Electrochemical Behaviour of Some Thiazolo[3,2-*a*]benzimidazol-3(2*H*)-one Derivatives. Part 1. Electroreduction of a Series of 2-Arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-ones

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The electrochemical reduction of a series of 2-arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-ones has been investigated. A mechanism for the electrode process covering a wide range of pH values is proposed, discussed, and clarified *via* model compounds, polarographic analysis, pK_a determination, and interpretation of Hammett's $\sigma/E_{\frac{1}{2}}$ relations. Large-scale preparative electrolysis of the title and model compounds was carried out and the products were isolated and identified.

The sequence –S–CO–CO–N–, present (in masked form) in 2-arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-ones (1a—g), is of interest from a pharmaceutical point of view.[1-3] Our laboratory has been involved for some time in the electrochemical study of heterocyclic azo systems.[4,5] Recently several unsuccessful attempts[6] have been made to reduce these compounds by classical synthetic routes. We report here the polarographic behaviour of compounds (1a—g) in 50% aqueous alcoholic buffers covering a wide range of pH values. We hoped to shed light on the mechanism of the electrode process in order to define optimum experimental conditions for the electrochemical reduction of these compounds.

Experimental

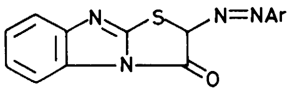
(1) *Synthesis of* 2-*Arylazothiazolo*[3,2-a]*benzimidazol*-3(2H)-*ones* (1a—g).—The appropriate aromatic amine (0.0034 mol) dissolved in concentrated hydrochloric acid (3 ml) and water (3 ml) was cooled to 0 °C and then treated with a cold solution of sodium nitrite (0.3 g) in water (3 ml). The diazotised amine was added gradually to an ice-cold solution of thiazolo[3,2-*a*]benzimidazol-3(2*H*)-one[7] (0.0034 mol) in anhydrous pyridine (30 ml). The mixture was set aside in a refrigerator overnight. The separated product was filtered off, washed with dilute hydrochloric acid and then water, dried, and finally recrystallized from acetic acid [compound (1e) from water] (see Table 1). Compounds (1a—e) showed no m.p. depression when mixed with authentic samples.[6,8]

(2) *Polarographic Investigations*.—(a) *Apparatus*. Polarographic curves were recorded with an LP60 polarograph (Laboratorni Pristrojé, Prague). A cell of our own design with a separated saturated calomel electrode was used. The capillary possessed the following characteristics in H_2O open circuit: t 3.75 s drop^{-1}, m 2.15 mg s^{-1} for h 57 cm.

(b) *Solutions and procedures*. Stock 10^{-3}M-solutions were prepared in absolute ethanol (n_D^{25} 1.359); Britton–Robinson modified universal buffers[9] (prepared from analytical grade chemicals) were used as supporting electrolytes. Ethanol and the appropriate buffer solution were introduced into the polarographic cell. The solution was then deaerated by bubbling a stream of H_2 for 10 min. The calculated amount of stock solution was then introduced into the cell so that the final concentration was 10^{-4}M in 10 ml of 50% v/v ethanolic buffer.

(c) *Measurements*. All experiments were carried out at 25 ± 2 °C. The half-wave potentials were measured graphically and expressed *vs*. saturated calomel electrode with an accuracy of ± 0.005 V. The accuracy of the applied voltage was checked by recording polarograms of standard Tl^+ in 0.1M-KNO_3 solutions for different concentrations ($E_{\frac{1}{2}} = -0.45$ V).

(3) *Controlled Potential Electrolysis* (*C.p.e.*) *and Identification of the Products*.—(i) Mercury pool electrolysis was



(1)

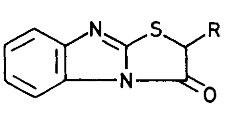
a; Ar = Ph
b; Ar = p-$CH_3C_6H_4$
c; Ar = m-$CH_3C_6H_4$
d; Ar = p-ClC_6H_4
e; Ar = p-$HO_3SC_6H_4$
f; Ar = p-$CH_3OC_6H_4$
g; Ar = m-$NO_2C_6H_4$

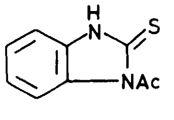
Table 1. 2-Arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-one derivatives (1a—g)

