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ELECTROCHEMICAL BEHAVIOUR OF 1-PHENYL-3-AMINO-4-(SUBSTITUTED BENZENEAZO)-PYRAZOLIN-5-ONES IN N,N'-DIMETHYLFORMAMIDE

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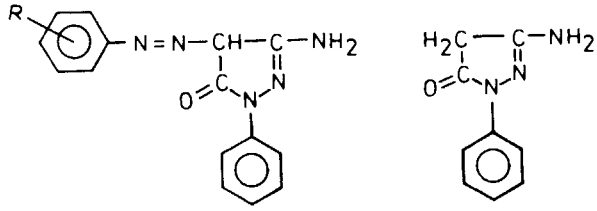
All the compounds exhibited a well-defined 4-electron reduction wave at dropping mercury electrode and one well-defined cathodic peak at hanging mercury dropping electrode in dimethylformamide. The products of electrolysis have been characterised and a plausible mechanism has been suggested. The effect of substituents and its correlation with Hammet substituent constant (σ) have also been studied.

Key Words: Benzeneazo-pyrazolin-5-ones; Dimethylformamide; Polarography; Cyclic Voltammetry

Introduction

Pyrazolin-5-one, pyrazoles and their derivatives possess interesting antidiabetic[1], anticancer[2] and antineoplastic[3] properties. Literature[4-7] survey reveals that little work has been carried out in non-aqueous media. In the present work, the electrochemical behaviour of a series of 1-phenyl-3-amino-4-(substituted benzeneazo)-pyrazolin-5-ones in dimethylformamide has been studied (Fig. 1).



(I)

Experimental

All the compounds are prepared by the literature method[8], purified by repeated recrystallization from acetic acid and characterised by spectral studies. Stock solutions (1.0×10^{-2} M) of the arylazo pyrazolin-5-ones are prepared in AR grade N,N'-dimethylformamide (AR H_2O 0.025%). Dimethylformamide is further purified[9] by distilling over P_2O_5. Tetra-*n*-butylammonium perchlorate

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is purified as required by reprecipitation from acetone-water followed by vacuum drying at room temperature.

Cell

A three compartment cell similar to that described by Kolthoff[10] is used throughout the experiment. The dropping mercury electrode is placed in the middle compartment containing the experiment solution and is separated from the secondary compartment by a No. 4 porosity glass sinter to prevent diffusion of water and potassium chloride from the salt bridge into middle compartment. Both the middle and secondary compartments are filled with the experimental solution. An aqueous saturated calomel electrode is used as a reference electrode and platinum wire is used as a counter electrode.

Apparatus

Polarograms are recorded with CL-25 ELICO, India dc Pen recording Polarograph. The capillary characteristic is 1.80 $mg^{2/3}\ s^{-1/2}$. The temperature of the solution is kept constant at $30 \pm 0.1°$. The cyclic voltammeter consists of *X-Y* recorder (Model RE 0074), PAR 173 Potentiostat and PAR 175 Universal Programmer. A hanging mercury (SMDE 303) drop electrode with drop area of 0.0096 cm^2 is used as the working cathode.

Procedure

Polarograms of all these compounds at concentration 1.0×10^{-3} M are recorded in dimethylformamide solution containing 0.10 M tetra-*n*-butylammonium perchlorate (TBAP). The dissolved oxygen is removed by passing purified nitrogen gas for about 30 minutes.

Results and Discussion

a. Polarography

1-Phenyl-3-amino-pyrazolin-5-one (I) has failed to exhibit a polarographic wave. Hence, the waves that are observed in 1-phenyl-3-amino-4-(substituted benzeneazo)-pyrazolin-5-ones are attributed to the polarographic reduction of *exo*-cyclic *azo* group. All the compounds exhibited a single reduction wave at DME. The nature of the wave is diffusion controlled as shown by the linear dependence of limiting current on square root of the mercury column height and the concentration of the depolariser. The diffusion controlled nature of the wave is confirmed by the low temperature coefficient (1.0-1.6% deg^{-1}, cf. Table I). The irreversible nature of the wave is established by semi-log plot and by shift of $E_{1/2}$ towards more negative potentials with increasing concentration of the depolariser.

