1.5062. Treatment of this oil with sulfuric acid in aqueous methanol gave 27.0 g (96%) of **16C** as a viscous oil which was subjected directly to sodium iodide in acetone solution. Distillation of this reaction product gave 18.6 g (84%) of yellow liquid, bp 97–99° (0.13 mm), n^{28}D 1.5399.

Anal. Calcd for $C_8H_{13}IO$: C, 35.02; H, 5.46. Found: C, 34.95; H, 5.54.

Cyclization of 17C. Dropwise addition of a solution of 29.3 g (0.15 mol) of **17C** in 500 ml of anhydrous ether to a rapidly stirred mixture of 75 g (0.32 mol) of silver oxide in 750 ml of the same solvent gave upon careful work-up 6.56 g (47%) of 2-cyclopropyltetrahydrofuran (**18**), bp 71–72° (70 mm), n^{25}D 1.4430; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.1–1.0 (broad multiplet, 5 H, cyclopropyl protons), 1.5–2.1 (multiplet, 4 H, ring methylene protons), and 3.1–3.8 (multiplet, 3 H, >C*H*O–).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.66; H, 10.77.

***trans*-7-(2-Tetrahydropyranyloxy)-3-hepten-1-ol (14T).** Sodium (13.8 g, 0.6 g-atom) in liquid ammonia (700 ml) reduction of **13** (42.5 g, 0.2 mol) gave rise to 37.4 g (87%) of **14T**, bp 105–106° (0.06 mm), n^{26}D 1.4723.

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.05; H, 10.38.

***trans*-7-Iodo-4-hepten-1-ol (17T).** From 20.0 g (0.09 mol) of **14T** and 19.1 g (0.10 mol) of *p*-toluenesulfonyl chloride in 60 ml of pyridine, there was obtained 23.1 g (67%) of **15T** as a clear oil, n^{26}D 1.4995. Partial hydrolysis of this oil with sulfuric acid in aqueous methanol gave 16.1 g (90.6%) of **16T**, n^{26}D 1.5091, which was treated directly with sodium iodide in acetone solution to afford 9.5 g (75%) of **17T** as a yellow liquid, bp 88–89° (0.05 mm), n^{25}D 1.5381.

Anal. Calcd for $C_7H_{13}IO$: C, 35.02; H, 5.46. Found: C, 35.08; H, 5.50.

Cyclization of 17T. A 7.1-g (0.030 mol) sample of **17T** was treated with powdered silver oxide (13.9 g, 0.06 mol) in the usual manner. Careful distillation of the reaction product led to the isolation of 1.90 g (57%) of **18**, bp 69–70° (65 mm), n^{24}D 1.4430, identical in all respects with the material obtained from **17C**.

***trans*-6-(2-Tetrahydropyranyloxy)-3-hexen-1-ol (22T).** To a solution of 24.2 g (1.05 g-atom) of sodium in 1500 ml of liquid ammonia was added dropwise a solution of 70 g (0.35 mol) of **20**[10,27] in 100 ml of ether. The resulting solution turned pink and an additional 14 g (0.61 g-atom) of sodium was added. The blue solution was worked up as described above to give 12.3 g (35%) of *trans*-3-hexen-1-ol (**21T**), bp 48–49° (2.4 mm), n^{23}D 1.4390, *p*-nitrophenyl urethan mp 84.0–84.5° [lit.[28] bp 51–53° (9 mm), n^{20}D 1.4374; *p*-nitrophenyl urethan mp 84–85°], and 17.5 g (25%) of **22T**, bp 102–103° (0.08 mm), n^{23}D 1.4748.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.79; H, 10.09.

***trans*-6-Iodo-3-hexen-1-ol (25T).** From 15.5 g (0.077 mol) of **22T** and 16.3 g (0.085 mol) of *p*-toluenesulfonyl chloride in 80 ml of pyridine, there was obtained 22.5 g (82%) of **23T** as a clear oil. Selective hydrolysis of this oil gave 16.0 g (94%) of **24T** which was converted directly to **25T** in the usual manner, 6.5 g (49%), bp 94–95° (0.05 mm), n^{23}D 1.5418.

Attempted Cyclization of 25T. Reaction of 5.3 g (0.023 mol) of **25T** with 12.7 g (0.055 mol) of powdered silver oxide in the customary fashion produced only a viscous, high-boiling liquid.

Cyclization of 17C with Aqueous Silver Nitrate. A solution of 3.0 g (12.5 mol) of **17C** in 25 ml of tetrahydrofuran was added dropwise during 30 min to a stirred solution of 2.53 g (15 mmol) of silver nitrate in 40 ml of water. A yellow precipitate of silver iodide formed rapidly. The mixture was stirred overnight, filtered, and treated with 100 ml of water. The filtrate was extracted with ether, and the combined organic layers were dried and carefully evaporated. Distillation of the residue gave 0.43 g (31%) of **18**, bp 60–61° (45 mm).

Cyclization of 17T with Aqueous Silver Nitrate. Treatment of 5.0 g (0.021 mol) of **17T** with 4.2 g (0.025 mol) of silver nitrate in the manner described above gave 0.68 (29%) of **18**, bp 66–67° (50 mm).

Acknowledgment. The authors wish to express their appreciation to the Army Research Office (Durham) for a grant which contributed to the financial support of this research.

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[27] R. A. Raphael and C. M. Roxburgh, *J. Chem. Soc.*, 3875 (1952).

[28] L. Crombie and S. H. Harper, *ibid.*, 873 (1950).

Kinetics and Mechanism of Oxidative Coupling of *p*-Phenylenediamines

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Abstract: Coupling reactions between quinonediimine, T^+, and coupler anions such as phenolates, C^-, have been analyzed within the framework of the scheme

$$T^+ + C^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} I \xrightarrow{k_3} P$$

where the second step may be elimination or oxidation. Values for k_1, k_2, and k_3, obtained for several systems, were found to be independent of pH. Coupling was examined from two points of view: (a) the reaction of nucleophiles, *i.e.*, C^-, with T^+ and (b) the reaction of electrophiles, *i.e.*, T^+, with C^-. In experiments related to a, the rates were found to increase with the basicity of C^-. In experiments related to b, reaction of two different couplers with various diimines produced similar rate effects. The reaction of diimines with bulky substituents *ortho* to the primary imino nitrogen deviated from a linear free energy relationship.

The oxidative coupling between *p*-phenylenediamine and a phenolic coupler is a three-component reaction if we consider the oxidant. It is known that the coupling reaction goes through the diimine;[1] however, it is expedient to use a mixture of oxidant and diamine[1c] instead of diimine because of the latter's instability. The oxidation step can be regarded as incidental to the

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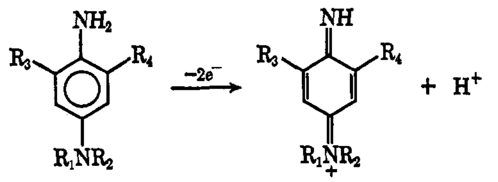
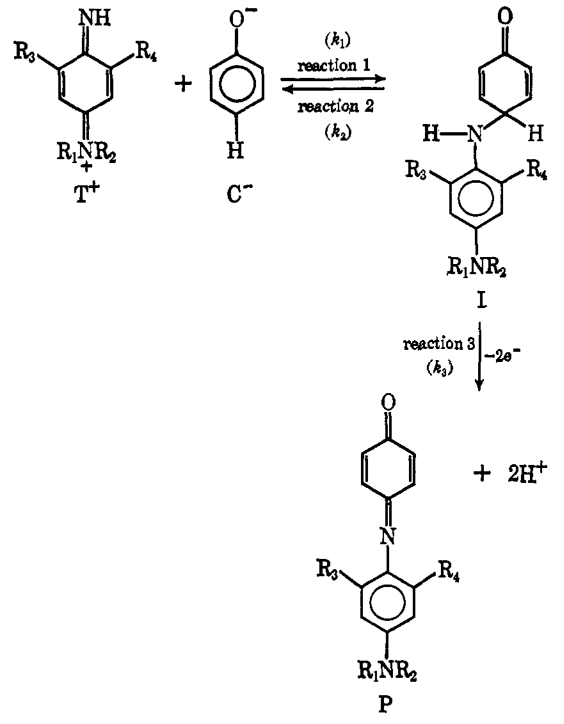
[1] (a) J. Eggers and H. Frieser, *Z. Elektrochem.*, 60, 372, 376 (1956). (b) L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, 79, 583 (1957). (c) In this report R_1 and R_2 are alkyl or substituted alkyl groups. R_3 and R_4 are selected from such substituents as H, alkyl, O-alkyl, halogen, etc.



