[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

A Polarographic Study of Azobenzene[1]

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It was found that the polarographic reduction of both the *cis* and *trans* isomers of azobenzene is reversible in certain buffers over the *p*H range 2.8 to 12.5. The conflicting results previously reported by various workers are explained by postulating a mechanism which involves the relative rates of the electrode process and the dissociation of the acid component of the buffer.

The polarographic reduction of azobenzene has been investigated by several workers with a general lack of agreement in results.

Shikata and Tachi[2] found the reduction involved hydronium ions but they did not obtain a linear relation between *p*H and reduction potential as is shown in Fig. 1. Volpi[3] reported that the half-wave potential was independent of *p*H. Shortly after Hartley prepared and established the identity of the *cis* isomer of azobenzene, Winkel and Siebert[4] reported the half-wave potential of the *cis* isomer as −0.80 volt and that of the *trans* as −0.97 volt. Hillson and Birnbaum[5] made a study of the half-wave potentials of both isomers as a function of *p*H using acetate buffers. Their results are shown in Fig. 1. The half-wave potentials of the two isomers are identical below a *p*H of 8.5 but diverge above this *p*H. They suggested that this divergence might be a characteristic property of systems exhibiting *cis–trans* isomerism, citing the similarity of the azo system to the maleic–fumaric acids system as shown in Fig. 1. We have confirmed the results of Hillson and Birnbaum. However, the behavior of the maleic–fumaric system has been satisfactorily explained[6] on the basis of the difference in dissociation constants for the two acids. Such an explanation cannot be applied to azobenzene. Since hydronium ions are used up in the reduction process the concentration of the acid component of the buffer must be sufficient to maintain a constant *p*H at the electrode interface. The solutions used by Hillson and Birnbaum with a *p*H greater than 8.5 had a concentration of the acid component less than that of the azobenzene.

It was thought that a study of the two isomers of azobenzene in solutions containing a higher concentration of the acid component of the buffer system might be valuable.

Experimental

The experimental work consisted of measuring the *c–v* curves for both isomers of azobenzene in solutions of various buffers over the *p*H range 2.8 to 12.5.

Apparatus.—The *c–v* curves were determined using a Sargent Model XXI Polarograph which was operated at a sensitivity of 0.003 microamp./mm. and a damping position of "off." All potentials were measured with a Rubicon potentiometer.

The electrolysis cell was an H-type, the anode arm containing a saturated calomel electrode. The constant for the capillary was $1.561\ \mathrm{mg.}^{2/3}\ \mathrm{sec.}^{-1/2}$ in 10% ethanol with an open circuit. The resistance of the cell was measured and in all cases found to be sufficiently small so that at the current used the *IR* drop was negligible.

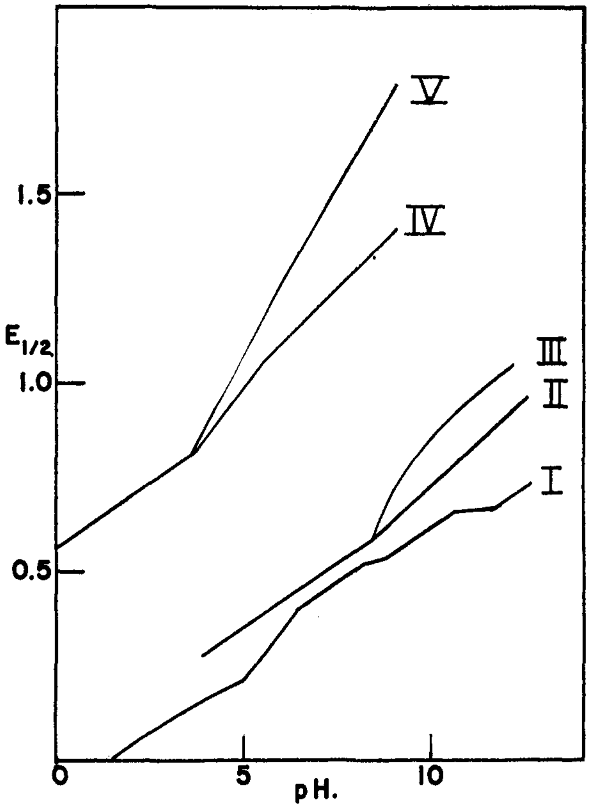

Fig. 1.—Half-wave potential *vs.* *p*H: II, *cis*-azobenzene; III, *trans*-azobenzene; IV, maleic acid; V, fumaric acid. Reduction potential *vs.* *p*H (I) for *trans*-azobenzene. Data are from ref. (5).

