Studies on Some Sulphonamoyl azopyrazoles at d.m.e. and g.c. Electrodes

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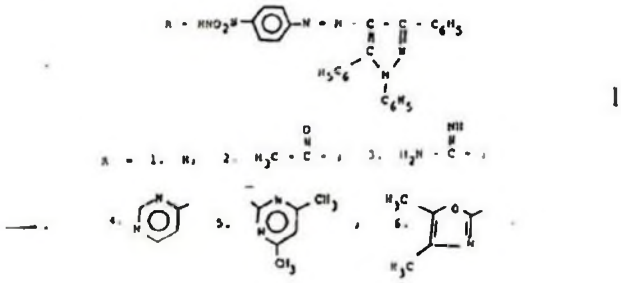
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The -N=N- group of 1-phenyl,3, 5-diphenyl[4'-sulphonamoyl] azopyrazoles is reduced in one step at d.m.e. and g.c. electrode in BR buffer solutions of pH 2.0-12.0. All these azopyrazoles give a well defined, diffusion-controlled and irreversible wave/peak corresponding to a 2 electron reduction of azo group to -NH-NH-. Effect of solvent composition on the electrode process was studied.

1-Phenyl,3,5-diphenyl-4-[4'-sulphonamoyl]azopyrazoles [A] are biologically important. Since their systematic electrochemical studies are not reported, such study of these compounds have been undertaken.

EXPERIMENTAL

All the compounds (I) were prepared by reported method [1].



I

Stock solutions [2.0 x 10^{-3} M] of all the compounds were prepared in dimethylformamide (AR). Buffer solutions of pH 2.5 - 12.0 [2] and potassium chloride (1.0 M KCl) solutions were prepared in double distilled water from AR grade chemicals. The test solutions for polarographic and cyclic voltammetric studies were prepared by mixing 1.0 ml stock solution of depolarizer (2.0 x 10^{-3} M), 3.0 ml of dimethylformamide (to prevent precipitation), 5.0 ml appropriate B.R. buffer and 1.0 ml of potassium chloride (1.0 M) as supporting electrolyte. The equipments used and other experimental details of polarographic and cyclic voltammetric studies are reported elsewhere [3].

The number of electrons consumed in the reduction of the compound (n) was determined by controlled potential electrolysis using 40 ml of the test solution.

In controlled potential electrolysis at mercury pool cathode, the test solution was electrolysed by the application of a specified potential lying on the limiting

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current of the polarographic wave. From the decrease of current with time during electrolysis, the number of electrons transferred was calculated. Progress of electrolysis was monitored by recording polarograms at different intervals of time, until only background current is realised. In controlled potential coulometry, the test solution was elctrolysed at a specified potential using glassy carbon cathode. The number of coulombs consumed were directly read on coulometer and 'n' was calculated.

RESULTS AND DISCUSSION

D.C. Polarography

Between pH 2.5 to 12.0, all sulphonamoylazopyrazoles of the series show a well-defined, 2e⁻ polarographic wave of practically constant height. The electrochemical characteristics of these compounds are compiled in Table 1. Comparing the observed half-wave potential with the one reported for the reduction of azo group [4], the observed wave has been attributed to the reduction of azo group.

The straight line plots of i_d vs $h^{1/2}$ and i_d vs concentration clearly shows the diffusion-controlled nature of the electrode process [5]. The same is also supported by the low value of temperature coefficient (below 1.62 %/deg). A comparison of limiting currents indicates that all compounds are reduced in the pH range 2.5 - 12.0 by consuming identical number of electrons. The value of slope of $E_{d.e.}$ *vs* log $[i/(i_d-i)]$ plots appreciably exceeds 0.059/n V. This finding, along with shift of $E_{1/2}$ towards negative potential with rise in concentration of depolarizer, suggest that the electrode process is irreversible [6] in nature. The $E_{1/2}$ shifts towards negative potential with rise in pH (upto 8.0) indicating proton participation in reduction process [6-8]. Between pH 8.0

