methoxyl groups into triphenylcarbinol do not yield as satisfactory agreement with experimental ratios. Thus models B and C yield calculated ratios that in no case agree with corresponding experimental ratios of K_{R^+} to within a factor of three. With p-methyl as substituent, according to model B, $K^{3x}_{R^+}/K^{x}_{R^+}$ equals 68 while the experimental value is 48. Model C yields a ratio of 170 in this case. Deviations from expectations based on model A are even greater. Part of the evidence which has been offered[24] in support of model B and/or C is the small dependence on the nature of the substituent of the ratio of K_{R^+} values for di- and triphenylcarbonium ions symmetrically substituted with identical substituents. Such behavior can, however, be rationalized in terms of model A.[31] Furthermore, inductive and field effects should produce substantial substituent-dependent variation in this ratio for ions of type B or C.

Neither the data on ionization equilibria in liquid sulfur dioxide nor hydrolysis equilibria in aqueous sulfuric acid provide a basis for unequivocal choice of model A or B and/or C. The present data are, however, least consistent with B.

Acknowledgment.—This work was made possible by support of the National Science Foundation under Grant NSF G 436. We are grateful to Professor M. S. Newman for providing a sample of mono-o-methyltriphenylcarbinol.

(31) This was pointed out to us by Prof. W. F. Sager as follows: "The constancy is really just one way of expressing the fact that the ratio of rho's for the two reactions is 3/2. A little simple algebra shows that either of these conditions implies the other. If the charge dispersal to the rings is extensive, if the stabilizing effect is proportional to the charge on the ring and if the substituent does not drastically alter the ring charge, then a value of 3/2 would be expected for the ratio of rho's. Similar considerations do not predict a constant ratio of K_{R^+} values for diarylphenylcarbonium and diarylcarbonium ions, as does model C, in cases where the aryl group is more effective than phenyl in stabilizing the ion. Deno's results show that the ratios are 4.47 for OCH_3, 6.0 for CH_3 and 6.7 for H. However, the third assumption made above requires that Deno's constant ratio should break down for ions in which the substituent is capable of bearing much of the charge. The large deviation found in the case of the dimethylamino substituent is in accord with this."

BOSTON 15, MASS.

[COMMUNICATION NO. 1835, FROM THE RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

The Mechanism of Dye Formation in Color Photography. III. Oxidative Condensation with p-Phenylenediamines in Aqueous Alkaline Solutions[1a,b]

BY L. K. J. TONG AND M. CAROLYN GLESMANN

RECEIVED AUGUST 7, 1956

The kinetics of the oxidative condensation of p-phenylenediamine and p-aminodialkylanilines with derivatives of α-naphthol in the pH range of 8 to 12 has been investigated by means of a steady-state flow method. The rates are proportional to the concentrations of the quinonediimines and of the naphtholate ions. It is suggested that the rate-determining step of the over-all reaction is the formation of the leuco dye by a bimolecular reaction of the above species. This is followed by rapid conversion of the leuco dye to the respective dyes. With different quinonediimines, approximate proportionality was found between rates of deamination and rates of coupling with a given coupler.

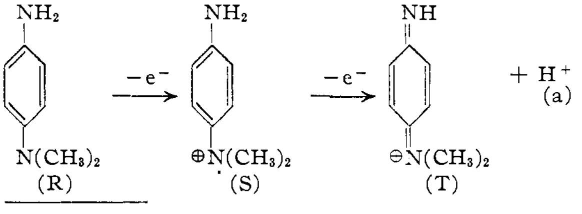
I. Introduction

In present-day color photography, the image dyes are most commonly formed by oxidative condensation (coupling) between p-phenylenediamine derivatives (developing agents), usually p-amino-N,N-dialkylanilines, and various compounds containing active methylene or methine groups (couplers), silver halide being the oxidant. The reaction as a whole, from the oxidation of the developer to the deposition of the dye, is heterogeneous, and can be very complex; the couplers may be present in various physical states in dilute aqueous solutions, as colloids, or as finely dispersed solid or liquid particles. The various phases of the process will be discussed separately. The subject of this paper is the homogeneous reaction between oxidized p-aminoalkylaniline and coupler in dilute aqueous solution.

In most of the previous research on coupling reactions, AgX was used as the oxidant.[2,3] This work has been reviewed adequately by Vittum and Weissberger.[2] Because of the complications just mentioned, such techniques[2,3] are not the most suitable ones for determining the mechanisms of the coupling reaction. For this purpose, the techniques used must produce the oxidized developing agent at a high rate and must be suitable for the observation of rapid reactions. Accordingly, ferricyanide was used as the oxidizing agent and most of the reactions were observed in the flow machine for rapid reactions designed by Ruby.[4]

II. Reactants

1. **Developing Agents.**—According to Michaelis,[5] the oxidation of p-phenylenediamines, R, takes place in two steps, each involving the removal of one electron, first to the semiquinone, S, then to the quinonediimine, T.



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(1) (a) Part I, L. K. J. Tong, *J. Phys. Chem.*, **58**, 1090 (1954); (b) Part II, L. K. J. Tong and M. C. Glesmann, THIS JOURNAL, **78**, 5827 (1956).

(2) P. W. Vittum and A. Weissberger, *J. Phot. Sci.*, **2**, 81 (1954).

(3) K. S. Lyalikov, B. A. Tsarev, Ya. L. Leibov and V. N. Kurnakov, *Otdel. Khim. Nauk*, **2**, 38 (1954).

(4) W. R. Ruby, *Rev. Sci. Instruments*, **26**, 460 (1955).

(5) L. Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940).

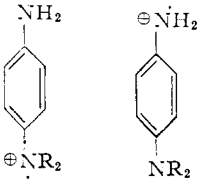
It is one of the objectives in this study to determine whether S or T is involved in the coupling rate reactions. The semiquinone, S, is capable of dimerization

$$2S \rightleftharpoons D \qquad (b)$$

and dismutation

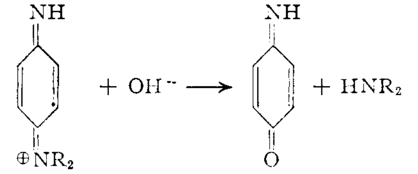
$$2S \rightleftharpoons R + T \qquad (c)$$

In dilute solutions as employed in our experiments, the concentration of D is likely to be very low. The equilibrium of reaction c depends upon the *p*H. Michaelis pointed out that the stability of S is highest in acid solutions where the resonating forms are equivalent.



Above *p*H 8, dismutation is almost instantaneous and complete; this is evidenced from deamination rate studies,[1] oxidation–reduction titrations[6] and the present coupling rate results.

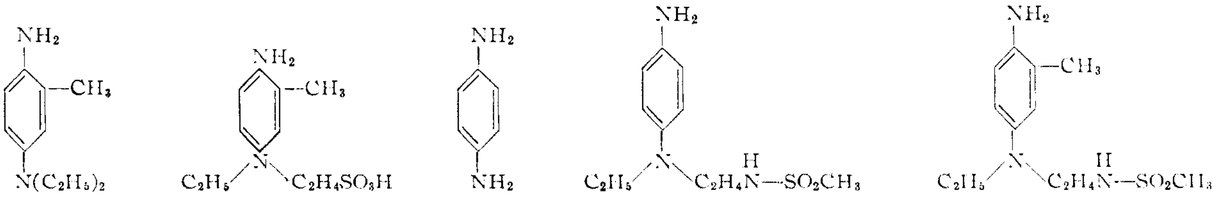
Oxidized developing agents also undergo deamination; this irreversible reaction can, when the *p*H is high or the coupler is unreactive, compete markedly with the coupling reaction. Corrections for this side reaction may therefore be necessary in the analysis of the data. It was principally with this in mind that we started our work with a study of the deamination reaction.



