Synthesis and electrochemical investigations on certain pyrazolin-5-ones

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Received 7 September 2011; revised 7 January 2012; accepted 28 February 2012

Abstract The electrochemical behavior of certain pyrazolin-5-ones was investigated at the dropping mercury electrode by employing DC polarography. The variables that influence the electrode process were extensively studied. All compounds under investigation gave two well defined polarographic waves. The mechanism for the electrode process was proposed in acid, as well as in basic media. The results obtained in polarography were compared with those obtained in cyclic voltammetry.

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1. Introduction

The chemistry of pyrazolone derivatives has received much attention, because of their interesting structural properties and applications to diverse areas [1]. Pyrazolin-5-ones are a very important class of heterocycles, due to their potential pharmacological and biological applications [2–4]. It is also well known that they have been used as therapeutic agents, such as anti-inflammatory, antibacterial, antifungal, analgesic and antipyretic etc. [5,6]. However antifungal drug discovery continues to be a crucial area [7]. This is due to the fact that, in recent years, the pathogenic microorganisms have developed excessive resistance to these drugs, due to widespread use [8].

Pyrazolin-5-ones are effective antifungal [9] agents. Pyrazolin-5-ones function as potential cdc25 inhibitors and are thought to be a good lead scaffold for developing an anticancer drug [10]. Some have shown preventive effects on myocardial injury [11] and acute myocardial infarction [12], and have been used in the treatment of cardiovascular disease [13].

In addition to these pharmacological applications, they have vital commercial significance. The design of photoluminescent lanthanide complexes of pyrazolones provide a suitable basis for sensitized near-infrared luminescence [14], and these materials are used in different kinds of light conversion and light-amplification devices [15,16]. The pyrazolin-5-ones are extensively used in the manufacture of commercial dyes, such as photographic dyes, textile dyes etc. The application is based on the fact that the pyrazolin-5-one system is an effective electron acceptor [17], and can also act as a weak electron
Table 1: Characteristics of pyrazolin-5-ones.

| Sample no | Substituent (R) | Color     | Melting point (°C) | Mol. wt. | Elemental analysis Found (Cal) % |
|-----------|-----------------|-----------|--------------------|---------|--------------------------------|
|           |                 |           |                    |         | C     | H     | N     | S     | Cl     |
| 1         | –H              | Orange    | 159–160            | 357     | 53.61 | 4.20  | 19.52 | 8.88  | (53.78) | (4.24) | (19.60) | (8.98) |
| 2         | 2′–CH₃         | Yellow    | 59–60              | 371     | 54.74 | 4.46  | 18.75 | 8.56  | (54.98) | (4.62) | (18.86) | (8.64) |
| 3         | 2′–OCH₃        | Yellow    | 67–68              | 387     | 52.61 | 4.39  | 18.01 | 8.09  | (52.71) | (4.43) | (18.08) | (8.28) |
| 4         | 2′–OH          | Black     | 251–252            | 373     | 51.35 | 3.98  | 18.65 | 8.51  | (51.47) | (4.05) | (18.76) | (8.59) |
| 5         | 2′–Cl          | Yellow    | 126–127            | 391     | 49.01 | 3.57  | 17.69 | 8.09  | 8.91    | (49.05) | (3.61) | (17.88) | (8.19) | (9.05) |

Scheme 1: Synthesis 2-pyrazolin-5-ones.

IR spectral details were obtained from a Perkin-Elmer 283 spectrometer.

All reagents used were of analytical reagent grade procured from Merck, India. The working solutions were prepared using double distilled water. The Britton–Robinson buffer was prepared from appropriate amounts of 0.04 M o-phosphoric acid, 0.04 M boric acid and 0.04 M acetic acid. The solutions of desired pH values were prepared by the addition of an appropriate volume of 0.2 M sodium hydroxide solution.

2.2. Preparation of toluene sulfonyl hydrazide (Scheme 1 (I)) [20]

A solution of p-toluene sulfonyl chloride in acetone and an appropriate amount of hydrazine hydrate were treated with 5% NaOH solution. The mixture was shaken vigorously for ten minutes, cooled and poured into 1:1 HCl. The precipitate formed was filtered, washed with water and recrystallized from alcohol.

2.3. Preparation of substituted aryl diazonium chloride (Scheme 1 (II)) [21]

The required amount of substituted aryl amine was dissolved in a suitable volume of dilute hydrochloric acid. The solution obtained was cooled to 0 °C and a little excess of an aqueous solution of sodium nitrite was added slowly. The addition of a little excess of sodium nitrite solution stabilizes the diazonium salt.

2.4. Preparation of aryl diazonium cyano esters (Scheme 1 (III)) [22]

The respective diazonium chloride solution was added to an ice cold solution of the mixture of sodium acetate and ethyl cyano acetate solutions in methanol. The addition of corresponding diazonium chloride was continued until yellow crystals were separated out. The crystals were filtered, washed with water and dried.

2.5. Synthesis of 2-pyrazolin-5-ones (Scheme 1 (IV))

A mixture of appropriate amounts of diazonium cyano ester and toluene sulfonyl hydrazide in ethanol was refluxed for six hours and cooled. The crystalline solid separated was filtered, washed with water, dried and recrystallised from dimethylformamide (1:1). The melting points of the different compounds synthesized are presented in Table 1. As these donor [18]. It is also reported that iron complexes of certain pyrazolin-5-ones are environmental friendly and are potential replacements for some important hazardous brownish black acid dyes [19].

