Polarographic Behaviour of Some Sulphonic-aryl-hydrazono Pyrazolin-5-one Dyes

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Summary: Polarographic studies of some sulphonic aryl (or napthol) hydrazono -1-phenyl-3-methyl-2-pyrazolin-5-one have been carried out in 10% ethyl alcohol B.R. buffer solutions in the pH range 1.8 - 12.0. The number of reduction waves was found to depend on the pH value of the solution and the structure of the dye stuff. All the compounds gave a single, well defined irreversible wave between pH values 2.0-9.0. The $\rm E_{l_2}$ of this wave is pH dependent but its identification almost constant throughout the entire pH range. The $\rm E_{l_2}$ was shifted towards more negative potential showing that protonation preceeds reduction. The sulphonic group causes a shift of the wave and plateau suffers a minimum at pH value higher than 9.0. The reduction corresponds to consumption of four electrons leading to the amine stage. A general mechanism for the reduction process is suggested and discussed.

Introduction

Pyrazolone and pyrazolin-5-one possess interesting antidiabetic [1-3] antineoplastic activity [4]. In view of the fact that the physiological activity of a molecule is closely related to its redox behaviour [5] in the cell membrane, therefore the study of some sulphonic arylhydrazones pyrazolin-5 -one dyes were investigated at d.m.e. As a simple relationship exists between structure, half wave potential and reactivity, a better understanding of the effect of structure on the redox behaviour of these compounds can be obtained [6]. The present work summarises the electrochemical behaviour of some sulphonic aryl hydrazono-pyrazolin-5 -one dyes with special reference to the effect of sulphonic group on their redox mechanims.

Materials and Methods

The organic ligands used in the present investigation were prepared as mentioned previously [7] by coupling the diazonium salts of 4-,3- and 2-sulphonic (4-methyl) acid compounds with pyrazolin-5-one in sodium acetate medium. Also, 2-hydroxy (4-sulphonic) naphthalene hydrazono -pyrazolin-5-one ligand was prepared by the same method [7]. The resulting dyes were recrystallized from the appropriate solvents. Elemental analysis and IR spectra confirmed the structure and purity of the compounds.

The stock solutions (0.01 M) of these compounds were prepared in 50% ethanol-50% water mixture (v/v). The

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$$R - N - N = C - C - CH_3$$

$$H \downarrow \qquad \downarrow \qquad \qquad \downarrow$$

$$C \qquad N$$

$$C \qquad N$$

$$C \qquad N$$

$$C \qquad 0$$

$$C \qquad 0$$

$$C \qquad 0$$

$$C \qquad 0$$

(4-Aryl-hydrazons, 1-phenyl-3-methyl pyrazolin-5-one)

(II)
$$R = C_6H_5$$
, (III) = $(2-SO_3Na, 4-CH_3) C_6H_3$, H_3C-

$$SO_3Na$$
(III) = $(3-SO_3Na) C_6H_4$, NaO_3S
(IV) = $(4-SO_3Na) C_6H_4$, NaO_3S

Britton Robinson buffers were prepared as described before [8]. The appropriate buffer solution (8.75 ml), ethanol (0.75 ml), (0.25 ml) gelatin 0.5% and dye solution (0.5 ml) were mixed in a polarographic cell. The solution was deoxygenated with purified nitrogen gas for 10 min, the gas allowed to pass over the surface on the solution and the polarograms was recorded.

All chemicals used in the present investigation are of A.R.grade, polarograms were recorded on a recording polarograph LP 60a. Perkin-Elmer 550S recording spectrophotometer was used for the u.v. and visible spectra. WTW digital pH meter 520 with combined electrode was used for measuring the [H] concentration.

The capillary used in the polagraphic study has the following characteristics, in oxygen-free universal buffer

in open circuit, $(m = 9 \times 10^{-3} g/drop, t=5.217 \text{ sec/drop at mercury height of } 45 \text{ cm})$.

Results and Discussion

The polarographic reduction of some dyes having the pyrazolin-5-one moiety was studied at d.m.e. in 10% ethanol universal buffer solutions, (except in case compound (1), 60% ethanol was used), covering pH range (1.8 - 12.0). The half wave potential $(E_{\frac{1}{2}})$ and the limiting current $(i_{\frac{1}{2}})$ for these compounds at different pH values are given in Table-1. The effect of the variation of pH on the half wave potential is represented in Fig. 1.

