

Studies on Bisazocompounds I.

Polarographic Behaviour of 1-[4-(4-Sodium-sulfonato-phenylazo)-3-sodiumsulfonato-phenylazo]-2-naphthol in Solutions of Varying pH at the Dropping Mercury Electrode

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The polarographic behaviour of the title compound in buffer solution of pH 2–12 is discussed. The two observed waves in alkaline media ($pH \geq 9.5$) are assigned to the formation of hydrazo and the bishydrazo derivatives, whereas in acid solutions the reduction leads to cleavage of both two azo groups. The nature of the waves is investigated and a general mechanism for the reduction process in alkaline and acid media is suggested. The values of the kinetic parameters for the electrode reactions are reported.

(*Keywords: Azo compounds; Bisazo compounds; Mechanism; Polarography; Reduction*)

Untersuchungen an Bisazo-Verbindungen I. Polarographisches Verhalten von 1-[4-(4-Natriumsulfonato-phenylazo)-3-natriumsulfonato-phenylazo]-2-naphthol in Lösungen mit verschiedenem pH an der tropfenden Quecksilber-Elektrode

Es wird das polarographische Verhalten der Titelverbindung in Pufferlösungen vom pH 2—12 diskutiert. Die zwei im alkalischen Bereich ($pH \geq 9,5$) beobachteten Wellen werden der Bildung der Hydrazo- bzw. Bishydrazo-Derivate zugeordnet, im sauren Bereich führt die Reduktion zur Spaltung beider Azo-Gruppen. Die Natur der Wellen wird untersucht, und ein genereller Mechanismus für die Reduktion im alkalischen und sauren Bereich wird vorgeschlagen. Die kinetischen Parameter der Elektrodenreaktionen werden angegeben.

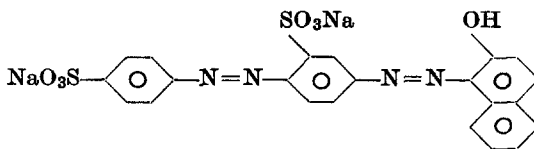
Introduction

The polarographic behaviour of azo compounds was studied by various authors in the past^{1–16}. Very little work has been carried out describing the polarographic behaviour of azo compounds substituted

with reducible groups^{8, 11-13, 15}. The present investigation is devoted to a study of this type with varying pH in order to throw light on the mechanism of the electrode process of bisazo compounds. The kinetic parameters of the electrode reactions are determined and discussed.

Experimental

Solution of the Bisazo compound



A 0.01M solution of 1-[4-(4-Sodiumsulfonato-phenylazo)-3-sodium-sulfonato-phenylazo]-2-naphthol (**1**; supplied by *Bidench, W. S.*; BDH grade) was prepared by dissolving the accurate weight of the solid in twice-distilled water. From this stock solution other lower concentrations were obtained by appropriate dilution.

Supporting electrolytes

The modified universal buffer series of *Britton* and *Robinson* (*pH* 2-12) was prepared as given by *Britton*. The *pH* was checked using a Radiometer *pH* meter, Model 28, accurate to ± 0.05 unit.

Working procedure and apparatus

The experimental technique and the electrolysis cell were as previously described¹⁷. The polarograph was a Radiometer P03. The capillary characteristics were $m = 2.11$ mg/s, $t = 4.09$ s at a height 45 cm Hg.

Results

The polarograms of Fig. 1 represent the polarographic reduction of **1** at different *pH* ranging from 2-12. All of these curves consist of two waves, representing the reduction of the two electroactives centers, which are the two azo groups. The height of the first wave in acid solutions (*pH* ≤ 6) retains its height, whereas the height of the second wave progressively increases. In alkaline solutions the height of the first wave attains a height (*pH* = 11) that is practically equal of the second wave. The total height of the polarogram decreases tremendously with increasing *pH* till it attains in alkaline solutions almost half its height in acid media (Fig. 2), whereas at intermediate *pH* the wave lies between the two values. Thus, it can be concluded that the