			Analysis (%)							
			C		H		N		S	
Compd.	M.p. (°C)	Formula	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
(1a)	255	$C_{15}H_{10}N_4OS$	61.2	61.3	3.4	3.4	19.05	19.1	10.9	10.8
(1b)	262	$C_{16}H_{12}N_4OS$	63.35	63.3	3.9	3.9	18.15	18.2	10.4	10.4
(1c)	252	$C_{16}H_{12}N_4OS$	63.35	63.4	3.9	3.9	18.15	18.1	10.4	10.4
(1d)	284	$C_{15}H_9ClN_4OS$ [a]	54.8	54.8	2.75	2.8	17.05	17.0	9.75	9.7
(1e)	>330	$C_{15}H_{10}N_4O_4S_2$	48.15	48.2	2.65	2.7	14.95	14.9	17.1	17.1
(1f)	242	$C_{16}H_{12}N_4O_2S$	58.05	58.1	3.85	3.9	18.05	18.0	10.3	10.3
(1g)	>300	$C_{15}H_9N_5O_3S$	53.1	53.0	2.65	2.7	20.65	20.7	9.45	9.4

[a] Found: Cl, 10.75. Calc. Cl.: 10.8%.

carried out in 10^{-3}M-HCl solution (200 ml) containing 50% v/v ethanol and substance (1a) (100 mg) (as a typical example). The electrolysis cell was a 250 ml conical flask on top of which were fixed the calomel, auxiliary, and hydrogen inlets. The mercury surface was stirred magnetically. The potential was controlled by a Tutorial T6 transistorized potentiostat (Birmingham) at −0.65 V *vs.* saturated calomel electrode (*i.e.* on the limiting current plateau of the wave). The progress of electrolysis was followed by recording the decrease in current with time. The pH was maintained at 3 during electrolysis by adding appropriate volumes of concentrated hydrochloric acid. After complete electrolysis the cell was disconnected, and the pH of the resulting solution was adjusted to 11 with aqueous ammonia. Evaporation *in vacuo* to half volume afforded a faint brown residue. After filtration, aniline was identified in the filtrate by diazotisation and coupling with β-naphthol. The faint brown residue, m.p. 135 °C, was identified as *2-aminothiazolo*[3,2-a]*benzimidazol*-3(2H)-*one* (2), $\nu_{max.}$ (KBr) 3 300 and 3 130 (NH_2), 2 960 (CH), and 1 680 cm^{-1} (C=O) (Found: C, 52.6; H, 3.45; N, 20.55; S, 15.55. $C_9H_7N_3OS$ requires C, 52.7; H, 3.4; N, 20.5; S, 15.6%).


(2) R = NH_2
(3) R = H


(4)

(ii) A similar electrolysis was carried out in 200 ml of HCl (pH 2) containing 50% v/v ethanol with thiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (3) as a model compound (100 mg). The potential was controlled at −1.0 V *vs.* saturated calomel electrode. After complete electrolysis, the remaining solution was evaporated *in vacuo* to half volume, and extracted with ether several times. The extract was evaporated and the pale yellow residue was identified as 1-acetyl-2,3-dihydrobenzimidazole-2-thione [10] (4). This compound can otherwise be obtained only in poor yield by tedious procedures; it is known to be protective and curative, and is particularly effective in control of apple scab and powdery mildew of apples.[10]

(4) *Determination of Apparent Dissociation Constants by Potentiometry.*—A solution containing 25% dimethylformamide, 25% EtOH, and 50% distilled H_2O, and 2 × 10^{-4}M in substrate, was titrated against standardized carbonate-free

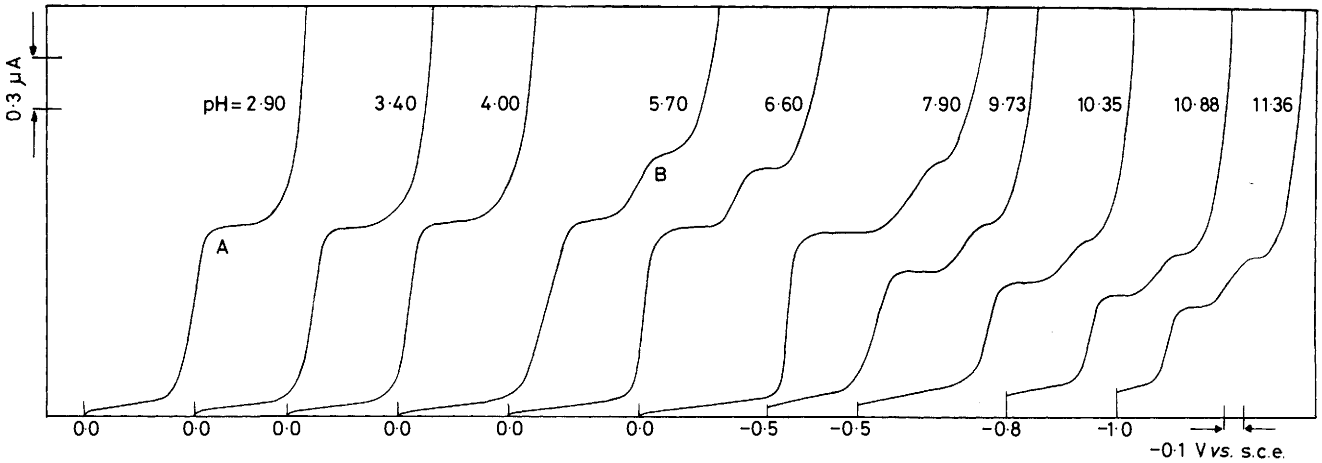


Figure 1. Polarograms of (1a)

