Kinetics and Mechanisms of Redox Reactions in Aqueous Solution. Part 4.[1] Oxidation of Diols by Aquamanganese(III) Ions in Aqueous Perchloric Acid

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The kinetics of oxidations of butane-1,4-, pentane-1,5-, and hexane-1,6-diols and of 3-methoxybutan-1-ol by aquamanganese(III) ions have been investigated in aqueous perchloric acid at constant ionic strength (4 mol dm^{-3}). The reaction has a first-order dependence both on [Mn^{III}] and [Substrate], but is independent of [Mn^{II}]. The rate decreases with increasing [H$^+$] at constant ionic strength, becoming less sensitive at >3 mol dm^{-3} HClO$_4$. The present rate data do not help to distinguish between inner- and outer-sphere mechanisms, although complex formation is indicated by spectrometry. A probable mechanism is suggested and the activation parameters are reported.

We have been interested in the oxidation of diols by vanadium(V) [2] and cerium(IV) in aqueous sulphuric,[3] nitric,[4] and perchloric acids.[1] This interest has now been extended to the use of aquamanganese(III) ions since a review of the literature [5] indicated that such a study had not been attempted.

EXPERIMENTAL

Reagents.—A stock solution of manganese(II) perchlorate (G. F. Smith) was prepared in perchloric acid solution of known strength. The solution was standardised against a standard ethylenediaminetetra–acetate (edta) solution (sodium salt, B.D.H.) in the presence of ammonium hydroxide using 4-(2-pyridylazo)resorcinol (par) indicator.[6] The colour change at the end-point was from red to yellow. Manganese(III) solutions were freshly prepared by the electrolytic oxidation of stock manganese(II) solutions under nitrogen.[5] The concentration of Mn^{III} was determined by treating a known volume of the solution with a known excess of iron(II) solution. The unchanged Fe^{II} was then estimated titrimetrically using a known solution of vanadium(V) (barium diphenylamine sulphonate indicator) in the presence of phosphoric acid. It was noted that the excess of Mn^{II} present in the manganese(III) solution did not affect the titrimetric estimation of Fe^{II} by V^{V}.

Perchloric acid (E. Merck, G.R., 70%) was diluted and standardised against standard alkali. Solutions of sodium and magnesium perchlorate (G. F. Smith) were prepared by direct weighing and dissolution of solid samples. Lithium perchlorate was prepared by the neutralisation of lithium carbonate with perchloric acid. The diols and 3-methoxybutan-1-ol were obtained from Fluka and used without further purification. Most of the diols were ' puriss ' grade reagents. The substrate solutions were prepared from known weights of samples. Other chemicals were used as received. Twice distilled water was used throughout.

Rate Measurements.—The reaction mixtures, containing Mn^{III}, Mn^{II}, perchloric acid, and sodium perchlorate (or other perchlorates used to adjust the ionic strength), and the substrate solutions were separately thermostatted in a water-bath maintained at the desired temperature (±0.1 °C) for thermal equilibrium. The reaction was initiated by the rapid addition of the desired volume of the substrate solution. In a few cases the reaction was also initiated by the addition of a manganese(III) solution. The order of mixing, however, did not affect the observed rate. At known intervals of time, a fixed volume of the reaction mixture was withdrawn and added to a known excess of iron(II) solution. The unchanged Fe^{II} was then back titrated with a standard vanadium(V) solution as described above. The concentrations of the reactants, Mn^{III} and the substrate, were so adjusted as to have substrate present in large excess over Mn^{III}. This ensured that there was very little contribution to the rate, if any, from the subsequent oxidation of any products which are more reactive than the substrate itself. The ionic strength (I) of the reaction mixture was kept constant at 4 mol dm^{-3}. High [Mn^{II}] was used to suppress [7] the formation of Mn^{IV} in the reaction mixture from the disproportionation of Mn^{III} through reaction (1).

$$2\text{Mn}^{III} \rightleftharpoons \text{Mn}^{II} + \text{Mn}^{IV} \qquad (1)$$

The observed first-order rate constant, $k_{obs.}$, with respect to Mn^{III} was obtained from the gradients of linear plots of log (change in titre) against time by the method of least squares. These first-order plots were linear for 80% completion of reaction, the maximum extent to which these reactions were studied. The correlation coefficient for the plots was, in general, >98% and so was the reproducibility of $k_{obs.}$ values from repeated runs.

