Kinetics of oxidation of iodide ion by trans-(cyclohexane-1,2-diamine N,N,N',N'-tetraacetato)manganate(III) in weakly acidic solution

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Kinetics of redox reaction between I\(^-\) and [Mn\(^{III}\)(cdta)]\(^+\) has been investigated in aqueous solution by a stopped-flow technique at pH 3.26 (acetate buffer) and at 30, 35, 40 and 45 °C. The overall reaction is third order—first order in [Mn\(^{III}\)(cdta)]\(^+\) and second order in [I\(^-\)]. Though no direct evidence has been obtained, an inner-sphere mechanism has been proposed based on the lability of the complex and is supported by the large negative value of ΔS° (−168 ± 6) J K\(^{-1}\) mol\(^{-1}\).

Recently, a number of studies involving [Mn\(^{III}\)(cdta)]\(^+\) (cdta= trans-(cyclohexane-1,2-diamine-N,N,N',N'-tetraacetic acid) with various organic and inorganic reducing agents appeared in the literature. The [Mn\(^{III}\)(cdta)]\(^+\) has been found to react by both inner- and outer-sphere mechanism. Iodide was found to be interesting reducing partner having variable mechanistic patterns which may be categorized as: (i) first order both in [oxidant] and [I\(^-\)]; (ii) first-order in [oxidant] and second order\(^{5,5}\) in [I\(^-\)]; and (iii) second order\(^{5}\) each in [oxidant] and [I\(^-\)].

In the case of (ii) and (iii), generally inner-sphere mechanism was found to be operative whereas for (i) outer-sphere mechanism has been proposed. The present note deals with the kinetic studies on the oxidation of iodide ion by the title complex in order to check the validity of the above propositions.

Experimental

The potassium salt of (trans-cyclohexane-1,2-diamine-N,N,N',N'-tetraacetato)manganate(III), K[Mn(cdta)]\(_2\)·2.5 H\(_2\)O (hereafter designated as [Mn\(^{III}\)(cdta)]\(^+\)) was prepared, characterized and standardized as reported earlier. Potassium iodide (KI) was of reagent grade (Fulka, AG) and was used without further purification. pH of the solution was maintained using acetate buffer (0.02 mol dm\(^{-3}\)) and adjusted using a Systronic digital pH-meter (model 335, India). Ionic strength was maintained by NaClO\(_4\).

Kinetics was carried out under pseudo-first order conditions using complex as the minor component and monitoring the disappearance of the complex at 510 nm in a stopped-flow apparatus (Otsuka Electronics, Japan) interfaced with data processor. The observed rate constants were evaluated by treating the kinetic curve of 5-6 runs by least-squares curve-fit method. The precision of the reported values is ± 5%. A Haake F-3 thermostat was used to maintain the reaction temperature at ± 0.1°C.

Results and discussion

The stoichiometry of the reaction was determined by reacting variable concentrations of iodide ion with a fixed and an excess concentration of the complex and determining the unreacted complex spectrophotometrically at 510 nm, the absorption maximum of the complex. In all the cases, the stoichiometry of the reaction was found to be 1:1 with iodine as the oxidation product of iodide ion and corresponds to reaction (1) which is also valid under the actual kinetic conditions.

\[
2[Mn^{III}(cdta)]^+ + 2I^- \rightarrow 2[Mn^{II}(cdta)]^2^- + I_2 \quad \ldots (1)
\]

Conditions adopted for the kinetics of reaction are: [Mn\(^{III}\)(cdta)]\(^+\) = 1.0×10\(^{-4}\) mol dm\(^{-3}\), [I\(^-\)] = 0.0001-0.01 mol dm\(^{-3}\), \(I = 0.20 \text{ (NaClO}_4)\), pH = 3.76 and temperature 30, 35, 40 and 45°C. The kinetic traces are single exponential decay curves and pseudo-first-order rate constants \((k_{\text{obs}})\) were determined by suitable computer-fit program by taking an average of atleast 5-6 kinetic traces. The dependence of rate on [I\(^-\)] was determined at pH 3.26 (0.02 M AcOH-NaOAc buffer) at variable temperatures and plots of \(k_{\text{obs}}\) versus [I\(^-\)] are ascending non-linear curves. The order of dependence of \(k_{\text{obs}}\) on [I\(^-\)] was determined by a non-linear fit of the experimental data to Eq. (2)

\[
k_{\text{obs}} = k[I^-]^n \quad \ldots (2)
\]
The evaluated values of $n$, the order of dependence on $[\Gamma]$ at different temperatures were found to lie in between 1.94-1.98 indicating a second order dependence on $[\Gamma]$. All these results indicate that the reaction is overall third-order—first-order in [complex] and second order in $[\Gamma]$. The values of $k$, the third order rate constants, at different temperatures were evaluated by the linear plots of $k_{\text{obs}}$ versus $[\Gamma]^2$ with no or negligible intercept.

