[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE RATE OF COUPLING OF DIAZONIUM SALTS WITH PHENOLS IN BUFFER SOLUTIONS

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In the coupling of diazonium salts with phenols the acidity of the solution is usually regulated by the addition of the salt of a weak acid; sodium acetate, sodium bicarbonate and sodium carbonate are thus commonly employed in the manufacture of azo dyes. In order for the reaction to proceed rapidly the acidity must be kept below a certain value; this value depends on the nature of the diazonium salt and the phenol. A great mass of qualitative information of this sort suggests that the rate of the coupling reaction is a function of the hydrogen-ion activity of the solution. Although many preparative and analytical procedures are practically based on such an assumption, the point never seems to have been tested by actual measurements. The previous work on the rate of coupling of diazonium salts[1] was carried out before the advent of the modern methods of preparing and studying buffer solutions; the results are, therefore, difficult to interpret and throw but little light on the role played by the hydrogen ion (or hydroxyl ion). We have now carried out a series of measurements of the rate of coupling of five diazotized amines with five phenols and naphthols in buffer solutions of known acidity. The results show that the reaction is remarkably free from complications and that the rate is a simple function of the hydrogen-ion activity of the buffer solution employed. As a result it becomes possible to reduce to simple equations a description of the coupling reaction of a number of substances under a variety of conditions.

Experimental Procedure

The course of the coupling reaction was followed colorimetrically, the extent of the reaction being determined by comparison with the color of an identical mixture in which the reaction was complete. The acidity of the solution was controlled by heavily buffering the reaction mixture. The concentration of buffering salt was of the order of tenth molar while the maximum concentration of the reactants was thousandth molar; the change in acidity of the solution during the reaction was thus negligible. The ionic strength of all the buffer solutions was 0.24; to obtain this value potassium chloride was added in some cases. The composition of the buffers is given in Table I. The *P*H values were determined by the usual electrometric method using a Clark rocking electrode and were repeatedly checked.

Purification of Material.—The amines which were employed were

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[1] Goldschmidt, *Ber.*, **30**, 670, 2075 (1897); **33**, 893 (1900); **35**, 3534 (1902); Veley, *J. Chem. Soc.*, **95**, 1186 (1909).

TABLE I

BUFFER SOLUTIONS OF CONSTANT IONIC STRENGTH (μ = 0.24)

Buffer	Constituent	Fraction	Constituent	Fraction	KCl per liter, g.	PH
Acetate I	0.50 *M* NaAc	0.48	0.52 *M* HAc	0.52	None	4.50
Acetate II	.10 *M* NaAc	.50	.10 *M* HAc	.50	14.2	4.50
Acetate III	.30 *M* NaAc	.80	.30 *M* HAc	.20	None	5.27
Phthalate II	.10 *M* $C_8H_4O_4HK$	.65	.10 *M* NaOH	.35	7.85	4.94
Phosphate I	.20 *M* Na_2HPO_4	.10	.20 *M* KH_2PO_4	.90	None	5.80
Phosphate II	.15 *M* Na_2HPO_4	.30	.15 *M* KH_2PO_4	.70	None	6.30
Phosphate III	.12 *M* Na_2HPO_4	.50	.12 *M* KH_2PO_4	.50	None	6.73
Phosphate IV	.10 *M* Na_2HPO_4	.70	.10 *M* KH_2PO_4	.30	None	7.08
Borate I	.10 *M* Borate	.60	.10 *M* HCl	.40	13.34	8.17
Borate II	.10 *M* Borate	1.00			10.37	9.15

sulfanilic acid, *p*-bromo-aniline, aniline, *p*-toluidine and *o*-anisidine; their purification presents no special problems and need not be described. The problem of purifying the sulfonated naphthols, on the other hand, is one of extreme difficulty because there are no simple criteria of purity such as boiling point or melting point. We wish to express our indebtedness in this connection to Dr. Hitch of the Jackson Laboratory of the du Pont Company for his assistance in supplying us with materials and suggesting methods of analysis; without his help we should not have been able to prepare the materials used in this research. Information in regard to the purification and analysis of the sulfonated naphthols is given below.

Sodium 1-naphthol-4-sulfonate (N and W Salt).—The zinc salt was recrystallized three times and converted into the sodium salt with sodium carbonate. Tests showed it to be free from naphthionic acid. The analysis by titration[2] with diazotized *p*-bromo-aniline and *p*-nitro-aniline gave values of 97.4 to 96.6% purity for the dry salt (dried over phosphorus pentoxide *in vacuo*).

