batch sampling.[17] Since the extinction coefficient for RR′ is the same in carbon tetrachloride and in benzene, it was assumed that the same value can also be used for styrene solutions.

The Yield of Tetramethylsuccinonitrile (RR) from ABN in the Presence of Scavengers. (1) **Isotope Dilution Analysis.**—ABN-d_{12} (1.71×10^{-3} mole) was added to 100 ml. of 0.038 *M* bromine in carbon tetrachloride. The solution was degassed three times at −78°, and the flask was filled with dry, oxygen-free nitrogen after each of the first two evacuations; it was finally sealed *in vacuo*. The mixture was heated at 65-74° for 44 hours (at least 7 half-lives). Bromine and solvent were removed by distillation at room temperature under reduced pressure after the addition of 0.3000 g. of tetramethylsuccinonitrile as a carrier. The carrier sample (m.p. 167-168°) was prepared independently by decomposition of unlabeled ABN. The residue from the distillation was sublimed four times yielding 0.313 g. of dinitrile, m.p. 163-165°, having 100 D/(D + H) = 0.16. The labeled material was therefore diluted to 0.173 times its original concentration. Since the carrier sample contained 2.21×10^{-3} mole there was 4.608×10^{-4} mole of labeled dinitrile in the reaction mixture, indicating a 26% yield.

A carbon tetrachloride solution (25 ml.) containing 0.171×10^{-3} mole of ABN-d_{12} was heated under gentle reflux for 24 hours. A slow stream of oxygen was passed over the solution, and the solvent was entirely lost after the 24-hour period. A 0.300-g. sample of dinitrile was added and the material was recrystallized from methanol giving 180 mg. of product, m.p. 157-160°, 100 D/(D + H) = 11.2; calculated yield of dinitrile in the decomposition, 18%.

(2) **Vapor Phase Chromatography.**—A solution of ABN (0.0558 *M*) in carbon tetrachloride was heated 133.5 hr. (8.2 half-lives) at 62.5°. Oxygen was bubbled slowly through the reaction mixture throughout the reaction. An aliquot from the mixture was subjected to vapor phase chromatography on a silicone column at 155°. A symmetrical peak was obtained at the retention time characteristic of RR. Comparison of the peak area with those obtained in chromatograms of solutions containing known amounts of RR indicated that the nitrile was produced in 20% yield.

Decomposition of ABN in the Presence of Bromine.—Bromine was determined spectrophotometrically using the absorption at 4300 Å. Runs at 62.5° were carried out by both the batch-sampling and sealed-ampoule techniques.[15] Solutions of bromine in carbon tetrachloride were shown to be stable under the reaction conditions. In a typical, sealed-ampoule run the carbon tetrachloride solution containing 0.0608 *M* ABN and 0.00245 *M* bromine was distributed into ampoules which were sealed *in vacuo* after five degassing cycles. The ampoules were placed in the constant temperature bath and removed at intervals, quenched by cooling, and analyzed by transferring part of the solutions to Beckman cells and reading the absorbance at 4300 Å.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

The Reactions of *p*-Phenylene-bis-diazonium Ion with Water[1]

BY EDWARD S. LEWIS AND MICHAEL D. JOHNSON[2]

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In water at *p*H between 2 and 4, *p*-phenylene-bis-diazonium ion (tetrazotized *p*-phenylenediamine) shows a reversible formation of a mono-*anti*-diazohydroxide and a mono-*anti*-diazotate. The mono-*syn*-diazotate is assumed to isomerize at a very rapid rate. The spectrophotometrically undetected mono-*syn*-diazohydroxide is shown to undergo a kinetically first-order reaction to give the phenol, *p*-hydroxybenzenediazonium ion, which is very probably formed by a reaction with a cyclic transition state, a true S_Ni reaction. The rate problem of a system of two substances interconverted reversibly, each one of which yields a third substance irreversibly as shown in the scheme below, has been integrated exactly in the form of explicit expressions of the concentration of each substance as a function of the four rate constants and time (see Scheme I). It is shown that this system fits within satisfactory precision the case of the tetrazonium salt hydrolysis.

Introduction

The reversible formation of *syn*-diazotates from diazonium salts has been a subject of recent study.[3] In the case of the diazonium ion with the powerfully electron-withdrawing *p*-nitro substituent, two additional features became apparent.[4] First was the rapid first-order reaction of the *syn*-diazotate to give the *anti*-diazotate. Second was the detection of a perceptibly slow kinetically second-order reaction between diazonium ions and hydroxide ion, presumably to give the *syn*-diazohydroxide. The fact that the extent of reaction is sufficient for rate measurement at a *p*H low enough to give a slow rate, with this substituent (which surely increases the rate constant) only means that the diazotate formation equilibrium is even more sensitive to substituents than is the rate constant. Another clearer example of this difference in sensitivity to substituents has also been found.[5] It has been observed recently that the *p*-diazonium ion group is far more powerfully electron withdrawing than is the *p*-nitro group[6]; it became of interest to study the diazonium salt with this influential substituent, especially because this diazonium salt had been reported to be the only *p*-substituted diazonium salt which gives nitrogen more rapidly than unsubstituted benzenediazonium ion.[7] We can anticipate that the *syn*–*anti*-isomerization will be even more rapid than in the case of the *p*-nitro substituted compound, that the diazotates will be formed at a much lower *p*H than with any other known compound, and that an unusual mechanism of decomposition will be involved. We may speculate that the substitution of hydroxide for nitrogen may be a bimolecular reaction[8] activated by the diazonium ion group, which promotes many other nucleophilic substitution reactions on the aromatic ring.[1]

Results

The following results were obtained by studying the absorption spectra of solutions never more than 10^{-4} *M* in tetrazonium salt. The experimental design was controlled by the failure to find a solvent in which the tetrazonium salt was soluble and

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(1) Paper VI of the series, "Reactions of Diazonium Salts with Nucleophiles," paper V, THIS JOURNAL, **82**, 862 (1960).

(2) Robert A. Welch Foundation Postdoctoral Fellow, 1957–1958.

(3) E. S. Lewis and H. Suhr, *Chem. Ber.*, **91**, 2350 (1958).

(4) E. S. Lewis and H. Suhr, THIS JOURNAL, **80**, 1367 (1958).

(5) E. S. Lewis and J. D. Saltiel, Paper presented at the Southwest Regional Meeting, American Chemical Society, Dec., 1959.

(6) E. S. Lewis and M. D. Johnson, THIS JOURNAL, **81**, 2070 (1959).

(7) C. C. Snow, *Ind. Eng. Chem.*, **24**, 1420 (1932).

(8) E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).

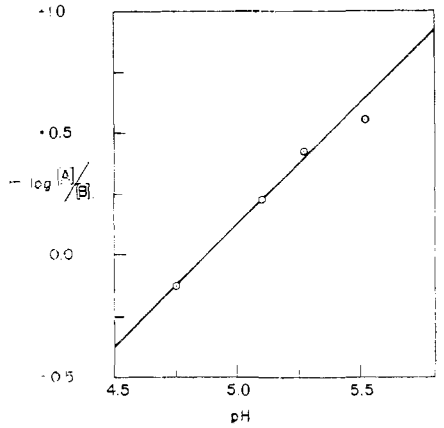

Fig. 1.—Variation in extent of ionization, $(ArN_2OH)/(ArN_2O^-) = A/B$, of *anti*-$ArN_2OH$ with *p*H.