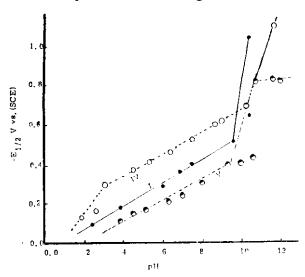


Fig. 1: Relation between $E_{\frac{1}{2}}$ and pH of different dyes in universal buffer solutions. (I) \longrightarrow PHP (IV) \longrightarrow 4-SPHP (V)- \bigcirc -2-OH(4-S) NHP

The polarographic behaviour of the compounds studied can be classified into three categories according to the number of waves in the polarogram and the structure of the organic dyes.

(1) The first cateogry: comprises the dye (I) without sulphonic group [phenylhydrazono-pyrazolin-5-one,

Table-1: Effect of pH on E and i of 0.5 mM. Organic Dye Solution 0.02% Gelatin in 10% Ethanol-Water at different pH's of Universal Buffer Solution.

PHy(1)						2-S(4-Me)PHP(II)				2-(OH)4-5 NHP(V)*				
			ana					on _a				·	αn _a	
pH	£ ¹² (A)	i _d / A	analysis	Tomas	рH	E ₁₅ (V)	i _d A	analysis	Tomas	pH	-E ₁ (V)	i _d A	analysis	Tomas
2.40	0.09	4.80	0.71	0.54	1.60	0.20	4.00	0.55	0.34	3.80	0.12	5.30	0.69	
3.85	0.18	4.75	0.71	0.90	2.10	0.14	4.80	0.34	0.34	4.50	0.16	5.40	0.69	-
6.00	0.35	4.80	0.95	0.90	2.80	0.34	4.35	0.35	0.34	5.15	0.17	4.90	0.88	-
5.80	0.39	4.90	0.54	0.90	3.40	0.40	4.70	0.31	0.32	6.40	0.21	5.40	0.79	0.90
7.50	0.42	4.95	0.78	0.83	4.40	0.42	4.15	0.57	0.49	7.00	0.24	5.45	0.79	0.90
8.60		4.25	0.77	0.83	5.40	0.46	4.25	0.57	0.45	8.00	0.31	5.20	0.82	0.54
9.60	0.52	5.40	0.50	0.54	6.40	0.46	3.73	0.74	0.54	9.35	0.41	5.05	1.28	0.45
			0.40	0.54	7.30	0.47	3.80	0.53	0.68					
10.4	0.66	3.10			8.40	0.47	4.05	0.69	0.49	10.10	0.42	4.10	0.65	0.45
	1.05	1.10	-	-	9.00	0.55	4.10		0.54		0.84	3.25	0.77	0.77
					9.60	0.60	4.20	0.69	0.49					
										10.70	0.45	3,20	0.63	0.90
											0.82	3.70	-	0.45
					10.40	0.62	3.72	0.31	0.54		_			
						1.33	1.00	0.56	-	11.60	0.47	0.65	-	-
											0.83	4.35	0.82	0.68
					12.00	0.62	1.15	0.71			**			
						1.08	3.05	0.31	0.41	12.00	0.81	3.75	0.69	0.60

Parameter of Ist wave (A_1) , Parameter of 2nd wave (A_2) , + Concentration of (V). 0.1 mM.

(PHP)] whose polarogram consists of one reduction wave. The $E_{\frac{1}{2}}$ of this wave shifted towards more negative potentials on increasing the pH values as shown in Fig. (2a) and Table-1. A new ill defined second wave appeared at pH value 10.40.

(2) The second category comprises the compounds having sulphonic group in phenyl ring (compounds II-IV) whose polarograms consist of one well defined wave (A₁) at pH range (1.8-9.0). At

pH 9.0, a new reduction wave begins to appear accompanied with a distortion of the plateau by the appearance of a minimum. The hump followed by the minimum through the reduction polarograms takes its characteristic shape in case of compounds II, III and IV at negative potential ranges between (0.7 - 1.2), (0.9 - 1.4) and (0.8 - 1.2) V., vs. SCE and at pH values 10.4. 9.0 and 9.6 respectively. As a result of this behaviour (hump followed by a minium), a shifted rising portion leads to the formation of a new wave (A₂). The height of the first part

(A1) decrease while that of the second part (A2) increases with increasing pH, of the solutions (Fig. 2b).

(3) The third category is that of compound (V) which has a napthol moiety and is different from the previous category in that its polarogram consists of one reduction wave at pH values between (3.8-8.0) and at potential range (0.0 to 0.4V) vs. SCE. Increasing pH from 8.0 to 11.6, the polarogram has a hump followed by a minimum at potential range (-0.7 to - 10.0 V)similar to that observed SCE through the second category was also obtained (Fig. 2 b,c). This characteristic behaviour may be attributed to the presence of sulphonic group in the dye stuff compounds (II-IV).

