

Electrolytically Generated Manganese(III) Sulphate for the Oxidation of 6-Deoxyhexoses in Aqueous Sulphuric Acid Medium: A Kinetic Study

K.S. RANGAPPA*, N. ANITHA, M. AYESHA NIKATH and A. THIMME GOWDA¹

*Department of Studies of Chemistry, University of Mysore
Manasagangotri, Mysore-570 006, India*

Manganese(III) sulphate was prepared by the electrolytic oxidation of manganese(II) sulphate in aqueous sulphuric acid. The electrolytically generated Mn(III) species was characterised by spectroscopic and redox potential studies. Conditions for the study of kinetics of oxidation of 6-deoxy hexoses namely L-rhamnose and L-fucose by Mn(III) in aqueous sulphuric acid were investigated at $\lambda_{\text{max}} = 500 \text{ nm}$ spectrophotometrically. The rate shows first order dependence on $[\text{Mn(III)}]_0$ and $[\text{S}]_0$ but there is no dependence of rate on $[\text{H}^+]$. The effects of added anions like chloride, sulphate, fluoride, persulphate and reaction product Mn(II) were investigated. Kinetic and thermodynamic parameters were computed from Arrhenius and Eyring plots. A mechanism involving the formation of enediol from 6-deoxyhexose which react with Mn(III) in the rate limiting step is suggested.

INTRODUCTION

A great deal of attention has been focussed on the oxidation of organic substrates by high valent metal ions. Oxidation of organic substrates by manganese(III) are of special importance due to their biological relevance^{1,2}. Manganese(III) porphyrins have been studied as possible models for closely related and biologically significant systems. There are reports on the kinetics of oxidation of various substrates by manganese(III) in perchlorate, sulphate, acetate and pyrophosphate media³.

Although the kinetics of oxidation of sugars with various metal ions^{4,5} and strong oxidants⁶ in alkaline medium has been extensively studied, oxidation of reducing sugars with oxidants like Mn(III) is not found in literature. Hence as a part of broad investigations on the oxidation of 6-deoxy hexoses by transition metal ions, the kinetics and mechanism of oxidation of L-rhamnose and L-fucose by Mn(III) in aqueous sulphuric acid medium is reported.

EXPERIMENTAL

Solution of manganese(III) sulphate was prepared by anodic oxidation of 0.2 M solution of manganese(II) sulphate in 5 M H_2SO_4 using an undivided cell with a platinum foil electrode (generation area 4.0 cm^2) while the cathode was a thin platinum spiral (effective area 0.2 cm^2). Electrolysis was carried out at the cell voltage of 6 V and a current density of 2 mA cm^{-2} . The solution was continuously stirred and the electrolysis was continued till Mn(III) of

¹Department of Studies in Chemistry, AVK College for Women, Hassan-573 201, India.

approximately 0.05 M was generated. The concentration of Mn(III) was determined iodometrically. Further electrolysis resulted in a turbid suspension of sparingly soluble manganese(III) sulphate and is therefore stopped at the appropriate stage. When the oxidation is over, an aliquot portion is removed for the estimation of the generated manganese(III) sulphate. The clear cherry red coloured solution containing an excess but known concentration of Mn(II), to suppress the disproportionation reaction,



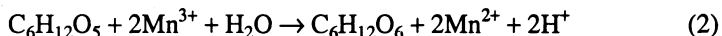
Though the solution appeared to be stable for more than one month at $[\text{H}^+] > 5.0 \text{ mol dm}^{-3}$ at a time, solution of Mn(III) always prepared afresh was used for the experiments.

The substrates L-rhamnose and L-fucose were used without further purification. Aqueous solutions of monosaccharides were prepared in triply distilled water whenever required. Sodium perchlorate (E. Merck) was used to keep the ionic strength of the medium at a constant high value.

Absorption spectra of Mn(III) solution is recorded using a Spectrochem MK II spectrometer, under the experimental conditions. Manganese(III) sulphate shows an absorption maximum at 500 nm.

