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The Polarographic Behavior of the Azobenzene–Hydrazobenzene System

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The system *trans*-azobenzene–hydrazobenzene has been found to be reversible at the dropping mercury electrode in a buffer range of 2 to 6. At higher pH values hydrazobenzene is oxidized at values which are about 0.07 v. more positive than those obtained for the reduction of *trans*-azobenzene. *cis*-Azobenzene is reduced at slightly more positive potentials than *trans*-azobenzene throughout the buffer range studied.

Azobenzene–hydrazobenzene, which has been found to be a reversible oxidation–reduction system potentiometrically[2,3] and at the mercury pool electrode,[4] has not yet been shown conclusively to be reversible at the dropping mercury electrode. Reversibility has been claimed for the reduction of azobenzene[5] solely from data obtained with this compound and without any work on the oxidation of hydrazobenzene. For a thermodynamically reversible system hydrazobenzene must oxidize at the same half-wave potential as that observed for the reduction of azobenzene.

The only comparison of the polarographic oxidation of hydrazobenzene with the corresponding reduction of azobenzene at the dropping mercury electrode has indicated that oxidation of hydrazobenzene occurs at more positive potentials than those for the reduction of azobenzene in the pH range studied.[6] A slope of 0.075 v. per pH unit for the linear plot of the half-wave potentials of azobenzene as a function of pH in view of other work,[5] pointed to inadequate buffering as a possible explanation for the differences in half-wave potentials between azobenzene and hydrazobenzene and suggested the present investigation.

Experimental

The current–voltage curves were obtained with a Sargent Model XII Polarograph having a current scale calibration of 0.00497 μa, per mm. at a sensitivity of 1.

Values were obtained from these current–voltage curves for the logarithmic analysis.

All measurements were made in a water thermostat at 25 ± 0.1° using an H cell. The compartment which held the saturated calomel electrode contained 1 M potassium nitrate.

The dropping mercury electrode unless indicated otherwise had the following characteristics. At a pressure of 70 cm. of mercury the drop time in 30% methanol solutions was 5.10 seconds (open circuit). The value of m was 1.10 mg. sec. $^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 1.413 mg.$^{2/3}$ sec.$^{-1/2}$.

Materials.—The various reagents used were of an analytical grade and were not purified unless specified.

Methanol was purified by distillation through a 28 inch Fenske column. Piperidine was distilled twice. Piperidine hydrochloride and piperidinium nitrate were recrystallized from a mixture of ethanol and ether containing a small amount of hydrogen chloride, and a mixture of acetone and ethyl acetate, respectively. *trans*-Azobenzene was recrystallized four times from 95% ethanol and chromatographed in petroleum ether (b.p. 45–70°) through a column of Alcoa

(1) Abstracted in part from the Ph.D. thesis, February, 1955, of J. D. Fredrickson.

(2) J. B. Conant and M. F. Pratt, THIS JOURNAL, **48**, 2468 (1926).

(3) E. Biilmann and J. H. Blom, *J. Chem. Soc.*, **125**, 1719 (1924).

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

(5) C. L. Castor and J. H. Saylor, THIS JOURNAL, **75**, 1427 (1953).

(6) A. Foffani and M. Fragiacomo, *Ricerca sci.*, **22**, S139 (1953).

activated Alumina, Grade F-20 mesh 80–200. *cis*-Azobenzene[7] and hydrazobenzene[8] were recrystallized from petroleum ether and carbon tetrachloride, respectively. The latter sample was stored in a sealed glass vial under reduced pressure (1 mm.) until it was used.

The maximum for azobenzene occurred at concentrations of azobenzene of 0.5 millimolar or higher. Cetylbenzyldimethylammonium chloride and technical grade cetyltrimethylammonium chloride were effective suppressors but also shifted the half-wave potentials to more negative potentials. To eliminate this effect, concentrations in the range of 0.25 millimolar were used throughout the work.