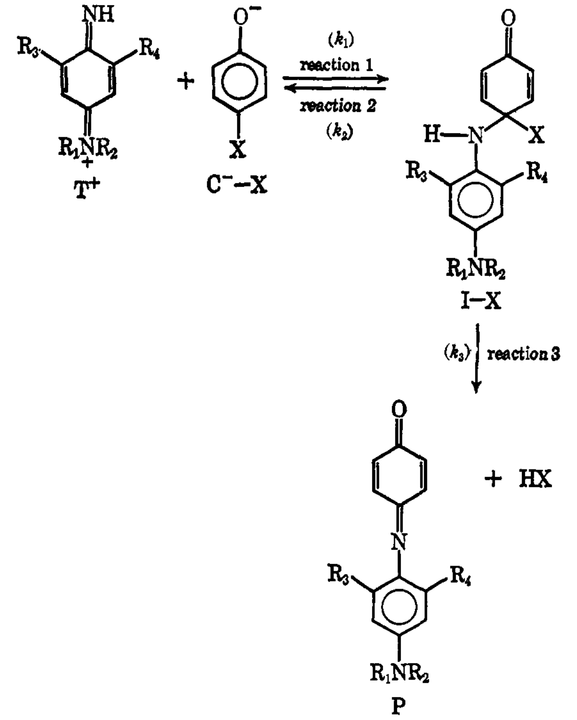
coupling mechanism. This is especially so if the oxidation step can be separated from the coupling step in the experiments. This is accomplished by the use of a flow machine[2] in which oxidation takes place in a separate chamber before the addition of the coupler. In the interval between the two mixings, the pH is kept low to reduce decomposition. Thus, in the following discussion, quinonediimine will be considered as the initial reactant.

Scheme I

Class A



Class B



Coupling reactions are separated into two classes, depending on whether the second step requires oxidation or whether it proceeds by elimination of a substituent other than hydrogen from the reaction site of the coupler.[3] These classes are designated A and B, respectively, in Scheme I.

In class B, X is usually a group capable of being eliminated as an anion, *e.g.*, CH_3O^-, $C_6H_5O^-$, halide, $SO_3{}^{2-}$, etc.[3b]

For simplification of subsequent discussion, we shall consider the symbolic reactions of Scheme I to be

$$T^+ + C^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_3} P$$

In principle, at sufficiently low concentrations of C^- (or a relatively small k_1), the rate of formation of P can be made proportional to the concentration of C^- in the first step, whereas, at high concentrations of C^- (or a relatively large k_1), it can be made independent of coupler and equal to the rate of the second step. With most systems, however, only one of these two extreme conditions could be attained by using practical concentrations. It is fortunate that some couplers were found to have borderline reactivity with several diimines so that all three elementary rate constants could be evaluated. The comparison of these constants was helpful in elucidating the mechanism.

Both the structure of the coupler and that of the diimine can be varied, allowing the reactions to be considered either as nucleophilic, with attack of the coupler on the diimine, or electrophilic, with attack of the diimine on the coupler ion.

Method and Treatment of Data. It would be impractical to obtain the elementary rate constants k_1, k_2, and k_3 experimentally by fitting the data to the solution of $(P)_t$ (eq 1) which was derived by using constant concentration of the diimine, $(T)_0$

$$(P)_t = (T)_0\left[1 - \frac{be^{-at} - ae^{-bt}}{b - a}\right] \tag{1}$$

where

$$a = H + \sqrt{H^2 - k_1k_3(C^-)}$$

$$b = H - \sqrt{H^2 - k_1k_3(C^-)}$$

in which

$$H = \frac{k_1(C^-) + k_2 + k_3}{2}$$

It is easier experimentally to evaluate the limiting cases as follows.

Case a. When the concentration of the intermediate (I) is small relative to the concentration of the diimine (T^+), the steady-state method may be applied by assuming $d(I)/dt = 0$. The experimentally obtained bimolecular rate constant k_{c^-} in eq 2 is a composite and

$$-\frac{d(T^+)}{dt} = k_{c^-}(T^+)(C^-) \tag{2}$$

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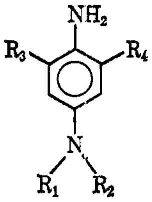
(2) W. R. Ruby, *Rev. Sci. Instr.*, **26**, 460 (1955).

(3) (a) P. W. Vittum and A. Weissberger, *J. Photogr. Sci.*, 6, 157 (1958). (b) G. W. Sawdey, M. K. Ruoff, and P. W. Vittum, *J. Amer. Chem. Soc.*, **72**, 4947 (1950).

Table I. Structures of Diamines



Diamine	Name	R_1	R_2	R_3	R_4
I	4-Amino-N,N-dimethylaniline	CH_3	CH_3	H	H
II	4-Amino-N,N-diethylaniline	C_2H_5	C_2H_5	H	H
III	N-(4-Aminophenyl)morpholine	$C_2H_4OC_2H_4$		H	H
IV	4-Amino-N-ethyl-N-β-hydroxyethylaniline	C_2H_5	C_2H_4OH	H	H
V	4-Amino-3-chloro-N,N-diethylaniline	C_2H_5	C_2H_5	H	Cl
VI	4-Amino-3-methyl-N,N-diethylaniline	C_2H_5	C_2H_5	H	CH_3
VII	4-Amino-3-methyl-N-ethyl-N-β-sulfoethylaniline	C_2H_5	$C_2H_4SO_3$-	H	CH_3
VIII	4-Amino-3-methyl-N-ethyl-N-(N′-methyl-β-methylsulfonamidoethyl)aniline	C_2H_5	$C_2H_4N(CH_3)SO_2CH_3$	H	CH_3
IX	4-Amino-3-ethyl-N,N-diethylaniline	C_2H_5	C_2H_5	H	C_2H_5
X	4-Amino-3-*n*-propyl-N,N-diethylaniline	C_2H_5	C_2H_5	H	$C_3H_7(n)$
XI	4-Amino-3-isopropyl-N,N-diethylaniline	C_2H_5	C_2H_5	H	$CH(CH_3)_2$
XII	4-Amino-3-*t*-butyl-N,N-diethylaniline	C_2H_5	C_2H_5	H	$C(CH_3)_3$
XIII	4-Amino-3-methoxy-N,N-diethylaniline	C_2H_5	C_2H_5	H	OCH_3
XIV	4-Amino-3-(β-methylsulfonamidoethyl)-N,N-diethylaniline	C_2H_5	C_2H_5	H	$C_2H_4NHSO_2CH_3$
XV	4-Amino-3,6-dimethyl-N,N-diethylaniline	C_2H_5	C_2H_5	CH_3	CH_3
XVI	4-Amino-3,6-dimethoxy-N,N-diethylaniline	C_2H_5	C_2H_5	OCH_3	OCH_3

is related to the elementary constants through eq 3.

$$k_{c^-} = \frac{k_1k_3}{k_2 + k_3} \tag{3}$$

The steady-state condition imposed on (I) implies $-d(T^+)/dt = d(P)/dt$ and therefore $k_{c^-}(T^+)(C^-) \cong k_3(I)$. With $(T^+) > (I)$, we obtain the inequality $k_3 > k_{c^-}(C^-)$ which we shall use in a later section to set a lower limit for k_3.

Case b. When $k_1(C^-) \gg k_2 + k_3$, diimine reacts rapidly with the coupler ions so that shortly after mixing (T^+) becomes very small and $(I) \cong (T^+)_0 - (P)$. This condition is equivalent to considering (I) as the initial reactant concentration which goes to (P) following first-order kinetics with rate constant k_3. If, soon after the induction period, another nucleophile, for example, a different coupler, is added to compete for the diimine which is in low concentration, part of the intermediate reacting by the reverse path (reaction 2 in Scheme I) will yield diimine which will react with the second nucleophile to form a new intermediate. Furthermore, if the kinetics involving the second nucleophile are already known, the elementary rate constants k_1 and k_2 can be determined from the yields of the two products.

A second coupler was chosen as the competing nucleophile, although any other nucleophile satisfying the same conditions could be used. The second coupler has (1) a rate comparable to that of the first, (2) produces a distinguishable dye, (3) whose intermediate is low in concentration at any particular time; therefore, eq 2 and 3 can be applied. The competitive reactions can be described by Scheme II. A double index is used for the constants in which the first refers to the couplers and the second refers to the steps.