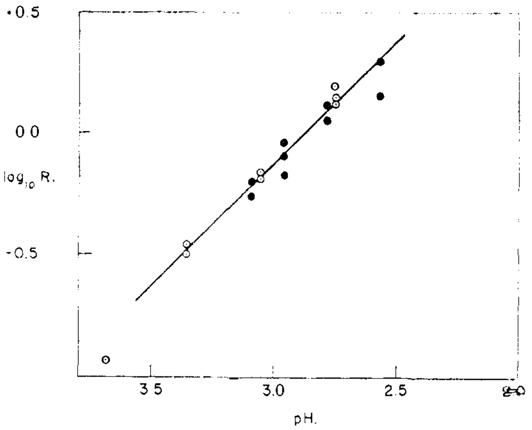

Fig. 2.—Variation in equilibrium ratio of ArN_2^+ to ArN_2OH, R, with *p*H; measured by 335 mμ absorption, ●; by coupling, ○.

stable, except concentrated perchloric or fluoroboric acids. In lower concentrations of acid the solubility was reduced, and at acidities below 0.1 *M*, decomposition was perceptibly rapid.

Several substances with distinguishable ultraviolet spectra could be detected in solutions containing initially only the tetrazonium salt. The pertinent spectral features are given in Table I, together with the structures ascribed to these substances. The accuracy of the extinction coefficients is limited by the presence of impurities both in the starting material and in the solutions containing any one of the substances.

TABLE I

SPECTRAL FEATURES OF THE SPECIES FROM *p*-PHENYLENE-BIS-DIAZONIUM ION

Compound[a]	λ_{max}[a]	ϵ_{max}	λ_{min}	ϵ_{min}	λ_{max}	ϵ_{max}
ArN_2^+	252	1.0×10^4	283	1×10^3	320	1.8×10^3
ArN_2OH	335	1.5×10^4	250	2.5×10^3		
ArN_2O^-[b]	370	4×10^4				
ArOH[c]	229	7.5×10^3	254	1.7×10^3	312	2.2×10^4
ArO^-[c]	250	4.5×10^3	280	....	350	4.2×10^4

[a] Ar– = *p*-N_2^+–C_6H_4–, all wave lengths in millimicrons. [b] The spectra of solutions containing this substance showed several maxima. Only the one in the table, the most intense one, was conclusively identified as belonging to a new substance in rapid equilibrium with the substance absorbing at 335 mμ; the extinction coefficient is clearly less than that of the diazooxide, but may be smaller than the number given. Other peaks coincided in position with the other maxima in the table above. [c] Spectra given here are identical with those of the materials synthesized from diazotization of *p*-aminophenol.[6]

The equilibrium between the *anti*-diazotate and the *anti*-diazohydroxide was determined by adding a solution at about *p*H 4 principally in the form of the latter compound to buffers of various higher *p*H, and measuring the absorbance as soon as possible after mixing at 370 mμ. An identical sample was in each case placed in a *p*H 8.2 buffer. If at *p*H 8.2 all the substance is in the diazotate form, the eq. 1 can be written, where $A_{8.2}$ = absorbance in the *p*H 8.2 buffer, A_x = absorbance in the *p*H *X* buffer, ϵ_A = extinction coefficient in the acid form, ϵ_B = extinction coefficient in the basic form, both in the *p*H *X* buffer, and C_A and C_B are the concentrations in the two forms.

$$\frac{C_A}{C_B} = \frac{A_{8.2} - A_x}{A_x - (\epsilon_A/\epsilon_B)A_{8.2}} \qquad (1)$$

Several reasonable values of ϵ_A/ϵ_B were tried, and plots were made of $-\log (C_A/C_B)$ *vs.* *p*H. The value $\epsilon_A/\epsilon_B = 0.2$ gave the linear plot of slope unity shown in Fig. 1, and yields for the acid dissociation constant of the *anti*-diazohydroxide, $K_a = 1.1 \times 10^{-5}$. This is 15 times as strong as the *anti*-*p*-nitrobenzene diazohydroxide,[4] again reflecting the powerful acid-strengthening effect of the diazonium ion group.

The equilibrium between the tetrazonium ion and the mono-*anti*-diazohydroxide was never quite attained, because irreversible reactions to give the phenol always occurred. Nevertheless, as will be shown later, in time a ratio of tetrazonium salt to *anti*-diazohydroxide was attained which was quite close to equilibrium. Two measurements of this ratio were used, in one, the absorbance at 335 mμ (the peak of the diazohydroxide) was measured after it had stopped increasing, then the solution was acidified and the concentration of *p*-hydroxybenzenediazonium ion was calculated from the spectrum. With an appropriate correction for this decomposition product, the absorbance at 335 mμ then yielded the ratio of tetrazonium salt to *anti*-diazohydroxide. The second measurement was based upon the direct measurements of the two substances by coupling as described later. A plot of the logarithm of this ratio *vs.* *p*H was satisfactorily linear and had a slope of one.

The approximate equilibrium constant calculated from this line is given in eq. 2.

$$K = (ArN_2OH)(H^+)/(ArN_2^+) = 1.2 \times 10^{-3} \qquad (2)$$

The plot is shown in Fig. 2.

The reaction rates were measured by a variety of spectrophotometric methods. Table II shows the rate of formation of *p*-hydroxybenzenediazonium ion from the tetrazonium salt at a variety of acid concentrations, followed by the increase in absorbance at 310 mμ. The last two columns, labelled k_{13} and λ_3, are based on the equations presented later. Because of the contribution of other fairly fast reactions, a first-order course was followed at the lower acidities only after several minutes. The rate constants reported are those for this later portion of the reaction.

TABLE II

DECOMPOSITION OF TETRAZOTIZED p-PHENYLENEDIAMINE IN ACID SOLUTION

(H^+), moles/l. $\times 10^3$	Pseudo-first-order rate constant, min.$^{-1}$ Obsd.	k_{13}	λ_3
6.92	0.00595	0.00635	0.00605
5.25	.00798	.00798	.00795
3.47	.0112	.0110	.0116
1.74	.0151	.0173	.0171

Table III shows in the second column the pseudo-first-order rate constants for the conversion of the *anti*-diazohydroxide to the tetrazonium ion which was followed by coupling the latter with 2-aminonaphthalene-6-sulfonic acid and measuring the concentration of the resulting monoazo compound at 575 mμ. The calculation of the last column is shown later.

TABLE III

RATE OF CONVERSION OF *anti*-DIAZOHYDROXIDE TO TETRAZONIUM ION

(H^+), moles/l.	Pseudo-first-order rate constant, min.$^{-1}$ Obsd.[a]	k_{21}
5.02×10^{-2}	1.14	1.13
2.51×10^{-2}	0.601	0.597
1.99×10^{-2}	.479	.485
1.26×10^{-2}	.334	.332
6.31×10^{-3}	.211	.207
2.57×10^{-3}	.146	.138

[a] All values except the first are averages of two or three runs with deviations from the mean of not more than 3%.

The faster initial stage of the reaction was followed more conveniently by the absorbance at 335 mμ, the absorption maximum of the *anti*-diazohydroxide. In the initial states of the reaction a first-order course was followed as shown by the linearity of a plot of log $(A_{t+\Delta} - A_t)$ *vs.* t according to Guggenheim.[9]

The observed pseudo-first-order constants are shown in Table IV, along with two columns calculated as shown later. The minimum in rate occurring near 2.69×10^{-3} M hydrogen ion is to be noted.

