Appendix

The initial rate equation was derived assuming the following

$$I_2 + h\nu \xrightarrow{\text{i}} 2I \tag{1A}$$

$$I_2 + C_5 \overset{K_c}{\rightleftharpoons} C_5 \cdot I_2 \tag{2A}$$

$$C_5 \cdot I_2 + h\nu \longrightarrow C_5 \cdot I + I\cdot \tag{3A}$$

$$C_5 \cdot I_2 + I\cdot \xrightarrow{k_1} C_5I_2 + I\cdot \tag{4A}$$

$$I + I \xrightarrow{\text{t}} I_2 \tag{5A}$$

$$C_5 \cdot I + I \xrightarrow{\text{t}} C_5 + I_2 \tag{6A}$$

For the purpose of this derivation, it was assumed that eq 4A was rate determining and irreversible. In addition, eq 3A was assumed to contribute to the production of iodine atoms in a manner similar to eq 1A.

The rate of formation of product according to eq 4A is given by

$$d[C_5I_2]/dt = k_1[C_5 \cdot I_2][I_2]_{\text{eff}}^{1/2} \tag{7A}$$

where $[I_2]_{\text{eff}}$ is the effective iodine concentration leading to the production of iodine atoms, which includes the contribution from eq 3A, as expressed by

$$[I_2]_{\text{eff}} = [I_2]_f + [C_5 \cdot I_2] \tag{8A}$$

and

$$\begin{aligned}[I_2]_f &= \text{concentration of uncomplexed iodine} \\ &= [I_2] - [C_5 \cdot I_2]\end{aligned} \tag{9A}$$

thus

$$[I_2]_{\text{eff}} = [I_2] \tag{10A}$$

The charge-transfer equilibrium constant is defined by

$$K_c = \frac{[C_5 \cdot I_2]}{[C_5][I_2]_f} \tag{11A}$$

Substituting the expression for $[I_2]_f$ into eq 11A and rearranging, we obtain the expression for the concentration of the complex

$$[C_5 \cdot I_2] = \frac{K_c[C_5][I_2]}{1 + K_c[C_5]} \tag{12A}$$

Substitution of eq 12A into eq 7A and rearrangement give

$$[I_2]^{-3/2}d[C_5I_2]/dt = \frac{k_1K_c[C_5]}{1 + K_c[C_5]} \tag{13A}$$

Since the observed rate constant is given by eq 14A

$$d[C_5I_2]/dt = k[I_2]^{3/2} \tag{14A}$$

it can be rewritten in terms of eq 13A to give eq 15A.[22]

$$\frac{[C_5]}{k} = \frac{1}{k_1K_c} + \frac{[C_5]}{k_1} \tag{15A}$$

According to eq 15A a plot of $[C_5]/k$ *vs.* $[C_5]$ would give a straight line whose slope would be equal to $1/k_1$ and the intercept equal K_c/k_1.

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[22] This rate expression is similar to the one arrived at by Keefer and Andrews in a study of the exchange reactions between organic halides and iodine monochloride. *Cf.* R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **75**, 543 (1953); **76**, 253 (1954).

Kinetics of Dye Formation by Flash Photolysis. In 1-Octanol

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Contribution from the Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650. Received May 29, 1970

Abstract: Azomethine dye is formed when *p*-azido-*N*,*N*-diethylaniline is photolyzed in the presence of 2,6-dimethylphenol derivatives in 1-octanol. Nitrene, formed in the photolysis, reacts at the position para to hydroxyl on the phenol to form a leuco dye or abstracts a proton to form quinonediimine. Leuco dye is converted to dye by elimination of a suitably positioned leaving group or by oxidation with quinonediimine. This rate-determining step (*i.e.*, conversion of leuco dye to dye) is accelerated by acidic materials and has only minor dependence on coupler ionization.

Azomethine dye is formed when quinonediimine reacts with a phenolic or naphtholic compound called a coupler. This reaction may occur in an aqueous phase or in a low dielectric organic solvent. The kinetics and mechanism of dye formation and the associated reactions of quinonediimine have been established for the aqueous phase.[1-4] The present work was undertaken to supply information regarding dye formation in organic solvents.