Oxidation of Hydrazobenzene with *p*-Benzoquinone.—Solutions of *p*-benzoquinone (0.278 g.) in the minimum amount of petroleum ether and of hydrazobenzene (0.6763 g.) in the minimum amount of benzene were deoxygenated with nitrogen, mixed together and stirred for five minutes. The hydroquinone formed was filtered and the filtrate was added to an alumina column with a volume of 4 ml. Elution of the column with petroleum ether (b.p. 45–60°) gave no colored band on the column. The eluate was added to a second alumina column with a volume of 13 ml. and the elution with petroleum ether repeated. No colored band appeared on the column. All operations were carried out in the presence of a 15-watt red lamp. These results indicated that no *cis*-azobenzene was present in the mixture.

Buffers.—The buffers in 30% methanol by volume had the following composition and pH values. The pH values were determined with both a pH meter and a hydrogen electrode and agreed in both instances.

Buffer	Composition	pH
1	0.0011 M HCl–0.02 M KCl	2.0
2	0.9 M HCOOH–0.1 M HCOONa	3.0
3	0.925 M CH$_3$COOH–0.075 M CH$_3$COONa	4.0
4	0.51 M CH$_3$COOH–0.49 M CH$_3$COONa	5.1
5	0.15 M CH$_3$COOH–1.35 M CH$_3$COONa	6.2
6	1.2 M NH$_4$Cl–0.012 M NH$_3$	7.2
7	2.4 M NH$_4$Cl–0.024 M NH$_3$	8.1
8	0.6 M NH$_4$Cl–0.602 M NH$_3$	9.2
9	0.4 M NH$_4$Cl–2.049 M NH$_3$	9.9
10	0.5 M C$_5$H$_{11}$NHCl–0.5 M C$_5$H$_{11}$N	11.1
11	0.97 M NH$_4$NO$_3$–0.03 M NH$_3$	7.7
12	1.0 M NH$_4$NO$_3$–0.18 M NH$_3$	8.5
13	0.6 M NH$_4$NO$_3$–0.6 M NH$_3$	9.2
14	0.2 M NH$_4$NO$_3$–1.0 M NH$_3$	9.9
15	0.4 M NH$_4$NO$_3$–2.0 M NH$_3$	9.9
16	0.5 M C$_5$H$_{11}$NHNO$_3$–0.5 M C$_5$H$_{11}$N	10.9

The resistances of the buffers were less than 1000 ohms. No correction in half-wave potentials for the iR drop was made.

Results

The behavior of *trans*-azobenzene, *cis*-azobenzene, and hydrazobenzene was studied in various buffered solutions in 30% methanol. The results are summarized in Fig. 1 and are given in more detail in Table I.

(7) G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

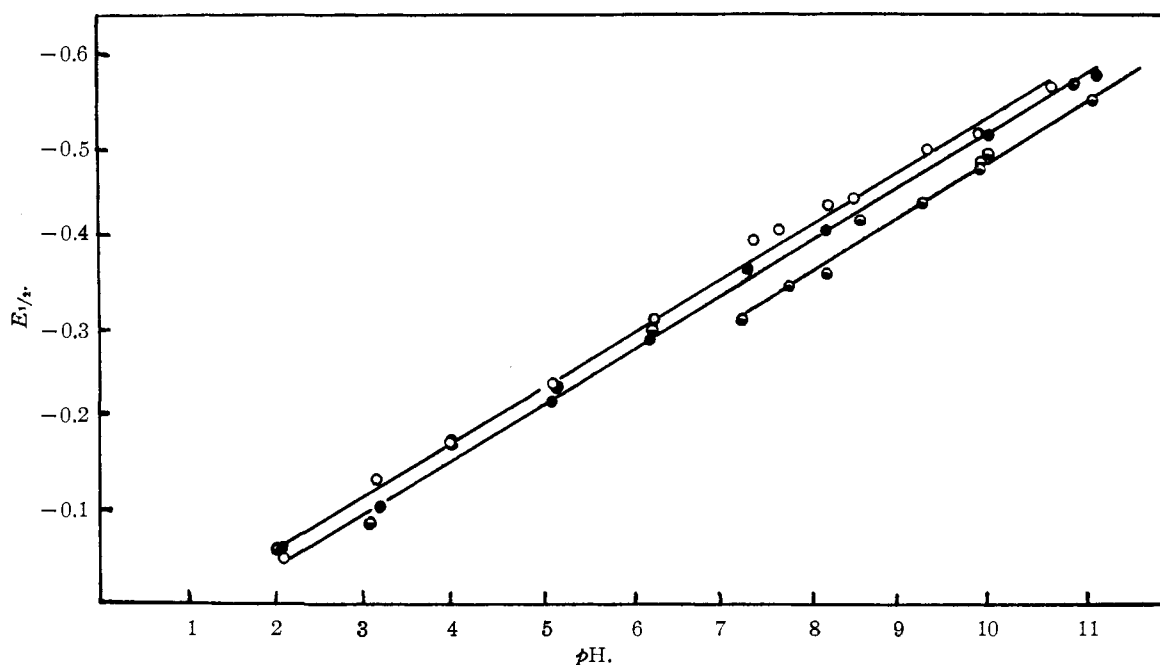(8) M. J. S. Dewar, *ibid.*, 777 (1946).