TABLE IV

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE APPEARANCE OF THE 335 mμ PEAK

(H^+), M	k_{335} obsd., min.$^{-1}$	$k_{12} + k_{12} + k_{21}$, min.$^{-1}$	λ_2, min.$^{-1}$
6.85×10^{-3}	0.255	0.282	0.276
2.69×10^{-3}	.240	.236	.232
1.62×10^{-3}	.241	.247	.239
1.10×10^{-3}	.280	.274	.270
8.13×10^{-4}	.301	.309	.305
5.50×10^{-4}	.380	.373	.397
4.07×10^{-4}	.446	.447	.445
2.69×10^{-4}	.615	.592	.591
1.35×10^{-4}	.990	1.02	1.02
6.85×10^{-5}	1.73	1.85	1.86

Measurements were also made by independent measurements of the concentration of the three species, the tetrazonium salt, the *anti*-diazohydroxide and the p-hydroxybenzene diazonium ion at various times after adding tetrazonium salt to water at different acidities. In these experiments, advantage was taken of the fact that 2-aminonaphthalene-6-sulfonic acid couples very rapidly with the tetrazonium salt,[1] but the *anti*-diazohydroxide and p-hydroxy benzenediazonium ion do not couple at a perceptible rate at the pH used. Furthermore, the conversion of the diazohydroxide to the tetrazonium ion is acid catalyzed, thus the tetrazonium ion couples rapidly, the *anti*-diazohydroxide couples after acidification, and p-hydroxybenzenediazonium ion does not couple at all. In Figs. 3, 4 and 5 are shown three examples of the concentration, *vs.* time curves, when the tetrazonium salt is labeled A_1, the *anti*-diazohydroxide is labeled A_2, and A_3 is p-hydroxybenzenediazonium ion. The concentration units are O.D./O.D.^{0}, where O.D. is the optical density of the coupled azo compound, and O.D.^{0} is the same optical density at zero time. A_1 is thus determined directly by coupling, and $A_1 + A_2$ is determined by coupling after acidification. A_3 is calculated as $A_1^0 - (A_1 + A_2)$, where A_1^0 is the concentration of A_1 at zero time, which is obtained by extrapolating $A_1 + A_2$ back to $t = 0$. The uncertainty of A_1^0 which enters into all the

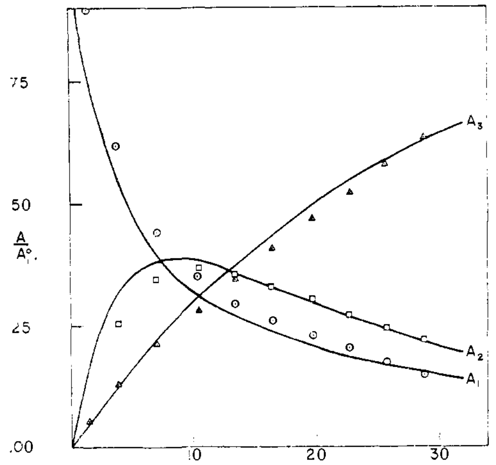

Fig. 3.—Time variation in concentration of ArN_2^+ (A_1), ArN_2OH (A_2), and ArOH (A_3) at $(H^+) = 8.71 \times 10^{-4}$ M.

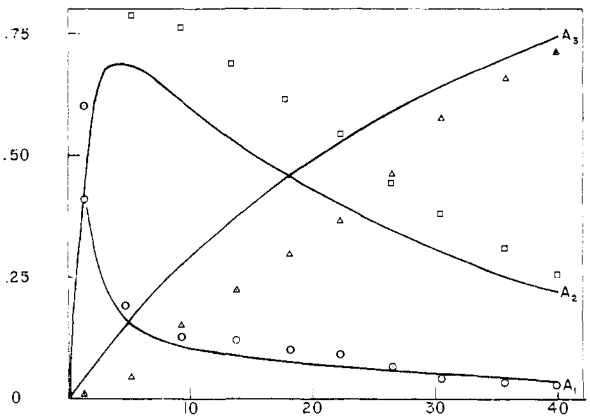

Fig. 4.—Time variation in concentration of ArN_2^+ (A_1), ArN_2OH (A_2) and ArOH (A_3) at $(H^+) = 2.09 \times 10^{-4}$ M.

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(9) E. A. Guggenheim, *Phil. Mag., Ser.* **7**, **2**, 538 (1926).

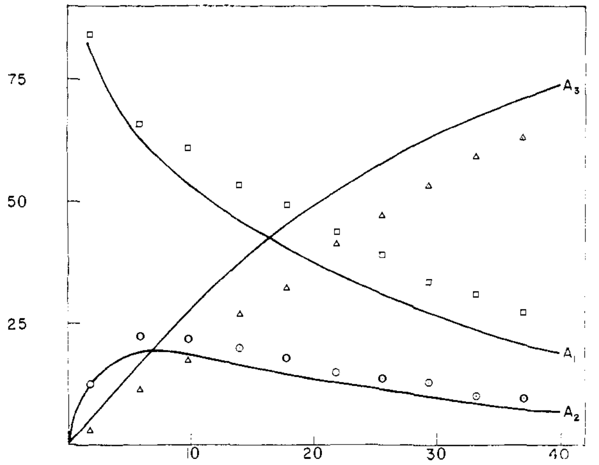


Fig. 5.—Time variation in concentration of ArN_2OH (A_1), ArN_2^+ (A_2) and ArOH (A_3) at (H^+) = 4.36×10^{-4} *M*.

concentrations in the O.D.^{0} term is one of the major uncertainties, since perceptible reaction occurs in the preparation of the samples, so that the time of starting the clock is poorly defined. Figure 3 (at (H^+) = 8.71×10^{-4} *M*) is selected as an example, illustrating fairly good agreement between the observed results and those calculated as shown later.

Figure 4 (at (H^+) = 2.09×10^{-4} *M*) shows a run at the lowest acidity, with somewhat poorer agreement between the observed and calculated curves. Figure 5 shows a run (at (H^+) = 4.36×10^{-4} *M*) in which the starting material was the *anti*-diazohydroxide rather than the tetrazonium salt. Duplicate runs (not shown in the figures or in Tables V, VI and VII) differed by not more than about 10% in concentration at any one time except when the concentration was very low. The sensitivity of the shape of the experimental curves to the value chosen for A_1^0 is illustrated in Fig. 6, which is derived from the same run as Fig. 4, but A_1^0 was given a 10% larger value. The change in the early portions of the A_2 and A_3 curves is to be noted. Tables V and VI show in more abbreviated form the results from experiments at five different acid concentrations. Table V gives the observed and calculated concentrations of A_1 and A_3 at 5, 10 and 20 minutes after the start of the reaction interpolated from smooth curves through the experimental and calculated points.

TABLE V

CONCENTRATIONS OF STARTING MATERIAL AT VARIOUS TIMES

	5 min.		10 min.		20 min.	
(H^+), *M*	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
6.61×10^{-3}	0.805	0.785	0.670	0.658	0.485	0.495
1.74×10^{-3}	.665	.614	.500	.450	.310	.300
8.71×10^{-4}	.535	.480	.358	.322	.225	.208
4.36×10^{-4}	.360	.298	.260	.195	.185	.132
4.36×10^{-4}	.680[a]	.658[a]	.602[a]	.532[a]	.460[a]	.375[a]
2.09×10^{-4}	.185	.156	.128	.103	.096	.071
2.09×10^{-4}[b]	.172	.156	.115	.103	.087	.071

[a] These concentrations are those of the starting material which in this run only was the *anti*-diazohydroxide, ArN_2OH. [b] This is the same run as the row above, but the value of A_1^0 was chosen 10% greater.

