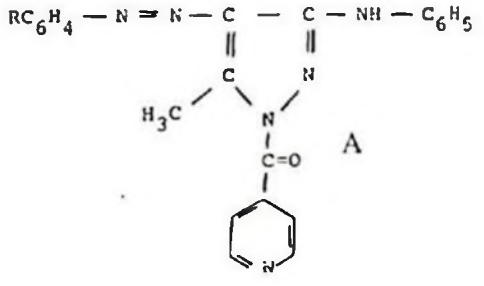
Voltammetry Studies of Some Isonicotinyl - Aryl - Azopyrazoles having Two Reduction Sites

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1-Isonicotinyl,3-phenylamino, 5-methyl, 4-arylazopyrazoles give two well-defined, diffusion-controlled, 2-electron, cathodic steps in B.R.buffers of pH 2.6 - 12.0 due to the reduction of -N=N- to -NH-NH- and >C=O to >CH-OH. Nitro substituted compounds gave one more 4 e⁻ wave / peak corresponding to the reduction of nitro to hydroxylamine group. The effect of substituents has been determined quantitatively by the application of Hammett equation.

Electrochemical techniques are adopted for investigating the biologically active compounds since they provide valuable information regarding their redox behaviour in living systems as demonstrated already [1,2]. In continuation of the studies of azo compounds [3-8], electrometric studies have been carried out on a series of 1-isonicotinyl,3-phenylamino, 5-methyl, 4-arylazopyrazoles (A) systematically and comprehensively.



A

R =

1. H; 2. 2'-CH_3; 3. 4'-CH_3;
4. 2'-OCH_3; 5. 4'-Cl; 6. 4'-Br;
7. 2'-NO_2; 8. 3'-NO_2; and 9. 4'-NO_2;

EXPERIMENTAL

The nine substituted azopyrazoles (Compound A 1 - 9) were synthesised by known method [4]. The equipments used and experimental details are reported earlier [5].

RESULTS AND DISCUSSION

The possible reduction sites in these compounds are the cyclic -C=C- and -C=N- groups of the pyrazole ring and exocyclic -N=N- and >C=O sites. In the case of nitro substituted compounds, -NO_2 is one more reduction site. Exocyclic -N=N- and >C=O (and in case of nitro compounds, -NO_2 group) are more susceptible for reduction. So, it can safely be concluded that these are the reduction sites.

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D.C.Polarography

All the azopyrazoles give two well-defined reduction waves whereas nitro substituted compounds give three reduction waves (Table 1).

All the waves were found to be diffusion-controlled on the basis of (i) low temperature coefficient (below 1.62% deg^{-1}), (ii) i_d is proportional to C and (iii) i_d is proportional to $h^{1/2}$ and irreversible on the basis of shift of $E_{1/2}$ with C and nature of log plots [7]. $E_{1/2}$ increases with pH and shows constancy at higher pH (Fig 1). It suggests the proton participation in the electrode process.