All *p*H measurements were made with a Beckman Model H *p*H Meter.

All measurements were carried out in a thermostat at 25 ± 0.01°.

Materials.—*trans*-Azobenzene was Eastman White Label which was purified by refluxing in ethanol for four hours followed by recrystallization from ethanol. The melting point was 68.0°. *cis*-Azobenzene was prepared and purified according to Hartley's method[7] and had a melting point of 71.5°. The visible absorption spectra were determined for both isomers and the curves obtained agree with those of Winkel and Seibert.[4] All other compounds were reagent grade.

All solutions, unless otherwise stated, were 1×10^{-4} *M* in azobenzene, 0.1 *M* in KCl and 10% ethanol by volume. The buffers used and their concentration in the final solution are given in Table I.

The solutions were deaerated with commercial nitrogen purified by passage through a solution of vanadyl sulfate in dilute sulfuric acid.

The *c–v* curves of all solutions were determined immedi-

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[1] This work was supported in part by a grant from the Duke University Research Council.

[2] M. Shikata and I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **17**, 45 (1931).

[3] A. Volpi, *Gazz. chim. ital.*, **77**, 473 (1947).

[4] A. Winkel and H. Siebert, *Ber.*, **74B**, 670 (1941).

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

[6] P. J. Elving and C. Teitelbaum, THIS JOURNAL, **71**, 3916 (1949).

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

TABLE I

BUFFER COMPOSITIONS

pH	Buffer system Citric acid, M	+ Na_2HPO_4, M	Acid component conc. M	Concn. ratio, acid to azobenzene
2.85	0.25	0.10	0.25	2500:1
3.65	.20	.20	.20	2000:1
4.80	.15	.30	.15	1500:1
6.26	.10	.40	.10	1000:1
7.10	.05	.50	.05	500:1
	NH_4Cl, M	+ NH_4OH, M		
8.08	1.0	0.20	1.0	10000:1
8.43	0.80	.40	0.80	8000:1
8.73	.60	.60	.60	6000:1
9.03	.40	.80	.40	4000:1
9.38	.20	1.0	.20	2000:1
11.70	1.0 M ethylenediamine		.009	90:1
12.20	1.0 M isoamylamine		.02	200:1
12.50	1.0 M piperidine		.04	400:1

ately after preparation in order to minimize thermal interconversion of the isomers. Photometric analysis of the solutions before and after the polarographic runs showed the conversion to be negligible.

Results

Thirteen measurements of the half-wave potential were made for each isomer over the pH range 2.85 to 12.50. A plot of the half-wave potentials of each isomer as a function of pH gave identical straight lines which are represented by the equation

$$E_{1/2} = 0.060 - 0.062p\text{H}$$

The average deviation from the equation for all measurements was ±0.006 volt.

Experiments run with varying amounts of added KCl in addition to the buffer gave results which indicated that the half-wave potential is independent of the ionic strength.

Hillson and Birnbaum obtained values of "n" somewhat less than 2 upon plotting log $(i_d - i)/i$ *vs.* E and reported that the reduction deviated further from reversibility as the pH was increased. In the present work, using the citrate–phosphate buffer system, a plot of log $(i_d - i)/i$ *vs.* E, gives a slope of 0.030 corresponding to a value of 2 for "n." This is in agreement with the potentiometric work by Biilmann and Blom,[8] who found the azo–hydrazo systems to be reversible.