Tong and Glesmann[1] have shown that, in aqueous systems, quinonediimine reacts reversibly with coupler ion to form an intermediate called a leuco dye. Colorless leuco dye is converted to dye by formation of a double bond through an elimination reaction or an oxidation reaction. If a leaving group (X) other than hydrogen is para to hydroxyl on the phenolic or naphtholic coupler, the dye forms by elimination, and the coupler is referred to as "two-equivalent." When hydrogen is para to hydroxyl, the leuco dye must be oxi-

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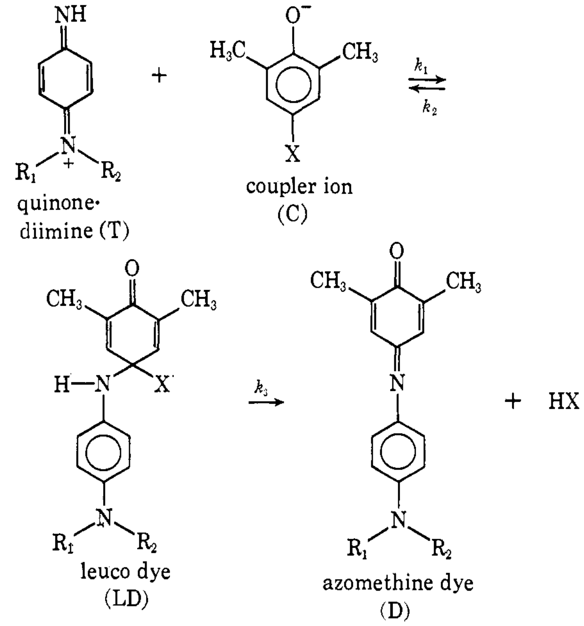
[1] L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, **90**, 5164 (1968).

[2] L. K. J. Tong and M. C. Glesmann, *ibid.*, **79**, 583 (1957).

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

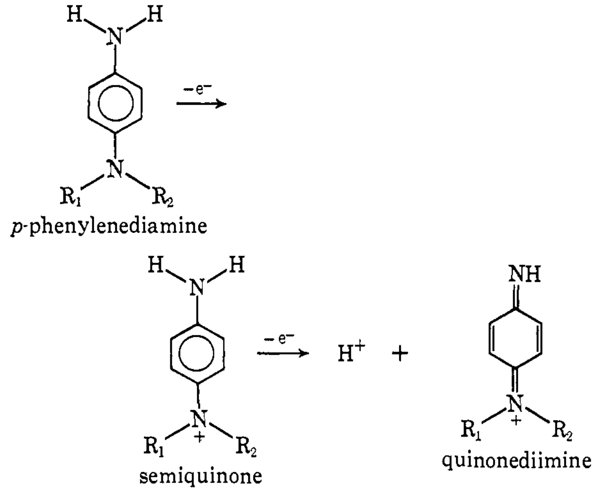
[4] L. K. J. Tong, M. C. Glesmann, and R. L. Bent, *J. Amer. Chem. Soc.*, **82**, 1988 (1960).

dized to dye and the coupler is called "four-equivalent." The coupler equivalency refers to the number of electrons that must be removed from the diamine-coupler pair to form one dye molecule. Some phenols do not form dye with quinonediimine, *e.g.*, when X = CH_3. The rate-determining step of dye formation in eq 1 involves leuco dye formation (k_1). X is a leaving group and R_1 and R_2 are alkyl groups.



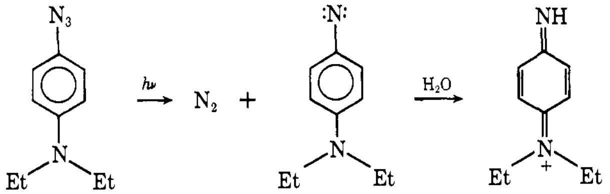
(1)

Quinonediimine is usually formed by chemical oxidation of *p*-phenylenediamine derivatives.[5] The reaction is rapid and complete for many oxidizing agents in water. In organic solvent, oxidation may be slow and equilibrium not completely in favor of quinonediimine. This makes interpretation of the kinetics of quinonediimine reactions difficult and led to the search for new means of producing quinonediimine in organic solvent.



(2)

Photolysis of *p*-azido-*N*,*N*-diethylaniline in aqueous media produces quinonediimine within a few microseconds and in quantitative yield.[6] This reaction is believed to proceed by the formation of nitrene, which is generally regarded as the primary product of azide photolysis.[7-9] The nitrene is highly reactive owing to an incomplete electronic octet on nitrogen and abstracts a proton from water to form quinonediimine.

