Electrochemical Studies on the Electron-transfer Reactions of Substituted Photoproducts of Potassium Octacyano-molybdate(IV) & Tungstate(IV) with 1,10-Phenanthroline

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Oxidation of substituted photoproducts of potassium octacyano-molybdate(IV) and -tungstate(IV) with 1,10-phenanthroline, Mo(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-}, W(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-}, Mo(CN)\textsubscript{4}(Phen)\textsuperscript{2-} and W(CN)\textsubscript{4}(Phen)\textsuperscript{2-}, has been carried out using Fe(III), Ce(IV), Cr(VI) and Mn(VII) as the oxidants. The determination of standard potential (E\textsuperscript{0}) for the redox reactions,

\[
\text{M(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} \rightleftharpoons M(CN)\textsubscript{4}(Phen)\textsuperscript{2-} + e},
\]

and

\[
\text{M(CN)\textsubscript{4}(Phen)\textsuperscript{2-} \rightleftharpoons M(CN)\textsubscript{4}(Phen)\textsuperscript{3+} + e},
\]

where M = Mo or W has been carried out by potential mediator method. The relationships,

\[
E = E^0 - \frac{2.303RT}{nF} \log \left(\frac{[\text{M(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-}]}{[\text{M(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} - ]}}\right)
\]

and

\[
E = E^0 - \frac{2.303RT}{nF} \log \left(\frac{[\text{M(CN)\textsubscript{4}(Phen)\textsuperscript{2-}]}{[\text{M(CN)\textsubscript{4}(Phen)\textsuperscript{2-}]}\right)
\]

have been found to hold good for these redox couples respectively. Values of thermodynamic equilibrium constant, standard free energy, enthalpy and entropy changes have been calculated for the above systems. The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) are higher and \(\Delta G^\circ\) lower for the oxidation of Mo(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} and Mo(CN)\textsubscript{4}(Phen)\textsuperscript{2-} than those for W(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} and W(CN)\textsubscript{4}(Phen)\textsuperscript{2-}.

Photochemical decomposition of Mo(CN)\textsubscript{4} and W(CN)\textsubscript{4} ions in aqueous solution gives initially red intermediates Mo(CN)\textsubscript{7}.H\textsubscript{2}O and W(CN)\textsubscript{7}.H\textsubscript{2}O which on further irradiation give final blue products [Mo(OH)\textsubscript{4}(CN)\textsubscript{4}]\textsuperscript{2-} and [W(OH)\textsubscript{4}(CN)\textsubscript{4}]\textsuperscript{2-} respectively; these have been isolated as MoO\textsubscript{2}(CN)\textsubscript{4} and WO\textsubscript{2}(CN)\textsubscript{4} respectively in the solid state. Protio
cation\textsuperscript{9,10}, crystallographic\textsuperscript{11,12} and polarographic\textsuperscript{13,14} studies on these complexes have been carried out extensively. Electrochemical studies on the electron transfer reactions\textsuperscript{1,16-18} reactions with simple and complexed metal ions\textsuperscript{19,20} and redox reactions\textsuperscript{21,22} have been studied earlier. Recent studies on these complexes involve photochemical substitution reactions of CN ligands in octacyano complexes\textsuperscript{24,25} and thermal substitution in dioxotetraacyano complexes\textsuperscript{26,27} by phenanthroline. This paper describes the oxidation of the photoproducts, Mo(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-}, Mo(CN)\textsubscript{4}(Phen)\textsuperscript{2-}, W(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} and W(CN)\textsubscript{4}(Phen)\textsuperscript{2-}, by Fe(III), Ce(IV), Cr(VI) and Mn(VII) and the determination of the standard potentials, equilibrium constants and the thermodynamic parameters.

Materials and Methods
Potassium octacyano-molybdate(IV) and tungstate(IV) dihydrates were prepared and purified by the method of Leipoldt\textsuperscript{28}. Their solutions were standardized potentiometrically by titrating against Ce(IV). Solution of 1,10-phenanthroline was prepared in doubly distilled water after dissolving in ethanol. Solutions of K\textsubscript{3}Fe(CN)\textsubscript{6}, Ce(SO\textsubscript{4})\textsubscript{2}, K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and KMnO\textsubscript{4} were prepared from BDH reagents of AR grade and standardized. The complexes M(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} and M(CN)\textsubscript{4}(Phen)\textsuperscript{2-}, where M = Mo or W, were prepared by mixing solutions of octacyano-molybdate(IV) and -tungstate(IV) dihydrates (0.05 mol dm\textsuperscript{-3}) and 1,10-phenanthroline (0.05 mol dm\textsuperscript{-3}) in 1:1 and 1:2 ratios respectively and irradiating them with visible light at \(\sim 365\) nm for 60 min.

