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# Inner-sphere Reduction of Tris(pyridine-2-carboxylato)manganese(III) by Glycolaldehyde in Sodium Picolinate–Picolinic Acid Buffer Medium†

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The reduction of tris(pyridine-2-carboxylato)manganese(III) by glycolaldehyde (GA) in sodium picolinate–picolinic acid buffer medium takes place by an inner-sphere mechanism

Manganese can adopt a wide variety of oxidation states and this ability is certainly related to the redox function of the metal ion in biological systems.[1] The tripositive state of the metal occupies an important position not only because of its biochemical relevance in diverse redox functions[1–3] but also because it is difficult to stabilize in aqueous media[4] and the fact that many of its complexes exhibit unusual magnetic and structural features.[5] The reactivities of manganese enzymes with binuclear active sites towards $H_2O_2$, $S_2O_3^{2-}$ glucose, DNA and RNA have been studied[6–9] and reviewed.[10] Monomeric glycolaldehyde or its enol form may react with oxidants, consequently the reaction between glycolaldehyde and manganese(III) has been selected which may be of special interest. While there are some reports on the kinetics of oxidation of different substrates by manganese(III) in perchlorate, sulfate, acetate and pyrophosphate media,[11] there are no literature data involving the reduction of tris(pyridine-2-carboxylato)-manganese(III) by glycolaldehyde and manganese(III) by glycolaldehyde in aqueous solution. The reaction was studied in sodium picolinate—picolinic acid buffer medium in the pH range 4.54–6.1, since the complex is unstable in more acidic or alkaline media. The possibility of ligand substitution reaction is minimized in this buffer medium.

The reactions were carried out at different $[\mathrm{Mn^{III}}]$ in the range $(1-5)\times10^{-4}\,\mathrm{mol\,dm^{-3}}$ but at constant concentrations of glycolaldehyde, pH and temperature of $2\times10^{-2}\,\mathrm{mol\,dm^{-3}}$, 6.1 and 313 K, respectively. The rate constants are independent $[(1.20\pm0.05)\times10^{-4}\,\mathrm{s^{-1}}]$ of $\mathrm{Mn^{III}}]$ concentration. The pseudo-first-order rate constants ($k_{\mathrm{obs}}$) were calculated at constant $[\mathrm{Mn^{III}}]$, pH and temperature but at different substrate concentrations. The results, recorded in Table 1, indicate that the reaction is first order with respect to [GA].

The influence of pH on the reaction rate was investigated at constant (GA), $[\mathrm{Mn^{III}}]$ and temperature and the values of $k_{\mathrm{obs}}$ were found to be independent of pH (4.54–6.1). The reaction can be expressed by eqn. (1).

$$-\frac{\mathrm{d}[\mathrm{Mn^{III}}]}{\mathrm{d}t}=k[\mathrm{GA}][\mathrm{Mn^{III}}] \qquad (1)$$

The values of $k$ are $(3.95\pm0.05)\times10^{-3}$, $(5.55\pm0.15)\times10^{-3}$ $(7.78\pm0.06)\times10^{-3}$ and $(10.44\pm0.04)\times10^{-3}\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ at 308, 313, 318 and 323 K, respectively. Least-squares treatment of a plot of log $(k/T)$ *vs.* $1/T$ were used to obtain the best straight line from which the enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were calculated using the theory of absolute reaction rate. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are $48\pm4\,\mathrm{kJ\,mol^{-1}}$ and $-136\pm12\,\mathrm{J\,K^{-1}\,mol^{-1}}$ respectively.