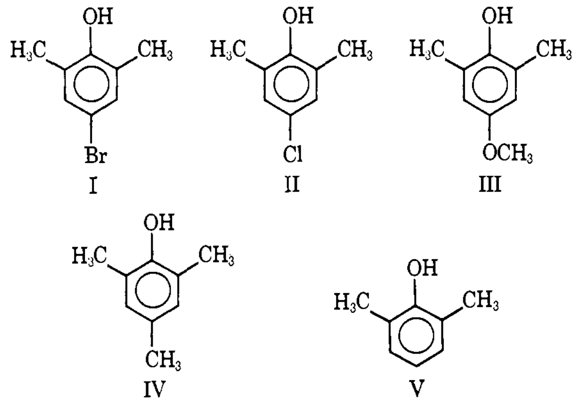


(3)

Photolysis of such an azide was investigated to determine whether the quinonediimine could be generated in organic solvent. In these cases nitrene reacts with itself, with oxygen, or with the organic solvent,[10] without necessarily deprotonating the latter. When a coupler with a highly dissociable proton is present, the acidic proton is not abstracted by the nitrene to form quinonediimine, yet the nitrene reacts with the phenol to form an azomethine dye.

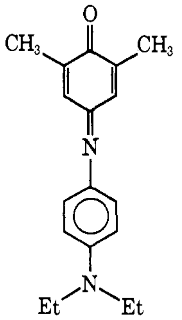
The azide and most of the phenols (Chart I) chosen for this work yield simple dyes. One of the phenols (IV) was selected to study the effect of a nondye-forming phenol on the rate.

Chart I. Couplers Studied



Results

This work was conducted in 1-octanol because of its stability, high viscosity, immiscibility with water, high boiling point, and low dielectric constant. When the azide is photolyzed in octanol with one of the couplers I, II, III, or V. the dye that forms is



No dye forms when coupler IV is photolyzed with the azide. The azomethine dye was identified by com-

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[5] L. Michaelis, *Chem. Rev.*, **16**, 243 (1935).

[6] R. C. Baetzold and L. K. J. Tong, submitted for publication.

[7] A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966).

[8] A. Reiser, G. C. Terry, and F. W. Willets, *Nature (London)*, **211**, 410 (1966).

[9] A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, **64**, 3265 (1968).

[10] Dr. W. J. Priest, private communication.

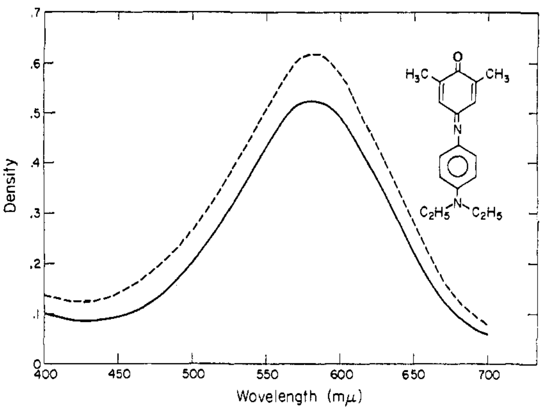


Figure 1. Spectra in octanol of dyes (different concentrations) formed by photolysis of azide I and coupler I (— — —) and authentic azomethine dye (———) by reaction of coupler and oxidized *p*-phenylenediamine.

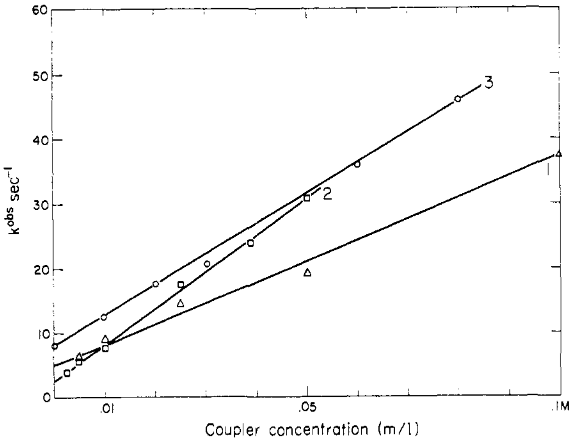


Figure 2. Dependence of pseudo-first-order rate constant on coupler concentration: curve 1, coupler V, slope = 338 l./mol sec; curve 2, coupler I, slope = 570 l./mol sec; curve 3, coupler I, 0.01 *M*, coupler IV concentration varied, slope = 487 l./mol sec.

paring its spectrum (Figure 1) with that of the dye formed by oxidative coupling of *p*-*N*,*N*-diethylaminoaniline with I, II, III, or V. Thin-layer chromatography further confirms this identification.