Fig. 1.—Half wave potentials *vs.* *p*H: O, *trans*-azobenzene; ●, *cis*-azobenzene; ◓, hydrazobenzene.

Studies with *cis*-azobenzene were carried out in the absence of light to prevent the isomerization of this compound to *trans*-azobenzene. This isomerization proceeded even slowly under these conditions and is demonstrated in Table I in a buffer of *p*H 6.20.

Polarograms in acid medium for hydrazobenzene were recorded within 20 minutes after preparation of the solution to minimize the disappearance of the hydrazobenzene by the benzidine rearrangement. The low diffusion current constants (I_d) in acid medium observed for this compound are due to this reaction. Oxidation of hydrazobenzene to azobenzene by oxygen in the manipulations (as indicated by the amount of the curve above the null line of the galvanometer) was not more than about 20% (curve E, Fig. 2).

Discussion of Results

In solutions containing 30% methanol it was found in agreement with previous investigators[5] that adequate buffering is necessary to secure a linear relationship between the half-wave potentials and *p*H with a slope of 0.059 v. per *p*H unit for the azobenzenes and that ionic strength had little effect on the reduction. This relationship held even in acetate buffers, contrary to the report of others,[5] if the acid component of the buffer was present in a concentration which was at least 500 times that of the azobenzene present. The results for *trans*-azobenzene are similar to those reported for this compound in 10% ethanol.[5] Slope analysis for this compound in buffer 4 gave a value of 0.033 which is in agreement with a two electron change.

The half-wave potentials for *cis*-azobenzene as a rule are more positive than those for *trans*-azobenzene in the same buffers. This difference in most cases is greater than the experimental error. The ease with which this compound isomerizes to *trans*-azobenzene, even in the absence of light (see
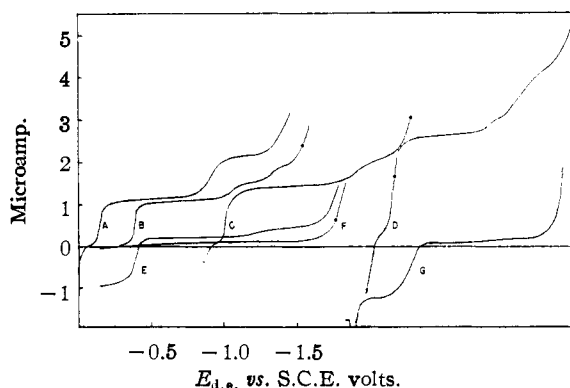

Fig. 2.—Polarograms for *trans*-azobenzene and hydrazobenzene in various buffers. All curves start at $E_{d.e.}$ (S.C.E.) = 0 volt. *trans*-Azobenzene in: A, *p*H 2.1; B, *p*H 3.1; C, *p*H 4 at 25°; D, *p*H 4 at 38.2°. Hydrazobenzene in: E, *p*H 5.1; G, *p*H 9.2. Curve F is the residual current for buffer *p*H 5.1.

