ELECTROREDUCTION OF SOME ARYLAZOMETHINE PYRAZOLONES

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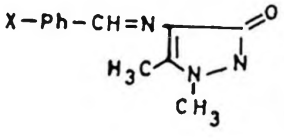
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DC polarography measurements with some 2,3-dimethyl-1-phenyl-4-(phenylazomethine)-3-pyrazolin-5-one and some of its derivatives show a single 4e, diffusion-controlled, irreversible wave in 30% ethanolic B.R.buffer, (pH < 8) while in strongly alkaline solutions (pH ≥ 10) a single 2e wave is observed. For m-and p-chloro derivatives, two single-electron waves are obtained. The voltammograms of these compounds at different sweep rates show two peaks in the cathodic scan in neutral or alkaline media, corresponding to two reduction steps.

In recent years the electrochemical reduction of hydrozones and azomethines was the subject of several investigations [1-5]. The reduction of arylhydrazones in buffered acidic media proceeds by a four-electron mechanism.

The present work deals with the polarographic and cyclic voltammetry studies of some arylazomethinepyrazolone compounds.

The compounds included in the present work have the general formula



x = H (I), p-OCH_3(II)
p - OH(III), p-$N(CH_3)_2$(IV).
m - Cl(V), p-C1 (VI)

The structural effects on the electrode process proper and the different kinetic parameters are discussed.

EXPERIMENTAL

Preparation of Organic Materials

Arylazomethinepyrazolone compounds under investigation were prepared by the method recommended for hydrazone and Schiff bases [7]. For this purpose, 4-aminoantipyrine was refluxed with the required quantity of the aldehyde derivatives in ethanol. On allowing the reaction mixture to cool, the solid separated out which was then filtered and recrystallized several times from ethanol and preserved in a desiccator over silica gel.

Voltammetric Measurements

The polarograms were recorded using a SARGENT WELCH Polarograph Model XVI. The characteristics of the capillary in 0.1 M KCl at open circuit was m = 1.7 mg/s, at h = 30 cm and t = 5 second per drop.

Polarographic Analyzer model 264 A (PARC) and SMDE electrode assembly (303 A) in HMDE mode (area = 2.6 x 10^{-2} cm^2) with Ag/AgCl (ref. electrode) and Pt counter electrode were used for cyclic voltammetry. The curves were recorded an a X-Y recorder model RE 0089 (Houstan instruments).

Solutions were prepared by mixing 2 ml ethanol, 5 ml of appropriate modified Britton Robinsons buffer [7] and calculated amount of depolarizer stock solution to give the final solution with 0.25 mM depolarizer. The pH of this was measured using orion pH meter model 901 with sensitivity of ± 0.05 pH. Polarograms and cyclic Voltammograms are recorded.

The number of electrons consumed in the overall reactions is measured by controlled potential coulometry using the system 380 PARC.

All experiments were carried out at 25° ± 1 C°.

The $E_{1/2}$ were measured graphically.

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RESULTS AND DISCUSSION

DC Polarography

The aryl azomethine pyrazolone (I-IV) in acidic media (pH < 6.01) do not show any defined reduction waves. Here H_2 evolution preceeds all other reductions. In media of higher pH, the polarogram consists of single reduction step (Fig. 1). The limiting current decreases gradually with increase in pH in the range of pH 8-10. Finally at pH > 10 the diffusion current is nearly half of its value at lower pH. Limiting currents at different heights of mercury column satisfies the relationship $i_l = K h^x$ with x varying in the range 0.32-0.75. Further i_d vs C in the concentration range 0.067-0.42 mM is linear and passes through the origin. All these indicates the waves are diffusion controlled.

