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 *p*H, 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

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

	D	
*p*H	Obsd.	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

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

	D	
*p*H	Obsd.	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.

Acknowledgment.—The authors are indebted to A. Weissberger and P. W. Vittum, of these Laboratories, for their encouragement and helpful discussions during the work, and to Dr. Weissberger, for his help in the preparation of the manuscript. They also wish to thank R. L. Bent, G. Brown and C. Barr, for the preparation and purification of the developing agents and couplers used in the experiments.

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[7] (a) J. E. LuValle, D. B. Glass and A. Weissberger, THIS JOURNAL, **70**, 2223 (1948); (b) R. L. Bent, J. C. Dessloch, F. C. Duennebier, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum and A. Weissberger, *ibid.*, **73**, 3100 (1951).

[8] A. Weissberger, Eastman Kodak Co., U. S. Patent 2,193,015 (1940).

[9] H. Hodgson and H. Turner, *J. Chem. Soc.*, 9 (1944).

[10] H. Kast, *Ber.*, **44**, 1337 (1911).

[11] Chemische Fabrik, Griesheim-Elektron, German Patent 291,139 (1914), *Chem. Zentr.*, **87**, I, 815 (1916); "Beilstein's Handbuch," Vol. XIV, 1933, p. 563.

ROCHESTER, N. Y.

[COMMUNICATION NO. 1836, FROM THE RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

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

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

RECEIVED AUGUST 7, 1956

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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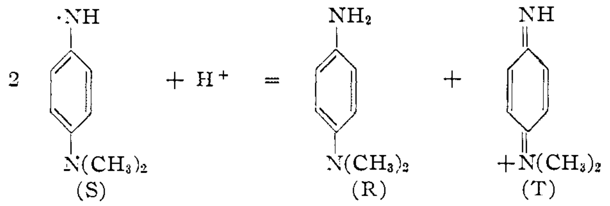
[1] S. Hünig and W. Daum, *Ann. Chem.*, **595**, 131 (1955).

[2] L. K. J. Tong and M. C. Glesmann, Part III, THIS JOURNAL, **79**, 583 (1957).

[3] L. Michaelis, M. P. Schubert and S. Granick, *ibid.*, **61**, 1981 (1939).



with the equilibrium constant at constant *p*H

$$\frac{1}{K} = \frac{[R][T]}{[S]^2} \qquad (1)$$

where [R], [S] and [T] are the sum of the concentrations of all species of the reduced, semi-oxidized and totally oxidized forms of the *p*-phenylenediamine. If S and R are added in initial concentrations of *a* and *b*, respectively, the following relationship holds at equilibrium

$$(a - 2[\mathrm{T}])^2 = K(b + [\mathrm{T}])[\mathrm{T}] \qquad (2)$$

In the special case when $b = 0$

$$[\mathrm{S}] = \frac{\sqrt{Ka}}{2 + \sqrt{K}}$$

and

$$[\mathrm{T}] = \frac{a}{2 + \sqrt{K}}$$

The equations state that if no R is added, both the semiquinone and the quinonediimine concentrations are proportional to the original semiquinone added. Since this was the experimental condition in which Hünig and Daum found the coupling rates to be proportional to the semiquinone, their results cannot be used to support either the SQ or the QDI mechanism.

Another point overlooked by Hünig and Daum is the increase in optical density by condensation of oxidized N-dimethyl-*p*-phenylenediamine to itself (autocoupling), which, under some of their experimental conditions, is the main observable phenomenon. In any case, correction must be made for this side reaction before the true coupling rate can be obtained.

Michaelis and Granick[4] observed similar color changes of the semiquinone solution, one, which was cooled suddenly to −10° and another, less rapid, at room temperature. They attributed both changes to the dimerization of the quinhydrone, but different reactions must be involved, since the color change by cooling is reversible, but the spontaneous change at room temperature is not. The reversible reaction is probably a dimerization, as suggested by Michaelis and Granick, but the irreversible reaction is autocoupling.

The difference in the two reactions is demonstrated by the following experiments.