(d)

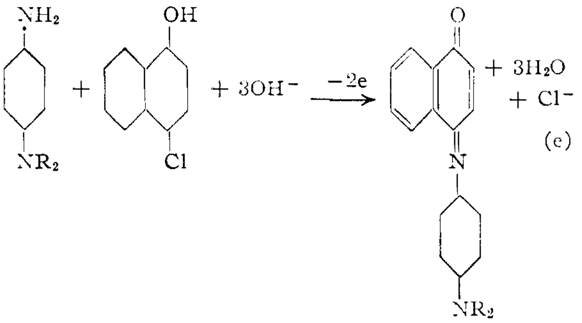
The developing agents used in this investigation are listed

Developing Agents



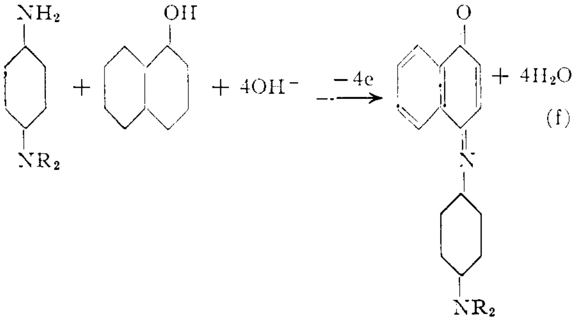
I II III IV V

2. **Couplers.**—Couplers may require two or four equivalents of oxidant to form one mole of dye; examples are 4-chloro-1-naphthol and α-naphthol, respectively, which react according to eq. e and f.



(e)

and



(f)

Several classes of organic compounds, such as pyrazolones and acetoacetic esters, as well as phenols and α-naphthols,[2] are used as couplers in color photography. Only the last type is used in the experiments discussed in this paper, since the other classes of couplers have intrinsic complications which are better treated separately after the fundamentals of the reaction are established for the simplest type.

Phenols and α-naphthols are dissociated to a large extent at the *p*H generally employed in color development (*p*H 10 to 12). Reactions were studied over a wide range of *p*H to determine the charge of the reactive species.

The couplers used in this investigation are listed below (α, β, γ, δ).

III. Procedures and Treatment of Data

1. **Methods of Measurement.**—In general, the reactions were followed by determining the amount of dye formed at any given time. Three methods were used: two employed the flow machine, and the third employed the conventional mixing technique appropriate for relatively slow reactions. The methods using the flow machine are identified as the chemical-stop method and the continuous method; both operate on the principle of the steady state. In both methods, oxidant and developer are mixed in chamber 1, and the coupler, dissolved in a buffer, is added in chamber 2. The coupling reaction is initiated at this point. The chemical-stop method provides for the introduction of a fourth solution, of hydroquinone (HQ) and acetic acid, in chamber 3 to stop the coupling. In the continuous method, the dye density is measured spectrophotometrically as the reaction mixture

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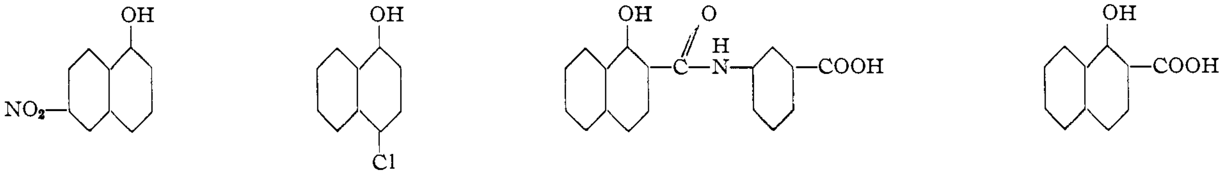
(6) W. R. Ruby, private communication.

Couplers



α β γ δ

passes a glass window along the reaction channel. In the stop method, the dye density is measured after the reaction is stopped, either as it passes the window or at a later time. The reaction time for the continuous method is the flow time from chamber 2 to the glass window, and that for the stop method is the flow time between chambers 2 and 3. The stop method permits the partly reacted mixture to be treated further. This is important, especially in cases where the dye solutions do not obey Beer's law, *e.g.*, because of their colloidal nature. In such cases, the dyes may be extracted into butyl acetate for analysis. Some dyes, however, are degraded in the stopping solution by the hydroquinone, the use of which is necessary because acid alone does not reduce the reaction rate sufficiently.

2. Kinetic Equations.—A few preliminary rate measurements indicate that, at high *p*H, the dismutation of semiquinone is almost complete. and that the rate of coupling is proportional to the quinonediimine (QDI) concentration [T] and not to the semiquinone concentration [S]. These deductions are based on the assumption that (1) ferricyanide oxidizes the developing agent to QDI if added in stoichiometric quantity, and (2) the coupling rate is proportional either to [S] or [T]. The first assumption is well supported for the region of high *p*H. In two experiments, the coupler concentration $[C]_0$ and the ferricyanide concentration q were kept constant, but the developing agent in experiment 1 was added in a concentration $q/2$ and in experiment 2 in a concentration q. The rates of dye formation in both experiments were identical.

The following tabulation shows the results of these experiments which can be expected under various conditions.

A. Semiquinone dismutates slightly, *i.e.*, K is large, in the equation

$$\frac{[S]^2}{[R][T]} = K$$

Experiment 1	Experiment 2
$[R]_1$ very small	$[R]_2$ very small
$[S]_1$ very small	$[S]_2 \sim q$
$[T]_1 \sim q/2$	$[T]_2$ very small

If the rate is proportional to [S], then $\text{rate}_2 > \text{rate}_1$. If the rate is proportional to [T], then $\text{rate}_1 > \text{rate}_2$.

B. Semiquinone dismutates extensively, *i.e.*, K is small.

Experiment 1	Experiment 2
$[R]_1$ very small	$[R]_2 \sim q/2$
$[S]_1$ very small	$[S]_2$ very small
$[T]_1 \sim q/2$	$[T]_2 \sim q/2$

But $[S]_2 >> [S]_1$, since $[R]_2 >> [R]_1$ and $[T]_2 \doteq [T]_1$.

If the rate is proportional to [S], then $\text{rate}_2 >> \text{rate}_1$; if the rate is proportional to [T], then $\text{rate}_2 \doteq \text{rate}_1$.

Of these possibilities, only the last one agrees with the results. Therefore, assumptions consistent with these results were used in deriving the following rate equations.

a = concn. of developing agent, as added
$2b$ = concn. of $Fe(CN)_6^{-3}$, as added
[C] = concn. of coupler, as added
[X] = concn. of dye

Mixing and oxidation can be assumed to be complete instantaneously. This assumption was borne out by the known efficiency of the apparatus from deamination rate studies (Note 1, Part I).

