A revisit to the oxidation of the 12-tungstocobaltate(II) ion by permanganate ion and comparison with the oxidation of octacyanomolybdate (IV) ion

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The oxidation of 12-tungstocobaltate(II) ion, [Co\(^{11}\)W\(^{6-}\)]\(^-\), abbreviated as [Co\(^{11}\)W\(^{6-}\)], have been a subject of recent interest and the oxidation by halate ions such as BrO\(_3^–\) (ref. 1), ClO\(_4^–\) (ref. 2), IO\(_4^–\) (ref. 3) and HSO\(_3^–\) ions have been reported. We have been interested in the oxidations of [Co\(^{11}\)W\(^{6-}\)]\(^-\), e.g. by S\(_2\)O\(_8^2^–\) and in the Ag\(^+\)-catalysed oxidation by peroxydisphosphate ion. While the title reaction was under investigation, a report on its oxidation was published. The mechanism proposed by the authors and the deducted rate law is given below:

\[
\text{MnO}_4^- + H^+ \rightleftharpoons \text{HMnO}_4 \quad \text{(1)}
\]

\[
[\text{Co}^{11}\text{W}]^{6-} + \text{HMnO}_4 \longrightarrow [\text{Co}^{11}\text{W}]^{5-} + \text{HMnO}_4^- \quad \text{(2)}
\]

\[
\frac{-d[\text{Co}^{11}\text{W}]^{6-}}{dt} = 5k_3K_2[\text{Co}^{11}\text{W}]^{6-}[\text{MnO}_4^-][H^+] \quad \text{(3)}
\]

The results of the present study especially the dependence of the observed rate on [H\(^+\)]. \(k_{\text{obs}} = (a + b[H^+])\,[\text{Co}^{11}\text{W}]^{6-}\), however, indicated that MnO\(_4^–\) ion is a slow co-oxidant along with HMnO\(_4\) which is ca. 4.72 \times 10\(^4\) times more reactive, giving it a close resemblance to the permanganate oxidation of Mo(CN)\(_6^{4-}\) ions. Yet another result of considerable importance obtained in this study is the spectrophotometric evidence for complex formation between the oxidant species, MnO\(_4^–\) and HMnO\(_4\), and the [Co\(^{11}\)W\(^{6-}\)]\(^-\) ion. Thus the basic nature of the previously proposed mechanism has altogether changed. The rate determining steps are no longer the bimolecular collisions between HMnO\(_4\) and [Co\(^{11}\)W\(^{6-}\)]\(^-\), and HMnO\(_4\) and [MCo\(^{11}\)W\(^{5-}\)]\(^-\). A linear dependence of the observed rate on the concentration of added alkali metal ion (M\(^+\)) increased in the order K\(^+\) > Na\(^+\) > Li\(^+\), led to the ambiguous suggestion of ion pairing of the M\(^+\) ion, either with the anionic reductant or oxidant. The alkali metal ion concentration, [M\(^+\)], was not included in the rate law. In the oxidation of arsonous acid by [Co\(^{11}\)W\(^{6-}\)]\(^-\) ion a similar acceleration of the rate by alkali metal ions, in the same order, was noted and the ion pair formation between M\(^+\) and [Co\(^{11}\)W\(^{5-}\)]\(^-\) ions was inferred. The spectrum study of a fixed [Co\(^{11}\)W\(^{6-}\)]\(^-\) in the presence of varying [NaClO\(_4\)] provided evidence for the attainment of equilibrium (4) probably in few ms as suggested by the rapid scans.

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*Extracted from the thesis of Rupa Saha submitted to JNV University in 1996.
obtained over few ms after the two solutions were mixed in the stopped-flow cell.

\[ \text{M}^+ + [\text{Co}^{ll}W]^{6-} \rightleftharpoons K \quad [\text{MCo}^{ll}W]^{7-} \quad \ldots \quad (4) \]

The experimental rate constants, \( k \) and \( k_{\text{irr}} \), corresponding to the oxidation by the \( \text{MnO}_4^- \) ion and \( \text{HMnO}_4 \) respectively, are in fair agreement with the values calculated by the Marcus cross-relation\(^{10}\). The reaction is thus an outer-sphere process.

Materials and Methods

Potassium 12-tungstocobaltate(II) and (III) were prepared as described elsewhere\(^{11}\). The purity of \([\text{Co}^{ll}W]^{6-}\) and \([\text{Co}^{lll}W]^{5-}\) solutions was checked spectrophotometrically. \(([\text{Co}^{ll}W]^{5-} : \varepsilon_{388} = 1215 \ \text{V} \ 5 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1} ; \ \text{lit.} \ \varepsilon_{390} = 1225 \ \text{and} \ 1207 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1} \) respectively\(^{12,13}\) and for \([\text{Co}^{ll}W]^{6-} : \varepsilon_{625} = 212 \pm 4 ; \ \text{lit.} \ \varepsilon_{625} = 214 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1})^8\). Permanganate solution was prepared and standardized as described earlier\(^{14}\). Solutions older than 72 h were discarded.

