Electrochemical Behaviour of Sulphonamoylhydrazono-pyrazolin-5-ones

Rajeev Jain, Jyoti Bhadauria and Sandeep Tomar

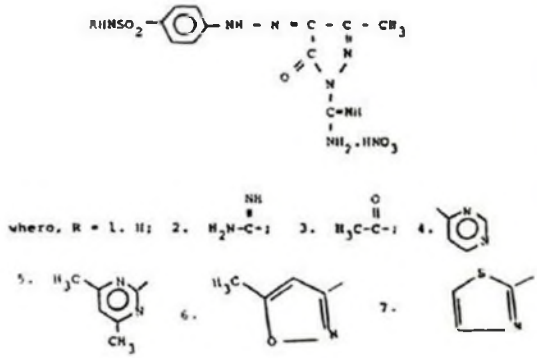
School of Studies in Chemistry, Jiwaji University, GWALIOR - 474 011.

The electrochemical behaviour of 1-guanylnitrate-3-methyl-4-[4-(substituted) sulphonamoyl] hydrazono-2-pyrazolin-5-ones have been investigated at dme and g.c. electrodes in Britton-Robinson buffer solutions of pH 2.6-12.0 using d.c. polarography, cyclic voltammetry and coulometry. The reduction gives one well-defined, irreversible and diffusion-controlled 4 electron wave/peak corresponding to the reductive cleavage of -NH-N= center. The mechanism of the reduction has been deduced. The effect of ionic-strength and solvent compositions has also been studied.

Many pyrazolone derivatives are well known for their biological activity. A knowledge about the redox behaviour of such biological substances may provide valuable information about redox behaviour in living systems [1-2]. In view of the biological activity of pyrazolones and usefulness of electrochemical techniques in studying biological molecules, some 1-guanylnitrate-3-methyl-4-[4'-(substituted) sulphonamoyl] hydrazono-2-pyrazolin-5-ones have been studied at dropping mercury and glassy carbon electrodes.

EXPERIMENTAL

All the compounds were synthesised in the laboratory [3] and purified by recrystalization. The structure of these compounds were confirmed by elemental and spectral analysis. Stock solutions (2.0×10^{-3}M) of all the compounds were prepared in dimethylformamide (AR). Buffer solutions at pH 2.6-12.0 [4] and potassium chloride (1.0M KCl) solution were prepared in double distilled water from AR grade chemicals. The equipment used and experimental details are reported elsewhere [5].



RESULTS AND DISCUSSION

D.C.Polarograpy

Each compound of the series (compounds 1-7) gave one 4e⁻ reduction wave in the entire pH range (pH 2.6-12.0).

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This wave has been assigned to the reduction of the hydrazono group on the basis of relative ease of reduction of hydrazono group at dme. The electrochemical characteristics of the compounds are compiled in Table 1.

Table 1

Electrochemical Characteristics of 1-guanylnitrate-3-methyl-4 -[4'-(substituted)-sulphonamoyl] hydrazono-2-pyrazolin-5-ones

pH 4.2; Conc = 2.0x10^{-4}M; Height 70 cm

Comp no	$-E_{1/2}$ V	i_d μA	$dE_{1/2}/dpH$ V/pH	αn_a	I	P
1	0.62	0.98	0.070	0.74	0.11	0.89
2	0.78	0.68	0.068	0.86	0.14	1.00
3	0.88	0.98	0.068	0.86	0.16	1.00
4	0.60	1.05	0.080	0.65	0.11	0.88
5	0.88	1.35	0.060	0.74	0.16	0.75
6	0.88	1.13	0.071	0.86	0.16	1.03
7	0.82	1.35	0.089	0.74	0.15	1.11

The low value of temperature coefficient (below 1.62% deg) and direct proportionality between i_d vs concentration and i_d vs $h^{1/2}$ clearly indicate the diffusion-controlled nature of the electrode process. The shift in $E_{1/2}$ towards more negative potential with increase in concentraion of the depolarizer and log plots [6] confirmed the irrreversible nature of the wave. The two segments in $E_{1/2}$ vs pH plots with break at pH 7.7 (Fig.1) clearly shows the proton participation in the reduction process.