Glycolaldehyde is known to be a dimer in the crystalline state. In dilute solution ($<0.1\,\mathrm{mol\,dm^{-3}}$) dimeric glycolaldehyde undergoes rapid dissociation to give monomers.[12] Consequently, solid glycolaldehyde, after dissolution in water, was allowed to stand for 1 h before kinetic experiments were performed. Absorption of 20% glycolaldehyde solution in 0.1% NaOD in $D_2O$ has been studied by FTIR spectroscopy[13] which also indicated that the dimer is dissociated into monomeric glycolaldehyde (1744 $\mathrm{cm^{-1}}$) in equilibrium with the enediol form (1703 $\mathrm{cm^{-1}}$). Enol forms of certain sugar derivatives in biological systems are the active forms with which enzymes react.[14,15] Enediols are also known[16] to play an important role in metal catalyzed oxidative degradation of reducing sugars, The enol form of the aldehyde reacts with the manganese(III) complex the structure of which has been reported[17] to be a pseudo-tetragonally distorted octahedron with slightly elongated axial bonds. Since $\mathrm{Mn^{III}}$ is an one–electron transfer oxidant, the reaction is likely to proceed through the intermediate formation of free radicals in the rate determining step. The free radicals are then rapidly oxidised by reacting with another $\mathrm{Mn^{III}}$ centre to give the products (Scheme 1).

The reaction rate is much slower compared to those found for reactions which occur by a typical outer-sphere mechanistic pathway.[18,19] The activation parameters obtained in this reaction are different from those found in sulfuric acid, acetic acid and pyrophosphate media. Since the present reaction has been studied in the pH range 4.54–6.1, the obtained values of activation parameters can not be compared with those obtained previously.[20] However, the activation enthalpy of 48 $\mathrm{kJ\,mol^{-1}}$ obtained here lies within the range found for reactions (47.7 − 54.4 $\mathrm{kJ\,mol^{-1}}$ which occur by an inner-sphere mechanism,[21] lending further support to the fact that the oxidation of glycolaldehyde by tris(pyridine-2-carboxylato)manganese(III) takes place by an inner-sphere mechanism.

**Table 1** Pseudo-first-order rate constants at different temperatures, $[\mathrm{Mn^{III}}]=2\times10^{-4}\,\mathrm{mol\,dm^{-3}}$, pH = 6.1[a]

| | $10^{-4}k_{\mathrm{obs}}/\mathrm{s^{-1}}$ | | | |
|---|---|---|---|---|
| $10^2[\mathrm{GA}]/\mathrm{mol\,dm^{-3}}$ | 308 | 313 | 318 | 323 |
| 1 | 0.40 (4.00) | 0.55 (5.5) | 0.78 (7.80) | 1.05 (10.50) |
| 2 | 0.78 (3.9) | 1.20 (6.00) | 1.55 (7.75) | 2.05 (10.25) |
| 3 | 1.19 (3.97) | 1.71 (5.70) | 2.30 (7.67) | 3.05 (10.17) |
| 4 | 1.58 (3.95) | 2.19 (5.48) | 3.07 (7.68) | 4.09 (10.23) |
| 5 | 2.01 (4.02) | 2.74 (5.48) | 3.86 (7.72) | 5.20 (10.40) |

[a] Values in parentheses are $10^{-3}k/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ ($k=k_{\mathrm{obs}}/[\mathrm{GA}]$).

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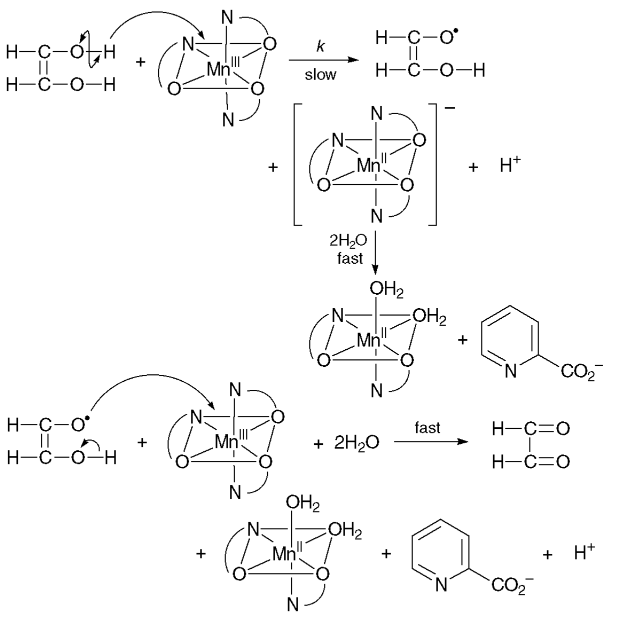

**Scheme 1**

## Experimental

*Reagents.*—Pyridine-2-carboxylic acid (Lancaster) and glycolaldehyde (Sigma) were used as received. All other materials were of reagent grade.