Disodium 1-Naphthol-3,8-disulfonate (Epsilon Salt).—The sodium salt was recrystallized four times from hot water and dried *in vacuo* over sulfuric acid for three weeks. The test for nitrogen by means of a potassium fusion was negative. Titration with benzene diazonium chloride showed a purity of 90.2 to 91.2%.

Disodium 2-Naphthol-3,6-disulfonate (R salt).—We are indebted to Dr. Hitch of the du Pont Company for a purified sample of this material which contained no G salt or Schaeffer's salt. By diazometric titration it was found to be 76.0 to 77.6% pure.

Disodium 2-Naphthol-6,8-disulfonate (G salt).—A good grade of commercial material was extracted with 80% alcohol at 70–75° and the soluble material obtained by cooling the solution. The crystals thus obtained were again extracted in the same manner and the less soluble material (R salt) discarded. The crystals were dried *in vacuo* over sulfuric acid; titration with diazotized *p*-nitraniline showed them to be 94.7 to 95.3% pure. The absence of any large amounts of R and Schaeffer's salts was demonstrated by the fact that no color developed with diazotized sulfanilic acid in a buffer of PH 5.6 and at a concentration of reactants at which both these salts couple rapidly.

Preparation of Solutions.—The results of the analyses given above were the basis for the preparation of the solutions of the sulfonated naphthols; it was assumed that the rest of the material was inert inorganic salt.

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[2] *Ann.*, **247**, 341 (1888); *Ber.*, **24**, 3160 (1891); *ibid.*, **18**, 46 (1885).

The diazonium salt solutions were always freshly prepared by diazotizing a solution of the corresponding amine at 0°. A solution of the amine of known concentration in standard hydrochloric acid was prepared and treated with sodium nitrite in the usual way. The concentration of the amine was usually 0.20 molar, the acid 0.52 molar. After the addition of the requisite amount of 0.20 M sodium nitrite (standardized by titration), the mixture was kept at 0° for about fifteen minutes and then diluted with water so that the resulting solution was 0.02 M in diazonium salt (it being assumed that the diazotization was quantitative) and about 0.012 M in free hydrochloric acid. This low concentration of hydrochloric acid may be still further decreased by the cautious addition of standard sodium hydroxide but this was not usually done since the high concentration of the buffering salt in the reaction mixture was sufficient to neutralize the small amount of free acid without materially affecting the P_H of the mixture. In the diazotization of sulfanilic acid the material was dissolved in just as little ammonia as possible (60–70 cc. of 8 M NH_4OH per mole) and the solution diluted to a 0.50 molar solution. Ten cc. was then rapidly acidified with 10 cc. of 1.566 M hydrochloric acid at 0° and 10 cc. of 0.50 molar nitrite slowly added. After shaking for three hours at 0°, the mixture was diluted to 100 cc. The resulting solution was 0.050 M in diazonium salt and approximately 0.006 M in free hydrochloric acid, if there were no excess of ammonia in the initial solution.

Colorimeter.—A Campbell–Hurley colorimeter[3] was modified so that one of the two tubes was placed in a small thermostat the temperature of which was kept constant within 0.03°. The tube fitted through a hole in the bottom of the thermostat box and was made water-tight by means of a rubber gasket. The other tube which was connected with the glass piston contained the standard solution and was not thermostated. Light from a 75-watt "daylight lamp" passed through a ground glass plate onto the mirror which reflected the beam through the two tubes. By moving the piston up and down the level of the standard solution was altered; the comparison of the two colors was made by means of the mirror and telescope characteristic of this type of colorimeter. Exactly 50 cc. of reaction mixture was always placed in the thermostated tube and the color matched by changing the level of the standard solution in the other tube, which was graduated from 1 to 100 cc. The readings of the level of the solution in this tube were a measure of the extent of the reaction.

Procedure

A color standard was first prepared from a reaction mixture (identical with the one under investigation) which had been allowed to stand at room temperature for at least fifteen hours to insure complete reaction. (Calculations using the velocity constants found and the temperature coefficient showed that the reaction would be 99% complete in less than twelve hours in every case.) Such a solution was diluted with an equal volume of the buffer solution and placed in the tube connected with the movable piston. The readings of the level in this tube (1 to 100) then corresponded directly to the extent of the reaction in the other tube. The validity of such a standard was shown by preparing many and comparing them with each other from time to time and also by allowing some reactions to proceed practically to completion, when the reading was found to be 100% within the experimental error. Although one standard might