Laitinen and Wawzonek[9] report a value of 0.33 × 10^{-5} cm.^{2}sec.$^{-1}$ for the diffusion coefficient of stilbene. It might be expected that azobenzene would have a diffusion coefficient of about the same magnitude. Upon solving the Ilkovic equation for *trans*-azobenzene a value of 0.41 × 10^{-5} cm.^{2}sec.$^{-1}$ for the diffusion coefficient was obtained for "n" equal to 2.

The three facts, (1) the diffusion coefficient of azobenzene can only have a reasonable value when a value of 2 for "n" is substituted in the Ilkovic equation, (2) the work of Biilmann and Blom showing the azo–hydrazo system to be reversible and (3) a value of 2 having been obtained by plotting log $(i_d - i)/i$ *vs.* E, offer satisfactory evidence that the polarographic reduction of azobenzene is reversible.

A slight difference was observed in the values of diffusion coefficients of the two isomers as calculated from the Ilkovic equation. The *cis* isomer had a diffusion coefficient of 0.57 × 10^{-5} cm.^{2}sec.$^{-1}$ and that of the *trans* isomer was 0.41 × 10^{-5} cm.^{2} sec.$^{-1}$.

Discussion

It is to be noted that the reduction of azobenzene is reversible in a citrate–phosphate buffer system whereas it is not reversible in an acetate buffer system at the same pH. Also, both isomers are found to exhibit an identical linear relationship between half-wave potential and pH, while Hillson and Birnbaum found a greater deviation for the *trans* form than for the *cis*. It appears that the explanation of these facts might be found by considering the role of the buffer system in the over-all reduction process.

The following reactions may be assumed to occur at the mercury interface during the reduction process

$$R + 2e \rightleftharpoons R^{=} \qquad (a)$$

$$R^{=} + 2H_3O^+ \rightleftharpoons RH_2 + 2H_2O \qquad (b)$$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (c)$$

If it is assumed that reactions (a), (b) and (c) are reversible and at equilibrium, with reaction (a) being the rate controlling and hence the potential determining step, the following equation is obtained

$$E = E_0 + \frac{RT}{2F}\ln\frac{i_d - i}{i} + \frac{RT}{F}\ln\,[H^+]$$

This equation is in agreement with the experimental facts.

The conditions involved in the above assumptions may be satisfied in two ways.

The dissociation of the acid component of the buffer may be slower than the electrode reaction (reaction a) but compensated for by a larger diffusion coefficient for the acid than for the azobenzene. On the other hand, the diffusion coefficient of both the acid and the azobenzene may be of the same order of magnitude with the dissociation of the acid being more rapid than the electrode process. These two possibilities were pointed out by Muller[10] in his study of the effect of buffers on the reduction of quinone.

Kemula and Chodkowski[11] in a study of the reduction of acetic acid report a value of 0.39 × 10^{-5} cm.^{2}sec.$^{-1}$ as the diffusion coefficient of acetic acid. Since the diffusion coefficients of acetic acid and azobenzene are of the same order of magnitude, the first explanation does not seem valid.

The second possibility can be examined qualitatively and a significant conclusion reached. Delahay[12] has recently pointed out the importance of considering the kinetics of buffer dissociation in electrode processes. Muller[10] has considered the effect of the slow dissociation of carbonic acid on the reduction of quinone. Let it be assumed that the dissociation of the acid component of the buffer

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

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

[10] O. H. Muller, *ibid.*, **62**, 2434 (1940).

[11] W. Kemula and J. Chodkowski, *Collection Czech. Chem. Communs.*, **15**, 1091 (1950).

[12] P. Delahay, THIS JOURNAL, **74**, 3497 (1952).

is slower than the electrode process. There exists in the solution a definite hydronium ion concentration as determined by the buffer system. As the reduction potential of the azobenzene is reached the reduction of R to R^- begins. The R^-, as it is formed, reacts with the H_3O^+ present to form RH_2. However, if it is assumed that the R^- is being formed more rapidly than the hydronium ions, as the process continues, the R^- concentration increases and the hydronium ion concentration decreases. The Nernst equation predicts that this excessive build-up of R^-, in increasing the R^- concentration above the expected equilibrium value, should shift E to a more negative value.

