Kinetics and Mechanism of Oxidation of D-Xylose by Mn(III) Pyrophosphate

By

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The oxidation of D-xylose by Mn(III) pyrophosphate in sulphuric acid has been found to be first order with respect to [Mn(III)]. Variation of rate with [D-xylose] suggests the rapid formation of reversible cyclic complex between Mn(III) and D-xylose, which further disproportionates in a slow rate determining step. Oxidation rate has been found to increase with [H$^+$]. Retardation of rate due to [pyrophosphate] and increase due to [Mn(II)] have been also observed. The value of thermodynamic parameters ΔE, $\Delta S^{\pm}$, and $\Delta G^{\pm}$ have been found to be 17.6 $\pm$ 0.1 kcal/mole, — 10.1 $\pm$ 0.1 e.u. and 20.6 $\pm$ 0.1 kcal/mole respectively. A mechanism involving a free radical has been proposed for the reaction under study.

The kinetics of many oxidation reactions involving Mn(III)[1] including those with Mn(III) pyrophosphate[2, 3] have been studied. Amongst the carbohydrates, only the oxidation of D-glucose[4] has been studied by this potent oxidant. Survey of literature shows that oxidation of pentoses, which constitute an important group of compounds among monosaccharides have received little attention in comparison with that of hexoses. We, therefore, carried out oxidation studies of D-xylose with Mn(III). The results have been reported here.

Experimental

Mn(III) pyrophosphate was prepared by the method of *Lingane* and *Karplus*[5]. D-Xylose (B.D.H. Biochemical) solution was prepared fresh daily. Other reagents like $MnSO_4$, $KMnO_4$, sodium pyrophosphate, H_2SO_4, chromotropic acid etc. were of AR/BDH grade.

Reactions were followed by quenching aliquots withdrawn at regular known intervals of time in slight excess of ferrous ammonium sulphate solution and estimating unreacted Fe(II) with Ce(IV) using N-phenyl-anthranilic acid as an indicator.

Stoichiometry

It was observed that one mole of D-xylose required 6 moles of Mn(III) for oxidation. The overall reaction may be represented as follows:

$$C_5H_{10}O_5 + 6\,Mn(III) + 3\,H_2O \rightarrow 3\,HCOOH + 2\,HCHO + 6\,Mn(II) + 6\,H^+$$

The formation of formaldehyde was confirmed by chromotropic acid spot test[6], whereas formic acid was confirmed by $HgCl_2$ test. The formation of free radicals was also confirmed during the reaction by the induced polymerisation reaction with acrylonitrile.

Results and Discussion

When the concentrations of D-xylose and H_2SO_4 acid were in excess, the fading of [Mn(III)] followed first order rate law. The pseudo first order rate constants, k_1, have been found to increase with [Mn(III)] (Table 1) but the order with respect to [D-xylose] has been found to be less than one.

Table 1. *Effect of Mn(III) and* D-*Xylose Concentrations.* $[H^+] = 1.0 M$; $[Na_4P_2O_7] = 5.33 \times 10^{-2} M$; Temp. $= 25\ °C$

$[Mn(III)] \times 10^3 M$	$[D\text{-xylose}] \times 10^2 M$	$k_1 \times 10^4\ sec^{-1}$
2.0	5.0	0.60
3.0	5.0	0.79
4.0	5.0	0.93
5.0	5.0	1.80
5.0	10.0	2.57
5.0	20.0	3.72
5.0	30.0	5.15
5.0	40.0	6.01

These results of substrate dependence of rate suggest also the formation of a complex between D-xylose and Mn(III) prior to slow rate determining step. This has been further confirmed by obtaining a linear plot if drawn between $1/k_1$ and $1/[D\text{-xylose}]$ with a positive intercept.

It was also observed that rate increased with the H_2SO_4 concentration. The rate has been found to increase with the first power of $[H^+]$ in runs (Table 2) where ionic strength was maintained by bisulphate addition.

Table 2. *Effect of* H^+ *Concentration.* $[Mn(III)] = 5.0 \times 10^{-3} M$; $[D\text{-xylose}] = 5.0 \times 10^{-2} M$; $[Na_4P_2O_7] = 5.33 \times 10^{-2} M$; $[HSO_4^-] = 3.0 M$; Temp. $= 25\ °C$

$[H^+]\ M$	1.0	1.5	2.0	2.5	3.0
$k_1 \times 10^4\ sec^{-1}$	2.09	3.10	3.72	4.63	5.53

Zucker-Hammett[7] and *Bunnett*[8] treatments were found to be applicable for the results obtained in Table 2. The slope values of *Zucker-Hammett* and *Bunnett* plots were found to be — 0.40 and 10.69 respectively.

The oxidation reaction was studied at five different temperatures. The temperature effects have been summarised in Table 3. The various thermodynamic parameters evaluated have been also given.

Table 3. *Effect of Temperature.* $[Mn(III)] = 5.0 \times 10^{-3}M$; $[D\text{-xylose}] = 5.0 \times 10^{-2}M$; $[Na_4P_2O_7] = 5.33 \times 10^{-2}M$; $[H^+] = 1.0M$

| Temp., °C	$k_1 \times 10^4$, sec^{-1}	ΔE kcal/mole	$\Delta S^{\neq}$ e.u.	$\Delta G^{\neq}$ kcal/mole
20	1.04	17.5	— 10.0	20.4
25	1.80	17.5	— 10.1	20.6
30	2.79	17.5	— 10.1	20.6
35	4.24	17.6	— 10.3	20.7
40	6.79	17.7	— 10.1	20.8
Average		17.6 ± 0.1	$— 10.1 \pm 0.1$	20.6 ± 0.1

Kolthoff and *Watters*[9] have described various forms of Mn(III) pyrophosphate depending on the pH ranges. The active form in pH range 0 to 3 was described as $Mn(H_2P_2O_7)_3{}^{3-}$. Thus, in the present studies this anion form can be regarded as active oxidant species of Mn(III). But at higher acidities this form can also change depending on the extent of association of H^+ with pyrophosphate ligand.