A moderately concentrated solution of semiquinone in *p*H 5.5 sodium acetate–acetic acid buffer (nearly saturated with sodium chloride to lower the freezing point) was divided into three parts. One part was kept at 25°, the second part was warmed to 50°, and the third part was cooled to −10°. After one hour, all samples had a purple cast. On returning to room temperature, the chilled sample reverted to its original red color, while the warmed solution remained purple. The sample that had been kept at room temperature was slightly more purple than the sample that had been chilled and subsequently warmed to room temperature.

We have measured the coupling rate of 2-methyl-4-chlorophenol with 4-amino-N-dimethylaniline under conditions very similar to those described by Hünig and Daum, but using variables which allowed us to discriminate between the SQ and the QDI mechanisms. The over-all reaction is

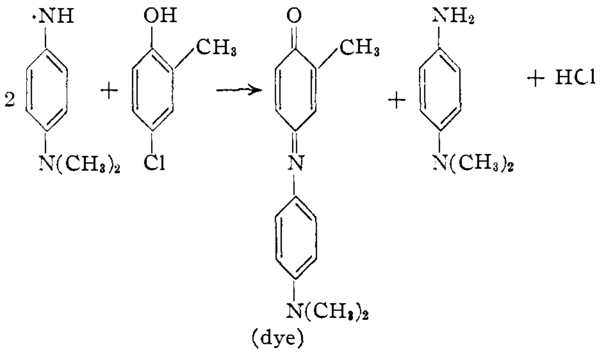


Figure 1B shows the density change in systems initially containing *a* and *b*, but devoid of coupler (autocoupling), while Fig. 1A shows the change in the corresponding systems, to which coupler had been added (autocoupling and coupling). The initial coupling rates (*m*) were therefore taken as the difference between the initial slopes of the two sets of curves. When *K* is large

$$[\mathrm{S}] \sim a \qquad [\mathrm{R}] \sim b$$

and eq. 1 becomes

$$[\mathrm{T}] \sim 1/K\left(\frac{a^2}{b}\right) \qquad (3)$$

With experimental conditions where *a* is kept constant and *b* varied, if the rate is proportional to [S], it should remain constant or slightly increase with the increase of *b*, but if the rate is proportional to [T], it is necessarily proportional to $1/b$. A set of experiments has been performed under these conditions with the results shown in Fig. 2, where

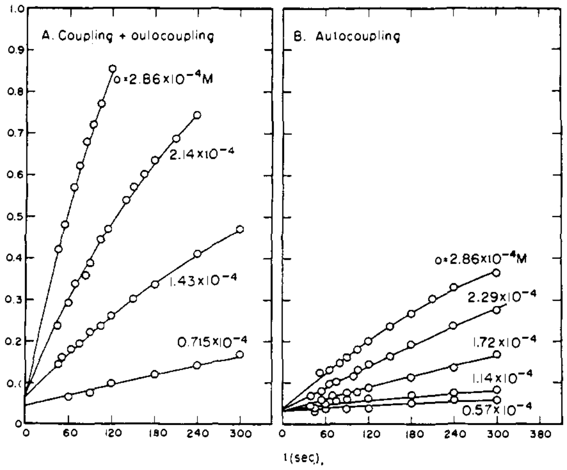


Fig. 1.—Coupling and autocoupling at *p*H 6.56, with dimethyl-*p*-phenylenediamine constant and semiquinone varied: *p*-phenylenediamine, $b = 0.525 \times 10^{-3}\,M$; (1A) coupler, $[\mathrm{C}]_0 = 1.43 \times 10^{-2}\,M$; (1B) coupler, $[\mathrm{C}]_0 = 0$.

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[4] L. Michaelis and S. Granick, THIS JOURNAL, **65**, 1747 (1943).