The solution of NaClO\(_4\) was prepared by neutralizing \( \text{Na}_2\text{CO}_3 \) with \( \text{HClO}_4 \) (E. Merck, GR) as described\(^{15}\). LiClO\(_4\) solution was prepared from a G.F. Smith sample. HClO\(_4\) was used as the proton source. All other reagents were of highest purity and were used as received. Twice distilled H\(_2\)O was used throughout.

Treatment of the data

The Excel 97 program was used to calculate the least square values of the intercept and slope of the linear trend line passing through the data points on the X and Y axis and to draw the linear plots.

Rate measurement.

The desired solutions were thermally equilibrated in two separate stock syringes immersed in water circulated from a Haake D8 G water bath. The reaction was initiated by pushing the solutions from the syringes into the reaction cell the temperature of which was maintained constant (± 0.1°C) as shown by a sensor placed near it. The kinetics were studied at constant ionic strength (0.60 mol dm\(^{-3}\)) under pseudofirst order conditions \(([\text{Co}^{ll}W]^{6-} >> [\text{MnO}_4^-])\) by monitoring the disappearance of \( \text{MnO}_4^- \) at 525 nm using a MK II Spectrochem spectrophotometer. The pseudo-first order rates, \( k_{\text{obs}} \) (= 2.3 x slope), were obtained from the plots of log \((A_\infty - A_t)\) against time that were linear (\(r > 0.99\)) for more than two half-lives of the reaction where \( A_\infty \) and \( A_t \) are the optical densities at infinite time and any time \( 't' \). The slope values were obtained using a least-squares linear regression programme. The \( k_{\text{obs}} \) values were reproducible within ± 3-5%. The mean values from two to three independent runs are reported in the Tables.

Spectrophotometry

The spectral studies were made using a HP 8452A spectrophotometer having a bandwidth of 2 nm at room temperature (25°C). The optical density was measured with quartz cell (1 cm) using the water, distilled twice, as the reference.

Spectral study of \([\text{Co}^{ll}W]^{6-}\) in the presence of \( \text{H}^+ \) ion

On an earlier occasion it was demonstrated that \([\text{Co}^{ll}W]^{5-}\) solution is not protonated\(^6\) by studying the rapid scans of the solutions in the pH range 4.05-5.23. Hence, by analogy the inference could be that \([\text{Co}^{ll}W]^{6-}\) ion is unlikely to be protonated. Since a more concentrated acid solution and the lower valent heteropoly ion \([\text{Co}^{ll}W]^{5-}\) is involved, a recheck was considered worthwhile. Therefore, the changes in the spectrum of a \(10^3[\text{Co}^{lll}W]^{6-} = 2 \ \text{mol dm}^{-3}\) solution were recorded over 500-700 nm first in an aqueous solution and then in the presence of \( \text{HClO}_4 \) which was varied from 0.01 to 0.1 mol dm\(^{-3}\) in a number of steps. It was noted that the optical density of the aqueous solution did not change with the increase in \([\text{H}^+]\) ion. The fact that there was no variation in the optical density over the investigated range of \([\text{H}^+]\) suggested that \([\text{Co}^{ll}W]^{6-}\) species is not protonated in acid solutions.

Spectral study of \([\text{Co}^{ll}W]^{6-}\) in the presence of \( \text{Na}^+ \) ion

The spectra of a \(10^4[\text{Co}^{lll}W]^{5-} = 2.44 \ \text{mol dm}^{-3}\) solution in the presence of different \( \text{NaClO}_4 \), Fig. 1, indicated that the optical density increased with the increase in \([\text{Na}^+]\) indicating the formation of a newer species probably \([\text{Co}^{ll}W]^{6-} \ \text{Na}^+]\) ion pair. It may be noted that the spectra had not shown the presence of any isosbestic point.

Spectral changes in \( \text{MnO}_4^-\) solution in presence of \( \text{Na}^+\)

This study was necessitated by an ambiguity about \( \text{MnO}_4^-\) ion forming an ion pair with \( \text{M}^+ \) ion\(^7\).
spectra of a $10^5\text{[MnO}_4^-\text{]}$ = 7.66 and $[\text{HClO}_4]$ = 0.01 mol dm$^{-3}$ solution in the presence of different $[\text{NaClO}_4]$ did not show any change in the optical density (0.196 ± 0.004). Hence the conclusion is that MnO$_4^-$ does not form ion pair with Na$^+$ ion.