Then $[T]_0 = b$ when $b \leq a$ and $[T]_0 = a$ when $b \geq a$.

C. 2-Equivalent Couplers.—

$$T + C \xrightarrow{k_1} \text{Leuco dye} \xrightarrow{k_3\text{ (fast)}} \text{Dye}$$

$$T \xrightarrow{k_2} \text{Quinonemonoimine (QMI)}$$

$$\frac{d[T]}{dt} = -(k_1[C] + k_2)[T] \qquad (1)$$

$$\frac{d[X]}{dt} = \frac{-d[C]}{dt} = k_1[C][T] \qquad (2)$$

Combining eq. 1 and 2, we obtain

$$\frac{d[T]}{d[C]} = 1 + \frac{k_2}{k_1[C]} \qquad (3)$$

Integrated from the limits $[T] = [T]_0$, and $[C] = [C]_0$, we obtain the expression for the QDI at the corresponding concentration of dye.

$$[T] = [T]_0 - [X] + \frac{k_2}{k_1}\ln\frac{[C]_0 - [X]}{[C]_0} \qquad (4)$$

Equation 4 can be simplified by assuming that

$$\ln\left(1 - \frac{[X]}{[C]_0}\right) \doteq \frac{-[X]}{[C]_0} \qquad (5)$$

This approximation is valid at the early part of the reaction or in the presence of coupler in large excess. Also, let

$$1 + \frac{k_2}{k_1[C]_0} = m \qquad (6)$$

When eq. 4, 5 and 6 are combined and substituted in eq. 2, we obtain

$$\frac{d[X]}{dt} = mk_1([C]_0 - [X])([T]_0/m - [X]) \qquad (7)$$

After integration within proper limits

$$k_1 = \frac{2.303}{t(m[C]_0 - [T]_0)}\log\frac{[T]_0([C]_0 - [X])}{m[C]_0([T]_0/m - [X])} \qquad (8)$$

When $[T]_0/m = [C]_0$, we obtain the equation

$$k_1 = \frac{[X]}{m[C]_0([C]_0 - [X])t} \qquad (8a)$$

D. 4-Equivalent Couplers.—With 4-equivalent couplers, the conversion of leuco dye (L.D.) to dye requires two further equivalents of oxidant. In the presence of excess oxidant, the ferricyanide is reduced; otherwise quinonediimine is reduced. In the latter case, the QDI disappears twice as fast as dye is formed.

a. When $b \leq a$

$$\mathrm{T} + \mathrm{C} \xrightarrow{k_1} \mathrm{L.D.}$$

$$\mathrm{L.D.} + \mathrm{T} \xrightarrow{k_3(\mathrm{fast})} \mathrm{Dye}$$

$$\mathrm{T} \xrightarrow{k_2} \mathrm{QMI}$$

$$\frac{\mathrm{d}[\mathrm{T}]}{\mathrm{d}t} = -(2k_1[\mathrm{C}] + k_2)[\mathrm{T}] \tag{9}$$

$$\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = \frac{-\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_1[\mathrm{C}][\mathrm{T}], \text{ which is eq. 2}$$

As in the case of 2-equivalent couplers, we obtain

$$[\mathrm{T}] = [\mathrm{T}]_0 - 2[\mathrm{X}] + \frac{k_2}{k_1} \ln \frac{[\mathrm{C}]_0 - [\mathrm{X}]}{[\mathrm{C}]_0} \tag{10}$$

and

$$k_1 = \frac{2.303}{t(2m'[\mathrm{C}]_0 - [\mathrm{T}]_0)} \log \frac{[\mathrm{T}]_0([\mathrm{C}]_0 - [\mathrm{X}])}{2m'[\mathrm{C}]_0([\mathrm{T}]_0/2m' - [\mathrm{X}])} \tag{11}$$

where

$$m' = \left(1 + \frac{k_2}{2k_1[\mathrm{C}]_0}\right)$$

When

$$2m'[\mathrm{C}]_0 = [\mathrm{T}]_0$$

$$k_1 = \frac{[\mathrm{X}]}{2m'[\mathrm{C}]_0([\mathrm{C}]_0 - [\mathrm{X}])t} \tag{11a}$$

When deamination is slow compared to coupling, $m' \doteq 1$, and eq. 8, 8a, 11 and 11a are reduced to the familiar second-order rate equations.

b. When $b \geqq 2a$, the equations are identical with those for 2-equivalent couplers.

c. When $a < b < 2a$, the situation is more complicated. Since this case does not impart any information not obtainable from cases A and B, no experiments were made.

3. Rate Constants by Competition between Deamination and Coupling.—If QDI and coupler are introduced at known initial concentrations and the reaction is allowed to proceed until the QDI is exhausted, and the dye yield is then measured, k_1 can be obtained from either eq. 4 or eq. 10, whichever is appropriate, provided k_2 has been previously determined in the given buffer.

Setting $[\mathrm{T}] = 0$ in eq. 4 and 10, we obtain eq. 12 and 13, respectively.

$$k_1 = \frac{2.303k_2}{([\mathrm{T}]_0 - [\mathrm{X}])} \log \frac{[\mathrm{C}]_0}{[\mathrm{C}]_0 - [\mathrm{X}]} \tag{12}$$

and

$$k_1 = \frac{2.303k_2}{[\mathrm{T}]_0 - 2[\mathrm{X}]} \log \frac{[\mathrm{C}]_0}{[\mathrm{C}]_0 - [\mathrm{X}]} \tag{13}$$

Equation 12 is applicable to 2-equivalent couplers, and to 4-equivalent couplers when $b \geqq 2a$. Equation 13 is applicable to 4-equivalent couplers when $b < a$

IV. Mechanism of the Coupling Reaction

In the following discussion, each dye is designated by a Roman numeral and a Greek letter corresponding to the developing agent and the coupler, respectively.

1. Precision of Data and Validity of Rate Equations.—The precision of the data can be judged from the scattering of points in Figs. 1 to 4. Most of these data were obtained with different combinations of flow rates and reaction path lengths which gave overlapping reaction times. The validity of the equations used to calculate the rate constants can be judged from the agreement of these points with the theoretical straight lines.

Figures 2 to 4 represent the results for the formation of dye Iα. In Fig. 3, for reaction at pH 12, the second-order rate plot without correction for deamination ($m = 1$) is curved, but, after correction ($m = 1.10$), it is approximately linear. At pH 11 (Fig. 2), although uncorrected for deamination, the curve is quite linear. This difference is caused mainly by a differential change in coupling and deamination rates with pH. In addition, owing to the high $[\mathrm{C}]_0$ required for application of eq. 11, the coupling rate became faster, and the data, therefore, represent only the latter part of the reaction where the effect of deamination is most apparent. In Fig. 2, eq. 8 is applied because the oxidant was in excess. Table I shows that the rate constants obtained with both conditions are in good agreement. Linear relationship was also obtained using eq. 13 (see Fig. 4, curve A). The rate constants obtained at pH 12 by the two methods (Figs. 3 and 4) are also in good agreement, supporting the contention that the only important side-reaction reducing dye yield is the deamination of the QDI.