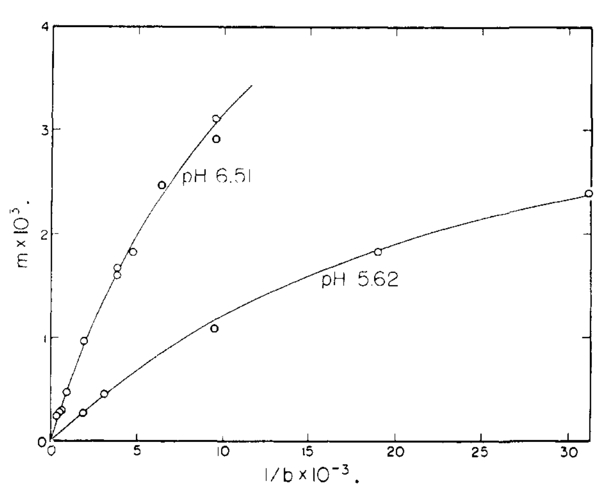

Fig. 2.—Coupling rate as a function of the initial concentration of dimethyl-*p*-phenylenediamine: semiquinone, $a = 0.143 \times 10^{-3}$ *M;* coupler, $[C]_0 = 7.15 \times 10^{-3}$ *M.*

m approaches zero almost linearly with decreasing 1/*b*. This shows that coupling can be stopped by a large excess of [R], as would be expected if the rate is proportional to [T], *i.e.*, the reaction follows the QDI mechanism. We can therefore set

$$m = \alpha[\mathrm{T}] \qquad (4)$$

Since the curvatures in the lines of Fig. 2 depend on the value of *K*, these curves can be used to estimate *K* by the following procedure.

Equation 2 was rearranged into the dimensionless form

$$\frac{b}{a} = \left(\frac{4-K}{K}\right)\frac{[\mathrm{T}]}{a} + \frac{1}{K\dfrac{[\mathrm{T}]}{a}} - \frac{4}{K} \qquad (5)$$

A set of reference curves relating to log [T]/*a* and log *a*/*b*, each with a given value of *K*, were calculated and drawn on transparent graph paper. The experimental points relating log *m* and log *a*/*b* are plotted to the same scale. The values of *K* and α were obtained by matching the curves on the two graphs, superimposing the same values of log *a*/*b*. *K* was obtained directly from the curve having the best fit, and α from the relative position of the log *m* and log [T]/*a* scales when the curves matched. From eq. 4 we obtain

$$\log \alpha = \log m - \log \frac{[\mathrm{T}]}{a} - \log a \qquad (6)$$

At *p*H 6.51, the constants estimated by this method were $K = 8$ and $\alpha = 220$; at *p*H 5.62, they were $K = 25$ and $\alpha = 190$. The curves shown in Fig. 2 were calculated by the use of these constants.

Figure 1 shows the results of experiments in which *b* was kept constant and *a* was varied. When *m* is plotted against *a*, as shown in Fig. 3, it increases approximately with the square of *a*. The curve shown in this figure was calculated using eq. 2 and 4 and the constants given above for α and *K* at *p*H 6.51.

The *K* values obtained by this method seem reasonable since, according to Michaelis and coworkers,[3] S should have maximum stability near *p*H 4. However, the almost identical values for the rate constant α at *p*H 6.5 and 5.6 were unexpected. A possible explanation is that the QDI becomes more reactive by acquiring a proton in the acid region or because the undissociated form of the coupler has a finite reaction which manifests itself when the ionic reaction is sufficiently suppressed. Possibly, both effects are produced. This uncertainty, however, does not alter the conclusion that, in acid solutions where the formation of SQ is at an optimum, the coupling rate is proportional to the concentration of the QDI and not to the concentration of the semiquinone.

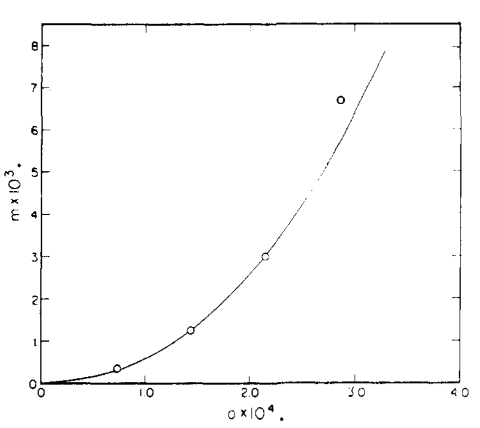

Fig. 3.—Dependence of coupling rate on semiquinone concentration: *p*-phenylenediamine, $b = 0.525 \times 10^{-3}$ *M;* coupler, $(C)_0 = 1.43 \times 10^{-2}$ *M; p*H 6.56.