Polarographic Behaviour of Nitro Compounds: In contrast to the reduction behaviour of the other compounds of the series, the nitro substituted compounds exhibited three waves. In general the *nitro* group undergoes reduction at more negative[11] potentials than the *azo* group. The first wave at less nega-

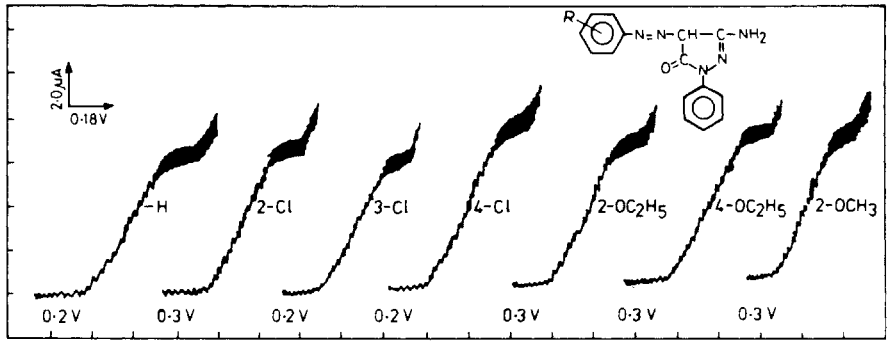


Fig 1 Polarograms of 1-phenyl-3-amino-4-(substituted benzeneazo)pyrazolin-5-ones (1×10^{-3} M) in N,N'-dimethylformamide

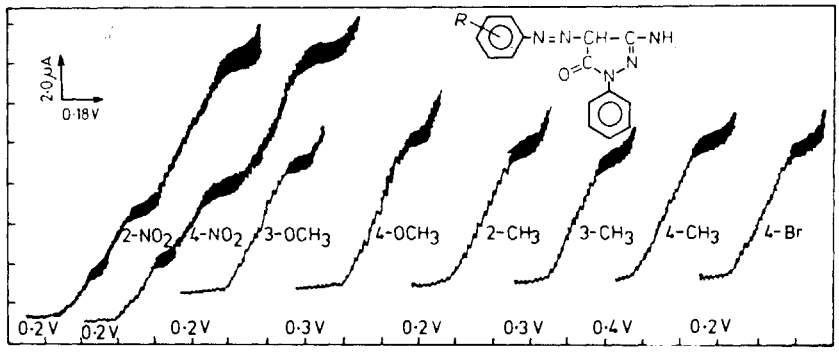


Fig 2 Polarograms of 1-phenyl-3-amino-4-(substituted benzeneazo)pyrazolin-5-ones (1×10^{-3} M) in N,N'-dimethylformamide

Table I

Effect of temperature on the polarographic characteristics of 1-*phenyl*-3-*amino*-4-(*benzeneazo*)*pyrazolin*-5-*one*
[Concentration] = 1×10^{-3} M

Temperature K	$-E_{1/2}$ *V* vs *SCE*	Limiting current μA	Temperature coefficient % deg^{-1}	αn_a	$D \times 10^6$ cm^2 sec^{-1}
303	0.58	6.3	—	0.60	1.4
313	0.62	7.2	1.30	0.55	1.6
323	0.65	8.3	1.41	0.49	1.9
333	0.70	9.6	1.45	0.46	2.2

tive potential is attributed to the reduction of the *azo* group. The second wave is therefore ascribed to the reduction of the *nitro* group. The third wave is attributed to the reduction of the compound formed in the interaction between the products formed in the electrode reactions responsible for the first and the second waves.

b. Cyclic voltammetry

Cyclic voltammetry at the HMDE showed that the compounds exhibit one well defined cathodic peak. However, *nitro* substituted arylazo pyrazolin-5-ones exhibit three cathodic peaks. The results are presented in Table II and ty-

Table II

Polarographic and cyclic voltammetric characteristics of 1-*phenyl*-3-*amino*-4-(*substituted benzeneazo*)*pyrazolin*-5-*ones in N,N-dimethylformamide*
[Concentration] = 1×10^{-3} M