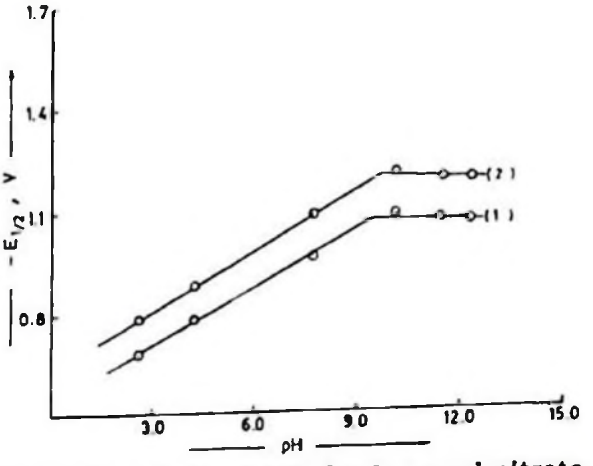


Fig 1 Plot of $-E_{1/2}$ *vs* pH for 1-guanyl-nitrate-3-methyl-4-[4'-(substituted)sulphonamoyl] hydrazono-2-pyrazolin-5-ones

Curve 1 Compound 2 Curve 2 Compound 3
Conc = 2.0x10^{-4}M;

The value of αn_a (product of transfer coefficient and number of electrons transferred in the rate determining step) and P (number of protons involved in the rate determining step) are determined using following expressions [6-9].

$$E_{3/4} - E_{1/4} = 0.0517/\alpha n_a$$

$$\frac{dE_{1/2}}{dpH} = \frac{0.05917}{\alpha n_a} P$$

Linear Sweep and Cyclic Voltammetry

1-Guanylnitrate-3-methyl-4-[4'-(substituted) sulphonamolyl] hydrazono-2-pyrazolin-5-ones gave a single four electron peak at Glassy Carbon (GC) electrode in the pH range 2.6-12.0. No anodic peak was observed in any media indicating irreversible nature of the electrode process (Fig.2). This is further supported by the negative shift in the peak potential with increasing sweep rate (50-200 mV/sec). The plots of

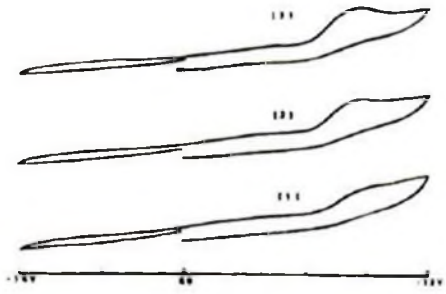


Fig 2 Cyclic Voltammograms of 1-guanyl-nitrate-3-methyl-4-[4'-(substituted)-sulphonamoyl] hydrazono-2-pyrazolin-5-one
1 pH 12.3 2 pH 11.4 3 pH 10.1
Scan rate = 50 mV/sec Conc = 2.0x10 $^{-4}$M;

i_p vs concentration and i_p vs $v^{1/2}$ (Fig.3) fulfil the criteria of diffusion controlled nature [8 - 9] of the electrode process. The plots E_p vs pH (Fig.4) are similar to $E_{1/2}$ vs pH plots and this lends support to the findings of d.c. polarography.

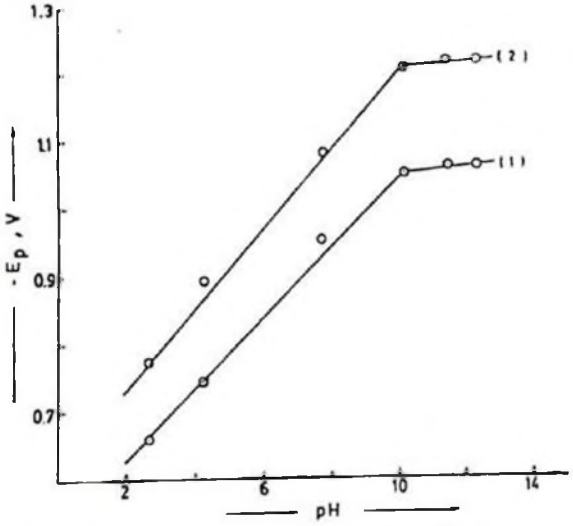


Fig 3 Plot of -E_p vs pH for 1-guanyl-nitrate-3-methyl-4-[4'-(substituted)sulphonamoyl] hydrazono-2-pyrazolin-5-one
Curve 1 Compound 2 Curve 2 Compound 3
Conc = 2.0x10^{-4}M;