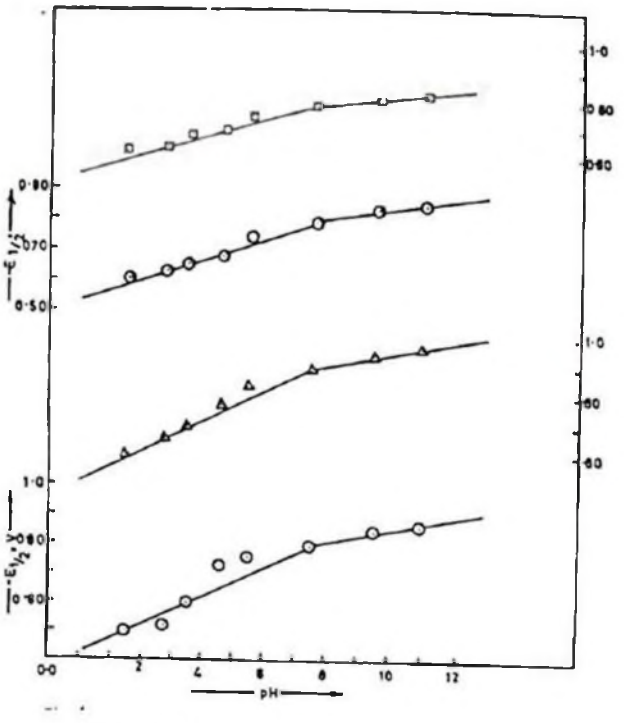


Fig 1. Plot of $E_{1/2}$ *vs* pH
Depolariser Conc. 2.0 X 10^{-4}M
a. Compound 1; b. Compound 2;
b. Compound 3; d. Compound 5

Table 1

Polarographic Characteristics of Typical Compounds at Different pH Values

Depolarizer: 1-(isonicotinoyl) 3 phenylamine- 5-methyl-4- aryl azopyrazoles
Conc = 2.0 x 10^{-4} M; Solvent DMF; Temp 30°C ; Supporting Electrolyte Concentration = 0.1 M

	Compound 1				Compound 7					
pH	Step 1 -N=N-		Step 2 C=O		Step 1 $-NO_2$		Step 2 -N=N-		Step 3 C=O	
	$-E_{1/2}$V	i_d μA	$-E_{1/2}$V	i_d μA	$-E_{1/2}$V	i_d μA	$-E_{1/2}$V	i_d μA	$-E_{1/2}$V	i_d μA
2.5	0.50	0.85	0.75	0.65	0.21	0.53	0.82	1.40	0.75	0.70
3.8	0.52	0.88	0.75	0.70	0.26	0.65	0.85	1.30	0.70	0.65
4.5	0.60	0.96	0.70	0.70	*	0.72	0.91	*	0.70	0.65
5.6	0.74	1.00	0.75	0.75	0.40	0.82	0.95	1.35	0.75	0.70
6.5	0.76	1.03	0.75	0.65	0.46	0.90	0.98	1.40	0.75	0.70
8.5	0.80	1.07	0.70	0.70	0.50	0.94	1.01	1.35	0.70	0.70
10.5	0.85	1.09	0.70	0.70	0.52	0.96	1.03	1.30	0.70	0.70
12.0	0.86	1.10	0.70	0.65	0.52	0.97	1.03	1.30	0.70	0.70

* waves not clear

Linear Sweep and Cyclic Voltammetry

Typical cyclic voltammogram of the compounds are dipicted in Fig 2. The behaviour of all the compounds are similar to that in D.C.Polarograms. The results are given in Table 2.

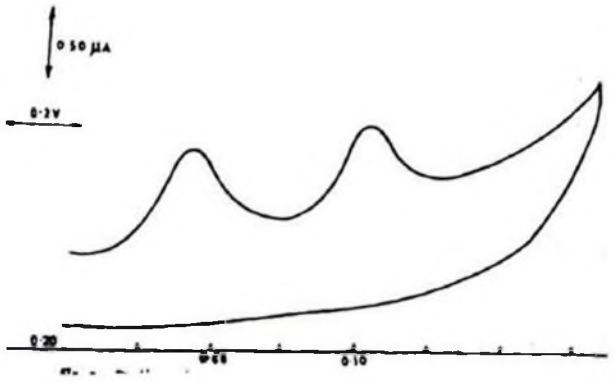


Fig 2 Cyclic Voltammogram of Compound 1 pH 3.8; Conc. 2.0 X 10^{-4}M; Scan 50 mV.sec^{-1}.