Photolysis of the azide in the presence of a "two-equivalent" coupler in octanol forms azomethine dye by a reaction path not involving quinonediimine. The dye is formed in milliseconds. On the other hand, formation of dye *via* the reaction of quinonediimine with coupler requires *minutes* in neutral octanol The latter experiment was performed by mixing coupler I with quinonediimine formed by oxidation of the *p*-phenylenediamine by bromine (eq 1). Alkali speeds up the reaction as expected if coupler ion is the reactive species. Base has only a minor effect on the dye formation rate in the azide photolysis system, as will be described later.

Rates were measured with coupler in excess relative to the photolysis product of the azide. This excess of coupler leads to first-order dye formation for up to three half-lives, as shown by a plot of time *vs.* the log of final dye density minus dye density at a given time.

Results for couplers I and V are presented since they are representative "two-equivalent" and "four-equivalent" couplers, respectively. The dependence of the first-order rate constant on coupler concentration is shown in Figure 2. The linear relation of rate constant to coupler concentration indicates coupler involvement in the rate-determining step. The extrapolated nonzero intercept corresponds to a finite rate at zero coupler concentration and suggests that coupler catalyzes the rate-determining step of the reaction, but that dye can form without catalysis of this step by coupler.

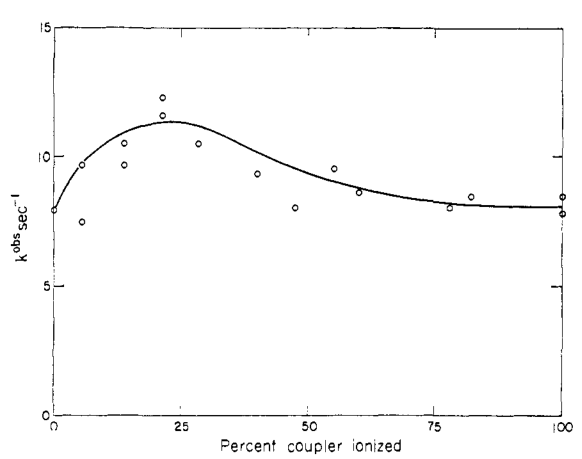


Figure 3. Dependence of dye-formation rate constant for azide I and 0.01 *M* coupler I on percentage coupler ionized by KOH.

The effect of coupler concentration on the dye-formation rate is nearly the same for dye-forming coupler as for nondye-forming coupler. Figure 2 shows the rate of dye formation for the azide and 0.01 *M* coupler I as the concentration of nondye-forming coupler IV is changed. The slope of this plot is 487 l./mol sec compared to a slope 570 l./mol sec when only coupler I is present. This experiment shows that the role of coupler in the rate-determining dye-formation step is catalytic since both dye-forming and nondye-forming couplers have similar effects.

Acetic acid increases the dye-formation rate in the azide-coupler photolysis system. In 0.01 *M* coupler I the rate constant increases linearly with acid (slope = 43.4 l./mol sec), passes through a maximum at 0.2 *M* acetic acid, and then decreases. In the concentration region beyond the maximum, the kinetics deviate from first order so this region was not examined in detail.

Coupler ion is not involved in the rate-determining dye-formation step in the azide photolysis system, unlike dye formation in water or octanol when quinonediimine is generated by oxidation of *p*-phenylenediamine. Figure 3 shows that the rate of dye formation has little dependence upon coupler ionization when KOH is added to octanol to ionize coupler I before photolysis. There must be a catalytic effect of KOH, however, to make up for the loss of catalysis by ionizing coupler. The catalyzing species could be coupler ion or excess KOH. The curvature in Figure 3 suggests that coupler ion is not the catalyzing species since the sum of coupler and its ion should be constant.

The primary photolysis product of the azide (nitrene) must react with coupler in order to account for the reaction leading to dye. Transient absorption attributable to the nitrene is not detected whether coupler is present or absent during photolysis of azide. This supports the contention that the nitrene reacts rapidly with coupler, forming an intermediate which is converted to dye in the rate-determining step of the reaction.

The reaction of nitrene with coupler is irreversible. This point is demonstrated by the kinetics of dye formation for photolysis of the azide and a mixture of two couplers, both forming the same dye. The couplers have different reactivity in the mixture, but dye appears as shown in Figure 4. The data were resolved into a sum of two concurrent, independent first-order reactions. The data show that (1) the rate-limiting step is dye formation from a coupler–nitrene intermediate and (2) the intermediates formed from nitrene and each coupler do not interconvert once they are formed. If interconversion were possible, all dye would be formed from the intermediate that decomposes most rapidly to dye. This would result in dye formation by simple first-order kinetics. First-order kinetics would also be observed if these two reactions were simple competition for couplers by nitrene in the rate-limiting step.