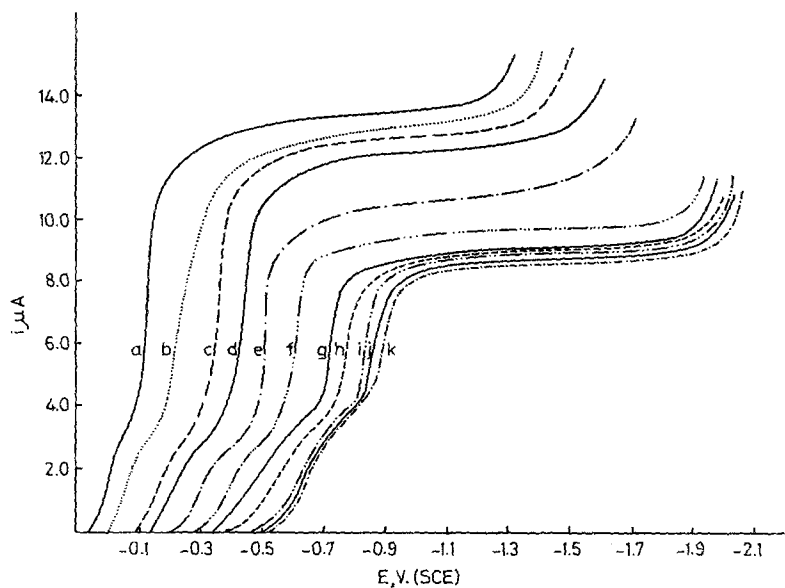


Fig. 1. Polarograms of mM I in universal buffer solutions of different pH . a) 2.0; b) 3.0; c) 4.0; d) 5.0; e) 6.0; f) 7.0; g) 8.0; h) 9.0; i) 10.0; j) 11.0; k) 11.8

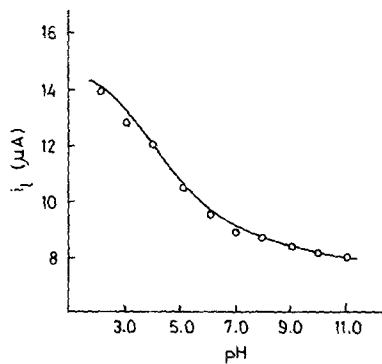


Fig. 2. Effect of pH on the limiting current (i_l) for the total polarogram

electrons involved in the electrode reaction in acid media are double those consumed in the alkaline side. Also, lowering the pH of the solutions causes both waves to shift towards less negative potentials and simultaneous rise of the polarogram.

Discussion

Mercury Pressure

The effect of mercury pressure on the limiting current in buffer solutions of *pH* 3.0 and 11.0 indicates that the values of the exponent α in the relation ($i_l = K h^\alpha$) are 0.40 and 0.50 for the first wave; whereas for the second wave these amount to 0.55 and 0.85. Thus, the reduction process is essentially diffusion controlled with a kinetic contribution along the first wave at *pH* 3.0 and adsorption component along the second wave at *pH* 11.0.

Reversibility of the Waves

Analysis of the waves was carried out by applying the fundamental equation for polarographic waves:

$$E = \frac{0.059}{n} \log i/i_d - i \quad (\text{at } 25^\circ\text{C}).$$

The plots for the first waves are straight lines at *pH* 3.0 and 11.0 with slopes amounting to 0.044 and 0.045 respectively. The second wave yields also straight lines at the same *pH* with slopes equal to 0.055 and 0.044. These data indicate irreversibility of the reduction process in the light of the fact that the total reduction current corresponds to eight

Table 1. *Data obtained for 1 at the mercury electrode at 25°C*

Wave	Slope = $0.059/\alpha n_a$	α		pH range	$\Delta E/\Delta \text{pH}$	$Z_{\text{H}^+} (n_a = 2)$
		$n_a = 1$	$n_a = 2$			
1st	0.044 at pH 3.0	1.34	0.67	2-10	0.080	1.82
	0.045 at pH 11.0	1.32	0.66	10-11.8	0.039	0.87
2nd	0.051 at pH 3.0	1.12	0.56	2-9	0.085	1.80
	0.045 at pH 11.0	1.32	0.66	9-11.8	0.045	1.01

electrons in acid solutions (two azo groups) and four in alkaline ones. On applying the equation for irreversible waves

$$E/\log i (i_d - i) = 0.059/\alpha n_a$$

The values of the transfer coefficient (α) obtained are less than unity, confirming the irreversible nature of the waves (Table 1). The most probable α values are obtained for $n_a = 2$ for the first or the second wave.

