

pounds which have been reported²³ as inhibitors and retarders for polymerization reactions.

Quantitatively, the quenching of these solutions corresponds to the modified²¹ Stern-Volmer equation $I_0/I = 1 + k_1[Q] + k_2[Q]^2$. Less exactly,

but apparently within the limits of experimental error, these data conform to the following empirical, one-constant equation $I_0/I = 1 + k[Q] + 1/8 k^2[Q]^2$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF NEW HAMPSHIRE]

A Polarographic Examination of Diazotized Amines¹

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In considering mechanisms by which reducing agents convert diazotized amines to biaryls,^{2,3} it was of interest to observe whether there was any difference in polarographic half-wave potentials between those diazo compounds which gave chiefly biaryl and those which gave chiefly azo compounds when treated with cupro-ammonia ion.² Polarographic information was also desirable in order that we might resume our study of large-scale electrolytic reduction at a mercury cathode⁴ under correct controlled potentials.

We have examined the polarographic behavior of diazo compounds derived from aniline and the three isomeric aminobenzoic acids. No polarographic examination of diazotized amines has been reported previously.⁵

Materials and Procedure

Benzenediazonium chloride was prepared by the method of Pray⁶; the crude salt was washed with anhydrous ether and reprecipitated once again from anhydrous ethyl alcohol by the dropwise addition of ether. After drying the salt was dissolved in ice water to prepare 0.1 *M* stock solutions which were stored at 0° in the dark and used within six hours of preparation. Suitable polarographic curves were obtained from solutions prepared by the direct diazotization of the amine provided that excess nitrous acid was eliminated by addition of urea; such solutions were not used throughout the work because of uncertainties concerning their exact concentration. The solid salt used by us was analyzed for chloride by an adsorption indicator technique⁷ and was found to be not less than 95% pure.

Benzenediazonium bisulfate and the analogous salts derived from the three aminobenzoic acids were prepared by a modification of methods used previously.^{6,8} The crudes were partially dissolved in water and reprecipitated by the addition of methyl alcohol, then ether. Stock solutions were 0.01 *M* and were preserved as described above

for chloride solutions. Sulfate analyses⁹ showed these solids to be pure diazonium bisulfates.

All other materials used in the preparation of solutions for polarographic or coulometric analysis were examined to insure freedom from reducible impurities in the potential range studied.

A Sargent-Heyrovsky Model XII polarograph was employed. Capillary constants and other similar data are included in Table I. Coulometric analysis was performed at 0° by conventional procedures.¹⁰ Pre-electrolysis of the supporting electrolyte and buffer solutions prior to the addition of the diazo solution was performed at a potential 0.1 to 0.2 v. more negative than that used in the actual coulometric analysis.

Results

Table I contains representative data obtained with the four diazo compounds under sixty diverse sets of experimental conditions. Figs. 1-3 indicate the quality of the curves obtained. Concentrations of 2 millimolar or less were used because at higher concentrations the maximum associated with the first wave could not be suppressed, intermediate waves appeared and the capillary activity of the diazo compound gave rise to minima (Fig. 3e). Streaming of the dropping electrode at -0.4 v. *vs.* S. C. E. occurred in 5×10^{-2} *M* solutions.

The important observable features of the polarographic results may be summarized conveniently as follows:

(1) All four substances exhibited two waves in the range from 0 to -1.5 v. *vs.* S. C. E. In selected cases more negative potentials were examined but no additional waves were detected prior to discharge of the supporting electrolyte. The first wave exhibited a pronounced maximum which was best suppressed by gelatin.

(2) Diffusion currents for the total second wave decreased rapidly in the higher *pH* range. Diazotized aniline, *m*- and *p*-aminobenzoic acids showed little or no diffusion currents above *pH* 11.5; diazotized anthranilic acid retained the typical two-wave curve as high as *pH* 12.5.

(3) At a given *pH*, or over a limited range of *pH*, diffusion currents for each wave were proportional to concentration of diazotized aniline, the only compound so examined (Fig. 3).

(4) Half-wave potentials for each wave varied

(1) Presented before the Division of Organic Chemistry at New York, N. Y., September, 1947, and Atlantic City, September, 1949.

(2) Atkinson, Morgan, Warren and Manning, *THIS JOURNAL*, **67**, 1513 (1945).