*Preparation of the Manganese*(III) *Complex.*—The complex tris(pyridine-2-carboxylato)manganese(III) was prepared[22] as follows. Freshly precipitated manganese dioxide was warmed with an aqueous solution of excess pyridine carboxylic acid with vigorous stirring and filtered through a sintered glass funnel. The scarlet-red solution gave red crystals on cooling (Found: C, 49,95; H, 3.30; N, 9.36. Calc. for $[Mn(C_5H_4NCO_2)_3]\cdot H_2O$, C, 49.22; H, 3.2; N, 9.56%). Thermogravimetry of the solid manganese(III) compound was carried out by heating a sample (9.3 mg) at a rate of $15\,^{\circ}C\,min^{-1}$ up to 200 °C and indicates that loss of crystallization water occurs in one step. The magnetic moment of the solid compound at room temperature (25 °C) was $4.92\,\mu_B$ similar to the value reported earlier.[23]

*Instruments.*—UV–VIS spectral measurements were carried out using a Systronics (India) spectrophotometer. Magnetic susceptibility was measured at room temperature by a Princeton Applied Research Vibrating sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. EPR of the product solution was recorded with a Varian (Model E112) spectrophotometer having the following instrumental setting: field, 3700 G; microwave frequency, 9.45 GHz; receiver gain $6.3\times10^3$ dpph was used as an internal field marker. C, H and N, analysis was performed using a Perkin–Elmer 240 CHN Analyser. Thermogravimetry were performed with a Shimadzu Corporation (Japan) TG 50 instrument in a normal atmospheric environment. pH measurements were carried out with an Elico LI 120 (India) pH meter.

*Kinetic Measurements.*—Since the adsorption coefficient of the manganese(III) solution is low in the visible region, the progress of the reaction was followed in the UV region where $Mn^{III}$ absorbs appreciably in the concentration range $(0.5-5.0)\times10^{-4}\,mol\,dm^{-3}$ under which Beer's law is obeyed. The reaction rate was monitored spectrophotometrically at 350 nm under pseudo-first order conditions, *i.e.* $[GA] \gg [Mn^{III}]$ which was initiated by adding the requisite quantity of the substrate, maintained at the desired temperature to the solution of $Mn^{III}$ and buffer. The reactions were followed for at least 75% conversion of the initial $Mn^{III}$. The pseudo-first-order rate constant ($k_{obs}$) was determined from the plot of log $A$ ($A$ = absorbance) *vs.* $t$. The rate constants ($k_{obs}$) calculated by a graphical method were reproducible to within ±3%.

*Product Studies.*—The reaction mixture containing excess glycolaldehyde ($2\times10^{-2}\,mol\,dm^{-3}$ ($[Mn^{III}] = 2\times10^{-3}\,mol\,dm^{-3}$) at pH 6.1 was allowed to stand for 2 h. An excess of aqueous sodium hydrogen sulfite solution (containing 5% ethanol) was then added followed by a known excess of iodine solution. The excess of iodine was back titrated against standard thiosulfate using starch as an indicator and unreacted glycolaldehyde measured.[24] From this result, the reaction obeys the following stoichiometry [eqn. (2)] with the products identified by standard tests.[25–27]

$$CH_2(OH)CH{=}O + 2[Mn^{III}(C_5H_4NCO_2)_3] + 4H_2O \rightarrow$$
$$(CH{=}O)_2 + 2[Mn^{II}(C_5H_4NCO_2)_2(H_2O)_2] + 2C_5H_4NCO_2^- + 2H^+ \quad (2)$$

The presence of $Mn^{II}$ in the reaction mixture was confirmed by the appearance of a typical six-line signal[28] in the EPR spectrum.

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