{-Diamine}]_0$.

TABLE 9

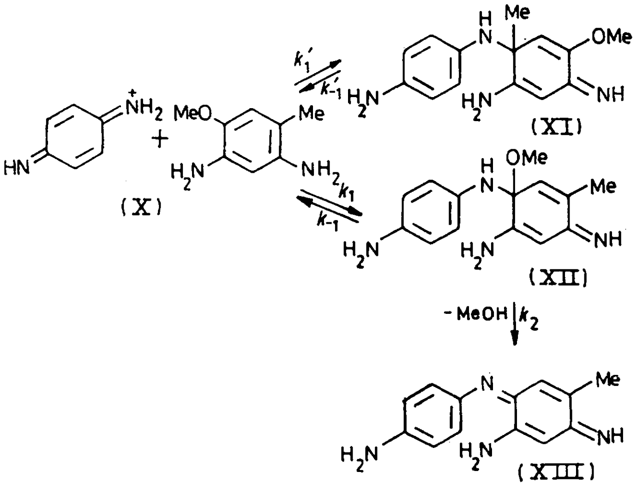
Rate data for the reaction of *p*-benzoquinone di-imine with 5-methoxytoluene-2,4-diamine at 30 °C

Expt.	pH (±0·01)	[Di-imine] (10^4M)	[*m*-Diamine] (10^4M)	Reaction times (s)* 25%	50%	75%	87·5%	Kinetic order
1	11·20	2·0	2·0	54	163	490		2nd
2	10·85	2·0	2·0	25	72	220	520	2nd
3	10·87	1·0	1·0	53	160	475		2nd
4	10·24	2·0	2·0	12	32	78	125	Mixed
5	9·53	1·0	1·0	22	60	130	210	Mixed
6	8·68	1·0	1·0	43·5	134	300	460	‡
7	8·60	1·0	2·0	40	103	200	294	1st
8	8·58	1·0	3·0	40	105	205	305	1st
9	8·48	1·0	4·0	42	105	205	304	1st
10	8·10	2·0 †	2·0	50	124	240		‡
11	7·15	2·0 †	2·0	32	80	180		‡
12	5·90	2·0 †	2·0	19	61	160		‡

* Based on quantitative formation of dye. † Using pure di-imine, others used *p*-diamine with two molar proportions of ferricyanide. ‡ First-order for *ca.* 84% dye formation followed by slow formation of the remaining 16% of dye.

The reaction of *p*-benzoquinone di-imine with 2,4-diamino-5-methoxytoluene (X) gives 2-amino-5-methylindamine (XIII), and the stoicheiometry of the reaction indicates that the diamine (X) is a 2-equivalent coupler. Since this diamine is less reactive than 4,6-dimethoxybenzene-1,3-diamine it was possible to make a more detailed study of the rate of formation of the dye (XIII).

Kinetic data are given in Table 9. From the data for experiments 1—3, it can be seen that dye formation follows second-order kinetics and that the pH dependence is consistent with an initial rate-controlling step involving the conjugate acid of the di-imine and the neutral *m*-diamine. Experiments 7—9 show that, at pH *ca.* 8·5, dye formation follows first-order kinetics and the rate is independent of *m*-diamine concentration, indicating that elimination of methanol from the intermediate (XII) is the slow step. However, the situation is further complicated by consideration of experiment 6, where stoicheiometric quantities of reactants are used. Under these circumstances, the rate of dye formation is considerably slower beyond 25% reaction, than when an excess of *m*-diamine is used. Examination of the rate plot shows a sharp break at *ca.* 85% reaction and it appears that a second intermediate, which can ultimately be converted into dye, is formed in the fast step. In a study of the reaction of di-imine with 2-methyl-5-aminophenol,[1] it was necessary to postulate the reversible formation of an adduct formed by coupling of the di-imine at the methylated carbon. The formation of a similar adduct (XI) in the present case would account for the observed deviation. Thus, in Scheme 4, the adducts (XI) and (XII) will be formed in the ratio k_1/k'_1 and, since the rate of dye formation with an excess of *m*-diamine (experiments 10—12) is independent of *m*-diamine concentration, it must be concluded that $k_2 \gg k_{-1}$ and that $k_1[m\text{-diamine}] >$