Stoichiometry

A known amount of sugar is allowed to react completely with excess of manganese(III) in the presence of excess of manganese(II) and H_2SO_4 at desired temperature. The unreacted manganese(III) concentration was determined by the iodometric titration with standard sodium thiosulphate solution using starch indicator near the end point. Two moles of oxidant were sufficient to oxidise one mole of 6-deoxyhexose leading to the formation of the corresponding acids namely 6-deoxy-L-mannonic acid, 6-deoxy-L-gluconic acid, 6-deoxy-L-galactonic acid and 6-deoxy-L-tartaric acid. Based on these results the following stoichiometric equation is suggested:



The products were analysed by paper chromatography using the solvent system, 1-butanol : water : acetic acid (4 : 5 : 1 v/v/v) and detected with *p*-anisidine hydrochloride. The R_f values obtained were compared with the corresponding products obtained by the oxidation of corresponding sugars using Fehling's⁷ method. The oxidation products were namely 6-deoxy-L-mannonic acid and 6-deoxy-L-gluconic acid for L-rhamnose; 6-deoxy-L-galactonic acid and 6-deoxy-L-tartaric acid for L-fucose.

RESULTS AND DISCUSSION

The kinetics of oxidation of sugars by Mn(III) was investigated at several initial concentrations of the reactants. At fixed [sugar], $[\text{H}_2\text{SO}_4]$, $[\text{Mn(II)}]$ and temperature, plots of log (absorbance) vs. time were linear even beyond 75% of the reaction. The rate increased with increase in $[\text{deoxyhexoses}]_0$ (Table-1). Plots of $\log k_{\text{obs}}$ vs. $\log[\text{deoxyhexoses}]_0$ were linear with slopes 1.03 and 1.0 for L-rhamnose respectively (Fig. 1).

TABLE-1
FIRST ORDER RATE CONSTANT FOR THE OXIDATION
OF 6-DEOXYHEXOSSES BY MANGANESE(III) SULPHATE AT 30°C

$[H_2SO_4] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[Mn(II)] = 0.01 \text{ mol dm}^{-3}$

$10^4 [Mn(III)]_0$ mol dm^{-3}	$10^4 [\text{deoxyhexose}]$ mol dm^{-3}	$10^4 k_{\text{obs}} \text{ s}^{-1}$	
		L-fucose	L-rhamnose
2.5	2.0	1.45	1.03
3.0	2.0	1.61	1.19
3.5	2.0	1.57	1.12
4.0	2.0	1.63	1.04
4.5	2.0	1.53	1.25
5.0	2.0	1.68	1.12
5.5	2.0	1.38	1.08
6.0	2.0	1.76	1.32
4.0	1.0	0.79	0.51
4.0	1.5	1.18	0.78
4.0	2.5	2.06	1.27
4.0	3.0	2.35	1.49
4.0	3.5	2.88	1.82

