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Note

Kinetics of reactions of manganese(III) pyrophosphate with some hexitols

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Alditols are acyclic, polyhydric alcohols that are derived from aldoses and ketoses by reduction. Their wide-spread occurrence in Nature, particularly in the lower forms of life, points to their biological importance. Compared to studies of the metal-ion oxidation of sugars, it seems that the oxidation of alditols has received little attention. Earlier, the oxidation of hexitols with cerium(IV) (ref. 1), cobalt(III) (ref. 2), and vanadium(V) (ref. 3) was reported, and we now describe oxidations with manganese(III) pyrophosphate.

EXPERIMENTAL

Experimental details and kinetic procedures have been described[4].

One mole of each hexitol examined, *i.e.*, D-mannitol, D-glucitol, and galactitol, consumed ~2 equivalents of oxidant under kinetic conditions. Presence of the respective aldohexose resulting was confirmed by paper chromatography, using authentic samples as standards, and also by the usual tests and preparation of their osazones.

The stoichiometric equation can, therefore, be represented as in Eq. *1*.

$$C_6H_{14}O_6 + 2\ Mn(III) \rightarrow C_6H_{12}O_6 + 2\ Mn(II) + 2\ H^+ \qquad (1)$$

In the presence of an ~20-fold excess of oxidant, one mole of each hexitol required ~8 equivalents of Mn(III), and therefore, the overall reaction can be given as in Eq. *2*.

$$C_6H_{14}O_6 + 8\ Mn(III) + 3\ H_2O \rightarrow 3\ HCO_2H + 3\ HCHO + 8\ Mn(II) + 8\ H^+ \qquad (2)$$

The products, HCHO and HCO_2H, were respectively confirmed by the chromotropic acid spot-test[5] and by the $HgCl_2$ test. Formation of free radicals during these reactions was confirmed by the polymerization reaction induced with acrylonitrile.

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KINETIC RESULTS

In all of the kinetic experiments, [hexitol] and [H_2SO_4] were $\gg$ [Mn(III)]; the disappearance of [Mn(III)] with time is given as in Eq. 3.

$$-\frac{d\,[\mathrm{Mn(III)}]}{dt} = k_{obs}\,[\mathrm{Mn(III)}] \tag{3}$$

TABLE I

VALUES OF k_{obs} (s^{-1}) AT DIFFERENT VALUES OF [HEXITOL] AND [Mn(III)] AT pH 1.15 AND 35° [free pyrophosphate] = 7.2 × 10^{-2}M

[Mn(III)] 10^3M	[Hexitol] 10^2M	k_{obs} × 10^4 (s^{-1}) D-Mannitol	D-Glucitol	Galactitol
2.0	6.6	0.53	2.45	1.44
3.0	6.6	0.94	2.77	1.67
4.0	6.6	1.03	3.52	1.82
5.0	6.6	1.16	3.89	1.98
6.0	6.6	1.72	4.49	2.46
6.0	13.0	1.82	7.23	3.05
6.0	20.0	2.79	7.92	4.61
6.0	26.0	3.58	10.12	5.71
6.0	33.0	4.28	11.65	6.12

TABLE II

VALUES[a] OF k_{obs} (s^{-1}) AT DIFFERENT VALUES OF pH AND [FREE PYROPHOSPHATE]

pH	[Free pyrophosphate] × 10^2M	k_{obs} × 10^4 (s^{-1}) D-Mannitol	D-Glucitol	Galactitol
1.20	7.2	1.08	1.69	2.57
1.10	7.2	2.48	4.96	4.99
1.05	7.2	3.13	5.35	5.14
1.00	7.2	3.21	6.42	7.65
1.15	1.2	17.81	33.20	22.01
1.15	2.7	8.33	12.83	9.74
1.15	4.2	5.38	8.74	6.95
1.15	5.7	2.77	5.27	3.04
1.15	7.2	1.72	4.49	2.46
1.15	8.7	1.61	2.94	2.23

[a][Mn(III)] = 6.0mM; [hexitol] = 66mM; temp. 35°.

TABLE III

VALUES[a] OF k_{obs} AT DIFFERENT TEMPERATURES

Hexitol	$k_{obs} \times 10^4$ (s^{-1})					$\Delta H^{\ddagger}$ ($kJ.mol.^{-1}$)	$\Delta S^{\ddagger}$ ($kJ^{-1}.mol.^{-1}$)
	35°	*40°*	*45°*	*50°*	*55°*		
D-Mannitol	1.72	2.59	8.10	11.54	18.25	106.67 ±1.63	+20.44 ±4.97
D-Glucitol	4.49	5.08	7.70	14.88	26.33	88.44 ±0.33	−33.10 ±0.16
Galactitol	2.46	2.81	7.98	12.34	19.31	88.90 ±0.29	−34.56 ±0.16

[a][Mn(III)] = 6.0mM; [hexitol] = 66mM; pH = 1.15; [free pyrophosphate] = 72mM.