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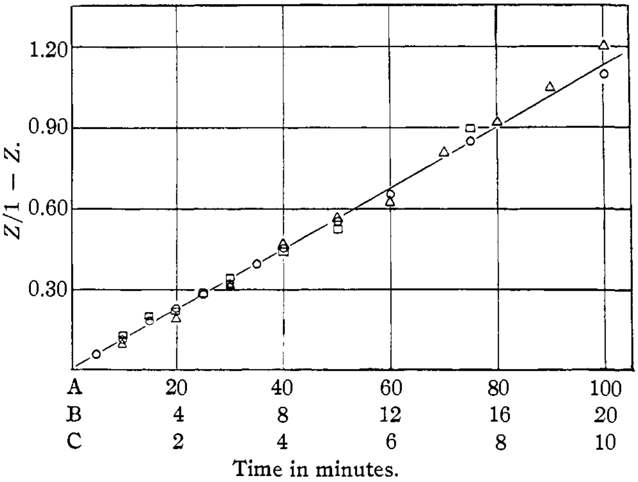
[3] Campbell and Hurley, THIS JOURNAL, **33**, 1112 (1911).

be used for many experiments days apart, fresh standards were actually prepared for each set of measurements. It is not possible to use a standard in one buffer for comparison with a reaction mixture in another buffer, as there is often a perceptible change in shade.

After the color standard had been introduced into one tube 48 cc. of buffer solution and 1 cc. of a solution of the hydroxy compound of requisite strength were placed in the other tube in the thermostat. After thermal equilibrium was established (twenty to thirty minutes), 1 cc. of the dilute diazonium salt solution, which had been kept in the thermostat for a short time, was rapidly introduced by means of a rapid-delivery pipet which reached to the bottom of the tube and through which a gentle stream of air was blown for a few seconds to stir the mixture. The time of mixing is estimated as less than five seconds. The time was recorded with a stop watch. Readings were usually made every minute for the first eight and then every two or three minutes, except in the case of very slow reactions. As a rule the measurements were continued until the reaction was 70–75% complete. The corresponding readings in duplicate experiments agreed well within 2 units (an error of 10 for 20% reacted).



□, Scale A, 0.0001 *M;* ○, Scale B, 0.0005 *M;* △, Scale C, 0.001 *M*.

Fig. 1.—Graphical representation of the rate of reaction of diazotized sulfanilic acid with sodium 1-naphthol-4-sulfonate. Equimolecular concentration of reactants. *P*н, 4.50; μ, 0.24; temp., 15°; slope, 0.0112; *k*, 112.

Results

Over a wide range of concentrations the reaction rate corresponds closely to the usual bimolecular equation. When the two reactants are present in equal amounts this takes the form of Equation 1 where C is the concentration of the reactants and Z the fraction reacted in the time, t (in minutes).

$$kC = \frac{1}{t}\frac{Z}{1 - Z} \tag{1}$$

The results of a number of experiments with diazotized sulfanilic acid and sodium 1-naphthol-4-sulfonate at *P*H 4.5 are shown graphically in Fig. 1. The value of $Z/(1 - Z)$ is plotted against t. The points fall well on a straight line which corresponds to a value of 112 for k. The same components taken in different proportions under the same conditions give results shown in Fig. 2. The integrated equation here takes the form of Equation 2, where C is the concentration of the reactant present in smallest amount, m the ratio of the two reactants (a whole number) and Z the fraction which has reacted.

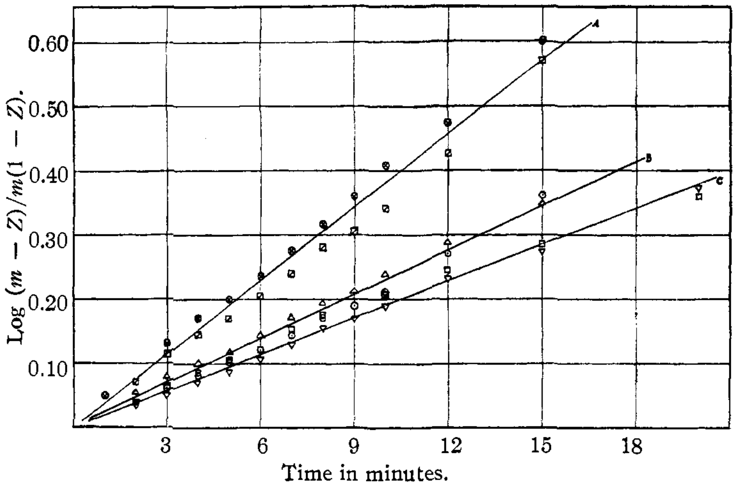


Fig. 2.—Graphical representation of rates of reaction of diazotized sulfanilic acid with sodium 1-naphthol-4-sulfonate at varying concentrations of reactants. *P*H, 4.50; temperature, 15°; μ, 0.24.