Table 2. Polarographic data of 2-arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-ones (1a—g)

Compd.	$\Delta E_{\frac{1}{2}}$ [a,b]/ΔpH (V/pH) Wave A	Wave B	pH [c]	*RT*/α*n*F [d] Wave A	Wave B	α*n* [e] Wave A	Wave B
(1a)	$E_{\frac{1}{2}}{}^a = -0.52 - 0.033$pH	$E_{\frac{1}{2}} = -0.26 - 0.152$pH	2.9	0.061		0.984	
	$E_{\frac{1}{2}}{}^b = +0.39 - 0.151$pH		10.4	0.062	0.106	0.968	0.566
(1b)	$E_{\frac{1}{2}}{}^a = -0.49 - 0.044$pH	$E_{\frac{1}{2}} = -0.31 - 0.142$pH	5.6	0.057	0.119	1.053	0.504
	$E_{\frac{1}{2}}{}^b = +0.50 - 0.161$pH		7.9	0.055	0.109	1.091	0.594
(1c)	$E_{\frac{1}{2}}{}^a = -0.59 - 0.031$pH	$E_{\frac{1}{2}} = -0.52 - 0.108$pH	2.5	0.052		1.154	
	$E_{\frac{1}{2}}{}^b = +0.81 - 0.181$pH		8.5	0.061	0.085	0.984	0.706
(1d)	$E_{\frac{1}{2}}{}^a = -0.53 - 0.037$pH	$E_{\frac{1}{2}} = -0.25 + 0.147$pH	2.5	0.066		0.909	
	$E_{\frac{1}{2}}{}^b = +0.51 - 0.169$pH		5.6	0.051	0.089	1.176	0.674
(1e)	$E_{\frac{1}{2}}{}^a = -0.57 - 0.030$pH	$E_{\frac{1}{2}} = -0.48 - 0.126$pH	5.6	0.064	0.096	0.938	0.625
	$E_{\frac{1}{2}}{}^b = +0.54 - 0.182$pH		10.2	0.061	0.095	0.984	0.632
(1f)	$E_{\frac{1}{2}}{}^a = -0.56 - 0.031$pH	$E_{\frac{1}{2}} = -0.54 - 0.103$pH	2.5	0.056		1.071	
	$E_{\frac{1}{2}}{}^b = +0.82 - 0.178$pH		5.6	0.043	0.079	1.395	0.759
(1g)	$E_{\frac{1}{2}}{}^a = -0.53 - 0.036$pH	$E_{\frac{1}{2}} = -0.37 - 0.132$pH	2.5	0.057		1.053	
	$E_{\frac{1}{2}}{}^b = +0.39 - 0.154$pH		5.6	0.050	0.076	1.200	0.779

[a] Equation of first segment. [b] Equation of second segment. [c] Individual pH value at which logarithmic analysis was carried out. [d] Slope of logarithmic analysis. [e] Transition coefficient.