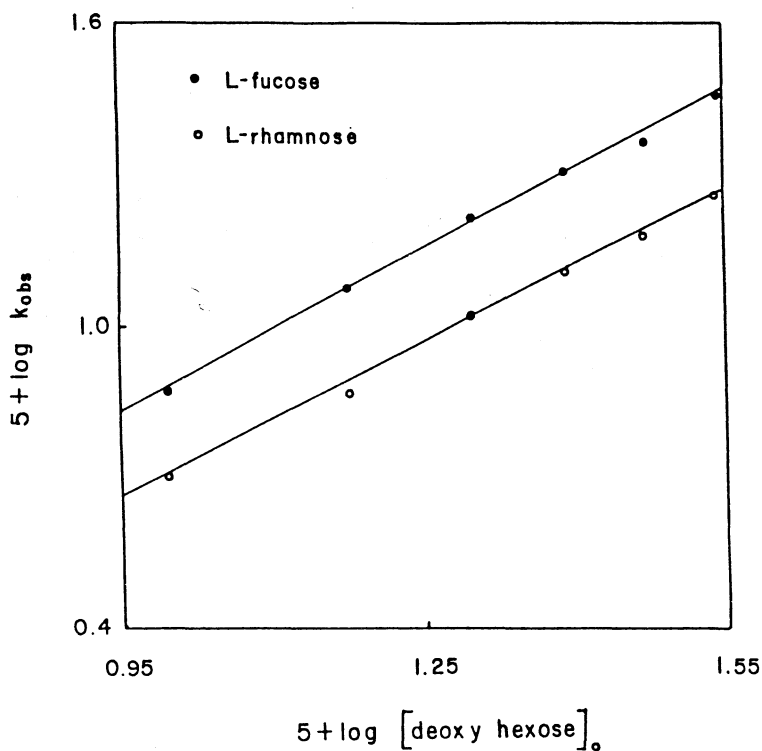


Fig. 1

Kinetic measurements were made in $\text{H}_2\text{SO}_4\text{-NaHSO}_4$ solutions of different $[\text{H}^+]$. The effective $[\text{H}^+]$ of each solution was evaluated using standard curve⁸ of $[\text{H}_2\text{SO}_4]$ vs. $[\text{H}^+]$. Increase in $[\text{H}^+]$ had no effect on the reaction rate.

The effect on the rate of reduction product Mn(II) of the oxidant was investigated and it was observed that the product had no effect on the reaction, indicating that it is not involved in the pre-equilibrium with the oxidant. Similarly the effect of anions such as chloride, fluoride and sulphate on the rate was insignificant.

The solvent composition of the reaction medium was varied by the addition of methanol (0–15%) to the reaction mixture. The rate increased with increase in methanol content. Plots of $\log k_{\text{obs}}$ vs. $1/D$ where D is the dielectric constant of the medium were linear with positive slope (Fig. 2).

TABLE-2
EFFECT OF DIELECTRIC CONSTANT OF THE MEDIUM OF THE RATE OF THE REACTION AT 30°C

$[\text{Mn(III)}]_0 = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{deoxyhexose}]_0 = 2 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{H}_2\text{SO}_4] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Mn(II)}] = 0.01 \text{ mol dm}^{-3}$

% MeOH	$10^4 k_{\text{obs}} \text{ s}$	
	L-fucose	L-rhamnose
0	1.63	1.04
2.5	2.14	1.38
5.0	2.64	1.75
7.5	3.83	2.52
10.0	4.66	3.12
12.5	7.78	5.63

TABLE-3
KINETIC AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF 6-DEOXYHEXOSSES BY Mn(III) IN ACID MEDIUM

6-deoxyhexoses	E_a kJ mol^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔG^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{JK}^{-1} \text{ mol}^{-1}$	$\log A$
L-fucose	56.7	54.1	96.9	-140.1	9.4
L-rhamnose	72.6	70.1	97.9	-91.4	12.2

The reaction was studied at different temperatures (297–313 K) to determine the activation parameters. Arrhenius plots of $\log k_{\text{obs}}$ vs. $1/T$ were found to be linear. The activation energy E_a was calculated from the slope of the plots. Values of the other kinetic parameters, ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger and $\log A$ were computed from the measured E_a values.

Olefinic monomers such as acrylonitrile and freshly prepared 10% acrylamide solution under nitrogen atmosphere were added to the reaction mixture to initiate

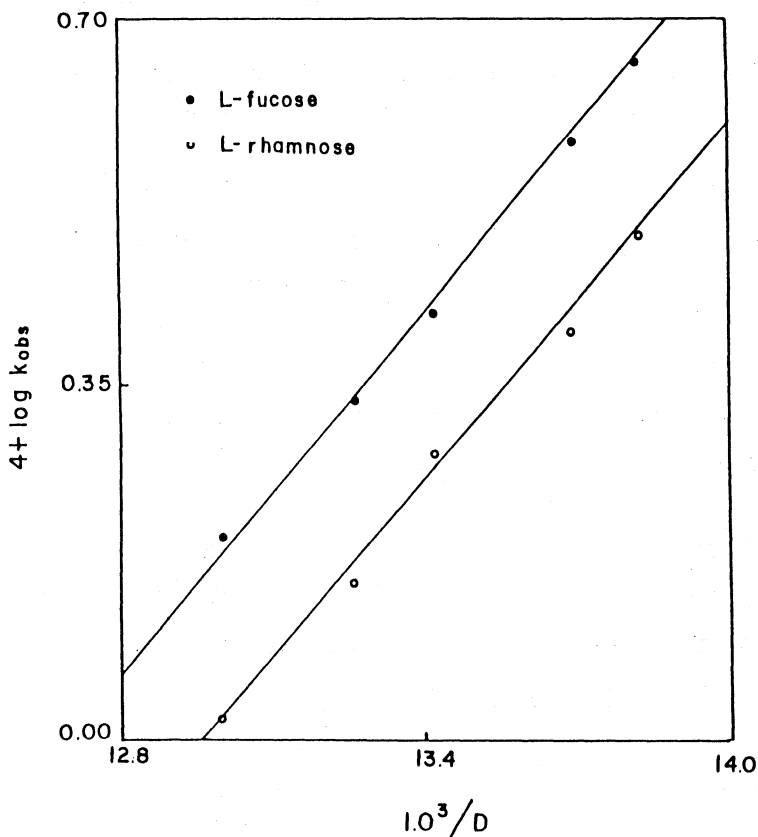
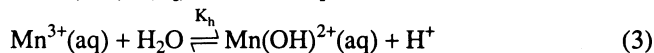