The diverse applications of pyrazolin-5-ones in different fields have inspired the authors to investigate the reduction behavior of these compounds. Particularly, the knowledge of the electrochemical reduction of pyrazolin-5-ones is a prerequisite for understanding the metabolic pathway leading to biological or pharmacological activity.
Figure 1: Plot of pH vs. $-E_{1/2}$ for pyrazolin-5-ones. [pyrazolin-5-one] = $1 \times 10^{-3}$ M; Medium = Dimethylformamide (40% v/v). I indicates first wave and II indicates second wave.

compounds are synthesized by already reported methods, the authors have characterized these compounds by elemental analysis, melting points and characteristic IR spectral bands. The IR spectrum of the compounds showed bands characteristic of the cyclic carbonyl group at around $1670 \text{ cm}^{-1}$ [23]. The band at around $1555 \text{ cm}^{-1}$ confirms the presence of $>\text{C}=\text{C–NH–N}=$ vibration [24]. The bands mentioned above are attributed to the presence of the 2-pyrazolin-5-one structure.

2.6. General experimental procedure employed for polarographic and cyclic voltammetric studies

10 mL of the buffer solution of the required pH, 2.5 mL of pyrazolin-5-one ($1 \times 10^{-2}$ M) and 10 mL of dimethylformamide were taken into the polarographic cell. The solution was made up to a total volume of 25 mL with distilled water. Polarograms and cyclic voltammograms were recorded after deaeration with nitrogen gas.

3. Results and discussion

3.1. Polarographic behavior of 1-(Toluenyl sulfonyl)-3-amino-4-(aryl hydrazono)-2-pyrazolin-5-one

1-(Toluenyl sulfonyl)-3-amino-4-(2′-substituted aryl hydrazono)-2-pyrazolin-5-ones (1–5) exhibits two waves in the entire pH range of study (1.1–10.1). The wave height decreases with an increase in pH. A decrease in wave height with an increase in pH was observed for all compounds. An inspection of the structure of the compounds suggests that the sites susceptible to reduction are exocyclic $>\text{C}=\text{N}$, cyclic $>\text{C}=\text{N}$ and cyclic amide. However, exocyclic $>\text{C}=\text{N}$ was more susceptible to reduction than cyclic $>\text{C}=\text{N}$ and cyclic amide. This was experimentally confirmed by the fact that 1-(Toluenyl sulfonyl)-3-amino-2-pyrazolin-5-one fails to undergo reduction under experimental conditions. Hence, the polarographic reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones was attributed to the reduction of the exocyclic $>\text{C}=\text{N}$ group.

3.1.1. Effect of pH on half-wave potential

All compounds (1–5) exhibit two well-defined waves in the entire pH range (1.1–10.1) of study. As indicated in Table 2, the half-wave potentials of the first and second waves for all compounds shift to more negative values with an increase in pH, in the range 1.1–7.1, and remain constant in alkaline medium. The $E_{1/2}$–pH plots (Figure 1(a)–(d)) have two linear portions. As revealed from Figure 1, the $E_{1/2}$–pH relationship for the first wave is represented by:

\begin{align*}
(1) & \quad -E_{1/2} = 0.06 + 0.09868 \times \text{pH V vs. SCE}; \\
(2) & \quad -E_{1/2} = 0.04 + 0.08148 \times \text{pH V vs. SCE}; \\
(3) & \quad -E_{1/2} = 0.02 + 0.07879 \times \text{pH V vs. SCE}; \\
(4) & \quad -E_{1/2} = 0.08 + 0.08186 \times \text{pH V vs. SCE}; \\
(5) & \quad -E_{1/2} = 0.07 + 0.08372 \times \text{pH V vs. SCE}.
\end{align*}

The $E_{1/2}$–pH relationship for the second wave is represented by:

\begin{align*}
(1) & \quad -E_{1/2} = 0.21 + 0.09135 \times \text{pH V vs. SCE};
\end{align*}
3.1.2. Effect of pH on wave height

The wave height for compounds (1–5) in different pH media is presented in Table 2, and in Figures 2 and 3. The plots of wave height vs. pH for the first and second waves, for all compounds under study, assume the shape of a dissociation curve. This type of behavior is expected if the depolarizer undergoes chemical cleavage in the acidic or alkaline medium.

The heterogeneous rate constant, $K_{f,h}$, and activation free energy change, $\Delta G^*$, at different pH values for compounds 1–5 are presented in Table 2. The results revealed that the electrode reaction was turning increasingly irreversible with an increase in the pH of the medium. This fact was confirmed by the decrease in $K_{f,h}$ and the increase in the $\Delta G^*$ value with an increase in pH.

3.1.3. Effect of mercury column height (h) on the wave height (H)

It is evident from Figure 4(a)–(c) that wave height (H) is linearly dependent on $h^{1/2}$. The constant values of $H/h^{1/2}$ indicate the diffusion controlled nature of the wave [26].