Equation 4 was derived by assuming the steady-state for both (T^+) and (I_2) and the following experimental conditions: (1) the concentration of each coupler ion is kept constant during any one experiment; (2) the second coupler is added at a precisely known time (t') when (T^+) has become small and an amount of the first dye $(P_1)'$ has been formed (observed in separate experiments).

Scheme II

$$T^+ + C_1^- \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} I_1 \xrightarrow{k_{13}} P_1$$

$$T^+ + C_2^- \underset{k_{22}}{\overset{k_{21}}{\rightleftarrows}} I_2 \xrightarrow{k_{23}} P_2$$

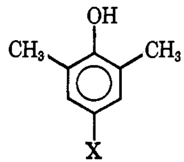
$$\frac{(P_1)_\infty - (P_1)'}{(P_2)_\infty} = \frac{k_{13}k_{11}\alpha_1(C_1)}{k_{12}k_{c^-}\alpha_2}\frac{1}{(C_2)} + \frac{k_{13}}{k_{12}} \tag{4}$$

In eq 4, (C_1) and (C_2) are the total concentrations of the two couplers, α_1 and α_2 are the degrees of ionization of these couplers, $(P_1)_\infty$ and $(P_2)_\infty$ are the final concentrations of the two dyes, and k_{c^-} is the bimolecular rate constant for the second coupler. All these quantities were obtained from independent experiments, including k_{c^-}, which is related to Scheme II through the approximation

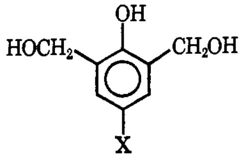
$$k_{c^-} \cong \frac{k_{21}k_{23}}{k_{22} + k_{23}}$$

The ratios k_{13}/k_{12} and k_{11}/k_{c^-} can be obtained graphically from a plot of $[(P_1)_\infty - (P_1)']/(P_2)_\infty$ *vs.* $((C_1)\alpha_1/\alpha_2 \cdot (1/(C_2))$; since k_{13} and k_{c^-} were obtained from independent experiments, k_{12} and k_{11} could be calculated.

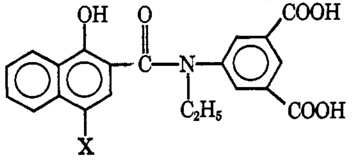
Because of the many combinations of couplers and diimines used in this study, some temporary codes have been devised. Both the diimine and diamine from which it was derived are identified by attaching a roman numeral to the class name, *e.g.*, "diamine IV" or "diimine IV." The numerals, chemical names, and chemical structures appear in Table I. The structures and the temporary codes (in parentheses) of the couplers are



coupler D-X



coupler A-X



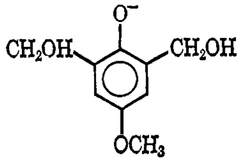
coupler B-X

where X = CH_3O–, Cl–, etc.

Results and Discussion

A. Coupling with the Elimination of CH_3O^-. The reaction between coupler A-OCH_3 and various diimines (except V) are bimolecular with rate constants k_{c^-} calculated from eq 2 by using the relationship $(T^+) \cong (T^+)_0 - (P)$. The results are summarized in Table II. In the table $(C^-)_0$ is the initial equilibrium concentration of coupler anion, and the total coupler concentration is $\geq (T^+)$ in all cases. Note that k_{c^-} increases toward what appears to be a limit as $(C^-)_0$ decreases. The deviations are related to (C^-) and are only indirectly related to pH. This suggests that the errors are due to a slight accumulation of intermediate at high (C^-). Reaction with diimine V was found to cover both extremes of conditions, depending on the coupler ion concentration (C^-). When (C^-) was large, the reactions were first order with constants independent of (C^-), and when (C^-) was small (at lower pH), the rates were bimolecular and similar to the other diimines. Further comments on the values of k_{c^-} will be made later.

Table II. Rate Constants[a] for Coupling of



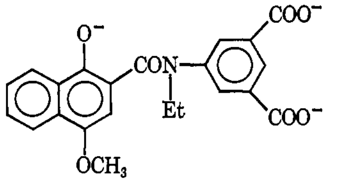
Diimine	pH	$(T)_0 \times 10^4$, M	$(C^-)_0 \times 10^6$, M	k_{c^-}, l./mol sec
III	8.24	1.00	2.4	1.7×10^7
	8.13	2.00	3.7	1.5×10^7
	8.26	1.00	4.9	0.8×10^7
				$(1.6 \times 10^7)^b$
VII	8.21	1.00	4.4	1.3×10^6
	8.22	1.00	8.8	1.4×10^6
	10.13	1.00	65.0	1.3×10^6
	10.12	1.00	130	1.1×10^6
	10.07	1.00	310	0.73×10^6
				$(1.3 \times 10^6)^b$
II	8.21	1.00	4.4	1.1×10^6
	8.22	1.00	8.8	1.0×10^6
	10.13	1.00	65.0	0.79×10^6
	10.10	1.00	126	0.71×10^6
	10.08	1.00	310	0.47×10^6
				$(1.1 \times 10^6)^b$
XIII	11.10	1.00	2000	1.3×10^3
	9.74	0.625	2200	1.3×10^3
	11.10	1.00	4000	1.2×10^3
	11.13	0.50	5000	1.3×10^3
				$(1.3 \times 10^3)^b$
XV	9.96	2.50	2800	250
	9.99	1.00	2900	250
	9.90	2.50	5200	300
				$(270)^b$
VI	10.16	1.00	130	2.8×10^4
	10.13	1.00	260	3.0×10^4
	9.74	0.625	2100	2.4×10^4
				$(2.9 \times 10^4)^b$
XII	9.96	2.50	2800	9.0
	9.90	2.50	5300	9.8
				$(9.4)^b$
XI	10.14	1.00	260	8.5×10^3
	10.05	1.00	490	8.9×10^3
				$(8.7 \times 10^3)^b$
V	8.01	0.500	0.71	2.7×10^6
	8.07	0.625	1.00	2.9×10^6
	8.18	0.625	1.25	2.9×10^6
	8.13	0.625	2.34	2.7×10^6
				$(2.8 \times 10^6)^b$
	10.10	1.00	128	$k_3 = 94\ sec^{-1}$
	10.04	1.00	570	$k_3 = 94\ sec^{-1}$
I	8.09	1.00	3.8	2.9×10^6
	8.14	1.00	6.8	2.8×10^6
				$(2.9 \times 10^6)^b$

[a] $pK_a = 9.86$. [b] Estimated upper limit for the value of k_{c^-}; see text.

In contrast with coupler A-OCH_3, coupler B-OCH_3 reacted with most diimines with rates independent of (C^-) (Table III). However, not all of these were first order; some have breaks in the first-order plot near the middle of the reaction. *The values of k_3 for only those diimines which show no break in the plots* (reactions usually analyzed to 75–90% completion) are recorded in Table III. It is interesting that the type of kinetics observed depends largely on the substituents R_3 and R_4 on the diimine. Those diimines with good first-order rates are the ones in which both R_3 and R_4 represent H or one of them represents Cl or OCH_3. The diimines with breaks in the curves were VI, VII, IX, and XIV; these have alkyl or substituted alkyl groups for R_3. This suggests that steric effects play a part. Diimine XV, in which both R_3 and R_4 represent methyl groups, however, follows bimolecular kinetics. Apparently, the large steric effect produces a small k_1 and/or a large k_2 and the rate is proportional to the coupling rate. The independence of rates on (C^-), combined with decreasing first-order rate, suggested the existence of more than one intermediate with the same composition: one leads directly to dye, the other leads to the same product indirectly through slow conversion to the former. Since there is more than one possible reaction site in each diimine and coupler ion, the existence of multiple addition compounds is not very surprising, although the most favorable one cannot be suggested at present.

