

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<sup>12</sup> 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,<sup>13</sup> 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).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

## The Polarographic Behavior of an Equimolar Mixture of Azoxybenzene and Hydrazobenzene

BY S. WAWZONEK AND J. D. FREDRICKSON<sup>1</sup>

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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<sup>2</sup> has been disproved recently by absorption spectra studies,<sup>3</sup> thermal data and X-ray studies.<sup>4</sup>

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.<sup>5</sup> The buffers and dropping mercury electrode used in 30% methanol were the same as described previously.<sup>5</sup> The polarographic results for the hydrazobenzene and *cis*-azobenzene are from this paper.<sup>5</sup>

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.<sup>-1</sup> with a calculated value of  $m^2/t^{1/2}$  of 1.880 mg.<sup>2</sup>/sec.<sup>-1/2</sup>.

**Materials.**—Azoxybenzene was recrystallized from 95% ethanol three times. 2-Hydroxyazobenzene<sup>6</sup> was recrystallized from 50% isopropyl alcohol. Isopropyl alcohol was purified by distillation. Cetyltrimethylammonium bromide

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.)	$i_{d,c}$
Azoxybenzene				
I Sorenson	0.0176	1.6	-0.29	6.84
II 0.0925 M CH <sub>3</sub> COOH- 0.0075 M CH <sub>3</sub> COONa	.0176	4.5	- .63	5.48
III 0.051 M CH <sub>3</sub> COOH- 0.049 M CH <sub>3</sub> COONa	.0176	5.5	- .72	6.04
IV 0.0095 M CH <sub>3</sub> COOH- 0.0905 M CH <sub>3</sub> COONa	.0176	6.5	- .93	6.68
II <sup>a</sup>	.0116	4.6	- .63	6.72
III <sup>a</sup>	.0116	5.5	- .70	6.82
IV <sup>a</sup>	.0116	6.5	- .80	5.58
IV <sup>b</sup>	.0116	6.5	- .47	2.20
			- .79	2.28
2-Hydroxyazobenzene				
IV	0.0116	6.5	-0.48	3.00

<sup>a</sup> Exposed to daylight for 24 hours. <sup>b</sup> 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

(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).

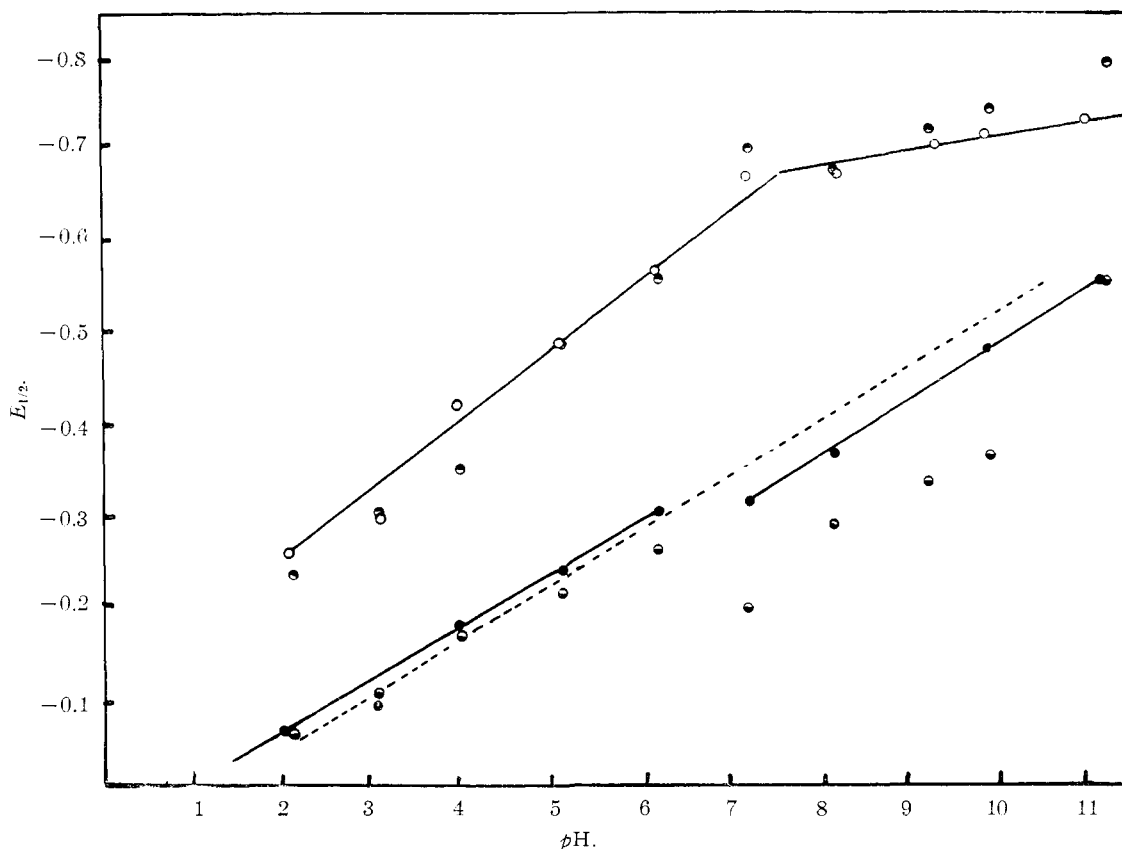


Fig. 1.—Half-wave potentials vs. pH: ○, azoxybenzene; ●, hydrazobenzene; ---, *cis*-azobenzene; ●, azoxybenzene in a mixture of azoxybenzene and hydrazobenzene; ●, hydrazobenzene in a mixture of hydrazobenzene and azoxybenzene.