3.1.4. Effect of concentration (C) of the depolarizer on the wave height (H)

The effect of concentration of 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones on
| Substance | \( \Delta_
olimits{E} \) | Number of protons | Number of electrons | \( \log_{10} \text{M.F.} \) | \( \log_{10} \text{M.F.} \) |
|-----------|----------------|------------------|--------------------|----------------|----------------|
| \( \text{H}^+ \) | 2.1 | 0.22 | 0.38 | 4.8 | 10 | 0.60 | 0.48 | 0.32 | 0.18 | 0.10 | 0.07 |
| \( \text{OH}^- \) | 3.3 | 0.69 | 0.77 | 5.1 | 0.54 | 0.58 | 0.51 | 0.45 | 0.39 | 0.33 | 0.27 |
| \( \text{Cl}^- \) | 5.0 | 0.09 | 0.11 | 6.3 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| \( \text{Br}^- \) | 5.8 | 0.10 | 0.11 | 6.6 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| \( \text{NO}_2^- \) | 7.6 | 0.11 | 0.12 | 8.9 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| \( \text{SO}_4^{2-} \) | 9.4 | 0.12 | 0.13 | 11.1 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |

**Note:** All values are in \( \log_{10} \) units.
wave height in the range 0.5–4.0 mM has been studied at pH 4.1 and 8.1. The wave height–concentration plots (Figures 5 and 6) were linear and were passing through the origin. This fact suggests that the reduction process was diffusion controlled, and the linear plots can be used for determination of trace amounts of 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones.

3.1.5. Nature of the electrode process

The semi-logarithmic plots (Figures 7 and 8) of the first and second waves for all compounds under study were linear, with slopes 0.049–0.051 and 0.048–0.053, respectively. The fractional value of the slope suggests that the reduction process was irreversible in nature. The irreversible nature of the polarographic waves was further confirmed by employing Tome’s criteria [27]. The $\alpha_n$ values obtained from Tome’s method are presented in Table 2 ($\alpha$ is the transfer coefficient and $n_a$ is the number of electrons involved). $\alpha_n$ values were almost equal to those obtained from conventional logarithmic plots. The irreversible nature of the waves may be attributed to the bulky aryl hydrazono group at the end of $\text{C}=\text{N}$ linkage [28].

### 3.1.6. Effect of temperature on the polarographic reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones

The polarograms of 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones in media of pH 4.1 were recorded at 303, 313, 323 and 333 K to study the effect of temperature on the half-wave potential and wave height. The results are presented in Table 3.

All compounds (1–5) exhibit two well-defined waves in the temperature range of study (303–333 K) at pH 4.1. The wave height increases with an increase in temperature and the temperature coefficient values were in the range 0.734%–1.495% deg$^{-1}$. The values were in good agreement with those reported in the literature for similar compounds by Meites [29].

The results presented in Table 3 revealed that the half-wave potentials shift to more negative values with an increase in temperature. This fact is an indication of the enhanced irreversible nature of the reduction process with the increase in temperature. Further, $\alpha_n$ values decrease with an increase in temperature from 303 to 333 K. The decrease in $\alpha_n$ values with the increase in temperature may be attributed to a decrease in the $\alpha$ value. The decrease in $\alpha$ values indicates that the transfer of electrons was increasingly difficult with the raise in temperature. Hence, the system tends to become
increasingly irreversible [30–33] with increase in temperature. The literature survey [34] reveals the same observations for similar compounds.

3.1.7. Thermodynamic parameters

The thermodynamic parameters, namely, the formal rate constant ($K'_f$), enthalpy of activation ($\Delta H^*$), activation free energy change ($\Delta G^*$) and the entropy of activation ($\Delta S^*$), were evaluated from the equations proposed by Meites and Israel [35], Oldham and Parry [36] and Gaur and Bhargava [37]. The diffusion coefficient necessary for calculation of the formal rate constant ($K'_f$) at different temperatures has been calculated from the Stoke–Einstein equation [38]. It was noticed from Tables 4 and 5 that the formal rate constant decreases with an increase in temperature. This fact suggests that the electrode reaction was rendered increasingly irreversible with the raise in temperature. This observation is in accordance with the conclusion arrived at on the basis of $\Delta H^*$ values. The negative $\Delta S^*$ values suggest that the activated state has a more rigid structure than the initial state. The thermodynamic parameters enthalpy of activation ($\Delta H^*$), free energy of activation ($\Delta G^*$) and entropy of activation ($\Delta S^*$) presented in Tables 4 and 5 reveal the following points:

1. The positive values of $\Delta H^*$ indicate that the process was endothermic.
2. The positive values of $\Delta G^*$ indicate that the process was not spontaneous.
3. The negative values of $\Delta S^*$ indicate that the process was entropically unfavorable.