Coulometry

Coulometric measurements [10] were carried out to calculate the number of

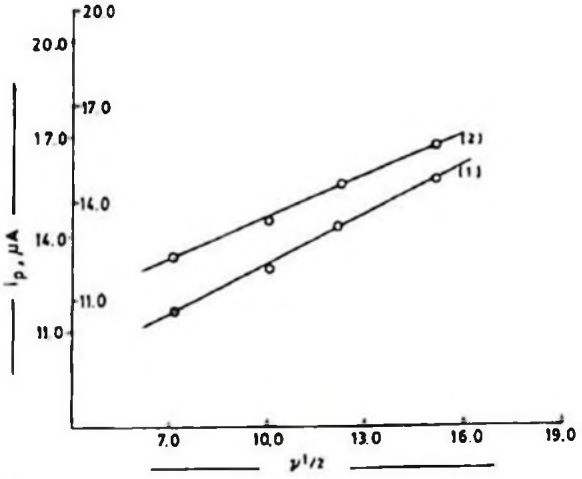


Fig 4 Plot of i_p vs $v^{1/2}$ for 1-guanyl-nitrate-3-methyl-4-[4'-(substituted)sulphonamoyl] hydrazono-2-pyrazolin-5-one

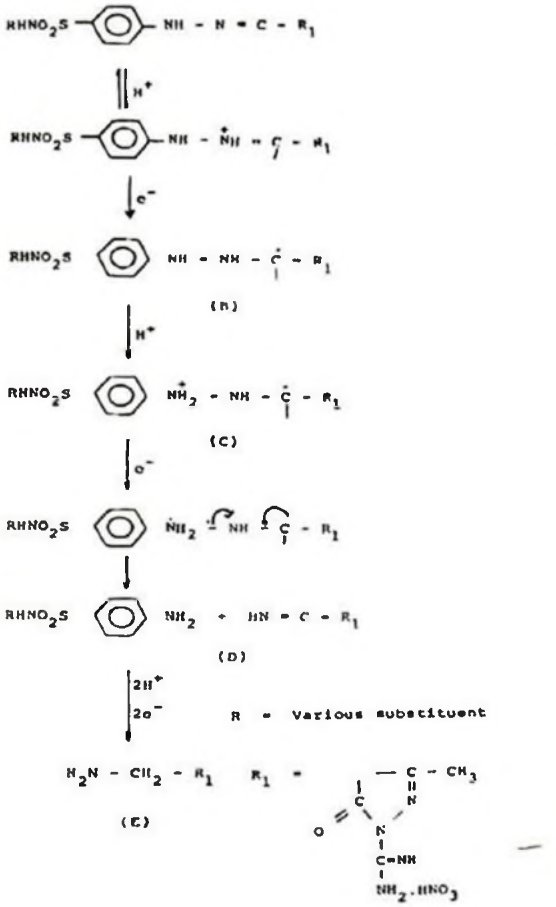
Conc = 2.0x10^{-4}M;

electrons taking part in the overall electrode process and was found to be four. Electrolysis was carried out at a slightly higher negative potential than peak potential. With progress of electrolysis, the colour of the solution gradually faded away and finally a colourless solution was obtained. After complete electrolysis, no peak could be observed in the cyclic voltammogram indicating complete reduction of -NH-N=C< group. During electrolysis, spectra were recorded at 425 nm (λ_{max}) at fixed intervals of time. Absorbance at 425 nm (due to -NH-N=C< grouping) showed a gradual decrease with time and finally peak disappeared, confirming the above findings.

Reduction Mechanism

Taking into consideration the findings of d.c. polarography, cyclic voltammetry, coulometry and the reports of earlier

workers, two general sequences [11-12] for the proton and electron addition (H^+, e^-, H^+, e^- and H^+, e^-, e^-, H^+) are possible. Out of these, former sequence is found plausible for these compounds.



Alternatively, the radical (B) could also combine with an electron instead of proton but this is not likely because such a reduction would involve only two electrons; in the present case, four electron process is indicated by coulometry.

This mechanism finds support from the $E_{1/2}/E_p$ *vs* pH plots (Fig.1 and 4). The constancy of half-wave potential value at higher pH can be explained as follows: both the acidic and basic forms of depolarizer are electroactive but in the range where the rate of protonation decreases, their $E_{1/2}$ are so close to each other that waves merge [6].

