CONCLUSIONS

1. A series of N'-(p-toluenesulphonyl)-3-methyl-4-(substituted arylhydrazono)pyrazolin-5-ones, and N'-(2-hydroxybenzoyl)-3,5-dimethyl-4-(substituted arylazo)pyrazoles have been synthesised and characterised by CHN analysis, IR and PMR spectral studies.

2. The compounds synthesized have been screened for antimicrobial activity against gram positive bacteria *S. aureus* and gram negative bacteria *E. coli* at a concentration 50μg/0.1ml. The results show that among Pyrazolin-5-ones 4'-Br, 4'-SO₂NH₂ and 4'-NO₂ exhibited maximum activity against both *S. aureus* and *E. coli*. Pyrazolin-5-ones with 2'-Cl and 2'-NO₂ exhibited moderate activity against *S. aureus* and *E. coli*.

   Among Pyrazole derivatives 4'-SO₂NH₂ exhibited moderate activity against *S. aureus* and *E. coli* and 4'-Cl, 4'-CH₃, 2'-Cl exhibited feeble activity.

   Pyrazolin-5-one and Pyrazole derivatives having substituents like –SO₂NH₂, -NO₂ and halogens in the benzene ring showed maximum activity in comparison with other substituents.

3. The electrochemical reduction of the following compounds have been studied at the dropping mercury electrode at 27° C

   N'-(p-toluenesulphonyl)-3-methyl-4-(4'-substituted arylhydrazono)-pyrazolin-5-ones, and

   N'-(2-hydroxybenzoyl)-3,5-dimethyl-4-(4'-substituted arylazo)pyrazoles.

4. A single well defined polarographic wave is observed for the compounds. The wave is found irreversible and E½ increases with pH of the medium. The half-wave
potential of the waves increase with rise in the pH of the medium. This suggests the involvement of protons in the reduction process.

5. The limiting current decreases with rise in the pH of the solution. This suggests that the reduction process is probably controlled by the rate of the proton transfer process or that a chemical reaction at the vicinity of the electrode process controls the electrode process.

6. The waves are diffusion controlled as indicated by the linear dependence of the limiting current on the square root of mercury column height ($h^{1/2}$). The plots pass through the origin.

7. The limiting current is directly proportional to the concentration and this confirms the diffusion controlled nature of the wave.

8. $E_{dme}$ vs log $\frac{i_d}{i}$ graphs are all linear. The slopes are however different from those expected for the reversible reductions. The irreversible nature is also confirmed by the Tome's criterion.\(^1\) This trend of irreversibility increases with rise in pH of the medium. The irreversible nature at any pH is further supported by the low k°\(_{th}\) (formal heterogeneous rate constant) values and the large ΔG* (activation free energy change) values.

9. The effect of temperature on the polarographic reduction of

(a) N'-(p-toluenesulphonyl)-3-methyl-4-(4'-substituted arylhydrazono)-pyrazolin-5-ones and

(b) N'-(2-hydroxybenzoyl)-3,5-dimethyl-4-(4'-substituted arylazo)pyrazoles

is studied at typical pH value (4.0) shows that the limiting current increases with rise in the temperature. The temperature coefficient is around 1.05-1.25% deg\(^{-1}\). The half-wave potential shifts to more negative values with rise in temperature and $\alpha_n$.
decreases with rise in temperature. These observations confirm that the irreversibility increases with the rise in temperature.\textsuperscript{2,7}

10. The activation free energy change ($\Delta G^*$) and the heterogeneous formal rate constant ($k_{f,h}$) is evaluated using the treatment proposed by Meites-Israel.

11. The number of electrons consumed in the reduction process is determined by controlled potential electrolysis and the results obtained are reported in the Table 1.

**TABLE 1**

**Number of electrons consumed in the reduction process**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the compound (s)</th>
<th>Group undergoing reduction at DME</th>
<th>Number of electrons involved in the reduction process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{N'}-(\text{p-toluenesulphonyl})-3\text{-methyl-} )</td>
<td>( \text{C=N-NH-} )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>( \text{4-(4'}\text{-substituted arylhydrazono)pyrazolin-5-ones} )</td>
<td>( 4\text{e}^-, 4\text{H}^+ )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{CH-NH}_2 + \text{-NH}_2 )</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>( \text{N'}-(2\text{-hydroxybenzoyl})-3,5- )</td>
<td>( \text{C=N=NH-} )</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>( \text{dimethyl-4-(4'}\text{-substituted arylazo)pyrazoles} )</td>
<td>( 2\text{e}^-, 2\text{H}^+ )</td>
<td></td>
</tr>
</tbody>
</table>

12. Literature survey reveals\textsuperscript{8-9} that the azo compounds exhibit azo-hydrazone tautomerism and that the nature of the aromatic ring or the substituent present in the heterocyclic system controls the same.
N'-(2-hydroxybenzoyl)-3,5-dimethyl-4-(4'-substituted arylazo)pyrazoles.

Pyrazoles fail to exhibit azo-hydrazone tautomerism and hence the azo group in these compounds undergoes a 2 electron reduction to the hydrazo stage.

Arylazo pyrazolin-5-ones found to exhibit azo-hydrazone tautomerism.

If \( R_1 \) and \( R_2 \) is OH or =O group the azo group in such compounds undergoes a 4 electron reductive cleavage in the azomethine (\( >C-N-NH^- \)) form.

13. In alkaline solutions (pH > pKa) the azomethine group (\( -NH-N=C< \)) exists in the anionic form and the azomethine anionic form(\( -N-N=C< \)) is susceptible for chemical
cleavage to the corresponding carbonyl compound. An equilibrium exists between the azomethine anion and the corresponding carbonyl compound as shown below.

\[
\begin{align*}
\text{R} & \text{N} & \text{N} & \text{CH} & \text{C} & \text{CH}_3 \\
& & & & & \\
\text{O} & \text{C} & \text{N} & \text{N} & \text{SO}_2 \\
\text{CH}_3 & & & & & \\
\text{R} & \text{N} & \text{CH} & \text{C} & \text{CH}_3 \\
& & & & & \\
\text{O} & \text{C} & \text{N} & \text{N} & \text{SO}_2 \\
\text{CH}_3 & & & & & \\
\end{align*}
\]

The wave observed in the present studies is therefore related to the polarographic reduction of the heterocyclic carbonyl compounds and this is not clearly differentiated. This is because that the reduction of the carbonyl compound occurs at such high negative potentials that they are observed at the decomposition potential of the buffer solution.

14. The cyclic voltammetric studies at glassy carbon electrode in aqueous buffer solutions of pH value (4.0 and 8.0) containing 65% dimethylformamide of the following compounds are taken up.

1. \(N'(p\text{-toluenesulphonyl})-3\text{-methyl}-4\text{-}((4'\text{-substituted arylhydrazono})\text{-pyrazolin-5-ones})\) and

2. \(N'(2\text{-hydroxybenzoyl})\text{-3,5-dimethyl}-4\text{-}((4'\text{-substituted arylazo})\text{pyrazoles})\)

A well defined cathodic peak is observed at all the scan rates studied (20, 50, 100 and 200 mV/s). The anodic peak in the reverse scan is absent. \(i_{pc}/v^{1/2}\) versus \(v\)
The mechanism proposed to explain the observed results is shown below.

R_4 = pyrazolin-5-ones ring system

The reason for the manifestation of a single four electron reduction wave in DC polarographic studies may be due to the fact that the reductive cleavage of N-N-bond and the reduction of imine occurs at the same potential.
\[ R_5 = \text{Pyrazole ring system} \]