The coulometric microcell of De Vries and Kroon [39], with mercury pool cathode, was employed to determine the value of $'n'$. The results are presented in Table 6.

| Table 3: Effect of temperature on the polarographic characteristics of 1-(Toluenyl sulfonyl)-3-amino-4-(2′-substituted hydrazono)-2-pyrazolin-5-one. pH: 4.1, [pyrazolin-5-one] = 1 × 10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v). |
| --- |
| Temperature | $-E_{1/2}$ V vs. SCE | Wave height $H$ (cm) | Temperature coefficient (% deg^{-1}) | $\alpha$ | $D \times 10^6$ (cm^2 s^{-1}) |
| −H | I wave | II wave | I wave | II wave | I wave | II wave | I wave | II wave | I wave | II wave |
| 303 | 0.35 | 0.47 | 3.1 | 3.3 | − | − | 0.66 | 0.54 | 2.01 | 2.28 |
| 313 | 0.37 | 0.53 | 3.6 | 3.8 | 1.49 | 1.41 | 0.61 | 0.48 | 2.71 | 3.02 |
| 323 | 0.41 | 0.62 | 4.1 | 4.3 | 1.30 | 1.24 | 0.55 | 0.43 | 3.52 | 3.87 |
| 333 | 0.47 | 0.69 | 4.7 | 4.9 | 1.37 | 1.31 | 0.51 | 0.39 | 4.63 | 5.03 |
| −CH₃ | 303 | 0.36 | 0.50 | 3.3 | 3.6 | − | − | 0.69 | 0.58 | 2.28 | 2.71 |
| 313 | 0.39 | 0.55 | 3.8 | 4.1 | 1.41 | 1.30 | 0.63 | 0.52 | 3.02 | 3.52 |
| 323 | 0.44 | 0.60 | 4.3 | 4.6 | 1.23 | 1.15 | 0.58 | 0.47 | 3.87 | 4.43 |
| 333 | 0.50 | 0.66 | 4.9 | 5.2 | 1.30 | 1.23 | 0.54 | 0.43 | 5.03 | 5.66 |
| −OCH₃ | 303 | 0.39 | 0.54 | 3.6 | 3.8 | − | − | 0.74 | 0.63 | 2.71 | 3.02 |
| 313 | 0.42 | 0.58 | 4.1 | 4.3 | 1.30 | 1.23 | 0.68 | 0.57 | 3.52 | 3.87 |
| 323 | 0.46 | 0.62 | 4.6 | 4.8 | 1.15 | 1.10 | 0.63 | 0.52 | 4.43 | 4.83 |
| 333 | 0.52 | 0.69 | 5.2 | 5.4 | 1.23 | 1.18 | 0.59 | 0.48 | 5.66 | 6.11 |
| −OH | 303 | 0.38 | 0.48 | 4.1 | 4.3 | − | − | 0.67 | 0.52 | 3.52 | 3.67 |
| 313 | 0.40 | 0.50 | 4.6 | 4.7 | 1.15 | 1.12 | 0.61 | 0.49 | 4.43 | 4.63 |
| 323 | 0.45 | 0.54 | 5.1 | 5.2 | 1.03 | 1.01 | 0.56 | 0.45 | 5.45 | 5.66 |
| 333 | 0.51 | 0.60 | 5.7 | 5.8 | 1.11 | 1.09 | 0.52 | 0.41 | 6.80 | 7.04 |
| −Cl | 303 | 0.31 | 0.48 | 2.9 | 3.1 | − | − | 0.61 | 0.47 | 1.76 | 2.01 |
| 313 | 0.34 | 0.51 | 3.3 | 3.6 | 1.29 | 1.50 | 0.55 | 0.44 | 2.28 | 2.71 |
| 323 | 0.39 | 0.55 | 3.8 | 4.1 | 1.41 | 1.30 | 0.50 | 0.40 | 3.02 | 3.52 |
| 333 | 0.45 | 0.62 | 4.4 | 4.7 | 1.47 | 1.37 | 0.46 | 0.35 | 4.05 | 4.63 |

![Figure 9: $-E_{1/2}$−$\sigma_p$ plots of pyrazolin-5-ones (first wave). [pyrazolin-5-one] = 1 × 10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v).](Image 335x247 to 567x414)

3.1.8. Effect of substituents on the polarographic behaviour of 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones

For the compounds in an aromatic series, structural correlations are usually done with $\sigma_p$ (substituent constant) values. The corresponding $E_{1/2}$−$\sigma_p$ plots are presented in Figures 9 and 10. It is observed from Table 2 that $\Delta E_{1/2}/\Delta \phi_H$, $\alpha_n$, and $l$ (diffusion current constant) values are practically in the same range for the entire reaction series. This fact made it possible to discuss the effect of substituents, in terms of the Hammett equation. The procedure reported in the literature [40] was
employed to compute Hamnett substituent constant values \((\rho)\). The \(\rho\) values are presented in Table 7. The values were found to be in the range of 0.10–0.30. Positive and low values \([41]\) of \(\rho\) indicate that the polargraphic reduction involves nucleophilic addition of electron to the substrate. This fact confirms that the electron uptake process was the potential rate determining step in all the reduction processes studied.

3.1.9. Reduction mechanism

The results reveal that the N–N bond in the hydrazono group \((>C=N-NH-)\) was reduced more easily than the azomethine \((>C=N-)\) group. Similar observations were made for semicarbazones and hydrazones [26,42].