The constants k_1 and k_2 for B-OCH_3 were evaluated by using the method described earlier, but only for those diimines for which reliable k_3's had been determined. The competing coupler, A-OCH_3, was used. The experimental conditions and results are recorded in Table IV. The graphs (one set of data was omitted to avoid confusion) used to determine the parameters in eq 4 are shown in Figure 1, each point representing duplicate experiments which were in good agreement. Measurements were made at several levels of pH and concentrations of couplers. For diimine I, two special sets of experiments were made: one with the competing coupler added at $t' = 0.022$ sec and $(P_1)' =$

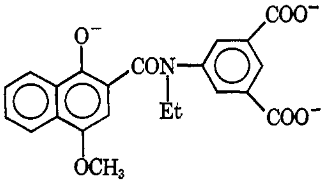
Table III. Rate Constants,[a] k_3, for Dye Formation with



Diimine	pH	$(T)_0 \times 10^4$, M	$[(C^-)_0 - (T)_0]$[b] $\times 10^4$, M	k_3, sec^{-1}
III	10.06	2.00	2.7	0.54
	10.07	2.00	7.2	0.55
XIII	10.17	1.00	36	1.53
	11.09	1.00	39	1.53
	11.11	1.00	79	1.55
II	9.93	1.25	3.3	3.2
	9.49	1.00	6.5	3.2
	10.05	1.25	7.8	3.2
	10.59	1.00	8.7	3.2
	9.74	1.00	15.6	3.0
V	9.00	1.25	3.8	0.46
	10.0	1.00	8.0	0.46
I	8.46	2.00	1.2	2.4
	10.0	1.00	3.6	2.4
	10.0	1.00	8.0	2.4
IV	10.12	1.00	1.38	4.3
	10.15	1.00	3.7	4.3
	10.14	1.00	8.3	5.0

[a] $pK_a = 9.07$. [b] The concentration of coupler anion in excess of intermediate immediately after the induction period.

Table IV. Rate Constants for the Elementary Reactions of Diimines and

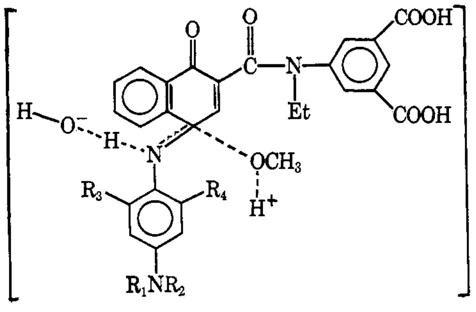


Diimine	pH	Intercept = k_{13}/k_{12}	Intercept/slope = k_{11}/k_{c^-}[a]	k_{13}, sec^{-1}	k_{12}, sec^{-1}	k_{11}, l./mol sec
I	8.46	...	..	2.4		
	9.50	2.0	24			
	10.00	...	..	2.4		
	10.07	2.0	24			
	10.05[b]	1.8	20			
	10.05[c]	1.8	20			
	10.55	2.0	22			
		Av 1.9	Av 22	Av 2.4	1.3	6.4×10^7
II	9.55	1.0	29			
	9.49	...	..	3.15		
	10.01	1.1	31			
	10.05	1.0	32			
	10.05	...	..	3.18		
	10.55	1.0	30			
	10.59	...	..	3.15		
		Av 1.0	Av 30	Av 3.16	3.2	3.3×10^7
V	9.54	0.4	18			
	9.00	...	..	0.46		
	10.00	0.4	20			
	10.00	...	..	0.46		
	10.56	0.5	19			
		Av 0.4	Av 19	Av 0.46	1.2	5.3×10^7
XIII	9.98	0.35	22			
	10.17	...	..	1.5		
	11.02	0.30	25			
	11.11	...	..	1.5		
		Av 0.33	Av 24	Av 1.5	4.6	3.1×10^4

[a] k_{c^-} is the upper limit of the rate constant for coupling of $AOCH_3$ from Table II. [b] $(P_1)' = 0.25 \times 10^{-5}$ M. [c] $(P_1)' = 0.55 \times 10^{-5}$ M.

0.25×10^{-5} M, and the other set at $t' = 0.049$ sec and $(P_1)' = 0.55 \times 10^{-5}$ M. Both the intercepts and the slopes were in good agreement. The alternative hypothesis that the second dye came from the residual (T^+) at t' and not by reversal of the first coupling reaction (*i.e.*, $k_2 = 0$ for coupler B-OCH$_3$) was refuted by the results of this pair of experiments as follows. The plots of $(P_2)_\infty$ *vs.* $(P_2)_\infty/(C_2)$ were both linear and did not differ by more than 2% when extrapolated to $1/(C_2) = 0$. Since, under the experimental conditions employed in the absence of C_2, the rate was independent of (C_1), it follows that $k_1(C_1^-)$ must be at least 24, *i.e.*, $10 \times k_3$, and the ratio of the two extrapolated values of $(P_2)_\infty$, if $k_2 = 0$ as postulated, should be less than 0.5, *i.e.*, $\exp(-24 \times 0.027)$.

It is significant that all three elementary rate constants were found to be independent of pH. This was more unexpected for k_3 than for the others, since it would be expected that deprotonation by a base would aid in the elimination of the MeO. The independence of rate on pH can be rationalized by postulating a concerted process in the elimination, the transition state including both H^+ and OH^-.



transition state of elimination step

From the observation cited below that the elimination of chloride and phenoxide is faster than that of methoxide, and the fact that the first two are more stable anions, it appears that the group being eliminated has already acquired ionic character. Bennett and Zahler[4] have postulated that, for nucleophilic displacement reactions, the rate of elimination increases with the stability of the ions being eliminated. The generalization seems to apply here also, although, unlike nucleophilic displacement, the elimination is from the nucleophile instead of from the electrophile.

$$ArX + Y^- \rightleftharpoons ArXY^- \longrightarrow ArY + X^-$$

nucleophilic displacement

B. Coupling with Elimination of Cl or OAr. The data for reactions with couplers B-Cl and B-OC$_6$H$_4$NO$_2$ are recorded in Table V. These reactions with one exception (B-Cl with diimine III) are bimolecular and their rates are proportional to coupling; the reactions with coupler B-OCH$_3$ (Tables II-IV), however, are usually first order and therefore limited by the elimination step. The value of k_3 measured for the re-

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(4) R. F. Bennett and K. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

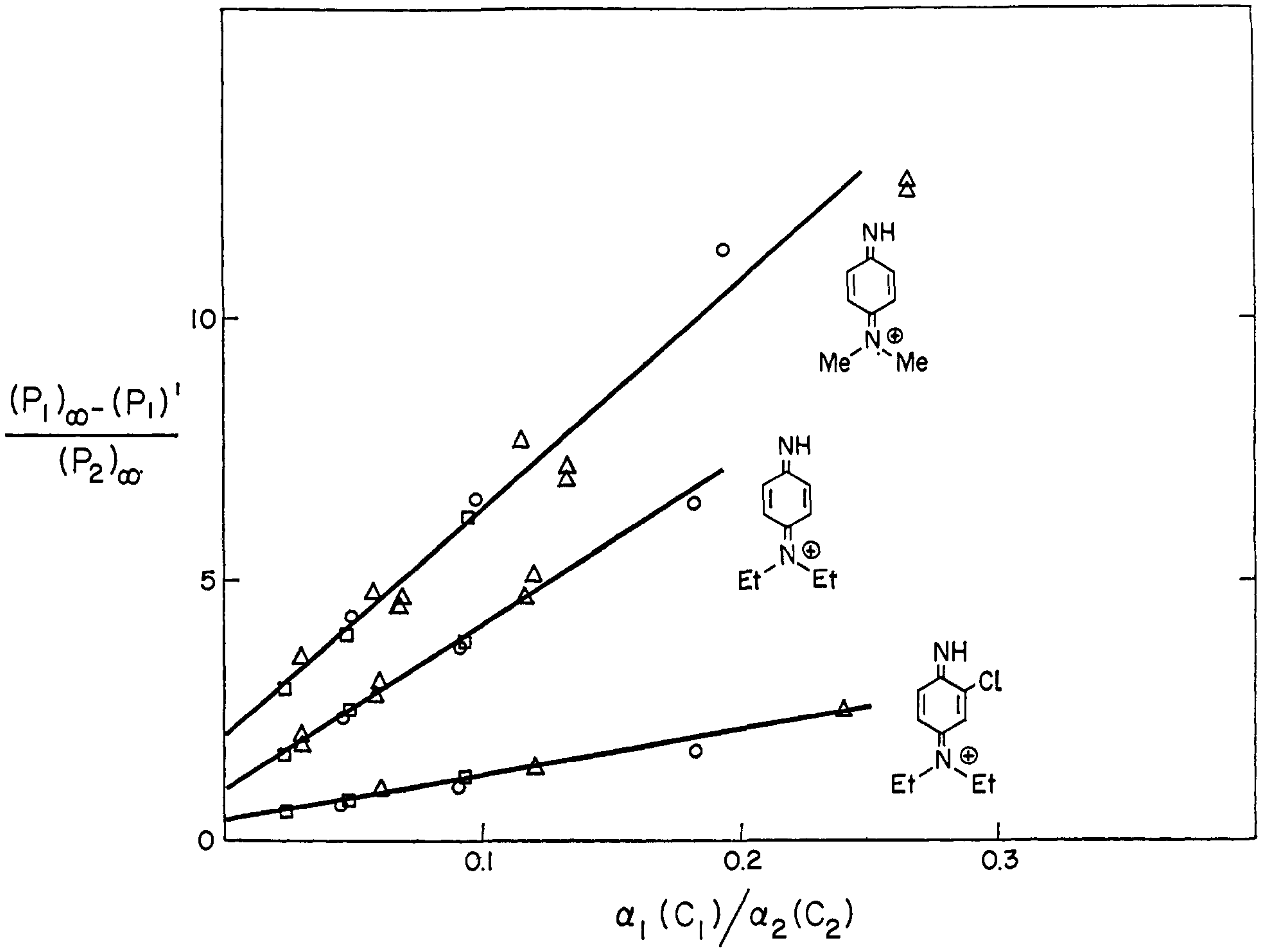
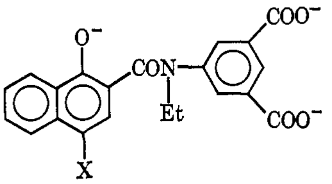