	A		B		C	
Concn. (diaz.)	0.0001	0.001	0.0005	0.001	0.0001	0.0005
Concn. (naphthol)	0.001	0.0001	0.001	0.0005	0.0005	0.0001

$$\frac{C\,(m - 1)}{2.30}\,k = \frac{1}{t}\log\frac{m - Z}{m\,(1 - Z)} \tag{2}$$

In Fig. 2 the value of $\log\,(m - Z)/[m(1 - Z)]$ is plotted against t. The slopes of the three lines (A, B, C) correspond to values of k of 105, 111 and 112, respectively, all in excellent agreement with each other and with the value obtained in the experiments in which equimolecular proportions of the reactants were employed. Similar results were obtained with other pairs of reactants in different buffer solutions; some of these are collected in Table II. The values of k were determined graphically as illustrated

TABLE II

REACTION VELOCITY CONSTANTS OBTAINED IN EXPERIMENTS WITH VARYING CONCENTRATIONS OF REACTANTS

Temp., 15.0° Ionic Strength, 0.24

Reactants	PH	Concn. in moles per liter × 10^3 Diazo salt	Hydroxy compound	k
Diazotized *o*-anisidine + disodium-2-naphthol-3,6-disulfonate	8.17	0.1	0.5	1000
	8.17	.1	.1	950
	8.17	.1	.1	970
Diazotized sulfanilic acid + disodium-2-naphthol-3,6-disulfonate	5.27	.5	1.0	95.6
	5.27	.1	0.5	97.5
	5.80	.1	.1	317
	5.80	.1	.5	350
	5.80	.5	.1	302
Diazotized sulfanilic acid + sodium *p*-phenolsulfonate	8.17	.1	.5	6.55
	8.17	.5	1.0	7.13
	8.17	.5	0.5	6.93
Diazotized aniline + disodium-1-naphthol-3,8-disulfonate	7.08	.5	.1	47.4
	7.08	.5	.5	52.7
	7.08	.1	.1	54.6

by Figs. 1 and 2. From all these results it is quite clear that the reaction is unusually free from complications and the rate is very closely expressed by the bimolecular equation.

The relationship between the rate of the reaction and the hydrogen-ion activity of the medium is shown in the results given in Table III and Fig. 3. Usually at least three experiments were performed with varying proportions of reactants, one in which equimolecular amounts were present and two in which the hydroxy compound was present in a 2 to 1 and 5 to 1 excess, the concentration of diazonium salt being 0.0005 and 0.0001 *M*, respectively. The value of k in each experiment was determined graphically. The range of the values of k thus obtained is given in the fourth column of Table III. It is evident from Fig. 3 that the values of log k fall closely on a straight line with unit slope. The reaction may thus be expressed by Equation 3

$$\log k = \log k_0 + P_H \qquad (3)$$

In the sixth column of Table III are given the values of k calculated from the best fit of Equation 3 to the data; the assumed value of k_0 is given in each case in the cross heading. The difference between the calculated and observed values is given in the last column. The agreement is within the experimental error (± 7%). It should be noted that in the case of the two acetate buffers of P_H 4.5 (see Table I) the concentration of base (acetate ion) and of free acid have been varied five-fold without changing the rate. This is of importance as showing that the hydrogen-ion activity (or something directly proportional to it) is the controlling factor.

TABLE III

RATE OF COUPLING IN DIFFERENT BUFFER SOLUTIONS

Temp., 15°; ionic strength, 0.24

*P*H	Buffer (see Table I)	No. of Expts.	Range of values of *k*	Av. *k*	*k* (calcd. from Eq. 3)	Deviation, %
(1) Diazotized *o*-Anisidine + 2-Naphthol-3,6-disulfonate; $k_0 = 6.28 \times 10^{-6}$						
6.30	Phosphate II	2[a]	11.7–12.8	12.3	12.4	+1
7.08	Phosphate IV	2[b]	68–73	70.5	75.5	+0.7
8.17	Borate I	3	950–1000	975	930	−5
(2) Diazotized *o*-Anisidine + 1-Naphthol-4-sulfonate; $k_0 = 1.43 \times 10^{-5}$						
5.80	Phosphate I	3	7.9–9.1	8.32	9.0	+8
6.30	Phosphate II	3	28.8–32.4	30.5	28.5	−7
6.73	Phosphate III	4	64.9–74.0	71.5	76.0	+6
7.08	Phosphate IV	3	152–165	158	170	+8
(3) Diazotized Sulfanilic Acid + 2-Naphthol-3,6-disulfonate; $k_0 = 5.06 \times 10^{-4}$						
4.94	Phthalate II	3	33–39.8	37.4	43.5	+14
5.27	Acetate III	2[c]	95.6–97.5	96.5	95.0	−1
5.80	Phosphate I	4	302–350	330	318	−4
(4) Diazotized Sulfanilic Acid + 1-Naphthol-4-sulfonate; $k_0 = 3.55 \times 10^{-3}$						
4.50	Acetate I	6	104–113	111	112	+1
4.50	Acetate II	2[a]	106–109	108	112	+4
4.94	Phthalate II	3	287–317	304	308	+1
5.27	Acetate III	4	648–690	665	660	−1