TABLE I

SUMMARY OF RATE CONSTANTS FOR FORMATION OF Iα

pH	Developing agent $\times 10^4$ (a)	$\frac{\mathrm{Fe(CN)_6^{\equiv}}}{2} \times 10^4$ (b)	Coupler $[\mathrm{C}]_0 \times 10^4$	k (l./mole sec.) $\times 10^{-4}$
12.00	2.5	2.5	10.0	8.1
12.00	2.5	2.5	(0.625–10.0)	7.9[a]
11.00	1.25	5.0	1.25	7.5
11.00	2.5	5.0	1.25	7.4
11.00	5.0	5.0	1.25	6.7
11.00	10.0	5.0	1.25	7.1
11.00	2.5	5.0	0.625	7.8
11.00	2.5	5.0	2.5	7.3
9.19	2.5	5.0	1.25	6.0
8.71	2.5	5.0	1.25	5.1
8.39	2.5	5.0	1.25	3.5
7.98	2.5	5.0	1.25	1.8

[a] Competition method.

The formation of dye IIβ is very fast, therefore, only coupling in solutions with a relatively low pH can be measured directly. At pH 8.9, with the shortest reaction time which can be measured in the machine, the reaction is 75% complete. At higher pH, therefore, only the competition method of rate determination could be used; the result is plotted in Fig. 4, curve B. Although the points are quite scattered, they lie reasonably close to the straight line; in this case, on extrapolation, the

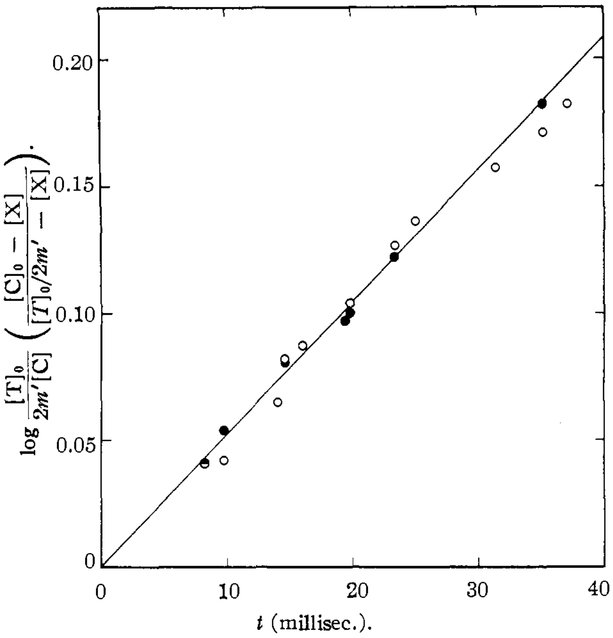


Fig. 1.—Formation of Vγ: $a = b = C_0 = 1.25 \times 10^{-4}$ M, calculated with $m = 1.013$. Duplicate runs.

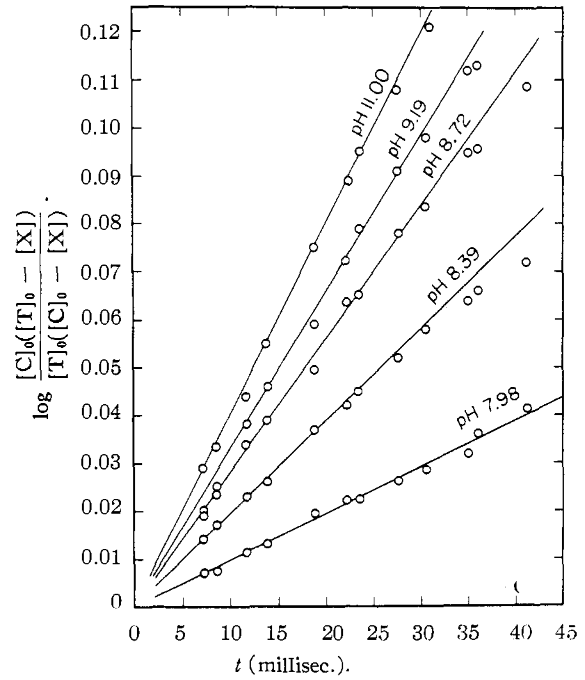


Fig. 2.—Formation of Iα at various pH values: $a = 2.5 \times 10^{-4}$ M; $b = 5.0 \times 10^{-4}$ M; $C_0 = 1.25 \times 10^{-4}$ M.

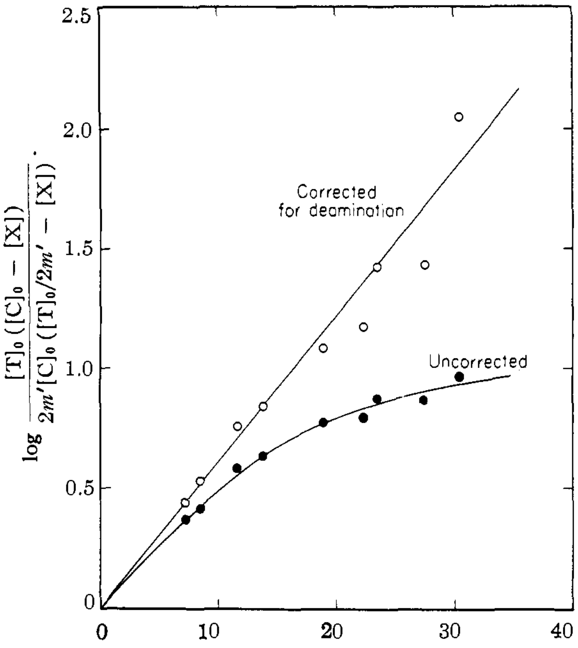


Fig. 3.—Formation of Iα at pH 12.00: $a = 2.5 \times 10^{-4}$ M; $b = 2.5 \times 10^{-4}$ M; $C_0 = 10^{-3}$ M. Uncor. curve, $m = 1.00$; cor. curve, $m = 1.10$.

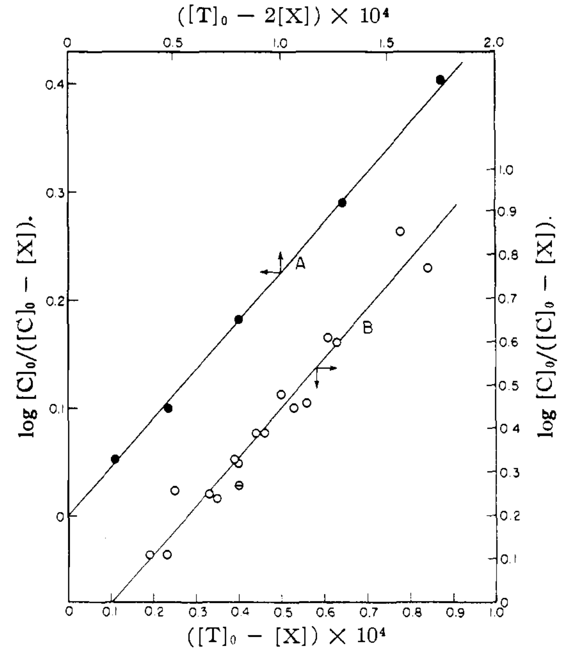
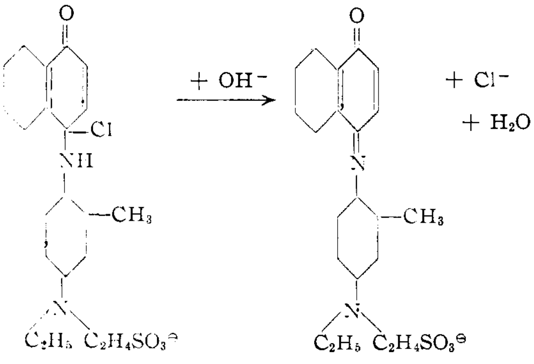


Fig. 4.—Curve A, formation of Iα by competition method at pH 12.00: $a = 2.5 \times 10^{-4}$ M; $b = 2.5 \times 10^{-4}$ M; $C_0 = 0.625 \times 10^{-4}$ M to 10.00×10^{-4} M. Curve B, formation of IIβ at pH 12.13: $a = 2.5 \times 10^{-4}$ M; $b = 3.125 \times 10^{-4}$ M; $C_0 = 2.0 \times 10^{-4}$ M to 10.0×10^{-4} M.