Stoicheiometry.—The stoicheiometry of the reactions was first investigated under the conditions used for the kinetic study. In these experiments the diols were present in excess over Mn^{III}. The reaction mixtures were treated with 2,4-dinitrophenylhydrazine after complete reduction of Mn^{III}, and the precipitated hydrazones were filtered off, washed, and dried. The yield of the hydrazone, in general, was 90—96% of the yield expected on the basis of reaction (2). The occurrence of reaction (2) was confirmed when it was found that the m.p. of the hydrazones separated from the oxidised reaction mixtures of butane-1,4-diol and pentane-1,5-diol corresponded to those of the hydrazones of 4-hydroxybutanal (lit.,[8] 118 °C; found 116 °C) and 5-hydroxypentanal (lit.,[8] 104 °C; found 105 °C) respectively.

$$\text{HOCH}_2[\text{CH}_2]_n\text{CH}_2\text{OH} + 2\text{Mn}^{III} \longrightarrow 2\text{Mn}^{II} + \text{HOCH}_2[\text{CH}_2]_n\text{CHO} + 2\text{H}^+ \qquad (2)$$

Next, reaction mixtures were prepared which contained a slight excess of Mn^{III} over diol ([Mn^{III}] $\sim$ 3[Diol]). In these experiments it was noted that the rate of consumption of Mn^{III} decreased when 2 equivalents of Mn^{III} had been used, indicating that further oxidation of the product, a hydroxyaldehyde as characterised above, was not competitive with substrate oxidation.

A set of fresh reaction mixtures was prepared and treated with 2,4-dinitrophenylhydrazine after the unchanged Mn^{III}, remaining after nearly 2 equivalents of it had been consumed, had been reduced with the minimum of Fe^{II}. The precipitated hydrazones were separated and their m.p.s determined, to be the same as stated above. There was no change in the m.p. of the hydrazone mixture, prepared by mixing the respective hydrazones obtained from the two experiments. This confirmed that the first oxidation product is a hydroxy-aldehyde. The stoicheiometry is thus represented by (2).

The absence of formaldehyde in the oxidised reaction mixtures in each case was confirmed by addition of 4,5-dihydroxynaphthalene-2,7-disulphonic acid.[9] This indicates that there is no C–C fission during the oxidation of the diols.

Spectrometric Measurements.—These measurements were undertaken to determine whether an intermediate complex was formed between aquamanganese (III) ions and the substrates. Solutions of the reactants were mixed and their absorbances noted at a preset wavelength on a Beckman DU-2 spectrophotometer. The process was repeated for different wavelengths. The method can, at best, be considered crude because there was some time-lag between the mixing of the solutions and their transfer to the cell compartment before noting the absorbance. However, the time-lag was kept to a minimum (<30 s) and the results illustrated in Figure 1 provide evidence in favour of the formation of an intermediate complex in each case. It is to be noted that in Figure 1 the absorbance increases for the 3-methoxybutan-1-ol solution but decreases in the other cases. Except for butane-1,4-diol, there was a clear shift in $\lambda_{\text{max.}}$ for the substrates.

