TABLE IV

VALUES OF $n\alpha$ FROM SLOPES OF LOG PLOTS

	Bi	Cd	Cr(III)	Cr(II)	Co	Cu	Fe(II)	Mn	Ni	Zn
Formamide	2.48	1.55	0.63							1.82
Water		1.70	0.68	1.27	0.68	1.50	1.79	1.98	0.61	1.89
Ethylene glycol	2.07	1.75		1.15	.59	0.43		2.25		0.68
Methanol	2.30	1.62	1.12	1.06	.72	1.70	1.02	2.07	.54	.68
Ethanol	2.47	1.45	1.02	1.09	.53	0.99	1.37	1.54		.44
Propanol	2.16	1.50	0.94		.51	1.10	1.07	1.35	.88	
Isopropyl alc.			1.11	0.79		0.86	1.07	0.79		
Butanol	2.04	1.28	1.19	.95	.49		1.27	1.05	.81	
Pentanol				.82	.43		1.13	0.93	.55	

magnetic susceptibility and large ionic radius contribute to complexation of the cation and this in turn contributes to the shift in the half-wave potential.

The Stokes–Einstein relation predicts that the diffusion coefficient is a linear function of the viscosity of the medium provided the diffusing species is large in comparison with the solvent molecules. Hence the ratio of the polarographic diffusion current and the square root of the fluidity should be a constant and such has been observed by others.[5-7] If the factors such as the change in the size of the solvated species are operative then the above ratio may not be constant. Such results were observed. The values used for the diffusion current were those obtained in 0.0005 *M* solutions and the results are shown in Fig. 2 where three separate effects seem to be evident. For the bismuth and copper ions, a plot of the diffusion current *versus* the square root of the fluidity gave a single line passing through the origin indicating that the viscosity of the solvent was the major factor affecting the diffusion coefficient. For cadmium, chromium, cobalt, ferrous iron, manganese and nickel, two parallel lines were obtained. These ions in water, formamide and ethylene glycol gave results which fell on a line which intercepted the origin. The results from the alcohol solutions fell on a parallel line which intercepted the fluidity axis. These data seem to suggest that for these ions the solvation species formed in the alcohols are similar but of a much larger sort than formed in the other solvents. A third effect can be seen for the results with zinc. The line formed by the alcohols was divergent and also intercepted the fluidity axis. The fact that reduction of zinc could not be obtained in the higher molecular weight alcohols seems to indicate a very large solvation species.

All of the polarographic waves were examined by plotting log $i/(i_d - i)$ *versus* the applied voltage, corrected for the potential drop through the solution. The slope of such lines gives $n\alpha/0.059$ and the values of $n\alpha$, when straight lines were obtained, are tabulated in Table IV. The reduction of chromium(III) in the alcohols, and manganese and zinc in water and formamide, gave values corresponding to the valence, but cobalt and zinc in the alcohols show some of the lowest values in the table.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarographic and Coulometric Study of *p*-Dimethylaminoazobenzene

BY H. A. LAITINEN AND T. J. KNEIP[1]

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In acid solution *p*H 1.9 in 50% ethanol, the polarographic reduction of *p*-dimethylaminoazobenzene involves a four-electron reaction to yield the amines, followed by a catalytic hydrogen wave. Coulometric measurements with a mercury poo cathode led to the same result. In strongly alkaline solution, *p*H 13.5, a two-electron polarographic wave was observed. Coulometric measurements indicated an unstable hydrazo compound, which gave an anodic polarographic wave, and which disproportionated slowly to give the original azo compound and the amines. At a *p*H of 9.5, the polarographic wave height corresponded to a little more than two electrons, while the coulometric measurement indicated a four-electron reduction. This disagreement is caused by a disproportionation rate which is slow compared to the polarographic drop life, but fast compared with the duration of a coulometric experiment. (NOTE: The *Chemical Abstracts* name of *p*-dimethylaminoazobenzene would be N,N-dimethyl-*p*-phenylazoaniline.)

