Electrochemical investigations on 5-methyl-4-(4|-substituted phenylhydrazono)- 2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-ones

5-metil-4-(4|-fenil hidrazon)-2-(5-tiyooko-4,5-dihidro-[1,3,4]oksadiazol-2-ilmetil)-2,4-dihidro-pirazol-3-on üzerine elektrokimyasal incelemeler

Research Article

Krishna Naik[1], Aluru Raghavendra Guru Prasad[2]*, Yadatai Narasimha Spoorthy[1], Lakshmana Rao Krishna Rao Ravindranath[1]

[1]Sri Kirshnadevaraya University, Anantapur, A.P., India.

[2]ICFAI Foundation For Higher Education, Hyderabad, A.P., India.

ABSTRACT

The electrochemical investigations on 5-methyl-4-(4|-substitute phenylhydrazono)- 2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-ones having substitutions namely -H, $-CH_3$, $-OCH_3$, $-OC_2H_5$, -Cl, -Br were carried out in Briton-Robinson buffer solutions. Investigations were carried to study the effect of pH, height of mercury column, effect of substituents based on which reduction mechanism was proposed in acid as well as in basic medium. The compounds under investigation exhibit a well defined single wave in the buffer solutions of pH 1.1-7.1 and two waves in solutions of pH 8.1-10.1 in polarographic studies at DME. In cyclic voltammetric studies at HMDE one cathodic peak in lower scan rates and two cathodic peaks in higher scan rates were obtained along with an inverted peak in solutions of pH 2.1-7.1. Cyclic voltammetric studies at MCPE leads to one cathodic peak in solutions of pH 2.1-7.1 and two cathodic peaks in pH range of 8.1-10.1 along with an anodic peak in solutions of pH 2.1-7.1. A detailed comparison of results obtained in polarographic studies with those obtained in cyclic voltammetry at HDME and MCPE were presented in the studies.

Key words

Pyrazol-3-ones, polarography, cyclic voltammetry, DME, MCPE, reduction mechanism

ÖZET

5-metil-4-(4-fenilhidrazon)-2-(5-tiyookso-4,5-dihidro-[1,3,4]oksadiazol-2-ilmetil)-2,4-dihidro-pirazol-3-,-H,$-CH_3$, $-OCH_3$, $-OC_2H_5$, -Cl, -Br) sübstitüe olmuş moleküller üzerinde elektrokimyasal incelemeler gerçekleştirilmiştir. Polarografik araştırmalar, hem asidik hem de bazik ortamlarda önerilen indirgenme mekanizmalarına dayalı pH etkisi, cıva kolon yüksekliği etkisi ve sübstitüsyon etkisi çalışmalarıyla gerçekleştirilmiştir. Polarografik çalışmalarda elde edilen sonuçlar, siklik voltametrede modifiye karbon pasta elektrot (MCPE) ve damlayan cıva elektrotu (DME) kullanılarak elde edilen sonuçlarla karşılaştırılmıştır.

Anahtar Sözcükler

Pirazol-3-on, polarografi, siklik voltametri, DME, MCPE, indirgenme mekanizması

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Corresponding author: A.R.G. Prasad, ICFAI Foundation For Higher Education, Hyderabad, A.P., India.

E-Mail: guruprasadar@yahoo.co.in

INTRODUCTION

The compounds containing oxadiazole [1-6] and pyrazole [6-9] moiety find extensive applications in medicinal chemistry. Further they have been used as precursors for the synthesis of many compounds demonstrating medicinal importance [6,10]. It has been a practice to understand the electrochemical behaviour of compounds to have knowledge of their metabolites when used as the drugs [11,12]. Electrochemical reduction of compounds containing azomethine group usually includes four electrons due to the cleavage of N-N bonds [13, 14]. The extensive medicinal applications of pyrazolin-3-ones in have inspired the authors to undertake the detailed polarographic and cyclic voltammetric studies of 5-methyl-4-(4^{l}-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazole-2-ylmethyl)-2,4-dihydro-pyr¬azol-3-ones.

EXPERIMENTAL

The chemicals employed in the studies were analytical reagent grade procured from Merck India Ltd. The pH measurements were made with pH meter model LI-10 manufactured by ELICO Private Limited, Hyderabad, India. A CL-25 Pen Recording Polarograph manufactured by ELICO Private Limited, Hyderabad, India was used to record current voltage curves. The cyclic voltammeter consists of an X-Y recorder (Model RE 0074), a PAR 175 Potentiostat and a PAR 175 Universal Programmer. A single compartment cell model 303 SMDE supplied by PAR with silver wire as reference electrode and platinum wire as counter electrode was used in the studies. A stationary mercury drop electrode (SMDE 303) with a drop area 0.0096 cm^2 was used as working electrode. The infrared spectra were recorded using Perkin–Elmer KBr spectrometer. ^{1}HNMR spectra were recorded using JEOL MODEL GSX 270 FT NMR Spectrometer and NMR 200 MHz Supercon machine, utilizing DMSO–d_6 as a solvents and TMS as an internal standard.

Preparation of Chemically modified electrode

Chemically modified carbon paste electrode was prepared by grinding the crown-ether crystals with a mortar and pestle. Graphite powder was added, finally ground, nujol oil was added and the whole was thoroughly mixed. The final composition of graphite/oil/modifier was 54:36:10% w/w. The paste was packed at one end of a glass tube (3 mm bore; 1mm wall), to make contact with a copper wire inserted into the tube.

General Procedure

8.0 mL of the buffer solution of desired pH (1.1 – 10.1), 2 mL of the stock solution of the substrate (1.0x10^{-2} M) in dimethylformamide (DMF), 6 mL of DMF and 4.0 mL of distilled water were mixed thoroughly in the polarographic cell/cyclic voltammetric cell and the polarograms/cyclic voltammograms were recorded after removing the dissolved oxygen by passing pure and dry nitrogen gas through the solution for 20 minutes.

Synthesis of pyrazol-3-ones

5-methyl-4-(4^{l}-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-ones (a-f) were synthesized by the procedure mentioned in the literature[15]. The compounds were characterized by elemental analysis, IR and ^{1}H NMR spectral data

Characterization of 5-methyl-4-(4^{l}-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazol-2-ylmethyl)-2,4-dihydro-pyrazol-3-one (a-f)

Table 1. Details of pyrazolin-3-ones synthesized.

Compound		-R
a		H
b		CH_3
c		OCH_3
d		OC_2H_5
e		Cl
f		Br

a: Mol. for. $C_{19}H_{16}N_6O_3S$; Yield 65; m.p°C 150; Element Calculated (Found)% C 55.87 (55.99); H 3.95(4.01); N 20.58(20.16); O 11.75(11.90) ; S 7.85(7.94), IR spectral data (ν_{max} in cm^{-1})- 3180 (NH); 3126 (oxadiazole NH); 1670(C=O); 1603(C=N); 1134(C=S), ^{1}H NMR spectral data (δ ppm)- 2.3 (s, 3H CH_3), 5.45 (s, 2H, N-CH_2-), 6.8 (s, H, Ar - NH) , 7.1–7.3 (m, 5H, Ar-H), 7.4 (d, 2H, C_6H_4), 7.7 (d, 2H, C_6H_4), 14.7 (s, H, thiol-thione tautomeric proton NH).

b: Mol. for. $C_{20}H_{18}N_6O_3S$; Yield 67; m.p°C 152; Element Calculated (Found)% C 56.86(56.91); H 4.29(4.32); N 19.89(19.74); O 11.36(11.48); S 7.59(7.55), IR spectral data (ν_{max} in cm^{-1})- 3160 (NH); 3110 (oxadiazole NH); 1655(C=O); 1600(C=N); 1125(C=S), ^{1}H NMR spectral data (δ ppm)- 2.0 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 5.40 (s, 2H, N-CH_2), 6.8 (s, H, Ar-NH), 7.1-7.3 (m, 4H Ar-H), 7.4 (d, 2H, C_6H_4), 7.7 (d, 2H, C_6H_4), 14.3 (s, H, thiol-thione tautomeric proton NH).

c: Mol. for. $C_{20}H_{18}N_6O_4S$; Yield 62; m.p°C 155; Element Calculated (Found)% C 54.79(54.81); H 4.14(4.04); N 19.17(19.27); O 14.60(14.46); S 7.31(7.42), IR spectral data (ν_{max} in cm^{-1})- 3165 (NH); 3120 (oxadiazole NH); 1660(C=O); 1602(C=N); 1130(C=S), ^{1}H NMR spectral data (δ ppm)- 2.2 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 5.42 (s, 2H, N-CH_2), 6.8 (s, H, Ar-NH), 7.1-7.3 (m, 4H, Ar-H), 7.4 (d, 2H, C_6H_4), 7.7(d, 2H, C_6H_4), 14.5 (s, H, thiol-thione tautomeric proton NH).