Table 1

Electrochemical characteristics of 1-phenyl-3,5-diphenyl-4-[4'-sulphonamoyl]azopyrazoles
pH 6.5; conc. 2.0×10^{-4} M; Height 65 cm

comp	Poloragraphy		CV		$\frac{dE_{1/2}}{dpH}$	αn_a	$IX10^3$
No.	$-E_{1/2}$,V	i_d,μA	$-E_p$,V	i_p,μA			
1.	0.73	1.46	0.73	7.94	0.040	0.54	3.19
2.	0.81	1.28	0.83	9.01	0.036	0.45	2.79
3.	0.77	1.64	0.79	9.68	0.038	0.35	3.50
4.	0.72	1.28	0.71	9.50	0.030	0.56	2.79
5.	0.89	1.24	0.72	10.03	0.046	0.81	2.71
6.	0.82	1.28	0.86	8.00	0.046	0.33	2.79

to 12.0 the $E_{1/2}$ remains nearly constant (Fig. 1). The shape of $E_{1/2}$ *vs* pH curve indicates that both acidic and basic forms of the depolarizer are electroactive [10] having almost the same half-wave potential.

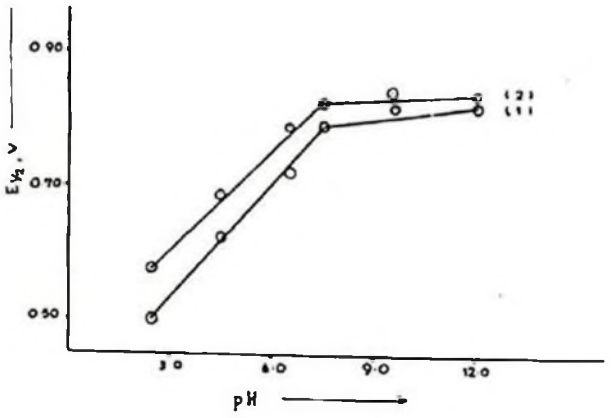


Fig. 1 : Plot of $-E_{1/2}$ *vs* pH
1. Compound 1 2. Compound 2
Concentration = 2.0 x 10^{-4}M.

The value of αn_a (product of transfer coefficient and number of electrons transferred in rate determining step) and P (number of protons involved in the rate determining step) are calculated using following expressions [5,10].

$$\alpha n_a = - 0.0517/(E_{1/4} - E_{3/4})$$

$$P = (dE_{1/2}/dpH)\ (\alpha n_a/0.0591)$$

The value of P was found to be one.

Linear Sweep and Cyclic Voltammetry

A single cathodic peak and no anodic peak in the cyclic voltammograms of the azopyrazoles in the pH range 2.5 - 12.0 indicates irreversible nature of electrode process (Fig. 2). This is further supported by the negative shift in the peak potential with increasing sweep rate (50-200 mV/sec). The direct proportionality between i_{pc} *vs* concentration of depolarizer and i_{pc} *vs* $v^{1/2}$ (Fig. 2B) pointed towards diffusion controlled nature of the electrode process [11]. The peak potential (E_p) values are dependent on pH and shifted cathodically with pH (Fig. 2C) indicating proton involvement in the electrode process. The peak potential shifted towards negative potential upto pH 7.7 and E_p was practically constant thereafter.

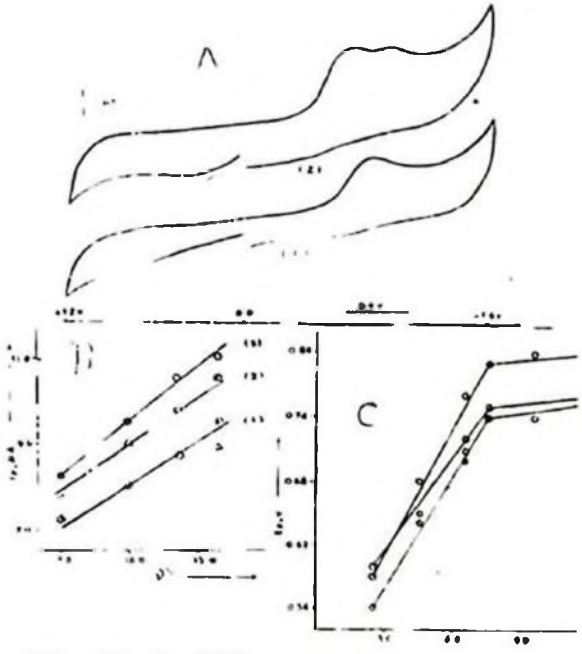


Fig. 2A : Cyclic Voltammograms
1. Compound 2 2. Compound 4
Scan Rate 100 mV/sec ; conc 2.0 x 10^{-4}M
2B Ip *vs* $v^{1/2}$ plots
1. Compound 6 2. Compound 2 pH6
2C - E_p *vs* pH plot.
1. Compound 2. Compound 4 3. Compound 5