3.1.9.1. Reduction in acidic medium

The first step involves the two-electron reductive cleavage of the \(>N-N<\) bond, leading to the formation of 1-(Toluenyl sulfonyl)-3-amino-4-(2-substituted hydrazono)-2-pyrazolin-5-one (Scheme 2 (B)) [43,44] and substituted aniline. The second step involves the two-electron reduction of ketimine (Scheme 2(B)) to the corresponding diamine (Scheme 2(C)). The wave height corresponding to both these steps were affected by acid–base equilibrium. The variation of wave height with pH is similar to the trend reported in the

Table 4: Kinetic and thermodynamic parameters for polargraphic reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(2-substituted hydrazono)-2-pyrazolin-5-one. (First wave); \(pH = 4.1\), [pyrazolin-5-one] = \(1 \times 10^{-3}\) M; Medium: Aqueous dimethylformamide (40% v/v).

| Compound | Parameter | Meites-Israël treatment | Oldham-Parry treatment | Gaur-Bhargava treatment |
|----------|-----------|-------------------------|------------------------|-------------------------|
| 2'-H     | \(K_a^{10^6}\) | 3.689 3.406 2.085 0.931 | 3.694 3.412 2.090 0.934 | 5.026 4.601 2.750 1.183 |
|          | \(\Delta H^\circ\) | 9.152 9.152 9.152 9.152 | 8.985 8.985 8.985 8.985 | 10.439 10.439 10.439 10.439 |
|          | \(\Delta G^\circ\) | 6.342 6.573 6.920 7.366 | 6.342 6.572 6.919 7.365 | 6.261 6.492 6.843 7.297 |
|          | \(-\Delta S^\circ\) | 7.287 6.252 4.923 3.375 | 7.367 5.722 4.409 2.877 | 11.802 10.623 9.145 7.447 |

Table 5: Kinetic and thermodynamic parameters of polargraphic reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(2-substituted hydrazono)-2-pyrazolin-5-one (Second wave); \(pH = 4.1\), [pyrazolin-5-one] = \(1 \times 10^{-3}\) M; Medium: Aqueous dimethylformamide (40% v/v).

| Compound | Parameter | Meites-Israël treatment | Oldham-Parry treatment | Gaur-Bhargava treatment |
|----------|-----------|-------------------------|------------------------|-------------------------|
| 2'-methyl| \(K_a^{10^6}\) | 2.645 1.894 0.912 0.395 | 2.650 1.898 0.915 0.397 | 3.547 2.495 1.161 0.485 |
|          | \(\Delta H^\circ\) | 15.646 15.646 15.646 15.646 | 15.604 15.604 15.604 15.604 | 16.437 16.437 16.437 16.437 |
|          | \(\Delta G^\circ\) | 6.429 6.731 7.150 7.612 | 6.429 6.731 7.149 7.611 | 6.352 6.657 7.083 7.553 |
|          | \(-\Delta S^\circ\) | 28.432 26.495 24.316 22.138 | 28.294 26.361 24.189 22.015 | 31.297 29.259 26.972 24.691 |
| 2'-methyl| \(K_a^{10^6}\) | 9.643 6.918 4.057 1.600 | 9.670 6.940 4.072 1.608 | 12.385 8.730 4.993 1.890 |
|          | \(\Delta H^\circ\) | 8.534 8.534 8.534 8.534 | 8.452 8.452 8.452 8.452 | 8.676 8.676 8.676 8.676 |
|          | \(\Delta G^\circ\) | 6.693 7.004 7.376 7.872 | 6.692 7.003 7.226 7.870 | 6.627 6.941 7.318 7.824 |
|          | \(-\Delta S^\circ\) | 4.089 2.901 1.598 0.260 | 3.822 2.642 1.808 0.240 | 4.776 3.556 2.217 0.570 |
| 2'-hydroxyl| \(K_a^{10^6}\) | 2.139 2.031 1.016 0.459 | 2.144 2.036 1.019 0.461 | 2.822 2.663 1.291 0.563 |
|          | \(\Delta H^\circ\) | 7.675 7.675 7.675 7.675 | 7.579 7.579 7.579 7.579 | 7.549 7.549 7.549 7.549 |
|          | \(\Delta G^\circ\) | 6.485 6.713 7.120 7.569 | 6.484 6.712 7.119 7.568 | 6.412 6.639 7.053 7.510 |
|          | \(-\Delta S^\circ\) | 1.941 1.086 0.269 1.669 | 1.627 0.783 0.563 1.955 | 1.766 0.902 0.452 1.871 |
| 2'-chloro| \(K_a^{10^6}\) | 1.103 0.763 0.396 0.194 | 1.104 0.764 0.397 0.195 | 1.573 1.068 0.537 0.255 |
|          | \(\Delta H^\circ\) | 11.333 11.333 11.333 11.333 | 11.503 11.503 11.503 11.503 | 11.525 11.525 11.525 11.525 |
|          | \(\Delta G^\circ\) | 6.056 6.235 6.741 7.154 | 6.056 6.335 6.741 7.154 | 5.963 6.264 6.656 7.076 |
|          | \(-\Delta S^\circ\) | 15.429 13.917 12.229 10.562 | 15.990 14.460 12.755 11.072 | 16.369 14.821 13.087 11.372 |

\(K_a^{10^6}\) expressed in cm s\(^{-1}\), \(\Delta H^\circ\), \(\Delta G^\circ\) and \(-\Delta S^\circ\) expressed in K cal mole\(^{-1}\).
Figure 10: $-E_{1/2} - \sigma_{P}$ plots of pyrazolin-5-ones (Second wave). [pyrazolin-5-one] = $1 \times 10^{-3}$ M; Medium: Aqueous dimethylformamide (40% v/v).

