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Electrochemical Behaviour of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles

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ABSTRACT

The electrochemical behaviour of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles has been investigated at dme and gc electrodes in buffer solutions of pH 2-10 using dc polarography and cyclic voltammetry and coulometry. The compounds exhibit one well defined wave in the entire pH range of study. The process is irreversible and diffusion controlled. Controlled potential electrolysis indicates the involvement of two electrons in the reduction process. The effect of solvent composition, cations and anions, temperature as well as the effect of the nature of the substituent on the mechanism of reduction has been investigated. Based on the results obtained the mechanism of reduction has been proposed.

Keywords: Pyrazoles, polarography, cyclic voltammetry, controlled potential electrolysis.

INTRODUCTION

Many pyrazoline derivatives are well known for their biological activity[1]. The redox characteristics of such biological substances may provide valuable information about the redox behavior in living systems[2]. In view of the biological activity of pyrazolines and the usefulness of electrochemical techniques in studying biological molecules, the electrochemical behavior of some N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles has been studies at dropping mercury electrode and glassy carbon electrodes.

MATERIALS AND METHODS

The synthesis of the compounds [1-4] involves following steps. The diazotized aromatic amines when condensed at active methylene position of benzoyl acetone, give 1-methyl-3-phenyl-2-phenyldrazono-1,2,3-propanetriones.The latter on cyclization with 2-hydroxy benzoic benzoylhydrazine gave N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles (1-4) on reflux ion in methanol for 6 h. The compounds were recrystallized from acetic acid. The homogeneity and purity of the compounds was tested through thin layer chromatography (TLC) and the structure confirmed elemental and spectral analyses. 1- m. p. 153-156; 2- 161-163; 3-181-182; 4- 100-102 ^{o}C. Stock solutions (1 x 10^{-2} M) of all the compounds were prepared in dimethylformamide (AR). Britton-Robinson buffer solutions pH 2-10 were prepared and used. Polarograms were recorded for deaerated solution containing 5 ml of the stock solution of the compound, 25 ml of dimethylformamide (the minimum volume necessary to keep the compound in solution), 20 ml of buffer solution of desired pH. A systronic polarograph model 1632 was used to record the polarograms. The polarograph consists of dropping mercury electrode (DME) assembly, a console and a printer interface. The DME assembly uses a three electrode system where it is used as a working electrode with saturated calomel electrode (SCE) as reference and platinum counter electrode. The polarographic console (1632) provides an accurately controlled and programmable DC ramp generator, a highly sensitive current monitor and facilities for controlling drop life of the mercury electrode. The capillary having the following characteristics in water: 3.27 mg sec^{-1}, t = 2.0 sec, $mg^{2/3}\ t^{1/6}$ = 3.66 $mg^{2/3}\ s^{-1/2}$ at h = 80 cm was employed as the working electrode. The pH measurements were made with ELICO digital pH meter having a glass electrode model LI 127. Cyclic voltammograms were recorded for deaerated solution containing 1 ml of the stock solution of the compound, 5 ml dimethylformamide and 4 ml of the buffer solution of desired pH with a Bio-analytical Systems CV-27 controller and conventional three electrode, Ag/Ag Cl reference electrode, glassy carbon working electrode and platinum counter electrode. Nitrogen gas was used as a purge gas.

The controlled potential electrolysis was carried out in a Lingane[3] H-type cell. A large pool of mercury is employed as the cathode at the bottom of the large compartment and a similar pool of mercury at the bottom of the smaller compartment is taken to serve as the anode. The cathode compartment contained 50 ml of DMF, 10 ml of 1.0 M KCl and 30 ml of buffer (pH 4). The solution in the cathode compartment is deaerated by bubbling pure nitrogen gas through it for about 15 minutes. The preelectrolysis is carried out for about 15 minutes with cathode potential fixed at a value which is to be used for subsequent reduction of the oxidant. When the back ground current reached a constant value, 10 ml of the 0.01 M N’-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(arylazo)pyrazole, was added to the cathode compartment and the electrolysis continued at -0.85 V. The decrease in the limiting current with time was recorded at regular intervals of time and the number of electrons involved in the reduction was calculated from the i-t curves following the procedure outlined by Lingane[3].