Fig. 2

polymerization if free radicals are present. The lack of polymerization indicated the absence of free radicals involvement in the reaction mixture.

It is interesting to note that there are speculations about the reactive species present in aqueous solution of Mn(III) salts. Data published by Diebler and Sutin⁹, Packler and Chawla¹⁰ and Wells and Davies¹¹ have shown that in the presence of F^- ion, aqueous solution of Mn(III) consists of hexamanganese(III)(aq), Mn(III)(aq), hydroxopenta(aq), $Mn(OH)^{2+}(aq)$ and $MnF^{2+}(aq)$. On the same lines it can be assumed with justification that Mn(III) species present in sulphuric acid medium are Mn(III)(aq), $Mn(OH)^{2+}(aq)$ and $MnSO_4^+(aq)$.

It has been established that manganese(III) sulphate¹² in aqueous sulphuric acid contains $Mn^{3+}(aq)$ and $Mn(OH)^{2+}(aq)$ as reactive species.

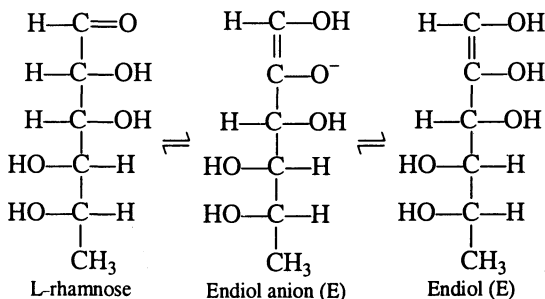


The hydrolysis constant calculated was $K_h = 0.93 \pm 0.03$.

In both visible and UV-region, the absorption spectra of both $Mn^{3+}(aq)$ and $Mn(OH)^{2+}(aq)$ have been reported to be similar. Our observation of the electronic absorption spectra is consistent with the values reported. Since there is no hydrogen ion dependence on the rate, it suggests that $Mn(OH)^{2+}(aq)$ is not the

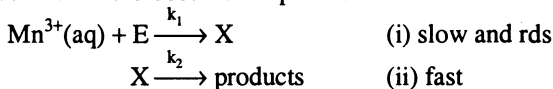
reactive species. Absence of sulphate effect on the reaction rate indicates that $\text{MnSO}_4^+(\text{aq})$ is not the active species in the present condition. Therefore $\text{Mn}^{3+}(\text{aq})$ is the reactive species as shown in the mechanism.

It is well known that in acid/alkaline solutions, sugars undergo the "Lobry de Bruyn-Alberda Van Ekenstein" transformation to form a complex mixture of products through an endiol intermediate. Since there is no $[\text{H}^+]$ dependence on rate, it is assumed that the 6-deoxyhexose is already converted into an endiol which reacts with the oxidant in the rate limiting step.



Scheme-1

The following scheme accounts for the observed experimental results.