Controlled Potential Electrolysis, Coulometry and Product Analysis

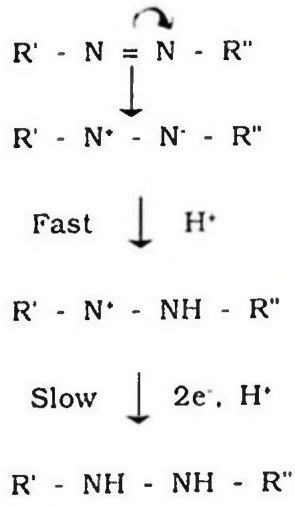
Controlled potential electrolysis of all these compounds at the plateau potential

using the mercury pool cathode consumed 2.0 ± 0.4 electrons. With the progress of electrolysis, the colour of the solution gradually faded away and finally a colourless solution was obtained. Coulometric studies at peak potential (E_p) using glassy carbon electrode also gave the value of 'n' as 2.0 ± 0.2. A cyclic voltammogram of completely reduced solution even at higher scan rate (200 mV/s) did not exhibit any oxidation or reduction peak. The progress of the electrolysis was also monitored by recording UV-VIS spectra at different intervals of time. With the progress of the electrolysis, absorbance at 340 nm systematically decreased and finally disappeared. These observations show that no intermediate with sufficient half-life is generated during electroreduction of the compound. The resulting solution was tested for amine present. Dye test indicated the absence of amine in the solution, which confirmed that further reduction did not take place. TLC analysis of the electrolysed solution gave only one spot, confirming that a product with -NH-NH- grouping is the end product of the electrolysis.

Mechanism

On the basis of DCP, CV, coulometric and CPE following mechanism (H^+, e^-, e^-, H^+) may be proposed for the reduction of these compounds at the N=N bond.

Initially, polarised molecule accepts a proton from the medium followed by taking up two-electrons and another proton from the medium. This



mechanism is supported by the shift of $E_{1/2}$ towards negative potential with pH as the reduction of -N=N- takes place at the expense of proton from the medium. The $E_{1/2}$ becomes constant, while the equilibrium tends to shift towards the unprotonated form. This is apparent from the fact that shift of $E_{1/2}$ with pH is not as marked above pH 8.0 as in acidic medium. Solution after controlled potential electrolysis did not give dye test, which shows that -N=N- group is being reduced to -NH-NH- and further reduction to amine is not taking place. Furthermore, TLC also indicated the presence of only one compound in the electrolysed solution. Cyclic voltammogram and polarographic waves recorded after controlled potential electrolysis did not give any peak, confirming the above reduction mechanism. Similar results for the reduction of comparable compound have been reported by other workers [12-15].

Influence of Solvent Composition on Polarographic Characteristics

Effect of solvent composition on the polarographic behaviour of 1-phenyl-3,5-

diphenyl-4-[4'-sulphonamoyl] azopyrazoles was studied at pH 6.5. The percentage of dimethylformamide was increased from 30% to 70%. It was found that half-wave potential shifted to more negative potential with increase in the percentage of solvent in the solution mixture. The i_d values continue to decrease and at very high percentage of organic solvent very ill defined waves were obtained (Table 2).

Table 2

Effect of Solvent Composition on Polarographic Characteristics

Depolariser; 1-phenyl-3,5-diphenyl-4-[4'-sulphonamoyl]azopyrazoles

pH 6.5; conc. 2.0 x 10^{-4} M;

DMF	$-E_{1/2}$ V	i_d,μA
30	0.72	1.28
40	0.74	1.18
50	0.77	1.10
60	0.78	1.02
70	0.63	0.98

The shift of half-wave potential towards negative potential may be due to rise in pH of the solution [16] which results in the increase in the dissociation constant of the protonated species [17]. Another possibility for the shift of $E_{1/2}$ may be the inhibition of the electrode process by the solvent molecules adsorbed [18] on the electrode. One more factor which causes great influence on the polarographic behaviour is viscosity. While increasing concentration of DMF in the solution, there is a gradual increase in viscosity upto certain concentration after which it becomes constant. All these factor retard the electrode process resulting in the difficult reduction with decreased diffusion current.

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Continued on page 22