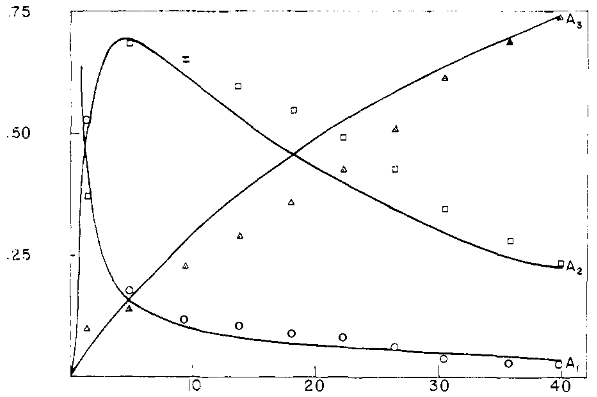


Fig. 6.—Same as Fig. 4, except A_1^0 increased by 10%.

Table VII shows the behavior of the intermediate A_2.

TABLE VI

CONCENTRATION OF ULTIMATE PRODUCT AT VARIOUS TIMES

Time	5 min.		10 min.		20 min.	
(H^+), *M*	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
6.61×10^{-3}	0.165	0.130	0.285	0.235	0.476	0.410
1.74×10^{-3}	.160	.160	.290	.290	.510	.490
8.71×10^{-4}	.160	.162	.270	.298	.480	.502
4.36×10^{-4}	.076	.167	.160	.298	.295	.499
4.36×10^{-4}	.105[a]	.148[a]	.180[a]	.282[a]	.370[a]	.487[a]
2.09×10^{-4}	.062	.161	.162	.292	.327	.492
2.09×10^{-4}[b]	.140	.161	.244	.292	.390	.492

[a] This run started with ArN_2OH instead of ArN_2^+. [b] This is the same run as the row above but the value of A_1^0 was chosen 10% greater.

TABLE VII

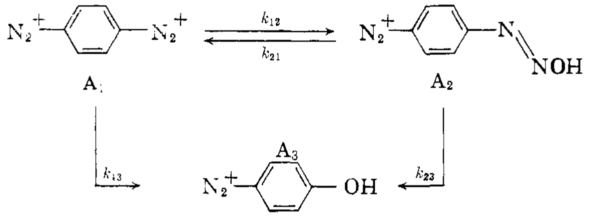
CONCENTRATION OF INTERMEDIATE PRODUCT

	A_2max		t[a]max		$A_1/A_2$40	
(H^+), *M*	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
6.61×10^{-3}	0.05	0.11	12	11	14	6
1.74×10^{-3}	.22	.26	12	10	1.7[b]	1.2[b]
8.71×10^{-4}	.40	.39	11	9	0.67[b]	0.73[b]
4.36×10^{-4}	.63	.53	8	8	.34	.37
4.36×10^{-4}[c]	.230[c]	.195[c]	5	7	.34	.37
2.09×10^{-4}	.79	.69	4	4	.118	.159
2.09×10^{-4}[d]	.69	.69	4	4	.116	.159

[a] The maxima are rather broad, so that t_{max} is not well defined; times are in minutes. [b] Values of ratio at 30 min., experiment not carried to 40. [c] Starting material is ArN_2-OH, intermediate concn. entered is that of tetrazonium ion, ArN_2^+. [d] Same as row above, except A_1^0 was 10% larger.

Discussion

Nearly all the experiments were conducted under conditions such that the only stable substances were the tetrazonium salt (which we shall call A_1), the *anti*-diazohydroxide (A_2) and *p*-hydroxybenzenediazonium ion and its conjugate base (the total of these species will be called A_3). By analogy with earlier work we may assume that the interconversions will be first order in the diazo species. This assumption is in keeping with rather limited observations showing that the course of all reactions did not depend on initial concentrations, and is made more reasonable by the consideration of the low concentrations used, which discourages higher order reactions. The only other important reagents in solution are water and its ions (and perchlorate and fluoborate ions, which may be assumed to be inert). Since the nitrogen loss reactions are certainly irreversible, scheme I is the most general one for these interconversions. In the subsequent treatment a k with two subscripts is a pseudo-first-order rate constant which may vary with acidity, a k with only one subscript is a rate-constant in the usual sense. The variation of concentration with time after certain initial conditions can be calculated from the rate constants if the differential equations are integrated. Since the above scheme may occur again, this integration is shown in the appendix, which also gives explicit expressions for the concentrations starting with pure A_1. While it is in principle possible to calculate the rate constants k_{12}, k_{21}, k_{13} and k_{23} from any measurement of concentration at at least four different times, the mathematics is cumbersome and the experimental error in the original data is sufficient to make such values almost worthless. Nevertheless, a crude evaluation of the constants could be made by graphical differentiation of curves such as are shown in Figs. 3 through 6, and it became clear that none of the constants was zero, that k_{13} and k_{23} were nearly equal and usually smaller than k_{12}. The reasonable requirement that all four pseudo-constants should be smooth functions of acidity was also applied, and it became clear that only k_{12} was strongly dependent on acidity over the range covered by these experiments. A set of constants at any one acidity could be checked by calculation of the concentration–time curves using the integrated rate expression, and comparing these with experimental data, such as those shown in Figs. 3–6.[10] It was not practical to determine exactly the form of the pH dependence of the rate constants in this way.



Scheme I

It proved practical to predict a reasonable acidity dependence for the pseudo-constants from a consideration of the mechanisms of the interconversions. This is based upon the series of intermediates and reactions indicated in Scheme II, to which the steady state principle was applied. In the scheme, Ar represents the p-$N_2^+C_6H_4$ group.

$$\begin{tikzcd}
ArN_2^+ + OH^- \arrow[r, shift left, "k_1"] \arrow[dd, shift right, "k_6"'] & syn\text{-}ArN_2OH \arrow[l, shift left, "k_2"] \arrow[r, shift left, "K_s"] \arrow[d, "k_D"] & syn\text{-}ArN_2O^- + H^+ \arrow[l, shift left] \arrow[dd, shift left, "k_3"] \\
 & ArOH + N_2 & \\
anti\text{-}ArN_2OH \arrow[uu, shift right, "(H^+)\ k_5"'] \arrow[rr, shift right] & & anti\text{-}ArNO_2^- + H^+ \arrow[ll, shift right, "K_a"'] \arrow[uu, shift left, "k_4"]
\end{tikzcd}$$

SCHEME II

With the exception of the omission of a direct, acidity-independent route from $anti$-ArN_2OH to ArN_2^+, and the introduction of a route to ArOH, this scheme is identical with that written for the reactions of p-nitrobenzenediazonium ion.[4] Assuming first that the ArN_2OH and ArN_2O^- are in very rapid equilibrium for both syn and $anti$ isomers, second that all syn-species may be considered unstable intermediates, and third that the extent of ionization of $anti$-ArN_2OH is minor in the range of interest, one can write for the steady state concentration of syn-ArN_2OH eq. 3. From

$$(syn\text{-}ArN_2OH) = \frac{k_1(OH^-)(ArN_2^+) + [k_4K_a/(H^+)](anti\text{-}ArN_2OH)}{k_2 + k_D + [k_3K_s/(H^+)]} \quad (3)$$