[a] Duplicate experiments only (no variation in concentration of reactants). [b] One expt. 0.0005 *M* (naphthol), 0.0001 *M* (diazo.); other, 0.0005 *M* each. [c] One expt. 0.0005 *M* (naphthol), 0.0001 *M* (diazo.); other expt. 0.001 *M* in naphthol and 0.0005 *M* diazo.

In addition to determining the effect of changing hydrogen-ion activity on the rate, two other variables were studied. In a number of cases the reactions were carried out at both 15 and 25° and in this way a temperature coefficient of the reaction velocity obtained. The results are summarized in Table IV. It is clear that there is nothing unusual about the temperature coefficient of this reaction. The consistency of the results is indicated in Part 2 of Table IV by the fact that the values of *E* determined at three different *P*H values agree within the experimental error, which we estimate to be ±500 cal. Probably the variations in *E* with the different pairs of components is to be attributed to experimental error except in the first case reported, where the value seems to be larger than the average. In all the experiments which we have been considering the ionic strength of the solutions was kept constant at 0.24. A few experiments were carried out to obtain a preliminary idea concerning the nature of the salt effect. A series of acetate and phosphate buffers of constant *P*H and varying ionic strength were prepared. The ionic strength of these buffers was varied from 0.022 to somewhat more than 1.0. In all the cases studied (4 combinations) an increase of the ionic strength from 0.25 to 0.9 had little effect on the reaction rate. Thus for practical purposes one may probably ignore the salt effect within an accuracy of ±10% in the value of *k*. We had hoped by decreasing the ionic strength of the solution to obtain data which could be interpreted by means of Brönsted's theory.[4] However, because of the necessity of having the solutions sufficiently buffered it was impossible to work with solutions more dilute than an ionic strength of about 0.022. This is hardly dilute enough for us to obtain the real limiting slope to a curve representing the change of log *k* with change in the square root of the ionic strength. The results obtained in the region between $\sqrt{\mu} = 0.15$ and 0.5 we have not been able to interpret according to Brönsted's theory by any mechanism we have been able to devise. This aspect of the research must be investigated further before any definite conclusions can be drawn. It is enough at this time to mention the fact that diazotized *o*-anisidine + 1-naphthol-4-sulfonate showed no salt effect whatsoever either in concentrated or dilute solution. The other three pairs, diazotized *o*-anisidine + 2-naphthol-3,6-sulfonate, diazotized sulfanilic acid + 2-naphthol-3,6-sulfonate, and diazotized sulfanilic acid + 1-naphthol-4-sulfonate, show a considerable salt effect in the dilute range, the value of log *k* increasing by about 0.18 from $\sqrt{\mu} = 0.15$ to 0.5.

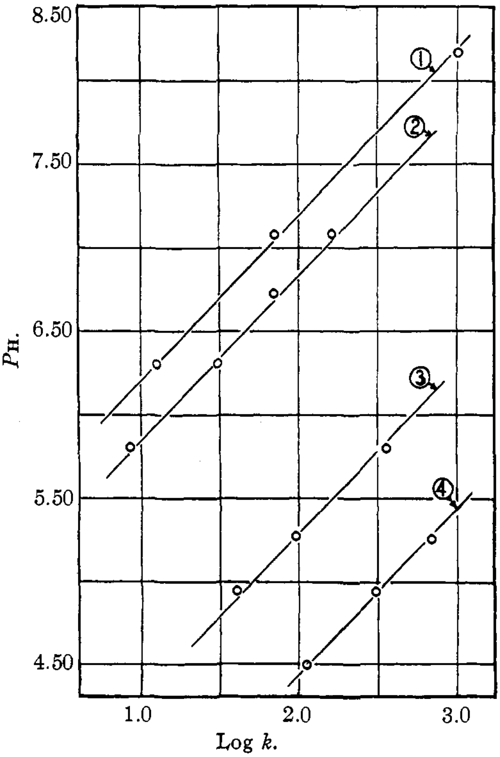


Fig. 3.—Rate of coupling of four pairs of components at different *P*H values. Temp., 15.0°; μ, 0.24. 1, Diazotized *o*-anisidine + R salt; 2, diazotized *o*-anisidine + N. and W. salt; 3, diazotized sulfanilic acid + R salt; 4, diazotized sulfanilic acid + N. and W. salt.