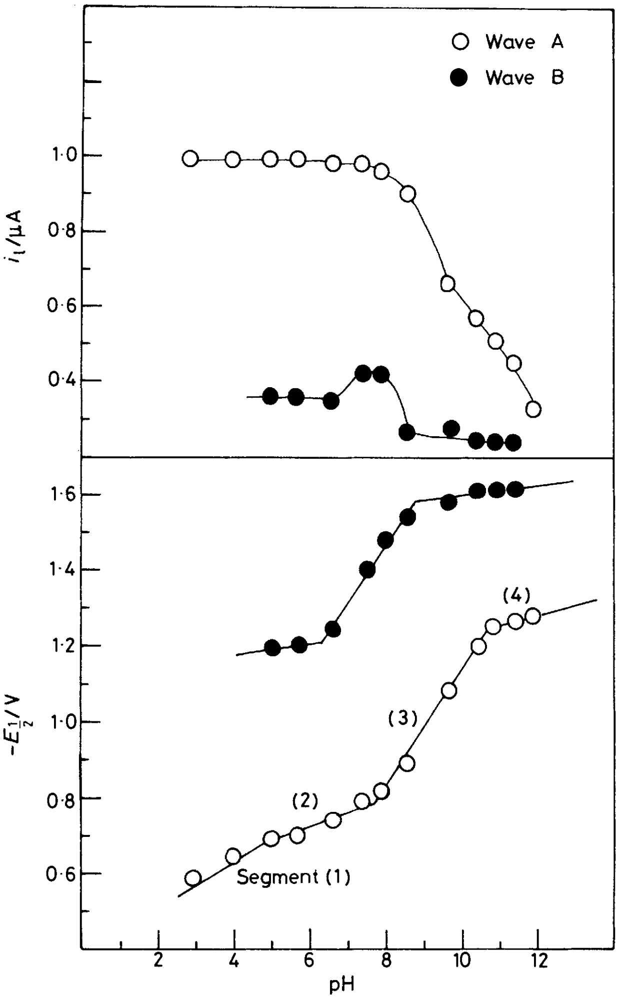


Figure 2. Variation of $E_{\frac{1}{2}}$ and i_l with pH for (1a)

aqueous 10^{-2}M-NaOH with continuous stirring. The apparent pH values were read on a Sargent-Welch PBL pH meter accurate to ±0.05 units. Values of pK_a were calculated using the Henderson-Hasselbalch equation [11] by plotting log [A^-]/[HA] *vs.* pH.

Results and Discussion

Polarographic Behaviour of Compounds (1a—g).—The polarograms of 10^{-4}M-solutions of (1a—f) in 50% v/v ethanolic buffers are exemplified by those of (1a) (Figure 1). At pH <5, compounds (1a—f) display a well defined polarographic wave A. The half-wave potential $E_{\frac{1}{2}}^A$ shifts to more negative values with increase of pH (Figure 2). The shifts in $E_{\frac{1}{2}}$ with pH are compiled in Table 2 in the form of linear equations. The $E_{\frac{1}{2}}$–pH plots show mainly two segments in which $E_{\frac{1}{2}}$ is sensitive to pH (segments 1 and 3), and two others in which $E_{\frac{1}{2}}$ is practically pH-independent (segments 2 and 4) (Figure 2). The limiting current decreases with increase of pH in the form of a well defined dissociation curve [12] (Figure 2). At pH >5 a more negative wave B appeared with an i_l value about half that of wave A. The dependence of both i_l and $E_{\frac{1}{2}}$ on pH is illustrated in Figure 2.

Polarographic Behaviour of (1g).—In addition to waves A and B, compound (1g) showed an additional 4 e^- irreversible diffusion-controlled wave C at more positive potential. The effect of pH on $E_{\frac{1}{2}}$ values of the different waves is shown in Figure 3. The behaviour of the additional wave can be described by the linear equation (i). Since the behaviour of this wave is similar to that of the well known aromatic *m*-nitro group,[13] it is not unreasonable to attribute the extra wave to the reduction of the nitro group to hydroxylamine [14] [equation (ii)]. At pH >8.5, a further ill defined 2 e^- wave appears which is attributed to further reduction of the hydroxylamine to amine [13] [equation (iii)].

$$E_{\frac{1}{2}} = +0.07 - 0.069\,\text{pH} \qquad \text{(i)}$$

$$-NO_2 + 4\,e^- + 4\,H^+ \xrightarrow{E_{\frac{1}{2}}} -NHOH + H_2O \qquad \text{(ii)}$$

$$-NHOH + 2\,e^- + 2\,H^+ \longrightarrow -NH_2 + H_2O \qquad \text{(iii)}$$

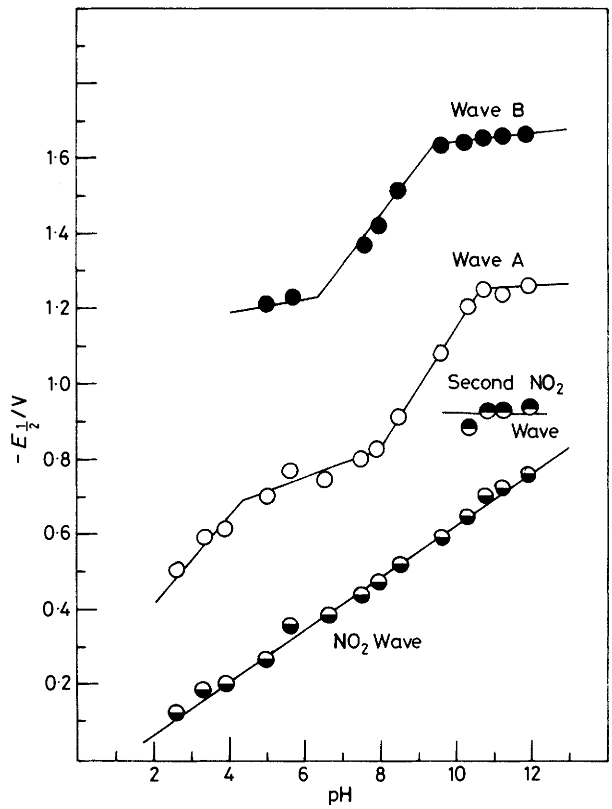


Figure 3. Variation of $E_{\frac{1}{2}}$ with pH for (1g)