Table 6: Millicoulometric data of 1-(Toluenyl sulfonyl)-3-amino-4-(2′-substituted hydrazono)-2-pyrazolin-5-one. [pyrazolin-5-one] = $1 \times 10^{-3}$ M; Medium: Aqueous dimethylformamide (40% v/v).

| pH | Wave height ($H$) (cm) | Time (s) | $n$ value | Wave height ($H$) (cm) | Time (s) | $n$ value |
|----|------------------------|----------|-----------|------------------------|----------|-----------|
| $-H$ | I wave | II wave | $\times$ | I wave | II wave | $\times$ |
| 4.1 | 3.6 | 3.8 | 0 | - | - | - | 3.8 | 4.1 | 0 | - | - |
| 2.9 | 3.1 | 3.3 | 7200 | 1.8 | 2.0 | 3.3 | 3.4 | 7200 | 2.0 | 1.9 |
| 1.3 | 1.2 | 1.2 | 10800 | 1.9 | 2.1 | 2.9 | 3.2 | 10800 | 2.1 | 1.9 |
| 8.1 | 3.1 | 3.2 | 7200 | 1.7 | 1.8 | 1.5 | 1.5 | 7200 | 1.6 | 1.6 |
| 1.2 | 1.2 | 1.1 | 10800 | 1.7 | 1.7 | 1.4 | 1.4 | 10800 | 2.2 | 2.2 |

| $-CH_3$ | I wave | II wave | $\times$ | I wave | II wave | $\times$ |
| 4.1 | 4.1 | 4.3 | 3.7 | 3.5 | 2.0 | 2.1 | 3.9 | 4.1 | 7200 | 2.1 | 2.3 |
| 3.1 | 3.3 | 3.7 | 10800 | 2.2 | 2.1 | 3.6 | 3.8 | 10800 | 2.1 | 2.3 |
| 2.9 | 2.9 | 2.5 | 7200 | 2.3 | 2.0 | 2.3 | 2.3 | 7200 | 1.9 | 2.2 |

| $-OCH_3$ | I wave | II wave | $\times$ | I wave | II wave | $\times$ |
| 4.1 | 4.1 | 4.2 | 3.6 | 3.8 | 7200 | 2.0 | 2.1 | 3.9 | 3.8 | 7200 | 2.1 | 2.3 |
| 3.1 | 3.3 | 3.7 | 10800 | 2.2 | 2.2 | 3.6 | 3.8 | 10800 | 2.1 | 2.3 |
| 2.9 | 2.9 | 2.5 | 7200 | 2.3 | 2.0 | 2.3 | 2.3 | 7200 | 1.9 | 2.2 |

| $-Cl$ | I wave | II wave | $\times$ | I wave | II wave | $\times$ |
| 4.1 | 4.3 | 4.4 | 3.2 | 3.6 | 7200 | 2.0 | 2.2 | 3.9 | 4.1 | 7200 | 2.1 | 2.3 |
| 3.1 | 3.3 | 3.7 | 10800 | 2.2 | 2.2 | 3.6 | 3.8 | 10800 | 2.1 | 2.3 |
| 2.9 | 2.9 | 2.5 | 7200 | 2.3 | 2.0 | 2.3 | 2.3 | 7200 | 1.9 | 2.2 |

Table 7: Effect of pH on the reaction constant for the reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(2′-substituted hydrazono)-2-pyrazolin-5-one. [pyrazolin-5-one] = $1 \times 10^{-3}$ M; Medium: Aqueous dimethylformamide (40% v/v).

| pH | $\rho$ value | I wave | II wave |
|----|--------------|--------|--------|
| 1.1 | 0.12 | 0.097 |
| 2.1 | 0.13 | 0.099 |
| 3.1 | 0.13 | 0.099 |
| 4.1 | 0.15 | 0.095 |
| 5.1 | 0.16 | 0.125 |
| 6.1 | 0.14 | 0.127 |
| 7.1 | 0.13 | 0.097 |
| 8.1 | 0.13 | 0.077 |
| 9.1 | 0.13 | 0.077 |
| 10.1 | 0.13 | 0.077 |

3.1.9.2. Reduction in alkaline medium. In alkaline medium, 1-(Toluenyl sulfonyl)-3-amino-4-(substituted aryl hydrazono)-2-pyrazolin-5-ones exist in azomethine anionic form [26] ($\geq C=N−_N−$).

The first wave may be ascribed to the two-electron reductive cleavage of the N–N bond in azomethine anionic form ($\geq C=N−_N−$). This anionic form (Scheme 3 (D)) is susceptible to cleavage, to form a heterocyclic carbonyl compound. The second wave is due to the two-electron reduction of the heterocyclic carbonyl compound to corresponding alcohol. The reduction mechanism observed in alkaline medium is similar to that reported in literature [46] and is given in Scheme 3.

3.2. Cyclic voltammetric behaviour of 1-(Toluenyl sulfonyl)-3-amino-4-(aryl hydrazono)-2-pyrazolin-5-one

The cyclic voltammograms were recorded using HMDE in dimethylformamide (40% v/v) in Britton–Robinson buffer solutions of pH 2.1, 4.1, 6.1 and 8.1 at scan rates of 10, 20,
3.2.1. Effect of scan rate on peak potential and peak current

In media of pH 2.1–8.1, the peak potentials shift to more negative values and the peak currents increase with an increase in the scan rate. The results are presented in Table 8.