Relation between Chemical Constitution and Coupling Tendency

In order to save space we have summarized in Table V all the final values

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[4] J. N. Brönsted, *Chem. Rev.*, **5**, 265 (1928); *Z. physik. Chem.*, **102**, 169 (1923); *ibid.*, **115**, 337 (1925).

TABLE IV

DETERMINATION OF TEMPERATURE COEFFICIENT OF CERTAIN COUPLING REACTIONS

P_H	Concn. of naphthol, mole per liter	Concn. of diazo, mole per liter	$k_{15°}$	$k_{25°}$	$k_{25°}/k_{15°}$	E, cal.
(1) Diazotized *o*-Anisidine + R Salt						
7.08	0.0005	0.0005	78	208	2.66	16,700
7.08	.0005	.0001	71	195	2.75	17,200
(2) Diazotized *o*-Anisidine + N and W Salt						
5.80	.001	.0005	8.2	19.7	2.40	15,000
6.30	.0005	.0005	30.5	76.5	2.51	15,500
6.73	.0005	.0005	73	185	2.54	15,900
(3) Diazotized Sulfanilic Acid + R Salt						
5.27	.001	.0005	95.6	230	2.41	15,000
5.27	.0005	.0001	97.5	223	2.29	14,200
(4) Diazotized Sulfanilic Acid + N and W Salt						
4.50	.0005	.0005	108	262	2.42	15,100
4.50	.0005	.0001	116	272	2.34	14,600

In all the experiments acetate and phosphate buffers of the same ionic strength (0.24) were employed. The rates were measured at 15 and 25° in the same buffer solution on the same day. The value of E was calculated from the equation $2.303\ (\log k_2 - \log k_1) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

of k obtained in all the measurements carried out at ionic strength 0.24 and 15°. These include the combinations with 5 amines and 4 naphthols. The values of k given in the fifth column are averages of at least three different experiments in each of which the value of k was obtained graphically as illustrated in the cases given in full above. The measurements were always made between 8 and 70% reaction, an average of at least ten observations being made in each experiment. The average range of the values of k may be taken as ±7%, although in many cases the agreement was even better. In the two cases indicated by stars (*) measurements were made in quite alkaline solutions. The reaction in this case did not follow the bimolecular equation. There was a definite falling off in rate as the reaction proceeded. The numbers given are thus mere approximations to a mean rate. In all other cases the measurements agreed within the experimental error with the bimolecular formulation.

A convenient method of comparing the results obtained with a given pair of substances in two or more buffers is to calculate the P_H at which $k = 10$ ($\log k = 1$), assuming the linear relationship between log k and P_H. This has been done in every case in Table V and the results are given in the last column. It is evident that in every case except the two in which the results are uncertain there is excellent agreement between the values obtained in the different buffers. Thus the relationship between rate of

TABLE V

SUMMARY OF DATA OBTAINED IN COUPLING EXPERIMENTS WITH A VARIETY OF NAPHTHOLS AND DIAZOTIZED AMINES (TEMP., 15.0°; IONIC STRENGTH, 0.24)