Spectral changes in MnO$_4^-$ solution in presence of $[\text{Co}^{\text{III}}\text{W}]^{6-}$ ion

The spectral changes in a $10^5\text{[MnO}_4^-\text{]}$ = 7.7 mol dm$^{-3}$ solution in the presence of different $[\text{Co}^{\text{III}}\text{W}]^{6-}$ in the absence of [H$^+$ ] are shown in Fig. 2. It is noted that the optical density of the reaction mixture increased with the increase in $[\text{Co}^{\text{III}}\text{W}]^{6-}$ ion without affecting the $\lambda_{\text{max}}$ of MnO$_4^-$ ion (525 nm). Similar spectral changes were also noted in the presence of $[\text{HClO}_4]$ = 0.1 mol dm$^{-3}$. The spectra in either case did not show the isosbestic point suggesting the formation of some new species, probably a complex is formed between MnO$_4^-$ and $[\text{Co}^{\text{III}}\text{W}]^{6-}$ ions.

Estimation of equilibrium constants from spectral data

The equilibrium constants $K$, $K^o$ and $K^h$ for the reactions 4, 8 and 9 respectively were estimated from the related linear plots of $(A_o-A_i)$ against [ligand]$^{-1}$, (NaClO$_4$, $K$ = 586 ± 16 dm$^3$ mol$^{-1}$, $r = 0.995$), and ([Co$^{\text{III}}\text{W}]^{6-}$, $K^o$ = 156 dm$^3$ mol$^{-1}$ and $K^h$ = 465 dm$^3$ mol$^{-1}$).

Test of free radicals

The formation or otherwise of the free radicals during the reaction was ascertained by adding 2 cm$^3$ acrylonitrile to the reaction mixture prepared from reactant solutions that had been purged with pure dry N$_2$ gas. The reaction mixture was shaken vigorously and left for some time. The precipitation of the polyacrylonitrile was not visible even after completion of the reaction suggesting that free radicals were not generated in the reaction.

Stoichiometry

The remaining $[\text{MnO}_4^-\text{]}$ and $[\text{Co}^{\text{III}}\text{W}^{5-}]$ formed in any given reaction mixtures were estimated at 525 nm and 388 nm respectively. The results of several such estimations indicated that $\Delta[\text{Co}^{\text{III}}\text{W}]^{6-}/\Delta[\text{MnO}_4^-] = 5.06 ± 0.04$ which is independent of initial [H$^+$]. The stoichiometry ratio is in agreement with the previous report$^7$. The stoichiometric equation of the reaction is thus given by Eq. (5). The resemblance of the spectra of the spent reaction mixture with the spectra of an authentically prepared solution$^{11}$ of $[\text{Co}^{\text{III}}\text{W}]^{5-}$ confirmed that $[\text{Co}^{\text{III}}\text{W}]^{5-}$ is the oxidation product.

$$5[\text{Co}^{\text{III}}\text{W}]^{6-} + \text{Mn}^{2+} \rightarrow 5[\text{Co}^{\text{III}}\text{W}]^{5-} + \text{Mn}^{2+} \quad \ldots \quad (5)$$

Results

Dependence on $[\text{MnO}_4^-]$

The almost constant value of $10^6k_{\text{obs}} = 3.31 ± 0.10$ s$^{-1}$ ($10^4[\text{Co}^{\text{III}}\text{W}]^{6-} = 5.0$, [H$^+$] = 0.01 and [it] = 0.60 mol dm$^{-3}$ at 40°C) over a ten-fold variation in the initial $[\text{MnO}_4^-]$ is consistent with first order dependence of the reaction in $[\text{MnO}_4^-]$ ion.
Dependence on $[\text{Co}^{II}\text{W}^6^-]$

The proportionate increase in the $k_{\text{obs}}$ values with the initial $[\text{Co}^{II}\text{W}^6^-]$ is indicated by the constancy of the factor $10^2k_{\text{obs}}/[\text{Co}^{II}\text{W}^6^-]$ (6.74 ± 0.20 dm$^3$ mol$^{-1}$ s$^{-1}$). The plot (not shown) of $k_{\text{obs}}$ versus $[\text{Co}^{II}\text{W}^6^-]$ is linear and passes through the origin, confirming a strict first-order dependence in $[\text{Co}^{II}\text{W}^6^-]$.

Dependence of $k_{\text{obs}}$ on $[\text{H}^+]$

There is no proportionate increase in $k_2$ ($= k_{\text{obs}}/[\text{Co}^{II}\text{W}^6^-]$), Table 1, with increase in $[\text{H}^+]$. The linear plots of $k_{\text{obs}}$ versus $[\text{H}^+]$ with positive intercepts on the rate ordinate indicated that the empirical rate law is given by Eq. (6) where $a$ and $b$ are empirical constants and is different from Eq. (3) reported by the previous authors.

$$k_{\text{obs}} = (a + b[\text{H}^+])[\text{Co}^{II}\text{W}^6^-]$$  \hspace{0.5cm} \ldots (6)

Dependence on [alkali metal ion]

The rate measurements at constant $[\text{ClO}_4^-]$, Table 2, show that the rate for the same $[\text{Na}^+] > [\text{Li}^+]$ and is consistent with the previous report$^7$: rate for $K^+ > Na^+ > Li^+$ ion. The linear plot of $k_{\text{obs}}$ against $[\text{Na}^+]$ has an intercept equal to the rate in the presence of LiClO$_4$ alone.