S.No.	Polarographic characteristics						Cyclic voltammetric characteristics		
	R	$-E^{1/2}$ *V* vs *SCE*	i_d μA	$I^* \times 10^3$	αn_a	$D \times 10^6$ $cm^2\ sec^{-1}$	Sweep rate VS^{-1}	$-E_{pc}$ *V*	i_{pc} μA
I	-H	0.58	6.3	3.5	0.60	1.40	0.100	0.71	2.2
II	2-Cl	0.63	6.5	3.6	0.63	1.48	"	0.70	1.8
III	3-Cl	0.50	5.9	3.3	0.63	1.48	"	0.59	2.1
IV	4-Cl	0.53	7.3	4.0	—	—	"	0.62	1.7
V	2-OC_2H_5	0.62	6.4	3.5	0.63	1.46	"	0.71	1.8
VI	4-OC_2H_5	0.66	6.7	3.7	0.60	1.51	"	0.75	1.8
VII	2-OCH_3	0.57	6.5	3.6	0.63	1.48	"	0.66	2.0
VIII	3-OCH_3	0.59	6.2	3.4	0.60	1.61	"	0.68	2.0
IX	4-OCH_3	0.69	7.1	3.9	0.59	1.62	"	0.76	2.1
X	2-CH_3	0.56	6.7	3.7	—	—	"	0.65	1.5
XI	3-CH_3	0.60	6.1	3.4	0.60	1.57	"	0.72	2.0
XII	4-CH_3	0.64	6.8	3.8	0.64	1.55	"	0.74	2.1
XIII	4-Br	0.50	6.5	3.6	0.59	1.48	0.100	0.62	1.9
XIV	2-NO_2	0.47	2.4	—	—	—	"	0.56	1.7
		0.67	3.0	—	—	—	"	0.75	1.7
		0.98	7.3	—	—	—	"	1.20	2.6
XV	4-NO_2	0.50	3.0	—	—	—	"	0.63	1.9
		0.71	3.5	—	—	—	"	0.84	1.9
		1.10	7.1	—	—	—	"	1.29	2.9

$I^* = i_d/cm^{2/3}t^{1/6}$

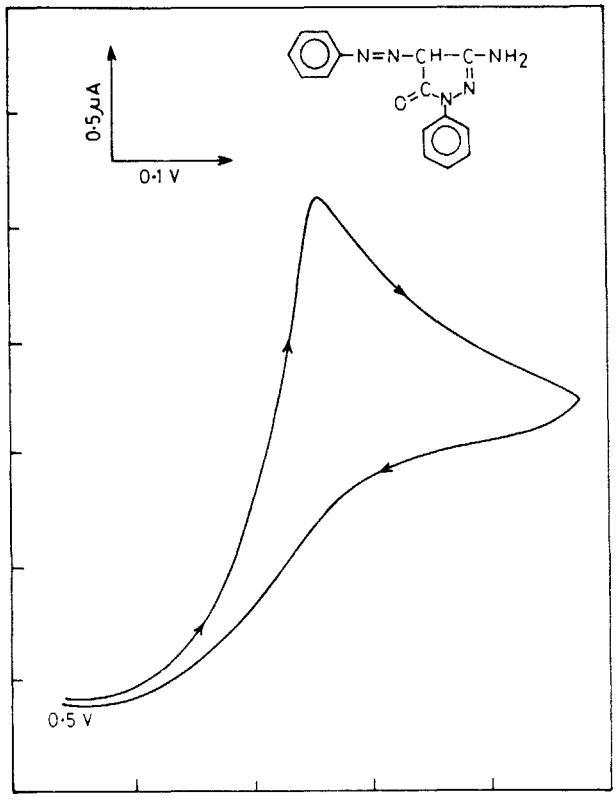


Fig 3 Cyclic voltammogram of 1-phenyl-3-amino-4-benzeneazo)pyrazolin-5-one (1×10^{-3} M) in N,N'-dimethylformamide, Sweep rate 0.100 VS^{-1}

pical cyclic voltammogram of 1-phenyl-3-amino-4-(benzeneazo)pyrazolin-5-one is shown in Fig. 3 recorded at a sweep rate of 0.100 VS^{-1}. The reduction is shown to be diffusion controlled by the linear plots of peak current, i_p versus $v^{1/2}$ passing through the origin. The cathodic peak potentials shifted towards negative potentials with increase in scan rate. This indicates the irreversible electron transfer process. The absence of anodic peak in the reverse scan under the experimental conditions, further supports the irreversibility of the electrode process.