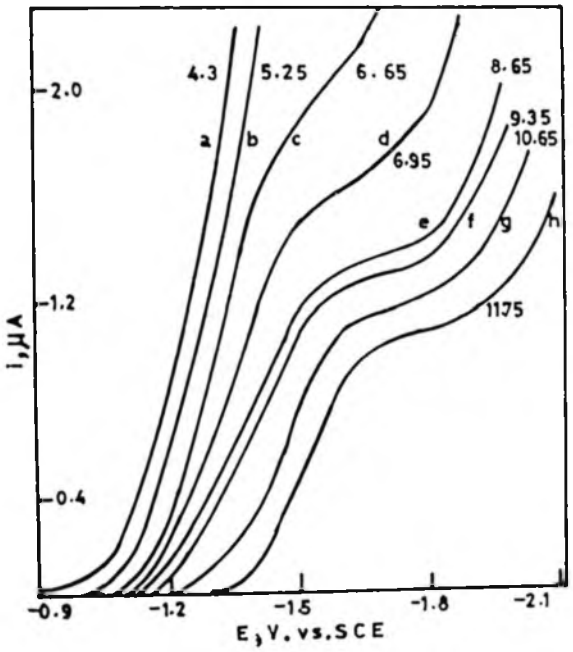


Fig. 1 Polarograms of the parent pyrazolone. Different pH values are marked on the curves.

The number of electrons used up in the overall reaction is shown to be 4 by coulometry. The TLC of the etherial extract of the completely electrolysed solution in slightly acidic medium shows that toluene or its corresponding derivatives is one of the main products indicating a cleavage of -C=N- bond through the uptake of 4 electrons.

In solutions of pH < 8, the reduction is through the uptake of 4 electrons. At pH > 10, the reduction corresponds to 2 electrons.

The polarograms for m-and p-chloro derivatives (V and VI), consist of two waves of almost equal height and the height of each wave corresponds to 2 electrons in slightly acidic or neutral solutions, whereas each of the two waves corresponds to one electron only in strong alkaline ones.

It is observed that with increase of pH, the $E_{1/2}$ shifted towards more negative potentials (Fig.2) indicating that proton transfer is preceeding the electrode process. The number of protons (Z_{H^+}) involved in the rate determining step was determined from the value of the slope if $E_{1/2}$ vs pH plot and was found to be 1 (Table 2).

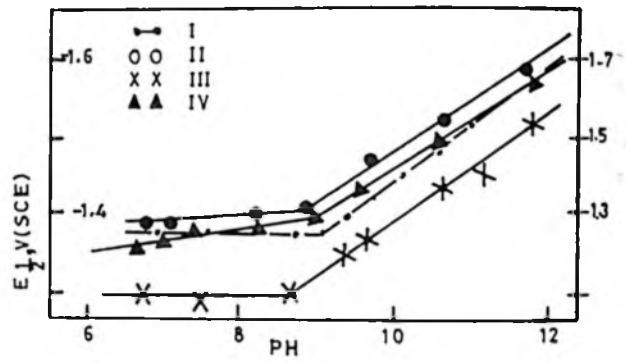


Fig. 2 The variation of half wave potential with pH.

The polarographic waves are found to be irrevesible as seen by the log plot analysis. The most probable value of α was obtained assuming n_α = 1 (Table 2). The irreversible nature is also confirmed by cyclic voltammetry.

Cyclic Voltammetry

The cyclic voltammograms of the compounds under investigation in neutral and alkaline media at different sweep rates (20-200 mV/S) show two peaks in the cathodic scan (Fig.3) and do not show any anodic peaks in the reverse scan, which indicates the irreversible nature of the reduction waves. This is further confirmed from the shift of peak potential (E_p) to more negative values with increasing sweep rate.

Using the number of electrons (n) consumed in the overall reduction process as calculated from coulometric measurements and values of the diffusion coefficient calculated by the

TABLE 1

DATA OF CONTROLLED POTENTIAL COULOMETRY MEASUREMENTS FOR ARYLAZOMETHINEPYRAZOLONES COMPOUNDS.

