Kinetics and mechanism of oxidation of [Mo(CN)₈]⁴⁻-[Mn(cdta)]⁻ complex ion: Application of the Marcus relationship in support of an outer-sphere mechanism

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Oxidation of [Mo(CN)₈]⁴⁻ by [Mrucdtaj]⁺, studied as a function of disappearance of [Mntcdta]⁻ at 510 nm, is a first order reaction with respect to both the ions. The linear plot between kobs and [H⁺] with intercept indicates two paths; one independent (k) of and the other (kH) dependent on [W]. These paths are ascribed to the protonation equilibrium between [Mntcdta]⁻ and H[Mn(cdta)], by analogy to the similar equilibrium existing in [Mn(III)edta]-complex, and is more likely than the equilibrium involving the protonation of [Mo(CN)₈]⁴⁻ ion. The alkali metal cations (M⁺) catalyze the observed rate in the order K⁺ > Na⁺ > Li⁺ ion. The data provide linear correlations between kobs/[Mo(CN)₈ 4⁻] and rM⁺], between kobs/[Mo(CN)₈ 4⁻) and μμ/(1 + μμ) with a predictable slope ~ 4 for the reaction between [Mn(cdta)]⁻ and [Mo(CN)₈]⁴⁻. The first correlation, indicative of the ion-pair formation, is not favoured because the kobs value did not show sign of saturation. The second correlation indicates the formation of a bridge by the alkali metal ion between the oxidant and reductant species. The rate constants k and kH at 25° C are (7.32 ± 0.17)x10⁻³ dm³ mol⁻¹ s⁻¹ and (1.3 ± 0.02)X10⁷ dm³ mol⁻² s⁻¹ respectively. The related values of the enthalpy and entropy are ΔHf° = 25 ± 2 kJ mol⁻¹, ΔS° = -70 ± 6 J K⁻¹ mol⁻¹, and ΔHf° = 28 ± 2 kJ mol⁻¹, ΔS° = 2 ± 5 J K⁻¹ mol⁻¹ respectively. The use of the Marcus theory supports the outer-sphere nature of the reaction.

The difficulty with the use of [Mn(aq)]³⁺ (aq = (H₂O)₆) ions is its hydrolysis even at high acid concentration (~4 mol dm⁻³). The Mn³⁺ oxidation state has been stabilized in neutral solution by such ligands as Schiff bases and polyaminocarboxylates. Mn³⁺ is coordinated to four carboxylato arms and two diamino nitrogen of the ligand Hcdta (trans-1,2-diaminocyclohexane-N,N,N',N'':ta?traacetic acid) and the seventh coordination site is occupied by a water molecule. The oxidation reactions of mononuclear Mn³⁺ complexes have been reviewed recently. We have been interested in the oxidations of SO₄²⁻ (ref.6), SO₃²⁻ (ref.7), and VO(aq)²⁻ (ref.8), by [Mn(cdta)]⁻. The oxidation of S₂O₅²⁻ was considered outer-sphere because the bond rupture between one of the carboxylato arms and the metal centre is less rapid than the rate of electron-transfer. Similarly, the oxidations of SO₃²⁻ and VO(aq)²⁻, have been shown to be outer-sphere by the use of Marcus treatment though the earlier studies on the oxidation of SO₃²⁻ (ref.10), and VO(aq)²⁻ (ref.11) were considered inner-sphere. The selective study on the oxidations of [Mo(CN)₈]⁴⁻ (M = Mo, W) by [Ag(OH)₄]⁻ (ref.12), S₂O₅²⁻ (ref.13, 14), 12-tungstocobaltate(III) ([Co(III)O₄W₁₂O₃₈]⁵⁻) (ref.15), and [Mo(CN)₈]⁴⁻ by MnO₄⁻ ion indicated an outer-sphere electron-transfer mechanism. A detailed study on the oxidation of [Mo(CN)₈]⁴⁻ by [Mn(cdta)]⁻ including the effect of alkali metal ions and its role in the mechanism is discussed. The Marcus treatment of the present results and those published previously indicated that the electron-transfer takes place through an outer-sphere mechanism.