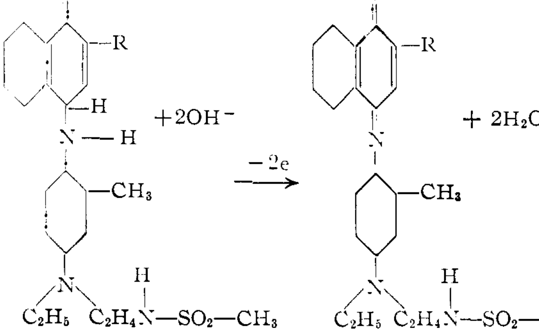
line does not go through the origin, as in curve A. The discrepancy can be accounted for by assuming a 4% impurity in this particular developing agent, which is not unreasonable. The scattering is due to the relatively high coupling rate compared to deamination rate, resulting in only a small difference between observed and theoretical dye yields.

2. **Leuco Dye Intermediate.**—Dyes from coupling reactions are commonly believed to form in two stages.[2] The first stage is the formation of the leuco dye and the second stage is the conversion of the leuco dye to the dye. The relative speed of the two stages can be judged by the shape of the rate curves, especially when the reactions are followed by the continuous method. If the rates of the first and of the second stage were of the same order of magnitude, there would be an accumulation of leuco dye, and the reaction, followed by measurement of the dye density of the reaction

mixture, would exhibit induction periods. It has been found that neither 2- nor 4-equivalent couplers exhibit noticeable induction periods. Probably the reactions of the leuco dyes from 2- and 4- equivalent couplers are represented by the equations



(g)



(h)

It is noteworthy that reaction h, involving oxidation, is also extremely rapid, even when ferricyanide is not present in excess. The absence of an induction period can mean either that step 1 is much faster than step 2, or *vice versa*. The former assumption predicates a rate-determining step whose rate is independent of the concentration of the reactant in excess, and is contradicted by the data in Table I.

3. Oxidation State of Reactant.—There has been much controversy over the oxidation state of the reactive form of the developing agent. Some arguments in support of the QDI mechanism have been presented in an earlier section. Experimentally, the QDI mechanism can be differentiated from the semiquinone mechanism by measuring the rates with excess of oxidant or excess of developing agent. These tests have been applied to most of the reactions described in this article and many more similar reactions yet unpublished. It has never been found that the rate constant could be greatly influenced at high pH by the variation of the oxidant-developing agent ratio. Where such variations were noticed, they usually could be traced to side effects, *e.g.*, the oxidation of coupler, when the ferricyanide concentration was in large excess, to produce colored materials which interfered with the absorption measurements. To conserve space, only the results for reaction Iα are given in detail in Table I. It is evident from the group of experiments measured at pH 11 that the maximum error in the rate constants did not amount to more than 10% of the average when the ratio of oxidant to developing agent changed from 0.25 to 2 and the concentration of coupler likewise underwent a 4-fold variation. In the same table is shown the agreement between the constants measured by the stop method and those by the competition method at pH 12.

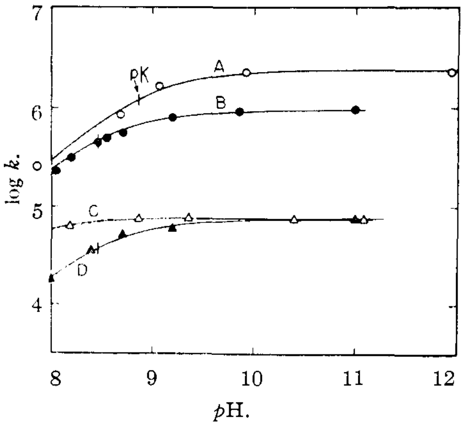


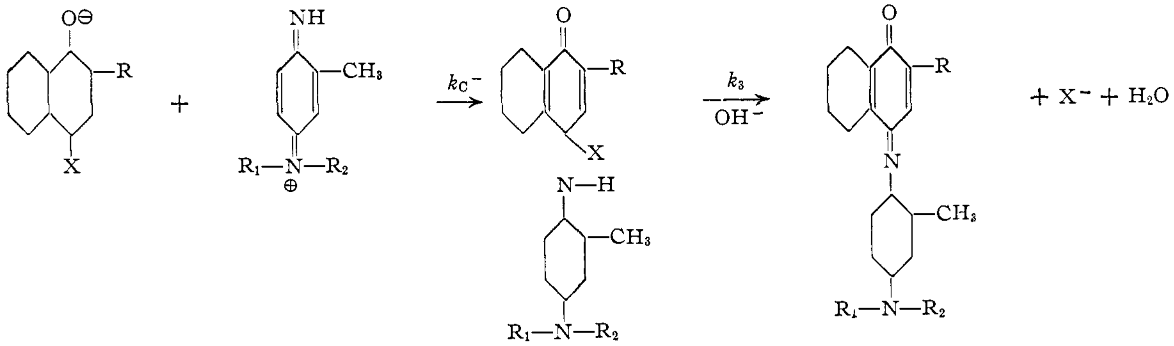
Fig. 5.—Second-order rate constants *vs.* pH for dye formation with N-substituted p-phenylenediamines; curves calculated from degree of ionization and specific rate constants for ions of the couplers: A, formation of IIβ; B, formation of IIα; C, formation of Iγ; D, formation of Iα.

4. Charge of the Reactants.—The charge of the reactive species of the reactants has been determined by the variation of the rate with pH. Figure 5 shows this relationship for the reactions forming Iα, Iγ, IIα and IIβ. The developing agent in all of these cases is a p-aminodialkylaniline. It should be pointed out that the predominating ionic species of the quinonediimine remains unchanged throughout this region. The lines were calculated on the basis of the degree of ionization of the corresponding couplers, using the pK's obtained by independent experiments. It is evident from the agreement of the experimental points with calculated lines that the rates are proportional to the coupler ions and the asymptotes correspond to the specific rate constants of the ions, k_{C^-}. Therefore, the kinetic expression for the reaction in this group is, in general

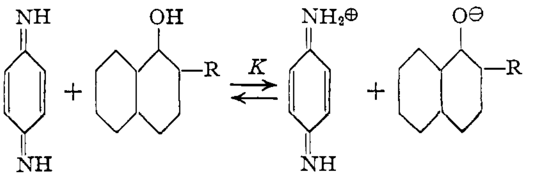
$$\frac{d[\text{dye}]}{dt} = k_{C^-}[C^-][QDI^+] \qquad (14)$$

It must be noted that the charge on the coupler and the QDI is the charge on their reactive sites and does not include the charge on substituent groups like $-CHCH_2SO_3^-$. These kinetics suggest that the rate-determining step is the first reaction below (i).