We have found that the amount of dye formed by each reaction depends upon the relative concentration of each coupler. As the ratio of coupler III concentration to coupler II concentration increases, more dye forms by the faster reaction.

Nitrene can form quinonediimine along with the dye upon azide photolysis in the presence of "four-equivalent couplers"; no quinonediimine is formed by reaction with "two-equivalent couplers." Quinonediimine is indicated by adding KOH to the photolysis products and observing a rapid increase in dye density; this effect comes from the acceleration of quinonediimine coupling by bases, as mentioned earlier. Formation of quinonediimine from nitrene and coupler V cannot be explained by the acidity of this coupler since the more acidic "two-equivalent" couplers (I and II) do not give quinonediimine.

Discussion

Nitrene would be expected to react with acidic protons on coupler, since in water nitrene can be exclusively protonated.[6] The exclusive reaction of nitrene with coupler at the position para to hydroxyl indicates that nitrene must react there before colliding with an acidic site on another coupler; otherwise, protonation to quinonediimine would have taken place. This suggests that a complex (AHC) is formed between azide and coupler and that, upon photolysis, it becomes a complex between nitrene and coupler (NHC). In this latter complex, the reaction of the nitrene at the para position of the coupler occurs.

Complexes like those postulated for AHC have been observed between aniline and phenol derivatives in other low dielectric organic solvents.[11] If the benzene rings are located in parallel planes, the reactive coupler position would come close to the reactive nitrene position through relative motions of the complexed partners.

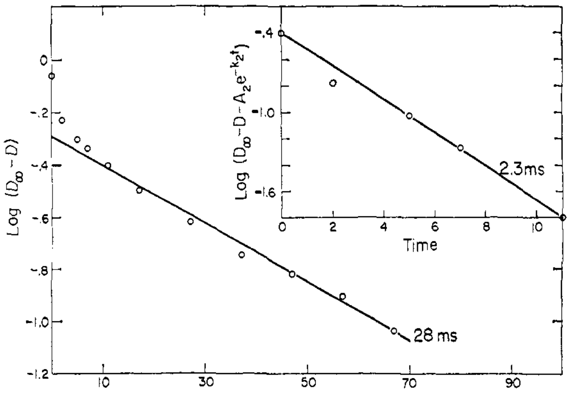
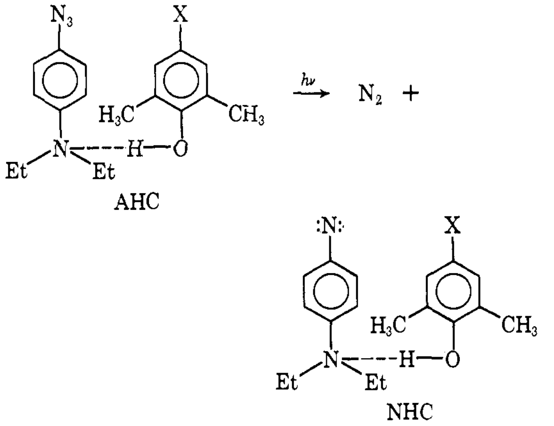


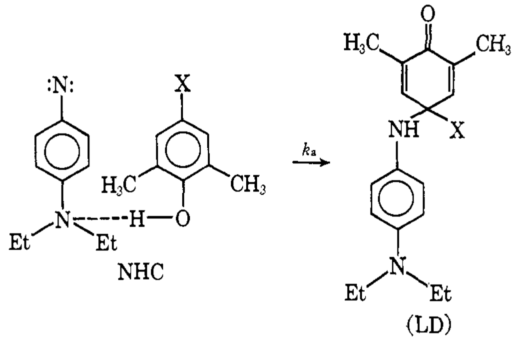
Figure 4. Plots showing kinetics of dye formation for azide I, 0.045 *M* coupler III, and 0.005 *M* coupler II. The slow reaction has a half-life of 28 msec, and the fast reaction has a half-life of 2.3 msec.