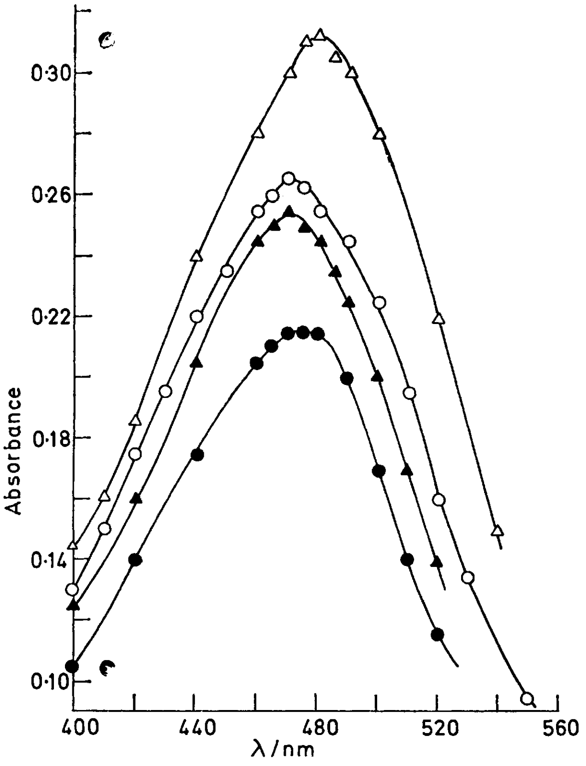

FIGURE 1 Spectrum of a manganese(III) solution (○, 0.002 6 mol dm^{-3}) and mixtures of Mn^{III} (0.002 6 mol dm^{-3}), and substrate solutions. The $\lambda_{\text{max.}}$ shifted in all cases except that of butane-1,4-diol. In all cases there was a change in the optical density. These features are evidence for the formation of a complex between manganese(III) ions and the substrates. Substrates (0.04 mol dm^{-3}): (▲) butane-1,4-diol; (●) pentane-1,5-diol; and (△) 3-methoxybutan-1-ol

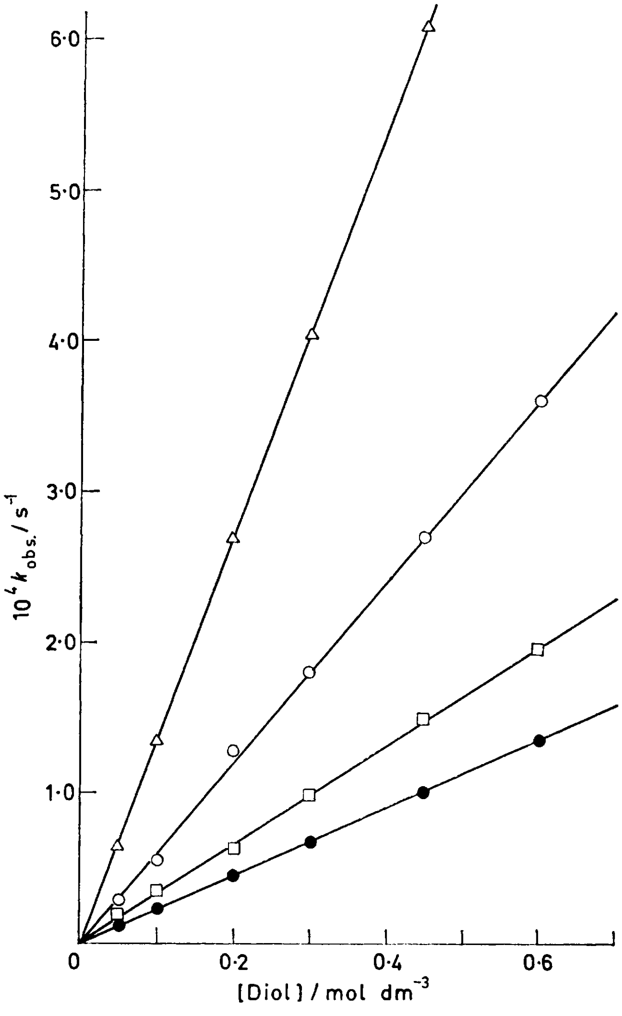

FIGURE 2 Plot of the observed first-order rate constant $k_{\text{obs.}}$ against [Substrate]; $[\text{Mn}^{\text{III}}] = 0.002$ mol dm^{-3}, $[\text{H}^+] = 3$ mol dm^{-3}, $I = 4$ mol dm^{-3}, and 25 °C; similar plots were obtained at other temperatures. Substrates: (●) butane-1,4-diol; (△) pentane-1,5-diol; (○) hexane-1,6-diol; and (□) 3-methoxybutan-1-ol