d: Mol. for. $C_{21}H_{20}N_6O_4S$; Yield 63; m.p°C 160; Element Calculated (Found)% C 55.74(55.87); H 4.46(4.32); N 18.57(18.36); O14.14(14.34); S 7.09(7.11), IR spectral data (ν_{max} in cm^{-1})- 3160(NH); 3115 (oxadiazole NH); 1650(C=O); 1600(C=N); 1125(C=S), ^{1}H NMR spectral data (δ ppm)- 2.1 (s, 3H, CH_3), 1.8 (t, 3H, $HOCH_3$), 3.16 (q, 2H, O-CH_2), 5.41 (s, 2H, NCH_2), 6.8 (s, H, Ar-NH), 7.1-7.3 (m, 4H Ar-H), 7.4 (d, 2H, C_6H_4), 7.7 (d, 2H, C_6H_4), 14.4 (s, H, thiol-thione tautomeric proton NH).

e: Mol. for. $C_{19}H_{15}ClN_6O_3S$; Yield 65; m.p°C 157; Element Calculated (Found)% C 51.53(51.71); H 3.41(3.53); N 18.98(18.72); O 10.84(10.94); S 7.24(7.12); Cl 8.01(7.98), IR spectral data (ν_{max} in cm^{-1})- 3195(NH); 3135 (oxadiazole NH); 1680(C=O); 1610(C=N); 1140(C=S), ^{1}H NMR spectral data (δ ppm)- 2.4 (s, 3H, CH_3), 5.47 (s, 2H, N-CH_2), 6.8 (s, H, Ar-NH), 7.1-7.3 (m, 4H, Ar-H), 7.4 (d, 2H, C_6H_4), 7.7 (d, 2H, C_6H_4), 14.8 (s, H, thiol-thione tautomeric proton NH).

f: Mol. for. $C_{19}H_{15}BrN_6O_3S$; Yield 68; m.p°C 162; Element Calculated (Found)% C 46.83(46.75); H 3.10(3.24); N 17.25(17.41); O 9.85(9.62); S 6.58(6.46); Br 16.40 (16.52), IR spectral data (ν_{max} in cm^{-1})- 3195(NH); 3140 (oxadiazole NH); 1685(C=O);1615(C=N); 1145(C=S), ^{1}H NMR spectral data (δ ppm)- 2.5 (s, 3H, CH_3), 5.48 (s, 2H, NOCH_2), 6.8 (s, H, Ar-NH), 7.1-7.3 (m, 4H, Ar-H), 7.4 (d, 2H, C_6H_4), 7.7(d, 2H, C_6H_4), 14.9 (s, H, thiol-thione tautomeric proton NH).

RESULTS AND DISCUSSION

Polarographic behaviour of pyrazol-3-ones (a-f)

Polarographic investigations of 5-methyl-4-(4^l-substituted phenyl hydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one were carried out in Briton-Robinson buffer solutions of pH 1.1-10.1. The compounds (a-f) under investigation exhibit a single wave in the pH range 1.1-7.1 and two waves in the pH range 8.1-10.1. An inspection of the structure of compounds shows that the sites susceptible for reduction at the dropping mercury electrode are cyclic azomethine >C=N-, cyclic > C = 0, cyclic C = S and exocyclic azomethine group. It is well known that the exocyclic azomethine group is more susceptible for the reduction than the other three groups. The reduction of the cyclic azomethine >C = N, cyclic >C = 0 and cyclic C = S generally occur at higher negative potentials at the dropping mercury electrode. However the polarographic studies of 5-methyl-2- [4-(-thioxo-4,5-dihydro-[1,3,4]oxadiazol-2-ylmethoxy)-phenyl]-2,4-dihydro-pyrazol-3-one studied under similar experimental conditions reveal that the compound does not exhibit any reduction wave under the experimental conditions. This could be assigned to the stabilization [16] of the pyrazoline-3-one ring by keto-enol tautomerism. This suggests that the waves observed with 5-methyl-4-(4^l-substituted

phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one (a-f) were due to the reduction of the exocyclic azomethine group.

The results shown in the Figure 1 reveal that the half wave potential increases with increase of pH in acidic media and remains unaltered in alkaline pH media. The graph drawn between the half wave potential and the pH was a straight line up to pH 8.1 and the slope lies between 180-230 mV. The half wave potential noticed in the present investigations was thus much more negative than that generally expected for the reduction of the simple azo group [17]. p values, the number of protons (Table 2) were low, non-integers. This suggests that the proton transfer taking place in the reduction process was heterogeneous in nature. There exists equilibrium between protonated form and unprotonated form [18]. Both protonated and unprotonated forms of the depolarizer were electroactive. The unprotonated form was reduced at more negative potential than protonated form of the azomethine group. As equilibrium was shifted towards the unprotonated form, the value of $E_{1/2}$ remains constant.

$$>C=N\text{-}NH \underset{-\,H^+}{\overset{+\,H^+}{\rightleftharpoons}} >C=\overset{+}{N}H\text{-}NH\text{-}$$

unprotonated form — protonated form

The $E_{1/2}$ becomes practically constant in alkaline pH range and this constancy in $E_{1/2}$ may be due to the fact that both acidic and basic forms of the depolarizer were electroactive. But in the pH range where the protonation rate decreases, the half wave potentials of both protonated form (acidic) and unprotonated form (basic) were so close to each other that the waves merge [19] and a single wave was observed. $E_{1/2}$vs pH graph consists of two linear segments intercepting each other and the point of interception of the two linear plots is approximately equal to pK_1. (Figure 1)

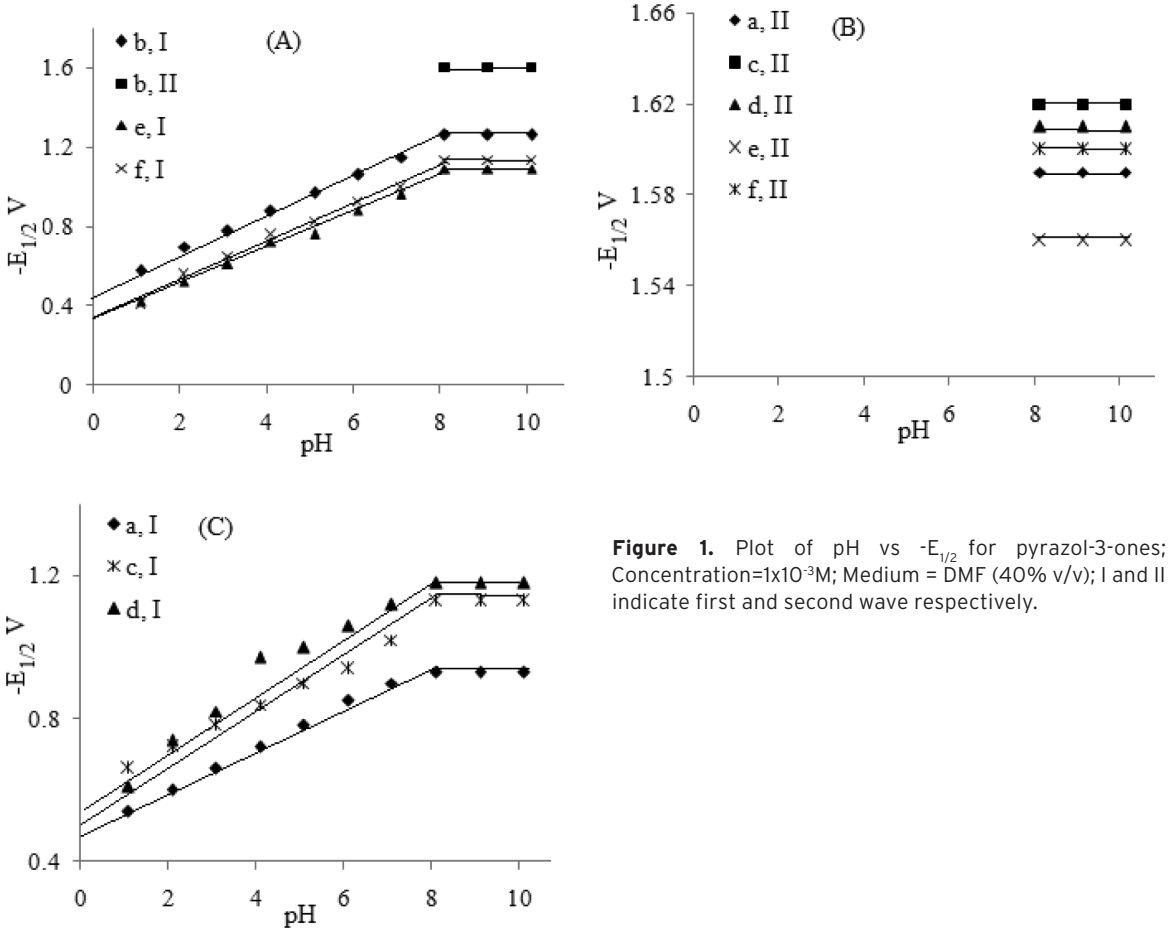


Figure 1. Plot of pH vs $-E_{1/2}$ for pyrazol-3-ones; Concentration=1x10^{-3}M; Medium = DMF (40% v/v); I and II indicate first and second wave respectively.