Table I), probably is the reason for the smaller differences observed in three of the buffers. A slope analysis of 0.027 for this compound in buffer 4 is in agreement with a two electron change in the reduction.

Hydrazobenzene in buffers with a *p*H range of 2 to 6 gave half-wave potentials which fell in between those of *cis*- and *trans*-azobenzene. A slope analysis in buffer 3 gave a value of 0.033 in agreement with a two-electron change. This behavior indicates that the hydrazobenzene–*trans*-azobenzene system is reversible thermodynamically at the dropping mercury electrode in this buffer region. *trans*-Azobenzene rather than the *cis* isomer must be involved because the former is the stable form. This relationship was verified further, chemically, by oxidizing hydrazobenzene with a mild oxidizing agent, benzoquinone, in the absence of light. Only *trans*-

TABLE I
POLAROGRAPHIC DATA IN 30% METHANOL

Buffer	C, mmoles/l.	I_d	$E_{1/2}$ (S.C.E.)
		trans-Azobenzene	
1	0.254	2.73	−0.05
		2.52[a]	− .79[a]
2	.255	2.83	− .14
		0.83[t]	− .77[a]
		1.03[b]	−1.02[b]
3	.252	3.48	− .18
		0.88[a]	−1.05[a]
	.255	3.83[c]	−0.18
		1.54[a,c]	−1.05[a]
	.255	4.60[c,d]	−0.18
		2.08[a,c,d]	−1.07[a]
	.255	7.04[c,e]	−0.19
		0.91[a,c,e]	−0.86[a]
		2.55[b,c,e]	−1.04[b]
4	.252	2.82	−0.24
5	.255	2.68	− .31
6	.255	2.83	− .40
7	.255	2.61	− .44
8	.255	2.69	− .50
9	.255	2.71	− .52
10	.254	2.41	− .57
11	.255	2.87	− .41
12	.255	2.77	− .45
		cis-Azobenzene	
1	0.307	3.11	−0.06
		2.50[a]	−0.81[a]
2	.274	2.95	−0.11
		1.45[a]	−0.73[a]
		0.72[b]	−1.11[b]
3	.252	2.83	−0.18
		0.74[a]	−1.01[a]
4	.296	2.80	−0.22
		0.29[a]	−0.97[a]
5	.252	2.46	−0.29[f]
		0.62[a]	−1.02[a,f]
		2.48	−0.30[g]
		0.56[a]	−1.02[a,g]
		2.43	−0.31[h]
		0.71[a]	−1.03[a,h]
		2.51	−0.31[i]
		0.22[a]	−1.04[a,i]
6	.263	2.26	−0.37
		0.77	− .99
7	.274	2.83	− .41
9	.274	2.80	− .52
10	.263	2.25	− .058
		Hydrazobenzene	
1	0.217	1.31	−0.06
		0.82[a]	− .77[a]
2	.283	2.16	− .09
		1.64[a]	− .67[a]
		0.41[b]	− .98[b]
3	.261	2.87	− .18
		1.56[a]	−1.05[a]
4	.261	2.89	−0.24
		0.48[a]	−1.06[a]
5	.304	3.07	−0.30
		0.76[a]	−1.05[a]
6	.282	2.74	−0.31
7	.282	2.77	− .36
9	.304	2.19	− .48
10	.250	2.07	− .55
11	.315	2.61	− .35
12	.293	2.15	− .42
13	.326	2.75	− .44
14	.304	2.43	− .49
15	.304	2.69	− .50
16	.250	2.22	− .57