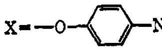
Figure 1. Graphical method for the determination of the rate constants for the elementary reactions of B–OCH_3 with diimines shown.

action between coupler B–Cl and diimine III is 100 times as large as that for the reaction between B–OCH_3 and the same diimine (Table III). The lower limits of k_3, estimated on the assumption that $k_3 > 5[k_{c^-}(C^-)]$ in these experiments, are more than 100 times as large for couplers B–$OC_6H_4NO_2$ and B–Cl as for coupler B–OCH_3 with diimine II.

Whereas k_3 is larger for couplers B–$OC_6H_4NO_2$ and B–Cl, k_{c^-} is larger for B–OCH_3. This implies that, for the former group of couplers, either k_1 is smaller or k_2 is larger, or both. The tendency for k_1 and k_2 to vary in opposite directions with variations in diimine structure is shown in Table IV. This relationship may not hold over wider variation of coupler structures, but there is more likelihood that the ratio k_1/k_2 (which would be the equilibrium constant for the formation of the intermediate, if measurable) varies in the opposite direction relative to that of k_3. The results can be interpreted by assuming that the free energy of the intermediate is insensitive to minor changes in structure and the free energy of the activated complex for the decomposition of the intermediate is parallel to that of the products (dye + anion). The latter is assumed to vary in the same direction as the initial reactants (diimine + coupler anion). Then the substituent which results in more stable anions also stabilizes the coupler anion, and a more stable diimine also results in a more stable dye. This interpretation has some justifications. The pK's for the couplers B–OCH_3, B–$OC_6H_4NO_2$ and B–Cl are 9.07, 8.08, and

Table V. Coupling Rates for



Di-imine	pH	$(T)_0 \times 10^4$, M	$(C^-)_0 \times 10^4$, M	k_{c^-}, l./mol sec	k_3, sec^{-1}
		X = Cl, pK_a = 7.7			
III	8.96	2.00	2.00	...	54
	10.00	1.00	2.00	...	54
	10.00	1.00	5.00	...	54
II	8.17	1.00	1.48	2.8×10^5	
	8.11	1.00	3.50	2.4×10^5	
VI	9.87	1.00	5.00	6.2×10^3	
	9.45	1.00	10.00	5.8×10^3	
VII	10.06	1.00	5.00	8.0×10^4	
	9.97	1.00	10.00	7.5×10^4	
		 X = –O–…–NO_2, pK_a = 8.08			
II	10.02	1.00	2.00	5.1×10^5	
	9.92	1.00	5.00	4.8×10^5	
VII	9.69	1.00	1.00	1.5×10^5	
	9.51	1.00	2.00	1.4×10^5	

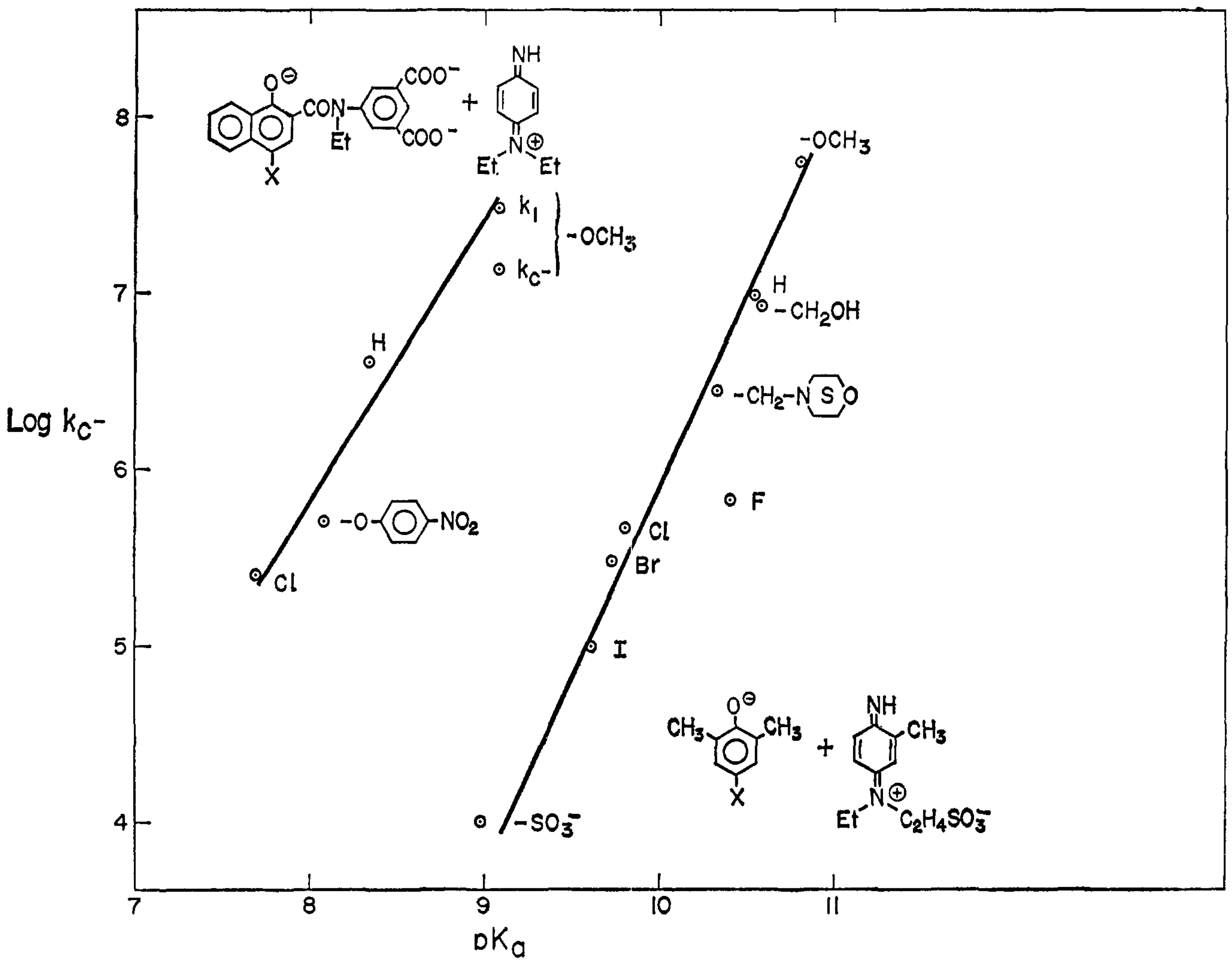


Figure 2. Coupling rates *vs.* pK_a of the couplers.

7.7, respectively, and the stability of the coupler anions should increase in this order. The relationship between the pK of the couplers and k_{c^-} will be examined in more detail later. The stability of the diimine should resemble that of the dye more than that of the intermediate because the dye has more quinonoid character.