The nitrene–coupler complex formed by photolysis is short-lived and not detected. It reacts to form an intermediate that may be leuco dye which is also formed when quinonediimine and coupler ion react. The decomposition of this intermediate to give dye is the rate-determining step of the reaction. These reactions can be represented as shown in eq 4a–4e. The initial step is



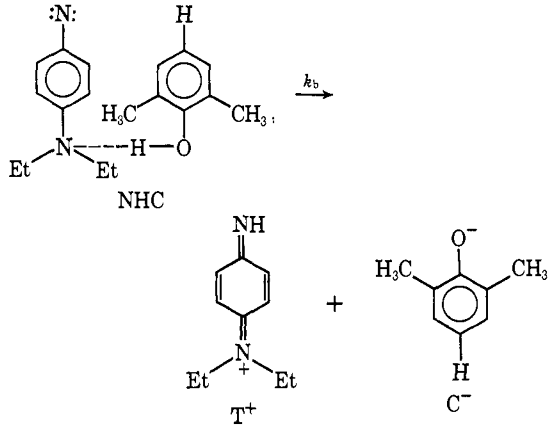
(4a)

Equation 4b shows fast C–N bond formation. When



(4b)

X = H, another path was followed besides eq 4b



(4c)

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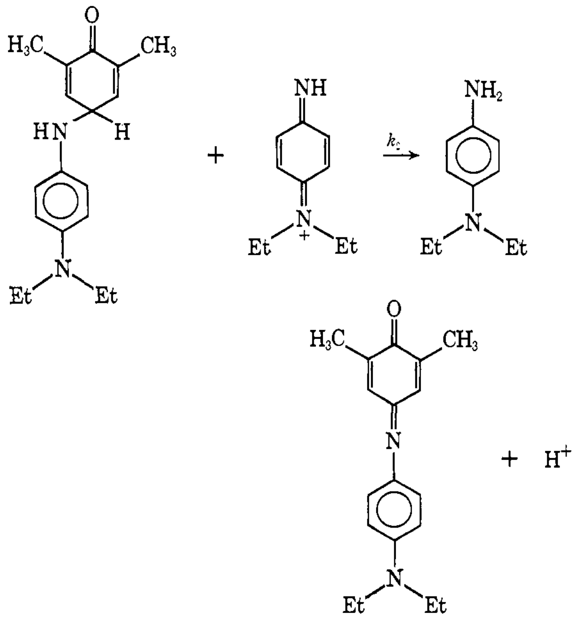
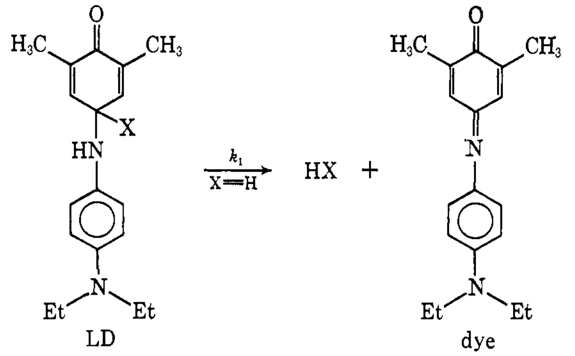
(11) "Acid-Base Behavior in Aprotic Organic Solvents," National Bureau of Standards, 1968, p 129.

When X = H, the dye is formed by oxidation by quinonediimine (eq 4d). When X can be eliminated, dye



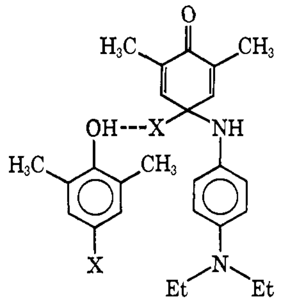
(4d)

is formed by a nonoxidation pathway.



(4e)

Two-Equivalent Couplers. Acid and coupler catalysis of the dye-formation rate is attributed to effects on the rate-determining reaction 4e. Catalysis by the acid function of these molecules could proceed through a transition state.



We believe the role of KOH in formation of dye from leuco dye may involve an ionization equilibrium of the latter. These effects can be used to write the general equation for the rate of dye formation (eq 5).

$$\text{LD} \xrightarrow{k_{\text{LD}}} \text{dye} + \text{HX} \qquad (5\text{a})$$

$$\text{LD} + \text{B} \xrightarrow{k_{\text{B}}} \text{dye} + \text{HX} + \text{B} \qquad (5\text{b})$$

$$k_{\text{obsd}} = k_{\text{LD}} + \sum k_{\text{B}}(\mathbf{B})$$

The summation includes all species B which represent either KOH, acetic acid (HAc), or coupler (HC). We evaluate k_{LD} from the intercept of Figure 2 and k_{B} from the slope ($\partial k_{\text{obsd}}/\partial(\mathbf{B})$).