Amine	Phenol or naphthol	Buffer	*P*H	Reaction velocity constant, k	Calcd. *P*H at which $k = 10$
Sulfanilic acid	Sodium *p*-phenol sulfonate	Borate	8.17	6.85	8.34
		Borate	9.15*	31.6*	8.65*
Sulfanilic acid	Disodium 2-naphthol-6,8-disulfonate (G salt)	Phosphate	6.30	6.93	6.46
		Phosphate	7.08	35.5	6.53
Sulfanilic acid	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Phosphate	5.80	78.4	4.90
		Phthalate	4.94	9.5	4.96
Sulfanilic acid	Disodium 2-naphthol-3,6-disulfonate (R salt)	Phosphate	5.80	330	4.28
		Acetate	5.27	96.5	4.29
		Phthalate	4.94	39.8	4.34
Sulfanilic acid	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phthalate	4.94	305	3.46
		Acetate	5.27	660	3.45
		Acetate	4.50	110	3.46
Sulfanilic acid	Resorcinol	Acetate	4.50	118	3.43
		Acetate	5.27	810	3.36
p-Toluidine	Disodium 2-naphthol-6,8-disulfonate (G salt)	Borate	8.17	15.8	7.97
		Borate	9.15*	72.0*	8.29*
p-Toluidine	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Borate	8.17	200	6.87
		Phosphate	7.08	19.7	6.79
p-Toluidine	Disodium 2-naphthol-3,6-disulfonate (R salt)	Phosphate	6.73	165	5.51
		Phosphate	5.80	12.7	5.70
p-Toluidine	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phosphate	6.30	95.0	5.32
		Phosphate	6.73	282	5.28
o-Anisidine	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Borate	8.17	62.5	7.36
		Phosphate	7.08	5.58	7.33
o-Anisidine	Disodium 2-naphthol-3,6-disulfonate (R salt)	Borate	8.17	985	6.18
		Phosphate	6.30	12.5	6.19
		Phosphate	7.08	71.1	6.23
o-Anisidine	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phosphate	5.80	8.32	5.88
		Phosphate	6.30	31.0	5.81
		Phosphate	7.08	158	5.88
		Phosphate	6.73	71.2	5.88
Aniline	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Phosphate	7.08	50.2	6.38
		Phosphate	6.30	8.10	6.39
Aniline	Disodium 2-naphthol-3,6-disulfonate (R salt)	Phosphate	5.80	35.7	5.25
		Acetate	5.27	10.5	5.25
Aniline	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phosphate	5.80	125.8	4.69
		Acetate	5.27	35.5	4.72
Aniline	Disodium 2-naphthol-6,8-sulfonate (G salt)	Borate	8.17	33.8	7.64
		Phosphate	7.08	3.19	7.58
p-Bromoaniline	Disodium 2-naphthol-6,8-disulfonate (G salt)	Phosphate	6.73	36.0	6.17
		Phosphate	5.80	5.63	6.06

TABLE V (*Concluded*)

Amine	Phenol or naphthol	Buffer	*P*H	Reaction velocity constant, *k*	Calcd. *P*H at which *k* = 10
p-Bromo-aniline	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Phosphate	5.80	107	4.77
		Acetate	5.27	31.7	4.77
p-Bromo-aniline	Disodium 2-naphthol-3,6-disulfonate (R salt)	Phosphate	5.80	222	4.45
		Acetate	5.27	62.2	4.48

All the experiments were carried out at 15° in buffered solutions of constant ionic strength (0.24) and measurements made between 8–10% reaction and 70–75% reaction. The values of k enumerated in the fifth column are averages of at least three experiments: one in which the components were in equivalent amounts, one in which the ratio of the reactants was in 2 to 1 (naphthol in excess) and one in which the reactants were 5 to 1 to each other (naphthol in excess). An average of 9 or 10 observations was made in each experiment. As indicated in Table II the average range in the value of k may be taken as ±7%.

coupling and hydrogen-ion activity illustrated in detail in Table III clearly holds in the case of all the substances investigated.

It is a matter of great interest to see to what extent it is possible to relate the coupling tendency of various compounds to their structure. As a measure of this coupling tendency one might use the value of log k_0 in Equation 3, but a somewhat more advantageous method of presenting the same results is to consider the *P*H at which log k has a definite value, for example 1. We may designate this *P*H as the "coupling value" of the pair of substances investigated at 15° and $\mu = 0.24$. It is evident that if one knows the coupling value for a pair of components it is possible to calculate the rate of reaction at any *P*H provided the ionic strength is fairly close to 0.24. Since the reaction follows the bimolecular equation so closely, the reaction velocity constant thus calculated may be turned directly into percentage reacted at a given time, provided the concentrations are specified. Furthermore, the rate at any temperature other than 15° may be estimated by using the usual equation for the temperature coefficient of the reaction velocity constant and a value of E of 15,000.

The coupling value of a given pair of components is determined both by the nature of the diazotized amine and the hydroxy compound. We have found that it is possible to assign constants to each amine and hydroxy component such that the sum of these numbers is approximately equal to the coupling value when the amine is diazotized and allowed to react with the hydroxy compound in question. This is illustrated by Table VI, in which the coupling value for each pair of components is given as calculated from a simple additive relationship of the two constants A and B arbitrarily assigned to the diazotized component and the hydroxy component, respectively. It will be noted that the agreement between the calculated and found coupling values is within a few tenths of a *P*H unit except in a few cases; that is, one may predict the rate from constants assigned to the individual components within an accuracy of 25%.