TABLE II  
POLAROGRAPHIC BEHAVIOR OF AZOXYBENZENE AND 2-HYDROXYAZOBENZENE IN 30% METHANOL

Buffer pH <sup>a</sup>	Concn., mmoles/l.	$i_{d,c}$	$I_d$	$E_{1/2}$ (S.C.E.)
Azoxybenzene				
2.0	0.262	8.58	6.14	-0.25
		3.56	2.54	-.83
3.0	.252	8.18	6.11	-.29
		1.26	0.94	-.79
		1.38	1.03	-1.02
4.0	.262	7.35	5.55	-0.42
		0.97	0.73	-1.04
5.1	.262	7.11	4.96	-0.49
6.2	.262	6.15	4.62	-.55
7.2	.252	7.72	5.49	-.67
8.1	.252	7.88	5.62	-.67
9.2	.252	8.16	5.82	-.70
9.9	.252	7.90	5.62	-.72
11.1	.252	6.62	4.72	-.73
2-Hydroxyazobenzene				
4.0	0.265	5.25	3.92	-0.22
5.1	.265	3.45	2.58	-.29
6.2	.265	2.53	1.89	-.35

<sup>a</sup> For the buffer compositions see reference 5.

enough 2-hydroxyazobenzene is formed to produce a polarographic wave for this compound (see Table I). This was confirmed further by the actual isolation of the compound. All the runs involving

azoxybenzene in methanolic solutions were subsequently carried out in the absence of daylight.

The results for equimolar mixtures of azoxybenzene and hydrazobenzene are given in Table III. The comparison between the mixture and pure compounds is shown in Fig. 1. The values for *cis*-azobenzene<sup>5</sup> are given by the dotted line.

TABLE III  
POLAROGRAPHIC BEHAVIOR OF EQUIMOLECULAR MIXTURES OF AZOXYBENZENE AND HYDRAZOBENZENE IN 30% METHANOL

Buffer pH	Azoxybenzene			Hydrazobenzene		
	Concn., mmoles/l.	$E_{1/2}$ (S.C.E.)	$i_{d,c}$	Concn., mmoles/l.	$E_{1/2}$ (S.C.E.)	$i_{d,c}$
2.0	0.206	-0.23	9.78	0.206	-0.06	2.19
3.0	.282	-.30	8.36	.282	-.10	1.96
4.0	.250	-.35	7.72	.250	-.16	3.96
5.1	.295	-.48	8.96	.282	-.21	3.70
6.2	.315	-.56	5.70	.315	-.26	3.17
7.2	.326	-.70	7.69	.326	-.19	2.79
8.1	.271	-.68	7.45	.271	-.29	3.66
9.2	.293	-.72	7.97	.293	-.33	3.97
9.9	.315	-.74	7.88	.315	-.41	3.95
11.1	.282	-.79	5.14	.282	-.55	2.85

### Discussion of Results

Comparison of the polarographic data for an equimolar mixture of azoxybenzene and hydrazobenzene in 30% methanol with those of *cis*-azobenzene, azoxybenzene and hydrazobenzene (Fig.

1) indicates that each compound shows its own polarographic behavior irrespective of the  $pH$  of the medium (Fig. 2). The diffusion currents obtained for the first wave of azoxybenzene at the same concentrations (Tables II and III) change very little when studied alone or in the presence of hydrazobenzene and indicate that very little reaction occurs between the two compounds. The results for hydrazobenzene in general substantiate this conclusion. Complications, however, arise in comparisons with this compound if traces of oxygen are present, since hydrazobenzene is very easily oxidized to azobenzene. The presence of the latter puts part of the polarographic curve observed for hydrazobenzene above the zero line of the galvanometer (polarograms E and D in Fig. 2). The occurrence of such a reaction was found only at  $pH$  2.0 (47%), 5.1 (19%), 6.2 (12%) and 11.1 (31%). The concentration of azoxybenzene in these buffers, as indicated by the diffusion currents, was decreased signifi-

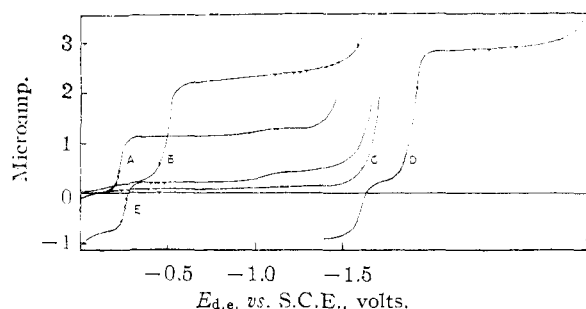


Fig. 2.—Polarograms for *cis*-azobenzene, azoxybenzene and hydrazobenzene in a buffer of  $pH$  5.1: A, *cis*-azobenzene; B, azoxybenzene; E, hydrazobenzene; C, residual current; D, mixture of hydrazobenzene and azoxybenzene.

cantly only in the buffer of  $pH$  11.1. The combined curve for hydrazobenzene and azobenzene under these circumstances was not materially increased and points to some other reason for the decrease in current observed.