Nature of the electrode process

The effect of mercury column height on the limiting current indicates the diffusion controlled nature of the polarographic wave. The i_l versus $h^{1/2}$ plots were linear and passing through the origin (Figure 2). The electrode processes was found to be irreversible in low acidic pH media unlike the reversible electrode process observed for simple azo and azomethine compounds [20] under similar conditions. The irreversible nature of >C=N-NH- group reduction in the present investigations was also further confirmed by the slopes of (0.08-0.15) of the semi logarithmic plots (E_{dme} vs log i/d–i, Figure 3) [21], the shift of $E_{1/2}$ towards more negative potentials with increase in the depolarizer concentration [21], the heterogeneous rate constant ($k^{o}_{f,h}$) calculated from the Meites–Israel equation, (Table 2) and the fact that the $K^{0}_{f,h}$ values were less than 10^{-5}. This may be due to the bulky group present at the end of >C=N-NH- linkage.

It is observed from the Figure 4 that the height of the wave decreases with increase of pH and this suggests that both the protonated form (acidic) and the unprotonated form (basic) were transported to the electrode surface and were electroactive.The decrease in the limiting current (Figure 4) with increase in pH may be ascribed to the decrease in H^{+} ion concentration with increase in pH. As the pH increases, the rate of the protonation decreases, thus the limiting current also decreases. The limiting current versus pH graph assumes the shape of a dissociation curve. This type of behaviour was observed for the electroreduction of substituted benzeneazo pyrazolin-5-one [22,23] and other substituted phenylazo compounds [24,25].

Electrode reaction

The plots of $-E_{dme}$ versus log i/i_d – i at typical pH 4.1 are shown in the Figure 3. The slope of the linear plots was not in agreement with the theoretical values (0.030 V and 0.015 V for 2 electron and 4

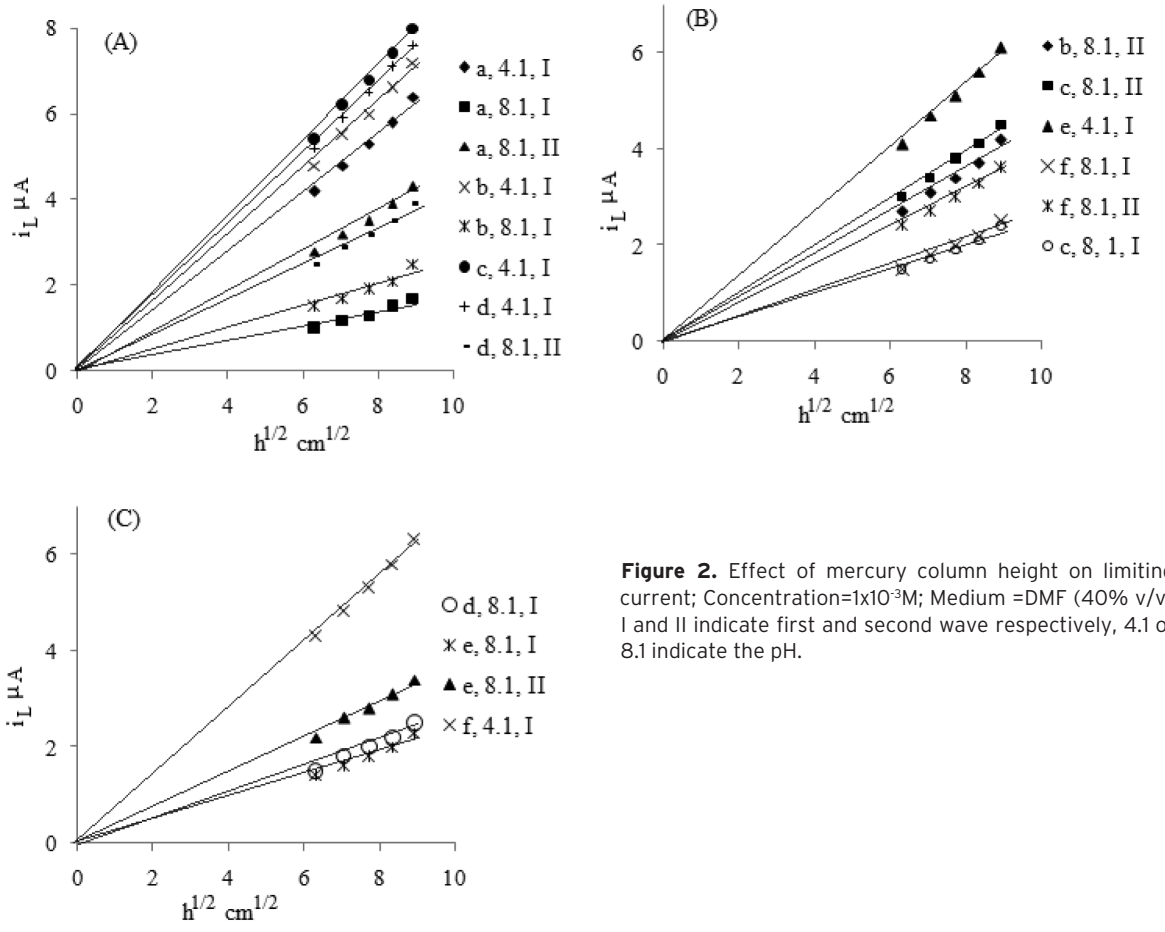


Figure 2. Effect of mercury column height on limiting current; Concentration=1x10^{-3}M; Medium =DMF (40% v/v). I and II indicate first and second wave respectively, 4.1 or 8.1 indicate the pH.

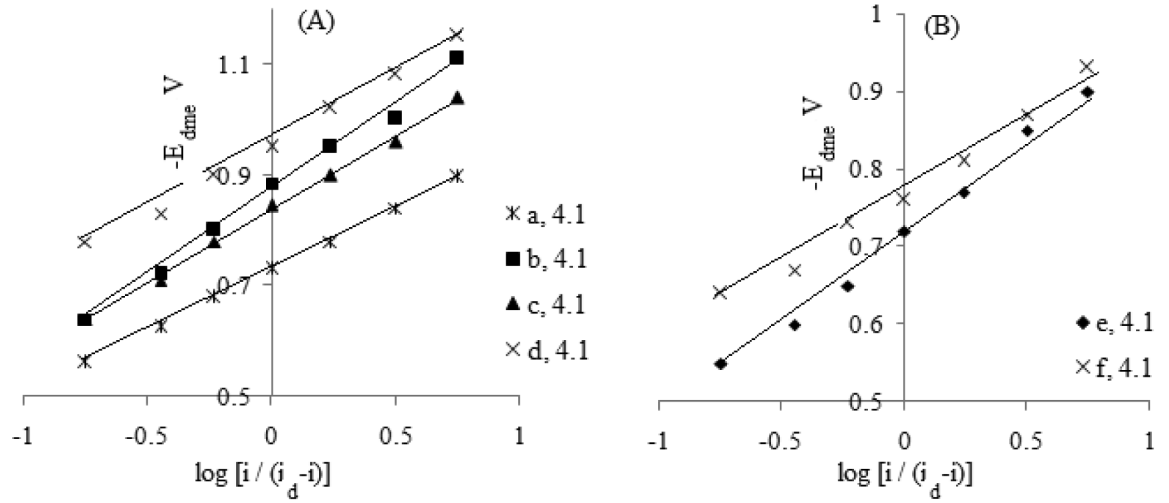


Figure 3. Semi log plots of pyrazol-3-ones. pH 4.1; Concentration=1x10^{-3}M; Medium = DMF (40% v/v).I indicate first wave.