On the basis of results obtained above the mechanism of oxidation of D-xylose by Mn(III) can now be proposed by considering the following steps.

In the first step, a reversible cyclic complex is expected to be formed between D-xylose and Mn(III). This complex then disproportionates in a slow step producing free radical and HCHO by a C—C bond fission.

$$\text{Complex} \xrightarrow[\text{Slow}]{k} \bar{R} + \text{HCHO} + H^+ + \text{Mn(II)}, \tag{1}$$
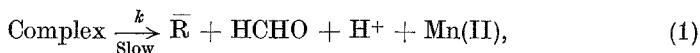
where $\bar{R}$ is $CHO \cdot CHOH \cdot CHOH \cdot \dot{C}HOH$. The free radical thus formed further breaks into products in a fast step.

$$\bar{R} + 5\,\text{Mn(III)} + 3\,H_2O \xrightarrow[\text{Fast}]{k'} 3\,\text{HCOOH} + \text{HCHO} + 5\,H^+ + 5\,\text{Mn(II)} \tag{2}$$
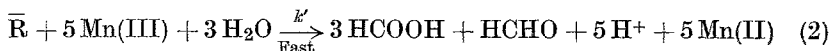
where $k' \gg k$. On the basis of above steps the rate expression at constant $[H^+]$ can be derived as: —

$$-\frac{d}{dt}[\text{Mn(III)}] = k[\text{Complex}] + k'[\bar{R}][\text{Mn(III)}]^5[H_2O]^3 \tag{3}$$

Applying a steady state treatment to free radical $\overline{R}$ it can be shown as: —

$$\frac{d}{dt}[\overline{R}] = k[\text{Complex}] - k'[\overline{R}][\text{Mn(III)}]^5[\text{H}_2\text{O}]^3 = 0 \qquad (4)$$

substituting (4) in (3) it follows

$$-\frac{d}{dt}[\text{Mn(III)}] = 2\,k[\text{Complex}] \qquad (5)$$

Considering that, of course,

$$[\text{Complex}] = \frac{K\,[\text{D-xylose}]\,[\text{Mn(III)}]}{1 + K\,[\text{D-xylose}]} = \frac{[\text{D-xylose}]\,[\text{Mn(III)}]}{1/K + [\text{D-xylose}]} \qquad (6)$$

Thus equation (6) can be represented as:

$$-\frac{d}{dt}[\text{Mn(III)}] = \frac{2\,k[\text{D-xylose}]\,[\text{Mn(III)}]}{1/K + [\text{D-xylose}]} = k_1[\text{Mn(III)}] \qquad (7, 8)$$

where k_1 (observed pseudo first order rate constant)

$$= \frac{2\,k[\text{D-xylose}]}{1/K + [\text{D-xylose}]} \qquad (9)$$

Applicability of equation (9) is evident from a linear plot which can be obtained if drawn between $1/k_1$ and $1/[\text{D-xylose}]$ with a positive intercept. The value of K, the formation constant for the D-xylose—Mn(III) complex was found to be $3.16\,\text{l}\cdot\text{mole}^{-1}$ at 25 °C under the experimental conditions (Table 1).

Further, a retardation of rate with $[\text{Na}_4\text{P}_2\text{O}_7]$ and increase with $[\text{Mn(II)}]$ were also observed (Table 4).

Table 4. *Effect of Sodium Pyrophosphate and Mn(II) Concentrations.* $[\text{Mn(III)}] = 5.0 \times 10^{-3}M$; $[\text{D-xylose}] = 5.0 \times 10^{-2}M°$ $[\text{H}^+] = 1.0M$; Temp. = 25 °C; $[\text{Na}_4\text{P}_2\text{O}_7] = 5.33 \times 10^{-2}M$

$[\text{Na}_4\text{P}_2\text{O}_7] \times 10^2 M$	$k_1 \times 10^4$, sec^{-1}	$[\text{Mn(II)}] \times 10^4$, M	$k_1 \times 10^4$ sec^{-1}
0.20	11.93	0.0	1.80
0.67	6.41	8.0	2.35
1.33	3.72	16.0	4.31
2.67	2.90	33.0	10.05
5.33	1.80		
8.00	1.10		

This retardation in rate with increase in pyrophosphate concentration can be attributed to the fact that the concentration of complex will be less at higher pyrophosphate concentration whereas Mn(II) when added

can form Mn(II) pyrophosphate reducing the concentration of free pyrophosphate. The concentration of the Mn(III)—D-xylose complex will increase on this account giving an increase in rate[10]. Further, the observed increase with [Mn(II)] may be due to presence of Mn(IV) as an impurity which with Mn(II) can gives additional Mn(III) as:

$$Mn(IV) + Mn(II) \rightleftharpoons 2\,Mn(III)$$
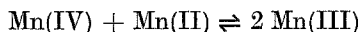
Thus, the proposed mechanism and rate expression are in accordance with the results obtained during studies.

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