C. **Effect of Variation of Couplers on Rates.** Figure 2 summarizes the results of coupling-rate measurements for two series of reactions: (1) between diimine VII and couplers D–X and (2) between diimine II and couplers B–X. The reactions are all bimolecular with constant k_{c^-} defined in eq 3. The reactions we have been discussing so far belong to class B in Scheme I. The results for D–H and B–H are included for comparison, and, since these reactions belong to class A which requires oxidation in the last step, the consistency of the data is surprising. Significantly, k_{c^-} was found to be independent of oxidant concentration for the last two reactions, which implies that k_3 is very large and therefore $k_{c^-} \cong k_1$. The unique correlation of both classes of reaction rates with the same parameter, pK, suggests that $k_{c^-} \cong k_1$ also holds for reactions of class B. That k_{c^-} is insensitive to k_3 is further substantiated by the observations that k_{c^-} for B-OCH$_3$ is much larger than k_{c^-} for D-Cl. It has already been shown that k_3 for the elimination of OCH$_3$ is much smaller than k_3 for elimination of Cl.

The linear relationship in Figure 2 can be expressed by eq 5

$$\log k_{c^-} = \log \rho + \beta \log K_a \qquad (5)$$

where $\beta < 0$. This expression shows that the reactivity increases with the basicity of the coupler anion. Correlations of this type are quite common for reactions with nucleophiles.[5]

The k_{c^-} in eq 5 may be replaced by k_1 to obtain eq 6

$$\log k_1 = \log \rho + \beta \log K_a \qquad (6)$$

where $\beta < 0$.

Since k_1 is the constant for the elementary reaction 1, it is not surprising that it is independent of subsequent reactions, and therefore applicable to both class A and class B reactions.

D. **Effect of Variation of Diimines on Rates.** Figure 3 summarizes the results of reaction rates for a collection of diimines with three different nucleophiles. The reactions were divided into three series, each with a common nucleophile. The first nucleophile was OH$^-$ which causes the diimine to deaminate, the second was coupler A-OCH$_3$, and the third was coupler B-H. Note that the two couplers have different reactions in the second step; coupler B-H reacts according to class

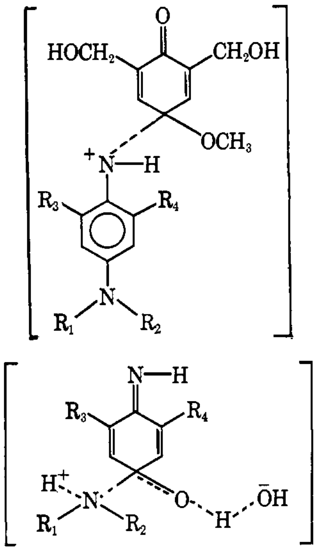
[5] (a) K. M. Ibue-Rosa, *J. Chem. Educ.*, **44**, 89 (1967); (b) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **60**, 271 (1963).

A and coupler A-OCH$_3$ reacts according to class B of Scheme I. However, both coupling reactions are bimolecular according to eq 3. In Figure 3, the log of k_{c^-} for the two coupling reactions is plotted *vs.* the log of k_{OH^-} defined by eq 7.

$$-\frac{d(T^+)}{dt} = k_{OH^-}(T^+)(OH^-) \qquad (7)$$

It is a coincidence that the two couplers have rates so similar that one set of data must be plotted with vertical displacement to avoid confusion. Two outstanding features were brought out graphically; one is the tendency of both coupling rates to vary in the same sense as the deamination rate when the structure of the diimine is varied. The other feature is the even closer parallelism between the rates of the two coupling reactions. If the data are replotted so that the two lines coincide, the average deviation of the two sets of data (when available for the same diimine) is 0.5 log unit. This also applies to those points with large deviations from the lines.

The general trend, represented by the lines, shows roughly the linear relationship between activation energy of each coupling reaction and that of the deamination reaction. But since the energies of the coupler ion and OH$^-$ are constant and that of the diimines are common for the two reactions, this also shows the linear relationship between the difference in the energy of the activated complexes for the two reactions and either one of the activation energies. Deviation of any point from the line indicates abnormality of one of these complexes. Based on the assumptions that the rate-determining step in coupling is reaction 1 of Scheme I, and that in deamination it is the decomposition of the intermediate,[6] the activated complexes can be represented as



Interestingly enough, the points lying below the lines (diimines XI, XII and XV) have bulky groups for R$_3$ or methyl groups for both R$_3$ and R$_4$. Thus it is reasonable to expect the steric effects to increase the energies of the activated complex for coupling but not for deamination. The positive vertical deviations of the points representing diimines XIII and XVI with coupler B-H are more difficult to understand, since the point for diimine XIII with coupler A-OCH$_3$ seems to be normal. Probably, the CH$_3$O group *ortho* to the coupling nitrogen stabilizes the transition state by a +R effect, thus making the diimine abnormally reactive. The effect is partially offset by interference between the two CH$_3$O groups, one on the diimine and one on the coupler in the reaction with coupler A-OCH$_3$. The rate of reaction between diimine XVI and coupler B-H may also be rationalized by saying that, with two CH$_3$O groups on the diimine, the acceleration should be greater than with diimine XIII with only one CH$_3$O group, but that this is compensated for by the extra steric hindrance of the double substitution.

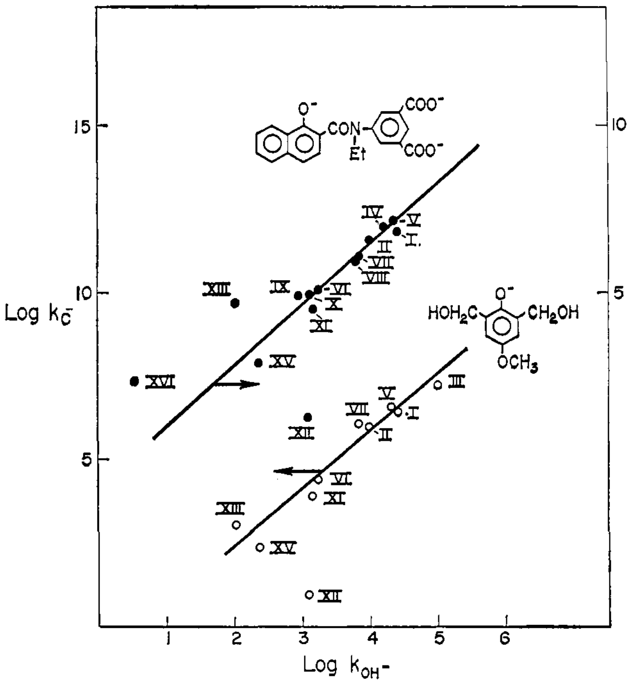


Figure 3. Coupling rate constants *vs.* deamination rate constants for numerous diimines.

Experimental Section

Reaction Rate Measurements. Dye Formation. Solutions of diamine, ferricyanide, and couplers in buffers were mixed in a jet mixing machine at 25°.[2] The flowing reaction mixture, after attaining a steady state, was analyzed for dye by means of a spectrophotometer unit with its cell in the flow channel.[1b] After mixing, and before any reaction, the concentrations were diamine 0.5 × 10^{-4} to 2 × 10^{-4} *M*, ferricyanide 2[diamine] for class B couplers and ≥4[diamine] for class A types of couplers, and 0.5 × 10^{-4} *M* to 10^{-2} *M* in coupler. The phosphate buffers, μ = 0.375, were in the pH range 8–11. The per cent transmittance at 650 mμ was measured at various times (7–800 msec) determined by the length of the spacer between the last mixing chamber and the flow cell and the flow speed. Shorter reaction times (between 1 and 7 msec) were achieved by quenching the reaction with acid in a third mixing chamber and modifying the chambers to shorten the reaction path. In the quenched solution (pH 6.5), no additional dye formed before the analysis in the flow cell. The ratios of optical density to dye concentration were determined in the same spectrophotometer. The dye solutions which were used for this purpose were prepared from known concentrations of the oxidized diamines in the presence of excess coupler. The pH of the reaction mixtures collected from the machine was measured with a Corning pH meter and a glass electrode.

Deamination Rates. With the exception of diamines XVI, XI, X, and XII, the deamination rates have been reported.[6] The deamination rates of these diamines were obtained by mixing the

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

diamine, ferricyanide, and pH 11 or 12 phosphate buffer in the jet mixing machine as described.[7] The analysis, however, was made in a scanning, double-beam uv spectrophotometer attached to the mixer.[8] The rate of disappearance of the diimine was followed by measuring the decrease in the absorbance at ~290 mμ, the λ_{max} of the diimine.

p*K* Measurements. Coupler p*K*'s were obtained spectrophotometrically. Uv absorptions of 10^{-4} *M* solutions of the couplers in pH 6, pH 12, and intermediate pH phosphate buffers, $\mu = 0.375$, were measured at the wavelength of maximum difference for the acid and ion forms.