The reduction of *p*-dimethylaminoazobenzene by chemical methods has been studied by Jacobson and Kunz.[1,2] They found that the products of zinc reduction in hydrochloric acid medium were amines from the splitting of the azo bond by the addition of four hydrogen atoms, an O-semidine and 2,4′-diamino-5-dimethylaminobiphenyl from the rearrangement of the intermediate hydrazo compound. Catalytic reduction of azo compounds to the amines or hydrazo compounds can be achieved by proper choice of catalyst.[3,4]

Water-soluble sulfonated azo dyes have been re-

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(1) P. Jacobson, *Ann.*, **428**, 76 (1922).

(2) P. Jacobson and R. Kunz, *ibid.*, **303**, 353 (1898).

(3) H. Mozingo, C. Spencer and K. Folkers, THIS JOURNAL, **66**, 1859 (1944).

(4) H. A. Strel'tsova and N. D. Zelinskii, *Bull. Acad. Sci. URSS, Classe sci. Chim.*, 401 (1941); *C. A.*, **36**, 418b (1942).

duced electrolytically to amines at a stirred mercury cathode in both acid and basic solutions.[5]

Shikata and Tachi[6] made the earliest polarographic study of azo compounds. Their principal interest was in the effect of various functional groups on the reduction potential of the azo bond. For *p*-dimethylaminoazobenzene they described three waves which varied in height and potential as the *p*H was changed. In the light of present knowledge, the first two waves can be attributed to a splitting of one wave due to insufficient buffering, and the third was most likely a catalytic hydrogen wave.

Pittoni,[7,8] also reported three waves in dilute acid solutions, and found in 0.1 *N* lithium chloride a single wave, of half-wave potential -0.88 volt, corresponding to that found in 0.1 *N* sodium hydroxide in the present investigation. This correspondence would be expected in view of the large *p*H shift at the electrode surface in unbuffered neutral salt solution.

Volpi[9] found similar results from azobenzene in unbuffered solution, with the exception that the third wave was absent. The total height of the two waves in acid solution was equal to the height of the single wave in neutral or alkaline solutions. Ruetschi and Trumpler[10] studied the effect of hydrogen ion concentration on the reduction of azobenzene in dilute solutions of strong acids and in buffer solutions of low buffer capacity. Castor and Saylor[11] studied azobenzene in buffered media, and found reversible two-electron slopes from *p*H 2.8 to 12.5. In acetate buffers, they observed irreversible slopes which were attributed to slow dissociation of acetic acid. On the other hand, Wawzonek and Frederickson[12] found reversible behavior in the *p*H range of 2 to 6 even in acetate buffers of sufficiently high concentration. Hillson and Birnbaum,[13] in a study of *cis*- and *trans*-azobenzene, found that in acid solution both forms are reduced at the same potential, while in alkaline solution the reduction potentials were different. Wawzonek and Frederickson[12] observed a slightly more positive reduction potential for the *cis* than the *trans* isomer at all *p*H values. A second wave was observed at *p*H 2 corresponding to the reduction to aniline. Streuli and Cooke[14] mentioned evidence for adsorption of azobenzene at a mercury pool electrode, as shown by an abnormally sharp current peak under linear voltage increase. Snowden and Page[15,16] have used an AC polarographic technique for azo and diazo compounds. In their studies of azo and azoxy compounds, Costa[17] and Wawzonek and Frederickson[18] discussed the reduction of azoxy compounds to hydrazo compounds and to amines.

In the present investigation, it is shown that the reduction products of *p*-dimethylaminoazobenzene are different in acid and alkaline media, and that at intermediate *p*H values the polarographic and coulometric values for *n*, the number of electrons per molecule, are different.