In reaction with p-phenylenediamine itself, however, the rate of the coupling reaction is proportional to the concentration of the undissociated coupler (Fig. 6). The constancy of the rate for the formation of III δ is due to the fact that δ has a pK of about 13 and is, therefore, essentially undissociated in the experiments. Although the kinetics with p-phenylenediamine seem to be exceptional, the mechanism of the coupling reaction need not be different. Although the QDI of unsubstituted p-phenylenediamine is predominantly in the neutral form, the following equilibrium exists



(i)



(j)

The product on the left is proportional to the product on the right; the rate can therefore be assumed to be proportional to the product on the right in agreement with mechanism i.

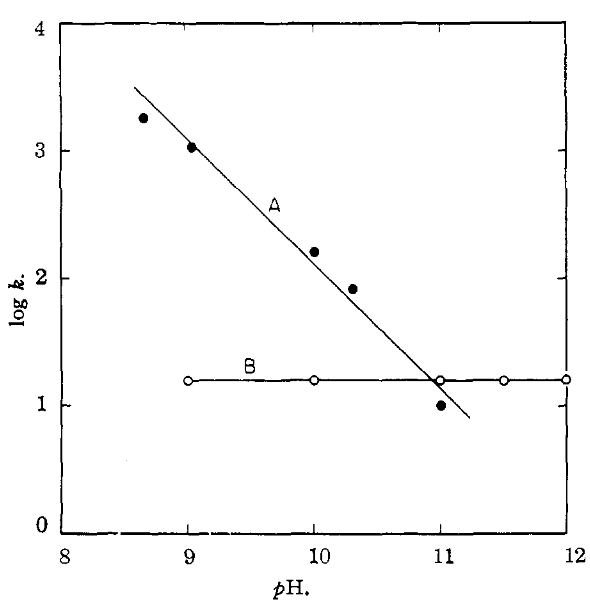


Fig. 6.—Second-order rate constants *vs.* *p*H for unsubstituted *p*-phenylenediamine with (A) coupler γ, (B) coupler δ.

Figures 7 and 8 represent reactions with QDI which have side groups with *pK*'s within the experimental region of *p*H. Coupler δ (Fig. 7) has *pK* 13 and coupler γ (Fig. 8) has *pK* 7.5. Both reaction rates can be resolved into a sum of two rates, one involving a positively charged QDI (reaction k) and the other a zwitterion (reaction l).

The dissociation constants for the QDI's were determined from the *p*H-dependence of the deamination rate.[1] For developing agents IV and V, $K = 1.3 \times 10^{-9}$ and 3×10^{-10}, respectively. Since the dissociation constant of δ is small and uncertain, the products of rate constants and dissociation constants are given (see Fig. 7). The calculated individual rates are plotted as dotted lines and the sums as solid lines. It is noteworthy that the ratios of rate constants of the cation to those of the zwitterion are quite large. This difference cannot be attributed entirely to electrostatic attraction between oppositely charged reactants, since the QDI of II, which is also a zwitter-

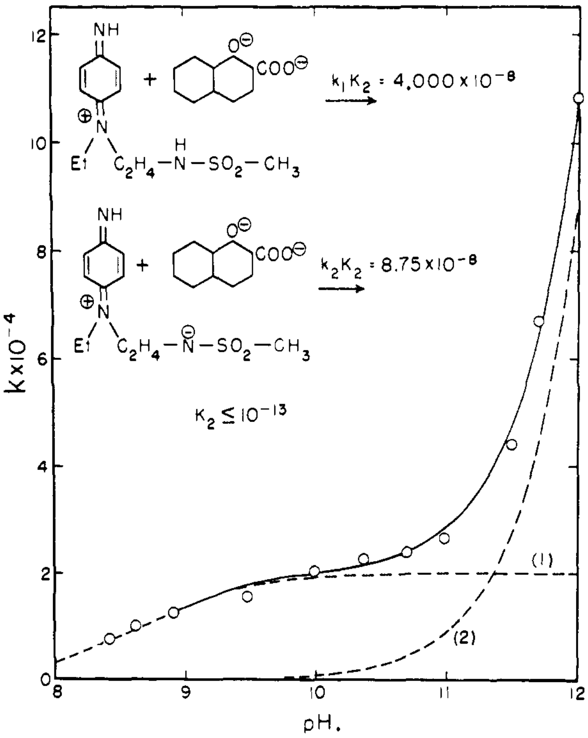
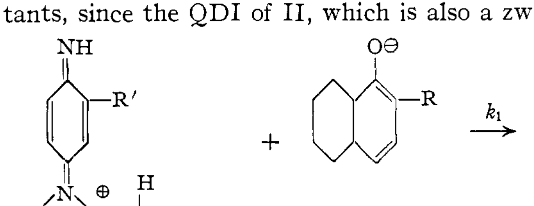
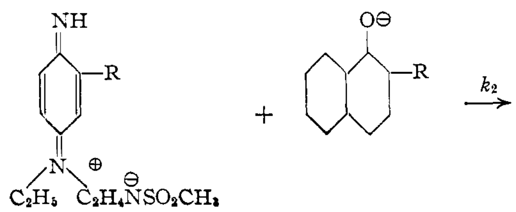


Fig. 7.—Second-order rate constants *vs.* *p*H for the formation of IV δ: dotted curves calculated, (1) for first reaction; (2) for second reaction.



(k)



(l)

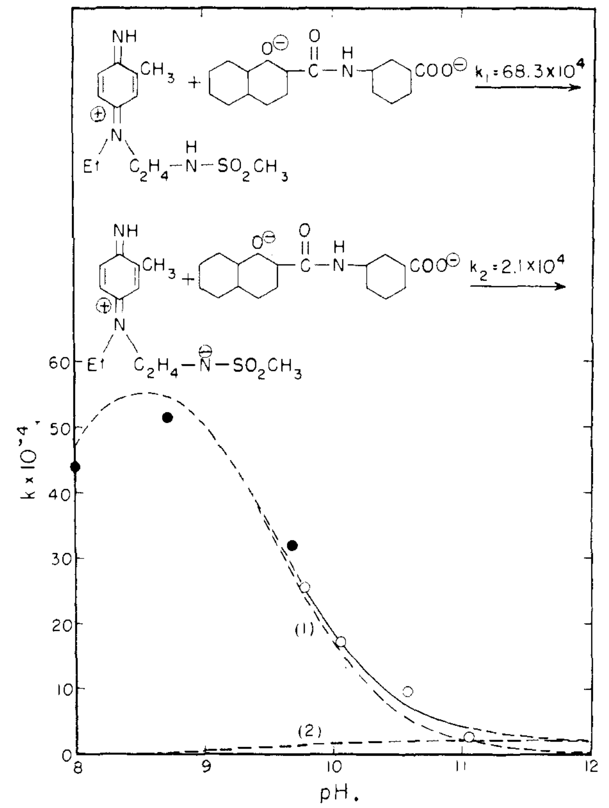
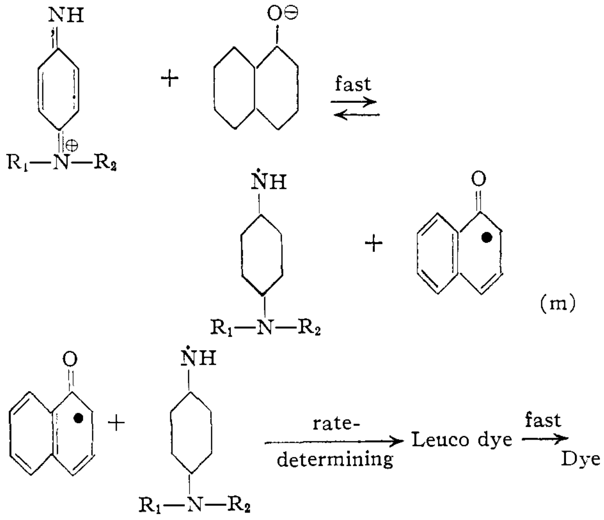