Scheme-2

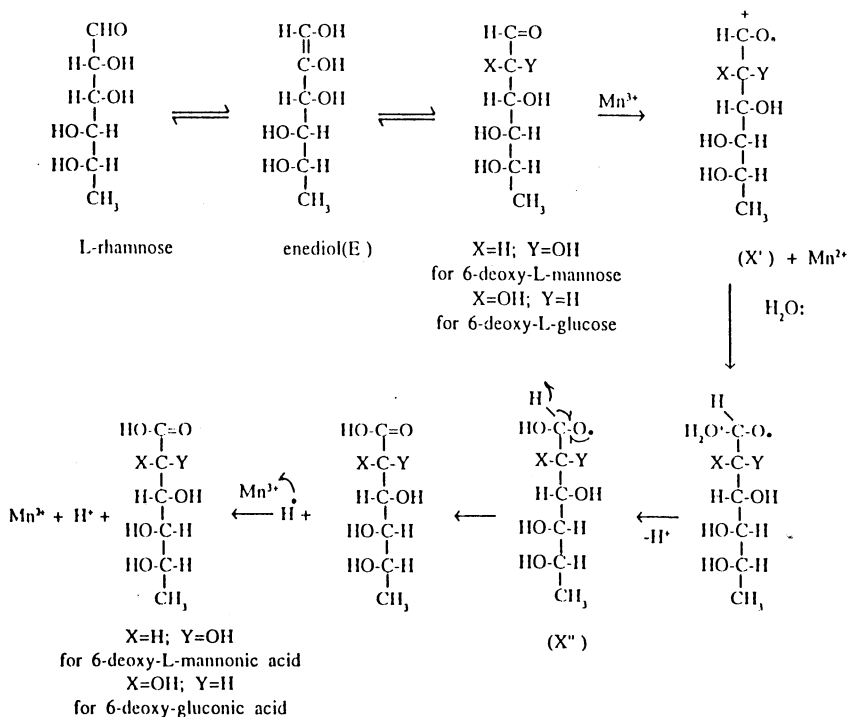
Here rate = $k_1[\text{Mn}^{3+}][\text{E}]$ (2)

Amis¹³ has shown that plot of $\log k_{\text{obs}}$ vs. $1/D$ gives a straight line with a positive slope for positive ion-dipole interactions. The positive dielectric effect in the present investigation shows a charge dispersal in the transition state, pointing towards a positive ion-dipole reaction and hence supports Scheme-2.

Spectral evidence for the formation of endiol-Mn(III) complex

The study of UV-visible spectra separately of pure Mn(III), L-rhamnose and L-fucose and mixture of Mn(III) and 6-deoxyhexoses shows deviations in peak wavelength and absorbance. Pure Mn(III) has λ_{max} at 500 nm and when mixed with L-rhamnose or L-fucose, it shifts to 450 nm. This observation indicates complex formation between the metal ion and sugar molecule. It is however probable that the shift in λ_{max} reflects the transient nature of the complex which breaks into products. The measurement of λ_{max} with time (for 2 h) was also observed indicating the change in λ_{max} from 450 to 410 nm suggesting the labile system (intermediate) is involved in the reaction sequence. A detailed mode of oxidation of L-rhamnose is given in Scheme-3. Similar type of mechanism can be proposed for L-fucose.

Endiol rearranges to give a mixture of L-deoxymannose or L-rhamnose and L-deoxyglucose. Now the carboxyl oxygen of these deoxyhexoses transfers one



Scheme-3

electron to Mn^{3+} forming Mn^{2+} and a radical cation species X' . The radical cation is further attacked by a molecule of water forming a transient free radical intermediate X'' with the elimination of a proton. This intermediate further gives away an electron to another molecule of Mn^{3+} forming a mixture of L-mannonic acid and L-gluconic acid. Similar explanation can be afforded for the oxidation of L-fucose which gives L-galactonic acid and L-tartaric acid.

It has been further noted that the rate of oxidation followed the trend: L-fucose > L-rhamnose. The probable explanation can be rationalized on the basis of their conformational stabilities, viz., L-rhamnose is more stable because there is no Δ -2 condition whereas in L-fucose there is Δ -2 condition. (Δ -2 condition means the presence of equatorial anomeric hydroxyl group and axial hydroxyl group at the second carbon atom).

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