Competition Method for Evaluation of k_1, k_2. Solutions of (1) 4×10^{-4} *M* diamine, (2) 8×10^{-4} *M* $K_3Fe(CN)_6$, (3) 10^{-3} *M* coupler B–OCH_3 in phosphate buffer ($\mu = 0.75$, pH 9.5–10.5), and (4) 0.00125–0.01 *M* coupler A–OCH_3 in phosphate buffer ($\mu = 0.375$ and same pH as 3) were mixed in this order in the mixing machine in the volume ratio 1:1:2:4, respectively. A spacer inserted between the last two mixing chambers gave reaction times of 0.02–0.05 sec before injection of the competing coupler. The reaction mixture was collected and an aliquot extracted into *n*-butyl acetate. The dye from A–OCH_3 was extracted almost completely, but the dye from B–OCH_3 remained mainly in the aqueous phase. The dye yields from the two couplers were calculated from the absorbance of the *n*-butyl acetate extract at 570 or 580 mμ and the apparent molar extinctions of the dyes. The latter were obtained from *n*-butyl acetate extractions of the individual dyes from aqueous solutions of known concentration. These extractions were made at the same pH and volume ratio as in the analysis.

Materials. The following couplers were prepared by methods reported in the literature: D–Br,[9] D–Cl,[10] D–I,[11] D–F,[12] D–OCH_3,[13] D–SO_3H,[14] D–CH_2–N-morpholinyl,[15] D–CH_2OH,[13] and A–OCH_3.[16] D–H was Eastman Grade recrystallized from petroleum ether (bp 35–60°) to mp 45.5

Coupler B–H was prepared by C. Snyder, formerly of these laboratories, as follows.

3′,5′-Dicarbomethoxy-N-ethyl-1-hydroxy-2-naphthanilide (A). An intimate mixture of 700 g (0.76 mol) of phenyl 1-hydroxy-2-naphthoate (Eastman Kodak Co.) and 180 g (0.76 mol) of dimethyl N-ethyl-5-aminoisophthalate (Eastman Kodak Co.) was heated to 160–190° under aspirator vacuum for *ca.* 2 hr. The nearly phenol-free residue was allowed to cool to room temperature and was triturated with two 200-ml portions of alcohol, yield 180 g (58%) of yellow crystals, mp 182–184°.

3′,5′-Dicarboxy-N-ethyl-1-hydroxy-2-naphthanilide (B–H). A mixture of 900 g (2.21 mol) of A, 5 l. of alcohol, and 300 g (7.5 mol) of NaOH in 1 l. of water was refluxed for *ca.* 2 hr. The hot solution was poured, with good stirring, into 7 l. of ice water containing 500 ml of concentrated HCl. The off-white precipitate which was formed was collected by filtration and washed well with water. The material was recrystallized from a mixture of 8.5 l. of alcohol and 6.5 l. of water, yield 475 g (56.5%) of yellow material, mp 248–249° dec.

Anal. Calcd for $C_{21}H_{17}NO_6$: C, 66.5; H, 4.5; N, 3.7. Found: C, 66.3; H, 4.8; N, 3.6.

Coupler B–Cl was prepared by A. Lurie, of these laboratories, according to the following procedures.

4-Chloro-3′,5′-dicarbomethoxy-N-ethyl-1-hydroxy-2-naphthanilide (B). By the procedure outlined for the condensation to make A, 89.6 g (0.3 mol) of phenyl 4-chloro-1-hydroxy-2-naphthoate (Eastman Kodak Co.) and 71.1 g (0.3 mol) of dimethyl N-ethyl-5-aminoisophthalate were used to prepare a dark oil which was dissolved in chloroform and washed with water. The dried chloroform solution was concentrated to dryness. The resulting dark oil was dissolved in 150 ml of hot acetic acid, yield 39 g (29.5%) of off-white crystals, mp 137–138°.

Impure second-crop material could be purified by column chromatography on Florisil and elution with various mixtures of benzene–chloroform.

4-Chloro-3′,5′-dicarboxy-N-ethyl-1-hydroxy-2-naphthanilide (B–Cl). B was hydrolyzed by a procedure analogous to that used to prepare B–H. The wet precipitate was slurried with 10 parts of acetic acid and then 10 parts of alcohol, giving a material, mp 255° dec, in 75% yield.

Anal. Calcd for $C_{21}H_{16}ClNO_6$: C, 60.9; H, 3.9; Cl, 8.6; N, 3.4. Found: C, 60.8; H, 3.8; Cl, 8.9; N, 3.4.

Coupler B–OCH_3 was prepared by A. Loria, of these laboratories, as follows.

1-Hydroxy-4-methoxy-2-naphthoic acid (C) was prepared according to a procedure described in the literature.[17]

3′,5′-Dicarbomethoxy-N-ethyl-1-hydroxy-4-methoxy-2-naphthanilide (D). A mixture of 26 g (0.12 mol) of C, 100 ml of thionyl chloride, and 5 ml of dimethylformamide was stirred for *ca.* 2 hr and then heated to 40° for an additional 0.5 hr. The excess thionyl chloride was removed under vacuum, yielding a yellow solid which is the acid chloride.

The acid chloride was suspended in 700 ml of dioxane and added to a vigorously stirred solution of 35 g (0.15 mol) of dimethyl N-ethyl-5-aminoisophthalate and 32 g (0.25 mol) of quinoline in 1 l. of dioxane. The mixture was heated at 50° for *ca.* 0.5 hr and poured into 4 l. of water which was then acidified with concentrated HCl. The resulting solid was isolated and triturated with hot methanol, yield 40 g (77%) of white material, mp 146–148°.

3′,5′-Dicarboxy-N-ethyl-1-hydroxy-4-methoxy-2-naphthanilide (B–OCH_3). A procedure analogous to that used to prepare B–H was used. The yellow powder obtained in 60% yield, mp 248–250°, was used without recrystallization.

Anal. Calcd for $C_{22}H_{19}NO_7$: C, 64.5; H, 4.7; N, 3.4. Found: C, 64.5; H, 4.9; N, 3.2.

Coupler B–OC_6H_4-*p*-NO_2 was prepared by A. Loria, of these laboratories.

1-Hydroxy-4-(*p*-nitrophenoxy)-2-naphthoic Acid (E). To a vigorously stirred solution of 20.4 g (0.1 mol) of 1,4-dihydroxy-2-naphthoic acid (Eastman Kodak Co.) in 150 ml of dimethylformamide under N_2, 20 g (0.2 mol) of 40% NaOH was added, followed 5 min later by 14.1 g (0.1 mol) of 1-fluoro-4-nitrobenzene. The temperature increased to *ca.* 60° during the addition of the nitro compound and was held at this point for an additional 0.5 hr by external heating. The reaction mixture was poured into 1 l. of 0.3 *M* HCl. The solid which formed was collected, slurried with water, dried, and recrystallized twice from large amounts of acetonitrile, yield 24 g (74%) of off-white crystalline material, mp 230° dec.

1-Hydroxy-4-(*p*-nitrophenoxy)-2-naphthoyl chloride (F). A mixture of 3.25 g (0.01 mol) of the acid E, 10 ml of thionyl chloride, and 5 ml of dimethylformamide was stirred at room temperature for 2 hr. The yellow solid which formed was recrystallized by dissolving it in a minimum amount of acetonitrile at 60° and cooling it to 5° to yield 2.5 g (73%) of yellow crystals, mp 145° dec.

3′,5′-Dicarbomethoxy-N-ethyl-1-hydroxy-4-(*p*-nitrophenoxy)-2-naphthanilide (G). To a stirred suspension of 2.4 g (0.007 mol) of the acid chloride F in 100 ml of dioxane, 1.7 g (0.007 mol) of dimethyl N-ethyl-5-aminoisophthalate was added. After complete solution, 1 ml of N,N-dimethylaniline (Eastman Kodak Co.) was added and stirring continued for 2 hr. The solution was allowed to stand for several hours and then was poured into 500 ml of water containing 1 ml of acetic acid. The solid formed was washed with water, dried, and recrystallized from a minimum amount of acetonitrile, yield 3 g (79%) of off-white powder, mp 182–184°.