Nature of the Polarographic Waves A and B.—The effect of mercury-height variation on i_l indicated that these waves are mainly controlled by diffusion in the pH range where i_l is practically constant (pH-independent). At pH values where i_l decreases in height, the slopes of the linear plots of log i_l *vs.* log h (h = mercury height) give values <0.5, a direct indication that these waves are of kinetic nature. Also, from the i_l–pH behaviour of compounds (1f) and (1g), it is possible to deduce that these compounds are adsorbed to some extent on the mercury surface at pH *ca.* 5—8; this is confirmed by the fact that the slope of log i_l *vs.* log h is $\gg$0.5. Further confirmation with the effect of concentration could not be obtained since these compounds precipitated at concentrations >2 × 10^{-4}M. Logarithmic analysis of these waves indicates that the processes are irreversible,[15] as can be observed from the transition and transfer coefficient values in Table 2.

Kinetic Parameters of the Acid–Base Equilibria in Compounds (1a—g).—The nature of the dissociation curves (Figure 2)

Table 3. Kinetic parameters of 2-arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-ones (1a—g)

Compd.	pK_a	pK'	10^{-13} k_r/ l mol^{-1} s^{-1}	10^{-5} k_d/s^{-1}
(1a)	7.80	10.80	3.396	8.524
(1b)	7.85	10.90	3.027	4.270
(1c)	7.80	10.50	5.383	8.532
(1d)	7.65	10.95	6.039	13.521
(1e)	7.80	10.05	0.067 76	0.1074
(1f)	7.90	10.55	5.383	0.6777
(1g)	7.55	10.78	3.396	9.571

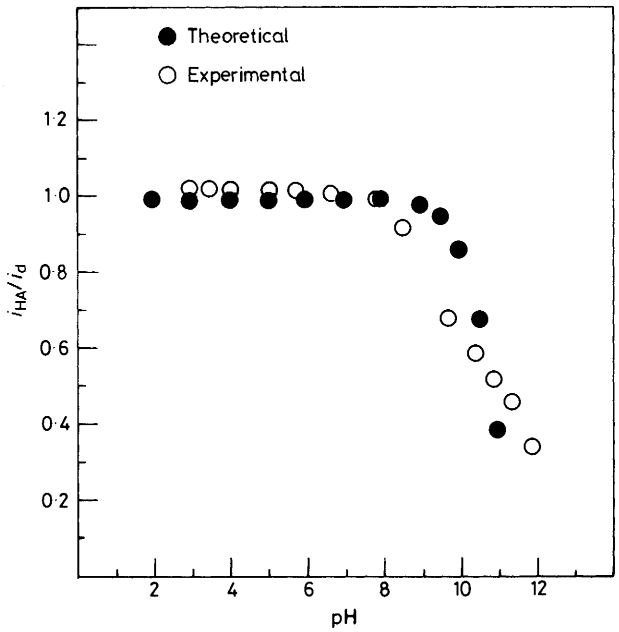


Figure 4. Comparison of theoretical and experimental i_{HA}/i_d values [equation (v)] for (1a—e)

raised the question as to whether these compounds are ionizable or hydrolysed in alkaline media. We therefore calculated the pK_a values of these compounds. The potentiometric pK_a values are compiled in Table 3 and are in good agreement with the intersection pH values of segments 2 and 3 of wave A;[16] the intersection value of segments 3 and 4 is in accord with pK'[13] (apparent polarographic dissociation constant, *i.e.* pH corresponding to $i_l/2$) obtained from the i_l-pH curves (Figure 2). By correlating pK' with the potentiometric pK_a values, it is possible to calculate the value of the rate constant k_r using equation (iv), and from k_r values one may obtain the appropriate theoretical curve using the relation (v).[12] The values of k_r and k_d are compiled in Table 3 ($k_d/k_r = K_a$).

$$\log k_r = 2\,\mathrm{p}K' - \mathrm{p}K_a - 2\log 0.886 - \log t \qquad \text{(iv)}$$

$$\frac{i_{HA}}{i_d} = \frac{0.886\left(\frac{k_r t}{K_a}\right)^{\frac{1}{2}}[\mathrm{H}^+]}{1 + 0.886\left(\frac{k_r t}{K_a}\right)^{\frac{1}{2}}[\mathrm{H}^+]} \qquad \text{(v)}$$

$$\mathrm{HA} \underset{k_r}{\overset{k_d}{\rightleftharpoons}} \mathrm{H}^+ + \mathrm{A}^- \qquad \text{(vi)}$$

Figure 4 shows that the theoretical curve is practically superimposed on the experimental results, indicating that these