Dependence on $[\text{Co}^{II}\text{W}^5^-]$ and $[\text{Mn}^{2+}]$

The separate addition of $[\text{Co}^{II}\text{W}^5^-]$ and $\text{Mn}^{2+}$ ions, the final products in the reaction, to the reaction mixture ($10^4[\text{MnO}_4^-] = 1.0$, $10^4[\text{Co}^{II}\text{W}^6^-] = 5.0$, $[\text{H}^+]= 0.01$ and $[\text{I}]= 0.60$ mol dm$^{-3}$ at 40°C) indicated that the rate is not altered indicating that these ions are not involved in any equilibrium prior to the rate determining step. $(10^4k_{\text{obs}} = 3.34 ± 0.10$ s$^{-1}$ over (0.5-5.0) × $10^{-3}$ mol dm$^{-3}$ of $[\text{Co}^{II}\text{W}^5^-]$ and $10^4k_{\text{obs}} = 3.30 ± 0.08$ s$^{-1}$ over the (1-10) × $10^{-5}$ mol dm$^{-3}$ range of $\text{Mn}^{2+}$ ion).

Discussion

The reaction is first order each in $\text{MnO}_4^-$ and $[\text{Co}^{II}\text{W}^5^-]$ ions though there is evidence for complex formation between $[\text{Co}^{II}\text{WM}]^+$ and $\text{MnO}_4^-$. The complex $[\text{Co}^{II}\text{WM}.\text{MnO}_4^+]$ evaded kinetics detection probably because it is not formed in sufficient concentration. Again, there is evidence for the ion pair formation between $M^+$ (alkali metal ion) and $[\text{Co}^{II}\text{W}^5^-]$ ions. It is calculated, using the deducted $K$ value (586 ± 16 dm$^3$ mol$^{-1}$), that $[\text{Co}^{II}\text{W}^5^-]$ ion is $\approx 96\%$ ion paired supporting the assumption that ion pair $[\text{Co}^{II}\text{WM}^5^+] = [\text{Co}^{II}\text{W}^5^-]$. In view of all this the most probable reaction mechanism is represented by the reactions (7)-(12) where reactions (10) and (11) are rate determining.

$$\text{MnO}_4^- + \text{H}^+ \xrightleftharpoons[K_h]{K_l} \text{HMnO}_4 \hspace{1cm} (K_h = 5.62 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}, 25°C^17)$$  \hspace{0.5cm} \ldots (7)

$$\text{MnO}_4^- + [\text{MCo}^{II}\text{W}]^5^- \xrightleftharpoons[K_l^0]{K_h^0} [\text{MnO}_4^-\text{..M..Co}^{II}\text{W}]^6^-$$  \hspace{0.5cm} \ldots (8)

$$\text{HMnO}_4 + [\text{MCo}^{II}\text{W}]^5^- \xrightleftharpoons[K_l^h]{K_h^h} [\text{HMnO}_4\text{..M..Co}^{II}\text{W}]^5^-$$  \hspace{0.5cm} \ldots (9)

$$[\text{MnO}_4^-\text{..M..Co}^{II}\text{W}]^6^- \xrightleftharpoons[K_l^6]{K_h^6} [\text{M..Co}^{III}\text{W}]^4^- + \text{MnO}_4^2^- \hspace{0.5cm} \text{or Mn(VI)}$$ (10)

$$[\text{HMnO}_4\text{..M..Co}^{II}\text{W}]^5^- \xrightleftharpoons[K_l^5]{K_h^5} [\text{M..Co}^{III}\text{W}]^4^- \hspace{0.5cm} \text{HMnO}_4^2^- \hspace{0.5cm} \text{or Mn(VI)}$$ (11)

$$\text{Mn(VI)} + 4[\text{MCo}^{II}\text{W}]^5- \xrightarrow{\text{fast}} \text{Mn(II)} + 4[\text{MCo}^{III}\text{W}]^4^- \hspace{0.5cm} \ldots (12)$$