Four-Equivalent Couplers. Oxidation of leuco dye (LD) by quinonediimine (T^+) is the rate-determining step for rapid dye formation initiated by photolysis of the azide in the presence of coupler V. A dye-formation reaction requiring several minutes is also observed and attributed to the coupling of quinonediimine and coupler in neutral octanol. This slow reaction is accelerated by base and results in the formation of 6.8 times more dye than is formed by the rapid reaction. This indicates that the initial concentration of quinonediimine is 14.6 times the initial concentration of leuco dye. Thus, the rapid appearance of dye takes place by a pseudo-first-order reaction with quinonediimine in excess of leuco dye concentration.

Coupler and acid increase the rate of dye formation. This can occur by increasing the ratio of quinonediimine to leuco dye initially formed. An intermolecular reaction between either acid or coupler with nitrene coupler intermediate (NHC), serving to protonate the latter and convert it to quinonediimine, is a possible explanation of this effect. We write the following equations (6a–e) to describe this mechanism.

$$\text{NHC} \xrightarrow{k_{\text{b}}} \text{T}^+ + \text{HC} \qquad (6\text{a})$$

$$\text{NHC} \xrightarrow{k_{\text{a}}} \text{LD} \qquad (6\text{b})$$

$$\text{NHC} + \text{HAc} \xrightarrow{k_{\text{H}}} \text{T}^+ + \text{HC} + \text{Ac}^- \qquad (6\text{c})$$

$$\text{NHC} + \text{HC} \xrightarrow{k_{\text{HC}}} \text{T}^+ + \text{HC} \qquad (6\text{d})$$

$$\text{T}^+ + \text{LD} \xrightarrow{k_0} \text{dye} + \text{R} + \text{H}^+ \qquad (6\text{e})$$

The rate constant for dye formation predicted by this mechanism is

$$k_{\text{obsd}} = (\text{dye})_{\text{f}}k_0\left\{\frac{k_{\text{b}}}{k_{\text{a}}} + \frac{k_{\text{H}}(\text{HAc})}{k_{\text{a}}} + \frac{k_{\text{HC}}(\text{HC})}{k_{\text{a}}}\right\} \qquad (7)$$

where $(\text{dye})_{\text{f}}$, the final concentration of dye formed, was kept at 5×10^{-6} M in all runs. Using eq 7 and the slope and intercept of Figure 2 for coupler V, we evaluate $k_{\text{HC}}/k_{\text{a}}$ and k_0. The slope of rate constant *vs.* acetic acid concentration (5250 l./mol sec) was used to evaluate $k_{\text{H}}/k_{\text{a}}$. These data appear in Table I.

Table I. Rate Constants for Dye Formation

Coupler	k_{LD}, sec^{-1}	k_{HC}, l./mol sec	k_{HAc}, l./mol sec	k_{KOH}, l./mol sec
I	2.3	570	43.5	1,410
II	4.3	570	23	1,680
III	3.5	475	403	335
V	$k_0 = 6.0 \times 10^4$ l./mol sec $k_{\text{b}}/k_{\text{a}} = 14.6$ $k_{\text{H}}/k_{\text{a}} = 1.74 \times 10^4$ l./mol $k_{\text{HC}}/k_{\text{a}} = 155$ l./mol			

Comparison of the rate constants in Table I indicates a minor effect of substituent on the rate constants k_{LD} and k_{HC}. The acid and base catalysis rate constants show more dependence on substituents.

Those leuco dyes formed from couplers with electron-releasing groups exhibit the greatest catalysis by acid. Apparently, the electron-releasing leaving group is better able to form a bond with a proton and be eliminated from the leuco dye.

A detailed mechanism of the formation of azomethine dye by azide photolysis in octanol is not possible to give at this time. The effect of acid, base, and coupler on the reaction mechanism is uncertain because the solvent properties of octanol are not well enough understood. The interaction between azide and coupler is great in this solvent since it causes nitrene to react by an intramolecular rather than an intermolecular path.

Experimental Section

Apparatus. The flash photolysis apparatus includes a variable bank of capacitors (1–8.5 μF), which can be charged to 10 kV; a xenon flashlamp is activated by a spark gap (EG + G GP42A), which is in turn fired by a trigger transformer whose action is initiated by an amplified delay pulse from an oscilloscope. Under typical operating conditions the photolysis flash has a half-life of 20 μsec; 100 μsec must elapse before accurate optical density measurements can be made.

Light in the analytical part of the system comes from a tungsten lamp (30 W) source and passes through the sample cell, a monochromator, and then into a photomultiplier. The cell is a 5-cm Pyrex capillary tube (1-mm i.d.) with caps at both ends to hold glass sides and restrict the light beam to go through the solution only. This design increases the uniformity of photolysis of azide compared with cells of larger cross-section.