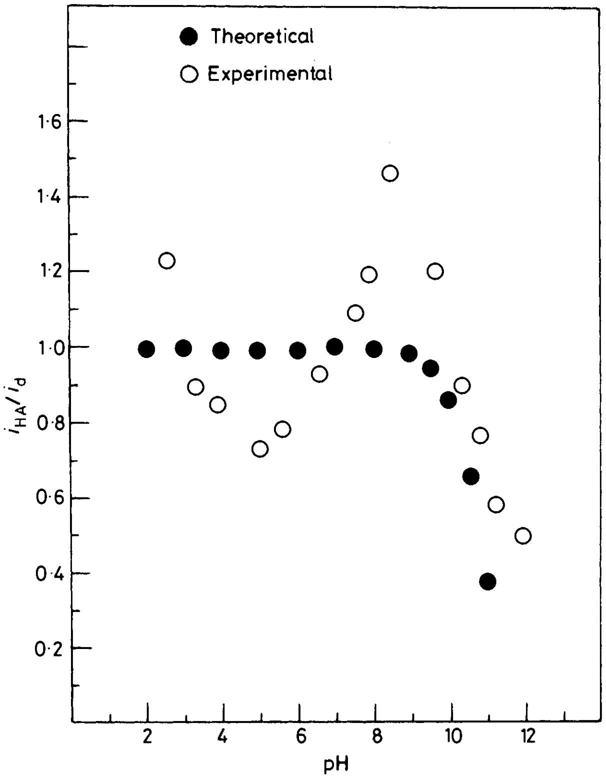
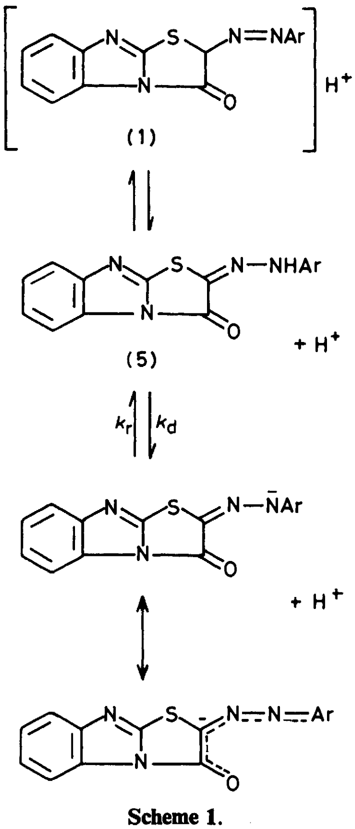
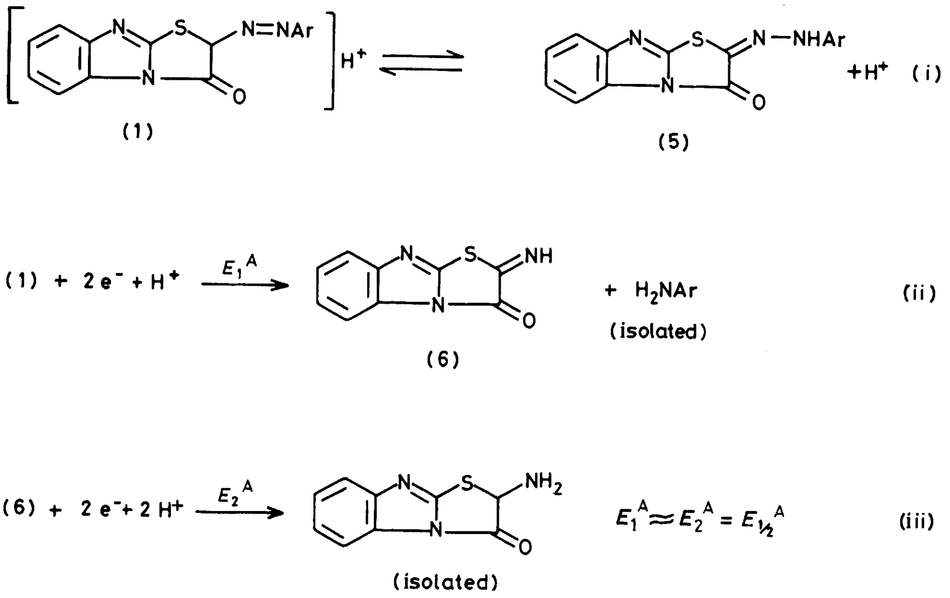


Figure 5. Comparison of theoretical and experimental i_{HA}/i_d values [equation (v)] for (1f)

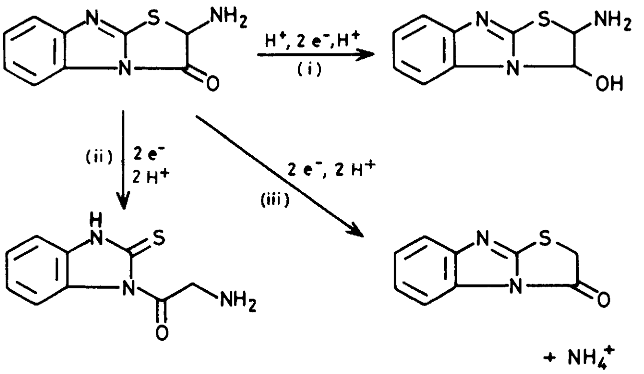


Scheme 1.