| Table 1—Dependence of $k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$) on $[\text{H}^+]$ at different temperatures. $10^4[\text{MnO}_4^-] = 1.0$, $10^4[\text{Co}^{II}\text{W}^6^-] = 5.0$ and $[\text{I}]= 0.60$ mol dm$^{-3}$ |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $[\text{H}^+]$ (mol dm$^{-3}$) | 20°C | 25°C | 30°C | 35°C | 40°C |
| 0.01 | 0.106 | 0.182 | 0.310 | 0.572 | 1.34 |
| 0.03 | 0.224 | 0.450 | 0.568 | 1.04 | 1.71 |
| 0.05 | 0.348 | 0.642 | 0.896 | 1.63 | 2.50 |
| 0.07 | 0.506 | 0.912 | 1.23 | 2.34 | 3.26 |
| 0.10 | 0.708 | 1.24 | 1.66 | 3.12 | 4.48 |
| 0.20 | 1.28 | 2.46 | 3.30 | 5.84 | 8.10 |
| 0.30 | 1.90 | 3.72 | 4.68 | 8.44 | 11.4 |
| 0.40 | 2.54 | 4.96 | 6.48 | 11.6 | 15.3 |
| 0.50 | 3.22 | 6.10 | 8.24 | 14.5 | 18.8 |

| Table 2—Dependence of $k_{\text{obs}}$ on $[\text{Li}^+]$ and $[\text{Na}^+]$ at constant $[\text{ClO}_4^-]$. $10^4[\text{MnO}_4^-] = 1.0$, $10^4[\text{Co}^{II}\text{W}^6^-] = 5.0$, $[\text{H}^+] = 0.02$ and $[\text{I}]= 0.60$ mol dm$^{-3}$ at 40°C |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $[\text{Li}^+]$ (mol dm$^{-3}$) | $[\text{Na}^+]$ (mol dm$^{-3}$) | $10^4k_{\text{obs}}$ (s$^{-1}$) |
| 0.48 | 0.00 | 3.89 |
| 0.40 | 0.08 | 5.43 |
| 0.30 | 0.18 | 7.46 |
| 0.20 | 0.28 | 9.44 |
| 0.10 | 0.38 | 11.2 |
| 0.00 | 0.48 | 13.3 |
The hexavalent manganese, MnO$_4^{2-}$, is stable in alkaline solutions. However, it seems that in acidic solution it oxidises [Co$^{III}$W]$^{6-}$. Since [Co$^{III}$W]$^{6-}$ is one electron oxidant, it is likely that each [Co$^{III}$W]$^{6-}$ molecule is oxidized by succeeding lower Mn valence states till it reaches the stable Mn$^{2+}$ state. This explains the stoichiometry of the reaction given in Eq. (5). Equation (12) is a combined representation of the process in which four [Co$^{III}$W]$^{6-}$ molecules are oxidised. The dissociation of MnO$_4^{2-}$ into Mn(VII) and Mn(V) through reaction (13) is highly unlikely because it suggests a regeneration of MnO$_4^{2-}$ ion impairing the observed stoichiometric ratio.

$$2\text{MnO}_4^{2-} \quad \underset{\text{fast}}{\longrightarrow} \quad \text{MnO}_4^{4-} + \frac{1}{3}\text{MnO}_4^{3-} \text{ or Mn(V)}$$

The rate law deduced in terms of reactions (7) to (12) is given by the eq. (14).

$$-\frac{d[\text{MnO}_4^{2-}]}{dt} = 5(k^{0}K^{0} + k^{T}K^{T}[H^{+}])[\text{MnO}_4^{2-}][\text{MCoo}^{5-}] 1 + K_{H}[H^{+}] + (k^{0} + k^{T}K^{T}[H^{+}])[\text{MCoo}^{5-}]$$

$$\text{or, } K_{obs} = 5(k + K_{H}[H^{+}])[\text{MCoo}^{5-}]$$

In view of the first order dependence of the reaction on [MCoo$^{5-}$], and in view of the empirical rate law (6) it is assumed that $K_{H}[H^{+}] + (k^{0} + k^{T}K^{T}[H^{+}])[\text{MCoo}^{5-}]$ when eq. (14) is reduced to eq. (15) where $k = k^{0}$ and $K_{H} = k^{T}K^{T}$. The assumption is valid because the order with respect to [MCoo$^{5-}$] is strictly one.

$$K_{obs} = 5(k + K_{H}[H^{+}])[\text{MCoo}^{5-}]$$

The plot of $k_{2}$ against [H$^{+}$] with intercept on the ordinate, consistent with the eq. (16), is in Fig. 3. The least squares values of $k$ and $K_{H}K_{H}$ at different temperatures, calculated separately from the intercepts and slopes of the plots in Fig. 3, are given in Table 3 wherein are also reported the respective activation parameters. A comparison of the eq. (15) with the eq. (6) indicates that $k = 0.2a$ and $K_{H} = 0.0b$.