Materials and Methods

The solutions were prepared in doubly distilled water deaerated with nitrogen at least for 20 min to check the oxidation by dissolved oxygen. MNO₃ (M = Li, Na and K), AcOH, NaOAc, HClO₄ and Na₂CO₃ were analytical grade reagents (Glaxo or E. Merck), and Mn(ClO₄)₂ was from G.F. Smith. KCN (purum), H₂WO₄ (purum), MoO₃ (puriss) were Fluka samples and Hcdta was from Sigma. These were used as received. NaClO₄ was prepared by neutralising Na₂CO₃ with HClO₄ to a pH 7 and standardised gravimetrically. The buffer solutions of desired pH were prepared from sodium acetate and acetic acid. The pH of the solutions was...
checked with an Agronic pH meter. The potassium salts of Mo(CN)$_6^{4-}$ (ref.18), and [Mn(cdtal)]$^-$ (ref.19) were prepared, characterised and standardised as described in the literature. The solution of [Mo(CN)$_5$]$^+$ was freshly prepared and protected from the diffused fluorescent room light.

In the investigation on the effect of alkali metal ions on the rate, the concentration of Na$^+$ ion is inclusive of its concentration present in the buffer solution. The ionic strength mentioned in Tables is the concentration of sodium perchlorate.

**Rapid scans**

The reaction mixture was rapid scanned using the RA-415 attachment with the Union Giken RA-401 stopped-flow spectrophotometer. The total span of the recorded spectrum is limited to 48 nm on either sides of the selected central wavelength 510 nm which is the $\lambda_{max}$ of [Mn(cdtal)]$^-$ ion. The rapid scan spectra, Fig. 1, were recorded using 1 ms gate time and zero interval time.

**Kinetics measurements**

The kinetics were studied under pseudo-first order conditions ([Mo(CN)$_5$]$^+$) >> [Mn(cdtal)] in acetic acid-sodium acetate buffer solutions of constant ionic strength (NaClO$_4$). The temperature of the reactant solutions and the reaction cell was maintained at the desired temperature (± 0.1°C) by circulating water from a Haake D8G refrigerated circulatory water bath. The reaction's progress was measured using Union-Giken RA-401 stopped-flow spectrophotometer interfaced with a RA-451 data processor which calculated the pseudo-first order rate constant, $k_{obs}$, by a least squares curve-fit method. The reported $k_{obs}$ values, evaluated from the averaged traces of at least 7-10 kinetic runs, were reproducible within ±5%.

The stopped-flow traces consisted of a short-lived ascending portion which acquired saturation in absorbency in time ≤ 10 ms and was followed by the main long-lived descending redox curve. That the ascending portion was real was confirmed by the rapid scan of the reaction mixtures, Fig. 1, in which the absorbency increased with time and reached the saturation value. The $k_{obs}$ values calculated from the descending portion both in the presence or absence of the ascending curve, which was later blanked from the stopped-flow trace either by increasing the response time or the delay time on RA-controller, were almost identical.

**Stoichiometry**

The stoichiometry was determined by preparing several reaction mixtures at room temperature using varying initial ratios of [Mn(cdtal)]$^-$ and [Mo(CN)$_5$]$^+$ at pH 4.27. The [Mn(cdtal)]$^-$ was always in excess. Since [Mn(cdtal)]$^-$ is photochemically stable and the reaction was complete in a very short time, the blanks were not prepared. However, solutions of [Mo(CN)$_5$]$^+$ ions were protected from the diffused light of the room because these ion can be converted photochemically to six coordinated trans-dioxo[MoO$_2$(CN)$_4$]$^+$ ions by the diffused room light. A Beckman DU spectrophotometer was used to estimate the unreacted [Mn(cdtal)]$^-$ at 510 nm (ε$_{510}$ = 345 dm$^3$ mol$^{-1}$ cm$^{-1}$).

**Results**

The rapid scan spectra, Fig. 1, corresponding to 3, 5, 8, 11 and 17 ms after mixing, show increasing absorbency tending to attain a saturation value with the time. It is thus consistent with the rising portion of the stopped-flow trace. The increase in the absorbency is indicative of the formation of a new species, probably, a weak complex between [Mo(CN)$_5$]$^+$ and [Mn(cdtal)]$^-$ ions. The result, $\Delta$[Mn(cdtal)]/\Delta[Mo(CN)$_5$]$^+$ = 1.02 ± 0.03, is represented by the stoichiometric Eq.(1)