RESULTS

The observed rate constant $k_{\text{obs.}}$ was found to be independent of the initial $[\text{Mn}^{\text{III}}]$ over a two-fold range (1.98×10^{-3}—3.96×10^{-3} mol dm^{-3}); a wider variation could not be obtained because of the difficulty in preparing more concentrated manganese(III) solutions. $k_{\text{obs.}}$ was also independent of the initial $[\text{Mn}^{\text{II}}]$; perchlorates of sodium, lithium, and magnesium were used to replace Mn^{II} at constant ionic strength.

The first-order dependence of $k_{\text{obs.}}$ on [Substrate] at 25 °C is shown in Figure 2. Similar plots were also obtained at other temperatures. Values of the second-order rate constant k'' (dm^3 mol^{-1} s^{-1}), obtained from the gradients of

TABLE 1

Values of the second-order rate constant k'' ($= k_{obs.}$/[Substrate]) at different temperatures, $[Mn^{III}] = 0.002$ mol dm^{-3}, $[HClO_4] = 3$ mol dm^{-3}, and $I = 4$ mol dm^{-3}

	θ_c/°C			
	20	25	30	35
Substrate	$10^4k''$/dm^3 mol^{-1} s^{-1}			
Butane-1,4-diol	3.12 ± 0.16	5.77 ± 0.23	10.92 ± 0.20	20.64 ± 0.31
Pentane-1,5-diol	1.16 ± 0.04	2.31 ± 0.06	5.14 ± 0.10	10.15 ± 0.06
Hexane-1,6-diol	1.70 ± 0.04	3.37 ± 0.09	7.05 ± 0.06	14.18 ± 0.28
3-Methoxybutan-1-ol	7.53 ± 0.08	13.48 ± 0.10	26.93 ± 0.36	46.92 ± 0.30

these plots, for each of the substrates at different temperatures are given in Table 1. Table 2 records the effect of $[H^+]$ on $k_{obs.}$ in the oxidations of butane-1,4- and hexane-1,6-diols. The precipitation of MnO_2 restricted rate measurements at <0.6 mol dm^{-3} $HClO_4$.

TABLE 2

Effect of $[H^+]$ on the observed, first-order rate constant $k_{obs.}$ in the oxidations of butane-1,4- and hexane-1,6-diols at $[Mn^{III}] = 0.002$ mol dm^{-3}, [Substrate] $= 0.2$ mol dm^{-3}, $I = 4$ mol dm^{-3}, and 30 °C

$[HClO_4]$/mol dm^{-3}	0.9	1.2	1.5	1.75	2.25	2.80	3.00	3.50
10^4 $k_{obs.}$/s^{-1}								
(Butane-1,4-diol)	4.74	4.10	3.61	3.27	2.75	2.35	2.20	2.00
(Hexane-1,6-diol)	2.92	2.56	2.26	2.14	1.75	1.50	1.41	1.25

It was noted that the reaction mixtures induced the polymerisation of acrylonitrile, suggesting that free radicals were generated during the course of oxidation. No polymerisation was observed when the monomer was added to separate solutions of Mn^{III} or substrates.

DISCUSSION

The invariance of the reaction rate with varying $[Mn^{II}]$ precludes (*i*) appreciable formation of a manganese(II)-substrate complex, (*ii*) a reversible rate-limiting step involving Mn^{II}, and (*iii*) involvement of Mn^{IV}, formed through reaction (1), in the oxidation. Thus the choice of the reactive manganese(III) species was restricted to either Mn^{3+}(aq) or $[Mn(OH)]^{2+}$(aq) or both. However, the observed dependence of $k_{obs.}$ on $[H^+]$, Figure 3, is more consistent with the assumption that $[Mn(OH)]^{2+}$(aq) is the reactive species. The other important feature to be included in any mechanism is the spectrophotometric evidence for the formation of complex(es) between manganese(III) ions and the substrates. There are two probable mechanisms [10] depending on whether or not the reaction proceeds through disproportionation of the complex(es).