(3) (a) Hodgson, *J. Chem. Soc.*, 348 (1948); (b) Waters, *ibid.*, 266 (1942); Saunders and Waters, *ibid.*, 1154 (1946); Hey and Waters, *ibid.*, 882 (1948); (c) Cowdrey and Davies, *ibid.*, 548 (1949).

(4) Atkinson, *et al.*, Buffalo meeting of the American Chemical Society, September, 1942.

(5) After this work had been completed, Elofson and Mecherly, *Anal. Chem.*, **21**, 565 (1949), stated that while diazo compounds exhibited a complex behavior, their polarographic activity at -0.3 v. *vs.* S. C. E. could be used in an amperometric titration.

(6) Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

(7) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947, p. 571.

(8) Hodgson and Mahadevan, *J. Chem. Soc.*, 325 (1947).

(9) Ref. 7, p. 840.

(10) Lingane, *THIS JOURNAL*, **67**, 1916 (1945).

TABLE I
 POLAROGRAPHIC BEHAVIOR OF DIAZOTIZED AMINES

 A single capillary was used: $m^2/s^2 = 2.17 \text{ mg.}^2/\text{sec.}^{-1/2}$, $t = 2.92\text{--}3.00 \text{ sec.}$ All solutions contained 0.01% gelatin and were studied at 0°

Diazo compound ^a	pH ^b	Concn., millimolar	First wave			Second wave		
			$E_{1/2}$ volts vs. S. C. E. ^c	i_d microamp.	i_d/C	$E_{1/2}$ volts vs. S. C. E. ^c	i_d microamp. ^d	i_d/C
A-1	9	0.5	-0.15	0.76	1.52	-1.06	3.49	6.98
A-2	9	1.0	- .15	1.50	1.50	-1.13	6.70	6.70
A-3	6.6	0.5	- .14	0.80	1.60	-1.03	4.00	8.00
A-4	6.8	1.0	- .14	1.40	1.40	-1.04	7.40	7.40
A-5	4.0	0.5	- .13	0.88	1.76	-0.97	4.60	9.20
A-6	4.4	1.0	- .16	1.73	1.73	-1.05	8.60	8.60
A-7	1.0	0.5	- .15	1.15	2.30	-0.75°
A-8	1.0	1.0	- .16	1.90	1.90	-0.82°
A-9	NHCl	0.5	- .25	0.84	1.68	-0.60°
A-10	NHCl	1.0	- .22	1.44	1.44	-0.67°
B-1	12.4	1.6	- .45	1.89	1.18	-1.13	4.60	2.88
B-2	11.3	1.6	- .39	2.16	1.35	-1.10	5.32	3.32
B-3	8.5	1.6	- .18	2.44	1.52	-1.01	6.32	3.95
B-4	6.7	1.6	- .19	2.44	1.52	-0.96	6.83	4.26
B-5	3.6	1.6	- .11	2.45	1.53	(-0.81)	8.74	5.46
B-6	0.9	1.6	+ .01	2.16	1.35	(-0.78)	8.95	5.60
C-1	11.5	1.6	- .38	1.86	1.16	-1.03	3.95	2.47
C-2	8.5	1.6	- .16	1.29	0.80	-0.96	3.59	2.24
C-3	6.7	1.6	- .08	2.52	1.57	(-0.85)	8.60	5.38
C-4	3.5	1.6	(- .09)	1.26	0.79	(-0.70)	7.40	4.63
C-5	0.9	1.6	+ .05	1.15	0.72	-0.70	11.9	7.42
D-1	11.4	1.6	- .38	0.41	0.26	-0.99	1.29	0.81
D-2	8.5	1.6	- .14	2.85	1.78	-1.02	6.90	4.31
D-3	6.7	1.6	- .09	2.77	1.73	(-1.00)	6.58	4.11
D-4	3.6	1.6	(- .05)	(-0.80)	7.65	4.78
D-5	1.0	1.6	(+ .04)	(-0.64)	7.30	4.56