RESULTS AND DISCUSSION

Wave in acidic pH’s: N’-(2-hydroxybenzoyl)-3-methyl-5-phenyl pyrazole failed to exhibit a polarographic wave under similar experimental conditions. Therefore the waves that are observed in compounds 1-4 (given in the Scheme 1) are attributed to the polarographic reduction of exocyclic azo group(>N=N<). These compounds exhibit a single wave in the entire pH range of study. The electrochemical characteristics of the compounds are presented in table 1 and 2. Polarogram of N’-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(arylazo)pyrazole at pH 4.0 is presented in fig. 1. The low value of temperature coefficient (below 1.62% K^{-1}) and the direct proportionality observed for i_d vs concentration and i_d vs $h^{1/2}$, indicate the diffusion-controlled nature of the electrode process. The shift in $E_{1/2}$ towards more negative potential with increase in concentration of depolarizer and semi-log plots[4] confirmed the irreversible nature of the wave. $E_{1/2}$ values were also found to become more negative with increase in pH before reaching a limiting value beyond a pH of 8.0. This clearly shows the participation of protons in the reduction process.

Table 1 Polarographic data of N’-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2’-substituted arylazo)pyrazoles (1-4)Conc. = 1 mM, Medium = 60% (V/V) DMF

pH	$-E_{1/2}$ V vs SCE				i_{lim} μA			
	1	2	3	4	1	2	3	4
2.0	0.75	0.78	0.82	0.71	11.5	15.7	17.6	20.6
4.0	0.93	0.96	1.02	0.92	8.2	11.8	14.0	18.0
6.0	1.10	1.12	1.14	1.07	7.8	9.6	10.4	15.2

8.0	1.27	1.30	1.35	1.23	5.4	8.0	5.6	14.0
10.0	1.27	1.30	1.35	1.23	5.2	7.8	5.3	13.8

Table 2 Polarographic characteristics and kinetic parameters of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles (1-4) at pH 4.0 and 8.0

pH	Comp-ound	$\Delta E_{1/2}/\Delta pH$	αn_a	Number of protons	Dx10^{6} cm^{2}/s	$k^{\circ}_{f,h}$ cm/s	ΔG^* kcal/mol
4.0	1	0.085	0.86	1.24	2.71	4.76x10^{-8}	17.16
	2	0.080	0.76	1.03	5.62	1.19x10^{-7}	16.47
	3	0.072	0.86	1.05	7.90	2.20x10^{-8}	17.62
	4	0.082	0.92	1.28	13.10	6.08x10^{-8}	17.01
8.0	1	0.085	0.89	1.28	1.18	1.32x10^{-10}	20.69
	2	0.080	0.58	0.78	2.59	3.23x10^{-8}	17.39
	3	0.072	0.86	1.05	1.28	7.31x10^{-11}	21.05
	4	0.082	0.90	1.25	7.91	5.30x10^{-10}	19.86

The value of αn_a (product of transfer coefficient and number of electrons transferred in the rate determining step) and P (the number of protons involved in the rate determining step) are determined using following expressions[4].

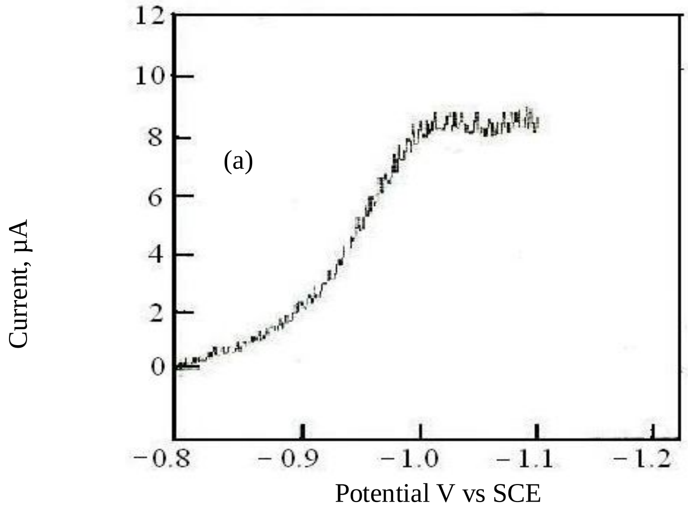


Fig. 1 Polarogram of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(arylazo)pyrazole . Concentration = 1mM; Medium=60% aqueous DMF; pH = 4.0

$$E_{1/2} - E_{1/4} = \frac{0.0517}{\alpha n_a} \qquad (1)$$

$$\frac{\Delta E_{1/2}}{\Delta pH} = \frac{0.05915}{\alpha n_a} P \qquad (2)$$

The value of diffusion coefficient has been determined by Ilkovic [5] equation.