A photomultiplier tube (EMI 9558), attached to the monochromator by a lighttight case, is coupled to the oscilloscope by an emitter–follower amplifier. The lamp firing is initiated by a delay pulse, which is generated a short time after the beginning of the oscilloscope sweep. The entire sweep showing buildup of dye is photographed for kinetic analysis.

Conditions of Experiment. All experiments were conducted at 25° with 2×10^{-5} *M* azide and at least fivefold excess of coupler. A photograph of the oscilloscope gave transmittance *vs.* time data, which were analyzed by first-order kinetics. The systems reported obey this rate law for up to three half-lives.

Chemicals. The azide used in this work was prepared by a literature procedure.[12] The couplers were the same samples studied by Tong and Glesmann.[4] Measurements of the dye yield (*ca.* 95%) obtained after completely photolyzing azide by repeated flashes indicate that azide is quantitatively converted to dye and that the purity of azide is high.

Anal. Calcd for azide ($C_{10}H_{14}N_4$): C, 63.2; H, 7.4; N, 29.4. Found: C, 63.3; H, 7.2; N, 29.0. Thin-layer chromatography of the azide on silica gel shows only one spot when the separation is performed in the absence of light. Azide was refrigerated in dark bottles when not being used.

For preparing the quinonediimine, the free base of *p*-*N*,*N*-diethylaminoaniline was oxidized by bromine in octanol. Excess bromine is mixed with free base, converting it to semiquinone in a few seconds. Semiquinone is detected by its characteristic pink color. The pink color fades, resulting in a colorless solution within a few minutes. This latter reaction corresponds to the oxidation of semiquinone to quinonediimine by bromine. Coupler is added to the colorless neutral solution causing the formation of azomethine dye within a few minutes.

The photolytic dye formation reaction was compared with the analogous reaction between quinonediimine and coupler ion in octanol. Quinonediimine, produced by oxidizing the free base of *p*-*N*,*N*-diethylaminoaniline with bromine, is mixed with coupler solution. Dye formation requires minutes in neutral octanol, but requires less than a few seconds when triethylamine is present to ionize coupler.

Kinetic Analysis. Kinetics of dye formation by two concurrent first-order reactions follows the rate law

$$(D_\infty - D) = A_1e^{-k_1t} + A_2e^{-k_2t} \qquad (8)$$

$$k_1 > k_2$$

where A_1 and A_2 represent the amounts of dye formed by reactions having rate constants k_1 and k_2, respectively. When t is large, only the term involving the slow rate is changing in eq 8 so the slope of Figure 4 at long times determines the slow rate constant k_2; the extrapolated intercept determines A_2. These known values are used in eq 8 to calculate

$$D_\infty - D - A_2e^{-k_2t}$$

for t small using the experimental data. Thus, the rate constant (k_1) is determined by plotting the logarithm of this quantity *vs.* time as in Figure 4.

Coupler Ionization. Coupler ionization has been determined spectrophotometrically utilizing the difference in the extinction coefficients of the ionic and neutral forms of the coupler at 320 mμ.

Conclusions

(1) The mechanism of azomethine dye formation from photolysis of azide I in the presence of 2,6-dimethylphenol-type couplers in octanol involves formation of leuco dye directly; the conversion of leuco dye to dye is rate determining in this system.

(2) The oxidation of leuco dye from the four-equivalent 2,6-dimethylphenol by quinonediimine has a bimolecular rate constant of 6.0×10^4 l./mol sec.

(3) The elimination of HX from leuco dye of two-equivalent 2,6-dimethylphenol-type coupler is catalyzed by coupler, acetic acid, and KOH. The rate of reaction in neutral octanol is nearly independent of leaving groups; acid-catalyzed rates are in the order: coupler III > I > II.

(4) Quinonediimine, produced by oxidation of developer by bromine in octanol, forms azomethine dye by reaction with coupler. The half-life of quinonediimine is several minutes in the presence of 0.1 *M* coupler in neutral octanol and indicates that coupling is the rate-limiting step. Preliminary results in other solvents suggest that this technique might be employed to study coupling reactions in low dielectric media.

(5) The formation of an azide–coupler complex prior to photolysis is responsible for the reaction of nitrene at the coupling position. If the nitrene were free, it would be expected to abstract the acidic proton from the coupler to form quinonediimine.

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[12] W. L. Evans, R. G. D. Moore, and J. E. Redding, *Anal. Chem.*, 34, 159 (1962).