3.2.2. Effect of pH on peak potential and peak current

An inspection of the data presented in Table 8 reveals that the cathodic peak potentials shift to more negative values, and peak currents decrease with an increase in pH of the solution. The number of cathodic peaks noticed in cyclic voltammetry was equal to the number of polarographic reduction waves observed in DC polarography. The results were similar to those observed in polarography. The diffusion-controlled nature of the electrode process is substantiated by following facts: (i) The plot of $i_{PC} \nu^{1/2}$ vs. $\nu^{1/2}$ was linear (Figures 11 and 12) and (ii) The values of $i_{PC}/\nu^{1/2}$ were nearly unaltered. The irreversible nature of the electrode process was confirmed by following facts: (i) The absence of anodic peak in the reverse scan. (ii) The value of $(E_{PC}/2 - E_{PC})$ was greater than 56.5 mV [47]. (iii) The current function $(i_{PC}/\nu^{1/2} \cdot C)$ was independent of the scan rate ($\nu$) and (iv) The plot of $(i_{PC}/\nu^{1/2})$ vs. $\nu$ graph was similar to the one expected for case II of Nicholson–Shain criteria [48].

Hence, the reduction mechanism observed at HMDE was assumed to be the same as that at DME, and is described in Schemes 2 and 3.

Cyclic voltammograms recorded (pH 2.1–8.1) under repeated cycles reveal that there is no change, either in the shape of the cyclic voltammogram or in the magnitude of the peak potential, even though the peak current diminishes with an increase in the number of cycles. This may be ascribed to the adsorption of substrate on the mercury solution interface. This behavior was similar to that normally expected under repeated cycles for irreversible systems.

3.2.3. Effect of substituent on the cyclic voltammetric behavior

Hammett’s linear free energy relations were applied to investigate the effect of substituent on cathodic peak potentials. Plots were drawn between the first/second cathodic peak potentials and the Hammett substituent constant ($\sigma_P$). The specific reaction constant ($\rho$) values obtained are given in Table 9. It was noticed from Figures 13 and 14 that plots $(E_{PC} - \sigma_P)$ were straight lines with a positive slope. The positive $'\rho'$ values suggest that nucleophilic addition of electrons plays a significant role.

4. Conclusion

Five pyrazolin-5-ones, namely;
(1) 1-(Toluenyl sulfonyl)-3-amino-4-(aryl hydrazono)-2-pyrazolin-5-one;
(2) 1-(Toluenyl sulfonyl)-3-amino-4-(2'-methyl aryl hydrazono)-2-pyrazolin-5-one;
(3) 1-(Toluenyl sulfonyl)-3-amino-4-(2'-methoxy aryl hydrazono)-2-pyrazolin-5-one;
Table 8: Cyclic voltammetric results of 1-(Toluenyl sulfonyl)-3-amino-4-(2′-substituted hydrazono)-2-pyrazolin-5-one.

| pH | Scan rate (V s⁻¹) | −E_{PC I} (V) | −E_{PC II} (V) | i_{PC I} (µA) | i_{PC II} (µA) | −E_{PC I} (V) | −E_{PC II} (V) | i_{PC I} (µA) | i_{PC II} (µA) |
|----|------------------|--------------|----------------|-------------|-------------|--------------|----------------|-------------|-------------|
| 4  | 0.010 0.020 0.050 | -H -CH₃ -OCH₃ -OH -Cl | 0.7 0.8 0.9 1.0 0.3 0.5 0.8 0.9 0.4 0.7 | 2.1 0.3 0.5 0.7 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 |
| 5  | 0.010 0.020 0.050 | -H -CH₃ -OCH₃ -OH -Cl | 0.7 0.8 0.9 1.0 0.3 0.5 0.8 0.9 0.4 0.7 | 2.1 0.3 0.5 0.7 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 |
| 6  | 0.010 0.020 0.050 | -H -CH₃ -OCH₃ -OH -Cl | 0.7 0.8 0.9 1.0 0.3 0.5 0.8 0.9 0.4 0.7 | 2.1 0.3 0.5 0.7 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 |
| 7  | 0.010 0.020 0.050 | -H -CH₃ -OCH₃ -OH -Cl | 0.7 0.8 0.9 1.0 0.3 0.5 0.8 0.9 0.4 0.7 | 2.1 0.3 0.5 0.7 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 | 0.3 0.5 0.7 0.9 0.3 0.5 0.7 0.9 0.3 0.5 |

Table continues with similar data for different pH values and scan rates.
Table 9: Effect of pH on the reaction constant for the reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(2′-substituted aryl hydrazono)-2-pyrazolin-5-ones. [pyrazolin-5-one] = 1 × 10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v).

| pH  | I wave | II wave |
|-----|--------|---------|
| 2.1 | 0.131  | 0.093   |
| 4.1 | 0.152  | 0.095   |
| 6.1 | 0.143  | 0.127   |
| 8.1 | 0.132  | 0.077   |

Figure 13: $-E_{1/2}$$\sigma_p$ plots of pyrazolin-5-ones (first wave). [pyrazolin-5-one] = 1 × 10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v).