The alkali metal ions (M$^{+}$) are known either to enhance or inhibit the rates of the reactions. The mediation of M$^{+}$ ions in the reactions is attributed to their forming ion pairs with the oppositely charged ions. It was first suggested in the electron exchange reaction between [Co$^{III}$W]$^{5-}$ and [Co$^{III}$W]$^{6-}$ ions since the rate was enhanced on replacing Li$^{+}$ by K$^{+}$ ion. The formation of [MFe(CN)$_6$]$_{2-}^{3-}$ ion pairs was suggested in a similar study between [Fe(CN)$_6$]$^{3-}$ and [Fe(CN)$_6$]$^{4-}$ ions for the rates enhanced by M$^{+}$ ions paralleled with the increase in ionic radii (Li$^{+}$: 0.60, Na$^{+}$: 0.95, K$^{+}$: 1.33, Rb$^{+}$: 1.48, and Cs$^{+}$: 1.69 Å). The same reaction in alkaline medium was, however, inhibited by the alkali metal ions. A similar enhancement of the rate$^{9,22}$ in the oxidations by [Co$^{III}$W]$^{5-}$ and the inhibition of the rate in the oxidation of [Co$^{III}$W]$^{6-}$ by S$_2$O$_8^{2-}$ and IO$_4^{-}$ ions had been observed$^{23}$ though the rate increased in the MnO$_4^{2-}$ oxidation of [Co$^{III}$W]$^{6-}$ ion.$^{7}$ The suggestion of ion pair formation in

Fig. 3—The linear plots of $k_{2}$ (k$_{obs}$/[Co$^{III}$W]$^{6-}$, dm$^{3}$ mol$^{-1}$ s$^{-1}$) against [H$^{+}$] at temperatures 20E( ), 25E( ), 30E( ), 35E( ) and 40E C( ).

<table>
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<th>Temp</th>
<th>20</th>
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<th>35</th>
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<td>k$_h$ (dm$^3$ mol$^{-1}$s$^{-1}$)</td>
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<td>0.74</td>
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<td>k$_h$ (kJ mol$^{-1}$)</td>
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<td>0.560</td>
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<tr>
<td>$\Delta H^\ddagger$ (kJ mol$^{-1}$)</td>
<td>107 ± 23</td>
<td>64 ± 5</td>
<td>107 ± 23</td>
<td>64 ± 5</td>
<td>107 ± 23</td>
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<tr>
<td>$\Delta S^\ddagger$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>71 ± 6</td>
<td>33 ± 18</td>
<td>55 ± 22</td>
<td>119 ± 25</td>
<td>177 ± 37</td>
</tr>
</tbody>
</table>

Table 3—Values of the rate constants $k$ (= $k^{0}$, dm$^3$ mol$^{-1}$ s$^{-1}$).
[Co\(^{11}\)W]\(^{5-}\) oxidations or oxidation of [Co\(^{11}\)W]\(^{6-}\) ion is at best an inference only and lacked any convincing support.

The formation of some newer species, most likely an ion pair [Co\(^{11}\)WM]\(^{5-}\) is supported by the spectral study shown in Fig. 1. The equilibrium constant \(K\) for the reaction (4), estimated from the plot of \((A_1 - A_0)^{-1}\) against [NaClO\(_4\)]\(^{-1}\), has a value 197 \(\pm\) 26 dm\(^3\) mol\(^{-1}\) and is of the same magnitude as reported for the formation of [Fe(CN),M]\(^{2-}\) ion pair\(^{25}\). However, the estimated value is several times the values 5.7 and 16.8 dm\(^3\) mol\(^{-1}\) in the presence of Na\(^+\) and K\(^+\) ions respectively in the oxidation\(^9\) of H\(_2\)AsO\(_4\). The probable reason for such a large difference could be due to the likely competition for M\(^+\) from H\(_2\)AsO\(_4\)\(^-\) ion. It has been shown that [Co\(^{11}\)W]\(^{6-}\) = [Co\(^{11}\)WM]\(^{5-}\). Since the plots constructed, using the data of the previous authors\(^7\), between \(k_2\) and [M\(^+\)] have some negligible intercepts, it is likely that [Co\(^{11}\)W]\(^{6-}\) ion is relatively poor oxidant compared to [Co\(^{11}\)WM]\(^{5-}\) ion.

There is no more ambiguity\(^7\) about M\(^+\) ion forming an ion pair with MnO\(_4\)\(^-\) ion because neither the optical density nor the \(\lambda_{\text{max}}\) of the MnO\(_4\)\(^-\) solution changed in the presence of Na\(^+\) ion. Further, the formation of a ternary complex between [Co\(^{11}\)W]\(^{6-}\) (in general term) and MnO\(_4\) /HMnO\(_4\) is supported by the spectral changes shown in Fig. 2. The estimation of the equilibrium constant in the presence of H\(^+\) ion suggested that its value is greater than that in aqueous solution.