[a] Second wave. [b] Third wave. [c] Capillary had a drop time of 5.72 sec. at 70 cm. The value of m was 0.897 sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 1.263 mg.$^{2/3}$ sec.$^{-1/2}$ at 25°. [d] At 92.5 cm. at 25°. [e] At 38.2°. [f] 30 minutes after the preparation of the solution in the absence of light. [g] 41 minutes after preparation of the solution in the absence of light. [h] 60 minutes after the preparation of the solution in the absence of light. [i] 21 hours and 15 minutes after the preparation of the solution in the absence of light.

azobenzene was detected chromatographically on alumina following the directions of Cook.[9]

In a higher pH range the use of a piperidine–piperidine hydrochloride and ammonia–ammonium chloride buffers gave half-wave potentials for hydrazobenzene which were shifted to more positive values from the theoretical values, calculated from data in the acetate buffers, by about 80 mv. A change of the anion from chloride to nitrate in these buffers decreased this difference in some of the buffers but was not consistent in its effect. The shape of the polarographic curves in these solutions is not symmetrical; the portion of the curve at more positive potentials, at which the diffusion current is attained, is slightly drawn out (see polarogram G, Fig. 2). Slope analyses subsequently in both nitrate and chloride buffers of pH 9.2 were found to be 0.0811.

The explanation for this behavior is not certain. The participation of the chloride ion in the electrode reaction may be involved by adsorption in a manner similar to that observed for phosphate ions in anodic reactions.[10] The same behavior in nitrate buffers is probably due to the traces of chloride ions present in these solutions. The use of concentrated phosphate buffers for the region of pH 7 and 8 in place of the ammonia–ammonium chloride buffers, for which the buffering capacity is poor, was prevented by precipitation of the salts from the 30% methanol solutions.

The second wave (polarogram A, Fig. 2) observed for the reduction of trans- and cis-azobenzenes and hydrazobenzene at a pH of 2 is for the further reduction of these compounds to aniline. The diffusion current constant is approximately equal to that of the first wave and is in agreement with the two electron change involved. The same type of reduction occurs at pH 3 (polarogram B, Fig. 2) but is complicated by the appearance of an adsorption wave. The latter persists in some of the acetate buffers (polarogram C, Fig. 2) and is similar in some respects to the example reported for phenosafranine[11]: the height is directly proportional to the height of the mercury reservoir and is decreased by the presence of gelatine. The effect of an increase in temperature, however, is different. Instead of

(9) A. H. Cook and D. G. Jones, J. Chem. Soc., 876 (1938).

(10) P. Zuman, Chem. Listy, 48, 1025 (1954); C. A., 49, 743 (1955).

(11) R. Brdička, Collection Czechoslov. Chem. Communs., 12, 522 (1947).

lowering the wave height the wave is split into two waves (polarogram D, Fig. 2). Interpretation of his behavior is difficult and complicated by the proximity of the wave to the discharge of the supporting electrolyte.

The possibility that this wave is similar to the anomalous wave often found in solutions of high ionic strength[12] is ruled out since dilution of the buffer does not change its height. The wave is likewise not caused by hydrogen ion depletion at the

(12) L. Meites, THIS JOURNAL, **75**, 3809 (1953).

electrode surface as suggested by Ruetschi and Trumpler,[13] since the wave height remains fairly constant with the change in pH. This independence with changes in pH and the low diffusion current constants eliminates the possibility that this wave represents further reduction of these compounds to aniline.

(13) P. Ruetschi and G. Trumpler, *Helv. Chim. Acta*, **35**, 1021, 1486 (1952).

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The Polarographic Behavior of an Equimolar Mixture of Azoxybenzene and Hydrazobenzene

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The polarographic behavior of an equimolar mixture of azoxybenzene and hydrazobenzene has been found to be different from that of *cis*-azobenzene in a pH range of 2.0 to 11.1. These results are in agreement with data obtained by others from absorption spectra studies, thermal data, X-ray studies and dipole moments, which confirm the structure of *cis*-azobenzene as a geometrical isomer and not as a double compound of azoxybenzene and hydrazobenzene. The polarographic results likewise show that no interaction occurs between azoxybenzene and hydrazobenzene in the buffer range 2.0 to 11.1.