^a A-1, etc., from aniline; B-, from anthranilic acid; C-, from *m*-aminobenzoic acid; D-, from *p*-aminobenzoic acid. Salt from aniline was chloride; all others were bisulfates. Runs A-1 to A-6 were 0.1 *M* in tetramethylammonium chloride in addition to buffer salts; all B, C and D runs were 0.1 *M* in potassium sulfate. Chloride and sulfate salts of a given diazo compound behaved alike. ^b Observed at 0° with conventional apparatus. Sodium phosphate buffers were used in the range pH 4 to 12; hydrochloric acid or sulfuric acid and sodium hydroxide were used for extremities of pH range. When used, total buffer salt concentration was 0.1 *M*. ^c Various common reference electrodes were used, all being calibrated against a standard S. C. E. No correction in $E_{1/2}$ values for iR drop was required. Values in parentheses are approximations. ^d For the total second wave. ^e Measured at steepest portion of wave (see Fig. 2). This type of curve was observed for A-7 to A-10 inclusive and made measurement of i_d inadvisable.

with concentration (Fig. 3). With the exception of the first wave of diazotized aniline, increasing

pH caused a shift of $E_{1/2}$ for both waves to more negative potentials.

(5) It has been observed that neither wave in the appropriate case can be assigned to common reduction products such as azobenzene,¹¹ phenylhydrazine,¹² aniline, diphenic acid, anthranilic acid or salicylic acid.

To aid in interpreting the above polarographic data we have performed coulometric analyses of benzenediazonium chloride solutions; $C_6H_5N_2Cl$, 10^{-3} to 10^{-2} *M*; potassium chloride, *M*; sodium phosphate buffer, *M*; pH, 7. Potentials used were -0.6 v. vs. S. C. E., which corresponds to the plateau between the first and second waves, and -1.3 v. vs. S. C. E. which lies well beyond the second wave. The maximum duration of electrolysis was two and one-half hours; solutions for analysis suffered negligible deterioration when stirred for this time in the electrolytic cell with no

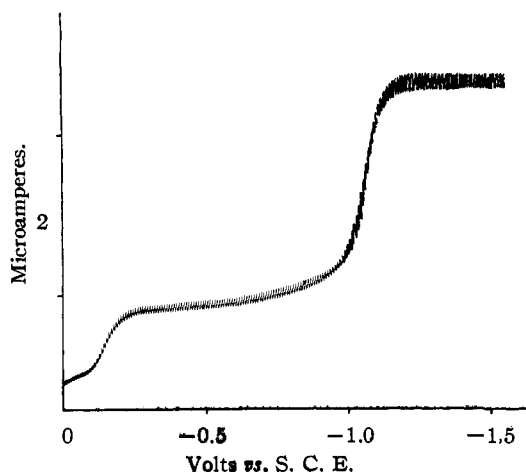


Fig. 1.—Run A-1 (see table).

(11) Previous work summarized by Volpi, *Gazz. chim. Ital.*, **77**, 473 (1947).

(12) Lupton and Lynch, *This Journal*, **66**, 697 (1944).

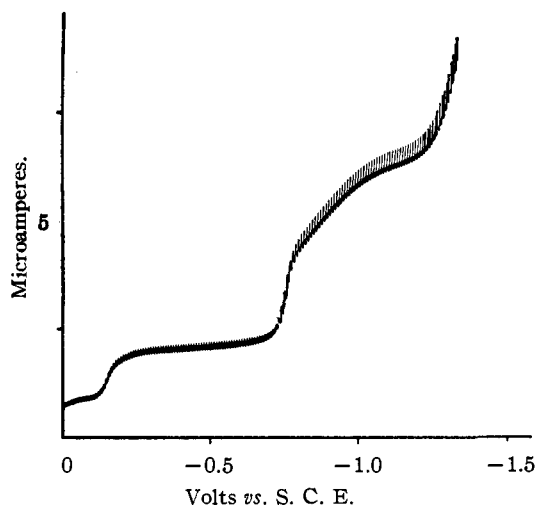


Fig. 2.—Run A-7 (see table).

current flowing, as shown by polarograms recorded before and after treatment.

The electron consumption at both potentials studied was 1 electron/mole RN_2X ; values in thirteen runs varied from 0.93 to 1.07. A polarogram prepared from partially electrolyzed solutions at either potential showed both waves to be present with diffusion currents diminished in proportion. At the conclusion of an analysis at either potential the solution possessed no polarographic activity. A dark red solid was observed to collect on the cathode; it contained a large proportion of mercury dust and tarry organic matter. From the latter we have isolated a small amount of phenylmercuric chloride, m. p. 248–250°, and a much larger quantity (approximately 50% of organic matter) of diphenylmercury, m. p. 115–120°, which we also isolated in our earlier large scale electrolyses.⁴ A convenient derivative was phenylmercuric chloride, m. p. 250–251°, prepared according to Steinkopf.¹³