Beside the ion pair formation M\(^+\) ion can act either as a bridge or as a charge buffer between the reacting species\(^7\). The larger size of M\(^+\) helps these ions to act as effective bridges between the oppositely charged ions and the same is supported by the fact that the rate enhancements are in the same order as their polarisabilities. A linear relationship between the rate and the polarisability\(^{25}\) \(\alpha_{\text{M}^+}\) was demonstrated in the oxidation of [Mo(CN)\(_5\)”\(^{1-}\) by [Mn(edta)]\(^+\) ion\(^26\). A similar plot, based on the data from the previous studies\(^7\), is shown in Fig. 4. Thus in a reaction between negatively charged donor and acceptor ions the M\(^+\) ions first form an ion pair with one of the acceptor or donor ion and subsequently this ion pair forms a bridged complex with the other reacting ion. The same is very well demonstrated in the electron transfer reactions of [Co\(^{11}\)W]\(^{6-}\) and [Co\(^{11}\)W]\(^{5-}\) ions\(^{18}\).

However, the enhancement of the rate by M\(^+\) ions of increasing ionic radii is faulted by the fact that the ionic radii of the strongly hydrated M\(_{\text{aq}}^+\) ions in aqueous solutions decrease with the increase in the size of the M\(_{\text{aq}}^+\) ions. This again supports the action of M\(^+\) ions as a bridge between the acceptor (A) and donor (D) pairs. The formation of the complex, A..M..D (charges not considered), is thus a prerequisite for the electron transfer between donor and acceptor pairs.

![Figure 4](image-url)
Since three species are involved, the complex so formed is named as a ternary complex. A three-body collision consistent with the first order dependence in each of the [Co(W)]$^{6-}$, MnO$_4^-$ and M$^+$ ions is required for the formation of the ternary complex. The formation of the [Co(W..M)]$^{5-}$ ion pair should not present any difficulty in assuming a first order dependence in M$^+$ and [Co(W)]$^{6-}$ ions because it is shown that [Co(W..M)]$^{5-} = [Co(W)]^{6-}$. Hence it is suggested that the ion pair [Co(W..M)]$^{5-}$ (MnO$_4^-$ does not form the ion pair vide supra) coordinates through the lone electron pair present on the outer most orbit of M$^+$ ion with MnO$_4^-$/HMnO$_4$. Thus larger the size of the M$^+$ ion, it is easier for the lone pair to coordinate because of the loose nature.

The accelerating effect of the H$^+$ ion cannot be attributed to the protonation of [Co(W)]$^{6-}$ ion in view of the unchanged nature of both optical density and the wavelength of the spectra of the [Co(W)]$^{6-}$ ion in the presence of HClO$_4$. This is consistent with the fact that the protonation of [Co(W)]$^{6-}$ ion is not reported in literature. The protonation of MnO$_4^-$ ion is reported in literature, and the participation of HMnO$_4$ species has been invoked in the oxidation of Mo(CN)$_8^{4-}$ ion, H$_3$PO$_4$ and aldehydes.

The parallelism between the oxidations of [Mo(CN)$_8^{4-}$] and [Co(W)]$^{6-}$ by acidic permanganate is noteworthy. The similarities include (a) similar dependence of $k_{obs}$ on [H$^+$], (b) MnO$_4^-$ ion being poor oxidant compared to H2MnO$_4$ and (c) the $k_1$/$k$ ratio is in the order: [Mo(CN)$_8^{4-}$] $>[Co(W)]^{6-}$ (3.9 x 10$^5$, 25EC) > [Fe(phen)$_2$]$^2+$ (4.72 x 10$^4$, 25EC) which is attributed to the respective redox potentials (EE, V) of [Mo(CN)$_8^{4-}$] $>[Co(W)]^{6-}$ (1.01V$^{35}$) $>[Fe(phen)$_2$]$^2+$ (1.06V$^{37}$).

Hence the oxidations of these ions by MnO$_4^-$ are likely to resemble one another. The $k_1$ for H2MnO$_4$/HMnO$_4$ is 1.3V$^{38}$ and 0.56V$^{39}$ for (MnO$_4^-$/HMnO$_4$ $^{2-}$).

Oxidation of [Mo(CN)$_8^{4-}$] by MnO$_4^-$ is considered outer-sphere because both MnO$_4^-$ and [Mo(CN)$_8^{4-}$] are inert to substitution and respond to the Marcus treatment. For a similar reason the present redox is expected to be outer-sphere and the same is tested using the Marcus cross relation, given by expressions (17) and (18).