Experimental

Apparatus.—A Sargent Model XXI polarograph and a Leeds and Northrup Model E Electrochemograph were used. A voltage span of 2 volts was used in all experiments; the Sargent voltage divider was standardized by means of a potentiometer at two widely separated points before each run.

A conventional H-type cell with a fritted glass diaphragm was used as the electrolysis vessel, using as a reference electrode an external saturated calomel electrode with a flexible sidearm terminated by an agar plug. The reference electrode was kept in a constant temperature bath with the sidearm immersed in saturated potassium chloride solution when not in use. All experiments except those concerned with temperature coefficients were carried out at 25 ± 0.05°.

A Sargent capillary was used, with a drop time of 6.71 sec. and mass rate of flow of 1.039 mg. sec.^{-1} measured at a corrected mercury head of 61.8 cm. at open circuit both in 50% ethanol, 0.2 *M* ammonia, 0.1 *M* ammonium chloride buffer, and in a 50% ethanol citrate buffer of *p*H 3.86.

The coulometric experiments were carried out under controlled potential using an apparatus described by Ziegler,[19] which was patterned after that of Lingane.[20] A hydrogen-oxygen coulometer[21] constructed from a 5-ml. buret was used to measure the total electrolysis current.

The electrolysis vessel was a larger version of an H-cell,[19] having a 300-ml. erlenmeyer flask as one arm of the cell. The cell was designed to permit introduction or removal of mercury through a three-way stopcock at one side of the bottom of the flask. Oxygen-free nitrogen could be passed through or over the solution as desired. The cross arm of the anode compartment was filled with potassium chloride-agar gel.

Materials.—A sample of *p*-dimethylaminoazobenzene[22] was twice recrystallized from 95% ethanol by addition of a small amount of hot distilled water. The product separated as a fine crystalline powder upon cooling. After filtration, washing and vacuum drying for 8 hours at 50°, the final

TABLE I

BUFFER SOLUTIONS IN 50% ETHANOL

Components		
Acidic	Basic	*p*H
0.1 *M* perchloric	....	1.48
.1 *M* sodium bisulfate	0.01 *M* sodium sulfate	1.90
.107 *M* citric acid	.0033 *M* sodium citrate	2.89[a]
.166 *M* citric acid	.033 *M* sodium citrate	3.86
.070 *M* citric acid	.040 *M* sodium citrate	4.72
.050 *M* citric acid	.050 *M* sodium citrate	5.02
.040 *M* citric acid	.070 *M* sodium citrate	5.68
.050 *M* potassium biphthalate	.050 *M* sodium phthalate	6.94
.100 *M* ammonium chloride	.010 *M* ammonium hydroxide	8.42
.100 *M* ammonium chloride	.040 *M* ammonium hydroxide	8.92
.100 *M* ammonium chloride	.200 *M* ammonium hydroxide	9.50
	.100 *M* sodium hydroxide	13.5

[a] 0.1 *N* potassium nitrate added as supporting electrolyte.

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[5] L. P. Hubbuch and A. Lowy, *Trans. Am. Electrochem. Soc.*, **LV**, 227 (1929).

[6] M. Shikata and I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **40**, 11 (1937); *C. A.*, **31**, 6087 (1937).

[7] A. Pittoni, *Atti soc. med.-chir Padova*, **25**, 125 (1947); *C. A.*, **43**, 7835g (1949).

[8] A. Pittoni, *Atti ist Veneto Sci. Venezia*, **106**, II, 29 (1948); *C. A.*, **44**, 8268a (1950).

[9] A. Volpi, *Gazz. chim. ital.*, **77**, 473 (1947); *C. A.*, **42**, 3346g (1948).

[10] P. Ruetschi and G. Trumpler, *Helv. Chim. Acta.*, **35**, 1021 (1952).

[11] C. R. Castor and J. H. Saylor, THIS JOURNAL, **75**, 1427 (1953).

[12] S. Wawzonek and J. D. Frederickson, *ibid.*, **77**, 3985 (1955).

