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Kinetics and mechanism of the oxidation of some aldoses, amino sugars and methylated sugars by tris(pyridine-2-carboxylato)manganese(III) in weakly acidic medium

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Abstract

The kinetics of oxidation of some aldoses, amino sugars and methylated sugars by tris(pyridine-2-carboxylato)manganese(III) have been studied spectrophotometrically in sodium picolinate–picolinic acid buffer medium. The reactions are first-order with respect to both manganese(III) and sugar concentrations, but independent with respect to sodium picolinate–picolinic acid buffer medium. The mechanisms for the reactions are discussed.

Keywords: Kinetics; Sodium picolinate–picolinic acid; Manganese

1. Introduction

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 requires special attention, not only because of its biochemical relevance in diverse redox functions [1,2], but also because it is difficult to stabilize it in aqueous medium [3], and many of its complexes exhibit unusual magnetic and structural features [4]. There are several reports on the kinetics of oxidation of various substrates by manganese(III) in perchlorate, sulfate, acetate and pyrophosphate media [5]. The important ones involve reactions of oximes [6], vitamins [7,8] and amino acids [9–12]. The kinetics of the oxidation of D-glucose by manganese(III) has been studied [13], and manganese(III) is shown to behave as a one-electron transfer oxidant. The present investigation was undertaken in order to clarify the mechanism of oxidation of some aldoses, amino sugars, and methylated sugars by tris(pyridine-2-carboxylato)manganese(III) in sodium picolinate–picolinic acid buffer medium. The tris-manganese(III) complex is very unstable in acid or alkaline medium, but it is stable in sodium picolinate–picolinic acid buffer medium in the pH range 4.22–6.45, which minimizes the possibility of a ligand substitution reaction.

2. Experimental

Reagents.—The aldoses, amino sugars and methylated sugars were obtained from BDH, E. Merck or Sigma Chemical Co. Pyridine-2-

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carboxylic acid was from Lancaster Synthesis. All other materials were of certified or reagent grade.

Preparation of the manganese(III) complex.—The complex, tris(pyridine-2-carboxylato)manganese(III) was prepared by a modified procedure from that reported in the literature [14]. $MnCl_2 \cdot 6H_2O$ (2.5 g, 10.7 mmol) was dissolved in water (25 mL). The solution was warmed, and H_2O_2 (25 mL, 808.8 mmol) was added to it. This was followed by the addition of NaOH (1 g, 25 mmol) dissolved in water (25 mL). The mixture was stirred vigorously for at least 30 min, and the precipitated MnO_2 was filtered through a sintered glass crucible. The precipitate was washed thoroughly with water and then warmed with an aq solution of excess pyridine-2-carboxylic acid with vigorous stirring. The mixture was then filtered through a sintered glass crucible. The scarlet–red filtrate deposited red crystals of tris-manganese(III) on cooling. Anal. Calcd for $[Mn(C_5H_4NCO_2)_3]H_2O$: C, 49.22; H, 3.21; N, 9.56. Found: C, 49.95; H, 3.30; N, 9.36.

Thermogravimetric analysis of the solid manganese(III) compound was carried out by heating a sample (19.39 mg) at the rate of 15 °C/min up to 400 °C. The result indicated that loss of water took place in one step, based on the weight-loss calculation for $[Mn(C_5H_4NCO_2)_3]H_2O$, confirming the loss of only one water molecule. The magnetic moment of the solid compound at room temperature (rt, 25 °C) has been found to be 4.92 BM. This value is not different from that mentioned earlier [15]. The structure of the manganese(III) complex has been reported [16] to be a pseudo-tetragonally distorted octahedron with the axial bonds slightly elongated. An attempt has been made to determine the redox potential in sodium picolinate–picolinic acid buffer medium. Mn^{3+} (2×10^{-4} mol dm^{-3}) at pH 6.1 and with NaCl as the supporting electrolyte is found to undergo an irreversible one-electron reduction at -0.80 V at 298 K.

Preparation of buffer solution.—The pK_a value of picolinic acid is 5.52 [17]. Buffer solutions were prepared from standard solutions of sodium picolinate and picolinic acid. The pH of the buffer solution was checked against a standard buffer solution with a pH meter.

Instruments.—Spectral measurements were carried out in the UV–vis region using a Systronics (India) spectrophotometer. Magnetic susceptibility was measured at rt by a Princeton Applied Research vibrating sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. Cyclic voltammograms were recorded by a Bio-Analytical System (BAS) CV-27. All experiments were carried out in a dry argon atmosphere using a three-electrode configuration. A planar Beckman model platinum electrode was used as the working electrode and SCE as the reference electrode. C, H and N analyses were performed by the microanalytical laboratory using a Perkin–Elmer 240 CHN Analyser. TGA studies were performed with a Shimadzu Corporation (Japan) TG 50 instrument in a normal atmospheric environment at a rate of 15 °C/min up to 400 °C. pH measurements were carried out in an Elico LI 120 (India) pH meter. The EPR spectrum was recorded with a Varian EPR spectrometer.