$$i_d = 607\ n\ D^{1/2}\ m^{2/3} t^{1/6}\ C \qquad (3)$$

where n = number of electrons transferred in the process, m = rate of mercury flow in mg/s, D = diffusion constant of depolarizer in cm^2/s, t = drop time in s, C = depolarizer concentration in mmol L^{-1}, i_d = diffusion current in micro amperes.The value of heterogeneous rate constant ($k^0_{f,h}$) has been evaluated by Meites and Isreal[6] equation.

$$E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n_a} \log \frac{1.349 k^0_{f,h}\ t^{1/2}}{D^{1/2}} \qquad (4)$$

The activation free energy change (ΔG^*) has been determined by the relationship

$$k^0_{f,h} = \frac{kT}{h} r_0 \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad (5)$$

Where k = Boltzmann constant, h = the Plank's constant, r_0 = the mean distance between the depolarized ions in the bulk solution, R = the gas constant and T = the absolute temperature. In general the value of r_0 is taken as 2×10^{-8} cm[7].

Wave in alkaline pH's: Each compound of the series (1-4) exhibits only one wave in the pH range 8 – 10. The half-wave potential of the wave in alkaline solutions is not altered with change in hydroxyl ion concentration. The height of the wave decreases with increase in pH and the wave height vs pH plot assumes the form of dissociation curve () in the pH range of study (2 – 10). This suggested that an acid base equilibrium governs the polarographic reduction.

Cyclic voltammetry: The compounds (1-4) gave one cathodic peak at all scan rates (0.020-0.200 V/s) at glassy carbon (gc) electrode at pH 4.0 and 8.0. No anodic peak is observed in the reverse scan in any media indicating irreversible nature of the electrode process (cf. fig. 2). This is further supported by the negative shift in the peak potential with the increasing scan rate (cf. table 3). The plots of i_{pc} vs concentration and i_{pc} vs $\nu^{1/2}$ fulfill the criteria of the diffusion controlled nature [8,9] of the electrode process. The plots of E_{pc} vs pH are similar to $E_{1/2}$ vs pH plots and this lends support to the findings of the dc polarography.

Controlled potential electrolysis: Progress of the electrolysis was followed by recording the decreasing current with time and the number of electrons per molecule was computed from i-t curves following the procedure outlined by Lingane[3] and found to be two. The electrolysis is carried out until the electrolyzed solution did not exhibit any polarographic wave or a cyclic voltammetric peak.

Table 3 Cyclic voltammetric data of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles (1-4) at pH 4.0, Conc. = 1 mM, Medium = 60% (V/V) DMF

pH	Compound	Scan rate Vs^{-1}	-Epc V	i_{pc} μA	$i_{pc}/\nu^{1/2}$
4.0	1	0.020	0.86	10.16	71.85
		0.050	0.88	15.90	71.10
		0.100	0.91	22.85	72.26
		0.200	0.95	33.14	74.10
	2	0.020	0.90	14.92	105.51
		0.050	0.92	23.40	104.65
		0.100	0.95	32.85	103.88
		0.200	1.00	47.40	105.99
	3	0.020	0.96	18.87	133.45

		0.050	0.98	29.74	133.00
		0.100	1.02	42.95	135.83
		0.200	1.05	60.41	135.08
	4	0.020	0.82	20.73	146.60
		0.050	0.85	32.90	147.13
		0.100	0.87	46.85	148.16
		0.200	0.90	66.48	148.65
8.0	1	0.020	1.17	16.74	47.66
		0.050	1.20	10.37	46.37
		0.100	1.23	14.90	47.12
		0.200	1.27	21.00	46.95
	2	0.020	1.20	10.24	72.41
		0.050	1.22	16.47	73.65
		0.100	1.26	23.46	74.91
		0.200	1.29	33.52	74.95
	3	0.020	1.25	6.84	48.37
		0.050	1.28	10.75	48.07
		0.100	1.31	15.40	48.70
		0.200	1.35	22.06	49.32
	4	0.020	1.14	17.14	121.21
		0.050	1.16	27.45	122.76
		0.100	1.19	38.62	122.13
		0.200	1.22	55.25	123.54