Fig. 8.—Second-order rate constants *vs.* *p*H for the formation of Vγ: dotted curves calculated for the reactions indicated; open circles indicate continuous methods; solid circles, stop method.

ion, reacts much faster with the same coupler (α) than does the QDI of I.

5. Reactivity and Mechanism.—These results established eq. 14 as the rate law for the coupling reaction. Two mechanisms are consistent with this rate law; the simpler one is the direct formation of leuco dye according to reaction i. However, it is also possible that the reaction goes through the aryloxyl free radical as



(m)

In this mechanism, the QDI and the coupler ion, instead of reacting directly to form leuco dye, first undergo a rapid and reversible electron exchange to form a pair of free radicals which then react relatively slowly to form the leuco dye. The pair of reacting radicals need not be the same pair which underwent electron exchange.

The two mechanisms cannot be differentiated by means of kinetics alone. The second mechanism seems less probable since, to satisfy eq. 14, the first equilibrium must be far toward the left, and this imposes an extremely large rate constant on the succeeding reaction. It is of interest to point out that for couplers which form free radicals readily, and if either mechanism holds, the rate would be more appropriately expressed as being proportional to the product of the semiquinone and the aryloxyl radical concentrations.

It is interesting to compare the reactivities of different QDI's in coupling and in deamination reactions. For this purpose, the rate constants are expressed in terms of the positively charged QDI. (The positive charge may be on the ring or on the imino nitrogen through resonance.) Therefore, it is necessary to convert the rate constants with *p*-phenylenediamine to this basis.

For deamination, the rate is assumed to be

$$\frac{d[\mathrm{III}]}{dt} = k'_2[\mathrm{III}^+][\mathrm{OH}^-] \qquad (15)$$

Therefore

$$k'_2 = \frac{k_2 K_{\mathrm{III}^+}}{K_w} \qquad (16)$$

where k_2 is the measured first-order rate constant and

$$K_{\mathrm{III}^+} = \frac{[\mathrm{H}^+][\mathrm{III}]}{[\mathrm{III}^+]}$$

III is the uncharged QDI of *p*-phenylenediamine, and III$^+$ is the QDI after acquiring a proton.

In the coupling between III and δ, the rates are expressed directly by eq. 17, but they can also be expressed by eq. 18 through the relationship of the constants in eq. 19.

$$\text{rate} = k_{\mathrm{HC}}[\mathrm{III}][\delta^-] \qquad (17)$$

$$\text{rate} = k_{\mathrm{C}^-}[\mathrm{III}^+][\delta^=] \qquad (18)$$

$$k_{\mathrm{C}^-} = \frac{k_{\mathrm{HC}} K_{\mathrm{III}^+}}{K_{\delta^-}} \qquad (19)$$

In these three equations, we let

$[\delta^-]$ = concn. of the couplers with the charge on the carboxylate alone
$[\delta^=]$ = concn. of the coupler with the charges on both the carboxylate and the naphthylate
K_{δ^-} = the dissociation const. for the naphthol-hydrogen

The values of k_{C^-} for γ and δ were calculated, using the constants

$$K_{\mathrm{III}^+} = 10^{-5}$$
$$K_{\gamma^-} = 3 \times 10^{-8}$$
$$K_{\delta^-} = 10^{-13}$$

To summarize and coördinate the data, the specific rate constants k_{C^-} for coupling and $k_2/(\mathrm{OH}^-)$ for deamination were plotted against each other in Fig. 9. The charges on the couplers and QDI's are shown. It is evident that the coupling rates are parallel to the deamination rates of the QDI, and for a given QDI they depend on the couplers. This relationship suggests additive contribution from both partners toward the coupling reactivity. Thus, log k_{C^-} may be expressed as the sum of two constants, A_D and A_C, corresponding to the QDI and the coupler, respectively. For this purpose, A_D may be taken as the deamination rate itself.

Although the deamination and coupling reactions are similar in that the same QDI reacts with the OH^- in one case and with the coupler ion in the other, they differ in the site of reaction. In deamination, the carbon atom in the ring bonded to the substituted-N is attacked, and in coupling it is the unsubstituted-N. Therefore, the additive rule for coupling reactivity is not expected to hold for cases where specific effects like steric hindrance are large.

V. Experimental Details

1. **Apparatus.**—The jet-mixing machine used to follow the fast reactions has been described in detail.[4] An absorption cell of the same cross-section as the channel was inserted in the path to measure densities of the flowing reaction mixture. The light source was made nearly monochromatic with approximately 10 mμ width at half transmission by the use of Corning Glass Filters and interference filters. A 16-mm. microscope objective was placed on either side of the absorption cell to give the desired optics. The transmitted light was focused on a photomultiplier tube and the current, after amplification, was recorded on an instrument. The photometer unit was calibrated against a Beckman Model DU spectrophotometer at wave lengths of 400, 530, 540, 600 and 650 mμ, using dye solutions. The densities were found to be proportional when below 1 in the first instrument. The calculated thickness of the cell is approximately 2.5 mm. For the stop method, both instruments were used to measure the densities.

To follow the slower reactions, a rapid-scanning spectrophotometer made by the American Optical Company was used.

2. **Solutions.**—The solutions were made up to produce the following concentrations in the reaction mixture: developing agents, 10^{-5} to 10^{-3} M; $K_3Fe(CN)_6$, 10^{-4} to 10^{-3} M; couplers, 10^{-5} to 10^{-3} M. The freshly prepared solutions of developing agent were protected from oxidation by deaeration with nitrogen.

The buffers, prepared by mixing the appropriate volumes of KH_2PO_4, K_2HPO_4 and K_3PO_4 solutions, gave a constant ionic strength of 0.375 in the reaction mixture. The pH of each reaction mixture was measured directly with a Beckman Model G pH meter. The stop solutions were generally 1% hydroquinone and 0.5% acetic acid to give a final pH of 6.5. The stop for Iγ also included 0.4% Triton X-100 to prevent precipitation of the dye.

3. **Procedure for Following the Reactions.**—Reactions forming Iγ, Iα and IIα were followed by the stop method, and those forming IIβ and IVδ by the continuous method. Formation of Vγ was followed by the continuous method in the pH range from 9.8 to 11 and by the stop method at lower pH, owing to the dye precipitation.