Kinetic measurements.—The electronic spectrum of the manganese(III) complex exhibited [15] two weak shoulders at 21,900 cm^{-1} ($\varepsilon = 257$ cm^{-1} mol^{-1} dm^3) and 24,800 cm^{-1} ($\varepsilon = 407$ cm^{-1} mol^{-1} dm^3). Since the extinction coefficient of manganese(III) solution is small in the visible region, the progress of the reaction was followed in the UV region where manganese(III) absorbs appreciably at the concentration region of $0.5–5.0 \times 10^{-4}$ mol dm^{-3}. Beer's law is also obeyed in this concentration range. The reaction rate was monitored spectrophotometrically at 350 nm ($\varepsilon = 2710$ cm^{-1} mol^{-1} dm^3) under pseudo-first-order conditions, i.e., [sugar] $\gg$ [tris-Mn(III)]. The pseudo-first-order rate constant (k_{obs}) was determined from the plot of log A (A = absorbance) vs time. The rate constants (k_{obs}) calculated by the graphical method were reproducible within $\pm 3\%$ error.

Stoichiometry and product analysis.—The reaction mixtures containing a known excess of tris[Mn(III)] of 1.3×10^{-3} mol dm^{-3} and [glucose] of 2×10^{-4} mol dm^{-3} at fixed pH 6.1 were made. After completion of the reactions, the unreacted [Mn(III)] was determined by iodometric titration with a standard sodium thiosulfate solution using starch indicator near the end point [15]. Determination

of unreacted [Mn(III)] showed that 1 mol of glucose consumes 2 mol of Mn(III). The reaction may be represented as follows:

$$\begin{aligned} R{-}CHO + 2[Mn(III)(C_5H_4NCO_2)_3] + 5H_2O \\ \rightarrow R{-}COO^- \\ + 2[Mn(II)(C_5H_4NCO_2)_2(H_2O)_2] \\ + 2C_5H_4NCO_2^- + 3H^+ \end{aligned} \quad (1)$$

where $R = -(CHOH)_4CH_2OH$.

After the kinetic experiments, the reaction mixtures of the aldoses and amino sugars were acidified and treated with 2,4-dinitrophenylhydrazine hydrochloride. The absence of any yellow precipitate indicates that neither the $-CH_2OH$ nor the =CHOH group is oxidized. The iron(III) chloride solution, colored violet with phenol, when added to the reaction mixture gave a bright yellow coloration [18], indicating that aldonic acids are formed in the oxidation of the aldoses. The aldoses were oxidized separately by the oxidant under kinetic conditions. After purification and concentration, the products were confirmed [18] by paper chromatography in comparison with the oxidation products of the respective aldoses by bromine. Similar experiments when carried out with the oxidation products of the amino sugars gave yellow colorations with the above iron(III) reagent. The amino sugars are also oxidized [19] by HgO to give aldosaminic acids, and when iron(III) chloride solution, colored violet with phenol, is added to an aldosaminic acid solution, a yellow coloration is also given. However, the addition of alkaline hydroxylamine solution to the reaction mixtures and subsequent addition of 2% $FeCl_3$ and 1% HCl failed to give any mauve coloration [20], which indicated that no lactone formation was taking place during the reaction. This is to be expected since primary products in the oxidation of cyclic aldoses are aldonic acids or γ- or δ-lactones in acidic solutions, but at $pH > 2.5$ the proportion of lactones is reduced [21]. Since the pK_a value of gluconic acid is 3.81, the thermodynamically stable species gluconate ion will be formed at pH 6.1.

That picolinic acid is generated [22a] during the reaction is confirmed by the following test. One drop of the test solution is mixed in a micro test tube with a drop of a solution of 1 g of $FeSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$ and 0.5 g of KF in 100 mL of 0.1 N acetic acid to give a light-yellow color, which is stable in acetic acid or dilute mineral acids. The colored reaction is due to the formation of the inner-complex cation between Fe^{2+} and the picolinate anion. The color intensity of the reaction mixture with the above reagents was much higher than that of the buffer mixture, and this was confirmed spectrophotometrically.