Compound	pH	Applied potential	Number of Electrons (n)
(I) Parent	6.9	-1.35	3.75 ≃ 4
0.72 mg	11.5	-1.65	1.68 ≃ 2
(II) p-OCH	7.1	-1.4	3.65 ≃ 4
0.208 mg	11.5	-1.65	1.87 ≃ 2
(III) P-OH	6.9	-1.39	4.19 ≃ 4
0.38 mg	11.5	-1.70	1.42 ≃ 2
(IV) p-$N(CH_3)_2$	7.1	-1.4	3.68 ≃ 4
0.208 mg	11.5	-1.65	1.87 ≃ 2
(V) m-Cl	7.1	-1.4	3.7 ≃ 4
0.2 mg	11.5	-1.55	1.85 ≃ 2

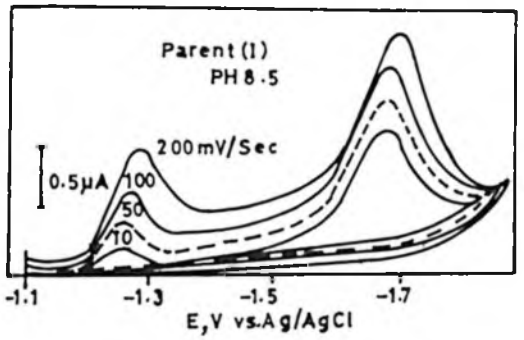


Fig. 3 Cyclic voltammograms at different scan rates.

aid of Ilkovic equation[9], the values of αn_a and heteterogeneous rate constants (k°_{fh}) were calculated from cyclic voltammetric data using the following equation [10], where all the terms have their usual significance,

$$E_p = (RT/\alpha n_a F)\,[\ln(k^{\circ}_{fh}/D^{1/2}) - \ln(\alpha n_a \nu)^{1/2} - 1.14]$$

Based on the above considerations, the mechanism of the electrode reaction of arylazomethinepyrazolones, may be proposed as shown in scheme (I)

a) In neutral and slightly acid solutions :

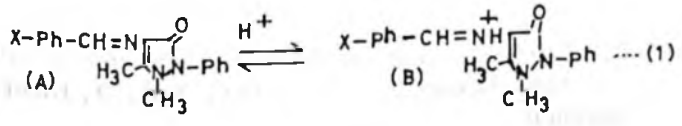


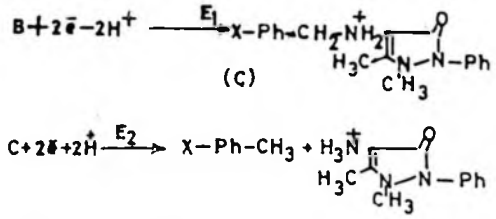
TABLE 2

POLAROGRAPHIC DATA OF ARYLAZOMETHINE PYRAZOLONE COMPOUNDS IN MEDIUM AQUEOUS ETHANOL

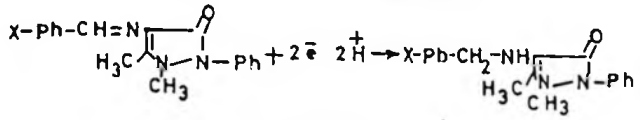
Temp. 25°

pH	$E_{1/2}$,	Slope mV		Z_{H^+}	αn_a
		S_1	S_2		
2,3-dimethyl-1-1-pheny1-4-(phenylazomethine)-3-pyrazoline-5-one(I)					
6.95	-1.365	75	93	0.81	0.635
8.65	-1.395	75	67	1.12	0.778
00.65	-1.510	75	77	0.97	0.768
2,3-dimethyl-1-pheny1-4-(p-methoxyphenylazomethine)-3-pyrazoline-5-one (II)					
7.0	-1.395	81	83	0.98	0.712
8.8	-1.410	81	86	0.95	0.687
10.45	-1.540	81	105	0.77	0.563
2,3-dimethy1-1-pheny1-4-(p-hydroxyphenylazomethine)-3-pyrazolin-5-one (III)					
6.85	-1.395	72	83	0.87	0.710
8.55	-1.410	72	84	0.86	0.704
10.50	-1.560	72	105	0.67	0.563
2,3-dimethy1-1-pheny1-4-(p-dimethylaminophenylazomethine)-3-pyrazolin-5-one (IV)					
7.35	-1.380	92	96	0.85	0.616
8.85	-1.380	82	109	0.75	0.542
10.50	-1.510	82	89	0.92	0.664
2,3-dimethy1-1-pheny1-4-(m-chlorophenylazomethine)-3-pyrazoline-5-one (V)					
6.70	-1.020	76	92	0.83	0.640
	-1.230	75	109	0.67	0.542
8.65	-1.150	76	72	1.06	0.813
	-1.320	75	91	0.82	0.650
9.85	-1.260	76	62	1.23	0.960
	-1.420	75	89	0.84	0.660
2,3-dimethy1-1-pheny1-4-(p-chlorophenylazomethine)-3-pyrazoline-5-one (VI)					
6.75	-1.050	81	109	0.74	0.542
	-1.260	93	100	0.93	0.591
8,65	-1.185	81	100	0.81	0.591
	-1.465	93	90	1.03	0.621
9.65	-1.260	81	94	0.86	0.628
	-1.500	93	89	1.04	0.664