c. Coulometry

The millicoulometric method of Devries and Kroon[12] using mercury pool in employed for determining the value of *n*. The number of electrons involved in the reduction is established to be 4 and the results are presented in Table III. Azobenzene in dimethylformamide is used as the standard.

d. Controlled Potential Electrolysis

(*i*) For controlled potential electrolysis (CPE) experiments a cell similar to that described by Manousek and Zuman[13] together with the PAR 173 Poten-

Table III

Millicoulometric data on 1-phenyl-3-amino-4-(benzeneazo)pyrazolin-5-one and azobenzene in N,N-dimethylformamide
[Concentration] = 1×10^{-3} M
Volume = 0.6ml

Current (μA)	Time (sec)	*n*-Value
Benzeneazo pyrazolin-5-one		
6.30	0	—
5.80	3600	3.9
5.10	7620	3.9
4.70	10800	4.0
Azobenzene		
3.20	0	—
2.90	3600	2.0
2.60	7620	2.0
2.40	10800	2.0

tiostat is used. This cell can hold upto 50ml of solution. It consists of three compartments: (*a*) Pool electrode, (*b*) Reference electrode (SCE) and (*c*) auxilliary platinum electrode which are separated by sintered glass disc of porosity *G* covered with a thin layer of agar-agar. The cathode compartment is filled with 10ml of 0.01 M 1-phenyl-3-amino-4-(benzeneazo)pyrazolin-5-one. 10 ml of 0.10 M tetra-*n*-butylammonium perchlorate and 30ml of dimethylformamide. The potential is controlled at the value corresponding to the limiting current plateau of the cathodic wave as taken from their polarograms under the same experimental conditions. The experiment is carried out twice at a controlled potential of -1.10 V (limiting current plateau of the wave). The progress of electrolysis is followed by recording the decrease in current with time and the number of electrons per molecule is computed from *i-t* curves following the procedure outlined by Lingane[14] and found to be 4*e*. After disconnecting electrolysis cell, 1ml of resulting solution is withdrawn and presence of aniline in the solution is revealed by standard spot test[15]. The remaining reaction mixture is partially evaporated on a water bath to half its volume, allowed to cool to room temperature and extracted with ether. The ether layer is evaporated in vacuo and the remaining yellow crystals are identified as 1-phenyl-3,4-diamino-pyrazolin-5-one ($C_9H_{10}N_4O$).

	Carbon %	Hydrogen %	Nitrogen %
Found	55.65	5.60	29.14
Calcd.	56.84	5.26	29.48

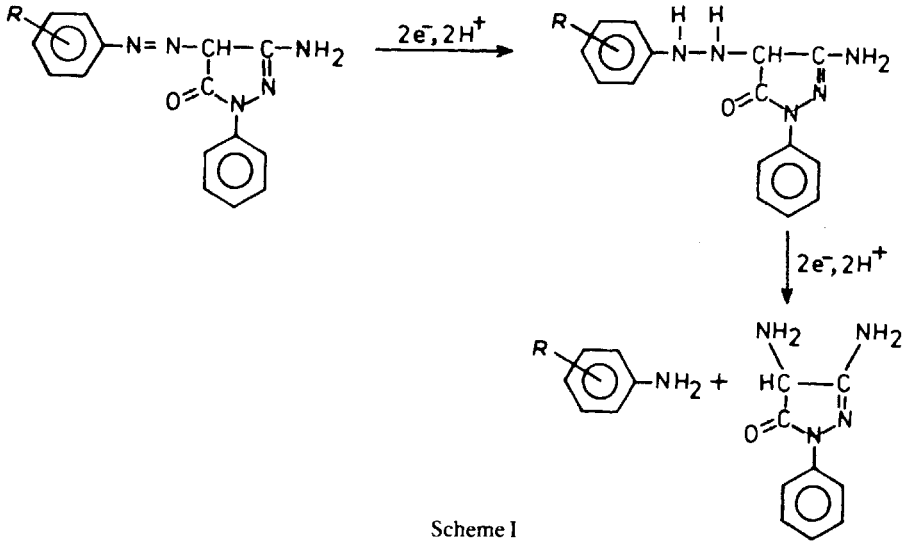
ν_{max}^{KBr} 1630cm^{-1} ($-C=O$ cyclic), 1210cm^{-1} ($-N-C_6H_5$); 1460 and

1495cm^{-1} (five membered heterocyclic ring); 3450 and 3320cm^{-1} (−NH stretching vibrations for primary amine).