Polymerization test.—Acrylamide (40%) was added during the course of the reactions. An immediate haziness appeared during the oxidation of the substrate by manganese(III). When an excess of methanol was added to the reaction mixture, a thick precipitate of polyacrylamide was formed, demonstrating that free radicals intervene in the oxidation process. The observation is to be expected since manganese(III) is a one-electron transfer oxidant that is reduced by the substrates to give free radicals and manganese(II). Blank experiments in which either the oxidant or the substrate were excluded gave no polymeric suspension. Moreover, the presence of manganese(II) in the reaction mixture was confirmed by the appearance of the typical six lines in the EPR spectrum as has been reported in the literature [22b].

3. Results and discussion

The reactions were carried out at different [Mn(III)] in the region $1-5 \times 10^{-4}$ mol dm^{-3} but at constant concentrations of substrates, pH and temperature. The rate constants were independent of oxidant concentration in each reaction (Table 1). The pseudo-first-order rate constants (k_{obs}) were calculated at constant [Mn(III)], pH and temperature but at different substrate concentrations. The results plotted in Fig. 1 indicate that each reaction is first order with respect to the [substrate]. The decrease in the rate with increase in asymmetric centre (n) is shown in Fig. 2. The plot of $\log k_2$ ($k_2 = k_{obs}$/[substrate]) vs 'n' is hyperbolic in character [23a]. The fact that the acyclic aldoses react at much faster rates than the cyclic ones is to be expected since the

Table 1
Effect of tris[Mn(III)] on the rate of oxidation[a]

Substrate	$k_{obs} \times 10^4$ (s^{-1})
D-Glucose	0.499 ± 0.01
D-Mannose	0.704 ± 0.01
D-Galactose	0.886 ± 0.02
D-Xylose	1.25 ± 0.05
L-Arabinose	2.23 ± 0.03
D-Ribose	3.33 ± 0.09
D-Erythrose	4.71 ± 0.10
DL-Glyceraldehyde	29.4 ± 0.12
D-Glucosamine hydrochloride	0.265 ± 0.01
D-Mannosamine hydrochloride	0.419 ± 0.01
D-Galactosamine hydrochloride	0.665 ± 0.01

[a] $T = 313$ K, [Mn(III)] = (1–5) $\times 10^{-4}$ mol dm^{-3}, pH 6.1, [substrate] = 0.3 mol dm^{-3}.

concentration of potential –CHO groups is higher in acyclic aldoses than the cyclic sugars.

The influence of pH on the reaction rate was investigated at different pH ranges but at constant [substrate], [Mn(III)] and temperature. The values of k_{obs} were found to be independent of pH (over the range of pH 4.22–6.45). The reaction may be described by the following rate expression:

$$-\frac{d[Mn(III)]}{dt} = k[S][Mn(III)] \quad (2)$$

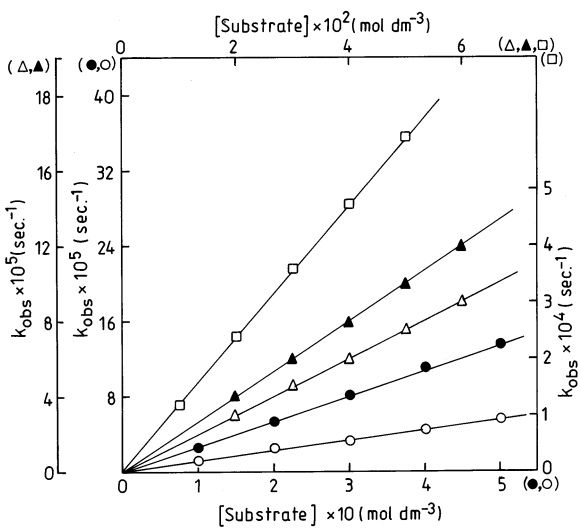


Fig. 1. Variation of the reaction rate with the [substrate]. Plots of k_{obs} vs [substrate] at pH 6.1, [Mn(III)] = 2.0×10^{-4} mol dm^{-3} and $T = 318$ K. (●) D-Glucose; (△) D-ribose; (▲) D-erythrose; (□) DL-glyceraldehyde; (○) D-glucosamine hydrochloride.

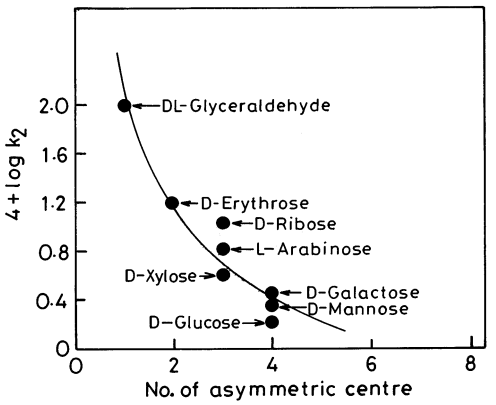


Fig. 2. Dependence of the reaction rate on the number of asymmetric centres (n). Plot of log k_2 vs 'n'.