$$[\text{Mn}^{2+} + [\text{Mo}^{4+}] + [\text{Mn}^{3+}] + [\text{Mo}^{2+}]$$

... (1)
Table 1- The dependence of $k_{obs}$ on the initial $[\text{Mo}(	ext{CN})_8^{4-}]$ at different temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$[\text{Mo}(	ext{CN})_8^{4-}]$ (mol dm$^{-3}$)</th>
<th>0.8</th>
<th>1.13</th>
<th>1.5</th>
<th>2.0</th>
<th>3.0</th>
<th>5.0</th>
<th>8.0</th>
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<td>10</td>
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<td>1.82</td>
<td>2.67</td>
<td>3.44</td>
<td>4.68</td>
<td>7.06</td>
<td>11.5</td>
<td>18.7</td>
<td>23.2</td>
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<tr>
<td>15</td>
<td></td>
<td>2.29</td>
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<td>4.37</td>
<td>5.54</td>
<td>8.53</td>
<td>14.9</td>
<td>22.1</td>
<td>28.4</td>
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<td></td>
<td>2.57</td>
<td>3.91</td>
<td>5.25</td>
<td>6.83</td>
<td>10.2</td>
<td>17.1</td>
<td>26.4</td>
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<td></td>
<td>3.24</td>
<td>4.56</td>
<td>6.10</td>
<td>8.50</td>
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<td>20.2</td>
<td>32.4</td>
<td>40.4</td>
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<tr>
<td>30</td>
<td></td>
<td>4.03</td>
<td>5.54</td>
<td>7.56</td>
<td>9.67</td>
<td>14.8</td>
<td>25.1</td>
<td>38.4</td>
<td>49.3</td>
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Table 2- The dependence of $k_{obs}$ on the initial pH of the reaction mixture at different temperatures.

<table>
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<th>pH (°C)</th>
<th>$[\text{Mo}(	ext{CN})_8^{4-}]$ (mol dm$^{-3}$)</th>
<th>0.8</th>
<th>1.13</th>
<th>1.5</th>
<th>2.0</th>
<th>3.0</th>
<th>5.0</th>
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<td>10</td>
<td>8.10</td>
<td>4.68</td>
<td>3.93</td>
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<td>3.29</td>
<td>3.25</td>
<td>3.25</td>
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<td>15</td>
<td>10.0</td>
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<td>15.3</td>
<td>8.50</td>
<td>6.85</td>
<td>6.31</td>
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<td>30</td>
<td>18.7</td>
<td>9.82</td>
<td>8.10</td>
<td>7.6</td>
<td>7.46</td>
<td>7.32</td>
<td>7.16</td>
<td>7.16</td>
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Table 3- The dependence of $k_{obs}$ on the alkali metal ion concentration at 25 °C.

<table>
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<tr>
<th>$[\text{M}^+](mol dm^{-3})$</th>
<th>$[\text{Mo}(	ext{CN})_8^{4-}]$ (mol dm$^{-3}$)</th>
<th>0.8</th>
<th>1.13</th>
<th>1.5</th>
<th>2.0</th>
<th>3.0</th>
<th>5.0</th>
<th>8.0</th>
<th>10.0</th>
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<td>Li$^+$</td>
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<td>1.44</td>
<td>2.11</td>
<td>2.79</td>
<td>3.47</td>
<td>4.14</td>
<td>4.82</td>
<td>5.46</td>
<td>5.46</td>
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<tr>
<td>Na$^+$</td>
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<td>2.77</td>
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<td>K$^+$</td>
<td></td>
<td>3.24</td>
<td>4.80</td>
<td>6.36</td>
<td>7.92</td>
<td>9.50</td>
<td>11.1</td>
<td>12.6</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Dependence on $[\text{Mo}(	ext{CN})_8^{4-}]$

The effect of the initial $[\text{Mo}(	ext{CN})_8^{4-}]$ on $k_{obs}$ at different temperatures and fixed pH 4.27 is given in Table 1. The plots between $k_{obs}$ and $[\text{Mo}(	ext{CN})_8^{4-}]$ were linear and passed through the origin indicating a first-order dependence in $[\text{Mo}(	ext{CN})_8^{4-}]$.