(ii) Controlled potential electrolysis is also carried out with 1-phenyl-3-amino-4-(4′-nitrobenzeneazo)pyrazolin-5-one. The potential is controlled at the value corresponding to the plateau of the more positive wave. After electrolysis, the resulting solution is extracted with ethyl acetate and the ethyl acetate extract is chromatographed on thin layer silica gel plates using benzene-methanol 4:1 (V/V) solvent. The extract exhibits two spots with R_f values 0.51 and 0.61. The products corresponding to these R_f values 0.51 and 0.61 are identified as *p*-nitroaniline and 1-phenyl-3,4-diamino-pyrazolin-5-one respectively by comparing with authentic samples.

Mechanism

Based on the foregoing results, the mechanism shown in Scheme I is suggested for the electro reduction of 1-phenyl-3-amino-4-(substituted benzeneazo)pyrazolin-5-ones.



Scheme I

Substituent Effects

A linear correlation between the half-have potential and the Hammett substituent constants (σ) is obtained as shown in Fig. 4. The *ortho* substituted derivatives deviate from the linear plot. This deviation of ortho derivatives may be attributed to the steric hindrance to the coplanarity[16,17]. The value of specific reaction constant (ρ) is found to be 0.26 V, which is in good agreement with the values reported in the literature for similar systems[18].

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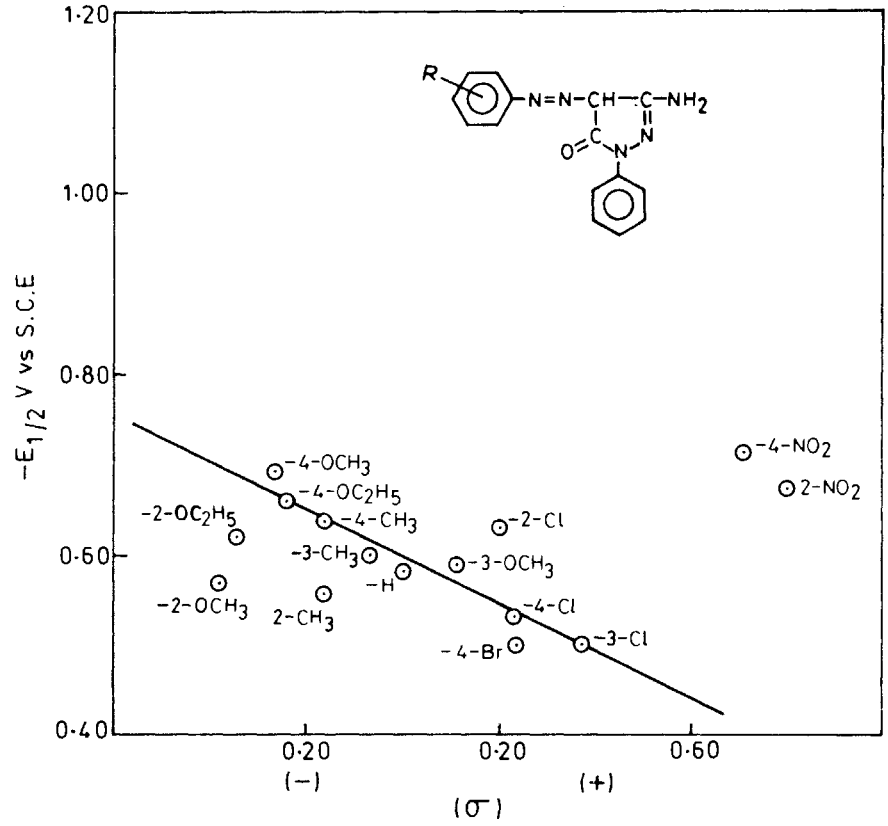

Fig 4 Plot of $E_{1/2}$ *versus* σ

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