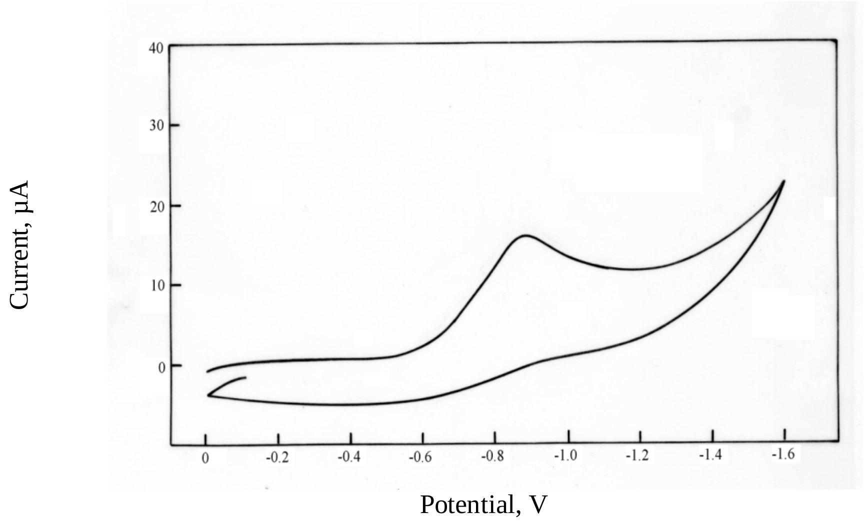


Fig. 2 Cyclic voltammogram of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(arylazo)pyrazole. pH = 4.0; Scan rate = 0.05 VS^{-1}

Effect of solvent composition : Effect of solvent composition on the polarographic characteristics of compounds 1-4 was studied by recording polarograms in 60 and 75% organic solvent solutions (dimethylformamide, dimethylsulphoxide, acetonitrile)-water solutions at pH 4 (cf. table 4). It was observed that half-wave potential shifted to more negative values[10] in the presence of organic co-solvent and the magnitude of the shift depends on the nature of the solvent. The order of the shift observed in the present study is CH_3CN>DMF>DMSO. The shift of half-wave potential towards more negative values with increase in the percentage of organic co-solvent, may be due to rise in pH of the solution[11] which results in an increase in the dissociation constant of the protonated species[13]. Both these factors lower the rate of protonation and consequently lead to a shift in $E_{1/2}$ of the reduction wave (in case where protonation precedes the electron transfer) towards more negative potential.

Table 4 Effect of organic co-solvent on $E_{1/2}$ of N'-(2-hydroxybenzoyl) -3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles (1-4) at pH 4.0 Conc. = 1 mM

Compound	$-E_{1/2}$ V vs SCE			$-E_{1/2}$ V vs SCE		
	DMSO 60%	DMF 60%	CH_3CN 60%	DMSO 75%	DMF 75%	CH_3CN 75%
1	0.86	0.93	1.02	0.95	1.03	1.12
2	0.89	0.96	1.04	0.98	1.06	1.14
3	0.92	1.02	1.07	1.02	1.08	1.17
4	0.83	0.92	0.99	0.92	1.00	1.08

Effect of cations and anions: To evaluate the effect of size of the cation and anion, the polarograms were recorded in supporting electrolytes having a common cation (KBr, KI, KCNS and KNO_3) and a common anion LiCl, NaCl, KCl and $N^+(CH_3)_4Br^-$. No change in limiting current and half-wave potential values were found in the former while lowering of $E_{1/2}$ and increase in limiting current was observed in the later. This can be explained in terms of the change of the structure of the double layer[13]. Size of anion has no effect on $E_{1/2}$ and i_l since the cations predominate in the electrical double layer at these potentials and increase in the size of cation lead to decrease in the rate making reaction more difficult[10] resulting in shift of $E_{1/2}$ towards more negative potentials (cf. table 5).

Table 5 Effect of cations and anions on the polarographic characteristics of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(2'-substituted arylazo)pyrazoles (1-4)
Conc. = 1 mM, pH = 4.0, Medium = 60% (V/V) DMF

Supporting Electrolyte (0.1 M)	$-E_{1/2}$ V vs SCE				i_{lim} µA			
	1	2	3	4	1	2	3	4
LiCl	0.86	0.91	0.92	0.83	6.8	10.4	11.2	16.2
NaCl	0.89	0.94	0.97	0.87	7.4	11.0	12.8	16.8
KCl	0.93	0.96	1.02	0.92	8.2	11.8	14.0	18.0
$N^+(CH_3)_4Br^-$	0.97	1.15	1.17	0.95	8.6	12.6	14.8	19.4
KBr	0.93	0.97	1.02	0.93	8.3	11.8	14.1	18.1
KI	0.93	0.97	1.03	0.93	8.3	11.9	14.2	18.1
KNO_3	0.92	0.98	1.03	0.94	8.4	11.8	14.2	18.2
KCNS	0.93	0.97	1.03	0.93	8.4	11.8	14.2	18.1