The polarographic results obtained not only indicate that *cis*-azobenzene is a definite compound but also preclude the occurrence of a reaction between hydrazobenzene and azoxybenzene in the  $pH$  region of 2.0 to 11.1 to form *trans*- or *cis*-azobenzene.

The shift in half-wave potentials of hydrazobenzene in the presence of azoxybenzene illustrates the sensitivity of this system to the presence of maximum suppressors and other compounds in the solution.

The polarographic behavior of azoxybenzene in this work parallels to a great extent the results reported recently.<sup>7</sup> Due to the more concentrated buffers employed in this work the half-wave potentials when plotted against  $pH$  in the range of 2 to 7.5 gave a line with a slope of 0.081 v. as against the 0.1 v. reported.<sup>7</sup> In the  $pH$  range of 7.5 to 11 the half-wave potentials were not constant but showed a slight increase with an increase in  $pH$ .

In the present investigation a second wave was obtained at a  $pH$  2.0 which was approximately equal to one half of the first wave in height and pointed to the further reduction of azoxybenzene to aniline. This wave appeared in the buffer of  $pH$  3.0 but was complicated by the appearance of the adsorption wave which has been found previously with hydrazobenzene and *cis*- and *trans*-azobenzenes.<sup>5</sup> The latter wave was found also in one of the acetate buffers.

(7) G. Costa, *Ann. triestini univ. Trieste*, **2**, 2223, 115 (1953).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

## The Partial Hydrolysis of Methyltriethoxysilane

BY M. M. SPRUNG AND F. O. GUENTHER

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The action of three molar equivalents of water and catalytic amounts of acid on a benzene solution of methyltriethoxysilane gave small yields of distillable liquids. These are principally cyclic polysiloxanes having both ethoxyl and hydroxyl "end groups." In alcohol solution, under similar conditions, only polymeric "methylsilicone gel" was obtained. Using 50 or 25% of the calculated quantity of water, complex mixtures of linear and cyclic products resulted. In the former case, the two major products isolated are a monocyclic polysiloxane (1,3,5,7-tetraethoxy-1,3,5,7-tetramethylcyclotetrasiloxane) and a closely related bicyclic structure. In the latter case the products are mixtures of the linear partial hydrolysis products,  $\text{EtO}[\text{CH}_3(\text{EtO})\text{SiO}]_n\text{Et}$ , with minor amounts of the cyclic products,  $[\text{CH}_3(\text{EtO})\text{SiO}]_n$ , where  $n$  is 3 to 5. Under certain conditions, it is possible to isolate small amounts of sublimable solids having the composition,  $(\text{CH}_3\text{SiO}_{1.5})_n$ , where  $n$  is probably 6 and 8.

### Introduction

Trifunctional silanes of general structure  $\text{RSiX}_3$ , where R is an alkyl or aryl group and X is a functional group such as halogen, alkoxy or acyloxy, produce cross-linked polymeric structures when hydrolyzed. Among organic silicon products, these structures are at present least well understood.

The characterization of partial hydrolysis products of trifunctional silanes was undertaken some years ago by Andrianov.<sup>1,2</sup> Several alkyltriethoxy-

silanes were hydrolyzed in alcohol with considerably less than equivalent quantities of water. The high-boiling, distillable products obtained were of the general type  $\text{C}_2\text{H}_5\text{O}[\text{R}(\text{C}_2\text{H}_5\text{O})\text{SiO}]_n\text{C}_2\text{H}_5$ , where R was ethyl, isobutyl, isoamyl and *n*-hexyl; and  $n$ , fixed roughly by the molar ratio of water to triethoxysilane, varied from 2 to 7. Andrianov and Breitman<sup>3</sup> hydrolyzed diphenyldichlorosilane, phenyltrichlorosilane and equimolecular mixtures of the two by passing moist air into heated chlorobenzene solutions. Diphenyldichlorosilane and the mixture gave crystalline products which were not

(1) K. A. Andrianov, *J. Gen. Chem. (USSR)*, **8**, 1235 (1938); *C.A.*, **33**, 4193 (1939).

(2) K. A. Andrianov, *J. Gen. Chem. (USSR)*, **16**, 633 (1946); *C.A.*, **41**, 1206 (1947).

(3) K. A. Andrianov and B. M. Breitman, *J. Gen. Chem. (USSR)*, **17**, 152? (1947); *C.A.*, **42**, 2239 (1948).