Substituents Effect



(b) In strongly alkaline solutions:



(Scheme 1)

TABLE 3

CYCLIC VOLTAMMETRIC DATA FOR SUBSTITUTED PYROZOLONES (pH 8.5, VOLTAGE SWEEP RATE 0.1 V/S, CONCENTRATION OF DEPOLARIZER = 0.1 mM. (a) 1ST PEAK, (b) 2ND PEAK.

Compound		E_p, V vs. Ag/AgC1	αn_a	$k^o_{f,h}$, cm/S
Parent (I)	a	-1.28	0.297	1.3×10^{-16}
	b	-1.960	0.535	1.42×10^{-17}
p-OCH_3 (II)	a	-1.35	0.340	6.58×10^{-16}
	b	-1.70	0.460	1.25×10^{-16}
p-OH (III)	a	-1.59	0.342	1.91×10^{-16}
	b	-1.78	0.454	1.22×10^{-16}
p-$N(CH_3)_2$ (IV)	a	-1.38	0.350	7.51×10^{-17}
	b	-1.70	0.520	6.58×10^{-18}
m-C1 (V)	a	-1.26	0.310	7.8×10^{-17}
	b	-1.68	0.580	6.4×10^{-18}
p-C1 (V1)	a	-1.27	0.278	7.91×10^{-17}
	b	-1.695	0.570	5.48×10^{-18}

In cases of compounds I to IV, in slightly acidic or neutral media, the potentials $E_1 \simeq E_2$ so that the reduction occurs through a single 4e reduction wave.

The most reliable values of $E_{1/2}$ at selected pH (pH ≃11) have been correlated with Hammett's [8] values as tabulated by Ritchie and Sagar [11]. Statistical treatment of the data was made using Jaffe calculations [12]. The data showed that the plot of $E_{1/2}$-σ (Fig.4) has a reasonable linearity with small $+\rho_{\pi,R}$ value (0.11). The evidence gathered from the above data supports the mechanism suggested in scheme (1) for the reductions of arylazomethine pyrazolone compounds (I-VI). Thus, on the basis of scheme (1) it would be anticipated that electron withdrawing groups would decrease the basicity of the unprotonated nitrogen atom linked to the pyrazolone moiety and consequently promote the reaction

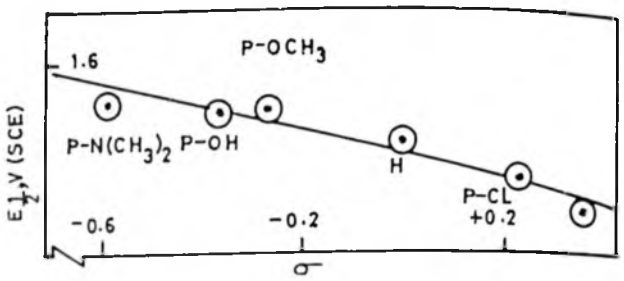


Fig. 4 Variation of half wave potential with Hammet constant

centre. However, the effect of groups on the reaction center was weak as realised from small $\rho_{\pi,R}$ value.

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