Scheme II one can write eq. 4 for the irreversible process

$$d(ArOH)/dt = k_D\ (syn\text{-}ArN_2OH) \quad (4)$$

and from Scheme I, eq. 5 can be written.

$$d(ArOH)/dt = k_{13}\ (ArN_2^+) + k_{23}\ (anti\text{-}ArN_2OH) \quad (5)$$

The combination of eq. 3, 4 and 5 leads directly to eq. 6, 7 and 8.

$$k_{13} = \frac{k_Dk_1(OH^-)}{k_2 + k_D + \frac{k_3K_s}{(H^+)}} = \frac{k_Dk_1K_W}{(k_2 + k_D)\left[(H^+) + \frac{k_3K_s}{k_2 + k_D}\right]} \quad (6)$$

$$k_{23} = \frac{k_Dk_4K_a}{(H^+)\left[k_2 + k_D + \frac{k_3K_s}{(H^+)}\right]} = \frac{k_Dk_4K_a}{(k_2 + k_D)\left[(H^+) + \frac{k_3K_s}{k_2 + k_D}\right]} \quad (7)$$

$$k_{13}/k_{23} = k_1K_W/k_4K_a \quad (8)$$

The reaction of the $anti$-diazohydroxide to give the tetrazonium ion was studied in the presence of coupling component so that the concentration of the tetrazonium ion was always very small. In general, eq. 9 can be written, but the terms in the right-hand side in (ArN_2^+) can be ignored when coupling component is present.

$$d(ArN_2^+)/dt = k_5\ (anti\text{-}ArN_2OH)(H^+) + k_2\ (syn\text{-}ArN_2OH) = k_5\ (anti\text{-}ArN_2OH)(H^+) + \frac{k_2k_4K_a(anti\text{-}ArN_2OH)}{(H^+)\left[k_2 + k_D + \frac{k_3K_s}{(H^+)}\right]} + \frac{k_2k_1(OH^-)(ArN_2^+)}{k_2 + k_D + \frac{k_3K_s}{(H^+)}} \quad (9)$$

Since from Scheme I one can write eq. 10 for the formation of tetrazonium salt from the $anti$-diazohydroxide, an expression, eq. 11, for k_{21} can

$$d(ArN_2^+)/dt = k_{21}\ (anti\text{-}ArN_2OH) \quad (10)$$

be written, and this is also the rate of conversion of the $anti$-ArN_2OH to the coupled product given in Table III. It has been rearranged from eq. 9 to conform to the form of eq. 6 and 7

$$k_{21} = k_5(H^+) + \frac{k_2k_4K_a}{(k_2 + k_D)\left[(H^+) + \frac{k_3K_s}{k_2 + k_D}\right]} \quad (11)$$

Finally the pseudo-constant k_{12} can also be derived from the steady state treatment, but it is more conveniently derived from the equilibrium expressions 12 and 13 derivable from Schemes I and II and experimentally measured.

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(10) These computations are rather tedious by hand, and we thank Mr. L. Shearer, who devised a program for the LGP-30 digital computer, and carried out all of these calculations.

$$K = (anti\text{-}ArN_2OH)(H^+)/(ArN_2^+) = 1.2 \times 10^{-3} \quad (12)$$

$$(anti\text{-}ArN_2OH)/(ArN_2^+) = k_{12}/k_{21} \quad (13)$$

From these one may write eq. 14

$$k_{12} = 1.2 \times 10^{-3} k_{21}/(H^+) \quad (14)$$

The fitting of the experimental data to eq. 6, 8 and 11, which define all the rate constants, was done rather unsystematically by fitting the entries in Table II to eq. 6 which determined the value of $k_1k_DK_w/(k_2 + k_D)$ rather well, and adding to this table a value of k_{13} from the experiments using the analyses by coupling, which fitted curves of the form of Figs. 3–6 fairly well, thus establishing also $k_3K_s/(k_2 + k_D)$. Using this latter value eq. 11 was fitted to the data of Table III, allowing evaluation of k_5 and of $k_2k_4K_a/(k_2 + k_D)$. A value at the lowest acidity derived from Table IV was also used. Several of the experiments using analysis by coupling showed that k_{13} was always slightly greater than k_{23} and the ratio from eq. 8 was estimated from a number of the experiments.

Equations 14, 15, 16 and 17 show the values ultimately chosen.

$$k_{13} = \frac{5.20 \times 10^{-4}}{(H^+) + 1.27 \times 10^{-2}} \quad (15)$$

$$k_{23} = 0.804k_{13} \quad (16)$$

$$k_{21} = 22.5(H^+) + \frac{1.23 \times 10^{-3}}{(H^+) + 1.27 \times 10^{-2}} \quad (17)$$

The rate constants calculated from eq. 14 through 17 give good agreement with experiment for the results in Tables II, III and IV. The calculated values of k_{21} are compared with the measured ones in Table III. The third column in Table II is k_{13}, and it shows reasonable agreement with the ultimate rate of formation of the 310 mμ absorption. In Table IV, the absorption at 335 mμ is due in part to the reversibly formed *anti*-diazohydroxide and in part to the irreversibly formed *p*-hydroxybenzenediazonium ion and its conjugate base. The pseudo constant for the irreversible process is k_{13}, and that for the first-order reversible process is $k_{12} + k_{21}$,[11] so the over-all rate may be well approximated by $k_{12} + k_{21} + k_{13}$. In both Tables II and IV, it should be noted that any part of the concentration–time curve which follows a first-order course should do so with a rate constant which is λ, a solution of the secular equation given in the appendix. For this reason λ_3 is included in Table II and λ_2 in Table III, and the fit is as good as it is to the individual rate constants.

It should be noted that all of the 26 independent kinetic runs and the eight independent equilibrium determinations are thus adequately fitted by the use of only six adjustable parameters.

Implicit in the equations 14 through 17 is the assumption that the rate constants combined in various ways to give the numbers are indeed constant. Since the reactions are those between ions, substantial salt effects are to be expected, and the above assumption must be in error. The ionic strengths of the solutions are almost exactly equal to the perchloric acid concentrations and these vary from about 7×10^{-2} *M* (in Table II) to about 7×10^{-5} *M* in Table IV. Salt effect corrections are artificially included in the coefficients of the empirical equations, and attempts to evaluate relations between the rate constants from experiments at different acidities will give only rather crude results. One of these, although crude, is of some value. The second term of eq. 17, divided by the expression for k_{23} (eq. 7) gives k_2/k_D; the numerical values lead to $k_2/k_D = 2.9$. The crudity is illustrated by the following calculations. The expression for the equilibrium constant for the formation of the *anti*-diazohydroxide from the tetrazonium salt, eq. 12, may be expressed in terms of rate constants from Scheme II as eq. 18.

$$K = \frac{(anti\text{-}ArN_2OH)(H^+)}{(ArN_2^+)} = \frac{k_1K_sk_3K_w}{k_2K_ak_4} = 1.2 \times 10^{-3} \quad (18)$$

Now by combining the steady state expressions with the corresponding numerical values, we can write the eq. 19, 20 and 21, and combining these in the obvious manner gives eq. 22.