E_i—pH Relation

The plot of E_i of the first and second waves versus pH yields broken lines covering the pH ranges 2-9.5 and pH 9.5-11.8 as shown in Fig. 3. This trend indicates some changes either in the reduction mechanism or in the species formed in these buffer solutions. The slopes of E_i — pH curves for the first section (pH range 2-9.5) for the first and second waves were used in the relation for irreversible waves:

$$\Delta E_i \neq \Delta pH = (0.059/\alpha n_a) Z_{H^+}$$

It seems that the number of hydrogen ions $Z_{H^+} = 2$, the number of electrons $n_a = 2$ (i.e., $Z_{H^+}/n_a = 2:2$) whereas the most probable transfer

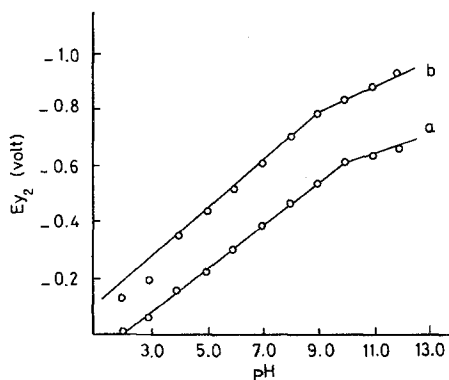


Fig. 3. Effect of pH on E_i : a) first wave; b) second wave

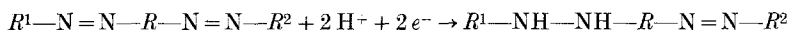
coefficient $\alpha = 0.67$ or 0.56 (obtained from the analysis of the waves). For the second section ($pH > 9.5$) $Z_{H^+} = 1$, $n_a = 2$ and $\alpha = 0.66$ (i.e. $Z_{H^+}/n_a = 1:2$). This shows that the variation of the slope of E_i — pH curves may be attributed to changes in the number of H^+ ions for both reduction centres.

The Electrode Reaction

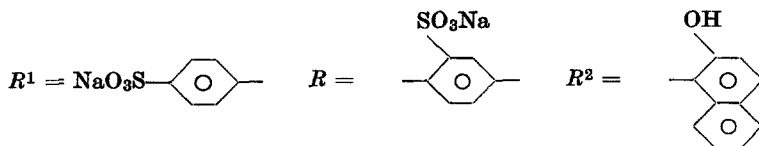
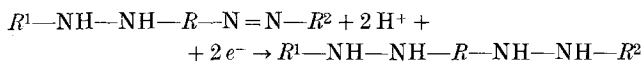
The reduction of **1** in buffer solutions of $pH > 9.5$ elucidated two waves of equal heights indicating that the same number of electrons participate in the two electrode reactions. The number of electrons n , involved in the reduction of these waves was established by comparing the limiting current of both waves with those of monoazo-compounds of known n -values¹⁴. 4-hydroxy-azobenzene for example is reduced in a single wave involving the transfer of two electrons per molecule. The

wave height of this monoazo-compound was found to be nearly half the total height of an equally concentrated solution of bisazo-compound under identical conditions. Thus it can be concluded that each of the two reduction waves of the bisazo-compound involves the transfer of two electrons and two protons per molecule and both azo groups are reduced to the corresponding bis-hydrazo-derivative:

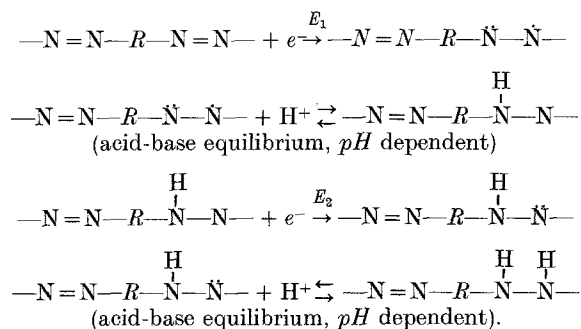
First wave



Second wave



The $\Delta E_{1/2}/\Delta pH$ relation of the first and second wave (Fig. 3) within the higher pH range 9.5-11.8 indicates that the number of protons Z_{H^+} equal one in the rate determining step and the electrode reaction is governed by both the rate of electron and proton transfer. Accordingly any one of the reactions given above may be take place in some steps each corresponding to one electron or one proton:

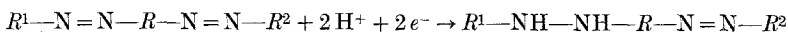


In buffer acid solution the reduction current is almost twice that of the limiting value in alkaline solution, indicating a change in the mechanism of reduction. Both waves together involve the transfer of 8 electrons and 8 protons per depolarizer molecule. The height of the first wave was equal in all buffer solutions and corresponding with two

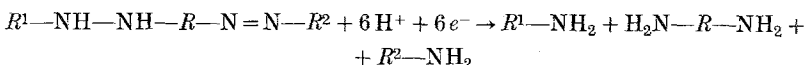
electrons per molecule. Whereas the second wave in acid buffer solutions attains a limiting height which is three times that of the first wave. This indicates the transfer of 6 electrons per molecule along the second wave in acid solutions and the reduction process occurs in a succession of acts involving most probably the transfer of pairs of electrons and protons at one time. A support of this assumption is gained from the $E_{\frac{1}{2}}-pH$ curves which indicate that the rate-determining step involves two electrons and $2H^+$ ions in acid solution.

Reduction in acid solution leads to the formation of β -naphthylamine, sodium sulphanilate and 2-sodium sulphonate-p-phenylenediamine.

first wave



second wave



Kinetic Parameters of the Electrode

The kinetic parameters of the electrode reaction along the first and second waves were calculated using the *Koutecky* equation¹⁸. Tables 1 and 2 include representative values for α , K_0 , ΔG^0 and $KD^{-\frac{1}{2}}$. The

Table 2. Results obtained for 1 in universal buffer solutions at 25°C

pH	Wave	i_l [μA]	$E_{\frac{1}{2}}$ [V]	$D_0 \times 10^{-6}$ [cm ² /sec]	K_0 [cm/sec]	ΔG^0 [kcal/mol]	$K_0 D^{-\frac{1}{2}}$ [s ^{-1/2}]
3.0	1st	3.3	-0.07	1.70 ^a	9.3×10^{-12}	93.19	7.1×10^{-9}
	2nd	9.6	-0.23	1.61 ^b	1.81×10^{-15}	114.7	1.43×10^{-12}
11.0	1st	4.1	-0.63	2.63 ^a	1.46×10^{-22}	155.6	9.9×10^{-20}
	2nd	4.3	-0.89	2.90 ^a	9.8×10^{-26}	174.0	7.6×10^{-23}

^a $n = 2$.

^b $n = 6$.

various parameters indicate that the process of reduction along the first and second waves is irreversible. This is shown by the fact that the value of α is less than unity when the rate determining step involves the uptake of two electrons. The values of $KD^{-\frac{1}{2}}$ are less than $0.05 s^{-\frac{1}{2}}$,

indicating the reduction process is controlled by the rate of electron transfer. The energy of activation generally increases with increasing pH denoting that the reduction process becomes more difficult at higher pH . Also the values of the rate constant decreases with rise of pH which is an indication for increased irreversibility at higher pH . This can be ascribed to the slow protonation of the intermediate free radical formed.

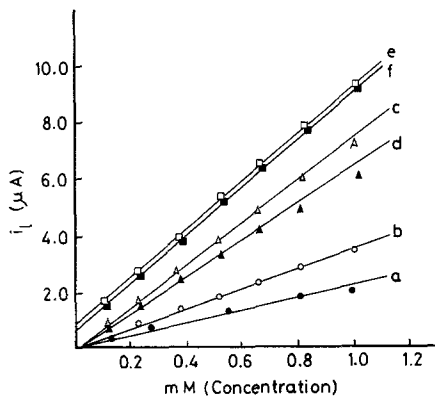


Fig. 4. Effect of concentration on the limiting current: first wave at pH 8.0 (a), pH 11.0 (b); second wave at pH 8.0 (c), pH 11.0 (d); total current at pH 8.0 (e), pH 11.0 (f)

Analytical Applications

To test the validity of the *Ilkovic* equation and accordingly the applicability of the polarographic method for the determination of the bisazo-compound under investigation, the values of the limiting current for the first and second waves, and also for the total current at pH 8.0 and 11.0 are plotted against the concentration of the organic compound. Satisfactory linear relations (Fig. 4) are obtained. Better linearity is observed when the net heights of the first and second waves are used. The constancy of i_d/c values indicates the validity of the polarographic method for the determination of the depolarizer.

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