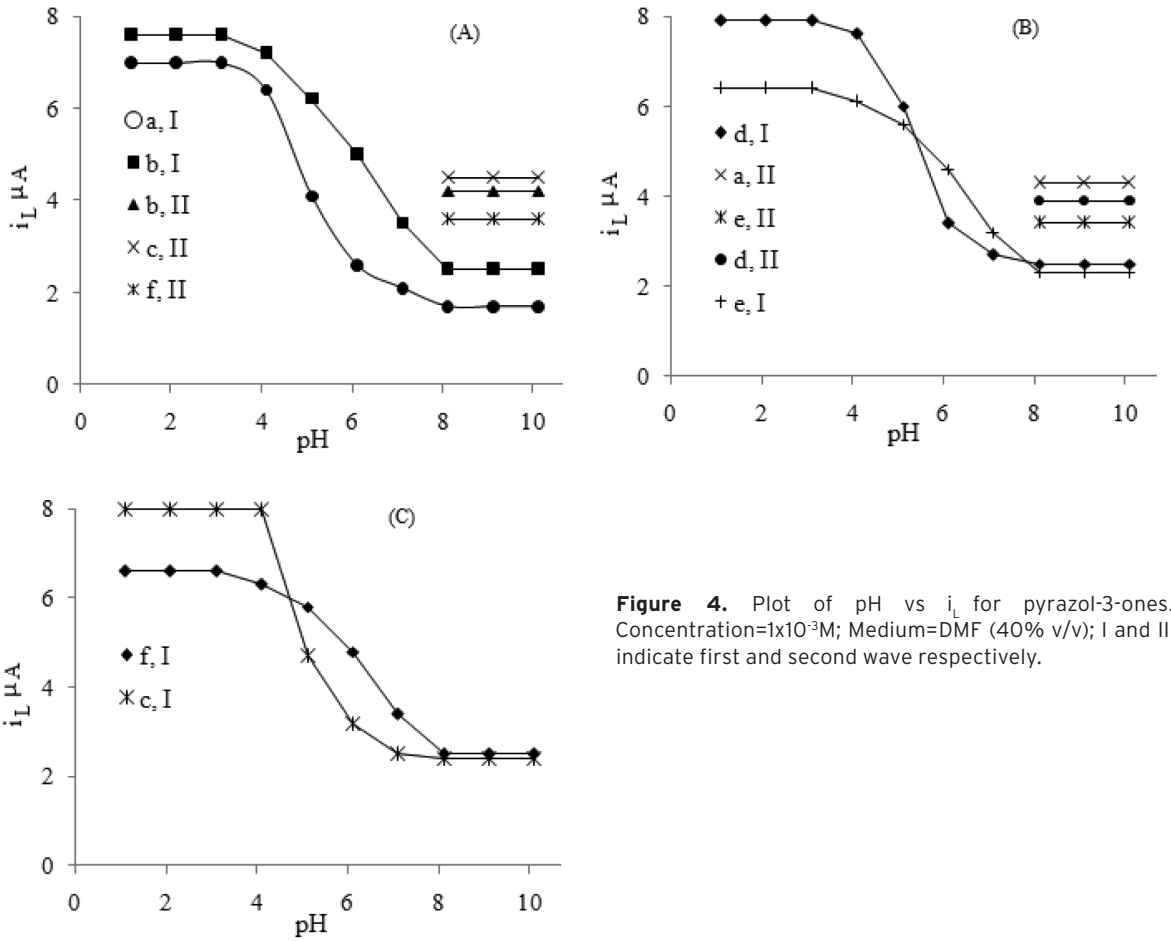


Figure 4. Plot of pH vs i_L for pyrazol-3-ones. Concentration=1x10^{-3}M; Medium=DMF (40% v/v); I and II indicate first and second wave respectively.

electron reduction (respectively) for the reversible waves. This indicates that the electrode reaction was irreversible. The αn_a values (α is the transfer coefficient and n_a is the number of electrons involved)obtained by applying Tome's criteria [26] were almost equal to the values obtained from conventional logarithmic plots (Table 2) indicating the irreversible nature of the polarographic wave.

Kinetic parameters of the electrode reaction

The kinetic parameters for the electrode reaction have been evaluated by Meites-Israel method.

Meites-Israel have extended the Koutecky [27] graphical method into a comparatively more precise mathematical form. The values obtained for $k^{o}_{f,h}$ and ΔG^* at various pH values are given in the Table 2. The $k^{o}_{f,h}$ values decrease with increase of the pH of the medium whereas ΔG^* values increase with the increase of pH. This trend shows that the electrode process was becoming incresingly irreversible with increase in pH of the solution.

Millicoulometric method

It is possible to determine the value of 'n' (number of Faradays per mole of electrode reaction) by the method developed by DeVris and Kroon [28]. The value of n was found to be 4 by comparison with $CdSO_4$ in Britton-Robinson buffers of pH 4.1 containing 40% (V/V) dimethylformamide. The results are shown in Table 3.

Controlled potential electrolysis

The controlled potential electrolysis of 5-methyl-4-(4^{l}-substituted phenylhydrazono)- 2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-oneawas carried out in a Lingane H-type cell. The cathode compartment contains 10 mL of 0.01 M compound 'a', 30 mL of DMF, 20 mL of 1.0 M KCl and 40 mL of the buffer solution (pH 4.1). A potential of -1.1 V was applied and maintained at constant potential by the control of the output from the battery. The electrolysis was followed by recording the decrease in current with time. The number of electrons per molecule was calculated from i-t curves following the procedure outlined by Lingane [29] and was found to be 4. After disconnecting the electrolysis cell, 1 mL of resulting solution was withdrawn and the presence of aniline in this solution was revealed by standard spot test [30]. The remaining reaction mixture was partially evaporated on the water bath to half its volume, allowed to cool to room temperature and was extracted with ether. The ether layer was evaporated under diminished pressure and the yellow crystalline solid was identified as 5-methyl-2-[4-(-thioxo-4,5-dihydro-[1,3,4]oxadiazol-2-ylmethoxy)-phenyl]-2,4-dihydro-pyrazol-3-one.

Reduction mechanism

The points mentioned below indicate that a totally different mechanism from the usual azo-hydrazo-amine mechanism must be operative in the present four electron reduction process.

1. The half wave potential of the wave observed was more negative than that expected for the reduction of the simple azo group [17,31].
2. The phenyl pyrazoles [32] were resistant to reduction under the experimental conditions.
3. The reduction of the azo and the hydrazo groups will not generally take place at the same potential.
4. In strong acidic aqueous solutions, the end products of the reduction of azobenzene are benzidine (70%) and diphenyline (30%) [33]. These compounds are not electroactive.In strong acid solutions, the limiting current of the polarogram of azobenzene should therefore be very much less than that observed in weak acidic solutions.
5. In the present investigations, the limiting current decreases with increase in HCl concentration.
6. Increase of half wave potential with increase in pH (Figure 1) and decrease of half wave potential with increase in HCl concentration prove that the acid-base equilibrium was playing a significant role in the reduction process. But as the wave was not kinetic in nature, acid-base equilibrium was a fast process.

The phenyl hydrazone pyrazoline-3-one (I) was protonated to yield the protonated form [25,34,35]. The weak (=N–NH-) single bond of the hydrazone was then cleaved [36,37] with the uptake of two electrons and two protons. The strength of the acid or alkaline medium employed for these reductions was approximately 0.4%. Hence it was not possible for the amide linkage in the pyrazole nucleus to get affected. Moreover, it was found in a separate experiment that 5-methyl-2-[4-(-thioxo-4,5-dihydro-[1,3,4]oxadiazol-2-ylmethoxy)-phenyl]-2,4-dihydro-pyrazol-3-one was not affected under even stronger acid or alkaline conditions. The unstable intermediate (II imine) produced in the

above process was then reduced to yield amine (IV) in a 2 electron process. It was reported [34,35] that the above mentioned two steps of reduction occur at the same potential and this fact substantiates the appearance of a single four electron wave as shown in Scheme 1.

The great decrease in the half wave potential with the rise in HCl concentration from 0.2 M to 1.0 M was a noteworthy fact since the change in pH corresponds to the influence of chloride ions rather than the acidity. It was reported [31,36] that adsorption of the depolarizer plays a significant role in the reduction of the azomethine compounds in protolyte media. Hence the observed positive shift in the half wave potential with increase of chloride concentration was probably due to the adsorption favoring conditions created with increase in the salt concentration.