$$k_3K_s/(k_2 + k_D) = 1.27 \times 10^{-2} \quad (19)$$

$$k_2k_4K_a/(k_2 + k_D) = 1.23 \times 10^{-3} \quad (20)$$

$$k_Dk_1K_W/(k_2 + k_D) = 5.20 \times 10^{-4} \quad (21)$$

$$\left[\frac{k_D}{k_2 + k_D}\right]\frac{k_1K_sk_3K_W}{k_2k_4K_a} = 5.36 \times 10^{-3} \quad (22)$$

Since the bracketted factor must be less than unity, we are driven to the inequality 23, which is incompatible with the eq. 18. This discrepancy

$$k_1K_Wk_3K_s/k_2k_4K_a > 5.36 \times 10^{-3} \quad (23)$$

which is about a factor of 20 if the above relation between k_2 and k_D is used, was at first disturbing, and efforts to reconcile the two methods of calculating the equilibrium constant were made. While this factor may be reduced, it became apparent that no completely consistent set of constants for equations such as equations 14 through 17 could be selected which would be consistent both with the equilibrium and kinetic data. The large salt effects anticipated make this sort of discrepancy probable, especially since the derivation of the inequality 23 invokes the combination of eq. 21 which is determined by experiments at the highest ionic strength with eq. 20, which is fixed by experiments at the lowest ionic strength. Since there are already six adjusted parameters, represented by the six different numbers in eq. 14 through 17, no attempt was made to try to apply ionic strength corrections to any of these, and the choice of the six numbers was uninfluenced by considerations of the apparent equilibrium discrepancy.

The individual rate constants which can in principle be calculated from the numbers in eq. 14 through 17 are, of course, uncertain because of the failure to correct for salt effects. They are presented to show the rough order of magnitude of these numbers.

$k_1 = 2 \times 10^{11}$ l./mole. min.
$k_4 = 2 \times 10^{2}$ min.$^{-1}$
$k_5 = 22.5$ l./mole. min.
$k_6 = 2.6 \times 10^{-2}$ min.$^{-1}$

Furthermore, from the fact that no *syn*-diazohydroxide was detected spectrophotometrically, one may deduce that its concentration was not

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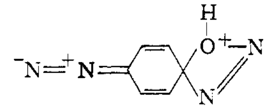
[11] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 172.

greater than 10% of the tetrazonium salt or the *anti*-diazohydroxide, hence $k_D > 10k_{13}$. Since k_{13} has a maximum value of about 0.041, we may conclude that $k_D > 0.4$ min.$^{-1}$. Aside from this minimum value, which is not very useful, it is not possible to say anything exact about k_2, k_D, k_3 or K_s, and the problem of the stability of the *syn*-diazohydroxides remains unsolved.

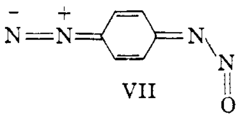
Scheme II is not unique in fitting the data. In particular it appears unsatisfactory in that k_1 is very much larger than any reasonable application of the Hammett equation to the corresponding value of 6×10^4 min.$^{-1}$ for the *p*-nitro compound.[4] An alternative mechanism for this step is a first-order reaction with water coupled with a reverse rate proportional to acid. This alternative alone gives a slightly less satisfactory agreement with experiment, especially the decomposition rates. It is likely that a mixture of the two may occur, so that the bimolecular constant k_1 can be reduced, but not eliminated. It is also possible to eliminate entirely the *syn*-diazotate, making diazotate a common conjugate base of the two diazohydroxides. However, in this treatment the analogy to k_4 becomes a proton transfer step, and the value given above for this appears too small. The addition of more interconversion paths, notably between tetrazonium ion and *anti*-diazohydroxide, analogous to that proposed in ref. 4, is not excluded; this was omitted only for simplicity.[12]

The most interesting feature of the scheme, the first-order decomposition of the *syn*-diazohydroxide, is firmly based. No alternative scheme which is kinetically distinguishable appears satisfactory.

The mechanism of this step is of considerable interest. One irreversible reaction of *syn*-diazohydroxides which has been proposed is the radical decomposition, a proposed step in the Gomberg–Bachmann reaction.[13] The ultimate formation of the phenol from the resulting ion-radical would require either a radical recombination reaction or the intervention of dissolved oxygen followed by a decomposition of the product peroxy radical. An alternative mechanism, which we at present prefer, is a form of SNi reaction with contributions of the structure VI or a larger ring analog containing a molecule of water in the transition state, analogous to a nucleophilic substitution activated by the *p*-diazonium ion group. It is at first not apparent that the *syn*-diazotate would not undergo this reaction even more rapidly, with attack by the anionic oxygen instead of the neutral OH group. However, the important contribution to the diazotate of the structure VII enforces a planar configuration on the whole molecule while it reduces the nucleophilic character of the oxygen and the electron deficiency of the ring. This character of the diazotate, which facilitates the *syn–anti* isomerization, may well inhibit the formation of the spirocyclic transition state.[14]



VI



VII

It is conceivable that the mechanism of this reaction follows the more conventional mechanism shown below in eq. 24 through 26 with the first rate determining. The previous argument about

$$syn\text{-}p\text{-}N_2{}^+\text{-}C_6H_4\text{-}N_2OH \xrightarrow{k_D'} N_2 + syn\text{-}p\text{-}{}^+C_6H_4N_2OH \qquad (24)$$

$$syn\text{-}p\text{-}{}^+C_6H_4N_2OH + H_2O \longrightarrow syn\text{-}p\text{-}HOC_6H_4N_2OH + H^+ \qquad (25)$$

$$syn\text{-}p\text{-}HOC_6H_4N_2OH \longrightarrow p\text{-}HOC_6H_4N_2{}^+ + OH^- \qquad (26)$$

the resonance in the diazotate also predicts that the bond to the diazonium group would have much more double bond character than that in the diazohydroxide, explaining why the nitrogen loss reaction would be much faster in the latter case. However, the lower limit set on k_D' of 0.4 min.$^{-1}$ is about 100 times as fast as any other *p*-substituted benzenediazonium ion. Furthermore, it was unnecessary to postulate any direct decomposition of the *anti*-diazohydroxide, yet it does not seem that the difference between stereoisomers would show up in the rate of loss of nitrogen from the *p*-position. In sum, the above route *via* the aryl cation is a plausible route for a small part of the reaction, but it is improbable that it could be the major path. It is also quite clear that the apparently favorable nucleophilic attack on the tetrazonium salt by hydroxide ion or water is not a major source of the phenol.

The mechanisms of the other steps do not call for much comment. It is clear that the isomerization must be very fast, as was anticipated; the rate constant of the reverse reaction, k_4, is nearly a million times as large as that calculated for the *p*-nitro compound from the rate of the forward process[4] and an isomerization equilibrium constant, calculated from equilibrium constants for the formation of the *anti*-diazotate[4] and the *syn*-diazotate.[3] The acid-catalyzed reaction of the *anti*-diazohydroxide is also faster with the *p*-diazonium ion group than with the *p*-nitro group.

Experimental

All spectra were determined using a Cary model 14 recording spectrophotometer. Unless otherwise stated, all the reactions were studied at 28.1 ± 0.1°.