Experimental

1. **Materials.**—Acetonitrile and methanol were Eastman White Label Grade; the potassium phosphate salts used for buffers were reagent grade. The 2-methyl-4-chlorophenol was prepared and recrystallized by A. H. Soloway, in these Laboratories; m.p. 45–47°. Wurster's Red or semiquinone of *p*-amino-N,N-dimethylaniline was recently prepared by R. Bent, also in these Laboratories; m.p. 123–125°. The *p*-amino-N-dimethylaniline sample was prepared in connection with earlier experiments[5] and stored under refrigeration.

2. **Coupling of *p*-Amino-N-dimethylaniline with 2-Methyl-4-chlorophenol.**—2-Methyl-4-chlorophenol, dissolved in a potassium phosphate buffer containing acetonitrile, was mixed with an aqueous solution of *p*-amino-N-dimethylaniline, and the coupling reaction was initiated by the addition of Wurster's Red dissolved in methanol. The concentration of both methanol and acetonitrile in the reaction mixture was 14.3% by volume. The ionic strength from the phosphate buffer was 0.43. The formation of the blue dye was followed by observing the change in transmission at 630 mμ in the American Optical Company Scanning Spectrophotometer. The *p*H of the reaction mixture was measured in a Beckman Model G *p*H meter. The reactants were kept at 25° in a water-bath, mixed and added to a 2.5-cm. cell around which 25° water was circulated.

Coupling measurements were made under three different sets of conditions, all having a large excess of coupler with initial concentration $[C]_0$; (1) *p*H 6.51, semiquinone constant, *p*-amino-N-dimethylaniline varied; (2) repeat of (1) at *p*H 5.62; (3) *p*H 6.56, *p*-amino-N-dimethylaniline constant, semiquinone varied. The density measured was the sum of the densities produced by two reactions: coupling of *p*-aminodimethylaniline with phenol and the autocoupling described in the previous section. The density from auto-

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(5) R. L. Bent, J. C. Dessloch, F. C. Duennebier, D. W. Fassett, D. B. Glass, T. H. James, D. B. Julian, W. R. Ruby, J. M. Snell, J. H. Sterner, J. R. Thirtle, P. W. Vittum and A. Weissberger, THIS JOURNAL, **73**, 3100 (1951).

coupling alone was determined by repeating the experiments in the absence of phenol.

It was found that the dye had the same extinction at *p*H 5.6 and *p*H 6.5, and that Beer's law was obeyed up to a density of at least 0.7 in the 2.5-cm. cell.

ROCHESTER 4, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Dye-sensitized Photopolymerization of Acrylamide[1]

BY GISELA K. OSTER, GERALD OSTER AND GIOVANNI PRATI

RECEIVED OCTOBER 1, 1956

The kinetics of polymerization of acrylamide by visible light using riboflavin as the sensitizer has been studied. The reaction proceeds so rapidly that the course of the polymerization can be followed by adiabatic thermal rise. The rate was found to be proportional to the one-half power of the absorbed light intensity, the square of the initial monomer concentration and the one-half power of the viscosity of the medium. The viscosity dependence of the rate was determined in glycerol–water mixtures. The molecular weights of the polymers were of the order of ten millions; they were independent of the initial monomer concentration but increased with increasing viscosity and decreasing intensity. These results are explained in terms of a kinetic scheme which involves the unimolecular disappearance of part of the initiating free radicals and the diffusion-controlled bimolecular termination of the growing chain radicals.

It has been found that vinyl compounds can be polymerized by visible light in the presence of certain dye-reducing agent combinations.[2,3] Dyes in the presence of mild reducing agents undergo photoreduction to their leuco forms.[4] If this photoreduction is carried out in the complete absence of oxygen no polymerization of vinyl monomer ensues. However, if oxygen is added after photoreduction has taken place, polymerization of the monomer commences. Therefore, the free radicals which initiate polymerization arise from the reaction between the leuco dye and oxygen.