\[
k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad \ldots \quad (17)
\]

\[
\ln f_{12} = \ln k_{12} + |4\ln (k_{11}k_{22}Z^2)| \quad \ldots \quad (18)
\]

\[
\begin{array}{cccccc}
10^{-3} k_{11} & 1.7 & 1.23 & 1.1 & 0.72 \\
\text{Acid independent path} & \log K_{12} (\text{MnO}_4^- + [Co(W)^{6-}]) = -7.45 \\
f_{12} & 0.215 & 0.218 & 0.218 & 0.221 \\
10^{-3} k_{12} & 0.362 & 0.310 & 0.293 & 0.239 \\
\text{Acid dependent path} & \log K_{12} (\text{HMnO}_4 + [Co(W)^{6-}]) = 5.08 \\
f_{12} & 0.490 & 0.492 & 0.493 & 0.496 \\
10^{-3} k_{12} & 9.96 & 8.49 & 8.03 & 6.52 \\
\end{array}
\]

where $k_{12}$ is the observed second order rate constant of the redox reaction, $k_{11}$ is the self-exchange rate for MnO$_4^-$/$MnO_4^{2-}$ pair, $k_{22}$ is the self-exchange rate for [Co(W)]$^{5-}$/[Co(W)]$^{6-}$ couple and has a value 1.0 dm$^3$ mol$^{-1}$ s$^{-1}$ (interpolated to $\mu = 0.6$ mol dm$^{-3}$ at 25EC from the data), $K_{12}$ is the equilibrium constant for the redox reaction and Z is the collision frequency for the uncharged species (10$^{12}$ mol$^{-1}$ s$^{-1}$). The $k_{11}$ value has been variously reported; the value (1.7 ± 0.22) x 10$^4$ is based on the isotopic-tracer technique, and the value (1.23 ± 0.25) x 10$^5$ is based on pulsed N.M.R. The recent value is 7.2 x 10$^2$ dm$^3$ mol$^{-1}$ s$^{-1}$ though a value 1.10 x 10$^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ is used in the oxidations of [Mo(CN)$_8^{4-}$] (ref.8) and [Co(W)]$^{6-}$ ion.

The calculated value of $k_{12}$ is dependent on the $k_{11}$ value since $k_{22} = 1.0$ (see Eq. 17). Since four $k_{11}$ values, mentioned above, are available in the literature, the $k_{12}$ values are calculated corresponding to each of the $k_{11}$ value. These values are reported in Table 5. The path independent of H$^+$ ion has an experimental value of $k$ ($k'$) = 0.46 x 10$^{-3}$ dm$^3$ mol$^{-1}$ compared to the calculated values of $k_{12}$ = 2.39 x 10$^{-3}$ and 2.93 x 10$^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ corresponding to $k_{11}$ = 720 and 1100 dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. Similarly, the experimental value of $k_{11}$ for the protonated path at 25EC is 0.122 dm$^3$ mol$^{-2}$ s$^{-1}$, the value of $k'$ ($k_1/k_{11}$) comes out to be 21.7 dm$^3$ mol$^{-1}$ s$^{-1}$ based on $k_{11}$ = 5.62 x 10$^{-3}$ dm$^3$ mol$^{-1}$ and $pK_a$ = -2.25 for MnO$_4^-$/HMnO$_4$ (ref. 21). The calculated value for the protonated path from the Marcus cross relation is 6.52 x 10$^4$ and 8.00 x 10$^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ corresponding to $k_{11}$ = 720 and 1100 dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. These values are given in Table 4.

Although the experimental value is about two orders of magnitude less than the calculated value from Marcus cross relation, yet the agreement is considered
good in view of a similar agreement in the oxidation of iodide ion by trans-dioxoruthenium(VI) ion (the calculated \( k_{12} = 7 \times 10^{-3} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \) and the experimental value \( k_3 = 1.92 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \)). Hence, an outersphere one-electron pathway for the reaction is supported by the Marcus cross relation. It may be mentioned that the previous authors\(^7\) reported almost an ideal agreement (calculated = \( 5.37 \times 10^3 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \) and experimental value = \( 2.01 \times 10^3 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \)).

Alternatively, one can opine that the reaction (19) could be a suitable replacement of reactions (9) and (11) in the proposed mechanism without affecting the nature of the rate law. The net result would be that \( k^h K_{10} \) is replaced by \( k_1 k_2 \) in the rate law. However, in doing so one cannot compare the experimental \( k_1 \) value with the corresponding value from the cross relation for the reason that the cross relation cannot be used to evaluate the rate constant for such a reaction. Hence reaction (19) is not considered.

\[
\text{[MnO}_4^- \cdot \text{Mn}^{2+} \text{W}^{6+} + \text{H}^+ \xrightarrow{k_1} \text{[MnO}_4^- \cdot \text{Mn}^{2+} \text{W}^{7+} + \text{HMnO}_4^- \text{ or Mn(VI)} \]
\]

\[\ldots \text{ (19)}\]

In conclusion, the agreement between the experimental rate constants and those calculated from the Marcus cross relation are found in good agreement and the experimental rate constants approximates the “outer-sphere” reaction.

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**References**