The redox potentials were measured using a Toshniwal portable potentiometer PL-52 (sensitivity \(\pm 0.1\%\)) in conjunction with an external multiflex galvanometer (current sensitivity \(2 \times 10^{-9}\) amp/mm). Bright platinum and saturated calomel electrodes were used in the cell. The measurements were made at a constant temperature of 313 K. The solution of M(CN)\textsubscript{4}(OH)\textsubscript{2}(Phen)\textsuperscript{2-} or M(CN)\textsubscript{4}(Phen)\textsuperscript{2-} was taken in the cell and the potential was measured after each addition of the oxidant, stirring the solution and allowing the potential to stabilize. Measurement of redox potentials at varying temperatures (276-323 K).
at intervals of 5° was carried out for evaluating thermodynamic parameters.

**Results and Discussion**

The photochemical substitution reactions of $\text{M(CN)}^{2-}$ with 1,10-phananthroline may be represented by the following reactions:

$$\text{hv} \quad \text{M(CN)}^{2-} + 2\text{H}_2\text{O} + \text{Phen} \rightarrow [\text{M(CN)}_4(\text{OH})_2\text{Phen}]^2^- + 2\text{OH}^- \quad \ldots (1)$$

$$[\text{M(CN)}_4(\text{OH})_2\text{Phen}]^2^- + \text{Phen} \rightarrow \text{M(CN)}_4(\text{Phen})_2 + 2\text{OH}^- \quad \ldots (2)$$

The oxidation of the photoproducts $[\text{M(CN)}_4(\text{OH})_2\text{Phen}]^2-$ and $\text{M(CN)}_4(\text{Phen})_2$ by $\text{K}_3\text{Fe(CN)}_6$, $\text{Ce(SO}_4)_2$, $\text{K}_3\text{Cr}_2\text{O}_7$ and $\text{KMnO}_4$ was studied potentiometrically which showed a sharp change in potential at the equivalence point. The oxidation-reduction potentials were measured after each addition of the oxidant. The following galvanic cells (A, B) were set for the above systems respectively.

$$\text{Pt} \mid \text{M(CN)}_4(\text{OH})_2\text{Phen})^2-, \text{M(CN)}_4(\text{OH})_2(\text{Phen})^1^-; \text{KCl (satd.)}, \text{Hg}_2\text{Cl}_2(S) \mid \text{Hg} \quad \ldots (A)$$

$$\text{Pt} \mid \text{M(CN)}_4(\text{Phen})_2, \text{M(CN)}_4(\text{Phen})^1_2; \text{KCl (satd.)}, \text{Hg}_2\text{Cl}_2(S) \mid \text{Hg} \quad \ldots (B)$$

The stoichiometry of the reaction was 1:1 for $\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2-$ or $\text{M(CN)}_4(\text{Phen})_2$ with Fe(III). The redox reaction may be represented by the following equations:

$$\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2- + \text{Fe(CN)}_6^{4-} \rightarrow \text{M(CN)}_4(\text{OH})_2(\text{Phen})^1^- + \text{Fe(CN)}_6^{3-} \quad \ldots (3)$$

$$\text{M(CN)}_4(\text{Phen})_2 + \text{Fe(CN)}_6^{4-} \rightarrow \text{M(CN)}_4(\text{Phen})^1_2 + \text{Fe(CN)}_6^{3-} \quad \ldots (4)$$

The value of standard potential ($E'$) was determined by potential mediator method$^{21, 23}$. The mean value of $E'$ for the redox couples, $\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2-$ and $\text{M(CN)}_4(\text{Phen})_2$, was determined graphically by plotting

$$\log \left( \frac{[\text{M(CN)}_4(\text{OH})_2(\text{Phen})^1^-][\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2]}{[\text{M(CN)}_4(\text{Phen})^1_2][\text{M(CN)}_4(\text{Phen})_2]} \right)$$

against electrode potential. The value of $E'$ was found from the plot; the value of $n$ was determined from the slope and it was equal to 1. Log $K$ values also show the completion of oxidation (Tables 1 and 2).
Ce(IV) shows a sharp change in potential at the equivalence point. Values of $E^\circ$, potential change at the equivalence point, $n$ and log $K$ are given in Tables 1 and 2.