Irreversible nature of the reduction steps is confirmed by the absence of the anodic peak and cathodic shift of the peak potential with increase in sweep rate (50 - 200 mV/sec). The ratio of i_p / C and $i_p/v^{1/2}$ were found to be constant for all the three peaks. The relationship between E_p *vs* pH was found to be similar to $E_{1/2}$ *vs* pH. The first wave at less negative potentials in the case of nitro substituted compounds was found to be a four electron reduction step whereas second and third steps were found to involve 2 electrons each in the reduction process. On the basis of number of electectons involved as well as the known easy reducibility of nitro group in both aliphatic and aromatic compounds, the first wave has been assigned to the reduction of nitro group. By comparison with reduction behaviour of compounds not

Table 2

Electrochemical Characteristics for the Reduction of Azo Group

Depolarizer: 1-(isonicotinoyl) 3 phenylamine- 5-methyl-4- aryl azopyrazole
Conc = 2.0 x 10^{-4} M; Solvent DMF; Temp 30°C; Supporting Electrolyte Concentration = 0.1 M

Comp. No.	$-E_{1/2}$ V	i_d µA	E_p V	i_p µA	αn_a	$Ix10^3$	P	σ
1	0.76	0.75	0.78	1.80	0.72	2.30	0.92	0.00
2	0.78	0.75	0.81	1.84	0.75	2.30	1.06	-1.17
3	0.75	0.70	0.77	1.82	0.78	2.10	1.05	-0.17
4	0.84	0.75	0.85	1.78	0.79	2.30	0.91	-0.30
5	0.74	0.75	0.76	1.80	0.71	2.30	1.03	+0.23
6	0.72	0.80	0.74	1.82	0.75	2.50	1.09	+0.23
7	0.90	0.75	0.93	1.84	-	2.30	-	-
8	0.86	0.70	0.90	1.80	-	2.10	-	-
9	0.76	0.75	0.78	1.82	-	2.30	-	-

having carbonyl group, the second of the waves has been assigned to the reduction of azo group. The remainig wave has been assigned to the reduction of carbonyl group.

Reduction Mechanism

The above results as well as coulometric and controlled potential electrolysis results confirm the reported mechanism for nitro [8] azo and carbonyl group.

Reduction of Nitro Group

At pH < 4, the reduction follows the pattern:

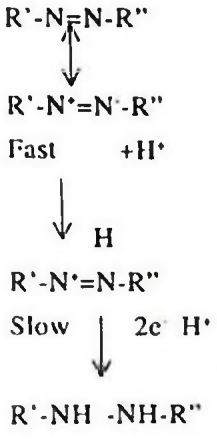
$C_6H_5NO_2 + 4e^- + 4H^+ \longrightarrow C_6H_5NHOH + H_2O$

$C_6H_5NHOH + 2e^- + 2H^+ \longrightarrow C_6H_5NH_2 + H_2O$

At pH > 4 only the first of the above reacton takes place.

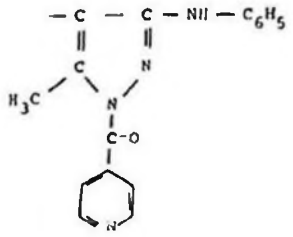
Reduction of azo Group

On the basis of number of electrons involved in the electrode process and number of protons involved in the rate determining step, following mechanism may be postulated for the reduction of these compounds.



Where R' = RC_6H_4 -

R" =



When the depolariser solution was tested after controlled potential electrolysis, it did not give dye test, thereby showing that -N=N- group is reduced to -NH-NH- and further reduction to amine is not taking place. TLC also indicated the presence of only one compound in the solution. Similar results have been reported by other workers [9] for the reduction of comparable compounds.

Reduction of Carbonyl Group

The two electron process for the reduction of the C=O group is probably similar to that found for other ketones [10].