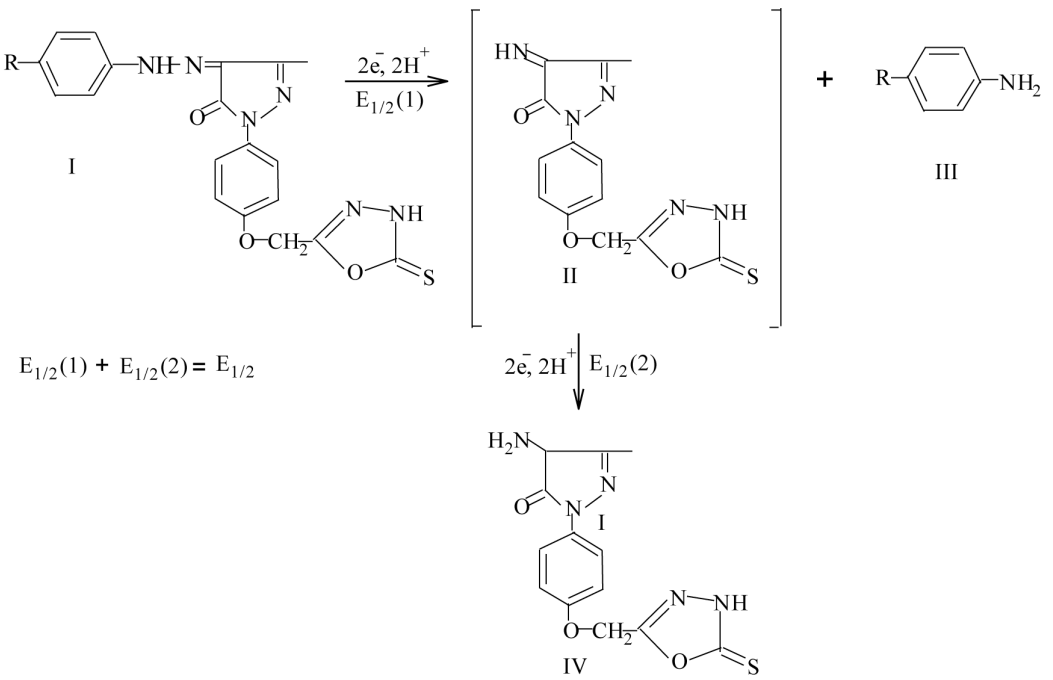
In alkaline medium, 5-methyl-4-(4^{l}-substituted phenyl hydrazono)-2-(5-thioxo-4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one (a-f) exists in the azomethine anionic form (II) and the latter was susceptible to chemical cleavage partially in alkaline solutions into the .corresponding carbonyl compound (IV) as shown in the Scheme 2.

The compounds exhibit two waves in the pH range 8.1-10.1. In strong alkaline medium (0.2 – 1.0 M NaOH), a single wave was observed whose height increases with increase in the alkali concentration. In alkaline medium (pH > pK_a), azomethine compounds (a-f) exists in the azomethine anionic form (II) and the latter undergoes chemical cleavage partially in alkaline into corresponding carbonyl compound (VI) as shown in Scheme 2. The carbonyl compounds were susceptible for reduction at the dropping mercury electrode. Therefore the second wave observed in the present studies has been ascribed to the two electron reduction of carbonyl compound and the first wave to the 4 electron reduction of azomethine anion.

A decrease in the height of the first wave and an increase in the height of the second wave with increase in pH supports to this conclusion. In strong

Mechanism in acidic medium

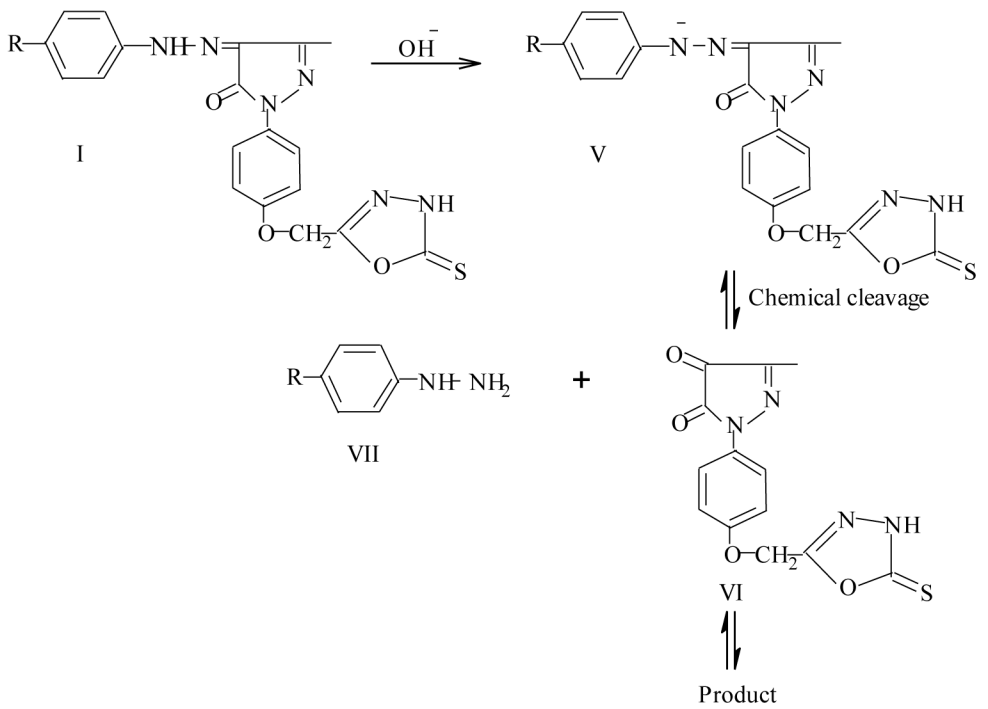
Mechanism in acidic medium



Scheme 1. Mechanism in acidic medium.

Mechanism in alkaline medium

Mechanism in alkaline medium



Scheme 2. Mechanism in basic medium.

alkaline solutions (0.2 – 1.0 M NaOH), the half wave potentials were observed in the range -1.40 to-1.56 V. It was due to the 2 electron reduction of carbonyl group to alcohols.

Substituent effect

The effect of substituent on the polarographic behaviour of 5-methyl-4-(4l-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazo1-2-ylmethyl)-2,4-dihydro-pyrazol-3-one is presented in the following lines. $E_{1/2}$-σ plots for the compounds investigated are presented in Figure 5. The values of specific reaction constant (ρ) are presented in Table 4.

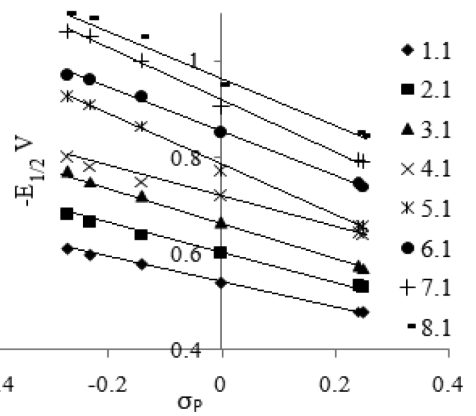


Figure 5. $E_{1/2}$ vs σ_p for the reduction of 5-methyl-4-(4l -substituted phenyl hydrazono-2-(5-thioxo 4,5 dihydro [1,3,4]-oxadiazole-2-ylmethyl) 2,4 dihydro-pyrazol-3-one ($1x10^{-3}$M).

As the values of $\Delta E_{1/2}$/pH, α_n and l (Table 2) are practically in the same range for the entire series, the effect of substituents were quantitatively discussed in terms of the Hammett equation. The values of the Hammett substituent constants were taken from the literature [37]. The values of specific reaction constant (ρ) were found to be in the range of 0.15 – 0.85. The specific reaction constant values were positive and low indicating that the nucleophilic reaction was taking place. This confirms that the electron uptake was the potential determining step.

Cyclic voltammetric studies at hanging mercury drop electrode (HMDE)

The cyclic voltammetric experiments of 5-methyl-4-

Table 2. Polarographic characteristics and kinetic parameters of 5-methyl-4-(4[|]-substituted phenyl hydrazono)- 2-(5-thioxo-4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one (1x 10^{-3}M).; Medium: Aqueous DMF(40%v/v).