The stoichiometry for the oxidation of $\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ or $\text{M(CN)}_4(\text{Phen})_2$ by $\text{Cr}_2\text{O}_7^{2-}$ is 1:1 and values of observed $E^\circ$, log $K$ and potential changes are given in Tables 1 and 2 for $\text{K}_2\text{Mo(CN)}_4(\text{OH})_2(\text{Phen})_2$, $\text{Mo(CN)}_4(\text{Phen})_2$, $\text{K}_2\text{W(CN)}_4(\text{OH})_2(\text{Phen})$ and $\text{W(CN)}_4(\text{Phen})_2$. The oxidation-reduction reactions for $\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ and $\text{M(CN)}_4(\text{Phen})_2$ by Mn(VII) may be represented by the Eqs (9) and (10).

$$\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2 - + \text{MnO}_4^- \rightleftharpoons \text{M(CN)}_4(\text{OH})_2(\text{Phen})_2 + \text{MnO}_4^- \quad \ldots (9)$$

$$\text{M(CN)}_4(\text{Phen})_2 + \text{MnO}_4^- \rightleftharpoons \text{M(CN)}_4(\text{Phen})_2 + \text{MnO}_4^- \quad \ldots (10)$$

The values of $E^\circ$, log $K$ and potential changes are also given in Tables 1 and 2.

The results on the oxidation of $\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ and $\text{M(CN)}_4(\text{Phen})_2$ with various oxidants show that Ce(IV) gives extremely sharp inflexion points as compared with other oxidants. The results show that Ce(IV) is a more efficient oxidant than Fe(III), Cr(VI) and Mn(VII) (Tables 1, 2).

The observed values of $E^\circ$ are quite comparable with the calculated values of $E^\circ$ and the relationships:

$$E = E^\circ - (2.303RT/nF) \log \left( \frac{[\text{M(CN)}_4(\text{OH})_2(\text{Phen})]}{[\text{M(CN)}_4(\text{Phen})_2]} \right) \quad \ldots (11)$$

$$E = E^\circ - (2.303RT/nF) \log \left( \frac{[\text{M(CN)}_4(\text{Phen})_2]}{[\text{M(CN)}_4(\text{Phen})_2]} \right) \quad \ldots (12)$$

hold good for the electrode reactions (5) and (6) respectively. The values of $E^\circ$ calculated from Eqs (11) and (12) are given in Tables 1 and 2. It is observed that the two sets of values are very close to each other.

The values of log $K$ show that oxidation of $\text{M(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ and $\text{M(CN)}_4(\text{Phen})_2$ with various oxidants is complete, but the extent of oxidation is more with Ce(IV) as is evident by the values of log $K$ reported in Tables 1 and 2. Thus, all the above results show that Ce(IV) serves as the most effective oxidant.

$E$ was measured at different temperatures in the range 276-323 K at interval of 5° for evaluating thermodynamic parameters. The values of $\Delta H^\circ$ and $\Delta S^\circ$ are higher and $\Delta G^\circ$ lower for the oxidation of $\text{Mo(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ and $\text{Mo(CN)}_4(\text{Phen})_2$ than those for $\text{W(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ and $\text{W(CN)}_4(\text{Phen})_2$ (Table 3). Although the $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ values for the oxidation of $\text{Mo(CN)}_4(\text{OH})_2(\text{Phen})^2 -$ or $\text{Mo(CN)}_4(\text{Phen})_2$, by Fe(II), Ce(IV), Cr(VI) and Mn(VII) are quite comparable, which is also found in the case of $\text{W(Ch)}_4(\text{OH})_2(\text{Phen})^2 -$ or $\text{W(Ch)}_4(\text{Phen})_2$, yet the values of all the thermodynamic parameters for all the above systems with Ce(IV) are slightly higher than those for other oxidants. The values of standard entropy changes are due to changes only in the oxidation state of the central metal of the complex ion and not in the molecular species.

### Table 3—Thermodynamic Parameters for the Oxidations of (A) $\text{Mo(CN)}_4(\text{OH})_2(\text{Phen})^2 -$,
(B) $\text{Mo(CN)}_4(\text{Phen})_2$, (C) $\text{W(Ch)}_4(\text{OH})_2(\text{Phen})^2 -$ and (D) $\text{W(Ch)}_4(\text{Phen})_2$ by the Oxidants at 313 K

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{Fe(CN)}_6$</td>
<td>212.0</td>
<td>216.0</td>
<td>212.0</td>
</tr>
<tr>
<td>$\text{K}_2\text{Cr}_2\text{O}_7$</td>
<td>35.43</td>
<td>36.02</td>
<td>35.43</td>
</tr>
<tr>
<td>$\text{K}_2\text{MnO}_4$</td>
<td>232.0</td>
<td>234.0</td>
<td>233.0</td>
</tr>
</tbody>
</table>

Values of $\Delta G^\circ$ and $\Delta H^\circ$ in kJ mol$^{-1}$; $\Delta S^\circ$ in J mol$^{-1}$ K$^{-1}$.