Dependence on pH

The increase in the initial pH, Table 2, decreased the $k_{obs}$ at different temperatures. The result is just opposite to that obtained in the oxidations of sulphite$^7$, vanadium(IV)$^8$, and other reducing agents$^{21}$ in which $k_{obs}$ increased with increase in pH. It has to be noted that the rate dropped significantly, almost by 50%, on changing the pH from 3.43 to 3.94 and thereafter uniformly. However, beyond pH 4.8 the drop in the rate was only perceptible and the most suitable value had to be chosen from a number of replicate runs for the linear relationship between $k_{obs}$ and $[\text{H}^+]$ shown in Fig. 2. The intercepts in the plots indicate the presence of a path independent of $[\text{H}^+]$. Hence, the $pK_a$ of the equilibrium between deprotonated and protonated complex species is expected around 3.

Dependence on alkali metal ion ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$). Table 3, shows that the rate increased with the concentration and size of the alkali metal ion.

Discussion

The data in Table 3 can be first interpreted as the effect of the ionic strength ($\mu$) on the rate. The linear plots of $\log k_{obs}/[\text{Mo}(	ext{CN})_8^{4-}]$ against $\sqrt{\mu}/(1 + \sqrt{\mu})$ have slope values of $3.93 \pm 0.06$, $3.94 \pm 0.05$, and $3.99 \pm 0.06$ in the case of $\text{Li}^+$, $\text{Na}^+$, and $\text{K}^+$ ions respectively. The slope values are in consonance with the predictable value 4 based on the reaction between $[\text{Mo}(	ext{CN})_8^{4-}]$ and $[\text{Mn}(\text{cdta})]^+$ ions though the ionic strength is far in excess than the permissible limits. However, the slope value is
Two distinct roles are assigned to alkali metal ions in the electron transfer reactions, viz. it acts either as a bridge for the electron-transfer or as a charge buffer between ionic species. Hence, a large sized alkali metal ion, associated with high value of polarisability, is likely to be more effective as a bridge between negatively charged reactant ions. The view is strengthened by the linear plots, between $k_{\text{obs}}/[\text{Mo(CN)}_6^{4-}]$ and the polarisability $\alpha_M$ of the alkali metal ions at different concentrations. Thus, the alkali metal ion is a part of the transition state, though this bridge differs entirely from an inner-sphere halide or cyano bridge between metal centres.

The kinetics is simple. The reaction is first order with respect to both $[\text{Mo(CN)}_6^{4-}]$ and $[\text{Mn(cdtal}]$ ions. That alkali metal ions act as a bridge for the electron-transfer in the transition state, is further supported by the rapid scanning of the reaction mixture. The dependence on $[\text{H}^+]$ has two paths; one is independent of and the other is dependent on $[\text{H}^+]$. It is indicative of a rapid pre-equilibrium between protonated and deprotonated forms and both forms are reactive. The effect of $pH$ on the $k_{\text{obs}}$ acquires significance in the sense that it is for the first time, as far as we know, that the $k_{\text{obs}}$ has decreased with increase in initial $pH$ of the reaction mixture. In earlier studies, the $k_{\text{obs}}$ had increased with increase in $pH$. However, the effect cannot be explained in terms of equilibrium (3) because the reactivity of $[\text{Mn(cdtal]OH]}^{-}$ cannot exceed that of $[\text{Mn(cdtal]OH}_2]$ because the deprotonation of $[\text{Mn(cdtal]OH}_2]$ results in a decrease in reduction potential. Therefore, the effect was invariably attributed to the equilibrium involving the protonation of the substrate. That it is so is supported by the fact that such an equilibrium is not possible for $\text{NO}_2^-$ ion, the $k_{\text{obs}}$ was found to be independent of the $pH$ in the oxidation of $\text{NO}_2^-$ ion. The other two equilibria that can exist are given in Eqs. (4) and (5) respectively.

$$K_{a2}$$
$$[\text{Mn(cdtal]OH]}^{-} \rightleftharpoons [\text{Mn(cdtal]}+ \text{H}^+]$$
(3)
$$K_{a1}$$
$$[\text{Mn(cdtal]OH}_2] \rightleftharpoons [\text{Mn(cdtal]}+ \text{H}^+]$$
(4)
$$K_{a1}$$
$$[\text{Mn(cdtal]}+ \text{H}^+]$$
(5)

Beside the reasons cited above, the equilibrium (3) is further not favoured since $[\text{Mn(cdtal]OH]}^{-}$ ion as the reactive species is likely to introduce a component of an inner-sphere mechanism.