[13] P. J. Hillson and P. P. Birnbaum, *Trans. Faraday Soc.*, **48**, 478 (1952).

[14] C. A. Streuli and W. D. Cooke, *Anal. Chem.*, **26**, 963 (1954).

[15] F. C. Snowden and H. T. Page, *ibid.*, **24**, 1152 (1952).

[16] F. C. Snowden and H. T. Page, *ibid.*, **22**, 969 (1950).

[17] G. Costa, *Ann. triestini univ. Trieste*, [2] **2223**, 115, 127, 151, 161 (1953); *C. A.* **48**, 4331 (1954); *Gazz. chim. ital.*, **83**, 875 (1953); *C. A.*, **48**, 10456 (1954).

[18] S. Wawzonek and J. D. Frederickson, THIS JOURNAL, **77**, 3988 (1955).

[19] W. A. Ziegler, Ph.D. Thesis, University of Illinois, 1952.

[20] J. J. Lingane, *Anal. Chem.*, **21**, 497 (1949).

[21] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

[22] Kindly furnished by Professor C. S. Marvel.

product showed a melting point of 117.6 to 119.0° with a hot stage microscope using a 2° per minute temperature rise.

The composition of the buffer solutions is given in Table I. The *p*H values were read with a Beckman Model G *p*H meter standardized with an aqueous buffer.

Results and Discussion

General Polarographic Behavior.—In acid buffers of *p*H 1.5 to 7, two waves were observed. The first wave was distorted by a prominent maximum; the second wave was approximately four times the height of the first at *p*H values below 5 (Fig. 1). Upon addition of gelatin in an attempt to suppress the maximum, the second wave disappeared at a gelatin concentration above 0.01% (Fig. 2), although traces of the maximum were still present at dye concentrations of 10^{-3} and 10^{-4} molar when the solubility limit of gelatin in the solvent was reached. Methylcellulose was more effective than gelatin; however, the solubility limit was again reached before all traces of the maximum had disappeared.

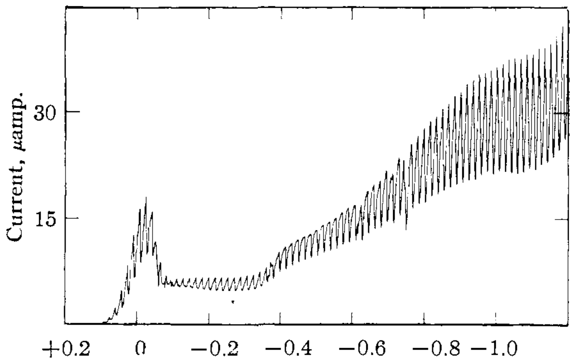

Fig. 1.—Polarogram of 10^{-3} *M* *p*-dimethylaminoazobenzene in 0.1 *M* perchloric acid.

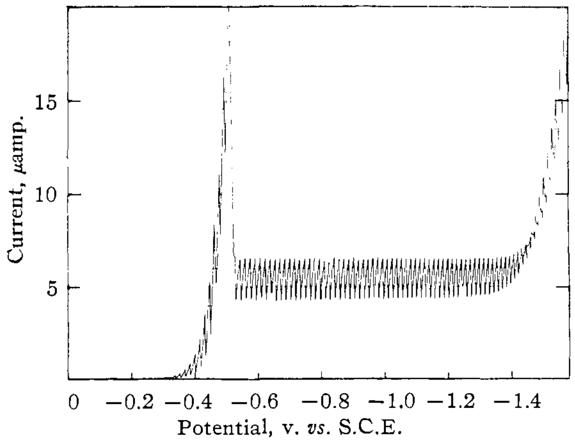

Fig. 2.—Polarogram of 10^{-3} *M* *p*-dimethylaminoazobenzene at *p*H 5.68, in presence of 0.016% gelatin.