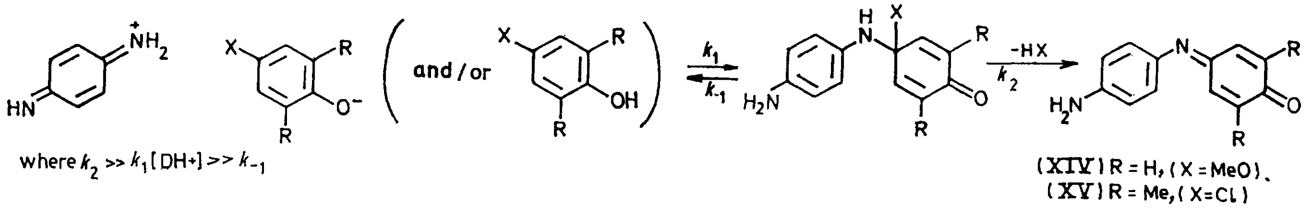


SCHEME 4

$k'_{-1} > k_2$. When stoicheiometric amounts are used, k_1[*m*-diamine] $\not\gg k'_{-1}$, and the conversion of (XI) into the dye becomes slow compared with the conversion of (XII) into the dye.

Similar breaks in the rate plots were observed at all pH values below, 8·5 although the overall rate of reaction increased. This is explained if it is assumed that k_1 and k'_1 have the same pH dependence and that k'_{-1} and k_2 have the same pH dependence. At pH values above 10·5, $k'_{-1} > k_2 > k_1$[*m*-diamine] and second-order kinetics, with $k_0 = k_1k_2/(k_{-1} + k_2)$, are observed. Although a quantitative evaluation of the rate constants in Scheme 4 cannot be made, certain qualitative conclusions can be drawn from the data in Table 9. Thus, k_1 and k'_1 increase 10-fold for each unit decrease in pH, k'_{-1}, k_2 and, probably k_{-1}, have minimum value at about pH 8·5.

Finally, the reaction of *p*-benzoquinone di-imine with 4-methoxyphenol and 4-chloro-2,6-xylenol has been examined. Both phenols behave as 2-equivalent couplers, yielding, respectively, indoaniline (XIV) and 3,5-dimethylindoaniline (XV). The dyes (XIV) and (XV) were obtained previously[4] by reaction of di-imine with the 4-equivalent couplers phenol and 2,6-xylenol. From the kinetic data in Tables 10 and 11, it is evident that the rate-controlling step is the coupling reaction, which is followed by rapid loss of methanol or hydrogen chloride (Scheme 5). The pH dependence of the rates is typical of that for the reaction of di-imines with phenols.[4]



SCHEME 5

TABLE 10

Rate data for the reaction of *p*-benzoquinone di-imine with 4-methoxyphenol at 30 °C

pH (±0·02)	Concentration (M) Di-imine	Concentration (M) Phenol	k_0 (l mol^{-1} s^{-1})
10·05	$1·0 \times 10^{-4}$	$5·0 \times 10^{-3}$	24·5
10·03	$1·0 \times 10^{-4}$	$1·0 \times 10^{-2}$	25·0
9·08	$1·0 \times 10^{-4}$	$1·0 \times 10^{-3}$	41·7
8·50	$1·0 \times 10^{-4}$	$1·0 \times 10^{-3}$	42·2
7·98	$1·0 \times 10^{-4}$	$1·0 \times 10^{-3}$	46·2
7·58 *	$1·0 \times 10^{-4}$	$1·0 \times 10^{-3}$	41·7
6·00 *	$2·5 \times 10^{-5}$	$1·0 \times 10^{-3}$	115·3

* Using pure di-imine, others use *p*-phenylenediamine with 2 molar proportions of ferricyanide.

The rate constants in Tables 10 and 11 can be expressed by the equation (10) where k_a is the specific second-order rate constant for the reaction of the conjugate acid of the di-imine (DH$^+$) with the phenolate ion (P$^-$), k_b is that for the reaction of DH$^+$ with neutral phenol (P), and the α values are the fractions of the reactants present as the designated species at the pH

$$k = k_a\alpha_{DH^+}\alpha_{P^-} + k_b\alpha_{DH^+}\alpha_P \qquad (10)$$

to which k pertains. Using pK_a values of 5·75, 10·15, and 9·70 for the di-imine,[8] *p*-methoxyphenol, and 4-chloro-2,6-xylenol respectively, the values of k_a and k_b were calculated using a computer program for the best solution to equation (10). The values are included in Table 12.