Compound	pH	$E_{1/2}$ / pH		α_{na}		No of protons		Dx10^{-6} cm sec^{-1}		I*x10^{-3} cm sec^{-1}		K^{0}_{fh} cm sec^{-1}		$\Delta^{*}G$ K cal $mole^{-1}$	
		I Wave	II Wave	I Wave	II Wave	I Wave	II Wave	I Wave	II Wave	I Wave	II Wave	I Wave	II Wave	I Wave	II Wave
a	2.1	0.06	-	0.48	-	0.486	-	10.24	-	3.88	-	1.678	-	2.861	-
	4.1	0.06	-	0.48	-	0.486	-	8.52	-	3.55	-	1.626	-	2.865	-
	6.1	0.06	-	0.44	-	0.446	-	1.39	-	1.44	-	1.493	-	2.875	-
	8.1	0.06	-	0.41	-	0.415	-	0.6	3.84	0.94	2.38	0.557	-	2.987	-
	10.1	0.06	-	0.41	-	0.415	-	0.6	3.84	0.94	2.38	0.557	-	2.987	-
b	2.1	0.09	-	0.53	-	0.806	-	12.04	-	4.22	-	11.505	-	2.641	-
	4.1	0.09	-	0.53	-	0.806	-	10.82	-	4	-	2.659	-	2.809	-
	6.1	0.09	-	0.48	-	0.73	-	5.19	-	2.77	-	2.21	-	2.83	-
	8.1	0.09	-	0.44	-	0.669	-	1.29	3.68	1.38	2.33	1.282	-	2.892	-
	10.1	0.09	-	0.44	-	0.669	-	1.29	3.68	1.38	2.33	1.282	-	2.892	-
c	2.1	0.06	-	0.53	-	0.537	-	13.39	-	4.44	-	8.03	-	2.683	-
	4.1	0.06	-	0.53	-	0.537	-	13.39	-	4.44	-	6.782	-	2.702	-
	6.1	0.06	-	0.48	-	0.486	-	2.13	-	1.77	-	1.333	-	2.888	-
	8.1	0.06	-	0.44	-	0.446	-	1.18	4.2	1.33	2.5	1.137	-	2.906	-
	10.1	0.06	-	0.44	-	0.446	-	1.18	4.2	1.33	2.5	1.137	-	2.906	-
d	2.1	0.08	-	0.53	-	0.716	-	13.03	-	4.38	-	5.243	-	2.731	-
	4.1	0.08	-	0.53	-	0.716	-	12.04	-	4.22	-	4.381	-	2.752	-
	6.1	0.08	-	0.48	-	0.649	-	2.4	-	1.88	-	1.503	-	2.874	-
	8.1	0.08	-	0.44	-	0.595	-	1.29	3.16	1.38	2.16	0.505	-	2.999	-
	10.1	0.08	-	0.44	-	0.595	-	1.29	3.16	1.38	2.16	0.505	-	2.999	-
e	2.1	0.09	-	0.59	-	0.897	-	8.52	-	3.55	-	2.069	-	2.837	-
	4.1	0.09	-	0.59	-	0.897	-	7.78	-	3.38	-	2	-	2.841	-
	6.1	0.09	-	0.53	-	0.806	-	4.41	-	2.55	-	1.679	-	2.861	-
	8.1	0.09	-	0.48	-	0.73	-	1.1	2.4	1.27	1.88	0.581	-	2.983	-
	10.1	0.09	-	0.48	-	0.73	-	1.1	2.4	1.27	1.88	0.581	-	2.983	-
f	2.1	0.09	-	0.61	-	0.928	-	9.12	-	3.66	-	6.664	-	2.704	-
	4.1	0.09	-	0.61	-	0.928	-	8.29	-	3.5	-	5.502	-	2.726	-
	6.1	0.09	-	0.55	-	0.836	-	4.79	-	2.66	-	4.57	-	2.747	-
	8.1	0.09	-	0.5	-	0.76	-	1.29	2.68	1.38	2	1.491	-	2.875	-
	10.1	0.09	-	0.5	-	0.76	-	1.29	2.68	1.38	2	1.491	-	2.875	-

Table 3. Millicoulometric data of 5-methyl-4-(4^{l}-substituted phenyl hydrazono)- 2-(5-thioxo-4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one ($0.8x10^{-4}$ M).

pH	Current (μ A)		Time (seconds)		n value	
	First wave	Second wave	First wave	Second wave	First wave	Second wave
4.1	6.4	-	0	-	-	-
	5.0	-	7200	-	3.1	-
	4.2	-	10800	-	5.4	-
8.1	1.7	4.3	0	0	-	-
	1.6	3.4	7200	7200	3.9	2.2
	1.8	2.9	10800	10800	3.4	4.0

Table 4. Effect of pH on the reaction constant for the reduction of 5-methyl-4(4^{l}-substituted phenylhydrozono)-2-(5-thioxo-4,5-dihydro[1,3,4] oxadiazol-2-ylmethyl)-2,4-dihydro-pyrazol-3-one; $C=1x10^{-3}$M.

pH	ρ	pH	ρ
1.1	0.29	6.1	0.58
2.1	0.29	7.1	0.66
3.1	0.45	8.1	0.66
4.1	0.33	9.1	0.66
5.1	0.50	10.1	0.66

(4^{l}-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one a-f were conducted at HMDE in buffer solutions of pH 2.1, 4.1, 6.1, 8.1 and 10.1 at different scan rates 10mVs^{-1}, 20 mVs^{-1}, 50 mVs^{-1}, 100 mVs^{-1}, 200 mVS^{-1}, 300 mVs^{-1}and 500 mVs^{-1}. A single cathodic peak in lower scan rates and two cathodic peaks in higher scan rates were noticed in solutions of pH 2.1-10.1. A cathodic peak in anodic cycle called inverted peak was noticed in solutions of pH 2.1-6.1. The cathodic peak potentials become more negative and the cathodic peak currents increase with the increase in the scan rate as shown in the Tables 5-7.The cathodic peak potentials were shifted to more negative values and the peak currents were decreased with the increase in the pH.

In solutions of pH 2.1-10.1, 5-methyl-4-(4^{l}-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-ones (a-f) exhibit one cathodic peak in lower sweep rates and two cathodic peaks in higher sweep rates. It may noticed from the Tables 5-7 that there is a negative shift in the peak potential with increase in sweep rates [38], the anodic peak was absent in the reverse scan rate [39], and the $i_{pc}/\upsilon^{1/2}$ versus υ plots were satisfying the Nicholson and Shain criteria [40] to confirm the irreversible nature of the electrode process.

The plots of i_{pc} vs $\gamma^{1/2}$ concentration and i_{pc} vs $\gamma^{1/2}$ fulfill the criteria for the diffusion controlled nature of the electrode process[41]. The plots of E_{Pc} vs pH were similar to $E_{1/2}$ vs pH plots and this lends support to the finding of the DC polarography. But in contrast to a single reduction wave observed in DC polarography in acidic solutions (pH 2.1-6.1), two cathodic peaks were observed at high scan rates (100-500 mVs^{-1}) in cyclic voltammetric studies and therefore suggest that the reduction was taking

place in two steps. The peak potential data showed that the potentials were very close to each other. Further two peaks observed in cyclicvoltammetric studies at high scan rates indicate that these steps were quite fast. This was probably the reason for the appearance of single wave in DC polarography. In alkaline solutions (pH 8.1-10.1), two polarographic waves in DC polarography and two cathodic peaks in cyclic voltammetric studies were observed. The first reduction step in DC polarography or the first cathodic peak in CV studies was attributed to 4 electron reduction of azomethine anionic form to amine (>C=N-N-to >C-NH_2 and NH_2–). The second reduction step in both the studies was ascribed to two electron reduction of ketone formed in the chemical cleavage of azomethine anion form into carbinol.

Inverted peaks

The peaks potentials were unaltered in lower sweep rates (10-50 mVs^{-1}) and increases in higher sweep rates (100-500 mVs^{-1}). The peak current increases with increase in sweep rates. However cathodic peak during anodic cycle (inverted peak, except in the solutions of pH 8.1-10.1 and in 0.1 M NaOH) was noticed in the present studies in buffer solutions of pH 2.1-6.10. The fact that a significant polarographic maximum was observed for the compounds under the chosen experimental conditions indicates that the inverted peak was due to the movement of the mercury surface due to uneven drop polarization [40,42,43].

Substituent effect on the cyclic voltammetric behaviour

A graph was drawn between the cathodic peak potential and the Hammett's substituent constant to assess the influence of substituent on the cathodic peaks corresponding to the azo group reduction. Typical plots obtained are presented in Figure6. The values are presented in Table 8. The slope (ρ) of the linear plots is positive and represents the nucleophilic reduction.

Cyclic voltammetric studies at crown-ether modified carbon paste electrode

The application of chemically modified electrodes in electro-analytical measurements is now a practical proposition. Chemically modified electrodes have been of considerable interest in the recent years. Wide spectrum of materials of diverse origin [22,44] can be analyzed using both CPE and chemically modified CPE.

Table 8. Effect of pH on the reaction constant for the reduction of 5-methyl-4-(4^{l}-chloro phenyl hydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one ($1x10^{-3}$M).

pH	ρ (First wave)	ρ (Second wave)
2.1	0.41	0.16
4.1	0.33	0.25
6.1	0.33	0.38
8.1	0.25	0.33
10.1	0.25	0.33

General voltammetric behavior

The cycle voltammetric experiments of 5-methyl-4-(4^{l}-substituted phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazol-2-ylmethyl)-2,4-dihydro-pyrazol-3-one a-f were conducted using a crown ether modified carbon paste electrode in Briton-Robsinson buffer solutions of pH 2.1, 4.1, 6.1, 8.1 and 10.1 at different scan rates viz 10 mVs^{-1}, 20 mVs^{-1}, 100 mVs^{-1}, 300 mVs^{-1} and 500 mVs^{-1}.