Materials. *p*-Phenylenebis-[diazonium Fluoroborate].—*p*-Phenylenediamine was tetrazotized by the method of Lewis and Johnson.[6]

Perchloric Acid.—The perchloric acid used was J. T. Baker analyzed reagent. Care was taken in the handling of solutions of *p*-phenylene-bis-[diazonium fluoroborate] in perchloric acid. Only small quantities were dealt with at a time and, when the solid material was in contact with the acid, open beakers were used. In one case a solution of the tetrazonium salt in concentrated perchloric acid did explode.

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(12) It should be noted that Table III is fitted not only by eq. 17 but also (like the *p*-nitro compound) by an expression of the form $k_{obs} = \alpha + \beta(H^+)$.

(13) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(14) We are indebted to Dr. M. G. Ettlinger for this suggestion.

Water.—All water used was distilled from deionized water in the presence of potassium permanganate.

Determination of Spectra.—The spectrum of the tetrazonium ion in greater than 10^{-2} M perchloric acid was determined using a solution made by adding 20 microliters of a solution of the salt in 8.72 M perchloric acid to an aqueous solution containing sufficient perchloric acid to bring the mixture to the required acidity. Solutions containing less than $10^{-2}M$ perchloric acid were made up by adding 20 microliters of a freshly prepared suspension of the salt in acid (of the correct molarity to bring the solution to the required *p*H) to 26 ml. of water. This volume was selected so that a 10-cm. cylindrical cell could be filled. This method provided satisfactory for solutions down to an acid concentration of approximately 6×10^{-5} M. Spectra in solutions below an acidity of 2.5×10^{-6} M could not be determined by direct addition of tetrazonium salt to any of the buffers attempted, because this produced rapid decomposition of the diazonium ion. However, when a solution of the salt was prepared at *p*H 4.2 as described above, allowed to stand for about 5 minutes and then added to a concentrated buffer solution, a reasonably stable solution was obtained. The spectra of solutions between *p*H 5.8 and 9.0 were obtained in the same manner, or by direct addition of 20 microliters of a suspension of the tetrazonium salt in approximately 0.1 M perchloric acid to the concentrated buffer solution. The *p*H of the solutions were checked in each case with a Beckman model D *p*H meter with calomel and glass electrodes. These checks gave satisfactory correlation at all *p*H's above 3, but below this value the *p*H reading was uncertain, probably because of the precipitation of potassium perchlorate in the potassium chloride bridge. Acid concentrations above $10^{-3}M$ were therefore calculated from the concentration of the perchloric acid used and the dilution factors.

Determination of the Relative Concentrations of *anti*-Diazohydroxide and *anti*-Diazotate.—A suspension (25 microliters) of the tetrazonium salt in 8.72×10^{-2} M perchloric acid was added to 50 ml. of water. This solution was divided into two equal parts and after about 5 minutes one part was added to 25 ml. of a buffer solution of *p*H 8.2 and the other part to 25 ml. of a buffer of *p*H between 4.75 and 5.52. The absorbance of the latter solution at 370 mμ was observed as soon as possible after mixing and for sufficient time to allow extrapolation of the observed values to the time of mixing with the buffer solution. The absorbance of the former solution at 370 mμ was similarly observed and extrapolated. The experiment was repeated under identical conditions each time with a buffer of *p*H 8.2 and one other buffer, giving a series of data with variable extents of conversion of the diazotate to its conjugate acid.

Determination of Reactant and Product Concentrations by Coupling (a).—A fresh suspension (50 microliters) of the tetrazonium salt in perchloric acid was added to 252 ml. of water and the clock was started. The concentration of the perchloric acid was that necessary to bring the final solution to the required acidity. Samples (25 ml.) were withdrawn and run into a 100-ml. beaker. To this was added 10 ml. of a solution containing 0.01 g. of 2-aminonaphthalene-6-sulfonic acid per liter (known henceforth as the coupling component), and the time of mixing was recorded. The solution was poured into a 10-cm. spectrophotometer cell and the absorbance of the solution at 575 mμ was noted for sufficient time to allow extrapolation to the time of mixing with the coupling component. This extrapolated absorbance is proportional to the tetrazonium ion concentration; 1.0 ml. of 8.72 M perchloric acid was then added and the sample was returned to the beaker and placed to one side. A second sample was removed and treated in the same way, but when it was placed to one side, the first sample was returned to the cell and its final absorbance was noted. The procedure was repeated with several samples, the absorbance of the previous sample being notified after acidification of each sample. The final sample was allowed to stand for about 3 minutes after acidification before reading its final absorbance. In a separate experiment it was found that the addition of 1 ml. of 8.72 M perchloric acid to the same volume of a solution of the pure azo compound decreased the extinction coefficient by approximately 7%. The final absorbance of each sample was therefore corrected by a factor of 1.07 so that the final values were on the same scale as the initial values. These final corrected absorbances are proportional to the sum of the concentrations of tetrazonium ion and the *anti*-diazohydroxide.

Determination of Reactant and Product Concentrations by Coupling (b).—In a similar experiment to that described above, the initial solution was prepared: 20 microliters of a suspension of the tetrazonium salt in 8.72×10^{-1} M perchloric acid was added to 252 ml. of water and allowed to stand for about 5 minutes. The clock was started at the same time as the correct amount of perchloric acid was added to bring the solution to an acidity of 4.36×10^{-4} M. Samples were then removed and treated as in (a) above.

Determination of Extinction Coefficient for the *anti*-Diazohydroxide and for *p*-Phenylenebis-[diazonium Fluoroborate].—The extinction coefficient of the tetrazonium salt was determined using a solution of a weighed quantity of the salt in 8.72 M perchloric acid. The extinction coefficient of the *anti*-diazohydroxide was determined as follows: 2 microliters of a suspension of the tetrazonium salt in 8.72×10^{-2} M perchloric acid was added to 2.29 ml. of water in a 1-cm. spectrophotometer cell and allowed to stand until the absorbance at 335 mμ was a maximum. The spectrum of the product was taken and 200 microliters of 8.72 M perchloric acid was added immediately to re-form the tetrazonium ion. The amounts of tetrazonium ion and of *p*-hydroxybenzenediazonium ion (the only products present in any quantity) were then calculated from their known extinction coefficients and the observed absorbances. The *p*-hydroxybenzenediazonium ion in the first solution was largely in the form of the diazo-oxide (*pK* 3.4) and the tetrazonium salt was assumed to be entirely in the form of the *anti*-diazohydroxide in this same solution. Thus the extinction coefficient of the *anti*-diazohydroxide was calculated by equating the observed absorbances in the first solution with the known concentrations of the components present.

Determination of the Ratio $[ArN_2^+]/[anti\text{-}ArN_2OH]$.—The concentrations of the tetrazonium ion and the *anti*-diazohydroxide, and hence their ratio, were calculated in a similar manner. The suspension of the tetrazonium salt in the correct acid solution was added to water and allowed to stand for 20–30 minutes until the absorbance at 335 mμ was approximately constant. The spectrum was taken and the solution was acidified and its spectrum taken again. The concentrations of tetrazonium ion and *p*-hydroxybenzenediazonium ion were determined for the acid solution, and the contributions of the latter and its conjugate base to the spectrum of the first solution were calculated and subtracted from the observed absorbance. The remaining absorbance was then equated with the known extinction coefficients of the *anti*-diazohydroxide and tetrazonium ion to give their respective concentrations. This experiment was repeated for various values of the *p*H between *p*H 2.17 and 3.26.