Effect of temperature: Compound 1 exhibits a single well-defined wave at pH 4.0 at all the temperatures studied (300.13 – 323.13°K). The unsubstituted N'-(4-hydroxybenzoyl)-3-methyl-5-phenyl pyrazole fail to exhibit the reduction wave under similar experimental conditions. So, the wave that has been observed in the present studies is attributed to the reduction of azo group. The diffusion controlled nature of the reduction wave has been indicated by the linear plots of i_d vs $h^{1/2}$ passing through the origin. The low temperature coefficient values (1.08 – 1.15 percent/degree) further supports the diffusion controlled nature of the wave. This is in agreement with the values predicated by Meites[4] for organic molecules. Semi-logarithmic analysis of the waves [4] confirmed the irreversible nature of the wave. It is seen from the table 6 that the half-wave potential values of the depolarizer shifted to more negative potentials with increase in temperature. The values of αn_a decrease with increase in temperature. But in the present studies it is observed that the values of n_a to be equal to 1. Since the decrease in values with increase in temperature is indiscrete and at no stage the two consecutive values vary by a factor of 1, the possibility of decrease in the value of product αn_a due to a change in n_a may be ruled out. A decrease in the value of α implies that the transfer of electron(s) is made increasingly difficult as the temperature is elevated. In other words, the electrode reaction of arylazo-pyrazole is rendered more irreversible. The shift of $E_{1/2}$ values to more negative potentials lends support to the above conclusion.

Knowing the value of n, the diffusion coefficient (D) values for the depolarizer at different temperatures have been calculated using the Ilkovic[5] equation. The values of heterogeneous rate constant ($k^0_{f,h}$) have been evaluated using Meites and Isreal[6] equation for the irreversible process and are presented in table 6. The values of $k^0_{f,h}$ are low and decreases with increase in temperature. This signifies that the electrode reactions are rendered more irreversible with increasing temperature. This observation is in harmony with the conclusion arrived at on the basis of αn_a values. The activation free energy change, ΔG* is positive for all the systems suggesting the non-spontaneous nature of the electrode process [14]. The high values of ΔG* also suggests that the reaction rate is slow [14] at all the temperatures of study.

Table 6 Effect of temperature on the polarographic characteristics of N'-(2-hydroxybenzoyl)-3-methyl-5-phenyl-4-(arylazo)pyrazole (1)

Conc.=1mM, pH=4.0, Medium=60% (V/V) DMF

Temperature K	$-E_{1/2}$ V vs SCE	i_{lim} µA	Temperature coefficient % deg^{-1}	αn_a	$D \times 10^6$ cm^2/s	$k^\circ_{f,h}$ cm/s	ΔG* kcal/mol
303.13	0.93	8.2	-	0.86	2.71	4.76×10^{-8}	17.16
310.13	0.98	9.2	1.15	0.82	3.42	4.28×10^{-8}	17.22
320.13	1.15	10.2	1.08	0.79	4.20	7.09×10^{-9}	18.30

Effect of substituents on reduction: To establish the effect of substituents on the polarographic reduction, $E_{1/2}$ was plotted against the Hammett substituent constant (fig. 3). The substituent constants, σ used were taken from the literature[15]. It is observed from the plot that the electron donating substituents, $-CH_3$ and $-OCH_3$ shifts $E_{1/2}$ towards more negative values while electron withdrawing group –Cl shifts $E_{1/2}$ towards more positive values. The correlation coefficient calculated for the $E_{1/2}$ σ vs plot (r = 1.0) show satisfactory application of Hammett's correlation to the system under study. The positive value of the specific reaction constant (ρ = 0.18 at pH 4) suggests that the electron addition step is more important than the addition of protons. The results also suggest that the presence of substituents makes the reduction either easier or more difficult depending on the nature of the substituent, without affecting the mechanism of reduction.