$R_1R_2\text{-}C{=}O \longrightarrow R_1R_2\text{-}C^{\bullet}\text{-}OH$

$\xrightarrow{+e^-} R_1R_2\text{-}C^-\text{-}OH \xrightarrow{+e^-,\ +H^+} R_1R_2\text{-}CH\text{-}OH$

Structural Effects

For the application of the modified Hammett equation to the half wave potentials of the substituted compounds of a given series, half wave potentials for the reduction azo group of the compounds (Table 1) were plotted against the Hammett substituent constants (σ) [11]. Nitro derivatives have not been included in this relationship, as this group is

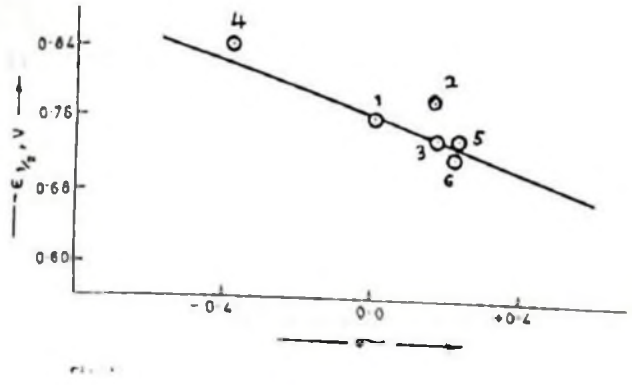


Fig 3. Plot of $E_{1/2}$ vs σ for Reduction of Azo Group Depolariser Conc. 2.0 X 10⁻³M pH = 6.5

reduced before the reduction of azo group. The plot of $E_{1/2}$ vs σ in B.R.buffer of pH 6.5 (Fig 3) is found to be linear. The meta and para derivatives fit in the straight line but the ortho derivative deviating from the regression line. This deviation may be attributed to the steric hindrence to coplanarity [12]. The value of specific reaction constant (ρ) for the wave of the azo group was found to be 0.08 V, which is in good agreement with the values reported in the literature [13] for similar systems. The effect of substituents on the reduction of >C=O group was found to be irregular (Table 1). This could be due to the substituents being far removed from the reduction site. However, a change in $E_{1/2}$ values may be attributed to the conjugated system in the series of compounds.

Effect of Double Layer

Ionic Strength

Ionic strength affects double layer and the latter affects the kinetics of the electrode process. In the present case, $E_{1/2}$ (of nitro, azo and carbonyl reduction) do not change in the series of polarograms with 1.0, 1.25, 1.87 and 2.5 M KCl; i_d also remains independent of ionic strength. Mairanovsky [14] has given an expression for $\Delta E_{1/2}$ consisting of two terms- the first depending on the charge of the electroactive species and the second term depending on pH dependence of $E_{1/2}$. Compounds under study are adsorbed at the mercury surface and their pre-protonation is also a surface reaction - they are present chiefly in non-ionised state in bulk; adsorbed species change to protonated form on the surface just before discharge. Thus for all practical purposes, charge on the reacting species may be considered as zero. Thus the first term in Mairanovsky expression for $\Delta E_{1/2}$ becomes unity. The second term could be just cancelling the first resulting in $\Delta E_{1/2} = 0$.

Effect of Solvent Composition

Polarograms are recorded in different percentages (40 - 70 %) of different solvents - DMF and acetonitrile at pH 6.5. It is observed that $E_{1/2}$ shifted towards more negative values with increasing concentration of the solvents. However, i_d decreased. At very high concentration (70 %) of the solvent, waves becomes ill defined. It appeares that it is the protonated species which get discharged on the electrode surface. The increase in solvent results in increase in pH [15] and increase in dissociation constant of the protonated species [16]. Both these factors lower protonation; consequence is the shift in $E_{1/2}$. It appears that these factors are

not the only factors responsible for the observed shift in $E_{1/2}$. The shift observed is greater than the shift expected due to change in pH and the dissociation constant. The extra shift in $E_{1/2}$ may be due to a decrease in adsorbability (and hence surface concentration) of the depolariser with increasing concentration of the organic solvent in aqueous - organic mixture [16]. Decrease in i_d could be due to increase in viscosity of the solvent.

ACKNOWLEDGEMENT

Authors are grateful to UGC, New Delhi for financial assistance to carry out this work.

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