The influence of temperature on the rate was determined for each reaction. The values of k_2 were calculated at different temperatures from 308 to 328 K. Least-squares analyses of log k_2/T against $1/T$ plots (Fig. 3) were used to obtain the best straight lines from which the enthalpies of activation ($\Delta H^{\neq}$) and entropies of activation ($\Delta S^{\neq}$) were calculated using the theory of absolute reaction rates.

The activation parameters are recorded in Table 2. The slower reactions are characterized by negative entropies of activation, unlike the fast reactions where entropies of activation are positive [23b]. The much slower rates and negative entropies of activation obtained in the present study, as compared to the oxida-

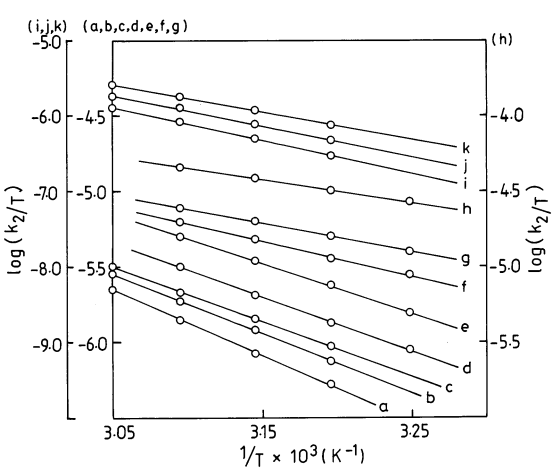


Fig. 3. Dependence of temperature on second-order rate constants for the oxidation of substrate by manganese(III). Plots of log (k_2/T) vs $1/T$. (a) D-Glucose, (b) D-mannose, (c) D-galactose, (d) D-xylose, (e) L-arabinose, (f) D-ribose, (g) D-erythrose, (h) DL-glyceraldehyde, (i) D-glucosamine hydrochloride (j) D-mannosamine hydrochloride (k) D-galactosamine hydrochloride.

Table 2
Values of activation parameters of the oxidations of some aldoses and amino sugars

Substrate	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
D-Glucose	83 ± 4	−52 ± 13
D-Mannose	74 ± 4	−79 ± 13
D-Galactose	71 ± 4	−86 ± 13
D-Xylose	66 ± 4	−99 ± 13
L-Arabinose	62 ± 4	−108 ± 13
D-Ribose	48 ± 2	−149 ± 7
D-Erythrose	35 ± 2	−186 ± 7
DL-Glyceraldehyde	26 ± 2	−200 ± 7
D-Glucosamine hydrochloride	87 ± 4	−45 ± 13
D-Mannosamine hydrochloride	76 ± 4	−74 ± 13
D-Galactosamine hydrochloride	73 ± 4	−82 ± 13

tions of anion of the aldoses by osmium(VIII) in alkaline medium [23c], justify the experimental observation. The enthalpy of activation is linearly related [24] to the entropy of activation ($r = 0.9988$) as plotted in Fig. 4 and the isokinetic temperature is 369.2 K. The isokinetic behavior is further supported [25] by the linear plot of $\log k_2'$ vs $\log k_2$ ($r = 0.9982$), where k_2' and k_2 are the second-order rate constants at the temperatures 323 and 313 K, respectively (Fig. 4). The isokinetic temperature, β, calculated from an Exner plot, is