The $[\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})]^+$ complex exists in protic equilibrium (3) with a $pK_m$ value 8.101.

$$K_m = [\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})]^+ \rightleftharpoons [\text{Mn}^{III}(\text{cdta})(\text{OH})]^2+ + \text{H}^+ \cdots (3)$$

So, at pH 3.26, $[\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})]^+$ is the sole reacting species of the complex. A reasonable mechanism fitting the overall third order dependence of reaction could be framed as shown in Scheme 1.

$$[\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})]^+ + \Gamma \rightleftharpoons [\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})]^+ + [\Gamma]^2$$

$$\text{fast} \quad [\text{Mn}^{II}(\text{cdta})(\text{H}_2\text{O})]^2+ + \Gamma$$

Scheme 1

The rate law derived from Scheme 1 is given as

$$d[\text{Complex}] / dt = \frac{k_2 k_1 [\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})^{-}] [\Gamma]^2}{k_1 + k_2 [\Gamma]} \quad \cdots (4)$$

Two special cases may arise:

(i) when $k_{1} >> k_2[\Gamma]$, the rate law turns to be

rate $= (k_2 k_1/k_{1})[\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})^{-}] [\Gamma]^2 \quad \cdots (5)$

$k_{\text{obs}} = (k_2 k_1/k_{1})[\Gamma]^2 \quad \cdots (6)$

prevailing first order dependence in complex and second-order in the iodide.

(ii) when $k_1 << k_2[\Gamma]$, rate law turns to be

$$\text{rate} = k_1 [\text{Mn}^{III}(\text{cdta})(\text{H}_2\text{O})^{-}] [\Gamma] \quad \cdots (7)$$

giving first order dependence both in complex and iodide.

In the present investigation, Eq. (6) is operative. Plots of $k_{\text{obs}}$ versus $[\Gamma]^2$ at different temperatures are shown in Fig. 1 and evaluated parameters from the slope values are: $k_2 K_1 (K_1 = k_1/k_{1}) = (8.31 \pm 0.27) \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, $(9.01 \pm 0.21) \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, $(10.2 \pm 0.28) \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ and $(12.2 \pm 0.03) \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ at 30, 35, 40 and 45°C respectively.

The thermodynamic parameters evaluated from the Eyring plot for the temperature dependence of $(K_1 k_2)$ are: $\Delta H^o$ = $(18.6 \pm 2.0) \text{ kJ mol}^{-1}$ and $\Delta S^o = (-168 \pm 6) \text{ JK}^{-1} \text{ mol}^{-1}$. The large negative value for $\Delta S^o$ is indicative of an associative mechanism.

The redox reactions of $[\text{Ni}^{III}(\text{L})]^3+$ (L= Cyclam=1,4,8,11-tetraazacyclotetradecane) with $\Gamma$ shows a first order dependence on both reductant and $[\text{Ni}^{III}(\text{L})]^3+$ (refs 2,3), and an outer-sphere mechanism has been proposed. The oxidation of $\Gamma$ ion by the nickel(III) complex of tri-$\alpha$-aminoisobutyric acid has been reported, and out of two reaction pathways, the major reaction involves two electron transfer in one concerted reaction step which proceeds via a transition state composed of two nickel centers and two iodides resulting an inner-sphere mechanism. The minor path is an outer-sphere type with first order
both in [oxidant] and [\(\Gamma\)]. Copper(III) peptide complexes react with iodide ion in a slightly different way. At higher concentration of iodide, the behavior is similar to the minor route as in [Ni\(^{III}\)(H\(_2\))\(\text{L}_2\)]\(^+\), however, at lower concentration of iodide, the reaction is first order in each of the reactants. This difference in reaction nature has been attributed to the nature of axial lability of the complexes\(^5\).

As no kinetic or spectral evidence in support of inner-sphere association was gathered, it is not possible to infer the mode of association between the complex and \(\Gamma\) ion. Another way to differentiate between the inner and outer-sphere mechanism is the application of Marcus cross-reaction relationships used for the calculation bimolecular rate constants\(^7\). However the over-all third order dependence of rate precludes this possibility here. Based on very high substitution lability of the loosely bound water molecule in [Mn\(^{III}\)(cdta)(H\(_2\)O)]\(^-\) (\(4.4\times10^{-8}\) s\(^-1\))\(^8\), it is likely that \(\Gamma\) displaces this water molecule to give iodomanganate intermediate, [Mn\(^{III}\)(cdta).I]\(^-\), a seven coordinated species, which reacts with another \(\Gamma\) ion in a rate determining step. Another mode of inner-sphere association is through the partial unwrapping of one of the coordinated carboxylate arms of the cdta ligand. The proposed inner-sphere mechanism is further supported by the large negative value of \(\Delta S^o\) (\(-168 \pm 6\) Jk mol\(^{-1}\)).

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References