The values of k_{obs}, the pseudo-first-order rate constant, at different values of [Mn(III)] and [hexitol] are given in Table I. The value of k_{obs} increases proportionally with [H^+], and decreases with [free pyrophosphate] (see Table II).

Added [Mn(II)] (6.0–26.0mM) had no effect on the oxidation rate. Thermodynamic parameters were computed from the data obtained by variation in temperature (see Table III).

DISCUSSION

Kolthoff and Watters[6] described various forms of Mn(III) pyrophosphate whose presence depends on the pH. In the pH range of 0–3, the active species was described as $Mn(III)(H_2P_2O_7)_3^{3-}$, but this form can change, due to association of H^+ with the free, as well as the complexed, pyrophosphate anion. Consequently, Mn(III) pyrophosphate may have any formula from $Mn(III)(H_2P_2O_7)_3^{3-}$ to $Mn(III)(H_3P_2O_7)_3$, involving various equilibria. In the present reaction, the variation of rate with [H^+] (see Table II) can be explained by considering the change in the formula of the active species, as in Eq. *4*.

$$Mn(H_2P_2O_7)_3^{3-} + H^+ \overset{K_1}{\rightleftharpoons} Mn(H_3P_2O_7)(H_2P_2O_7)_2^{2-} \qquad (4)$$

An isokinetic plot (β = 314 K) can be obtained from the data given in Table III, in accordance with Laffler's compensation law. Thus, an identical mechanism can now be proposed for all three of these hexitols.

The active form of Mn(III) as expressed in Eq. *4* can now be presumed to react with a hexitol molecule, to form a reversible, cyclic complex, as in Eq. *5*.

$$C_6H_{14}O_6 + Mn(H_3P_2O_7)(H_2P_2O_7)_2^{2-} \overset{K_2}{\rightleftharpoons} \underset{\text{Complex}}{Mn(H_3P_2O_7)(C_6H_{14}O_6)(H_2P_2O_7)} + H_2P_2O_7^{-2} \qquad (5)$$

Then, the complex disproportionates in a slow step, producing a free radical, which now reacts with another Mn(III) ion, to produce the aldohexose in a fast step, as in Eq. *6*.

$$\text{Complex} + H_2O\ (\text{slow}) \xrightarrow{k_s} \bar{R} + \mathrm{Mn(II)}(H_2P_2O_7)H_2P_2O_7^{-1} + H_3^+O, \quad (6)$$

where $\bar{R}$ = free radical = $HOH_2C(CHOH)_4\dot{C}HOH$

$$HOH_2C(CHOH)_4\dot{C}HOH + \mathrm{Mn(III)} + H_2O \xrightarrow{\text{fast}} (HOH_2C)(CHOH)_4CHO + \mathrm{Mn(II)} + H_3O^+ \quad (7)$$

When Mn(III) is present in excess, the aldohexose formed is further oxidized to formic acid and formaldehyde, as in Eq. *8*.

$$HOH_2C(CHOH)_4CHO + 6\ \mathrm{Mn(III)} + 3\ H_2O \xrightarrow{\text{fast}} 3\ HCHO + 3\ HCO_2H + 6\ \mathrm{Mn(II)} + 6\ H^+ \quad (8)$$

On the basis of steps *4–7* as proposed, the following rate expression (Eq. *9*) can be obtained.

$$-\frac{d[\mathrm{Mn(III)}]}{dt} = \frac{K_1 K_2\ [C_6H_{14}O_6][\mathrm{Mn(III)}][H^+]}{[H_2P_2O_7]^{2-} + K_2\ [C_6H_{14}O_6]} = k_{obs}\ [\mathrm{Mn(III)}] \quad (9)$$

From the data in Table I, linear plots were obtained between $1/k_{obs}$ and 1/[hexitol], in accordance with the rate expression (Eq. 7). The values of k_2, the equilibrium constant, for all three hexitols were computed (from the linear plots) as 0.45, 0.49, and 0.30 mol^{-1}, respectively.

Thus, the rate expression (Eq. *9*) and the mechanistic steps proposed are consistent with the results obtained during this study.

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