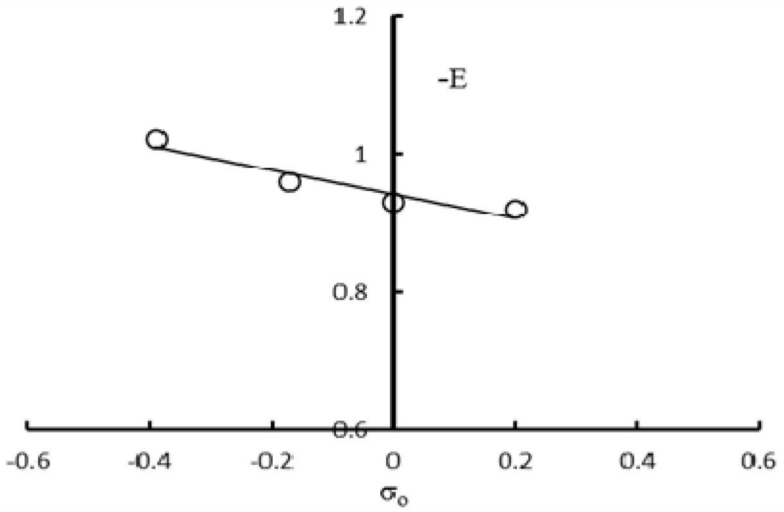
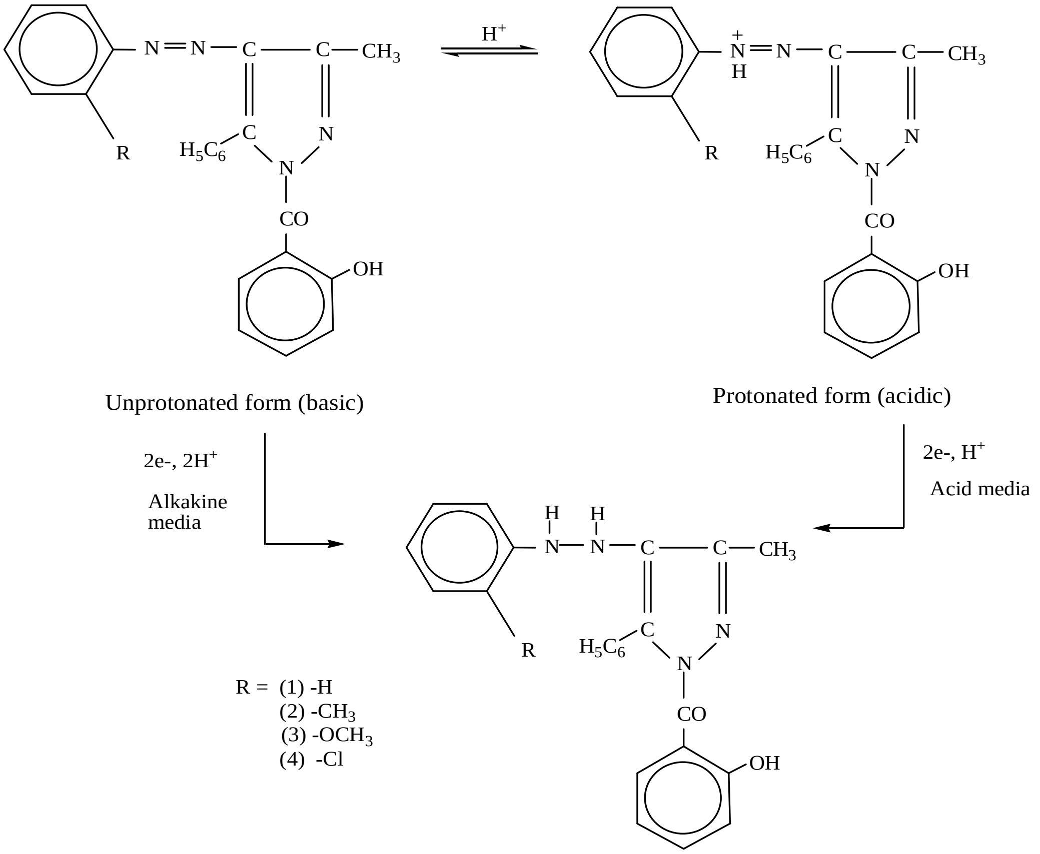


Fig. 3 Plot of $-E_{1/2}$ V vs σ_o

Mechanism of reduction: Based on the results obtained a mechanism of reduction shown in **Scheme 1** may be proposed for the present compounds.



Scheme 1 Reduction Mechanism

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