Scheme 2.

Wave B



Scheme 3.

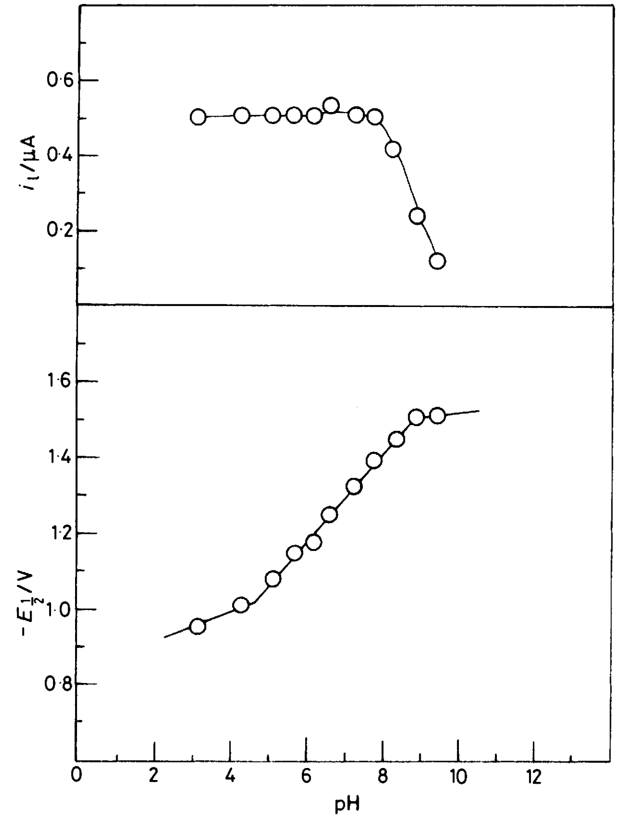


Figure 6. Variation of $E_{\frac{1}{2}}$ and i_l with pH for (3)

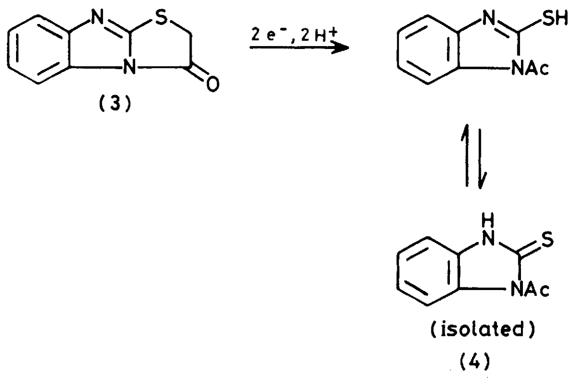
compounds behave as acids with one ionizable centre. However, compounds (1f) and (1g) behave somewhat differently: they both show an abnormal increase of i_l in the pH range 5—8 [see Figure 5 for compound (1f)]. This ionization process is only possible if these compounds exist in the hydrazone form. In fact the compounds behave as true hydrazones and the structural formula (5) is more stable than (1) owing to conjugation. That compounds (1a—g) are electroinactive in alkaline media could be attributed to the fact that the negative charge of the anion is delocalized over the carbonyl–hydrazone system (Scheme 1).

Assignment of Waves A and B of Compounds (1a—f).—(1) The behaviour of wave A is in good agreement with the reported behaviour of compounds containing the hydrazone linkage[17,18] and different from those containing the azo –N=N– moiety.[19-21] Thus, their $E_{\frac{1}{2}}$ values are similar to those of aromatic hydrazones, but more negative than those of azo compounds. This interpretation is confirmed by the fact that the wave corresponding to the reduction of the nitro moiety in compound (1g) appeared before wave A; if an azo function was the reducible species the nitro wave would appear at more negative potential. Scheme 2 illustrates the electroreduction sequence of wave A in acid media and is confirmed by isolation and characterization of 2-aminothiazolo[3,2-*a*]benzimidazol-3(2*H*)-one and aniline. That only one well defined wave is observed is due to the fact that the energies of the individual steps are very close; thus only one amalgamated four-electron wave is displayed. At highly alkaline media ($\mathrm{pH} \gg \mathrm{p}K_a$) the wave starts to decrease in height due to the