With increasing *p*H, the height of the first wave decreased gradually from *p*H 1 to 5, and more rapidly between *p*H values of 6 and 8. Above *p*H 8, the height decreased more slowly, until at *p*H 13.5 the wave height was about half of its value in acid solutions.

The second wave, very pronounced in acid solution, showed a rapid decrease in height in the *p*H range between 6 and 8, and had disappeared at *p*H values above 9.5.

The first wave shifted with *p*H, the second showed no significant change. Because of the presence of the maximum, accurate values of the half-wave potential could not be determined. Estimated values, listed in Table II, show about 0.108 v. change per *p*H unit below *p*H 6, and 0.051 v. above *p*H 7. Heights of the first and second waves are also listed in Table II. The combined heights of the two waves were measured in the absence of gelatin, and in certain experiments the second wave was suppressed to allow measurement of the first wave.

Table II

Wave Heights and Half-wave Potentials

	First wave		Second wave
*p*H	$E_{1/2}$ (v. *vs.* S.C.E.)	Wave height, μa./m. mole/l.	Current at −1.2 v., μa./m. mole/l.
1.48	+0.13	6.75	31.6[a]
1.90	.00	6.98	32.2
2.89	− .11	6.90	27.2
3.86	− .21	6.70[b]	26.3
4.72	− .34	6.60[b]	28.0
5.02	− .43	6.60[c]	28.0
5.68	− .46	6.50[b]	24.8
6.94	− .54	6.30[b]	19.7
8.42	− .62	4.75[b]	3.85
8.92	− .64	4.25	0.90
9.50	− .67	3.90	0.0
13.5	− .88	3.48	0.0

[a] Measured at −1.1 v. [b] 0.008% gelatin present to suppress the second wave. [c] 0.008% methylcellulose present.

Effect of Height of Mercury Column.—Heights of the first wave were determined at three *p*H values (1.90, 4.42 and 9.50) at various heights of mercury column from 39.2 to 99.2 cm. The height of mercury column was corrected for back pressure and the wave heights were corrected for variations of residual current with mercury head. The exponent x in the equation $i = kh^x$ was evaluated by log-log plots to be 0.42, 0.55 and 0.40 at the three *p*H values, respectively.

Similar measurements of the second wave at *p*H values of 1.90 and 4.42 showed the wave height to be independent of the height of mercury column.

Clearly, the first wave is governed by a diffusion process, while the second is kinetically controlled. The kinetic process is undoubtedly the catalytic discharge of hydrogen which becomes decreasingly important above a *p*H of 6 and disappears entirely above *p*H of 9.5. The suppressing effect of gelatin either indicates that the catalytic hydrogen discharge is caused by an absorbed layer of dye or reduction product, or that the kinetics of the catalytic process are affected by the presence of an adsorbed layer of gelatin. In this connection, Pech[23] has reported catalytic hydrogen waves in the presence of aliphatic amines. As will be shown below, the catalytic wave appears under conditions such that amines are the reduction product of the dye. Aniline (10^{-3} *M* in *p*H 1.9 buffer) failed to show a catalytic hydrogen wave. The other product, *p*-

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[23] J. Pech, *Coll. Czech. Chem. Communs.*, **6**, 126 (1934).

(N,N-dimethylamino)-aniline, was not available for testing.

Effect of Temperature.—The heights of the two waves were measured at a *p*H of 1.90 at 25 and 34°. The temperature coefficients, computed by means of the compound interest formula, were 1.9 and 5.2% per degree for the first and second waves, respectively. The wave height of the single wave at *p*H 9.5 showed a temperature coefficient of 2.1% per degree.

Clearly, the first wave in acid solution is diffusion controlled, while the high temperature coefficient of the second wave confirms the previous indication of kinetic control.

Polarographic Wave Heights.—The height of the first wave at *p*H 1.90, and that of the single wave at *p*H values of 9.5 and 13.5 were proportional to concentration over a concentration range of 10^{-4} to 10^{-3} molar.