It is clear from (Fig. 2c Table 1) that the height of the first wave decreases while that of the second wave increases with the variation of pH from 8.0 to 11.6. Polarogram at pH 12 differs from those in the second categories as in this pH range the polaro-

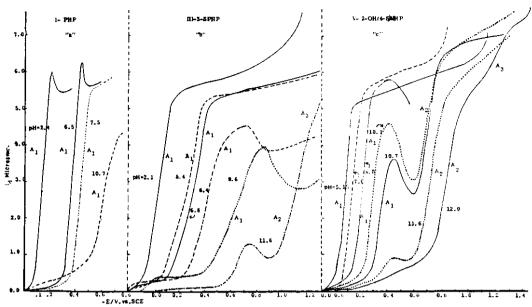


Fig.-2: Polarographic behaviour of I, II and V dyes at different pH's.

gram begins to split into two due to the ionization of hydroxyl group; the first wave nonionized species and the second wave $(E_{\frac{1}{2}}1.16 \text{ V.vs. SCE})$ for ionized species.

It is interesting to note that the half wave potential of the first wave obtained in case of compounds (II-V) shifts to more negative values (i.e. retarding effect) at high pH. This retarding effect was noticed in the case of compounds (II, III and IV) at pH values 9.0, and pH 8.0 for compound (V), (Fig. 2b and c). The splitting of the single wave into (A1 and A2) which may be due to nonionized-ionized forms or due to retardation of reduction due to adsorption of certain species. Since the values of id in acid medium about equal the summation of id of both waves in alkaline (Table-1). Therefore, medium number of electrons consumed in both media are equal, thus favouring adsorption of certain species. The presence of a hump followed by a minimum and then a rising portion (A_1) indicates that the reduction is hindered on the covered areas of the drop and unhindered on the bare portions [9]. The adsorbed species are the sulphonate anions probably associated with [10, 11] the buffer cation. It is clear now that the reduction behaviour of compound (I), (without sulphonic group) is not similar to that of the other dyes investigated (compounds II-V). The polarographic reduction obtained through the investigation of these compounds is similar to that obtained previously during the reduction of some 3-pyridyl azo dyes containing sulphonic group [9].

The half wave potential $(E_{\frac{1}{2}})$ vs.pH plots for the reduction waves obtained denote that hydrogen ions are consumed in the electrode process. The logarithmic analysis of the polarographic waves are linear plots with slopes amounting 0.07 to 0.18 denoting that the electrode process proceeds irreversibly. The effect of the mercury height (h) on the limiting current (i_d) for the investigated compounds at different pH values was studied. The plot of log (i_d) vs. log h is linear

with slopes ranging between 0.20 to 0.40 for the first and second waves indicating that these waves are almost kinetically controlled. Plots of the limiting current of the wave vs. molar concentration of the depolarisers are linear passing through the origin, indicating the validity of Ilkovic equation.

Mechanism of the electrode process

The organic ligands studied contain different groups liable to reduction at d.m.e. such as hydrazono-group and the carbonyl group of pyrazolin-5 -one moiety. The compounds (I-V) listed in Table-1 gave a single four electron reduction wave in B.R. solutions in the pH 2.8-12.0. This reduction was confirmed by comparing the height of the wave with that obtained with reduction of the azo benzene or the wave of reduction of Zn(II) which are known as four and two electrons respectively. The height of the wave is approximately constant in the pH range of investigation (Table-1). This is not in accordance with the fact that the reduction of azo compounds involved four and two electrons in acid and in alkaline solutions respectively [12]. Meanwhile Millefiori [13] found that the reduction of the azo compounds involved four electrons in both acid and alkaline media. Addition of pyrazolin-5-one through the reduction of the studied azo compounds does not affect the height of the wave. Moreover, the authors found that, pyrazolin-5-one itself is not reduced in the B.R. buffer solution.

The plots of $E_{\frac{1}{2}}$ vs pH for the compounds (II-IV) were linear with slopes ranged between 0.11 up to 0.14 till pH 3.4. Therefore a gradual change in $E_{\frac{1}{2}}$ to more negative values was also observed at higher pH's but the values of the slopes of the linear plots were smaller (Fi.g 1). The irreversible

nature of the waves was confirmed by log-log plots and shift of $E_{\frac{1}{2}}$ towards more negative potential with increasing concentration of depolarizer [14].