Table 4. Results of statistical treatment of $E_{\frac{1}{2}}/\sigma$ data for 2-arylazothiazolo[3,2-*a*]benzimidazol-3(2*H*)-ones (1a—g)

		σ			σ⁰			σ*		
pH	Wave	ρ [a]	*r* [b]	s.d. [c]	ρ	*r*	s.d.	ρ	*r*	s.d.
2.5	A	0.102	0.545	0.095	0.107	0.509	0.101	0.016	0.163	0.053
7.5	A	0.086	0.476	0.090	0.044	0.217	0.102	0.022	0.236	0.047
	B	0.023	0.127	0.091	0.026	0.091	0.020	0.211	0.211	0.047
11.0	A	0.149	0.608	0.136	0.026	0.097	0.154	0.011	0.082	0.077
	B	0.002	0.008	0.139	0.008	0.029	0.154	0.022	0.164	0.077

[a] Slope. [b] Correlation coefficient. [c] Standard deviation.



Scheme 4.

formation of the anion, which is stabilized by delocalization, thus preventing further reduction (Scheme 1).

(2) At a first glance one might deduce three possible assignments for wave B based on $E_{\frac{1}{2}}$ limits and i_l/pH dependence (Scheme 3).

(i) Reduction of the carbonyl group in the sequence H^+, $2\,e^-$, H^+.

(ii) Cleavage of the C–S bond in the heterocyclic portion of the molecule.

(iii) Cleavage of the $C-NH_2$ bond in the product of the first process wave A (Scheme 2).

To elucidate this we studied the polarographic behaviour of the model compound (3). This compound is reduced along a well defined polarographic two-electron wave which decreases in height with increase of pH in the form of a dissociation curve. The shift of $E_{\frac{1}{2}}$ with pH and the decrease of i_l with pH are illustrated in Figure 6. This behaviour is similar to the behaviour of wave B in the series under study; thus it is not unreasonable to infer that the mechanism of wave B is very similar to that of the model (3). Furthermore electrolysis was carried out at pH 2 at a controlled potential of -1.0 V *vs.* saturated calomel; based on the isolation and characterization of the product one can assume that Scheme 4 illustrates the electroreduction of compound (3) [mechanism (ii)].

Assignment (iii) is rejected since ammonium ion could not be detected in the solution; also if this were true it would result in the formation of compound (3), which in turn would be reduced in a further two-electron wave. No additional wave was observed. The carbonyl group in the isolated product (4) could be stabilized *via* hydrogen bonding.

Structure–Energy Relationships.—Hammett correlations of $E_{\frac{1}{2}}$ values with different σ sets are, in general, weak (*cf.* Table 4), but it is obvious that $E_{\frac{1}{2}}$ values of wave B (pH 7.5 and 11.0, Table 4) are practically independent of substituent effects. This can be readily understood from the fact that wave B corresponds to reduction of the molecule resulting from the reductive cleavage of the –C=N–NH– moiety (wave A) to give a substituted aniline. Thus the substituent has no further effect on the reducible centre. Since the nitro group is reduced prior to the hydrazone linkage, σ_{NHOH} values were used instead of $\sigma_{p\text{-}NO_2}$ in acid and neutral media. In highly alkaline media σ_{NH_2} values were used. On the other hand pK_a/σ correlations have reasonable linearity, with ρ 0.256—0.388 (Figure 7), in good agreement with previously reported values for monobasic weak organic acids.[22] In addition these correlations confirm that the ionizable centre (–NH–) is directly conjugated with the substituent.

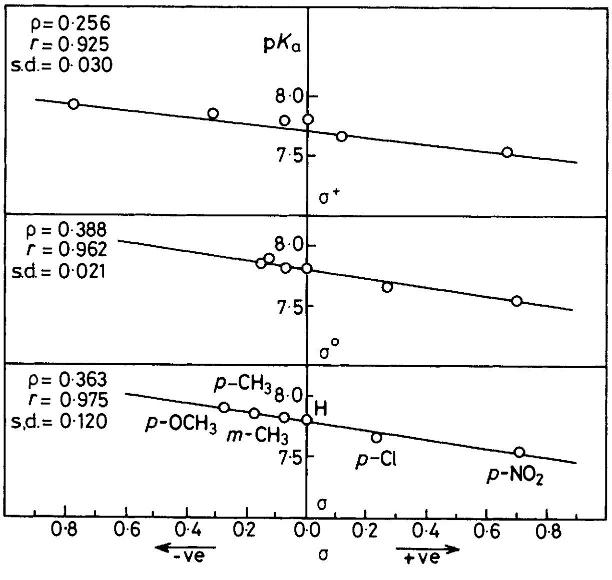


Figure 7. Correlation curves

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