The results in Table 3 can also be interpreted to mean that $k_{\text{obs}}$ increased with increase in alkali metal ion and the increase is in the order $K^+ > Na^+ > Li^+$. Indeed the plots between $k_{\text{obs}}/[\text{Mo(CN)}_6^{4-}]$ and $[\text{Mn(cdtal}]$ ions are linear with small intercepts (around 50 dm$^3$ mol$^{-1}$ s$^{-1}$) indicating rate is catalysed by alkali metal ions. The use of $\text{NaClO}_3$ or NaN$O_3$ resulted in almost identical rate constants suggesting the rate is independent of the nature of anion. Hence, the rate law for the reaction is represented by an empirical rate law in Eq. (2).

$$-d[\text{Mn(cdtal]}]/dt =$$
$$a + b[\text{M}^+] [\text{Mn(cdtal]}) [\text{Mo(CN)}_6^{4-}] (a > b)$$
(2)

The alkali metal ion can form an ion-pair with the cyano-complex, and by analogy with other cyano-complexes a value of the ion-pair association constant $25$ dm$^3$ mol$^{-1}$ is estimated for the formation of $\text{KMo(CN)}_6^{3-}$ (ref.22). Hence, the rate is expected to level off at high $[\text{M}^+]$ because calculations show $60% \ [\text{Mo(CN)}_6^{4-}]$ is present as $\text{M}[\text{Mo(CN)}_6^{3-}]$ at $[\text{K}^+] = 0.06$ and $70%$ at $[\text{K}^+] = 0.10$ mol dm$^{-3}$. Since there is no levelling of the rate, either the estimated value is in error or the alkali metal ion has some other role in the mechanism.
fourth proton of $H_{4}[Mo(CN)_{8}]$ is stated to be completely dissociated\(^{29}\) and, therefore, the $k_{\text{obs}}$ was expected to be independent of the pH as in the oxidation of nitrite ion\(^{29}\). Since it is not so, the equilibrium (4) is not to be considered.

The strong similarities such as spectrophotometric and the acid-base titration of $\text{Mn(III)}$-edta and $\text{Mn(III)}$-cdta complexes, and the chemical behaviour such as the decomposition of these complexes was independent of pH in the range 3-6 are compelling enough to provoke equilibrium (5) by analogy of the existence of an identical equilibrium in the $[\text{Mn(cdta)}](\text{OH}_{2})]$ complex with a $pK_{a1}$ value of 2.7.(ref31). The $pK_{a1}$; the $pK_{a2}$; the $pK_{a3}$; the $pK_{a4}$; the $pK_{a5}$; the $pK_{a6}$; the $pK_{a7}$; the $pK_{a8}$; the $pK_{a9}$; the $pK_{a10}$; the $pK_{a11}$; the $pK_{a12}$ are in fair agreement with those calculated \(\text{ref.32}\) from the plots of $k_{\text{obs}}/[\text{Mo(CN)}_{8}]^{4-}$ against $[\text{J-F}]$ and $[\text{H}]=10^{-4}$ dm$^{-3}$ mol$^{-1}$ and that of $k_{H}$ is $10^{-7}$ dm$^{-3}$ mol$^{-1}$ S$^{-1}$.

The values of the intercepts and slopes of the linear plots of $k_{\text{obs}}/[\text{Mo(CN)}_{8}]^{4-}$ against $[\text{H}]^{+}$ are calculated using a least squares program and are used to calculate the values of $k$ (= intercept/[M$^{+}$]) where $[\text{M}^{+}] = 0.4$ mol dm$^{-3}$ and $k_{H}$ (= slope). These values are in Table 4 wherein are also reported the values of the respective activation parameters. These values are typical of many outer-sphere reactions though there are $[\text{Mn(cdta)}]^{2+}$ in fair agreement with those calculated from the plots of $k_{\text{obs}}/[\text{Mo(CN)}_{8}]^{4-}$ against $[\text{H}]^{+}$ and reported in Table 4.

Marcus theory\(^{9}\) is the tool used to distinguish between outer-sphere and inner-sphere reactions. We recently used the theory to show that the oxidations of $S(IV)$ (ref.7), $[\text{SO}_{3}]^{2-}$, and $\text{VO}^{2+}(\text{aq})$ (ref.8) by $[\text{Mn(cdta)}]^{2+}$ are better placed with outer-sphere reactions. The Marcus cross-relation is given by Eq. (14) where $k_{12} = k_{\text{obs}}/[\text{Mo(CN)}_{8}]^{4-}$ is the second order rate constant and its value deduced.