Since the half wave potentials of these pyrazolin-5-one were pH dependent and the limiting current pH independent, through the range of pH studied, it was concluded that both acidic and basic forms of the compounds reached the electrode surface and were electroactive. The two general sequences [15] for the proton and electron addition viz H⁺, e, H⁺, e and H⁺, e,e, H⁺; the former sequence is more probable for these compounds in the light of their structural genesis. After the uptake of a proton and one electron radical (c) would accept a proton to form a protonated radical (d) which after taking one electron gets cleavage at nitrogen bond with the expulsion of aniline or its derivative. The imine (e) formed gets further protonated and reduced.

The mechanism of reduction obtained through the investigation of sulphonic aryl hydrazono-4-[(1-phenyl, 3-methyl)pyrazolin-5-one] dyes is similar to the polarographic reduction of 4-Aryl hydrazono-4-N'-Hipparyl-3-methyl-2-pyrazolin-5-ones [16]. This mechanism finds support from the more negative shift of $E_{\frac{1}{2}}$ with pH as protons are consumed in the reduction. As the dissociation constants of sulphonic

(1)
$$R - NH - N = C$$
 $C - CH_3$ $R - NH - NH = C - C - CH_3$

(a) $C - CH_3$

(b)

$$R - NH - NH - C - C - CH_3$$

$$C_6H_5$$

(c)

group K_1 of the compounds (II-IV) are expected at pH value about 3.0 [17], therefore, the tendency of shifting $E_{\frac{1}{2}}$ to more negative potentials decrease till pH value 10.4 and an increase in $E_{\frac{1}{2}}$ values indicates the formation of new ionized species "reduced form"

 $H_2A \longrightarrow HA^- + H^+$ (pH range 2.0 - 3.0)

 $HA \stackrel{-}{\rightleftharpoons} A^{-} + H^{+}$ (pH more than 10.6).

The plots of $E_{\frac{1}{2}}$ vs.pH (Fig.1) is composed of interesting three segments and the pH's at points of intersection approximately equal to pK₁ and pK₂ respectively.

These data are in good agreement with results obtained by both spectro-photometric and pH-metric determination of the dissociation constant of compound (V) [7].

It is important to note that, when the depolarizer solution was tested after controlled potential electrolysis, it gave the dye test indicating that at least one of the reduction products is an aromatic amine. Moreover, the u.v. and visible spectra of the solution was recorded during electrolysis at different time intervals. It was found that λ_{\max} at 390 nm (due to -NH-N=C

grouping) showed gradually decrease in peak height and finally the wave disappeared after 20 hrs. supporting the reduction mechanism proposed.

References

- R.F. Harmon, F.E. Dutton and H.D. Warren J.Med.Chem., 11, 627 (1968).
- D.C. Schroeder, Chem. Rev., 55, 181 (1955).
- 3. H.G.Grag and P.P. Singh, J.Med. Chem., 12, 612 (1969).
- 4. H.G.Grag and R.A.Sharma, J.Med.Chem., 12, 1122 (1969).
- B.Pullman and A. Pullman,
 "Quantum Biochemistry" John
 Wiley & Sons, New York (1963).
- P. Zuman,
 "Substituent Effects in Organic Polarography", Plenum Press,
 New York (1967).
- 7. B.A. El-Shetary, S. Labib, F. Zidan and M.S. Abdel-Moez, J. of the Chinese Chemical Society 33, 41 (1986).
- 8. H.S.T.Brilton,"Hydrogen ions" Vol.1, Chapman& Hall, London (1955)
- Y.M. Issa, B.E.El-Anadouli and B.A. El-Shetary, Ind. J. Chem., 23A, 183 (1984).
- 10. T.M.Florence and Y.J.Forrer, Aust. J. Chem. 17, 1085 (1964).
- 11. T.M.Florence, Aust.J.Chem., 18, 609, 618 (1965).
- 12. I.M.Issa, R.M.Issa, Y.M.Temerek and M.R. Mahmoud, Electro Chemica Acta, 18, 139 (1973).
- 13. A. Mellefiori and C. Giovanni, Ann. Chem. (Rome), 59, 128 (1969).

Techniques" Interscience, New York (1967). "The Elucidation of Organic Elec-

trode Process", Academic Press.

New York (1963).

16. R.Jain. J.Indian $(1985)_{-}$

(1985).

Chem.Soc., G.El-Inany, B.El-Shetary, Abo-Ali and A. Ramadan, J.Chem.Soc.Pakistan. 295

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