The present paper is concerned with the kinetics of the photopolymerization of acrylamide using riboflavin as the sensitizer. Of all the dyes, riboflavin is unique in that part of the dye itself, namely, the ribose group, acts as its own reducing agent. Under the influence of visible light the polymerization, which is an exothermic reaction, proceeds so rapidly that the course of the polymerization can be followed by adiabatic thermal rise. Some of the experiments described herein were designed to elucidate the role of diffusion-controlled processes in high polymer reactions.

Experimental

Materials.—Acrylamide (m.p. 84.5°) was obtained from American Cyanamid Co. Riboflavin 5′-phosphate sodium was obtained from Hoffman–LaRoche. This form of riboflavin is preferable to the non-esterified form in that it is more water-soluble and seems to be more stable to oxidation in solution. Glycerol was Fisher C.P. grade.

Procedure.—The aqueous solutions containing dye and monomer were placed in test-tubes having a diameter of $^3/_4$ in., the volume of the solution being 11 ml. In some cases glycerol–water mixtures were substituted for pure water.

The solutions were placed 12 in. from a 1000-watt Kodak Master projector using a blue cobalt glass (Corning number 5-58) as a filter. Using a calibrated thermopile, it was found that under these conditions 2.6×10^{16} quanta fell on an area of 1 cm.^{2} per sec. Variations in intensity were made using neutral density filters.

The thermal rise accompanying the polymerization was measured with a copper–constantan thermocouple which was placed at the center of the solution. The thermal e.m.f. was amplified by a Leeds and Northrup stabilized d.c. microvolt amplifier and was continuously recorded on a Leeds and Northrup Speedomax Type G recorder. The thermal rise was used to calculate the per cent. conversion of monomer. The polymerization was allowed to proceed until a certain temperature was reached; the resultant mixture was then quickly dissolved in water, and the polymer was precipitated in a large volume of methanol and was filtered, dried and weighed. Knowing the heat capacity of the original solution and assuming adiabatic conditions for this rapid polymerization, an average of ten experiments showed that 20 kcal. are evolved per mole of monomer converted. Hence, in our experiments a temperature rise of one degree centigrade corresponds to a conversion of 5.5×10^{-4} mole of acrylamide.

The viscosities of the mixtures prior to irradiation were measured in an Ostwald viscometer having a flow time for water of 15 sec. Intrinsic viscosities of the polymer produced were determined in an Ostwald dilution viscometer having a flow time for water of 300 sec. Light scattering measurements at various angles were carried out in an Aminco instrument using Ludox for standardization.[5]

Results

In Fig. 1 are illustrated some typical rate curves. After an initial period of illumination the polymerization commences and accelerates until it reaches a constant rate. At about 20% conversion for the systems illustrated in Fig. 1, the reaction is accelerated due to the Trommsdorff effect. If the light is turned off while the reaction proceeds at a uniform rate, the polymerization continues but at a rapidly diminishing rate. This post-polymerization is particularly prolonged in highly viscous solutions. In all cases the rate of the reaction is taken from the slopes of the linear portions of the curves. The induction period is chosen as the intercept of the time axis with the extrapolation of the linear portion of the rate curve.

The monomer concentration (21–64%) was varied keeping all other factors constant. It was found that the rate of monomer consumption was proportional to the second power of the initial monomer concentration. The induction period was not sensibly dependent on the initial monomer concentrations under the conditions described in Fig. 1.

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[1] Presented before the 130th National Meeting of the American Chemical Society, Atlantic City, September 20, 1956.

[2] G. Oster, *Nature*, **173**, 300 (1954).

[3] For other methods of sensitized photopolymerization see G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A189**, 481 (1947); M. G. Evans, M. Santuppa and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

[4] G. Oster, *Photo. Engr.*, **4**, 173 (1953).

[5] G. Oster, *Anal. Chem.*, **25**, 1165 (1953).