Cyclic voltammograms of 5-methyl-4-(phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4] oxadiazol-2-ylmethyl)-2,4-dihydro-pyrazol-3-one 'a' were recorded with plain (unmodified) carbon paste electrode. A well defined single cathodic peak was observed at high sweep rates (100 mVs^{-1}, 300 mVs^{-1} and 500 mVs^{-1}) and ill defined cathodic peak was noticed at lower sweep rates (10 mVs^{-1}, 20 mVs^{-1}, and 50 mVs^{-1}) in solutions of pH 2.1-7.1.The compounds a-f at MCPE exhibit one cathodic peak in the buffer solutions of pH 2.1-7.1 and two cathodic peaks in buffer solutions of pH 8.1-10.1. In addition to these peaks an anodic peak in buffer solutions of pH 2.1-6.1 was noticed. The cathodic peak potentials increases with increase in pH and it remains unaltered in alkaline solutions. The fact that the cathodic peak currents were proportional to square root of scan rates suggests the process was diffusion controlled and was further confirmed by the linear variationof i_{pc} with concentration. The irreversible nature of the peak is characterized by (1)dependence of peak potential on sweep rates, (2) the plot of $E_{pc}/\gamma^{1/2}$ vs sweep rate is straight line parallel to sweep rate

Table 5. Cyclic voltammetric results of Effect of pH on E_{+} and limiting current of pyrazol-3-ones (1x10^{-3}M); Medium : Aqueous DMF (40 % V/V)

pH	Scan rate (Vs^{-1})	$-E_{PCI}$ (V)	$-E_{PCI\,I}$ (V)	$-E_{PC}$ inv (V)	I_{PCI} (uA)	I_{PCII} (υA)	I_{PC} inv (uA)	E_{pcI} (V)	$-E_{pcII}$ (V)	$-E_{pa}$ (V)	I_{pcI} (μA)	I_{pcII} (μA)	I_{pa} (μA)
HMDC								**MCPE**					
5-methyl-4-(phenylhydrazono)- 2-(5-thioxo- 4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one													
4.1	0.010	0.72		0.63	0.5		0.3	0.87		1.23	1.1		0.8
	0.020	0.81		0.72	0.7		0.5	0.91		1.27	1.6		1.2
	0.050	0.87		0.78	1.1		0.7	0.95		1.31	2.4		1.8
	0.100	0.93	1.05	0.84	1.5	1.2	0.9	0.99		1.35	3.5		2.5
	0.200	0.99	1.17	0.90	2.8	1.8	1.4	1.03		1.39	4.9		3.6
	0.300	1.05	1.29	0.96	3.2	2.2	1.6	1.09		1.45	6.0		4.3
	0.500	1.11	1.47	1.02	4.3	2.8	2.2	1.15		1.50	7.8		5.6
8.1	0.010	0.96			0.2			1.08	1.59		0.5	0.8	
	0.020	1.05			0.3			1.12	1.63		0.7	1.2	
	0.050	1.11			0.5			1.16	1.67		1.1	1.8	
	0.100	1.17	1.29		0.6	0.6		1.20	1.71		1.5	2.5	
	0.200	1.23	1.41		0.9	0.9		1.24	1.75		2.3	3.6	
	0.300	1.29	1.53		1.1	1.1		1.30	1.81		2.8	4.3	
	0.500	1.35	1.65		1.4	1. 4		1.36	1.87		3.5	5.6	
5-methyl- 4-(4[-methyl phenylhydrazono)- 2-(5-thioxo- 4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one													
4.1	0.010	0.91		0.82	0.6		0.3	1.03		1.24	1.2		1.0
	0.020	0.97		0.88	0.8		0.4	1.07		1.28	1.7		1.4
	0.050	1.03		0.94	1.4		0.7	1.11		1.32	2.6		2.2
	0.100	1.09	1.21	1.00	1.9	1.6	0.9	1.15		1.36	3.7		3.1
	0.200	1.15	1.27	1.06	2.6	2.3	1.5	1.19		1.40	5.3		4.4
	0.300	1.21	1.33	1.12	3.3	2.8	1.6	1.25		1.46	6.6		5.4
	0.500	1.27	1.39	1.18	4.2	3.6	2.2	1.31		1.51	8.5		7.1
8.1	0.010	1.29			0.3			1.43	1.60		0.5	0.7	
	0.020	1.35			0.4			1.45	1.64		0.7	1.0	
	0.050	1.41			0.7			1.49	1.68		1.1	1.5	
	0.100	1.47	1.59		0.9	0.9		1.53	1.72		1.5	2.2	
	0.200	1.53	1.65		1.4	1.4		1.57	1.76		2.3	3.3	
	0.300	1.59	1.71		1.6	1.6		1.63	1.82		2.8	3.8	
	0.500	1.65	1.77		2.2	2.2		1.69	1.88		3.5	4.9	

Table 6. Cyclic voltammetric results of Effect of pH on E_+ and limiting current of pyrazol-3-ones ($1x10^{-3}$M); Medium : Aqueous DMF(40 % V/V

pH	Scan rate (Vs^{-1})	$-E_{PCI}$ (V)	$-E_{PCI\ I}$ (V)	$-E_{PC}$ inv (V)	I_{PCI} (uA)	I_{PCII} (uA)	I_{PC} inv (uA)	E_{pcI} (V)	$-E_{pcII}$ (V)	$-E_{pa}$ (V)	I_{pcI} (μA)	I_{pcII} (μA)	I_{pa} (μA)
HMDC								**MCPE**					
5-methyl-4-(4[l]-methoxy phenylhydrazono)- 2-(5-thioxo- 4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro pyrazol-3-one													
4.1	0.010	0.87		0.78	0.7		0.7	0.99		1.20	1.0		0.8
	0.020	0.93		0.84	0.9		0.9	1.03		1.24	1.4		1.2
	0.050	0.99		0.90	1.5		1.5	1.07		1.28	2.2		1.7
	0.100	1.05	1.17	0.96	2.2	2.2	2.2	1.11		1.32	3.1		2.5
	0.200	1.11	1.23	1.02	3.2	3.2	3.2	1.15		1.36	4.7		3.6
	0.300	1.17	1.29	1.08	3.8	3.8	3.8	1.21		1.42	5.4		4.3
	0.500	1.23	1.35	1.14	4.9	4.9	4.9	1.27		1.48	7.1		5.6
8.1	0.010	1.11			0.4			1.28	1.62		0.4	0.7	
	0.020	1.17			0.6			1.32	1.66		0.6	0.9	
	0.050	1.23			0.9			1.36	1.70		0.9	1.5	
	0.100	1.29	1.41		1.2	1.2		1.40	1.74		1.3	2.3	
	0.200	1.35	1.47		1.8	1.8		1.44	1.78		1.8	3.2	
	0.300	1.41	1.53		2.2	2.2		1.50	1.84		2.3	3.9	
	0.500	1.47	1.59		2.8	2.8		1.56	1.90		2.8	4.9	
5-methyl- 4-(4[l]-ethoxy phenylhydrazono)- 2-(5-thioxo- 4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one													
4.1	0.010	0.95		0.86	0.7		0.4	1.12		1.33	1.2		0.9
	0.020	1.01		0.92	0.9		0.6	1.16		1.37	1.7		1.2
	0.050	1.07		0.98	1.5		0.9	1.20		1.41	2.6		1.9
	0.100	1.13	1.25	1.04	2.2	1.9	1.2	1.24		1.45	3.7		2.8
	0.200	1.19	1.31	1.1	3.2	2.7	1.8	1.28		1.49	5.3		4.1
	0.300	1.25	1.37	1.16	3.8	3.2	2.2	1.34		1.55	6.6		5.0
	0.500	1.31	1.43	1.22	4.9	4.2	2.8	1.40		1.61	8.5		6.3
8.1	0.010	1.21			0.4			1.33	1.76		0.7	0.6	
	0.020	1.27			0.6			1.37	1.80		1.0	0.9	
	0.050	1.33			0.9			1.41	1.84		1.5	1.3	
	0.100	1.39	1.51		1.2	0.9		1.45	1.88		2.2	1.9	
	0.200	1.48	1.60		1.8	1.4		1.49	1.92		3.3	2.7	
	0.300	1.57	1.69		2.2	1.6		1.55	1.98		3.8	3.2	
	0.500	1.66	1.78		2.8	2.2		1.61	2.04		4.9	4.3	