Calculation of apparent diffusion coefficients from the Ilkovic equation led to the following values (Table III),

TABLE III

CALCULATED APPARENT DIFFUSION COEFFICIENTS

*p*H	$D \times 10^6$ Assuming $n = 4$	 Assuming $n = 2$
1.90	3.56	14.24
2.89	3.54	14.16
9.50	1.16	4.63
13.5	0.87	3.38

The data in Table III were calculated for solutions of very low and very high *p*H to avoid the use of diffusion current data obtained with gelatin present. In the acid solutions, the dye exists as a cation, while in the alkaline solutions it is present as neutral molecules. The calculated values of *D* in acid solution assuming a four-electron reduction, are in satisfactory agreement with the value for the *p*H 13.5 solution if a two-electron reaction is assumed in that medium. For the ammoniacal buffer of *p*H 9.5, the calculated values are anomalous no matter which reaction is assumed. Increasing the buffer concentration twofold had no noticeable effect either on the wave height or half-wave potential. Evidently, a mixed process is occurring.

The calculated value of 3.5×10^{-6} cm.^{2} sec.$^{-1}$ for *D* is in good agreement with the value of 3.3×10^{-6} cm.^{2} sec.$^{-1}$ for stilbene[24] in dioxane–water, for azobenzene[25] in approximately 50% ethanol, and for trans azobenzene[11] in approximately 10% ethanol.

Coulometric Measurements.—The coulometric experiments were carried out on solutions of the same composition as used for the polarographic experiments. For each experiment, 150 ml. of solution was deaerated, and a polarogram was recorded. Nitrogen was passed over the solution during the polarographic and electrolytic experiments. The dropping electrode was removed and the mercury pool cathode was introduced. A motor-driven glass rod stirrer was turned on, and electrolysis was carried out at a controlled cathode potential corresponding to the plateau of the polarographic wave. After 3.5 to 4 ml. of gas had collected in the coulometer, the mercury cathode was removed, and a second polarogram was recorded. The whole procedure was repeated if sufficient reducible material remained in the solution. Three buffer solutions were used, of *p*H values 1.90, 9.50 and 13.5. The data obtained are listed in Table IV.

TABLE IV

COULOMETRIC EVALUATION OF ELECTRONS PER MOLECULE

*p*H	i_d, initial μamp.	i_d, final μamp.	Moles removed $\times 10^5$	Equiv. found $\times 10^5$	n
1.90	7.90	5.05	5.39	21	3.9
1.90	5.05	2.12	5.56	20	3.7
9.50	4.82	3.38	4.47	19.6	4.4
9.50	3.38	2.03	4.20	18.8	4.5
13.5	3.98	2.02 -1.26^a	7.5	19.9	2.6
13.5	2.02 -1.26^a	0.78 -2.00^a	4.7	15.1	3.1

[a] Anodic waves.

Controlled potential electrolysis at *p*H 13.5 led to a solution which gave a composite anodic–cathodic polarographic wave passing through zero current with only a slight indication of decreased slope (Fig. 3). The resulting solution was not completely stable. Although the solution was air free and a stream of purified nitrogen was passed over it at all times, the anodic current was found to decrease in the last experiment in Table IV by 0.70 μ amp. in 15 minutes. On standing overnight, the anodic wave had disappeared, and a cathodic wave of 2.10 μ amp. was found. The net change in cathodic wave height after two electrolyses and standing overnight was 1.88 μ amp., corresponding to an over-all reaction of 4.8 electrons per molecule. It is apparent also from Table IV that the combined wave heights after the first electrolysis (3.28 μ amp.) is less than the initial wave height of 3.98 μ amp. If a mixed 2- and 4-electron reduction were assumed and the missing diffusion current attributed to the four-electron reduction, the calculated number of faradays of electricity in 2.13×10^{-4}, as compared with the observed 1.99×10^{-4} faradays.