This effect on the shape of the polarographic curve is shown in Fig. 2. The curves were obtained by reducing solutions of different azobenzene concentration. The solutions were not buffered in order to obtain maximum deviation from reversibility. In solutions of higher azobenzene concentration there should be a larger excess of R^- at similar points on the curve. This excess should give larger shifts of E for solutions of higher azobenzene concentration as is illustrated in Fig. 2. This may explain some observations in organic polarography in which the half-wave potential varies with concentration.

The relative rates of the electrode process and the dissociation of the buffer may also account for the fact that the azobenzene reduction is reversible in a citric acid–phosphate buffer while it is irreversible in an acetate buffer of the same *p*H. The rate of dissociation of the citric acid system may be more rapid than the electrode process whereas the dissociation of the acetic acid may be slower than the electrode process. This may explain the work of Day and co-workers[13] on the effect of different buffers on the polarographic waves of aromatic ketones. They found that in the case of the citrate–phosphate buffer system two distinct waves appeared in the reduction of fluorenone but in an acetate buffer the first wave sloped over into the second wave, combining to form a single wave.

The deviation from linearity of the half-wave potential *vs.* *p*H function for the *cis* and *trans* isomers, as seen in Fig. 1, may also be explained on the basis of such relative reaction rates. The half-wave potentials of the two isomers are identical in the citrate–phosphate buffer system. If the rate of the electrode process is more rapid for the *trans* isomer than for the *cis* isomer there might be expected, using a buffer with a relatively slow rate of dissociation, a greater deviation from reversibility for the *trans* isomer with an accompanying more negative value for the observed half-wave potential. This reasoning may be applied to previous results obtained with azobenzene in unbuffered solutions. In such cases water can be considered as the buffer system. The results shown in Fig. 2 indicate a slower rate of dissociation of water. In the cases reported[3,4] the *trans* isomer had an appreciably more negative half-wave potential than the *cis* isomer, the difference being greater than that found by Hillson and Birnbaum.

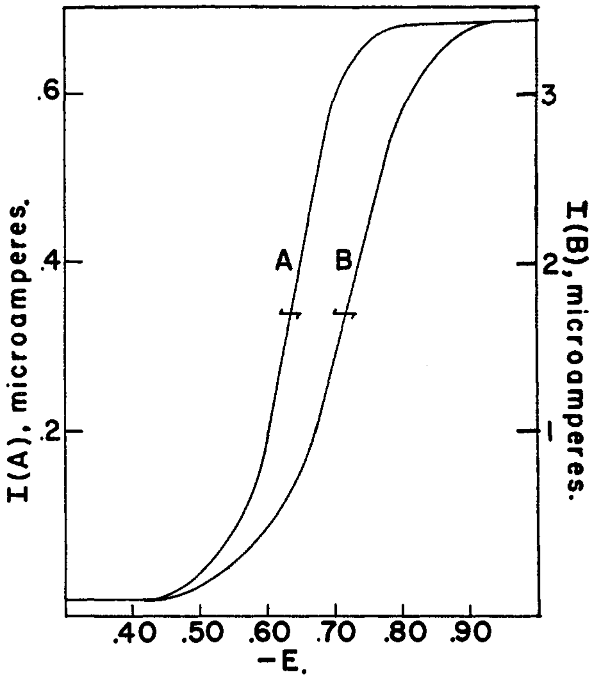

Fig. 2.—Polarograms of A, 2×10^{-4} and B, 10×10^{-4} *M* *trans*-azobenzene in unbuffered 40% ethanol solution. Supporting electrolyte is 0.1 *M* LiCl.

One of the referees has pointed out that the reaction

$$R^- + 2HA \rightleftarrows RH_2 + 2A^- \qquad (d)$$

should be considered. It does not seem possible to distinguish between it and the two reactions (b) and (c). The present results could be explained on the basis of either reactions (b) and (c) or (d).

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[13] R. A. Day, Jr., S. R. Milliken and W. D. Shults, THIS JOURNAL, 74, 2741 (1952).