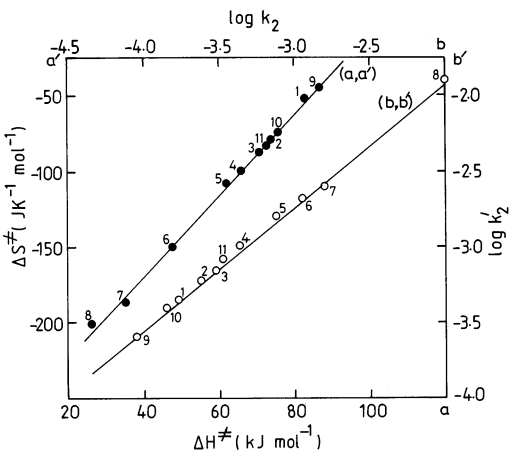
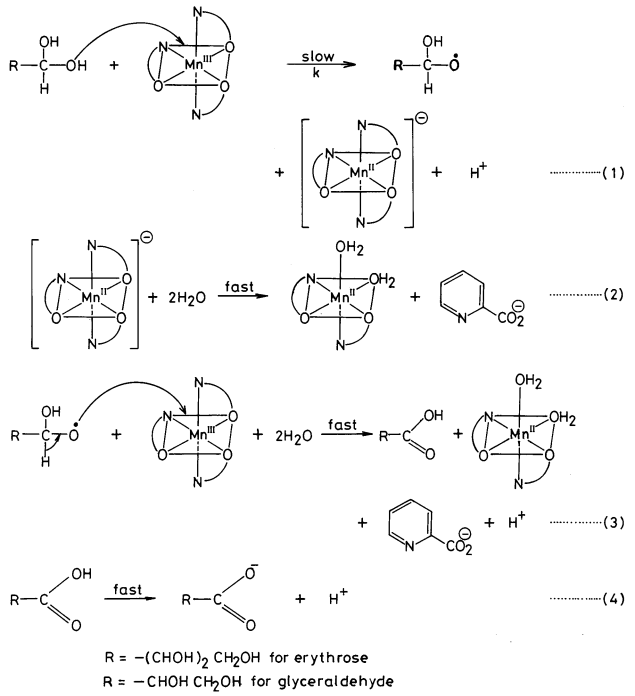


Fig. 4. Isokinetic plots for the oxidations of aldoses and amino sugars by tris[manganese(III)] in buffer medium. (a, a′), plot of $\Delta S^{\neq}$ vs $\Delta H^{\neq}$; (b, b′), plot of $\log k_2'$ vs $\log k_2$. (1) D-Glucose, (2) D-mannose, (3) D-galactose, (4) D-xylose, (5) L-arabinose, (6) D-ribose, (7) D-erythrose, (8) DL-Glyceraldehyde, (9) D-glucosamine hydrochloride (10) D-mannosamine hydrochloride (11) D-galactosamine hydrochloride.

370.3 K. The value of β, which is higher than T (318 K) (T = mid-point of the experimentally used range of temperatures), suggests that enthalpy is a controlling factor [26].

It has been shown [18,27] that cyclic pyranoid forms of hexoses and pentoses are involved in their oxidations with the metal ions. The pyranoid form in the $^4C_1$ conformation preponderates [28] in aqueous solution of hexose and the β anomer where the 1-OH equatorial is attacked by the oxidants [29]. However, the β anomer of a pentose exists as an equilibrium mixture of $^4C_1$ and $^1C_4$ forms, of which the former preponderates. These aldoses are believed to be preferentially oxidized in the $^4C_1$ β pyranoid form, and hence, initial product should be the corresponding lactone. In aqueous solution, the composition of D-erythrose is 25% α-furanose, 63% β-furanose, ~2% aldehyde, and ~10% aldehydrol [30]. Thus D-erythrose exists predominantly in the furanoid form as the β anomer. Glyceraldehyde, the simplest sugar, consists mainly of the aldehydrol in dilute solution; in the crystalline state (DL) or syrupy state (D), it is dimeric [31a]. Thus, as the length of the chain of the aldehydo form increases, the extent of hydration decreases [31b]. Again the pK_a values of some aldoses are known [32]. The values are 12.35, 12.29, 12.41, and 12.21 for D-glucose, D-xylose, L-arabinose and D-ribose, respectively. Consequently, the aldoses will remain in the undissociated form in the pH range 4.22–6.45.

The pseudo-first-order rate constants for the oxidations of both methyl α-D-glucopyranoside and methyl β-D-glucopyranoside have been determined. The values of k_{obs} obtained for the oxidations of the two methyl glucosides are 8.5×10^{-6} and 12.8×10^{-6} s^{-1} for methyl α- and methyl β-D-glucopyranosides, respectively, at [substrate] = 3.0×10^{-1} mol dm^{-3}, [Mn (III)] = 2×10^{-4} mol dm^{-3}, pH 6.1 and $T = 328$ K. The oxidations of methyl α-D-glucopyranoside and methyl β-D-glucopyranoside are too slow to be studied under the conditions at which other substrates are oxidized. Consequently, C-1 of the aldoses appears to be more reactive [33] than C-6. The reaction proceeds through the intermediate formation of a free radical between the reac-



Scheme 1.

tants in the rate-determining step. The free radical is then rapidly oxidized by another [Mn(III)] to give products. The different steps of the reactions involving the hydrated form of the acyclic aldoses and manganese(III) are shown in Scheme 1. Irrespective of whether the substrate is in the cyclic or acyclic form, the aldonic acids are converted to their anions at pH 6.1. The observed order with respect to each reactant and the formation of polymeric suspension in the presence of acrylamide corroborate the suggested mechanism.

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