Coupling of IIIγ and IIIδ was followed in the A.O. scanning spectrophotometer in a 1-cm. cell. The developing agent and the coupler in the buffer were mixed, and the reaction was initiated by the addition of $K_3Fe(CN)_6$ from a hypodermic syringe.

Coupling rates of Iα and IIβ at pH 12 were obtained by the competition method. The procedures for this method were similar to the continuous method except that the reaction was allowed to go to completion before analysis. The concentration of the coupler was varied while that of the developing agent and that of the oxidant were kept constant.

The temperatures of the coupling reactions were maintained at 25 ± 0.1°.

All the dyes were analyzed in aqueous solutions except Iα, which, because of its tendency to precipitate, was extracted into butyl acetate before analysis.

In most instances, the pure dyes were not available or could not be dispersed into the medium desired. The extinction coefficients were then obtained from the density measurements of freshly prepared dye solutions, using either limiting amounts of developer or coupler.

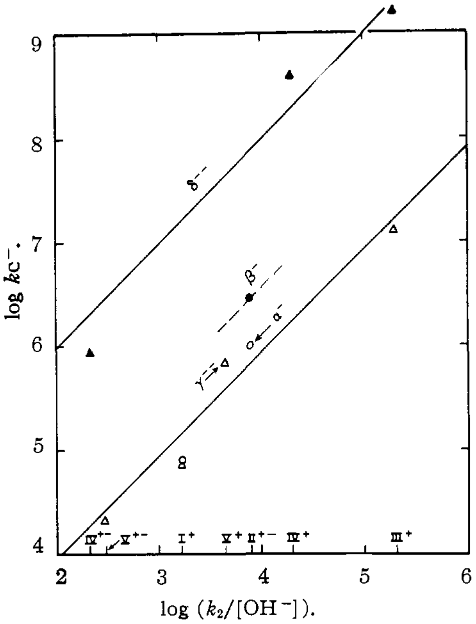


Fig. 9.—Specific rate constants (coupler ions) for dye formation *vs.* deamination rate constants for the corresponding QDI.

For Iα, the extinction coefficients calculated from experiments using a pure dye and from dyes produced by a limiting reactant were in good agreement. Table II lists the absorbancies of the dyes.

Obedience to Beer's law was established for several of the dyes.

TABLE II

ABSORBANCIES OF DYES

Dye	Medium	λ, mμ	Molar $\epsilon \times 10^{-4}$
Iα	Butyl acetate	650	2.10[a]
Iα	Butyl acetate	650	2.08
Iγ	Aqueous pH 6.5 0.2% Triton	735	3.44
IIα	Aqueous pH 6.5	660	1.38
IIβ	Aqueous pH 8–9	602	0.86
	Aqueous pH 6.5	600	0.78
IIIγ	Aqueous pH 8	600	1.51
IIIδ	Aqueous pH 8	530	0.70
IVδ	Aqueous pH 8–12	600	1.27
Vγ	Aqueous pH 8	652	2.27
	Aqueous pH 6.5	660	1.83

[a] Calcd. from pure dye.

4. **Measurements of Dissociation Constants.**—The dissociation constant of couplers α and β were calculated from absorption and pH measurements of solutions having the same coupler concentrations, according to the equation

$$pK = p\text{H} - \log \frac{D_a - D}{D - D_b}$$

where

D_a = density of the coupler in acid soln.
D_b = density of the coupler in basic soln.
D = density of the soln. at the measured pH

Table III lists the pK's and shows a comparison of the experimental and calculated densities.

Attempts were made to determine the dissociation constants of γ and δ by both absorption and titration. The accuracy was low in the case of γ, owing to precipitation of the coupler at low pH, and in the case of δ, because the pK was high. The pK's were estimated to be 13 for δ and 7.5 for γ.

5. Materials.—Potassium ferricyanide and the phosphates used for the buffers. KH_2PO_4, K_2HPO_4 and K_3PO_4, were reagent grade. The hydroquinone was of technical grade. Butyl acetate and glacial acetic acid were Eastman White Label grade. Triton X-100 was obtained from Rohm and Haas.

Table III

Dissociation of 4-Chloro-1-naphthol

$D_{\text{acid}} = 0.009$ (pH 6) $\lambda = 350$ mμ
$D_{\text{base}} = 1.026$ (pH 12) $pK = 8.64$

pH	D Obsd.	D Calcd.
8.36	0.355	0.358
8.52	.444	.447
8.69	.550	.556
9.00	.683	.719
9.12	.765	.774

Dissociation of 6-Nitro-1-naphthol

$D_{\text{acid}} = 0.021$ (pH 6.5) $\lambda = 520$ mμ
$D_{\text{base}} = 0.608$ (pH 12) $pK = 8.49$

pH	D Obsd.	D Calcd.
7.72	0.105	0.105
8.09	.192	.189
8.51	.328	.321
8.80	.415	.415
9.26	.523	.522

The developing agents and couplers used in our experiments were prepared and purified in accordance with procedures already described: 4-amino-N,N-diethyl-3-methylaniline hydrochloride, I^{7}; 4-amino-3-methyl-N-ethyl-N-(β-sulfoethyl)-aniline, II^{7b}; p-phenylenediamine dihydrochloride, III^{7}; 4-amino-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline sulfate, IV^{8}; 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline sulfate, V^{8}; 6-nitro-1-naphthol, α; m.p. 178–180°^{9}; 4-chloro-1-naphthol, β; m.p. 119–120°^{10}; 2-(m-carboxyphenylcarbamyl)-1-naphthol, γ^{11}; and 2-carboxy-1-naphthol, δ, which was obtained from Eastman Kodak Company and purified by successive recrystallizations in ethanol–water, ether and acetonitrile, and filtration through Darco and Supercel; m.p. 203–204°.

Dye Iα was prepared by coupling I with α and was purified chromatographically. Calcd.: C, 69.4; H, 5.8; N, 11.6. Found: C, 69.8; H, 6.0; N, 12.0.

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Rochester, N. Y.

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The Mechanism of Dye Formation in Color Photography. IV. Oxidative Condensation in Acidic Aqueous Solutions

By L. K. J. Tong and M. Carolyn Glesmann

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The kinetics of the oxidative condensation between p-amino-N,N-dimethylaniline and 2-methyl-4-chlorophenol in acid buffers have been investigated. As in alkaline solution and at variance with statements in the literature, the rates are proportional to the concentration of the holoquinoid oxidation product of the p-aminodialkylaniline. A method is described by which the rates of the coupling reaction are used in order to estimate the equilibrium constant of the semiquinone formation.

According to a recent paper by Hünig and Daum,[1] the oxidative condensation of p-amino-N,N-dimethylaniline with a coupler (2-methyl-4-chlorophenol) in acid solution proceeds by way of the semiquinone (SQ) of the p-phenylenediamine derivative. This conclusion was based on the observations that (1) the increase in optical density at 630 mμ is proportional to the SQ concentration, and (2) a large excess of N-dimethyl-p-phenylenediamine failed to stop the reaction.

In view of our findings[2] that the same condensation in the alkaline region proceeds by way of the quinonediimine (QDI), we have examined the dye formation in acid solution.

Michaelis[3] and co-workers have shown that a semiquinone of the Wurster Red type dismutates, according to the equation

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