TABLE 11

Rate data for the reaction of *p*-benzoquinone di-imine with 4-chloro-2,6-xylenol at 30 °C

pH	Concentration (M × 10^5) Di-imine	Concentration (M × 10^5) Xylenol	$t_{\frac{1}{2}}$ (s)	k_0 (l mol^{-1} s^{-1})
10·90	3·0 *	100	50·0	$1·38 \times 10^1$
10·00	3·0 *	100	8·75	$7·92 \times 10^1$
9·98	5·0 †	100	8·00	$8·67 \times 10^1$
9·91	20·0 †	20	49·0	$1·02 \times 10^2$
9·32	3·0 *	100	4·18	$1·66 \times 10^2$
7·95	3·0 *	100	2·50	$2·77 \times 10^2$
7·25	3·0 *	100	1·59	$4·35 \times 10^2$
6·84	3·0 *	50	1·40	$9·92 \times 10^2$
5·78	3·0 *	50	0·45	$2·97 \times 10^3$

* Using pure di-imine. † Using *p*-phenylenediamine with 2 molar proportions of ferricyanide.

TABLE 12

Second-order rate constants for the coupling reactions of quinone imines with various couplers at 30 °C

Imine:	Specific second-order rate constants (l mol^{-1} s^{-1}) Di-imine (DH$^+$)		Specific second-order rate constants (l mol^{-1} s^{-1}) Monoimine (M)
1,3-Diamine			
4-MeO	$5·0 \times 10^6$		$1·9 \times 10^2$
4,6-(MeO)$_2$	$1·6 \times 10^8$		$3·7 \times 10^3$
4-MeO-6-Me	$8·5 \times 10^6$		
Parent	$2·0 \times 10^5$		$1·1 \times 10^1$
4-Me	$6·0 \times 10^5$		$4·0 \times 10^1$
	k_a *	k_b †	k ‡
Phenol	$8·5 \times 10^4$		$8·5 \times 10^{-1}$
4-MeO	$1·1 \times 10^6$	$2·3 \times 10^2$	
2,6-Me$_2$	$8·0 \times 10^7$	$1·6 \times 10^4$	$6·3 \times 10^2$
4-Cl-2,6-Me$_2$	$2·2 \times 10^6$	$5·8 \times 10^2$	

* For DH$^+$ + Phenolate. † For DH$^+$ + Phenol. ‡ For M + Phenolate.

Support for the coupling mechanisms presented above is obtained from comparison of the various specific second-order rate constants deduced in the present work with those for the simpler couplers reported previously. From Table 12 it can be seen that 2,4-diaminoanisole is 20—25 times more reactive than the parent *m*-phenylenediamine, and 20—30 times less reactive than the dimethoxy-*m*-diamine towards both neutral monoimine and protonated di-imine. Methylation of both *m*-phenylenediamine and 2,4-diaminoanisole increases the reactivity by factors of 1·5—4·0. Similarly the 4-methoxyphenolate ion is 13 times more reactive than the phenolate ion, while the 4-chloro-2,6-xylenolate ion is 40 times less reactive than the 2,6-xylenolate ion. Conversely, the conjugate acid of the di-imine is some 10^4—10^5 times more reactive than the neutral monoimine towards all the couplers. Thus, the relative reactivities are in accord with the above treatment of the kinetic data.

EXPERIMENTAL

Materials.—*p*-Aminophenol, *p*-phenylenediamine, 2,4-diaminoanisole, 4-chloro-2,6-xylenol, and *p*-methoxyphenol were commercial samples, purified by recrystallization. The preparation of *p*-benzoquinone di-imine and of an ether solution of *p*-benzoquinone monoimine has been described previously.[8]

1,5-*Dimethoxybenzene*-2,4-*diamine Dihydrochloride.*—1,5-Dimethoxy-2,4-dinitrobenzene [9] m.p. 157·5° (lit.,[9] m.p. 154°) (5 g) in ethyl acetate, was hydrogenated over 10% Pd–C. The filtered solution was treated with dry hydrogen chloride to precipitate the *salt* as a pale pink powder (Found: C, 39·8; H, 5·8; N, 11·6. $C_8H_{14}Cl_2N_2O_2$ requires C, 39·6; H, 6·2; N, 11·8%).

5-*Methoxy*-2,4-*dinitrotoluene.*— 5-Chloro-2,4-dinitrotoluene [10] (17 g) in warm methanol (400 ml), was treated with potassium hydroxide (6 g) in the minimum amount of methanol. The mixture was refluxed for 1 h, and the product was then precipitated by addition of water. Two recrystallizations from methanol gave 5-*methoxy*-2,4-*dinitrotoluene*, m.p. 97° (lit.,[11] 101°).

5-*Methoxy*-2,4-*diaminotoluene Dihydrochloride.*—The dinitro-compound was reduced and worked up as above to give the *salt* (Found: C, 41·2; H, 6·5; N, 12·6; Cl, 30·5. $C_8H_{14}Cl_2N_2O$ requires C, 41·7; H, 6·2; Cl, 31·0; N, 12·5%).