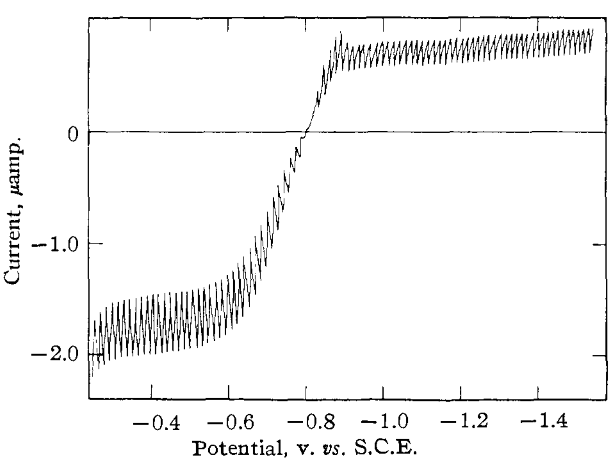

Fig. 3.—Polarogram of solution resulting from electrolysis of *p*-dimethylaminoazobenzene at *p*H 13.5.

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[24] H. A. Laitinen and S. Wawzonek, THIS JOURNAL, **64**, 1765 (1942).

[25] P. Ruetschi and G. Trumpler, *Helv. Chim. Acta*, **35**, 1021 (1952).

These observations may be accounted for by assuming that the primary reduction product in alkaline solution is the hydrazo compound, which forms nearly a reversible oxidation–reduction couple with the azo compound, as shown by the composite polarographic wave. However, the hydrazo compound undergoes disproportionation slowly, to yield from two moles of hydrazo compound one mole of azo compound and one mole of each of the two amines. The rate of disproportionation is so slow at *p*H 13.5 that the polarographic wave height corresponds to a two-electron process.

At *p*H 9.5 the disproportionation rate is so rapid that a 4-electron reduction is clearly observed at the mercury pool cathode, while a mixed process occurs at the dropping electrode.

At *p*H 1.9, both electrodes show a 4-electron reduction. Conceivably, the disproportionation rate could be so rapid that it is quantitative at the dropping electrode. Alternatively, the azo compound may accept four electrons in the primary reaction.

An experiment by Kivalo[26] in this Laboratory using an oscillographic technique is of interest in this connection. Using a 10^{-3} *M* solution of dye in a 0.1 *M* biphthalate buffer of *p*H 7.1, and applying a two cycle sine wave potential of two volt magnitude to a dropping electrode, it was found that both an anodic and cathodic current could be observed. However, an overvoltage of the order of 0.3 volt between the anodic and cathodic processes was observed. Since the amines, which are the reduction products, are anodically inert, this experiment strongly indicates the formation of an anodically active intermediate, probably the hydrazo compound, at *p*H 7. Further experiments of this type in solutions of lower *p*H would be of interest in the further elucidation of the reduction mechanism.

A disproportionation of the type postulated here has been noted by Hoffman[27] in heating hydrazobenzene above its melting point. Similar reactions have been reported by Lermontoff[28] for dinitrohydrazobenzene and by Stern[29] with acetylhydrazobenzene. Biehringer and Busch[30] found an irreversible disproportionation of hydrazobenzene upon heating a 1 *M* solution in absolute alcohol to about 120 to 130° for 6 to 8 hours. Apparently, N,N-dimethyl-*p*-phenylhydrazoaniline is so unstable that it has not been isolated.

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(26) P. Kivalo, private communication.

(27) A. W. Hoffman, *Proc. Roy. Soc. (London)*, **12**, 576 (1863); *Jahresbericht*, 425 (1863).

(28) J. Lermontoff, *Ber.*, **5**, 235 (1872).

(29) D. Stern, *ibid.*, **17**, 378 (1884).

(30) J. Biehringer and A. Busch, *ibid.*, **36**, 339 (1903).