TABLE VI

COMPARISON OF THE COUPLING VALUE CALCULATED FROM THE EMPIRICAL CONSTANTS AND FOUND EXPERIMENTALLY (TEMP., 15°, $\mu = 0.24$)

	Sulfanilic acid, $A = 0$		p-Bromo-aniline, $A = 0$		Aniline, $A = 1.1$		p-Toluidine, $A = 1.5$		o-Anisidine $A = 2.1$	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Naphthol-4-sulfonate, $B = 3.5$	3.5	3.45			4.6	4.70	5.0	5.31	5.6	5.85
2-Naphthol-3,6-disulfonate, $B = 4.2$	4.2	4.28	4.2	4.43	5.3	5.22	5.7	5.60	6.3	6.22
1-Naphthol-3,8-disulfonate, $B = 5.1$	5.1	4.90	5.1	4.77	6.2	6.37	6.7	6.83	7.3	7.35
2-Naphthol-6,8-disulfonate, $B = 6.4$	6.4	6.46	6.4	6.10	7.5	7.60	7.9	8.02		
p-Phenol-sulfonate, $B = 8.3$	8.3	8.35								

The numbers given above for each pair of components represent the coupling value (P_H at which log k = 1) as calculated according to the relationship $A + B$ = coupling value, and found experimentally as shown in Table V. The values of A and B for each component are given under the name and were assigned empirically so that the best agreement would result in this table.

In addition to the values given in Table VI, mention should perhaps be made of some very preliminary experiments which resulted in the assignment of the following constants: p-nitro-aniline, $A = -2$; salicyclic acid, $B = 8$; resorcinol, $B = 3.4$. To determine the coupling value of a pair of components within half a P_H unit it is not necessary in most cases actually to use a colorimeter. By working with carefully prepared solutions of known concentration and a series of graduated buffer solutions, it is possible in a series of test-tube determinations to give a very good estimate of the coupling value. If these values and the corresponding constants for the individual components have analytical or preparative application, the advantage of such a series of rough colorimetric measurements is obvious.

In interpreting the significance of the constants A and B of Table VI one needs to know the mechanism of the reaction. It seems probable that the reaction proceeds according to the following scheme although, as was stated above, an attempt to apply this mechanism to an explanation of the primary salt effect has not been successful.

$$\text{Ar N}_2\text{X} + \text{OH}^- \rightleftharpoons \text{Ar N}{=}\text{NOH} + \text{X}^- \text{ (Fast and reversible)}$$
$$\text{ArN}{=}\text{NOH} + \text{P} \longrightarrow \text{Ar N}{=}\text{NP} + \text{H}_2\text{O} \text{ (Relatively slow and irreversible)}$$

In the two equations Ar represents an aromatic residue and P a phenol or naphthol. The equilibrium in the first step would be a function of the hydroxyl-ion activity, which is a direct function of the measured P_H of the solution. Since the rate of the second step depends on the concentration of ArN=NOH this rate would be a function of the P_H value of the buffer. The empirical constant A would seem to be a measure of the position of the equilibrium in the first step, while the empirical constant B corresponds to the speed of the reaction of the hydroxy compound in the second step. The fact that these two constants are approximately additive in every case would seem to indicate, in terms of the mechanism given above, that the rate of reaction of a diazo hydroxide and a hydroxy compound was a function only of the nature of the hydroxy compound. An inspection of Table VI makes it evident that there is greater regularity in the effect of change of chemical structure on the constant *A* than on the constant *B*. This is in accord with the fact that the relationship between equilibrium constants and structure is usually more regular than the relationship between structure and reaction velocity constants.

Whether or not the mechanism given above is correct, it is evident that it is possible to reduce to a remarkably simple formulation the reaction between diazotized amines and hydroxy compounds in dilute solution.

Summary

1. The rate of coupling of diazotized amines with certain phenols and naphthols has been measured colorimetrically in buffer solutions of constant ionic strength. Over a wide range of concentration the reaction rate corresponds to that calculated by means of the usual bimolecular equations.

2. The rate of coupling is a simple function of the hydrogen-ion activity of the buffer solutions. Each pair of components may be characterized (at a given temperature and salt concentration) by means of a "coupling value" defined as the P_H at which $\log k = 1$. In the case of the 20 pairs of components studied, it was found possible to assign certain empirical constants to each amine and phenol such that the sum was approximately equal to the coupling value.

3. The temperature coefficient was measured between 15 and 25°; the average value of E was 15,000. Some preliminary experiments indicate that the salt effect between the ranges $\sqrt{\mu} = 0.5$ and 0.9 may be neglected for practical purposes but from $\sqrt{\mu} = 0.5$ to 0.2 there may be considerable decrease in the velocity constant. Attempts to interpret the data in terms of Brönsted's theory have not yet been successful.

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