Table 7. Cyclic voltammetric results of Effect of pH on E_{+} and limiting current of pyrazol-3-ones ($1x10^{-3}$M); Medium : Aqueous DMF (40% V/V)

pH	Scan rate (Vs^{-1})	$-E_{PCI}$ (V)	$-E_{PCI\ I}$ (V)	$-E_{PC}$ inv (V)	I_{PCI} (uA)	I_{PCII} (uA)	I_{PC} inv (uA)	E_{pcI} (V)	$-E_{pcII}$ (V)	$-E_{pa}$ (V)	I_{pcI} (μA)	I_{pcII} (μA)	I_{pa} (μA)
HMDC								**MCPE**					
5-methyl- 4-(4^{l}-chloro phenylhydrazono)- 2-(5-thioxo- 4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one													
4.1	0.010	0.73		0.64	0.4		0.2	0.87		1.08	1.0		0.7
	0.020	0.79		0.70	0.6		0.3	0.91		1.12	1.4		0.9
	0.050	0.85		0.76	0.9		0.5	0.95		1.16	2.2		1.5
	0.100	0.91	1.03	0.82	1.2	0.9	0.6	0.99		1.20	3.1		2.3
	0.200	0.97	1.09	0.88	1.8	1.4	0.9	1.03		1.24	4.7		3.2
	0.300	1.03	1.15	0.94	2.1	1.6	1.1	1.09		1.30	5.4		3.9
	0.500	1.09	1.21	1.00	2.8	2.2	1.4	1.15		1.36	7.1		4.9
8.1	0.010	1.12			0.3			1.24	1.56		0.4	0.6	
	0.020	1.18			0.4			1.28	1.60		0.6	0.9	
	0.050	1.24			0.7			1.32	1.64		0.9	1.3	
	0.100	1.30	1.42		0.9	0.9		1.36	1.68		1.3	1.9	
	0.200	1.36	1.48		1.4	1.4		1.40	1.72		1.8	2.7	
	0.300	1.42	1.54		1.6	1.6		1.46	1.78		2.3	3.2	
	0.500	1.48	1.60		2.2	2.2		1.52	1.84		2.8	4.3	
5-methyl- 4-(4^{l}-bromo phenylhydrazono)- 2-(5-thioxo- 4,5- dihydro-[1,3,4] oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one													
4.1	0.010	0.77		0.68	0.5		0.3	0.91		1.12	1.0		0.7
	0.020	0.83		0.74	0.7		0.5	0.95		1.16	1.4		0.9
	0.050	0.89		0.80	1.1		0.7	0.99		1.20	2.2		1.5
	0.100	0.95	1.07	0.86	1.5	1.2	0.9	1.03		1.24	3.1		2.3
	0.200	1.01	1.13	0.92	2.3	1.8	1.4	1.07		1.28	4.7		3.2
	0.300	1.07	1.19	0.98	2.7	2.2	1.6	1.13		1.34	5.4		3.9
	0.500	1.13	1.25	1.04	3.5	2.8	2.2	1.19		1.40	7.1		4.9
8.1	0.010	1.16			0.4			1.28	1.60		0.5	0.6	
	0.020	1.22			0.6			1.32	1.64		0.7	0.9	
	0.050	1.28			0.9			1.36	1.68		1.1	1.3	
	0.100	1.34	1.46		1.2	0.9		1.40	1.72		1.5	1.9	
	0.200	1.40	1.52		1.8	1.4		1.44	1.76		2.3	2.7	
	0.300	1.46	1.58		2.2	1.6		1.50	1.82		2.8	3.2	
	0.500	1.52	1.64		2.8	2.2		1.56	1.88		3.5	4.3	

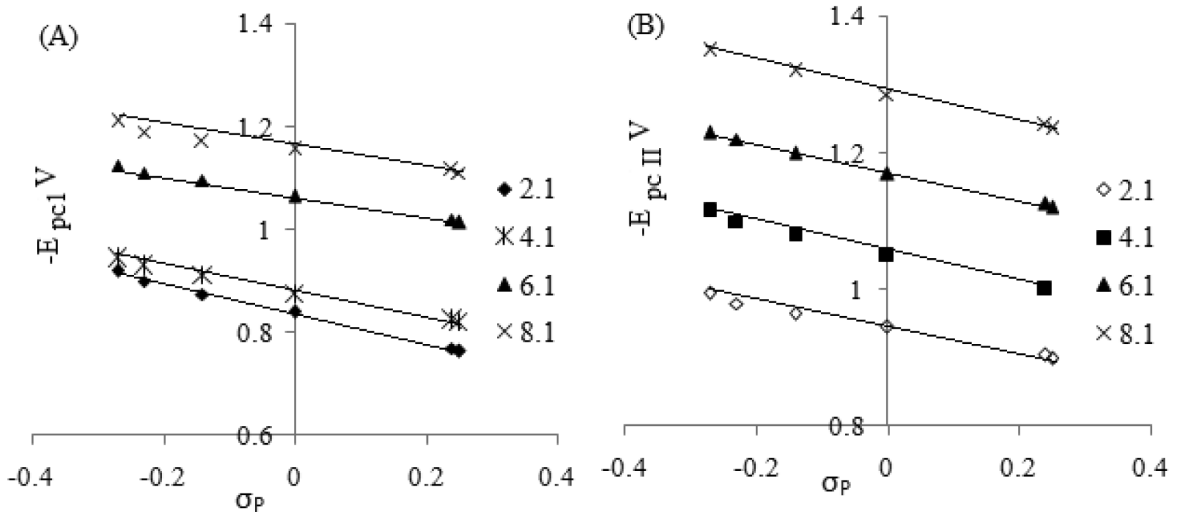


Figure 6. $E_{1/2}$ vs σ_p of 5-methyl-4(4^{l}-substituted phenylhydrozono)-2,(5-thioxo-4,5-dihydro-(1,3,4)oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-one at HMDE (A) and (B) represent the first and second cathodic peaks respectively; Concentration=1x10^{-3}M.

axis and (3) the shape of $i_{pc}/\gamma^{1/2}$ versus γ plot was in accordance with the Nicholson and Shain criteria (II).

Comparison between polarographic behavior and cyclic voltammetric behaviour

The compounds (a-f) exhibit a well defined single wave in the buffer solutions of pH 1.1-7.1 and two waves in alkaline solutions of pH 8.1-10.1 in polarographic studies at dropping mercury electrode. In cyclic voltammetric studies at HMDE one cathodic peak in lower scan rates and two cathodic peaks in higher scan rates were obtained alongwith an inverted peak in the acidic solutions of pH 2.1-6.1. However, one cathodic peak in solutions of pH 2.1-7.1 and two cathodic peaks in the pH range of 8.1-10.1 were observed in cyclic voltammetric studies at modified carbon electrode alongwith an anodic peak in acidic solutions of pH 2.1-7.1.

Nature of electrode process

The irreversible nature of the wave was further supported by negative shift in the peak potential with increase in sweep rates. The plots of i_{pc} vs concentration and i_{pc} vs $\gamma^{1/2}$ fulfil the criteria for the diffusion controlled nature of the electrode process. The plots of E_{pc} vs pH were similar to E_{pa} vs pH plots and this lends support to the finding of the DC polarography.

Reduction mechanism is acidic medium

The first polarographic wave in the solutions of pH 2.1-7.1 itself manifest as two cathodic peaks at higher sweep rates in cyclic voltammetric studies at HMDE and one cathodic peak at chemically modified carbon paste electrode under similar experimental conditions. This was attributed to the four electron reduction of azomethine group (>C=N-NH) to amine stage, in two steps through imine intermediate. An anodic peak was noticed in the acidic solutions of pH 2.1-6.1 at MCPE studies and it may be due to oxidation of amine formed in the reduction process.

Reduction mechanism in alkaline medium

In solutions of pH 8.1-10.1, two polarographic waves in DC polarography or two cathodic peaks in CVM studies at HMDE or MCPE were noticed. The first wave or peak was attributed to four electron reduction of azomethine anionic form to an amine (>C=N-N-to >C-NH_2 and NH_2). The second wave or peak was ascribed to two electron reduction of ketone formed in the chemical cleavage of azomethine anion form into carbinol.

CONCLUSION

Novel Pyrazolin-3-ones namely 5-methyl-4-(4^{l}-substitute phenylhydrazono)-2-(5-thioxo-4,5-dihydro-[1,3,4]oxadiazole-2-ylmethyl)-2,4-dihydro-pyrazol-3-ones were synthesized and

characterized by IR, ^{1}H NMR and elemental analysis. The polarographic investigations were carried out on the title compounds to deduce the reduction mechanism in acidic and basic media. The reduction was found to be reversible and diffusion controlled with the involvement of protons. The results were compared with those obtained in cyclic voltammetry at hanging mercury drop electrode and modified carbon paste electrode.

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