Discussion

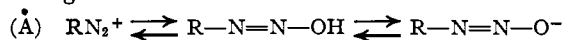
It is apparent that $E_{1/2}$ values for the four compounds examined do not differ significantly; with the exception of the first wave of diazotized aniline they all exhibit the same variation with $p\text{H}$. We may conclude that there is no relation between $E_{1/2}$ values and behavior on reduction with cupro-ammonia ion.²

The results of coulometric analysis indicate that the two waves observed correspond to ingredients of an equilibrium mixture; although the coulometric determination was carried out at a single $p\text{H}$ value, the small variation in i_d/C for the total second wave when $p\text{H} < 9$ indicates that the same electrode process is occurring at all $p\text{H}$ values.

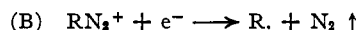
The polarographic results may be explained on

(13) Steinkopf, *Ann.*, **418**, 829 (1917).

the basis of the classical equilibrium (A). Considering



the specific case of diazotized aniline we may assign the first wave to the diazonium ion, RN_2^+ , which would discharge as follows



Such a process involves no hydrogen ions and would therefore exhibit no variation in $E_{1/2}$ with $p\text{H}$, even were it reversible, which is unlikely. The liberation of the free phenyl radical accounts for the observed disintegration of the mercury cathode and may also account for the erratic behavior of the dropping mercury cathode when more concentrated solutions are used; the liberation of nitrogen in a solution already saturated with the gas may also be involved in this erratic behavior. The discharge of RN_2^+ is a slow process, for even in strongly acid solutions where RN_2^+ is said to predominate a second wave, assigned below to the diazohydroxide, is observed. The slow discharge is also indicated by the positive slope of the curve following the first wave. In solutions of intermediate $p\text{H}$, where R-N=N-OH is believed to predominate,

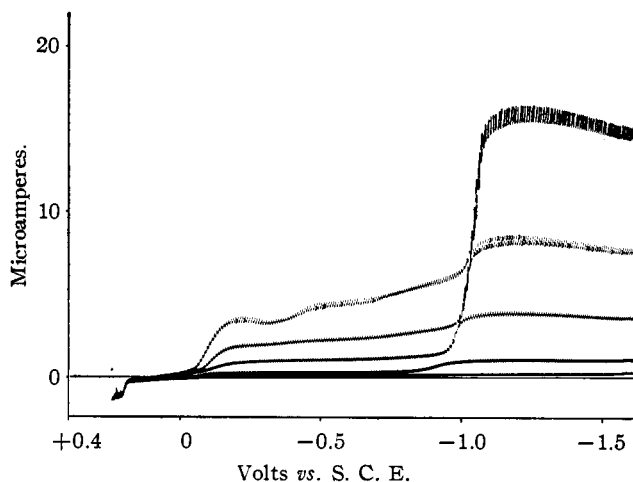
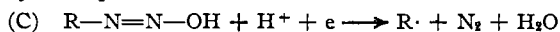


Fig. 3.—Polarograms of (a) 0, (b) 0.2, (c) 0.5, (d) 1.0 and (e) 2.0 millimolar benzenediazonium bisulfate in 0.1 *M* potassium sulfate at $p\text{H}$ 6.7.

the first wave would persist because of the speed with which RN_2^+ is regenerated from R-N=N-OH .

The second wave may be assigned to the undissociated diazohydroxide, R-N=N-OH . As mentioned above this wave would persist even in strongly acid solutions because of the slowness with which the predominant RN_2^+ discharges. The over-all process involved in the second wave may be represented as



The decrease in $E_{1/2}$ for this wave with decreasing $p\text{H}$ suggests that hydrogen ions are involved in

the reduction step but the process as a whole is irreversible since $E_{1/2}$ varies noticeably with concentration (Fig. 3).

When $pH > 9$ a pronounced diminution in diffusion currents occurs. Apparently the diazotate ion, $R-N=N-O^-$, reverts so slowly to the diazohydroxide that measurable concentrations of the latter cannot be maintained in the vicinity of the dropping electrode. The diazotate ion does not discharge at potentials available for study in solutions containing sodium ion.