4-*Hydroxy*-5′-*methoxy*-2′,4′-*dinitrodiphenylamine.*— 5-Chloro-2,4-dinitroanisole [12] (3·1 g), *p*-aminophenol (1·45 g), and anhydrous sodium acetate (1·2 g) in ethanol (100 ml) were heated under reflux for 2 h. On cooling, the *diphenylamine* separated as orange-red microcrystals, m.p. 264° (from acetone) (Found: C, 51·2; H, 3·95, N, 13·8. $C_{13}H_{11}N_3O_6$ requires C, 51·2; H, 3·6; N, 13·8%).

4-*Amino*-5′-*methoxy*-2′,4′-*dinitrodiphenylamine.*— 5-Chloro-2,4-dinitroanisole (4·64 g) and *p*-acetamidoaniline (3·0 g) were reacted as described above to give 4-*acetamido*-2′,4′-*dinitro*-5′-*methoxydiphenylamine* as yellow crystals m.p. 249° (from acetone) (Found: C, 52·2; H, 3·97; N, 16·2. $C_{15}H_{14}N_4O_6$ requires C, 52·0; H, 4·05; N, 16·2%). The amide (5·74 g) in ethanol (100 ml) and 20% v/v aqueous sulphuric acid (400 ml) was refluxed until solution was complete to yield the aminodiphenylamine as orange crystals, m.p. 207° (from acetone) (Found: C, 51·1; H, 3·8; N, 18·1. $C_{13}H_{12}N_4O_5$ requires C, 51·3; H, 3·95; N, 18·4%).

2,4-*Diaminodiphenylamines.*—Solutions of 2,4-diaminodiphenylamines were produced by quantitative catalytic reduction of the corresponding 2,4-dinitrodiphenylamines in ethyl acetate. Standard solutions were prepared by 100 : 1 dilution of the ethyl acetate solutions with aqueous phosphate buffers.

Attempts to isolate the hydrochloride salts of the triaminodiphenylamine and diaminohydroxydiphenylamine gave solid products whose analysis showed them to comprise a mixture of di- and tri-hydrochlorides.

Indamines and Indoanilines.—The dyes were prepared quantitatively, in aqueous buffer solution, by oxidation of the corresponding diphenylamine (leuco-dye), or of a mixture of *p*-phenylenediamine or *p*-aminophenol with excess of the appropriate coupler, with potassium ferricyanide. The spectra of the dyes were recorded at various pH, and comparison of supposedly identical dyes from differing starting materials was confirmed by t.l.c. Spectral data for the dyes is given in Table 13.

TABLE 13

Spectra of the indamine and indoaniline dyes in aqueous buffers

	$\lambda_{max.}$/nm (log ε)		
Dye	Conjugate acid	Free base * or Anion †	pK_a
(VI)	475 (4·00)	495 (*ca.* 4·0) †	*ca.* 11·2
		610 (*ca.* 4·3) *	*ca.* 8·7
(IX)	511 (4·04)	440 (3·91) *	10·8
(XIII)	549 (4·09)	450 (3·94) *	10·6
(XIV)		554 (4·05) *	
(XV)		525 (4·00) *	

Dissociation Constants.—The pK_a values of phenolic and *m*-diamine couplers were determined spectrophotometrically as described previously.[4] Results are given in Table 14.

TABLE 14

Spectral data and dissociation constants for *m*-diamines and phenols

	$\lambda_{max.}$/nm (log ε)			
2,4-Diamine	2nd Conj. acid	1st Conj. acid	Free base	pK_a (±0·05)
1-MeO	272 (3·30); 277^{s} (3·25)	287 (3·51)	297 (3·54)	3·15; 5·72
1,5-$(MeO)_2$	278 (3·49)	300 (3·61)	308 (3·72)	3·70; 5·80
1-Me-5-MeO	276 (3·48)	294 (3·58)	302 (3·62)	3·35; 5·75
Phenol	Neutral		Anion	(±0·03)
4-MeO	287 (3·44)		306 (3·50)	10·15
4-Cl-2,6-Me_2	277 (3·12); 284^{s} (3·09)		298 (3·54)	9·70

Kinetic Measurements.—All kinetic measurements were made in 0·1M-aqueous phosphate buffers at 30° ± 0·1° using previously described mixing and spectrophotometric techniques.[2,8] Rate constants for reactions with 4-equivalent couplers were calculated according to the kinetic equation appropriate for the stoicheiometry of the reaction mixture employed.[5] Rate constants for reactions with 2-equivalent couplers were calculated according to the kinetic equations for simple second-order reactions or for pseudo first-order reactions. Duplicate runs were reproducible to within ±3% and it is estimated that the derived rate constants are accurate to within ±8%.

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