The postulation that *cis*-azobenzene is not a geometrical isomer of *trans*-azobenzene but a double compound of azoxybenzene and hydrazobenzene[2] has been disproved recently by absorption spectra studies,[3] thermal data and X-ray studies.[4]

The polarographic behavior of an equimolar mixture of azoxybenzene and hydrazobenzene has now been studied, using aqueous methanol as a solvent and buffers ranging from pH 2.0 to 11.1, and compared with that of the pure components and of *cis*-azobenzene. Such an investigation was considered to be of interest in that not only would it study the system under different conditions from those used by the other physical methods, but it would also determine whether any interaction occurred between the two compounds under the influence of acids or bases to produce *cis*- or *trans*-azobenzene.

Experimental

The current–voltage curves were determined in a manner similar to that described in a previous paper.[5] The buffers and dropping mercury electrode used in 30% methanol were the same as described previously.[5] The polarographic results for the hydrazobenzene and *cis*-azobenzene are from this paper.[5]

The dropping mercury electrode used in isopropyl alcohol solutions had the following characteristics. At a pressure of 63 cm. of mercury the drop time was 3.4 seconds (open circuit). The value of m was 1.899 mg. sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 1.880 mg.$^{2/3}$sec.$^{-1/2}$.

Materials.—Azoxybenzene was recrystallized from 95% ethanol three times. 2-Hydroxyazobenzene[6] was recrystallized from 50% isopropyl alcohol. Isopropyl alcohol was purified by distillation. Cetyltrimethylammonium bromide

(1) Abstracted in part from the Ph.D. thesis, February, 1955, of J. D. Fredrickson.

(2) H. H. Hodgson, *J. Chem. Soc.*, 1097 (1948).

(3) R. J. W. LeFevre and J. Northcott, *ibid.*, 4082 (1952).

(4) N. Cambell, A. W. Henderson and D. Taylor, *ibid.*, 1281 (1953).

(5) S. Wawzonek and J. D. Fredrickson, THIS JOURNAL, **77**, 3985 (1955).

(6) W. M. Cummings and G. S. Ferrier, *J. Chem. Soc.*, **127**, 2474 (1925).

was used as a maximum suppressor and was obtained from Eastman Kodak Co.

Results

The polarographic behavior of azoxybenzene in 50% isopropyl alcohol and 30% methanol is given in Tables I and II. To avoid maxima the concentration of azoxybenzene in 30% methanol was kept below 0.5 millimolar.

TABLE I

POLAROGRAPHIC BEHAVIOR OF COMPOUNDS IN 50% ISOPROPYL ALCOHOL AT A CONCENTRATION OF 0.5 MILLIMOLAR

Buffer	Maximum suppressor, %	pH	$E_{1/2}$ (S.C.E.)	i_d
	Azoxybenzene			
I Sorenson	0.0176	1.6	−0.29	6.84
II 0.0925 M CH₃COOH– 0.0075 M CH₃COONa	.0176	4.5	− .63	5.48
III 0.051 M CH₃COOH– .049 M CH₃COONa	.0176	5.5	− .72	6.04
IV 0.0095 M CH₃COOH– .0905 M CH₃COONa	.0176	6.5	− .93	6.68
II^a	.0116	4.6	− .63	6.72
III^a	.0116	5.5	− .70	6.82
IV^a	.0116	6.5	− .80	5.58
IV^b	.0116	6.5	− .47	2.20
			− .79	2.28
	2-Hydroxyazobenzene			
IV	0.0116	6.5	−0.48	3.00

^{a} Exposed to daylight for 24 hours. ^{b} Exposed to sunlight for 3.5 hours.

Azoxybenzene when exposed in solution to daylight, rearranges slowly to 2-hydroxyazobenzene. Under these conditions the half-wave potentials are found to be shifted to more positive potentials. This behavior is shown in Table I. If the solution is exposed to direct sunlight for several hours