A similar analysis may be applied to the results obtained with the diazotized aminobenzoic acids. In these cases, however, $E_{1/2}$ for the first wave becomes more negative with increasing pH . We ascribe this increasing difficulty of reduction of RN_2^+ to the appearance of negative poles as the carboxyl groups become ionic with increasing pH .

In conclusion it must be pointed out that while the present work explains the formation of diphenylmercury in the coulometric analysis and in previous large scale electrolyses⁴ and possibly explains an isolated case in which biaryl has been formed by an electrolytic method,¹⁴ polarography cannot explain the formation of phenylhydrazine and its reduction products.^{4,15,16,17,18} In the cited cases large scale reductions were performed using cell potentials above 5 v. and currents as high as 7 amp. Under these conditions hydrogen

(14) Battagay and Beha, *Bull. soc. chim.*, [4] **33**, 1089 (1923).

(15) McClure and Lowy, *Trans. Am. Electrochem. Soc.*, **56**, 445 (1929).

(16) Fichter and Willi, *Helv. Chim. Acta*, **17**, 1416 (1934).

(17) Cook and France, *THIS JOURNAL*, **56**, 2225 (1934).

(18) Takayanagi, *J. Chem. Soc. Japan*, **57**, 64 (1936); *C. A.*, **30**, 5132 (1936).

was evolved, thus rendering an examination of this potential region by the polarograph impossible.

Acknowledgment.—This work was made possible by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences. We wish to acknowledge the advice and encouragement of Professor James J. Lingane of Harvard University during the early stages of this study, and the assistance which Dr. Louis Meites of Yale University kindly gave us in the interpretation of the polarographic results.

Summary

1. Diazo compounds derived from aniline and the three isomeric aminobenzoic acids exhibit two polarographic waves in the range of 0 v. to -1.5 v. *vs.* S.C.E. $E_{1/2}$ values for the four compounds do not differ significantly from one another.

2. At a single pH or over a limited range of pH diffusion currents are proportional to concentration of diazo compounds. When $pH > 9$ diffusion currents decrease markedly and in strongly basic solutions no waves are observed.

3. In general, $E_{1/2}$ values become more negative with increasing pH .

4. Coulometric analysis indicates that 1 electron/mole RN_2X is involved at all potentials.

5. The first wave is assigned to a slow irreversible reduction of the diazonium ion, RN_2^+ (B); the second wave to a rapid irreversible reduction of the diazohydroxide, $R-N=N-OH$ (C). The equilibrium $RN_2^+ \rightleftharpoons R-N=N-OH$ is mobile, while $R-N=N-OH \rightleftharpoons R-N=N-O^-$ is slow.

DURHAM, N. H.

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Hydrogen Fluoride as a Condensing Agent. III. Nuclear Alkylation of Thiophenes in the Presence of Hydrogen Fluoride¹

BY VIKTOR WEINMAYR

The action of hydrogen fluoride upon thiophene has been discussed in the literature on several occasions; Fredenhagen,² and Klatt³ reported that hydrogen fluoride polymerized thiophene violently, Kutz⁴ stated that hydrogen fluoride produced resinous products when used as an alkylating catalyst for thiophene.

We have discovered that thiophene did not polymerize at the instant it came in contact with hydrogen fluoride, but that a short, yet discernible time of stability existed. Although this period of stability was short it was sufficient to allow alkylation, and to convert the unstable, unsubstituted

thiophene to the much more stable alkylthiophenes.

Because two competing reactions, the polymerization and the alkylation, could take place, it was necessary, with the thiophenes that polymerized easily, to use olefins as the alkylating agents rather than the less reactive alcohols or ethers.

Thiophene has been reported to be more reactive than benzene, hence benzene had been used as a solvent for acylations of thiophene.⁵ However, when a solution of thiophene in benzene was alkylated with hexene-1 it was the benzene rather than the thiophene which was alkylated.

The constitution of the compounds obtained was not determined but was postulated upon

(1) For the previous paper of this series see Calcott, Tinker and Weinmayr, *THIS JOURNAL*, **61**, 1010 (1939).

(2) K. Fredenhagen, *Z. physik. Chem.*, **A164**, 176 (1933).

(3) W. Klatt, *Z. anorg. physik. Chem.*, **333**, 393 (1937).

(4) W. Kutz and B. B. Corson, *THIS JOURNAL*, **66**, 1477 (1946).

(5) G. Stednikoff and I. Goldfarb, *Ber.*, **61**, 2341 (1928).