The plots of $E_{1/2}$ *vs* pH are composed of two linear parts and the pH at the point of intersection of its two linear parts is pK_1. Similar steps of the reduction of hydrazonogroup involving cleavage of the N-N bond have also been proposed by other workers [13-14].

Effect of Ionic Strength

Following equation [15] represents the influence of structure of double layer on $E_{1/2}$ for a pre-protonation, irreversible electrode process.

$$\Delta E_{1/2} = \Delta\psi_1 = \frac{\alpha n_a - Z}{\alpha n_a} \cdot \frac{F}{2.3\,RT} \cdot \frac{dE_{1/2}}{dpH}$$

where ψ is variation in double layer potential, α is the trnasfer coefficient, n is the number of electrons transferred, Z is charge on the particle being discharged. It is pretty clear from the above equation that the factor which will alter structure of double layer may bring about a change in $\Delta E_{1/2}$.

The organic compound under study gets reduced at electrode surface immediately after protonation (RH^+). The pyrazolone compound remains almost in non-ionised state. Thus for all practicle purposes, Z may safely be considered as zero and first term within the bracket become equal to

unity. Since the second term in the bracket of the equation is approximately 1 and Z = O, $E_{1/2}$ will be almost independent of ionic strength. This theoretical predication was found true; these pyrazolones have been polarographed in solution of various molarities of KCl (0.5M to 2.0M) and no change in i_d and $E_{1/2}$ was observed.

Effect of Cations and Anions

To evaluate the effect of the size of cation and anion, the polarograms were recorded in supporting electrolyte having common cation (KBr, KI, KCNS and KNO_3) and common anion (LiCl, NaCl, KCl, CsCl) and tetraethyl ammonium bromide. No change in i_d and $E_{1/2}$ values were found in the former while lowering of $E_{1/2}$ and constancy in i_d was observed in the later. This can be explained in terms of the change of the structure of double layer [16-17]. Size of anions has no effect on $E_{1/2}$ and i_d since the cations predominate in the electrical double layer at these potentials and increase in size of cations lead to decrease in ψ_1, making reaction more difficult [18] resulting in shift of $E_{1/2}$ towards more negative potential (Table 2).

Table 2

Effect of Cations & Anions on Polarographic Characteristics of 1-guanyl-nitrate-3-methyl-4-[4'-(substituted)sulphonamoyl] hydrazono-2-pyrazolin-5-one

pH 4.2; Conc = 2.0×10^{-4}M; Height 70 cm

Sl No	Supporting Electrolyte	$-E_{1/2}$ V	i_d µA
1	LiCl	0.72	1.50
2	NaCl	0.78	1.43
3	KCl	0.82	1.35
4	$(C_2H_5)NBr$	0.78	1.21
5	KBr	0.80	1.43
6	KI	0.80	1.43
7	KNO_3	0.82	1.43
8	KCNS	0.80	1.43

Effect of Solvent Composition

On increasing the concentration of dimethylformamide from 30% to 70% at pH 4.2, a decrease in i_d and $E_{1/2}$ values were noticed. At very high concentration of the solvent, only an ill defined wave is obtained.

The protonated species get discharged on the electrode surface. The rise of the percentage of the solvent results in an increase in pH [19] and dissociation constant of the protonated species [20]. Both these factors lower the rate of protonation and consequently the shift in $E_{1/2}$ towards -ve potential was observed [20]. Schwabe [21] assumed this shift in $E_{1/2}$ due to the inhibition of the electrode process by the solvent molecules absorbed on the electrode. In addition to this, the decrease in adsorbability and hence surface concentration of the depolarizer with an increasing percentage of organic solvent in aqueous-organic mixture [22] would also retard the electrode reaction resulting in decrease in i_d and shift of $E_{1/2}$ towards more negative potentials (Table 3).

Table 3

Effect of Solvent Composition on Polarographic Characteristics of 1-guanyl-nitrate-3-methyl-4-[4'-(substituted) sulphonamoyl] hydrazono-2-pyrazolin-5-one

pH 4.2; Conc = 2.0x10^{-4}M; Height 70 cm

Sl No	% DMF	$-E_{1/2}$ V	i_d µA
1	30	0.82	1.35
2	40	0.84	1.36
3	50	0.88	1.27
4	60	0.90	1.12
5	70	0.94	0.97

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