Figure 14: $-E_{1/2}$$\sigma_p$ plots of pyrazolin-5-ones (second wave). [pyrazolin-5-one] = 1 × 10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v).

(4) 1-(Toluenyl sulfonyl)-3-amino-4-(2′-hydroxy aryl hydrazono)-2-pyrazolin-5-one;
(5) 1-(Toluenyl sulfonyl)-3-amino-4-(2′-chboro aryl hydrazono)-2-pyrazolin-5-one;

reported in this article, gave two well defined polarographic waves in the entire pH range of study (1.1–10.1). The reduction process was found to be irreversible and diffusion controlled with the involvement of protons. Cyclic voltammetry was performed in support of the results obtained in polarography. Based on the results obtained, the authors proposed a mechanism for the electrode reaction at the dropping mercury electrode; the same of which may be used for pharmacokinetic studies involving these pyrazolin-5-ones.

Acknowledgments

The authors are thankful to V. Sheshagiri, Professor (Emeritus), Sri Krishnadevaraya University, Anantapur, A.P., India, for his valuable suggestions during the entire course of this work.

Appendix

1. The number of protons involved in the reduction process was calculated by the following equation:

$$\frac{\Delta E_{1/2}}{\Delta \text{pH}} = 0.05915 \frac{\alpha n_a}{i_d - i}$$

where:

- $\alpha$ = transfer coefficient;
- $n_a$ = number of electrons involved in the rate determining step.

2. Tomes’ criterion for an irreversible process; the equation is given by:

$$E = E_{1/2} = -0.0542 \frac{\alpha n_a}{i_d - i} \log \left( \frac{i}{i_d - i} \right)$$

with: $E_{1/2} = -0.2412 + 0.05915 \frac{\alpha n_a}{i_d - i} \log \left( \frac{1.349 K_f^h t_{1/2}}{D^{1/2}} \right)$

where:

- $K_f^h$ = heterogeneous forward rate constant in cm/s;
- $D$ = diffusion coefficient of the depolariser in cm² s⁻¹.

3. $\alpha n_a$ value for an irreversible process can be calculated using the following equation:

$$E_{1/4} - E_{3/4} = \frac{0.05172}{\alpha n_a}$$

where $E_{1/4}$ and $E_{3/4}$ are potentials when $i = i_d/4$ and $3 i_d/4$, respectively.

4. The following formulae were employed for calculation of kinetic parameter ‘$K_f^h$’.

Meites–Israel’s method:

$$E_{\text{dme}} = \frac{0.05915}{\alpha n_a} \log \left( \frac{1.349 K_f^h}{D^{1/2}} \right) - 0.0542 \frac{\alpha n_a}{i_d - i} \log \left( \frac{i}{i_d - i} \right)$$

Oldham–Parry’s method:

Oldham–Parry have suggested alternatives to the usual log plots for the calculation of $K_f^h$:

$$E_{\text{dme}} = E_{1/2} = -0.05915 \frac{\alpha n_a}{i_d - i} \log \left[ \frac{\sqrt{\t}}{D} \frac{1.359}{D^{1/2}} \right]$$

Gaur–Bhargava’s method:

Gaur–Bhargava assumed that diffusion to the electrode surface is spherical, but not linear, as assumed by Meites–Israel.

$$E_{\text{dme}} = \frac{0.05915}{\alpha n_a} \log \left( \frac{1.349 K_f^h t_{1/2}}{1.128 D^{1/2}} \right) - 0.05690 \frac{\alpha n_a}{i_d - i} \log \left( \frac{i}{i_d - i} \right)$$

$\alpha n_a$ was calculated from the following equation:

$$\alpha n_a = -0.0517/(E_{3/4} - E_{1/4})$$
5. Stoke–Einstein equation:

\[ D = \frac{3.38 \times 10^{-5}}{V_m^{1/3} \eta} \] at 30 °C,

where:

\( \eta \) = viscosity of the solution;

\( V_m \) = apparent molar volume.

6. Hammett substituent constant (\( \sigma \)) for meta and para substituents are:

\[ E_{1/2}(X) = E_{1/2}(H) + 0.136\sigma(H); \]

where:

\[ E_{1/2}(X) = \text{half-wave potential of the substituted pyrazolin}; \]
\[ E_{1/2}(H) = \text{half-wave potential of the pyrazolin}; \]
\[ \sigma(H) = \text{Hammett substituent constant}. \]

Hammet quantified the effect of substituents on any reaction by defining an empirical electronic substituent parameter (\( \sigma \)).

The basic equation is:

\[ \log(K/K_0) = \sigma, \]

where \( K \) is the dissociation constant of unsubstituted reactant.

\( K_0 \) is the dissociation constant of substituted reactant. \( \sigma \) is the substituent constant, which depends only on the specific substituent.

The slope of the linear plot is referred to as \( \rho \) (reaction constant). The reaction constant is a measure of how sensitive a particular reaction is to changes in electronic effects of substituent groups. The reaction constant depends on the nature of the chemical reaction, as well as reaction conditions (solvent, temperature, etc.). Both the sign and magnitude of the reaction constant are indicative of the extent of charge build up during the reaction progress.

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