3′,5′-Dicarboxy-N-ethyl-1-hydroxy-4-(*p*-nitrophenoxy)-2-naphthanilide (B–OC_6H_4-*p*NO_2). A procedure analogous to that used to prepare B–H was used. The yellow powder obtained was recrystallized from *n*-propyl alcohol, giving a material, mp 227–229° dec, in 56% yield.

Anal. Calcd for $C_{27}H_{20}N_2O_9$: C, 62.7; H, 3.9; N, 5.4. Found: C, 62.7; H, 4.1; N, 5.5.

The following diamines have been described:[18] I, II, III, IV, V, VI, VIII, IX, XIII, XIV, XV. In addition, diamines X and XII have been described,[19] as well as diamine VII.[20]

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(7) L. K. J. Tong, *J. Phys. Chem.*, 58, 1090 (1954).

(8) C. A. Bishop, R. F. Porter, and L. K. J. Tong, *J. Amer. Chem. Soc.*, 85, 3991 (1963).

(9) K. Auwers and T. Markovits, *Ber.*, 41, 2336 (1908).

(10) G. Lockemann and T. Kunzmann, *Angew. Chem.*, 46, 296 (1933)

(11) K. Heicken, *ibid.*, 52, 263 (1939).

(12) A. S. Kende and P. MacGregor, *Chem. Ind.* (London), 460 (1962).

(13) E. Bamberger, *Ber.*, 36, 2028 (1903).

(14) H. Brückner, *Angew. Chem.*, 41, 1046 (1908).

(15) British Patent 941803 (Kalle, Nov 13, 1963).

(16) W. J. Moran, E. C. Schreiber, E. Engel, D. C. Behn, and J. L. Yamens, *J. Amer. Chem. Soc.*, 74, 127 (1952).

(17) A. Homeyer and V. H Wallenford, *J. Amer. Chem. Soc.*, 64, 799 (1942).

(18) R. L. Bent, *et al.*, *ibid.*, 73, 3100 (1951).

(19) R. L. Bent, *et al.*, *Photogr. Sci. Eng.*, 8, 125 (1963).

(20) L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, 78, 5827 (1956).

The remaining diamines, XI and XVI, were prepared by R. L. Bent, of these laboratories. Diamine XI was prepared as follows.

3-Isopropylaniline (H) was prepared from chlorobenzene and isopropyl alcohol, as described in the literature.[21] In our hands, however, the reduction of the intermediate, 2-chloro-5-isopropylnitrobenzene, gave 2-chloro-5-isopropylaniline rather than 3-isopropylaniline as reported. The chlorine had to be eliminated in a separate step by means of KOH, methanol, and Raney nickel catalyst, under reductive conditions.[22] The product had bp 93–95° (5 mm), n^{24}D 1.546.

N,N-Diethyl-3-isopropylaniline (I). A mixture of 30 g (0.222 mol) of H, 72 g (0.46 mol) of ethyl iodide, 84 g (0.46 mol) of sodium bicarbonate, 280 ml of ethanol, and 110 ml of water was refluxed for 18 hr. After removal of the ethanol, the product was extracted with ether and the latter dried and concentrated. The residual oil was treated with acetic anhydride to remove any primary or secondary amines, and distilled. The yield of I, bp 115–120° (7 mm), n^{25}D 1.5221, was 25.6 g (60%).

4-(2,5-Dichlorophenylazo)-N,N-diethyl-3-isopropylaniline (J). A total of 21.6 g (0.133 mol) of 2,5-dichloroaniline was dissolved in a mixture of 150 ml of concentrated hydrochloric acid and 500 ml of water on a steam bath. After cooling to 5°, the hydrochloride salt of the aniline precipitated out and slightly over the theoretical quantity of sodium nitrite was added, with stirring. When diazotization was complete, and after the excess nitrous acid was destroyed by sulfamic acid, the solution was filtered and at once added to a cold solution of 25.4 g (0.133 mol) of I in dilute hydrochloric acid. The coupling reaction was initiated by the addition of 180 g of sodium acetate. The azo dye precipitated as a gum but gradually became crystalline. The yield of J, mp 89–91° after two recrystallizations from ethanol, was 20 g (41.5%).

Anal. Calcd for $C_{19}H_{23}Cl_2N_3$: C, 62.6; H, 6.31. Found: C, 62.7; H, 6.2.

4-Amino-N,N-diethyl-3-isopropylaniline Hydrochloride (XI). The reduction of 3.64 g (0.01 mol) of J was carried out in absolute ethanol at 40 psi, with Raney nickel as catalyst. The catalyst was filtered off and washed on a funnel with alcohol, and 1 equiv of concentrated hydrochloric acid was added. The filtrate was then concentrated to a small volume and excess ether was added to precipitate the developer salt; the latter was dissolved in a small volume of absolute ethanol and again precipitated out with excess ether (the re-formed dichloroaniline remains in solution). The yield of XI, mp 215–217° after recrystallization from isopropyl alcohol, was 1.45 g (60%).

Anal. Calcd for $C_{13}H_{23}ClN_2$: C, 64.3; H, 9.48. Found: C, 64.4; H, 9.3.

Diamine XVI. N,N-Diethyl-3,5-dimethoxyaniline (K) was prepared by the dialkylation of 50 g (0.327 mol) of 3,5-dimethoxyaniline (mp 46.5–48°, from Aldrich Chemical Co.) with ethyl iodide, as already described for 3-isopropylaniline. The yield of K, bp 114–118° (1 mm) and mp 45.5–47 from petroleum ether, was 25 g (36.5%).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.8; H, 9.1. Found: C, 69.1; H, 9.3.

4-(2,5-Dichlorophenylazo)-N,N-diethyl-3,5-dimethoxyaniline (L) was prepared by the coupling of diazotized 2,5-dichloroaniline with 2.09 g (0.01 mol) of K, as already described for 3-isopropylaniline. The yield of L, mp 139–140.5° after two recrystallizations from ethanol, was 2.55 g (33%).

Anal. Calcd for $C_{18}H_{21}Cl_2N_3O_2$: C, 56.5; H, 5.49. Found: C, 56.4; H, 5.2.

4-Amino-N,N-diethyl-3,5-dimethoxyaniline Hydrochloride (XVI). The reduction of 3.82 g (0.01 mol) of L in absolute ethanol, with Raney nickel as catalyst, and the conversion of the developer base to hydrochloride salt, was carried out as described for the 3-isopropyl developer. The yield of XVI, mp 212–214° from isopropyl alcohol, was 1.25 g (48%).

Anal. Calcd for $C_{12}H_{21}ClN_2O_2$: C, 55.2; H, 8.06. Found: C, 55.6; H, 8.3.

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On the Mechanisms of Dediazoniation and Other Aromatic Denitrogenation Reactions Induced by Sodium Methoxide in Methanol

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Abstract: Reactions of compounds of types **1–4** with $NaOCH_3$ in CH_3OH afford substantial yields of products in which the nitrogenous substituent has been replaced by hydrogen. When these reactions are carried out in CH_3OD solution, the hydrogen which replaces the nitrogenous group is sometimes protium and sometimes deuterium. In this research, the percentage of monodeuteration of the denitrogenation product is determined as a function of the nitrogenous leaving group, of substituents in the parent aromatic ring, and of the $NaOCH_3$ concentration. The percentage of monodeuteration of the product is found to be greater from 1-aryl-2-benzenesulfonhydrazides (**1**) than from diazonium salts (**2**), greater at higher $NaOCH_3$ concentrations and greater from chlorine-substituted than from unsubstituted compounds. However, *p*-nitrobenzenediazonium ion gives virtually deuterium-free nitrobenzene under all conditions. Deuterated products are taken to be formed *via* aryl anion intermediates and deuterium-free products *via* aryl radicals. Radical and carbanionic mechanisms are suggested, and the factors governing competition between the mechanisms are discussed.

The mechanism of dediazoniation[2] of *o*-halobenzenediazonium ions by sodium methoxide in methanol is sharply dependent on the base concentration.[3,4] This is shown particularly by the products formed in CH_3OD solution. When only 1 equiv of $NaOCH_3$ is provided per mole of *o*-chlorobenzenediazonium ions, the chlorobenzene formed is nearly deuterium free. But when 2 *M* $NaOCH_3$ is used, it is mainly *o*-deuteriochlorobenzene.[3]

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(2) "Dediazoniation" means replacement of the diazonia group ($-N_2^+$) by hydrogen.

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