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### Table 4. The values of $k$ (dm$^{-3}$ mol$^{-1}$ s$^{-1}$) and $k_{H}$ (dm$^{-3}$ mol$^{-1}$ s$^{-1}$) at different temperatures and the related activation parameters

<table>
<thead>
<tr>
<th>(°C)</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3k$</td>
<td>4.03</td>
<td>4.98</td>
<td>6.04</td>
<td>7.32</td>
<td>8.73</td>
</tr>
<tr>
<td>$10^3k_{H}$</td>
<td>11.17</td>
<td>0.13</td>
<td>0.13</td>
<td>0.17</td>
<td>0.41</td>
</tr>
</tbody>
</table>

$\Delta H^{*} = 25 \pm 2$ kJ mol$^{-1}$; $\Delta S^{*} = 28 \pm 2$ kJ mol$^{-1}$; $\Delta G^{*} = -70 \pm 6$ J K$^{-1}$ mol$^{-1}$; $\Delta S_{R}^{2} = 2 \pm 2$ J K$^{-1}$ mol$^{-1}$

### Table 5. Rate data for the oxidation of $[\text{Mo(CN)}_{8}]^{4-}$ with one-electron oxidants at 25 °C

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>$E^*$</th>
<th>$k_{12}$</th>
<th>$k_{12}$</th>
<th>L.H.S</th>
<th>$k_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co(III)}W_{12}O_{4}]^{n-}$</td>
<td>4.03</td>
<td>5.84</td>
<td>3.13</td>
<td>6.91</td>
<td>3.21</td>
</tr>
<tr>
<td>$[\text{HMoO}_{4}]$</td>
<td>1.34</td>
<td>6.45</td>
<td>1.67</td>
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<td>8.28</td>
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<tr>
<td>$[\text{Mn(cdta)}(\text{OH}_{2})]$</td>
<td>0.81</td>
<td>0.79</td>
<td>4.05</td>
<td>2.88</td>
<td>0.17</td>
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</table>

$\text{H}_{2}^{+}$ is $10^{-4}$ dm$^{-3}$ mol$^{-1}$ S$^{-1}$.

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from Table 1 is $4050 \pm 12$ dm$^3$ mol$^{-1}$ s$^{-1}$ at pH 3.94 and 25 °C. The other symbols have their usual meaning. Equation (14) could be rearranged to Eq. (15).

$$ k_{12} = (k_{1}k_{2}k_{12})^{0.5}W_{12} \quad \ldots (14) $$

$$ 2\log k_{12} - \log k_{11} - \log k_{22} = \log f_{12} + 2\log W_{12} + \log K_{12} \quad \ldots (15) $$

Equation (15) is meant for a rigorous treatment if minimum number of three data points i.e., rates of oxidation of a single reductant by a number of oxidants are available and the self-exchange rates of oxidant and reductant ions are known. Fortunately with the present result three data points are available. The data corresponding to [Ag(OH)$_4$]$^-$ is excluded because the rate is known in a different (alkaline) medium$^{12}$. One estimate$^{33}$ is $3 \times 10^4$. Equation (15) could be written as Eq. (16) where L.H.S. = $(2 \log k_{12} - \log k_{11} - \log k_{22})$ and C = $(\log f_{12} + 2 \log W_{12})$.

$$ \text{L.H.S.} = \log K_{12} + C \quad \ldots (16) $$

Hence, a plot of L.H.S. against log $K_{12}$ is expected to be linear with an ideal slope of unity. The required plot, based on the data in Table 5, has a slope of $1.06 \pm 0.11$ ($r = 0.995$ ) which is in fair agreement with the predicted slope remembering that the data in Table 5 is at different ionic strengths. This, as well as the first order dependence in both oxidant and reductant ions, favours an outer-sphere electron transfer.

Acknowledgement

We are grateful to the Department of Science and Technology for the grant to purchase the stopped-flow instrument and financial assistance. A partial financial assistance to UC through a project sanctioned by the CSIR is also acknowledged with thanks. Thanks are also due to Prof. K.K. Banerji, Head of the Department, in extending all the laboratory facilities.

References