Determination of Conversion of *anti*-Diazohydroxide to Tetrazonium Salt by Coupling.—A fresh suspension (20 microliters) of the tetrazonium salt in 8.72×10^{-2} M perchloric acid was added to 25 ml. of water and allowed to stand for 5 minutes. This solution was then mixed with 10 ml. of the coupling component containing sufficient acid to bring the solution to the required acidity. The absorbance of this solution was then observed as a function of time. This was carried out between acid concentrations of 5×10^{-2} and 2×10^{-3} M.

In a similar experiment, 50 ml. of the initial solution was prepared and divided into two parts. The first part was treated as described above, and the second was simultaneously treated with a solution of the coupling component containing 2.0 ml. of 8.72 M perchloric acid. The maximum absorbance attained in each case at 575 mμ was observed. In a separate experiment in which 2.0 ml. of 8.72 M perchloric acid was added to the same volume of a solution of the azo compound alone, it was found that the extinction coefficient was reduced by about 17%. The corresponding absorbances after addition of acid were therefore increased by about 20% to correlate these values with those for the less strongly acid solutions. The corrected values (allowing also for the change in volume on adding 2.0 ml. of acid) agreed with those obtained in the less acid solutions to within 3%, showing that no side-reactions were being suppressed by the additional acid.

Appendix

The integration of the simultaneous differential eq. 27, 28 and 29 corresponding to Scheme I, may be accomplished by methods previously described. A recent description is by Frost and Pearson,[15] who have also given earlier references. The secular equation given by the method there described

$$\mathrm{d}(\mathrm{A}_1)\mathrm{d}t = k_{21}(\mathrm{A}_2) - (k_{12} + k_{13})(\mathrm{A}_1) \qquad (27)$$

$$\mathrm{d}(\mathrm{A}_2)/\mathrm{d}t = k_{12}(\mathrm{A}_1) - (k_{21} + k_{23})(\mathrm{A}_2) \qquad (28)$$

$$\mathrm{d}(\mathrm{A}_3)/\mathrm{d}\,t = k_{13}(\mathrm{A}_1) + k_{23}(\mathrm{A})_2 \qquad (29)$$

is eq. 30, with the roots given below as eq. 31, 32 and 33.

$$\begin{vmatrix} k_{12} + k_{13} - \lambda & -k_{21} & 0 \\ -k_{12} & k_{21} + k_{23} - \lambda & 0 \\ -k_{13} & -k_{23} & -\lambda \end{vmatrix} = 0 \qquad (30)$$

$$\lambda_1 = 0 \qquad (31)$$

$$\lambda_2 = \frac{1}{2}\left(k_{12} + k_{13} + k_{21} + k_{23} + \sqrt{(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{12}k_{23} + k_{13}k_{23} + k_{13}k_{21})}\right) \qquad (32)$$

$$\lambda_3 = \frac{1}{2}\left(k_{12} + k_{13} + k_{21} + k_{23} - \sqrt{(k_{12} + k_{13} + k_{21} + k_{23})^2 - 4(k_{12}k_{23} + k_{13}k_{23} + k_{13}k_{21})}\right) \qquad (33)$$

As described in ref. 15, the coefficients B can be deduced by setting $\mathrm{B}_{3r} = 1$. In this particular case, in contrast to the case illustrated by Frost and Pearson, setting B_{1r} or $B_2 = 1$ leads to some infinities for other B values. In matrix form, this may be written as eq. 34,[16] or in abbreviated form

$$\mathbf{B} = \left\{\begin{matrix} 0 & \dfrac{\lambda_2 - k_{21} + k_{23}}{k_{12} + k_{21} + k_{23} - \lambda_2} & \dfrac{\lambda_3 - k_{21} + k_{23}}{k_{12} + k_{21} + k_{23} - \lambda_3} \\ 0 & \dfrac{\lambda_2 - k_{12} + k_{13}}{k_{12} + k_{21} + k_{13} - \lambda_2} & \dfrac{\lambda_3 - k_{12} + k_{13}}{k_{12} + k_{21} + k_{13} - \lambda_3} \\ 1 & 1 & 1 \end{matrix}\right\} \qquad (34)$$

as eq. 35.

$$\mathbf{B} = \begin{pmatrix} 0 & B_{12} & B_{13} \\ 0 & B_{22} & B_{23} \\ 1 & 1 & 1 \end{pmatrix} \qquad (35)$$

The mechanics of the solution for the coefficients Q in Frost and Pearson's treatment can be made more routine by using matrix notation and methods throughout.[17]

Let us define the following matrices by eq. 36, 37 and 38.

$$\mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} \qquad (36)$$

$$\mathbf{A}_0 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \qquad (37)$$

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & e^{-\lambda_2 t} & 0 \\ 0 & 0 & e^{-\lambda_3 t} \end{pmatrix} \qquad (38)$$

Where A_1, A_2 and A_3 are the concentrations of the three substances, and the $\mathbf{A}_0$ matrix represents the conditions at $t = 0$ (we have selected $A_1 = a$, $A_2 = A_3 = 0$, but the method will accommodate another selection of initial conditions). Then the desired matrix **A** can be shown to be given by eq. 39.

$$\mathbf{A} = \mathbf{B}\,\mathbf{E}\,\mathrm{B}^{-1}\,\mathrm{A}_0 \qquad (39)$$

The explicit solution of this equation then gives the desired dependence of concentration on time, starting with pure A_1, now written in conventional form as eq. 40, 41 and 42.

$$A_1 = \frac{a}{B_{22} - B_{23}}(B_{12}B_{23}e^{-\lambda_2 t} - B_{13}B_{22}e^{-\lambda_3 t}) \qquad (40)$$

$$A_2 = \frac{a}{B_{22} - B_{23}}(B_{22}B_{23}e^{-\lambda_2 t} - N_{23}B_{22}e^{-\lambda_3 t}) \qquad (41)$$

$$A_3 = \frac{a}{B_{22} - B_{23}}(B_{22} - B_{23} + B_{23}e^{-\lambda_2 t} - B_{22}e^{-\lambda_3 t}) \qquad (42)$$

It can be shown, when the B's are defined according to eq. 34 and the proper λ values are given, that $B_{12}B_{23} - B_{13}B_{22} = B_{22} - B_{23}$; hence the initial condition of $A_1 = a$ is satisfied.[18]

Acknowledgment.—We wish to thank the Robert A. Welch foundation for the support of this work.

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[15] A. A. Frost and R. G. Pearson, ref. 11, p. 160.

[16] For computational purposes, several of the above differences are rather small, and the elements of the matrix can be more readily calculated by taking advantage of the identity $\lambda_2 + \lambda_3 = k_{12} + k_{21} + k_{13} + k_{23}$, which, at least in our case, led to more useful expressions for the terms above.

[17] We are very indebted to Professor J. E. Kilpatrick for pointing this method and for help in the application of it. While matrix methods are not familiar to many chemists (including the authors), the application of the methods led to the first correct solution of the equations, since the algebra in solving the coefficients Q was too cumbersome by conventional methods.

[18] Since chart I is symmetrical with respect to exchange of A_1 and A_2, experiments (such as that in Fig. 5) starting with the substance normally called A_2 can be covered by the same equations merely by exchanging the 1 and 2 subscripts in the compounds and the rate constants. It is also obvious that since the rates are independent of A_3 if $A_3 = b$ at $t = 0$ then at later times A_3 is increased by b over that given by eq. 42.