The rate law, for all the reactions studied, at a fixed $[H^+]$ is given by equation (3) where $k_{obs.}$, in view of its dependence on $[H^+]$, is defined by (4) where A and B are

$$-d[Mn^{III}]/dt = k_{obs.}[\text{Substrate}][Mn^{III}] \qquad (3)$$

$$k_{obs.} = A[H^+]/(1 + B[H^+]^{-1}) \qquad (4)$$

empirical constants related to the rate law of the proposed mechanism.

Consistent with the above features of the reaction, the following scheme can be proposed where K_h is the hydrolytic equilibrium constant and β_1 and K_1 are the equilibrium constants for the formation of complexes with Mn^{3+}(aq) and $[Mn(OH)]^{2+}$(aq) respectively. Here R = CH_2OH or MeCH(OMe) for the diol or 3-methoxybutan-1-ol respectively, which is itself represented by S.

$$Mn^{3+}(aq) + H_2O \xrightleftharpoons{K_h} [Mn(OH)]^{2+}(aq) + H^+ \qquad (5)$$

$$Mn^{3+}(aq) + S \xrightleftharpoons{\beta_1} [Mn\{HOCH_2(CH_2)_nR\}]^{3+}(aq) \qquad (6)$$

$$[Mn(OH)]^{2+}(aq) + S \xrightleftharpoons{K_1} [Mn\{OCH_2(CH_2)_nR\}]^{2+}(aq) + H_2O \qquad (7)$$

$$Mn^{3+}(aq) + S \xrightarrow{k} Mn^{II} + O\dot{C}H_2[CH_2]_nR + H^+ \qquad (8)$$

$$[Mn(OH)]^{2+}(aq) + S \xrightarrow{k_2} Mn^{II} + O\dot{C}H_2[CH_2]_nR + H^+ \qquad (9)$$

$$Mn^{III} + \dot{C}H_2O[CH_2]_nR \xrightarrow{\text{fast}} Mn^{II} + HOC[CH_2]_nR + H^+ \qquad (10)$$

In the above scheme the manganese(III)-substrate complex is not considered to be an intermediate. The rate of disappearance of Mn^{III}, from reactions (5)—(10), is given by equation (11).

$$\frac{-d[Mn^{III}]}{dt} = \frac{2(k + k_2K_h[H^+]^{-1})[\text{Substrate}][Mn^{III}]}{1 + K_h[H^+]^{-1} + (\beta_1 + K_1K_h[H^+]^{-1})[\text{Substrate}]} \qquad (11)$$

$$k_{obs.} = \frac{2(k + k_2K_h[H^+]^{-1})[\text{Substrate}]}{1 + K_h[H^+]^{-1} + (\beta_1 + K_1K_h[H^+]^{-1})[\text{Substrate}]} \qquad (12)$$

Since a plot of $k_{obs.}$ against [Substrate] passes through the origin, Figure 2, it is understood that $(1 + K_h[H^+]^{-1}) \gg (\beta_1 + K_1K_h[H^+]^{-1})$[Substrate]. Again, a plot of $k_{obs.}$-$(1 + K_h[H^+]^{-1})$ against $[H^+]^{-1}$, Figure 3, did not give any intercept on the rate axis which indicates that either k is zero or that it is negligibly small in comparison to k_2, the rate-limiting constant for the reaction between $[Mn(OH)]^{2+}$(aq) and the substrate. With these two approximations, equation (12) may be simplified to (13) which is considered to be the final rate equation for the reactions studied. Comparison of equation (13) with (4)

$$k_{obs.} = \frac{2k_2K_h[H^+]^{-1}[\text{Substrate}]}{1 + K_h[H^+]^{-1}} \qquad (13)$$

indicates that the empirical constants A and B are respectively equal to $2k_2K_h$ and K_h. Since the ΔH for K_h is known,[7b] values of K_h were calculated at the relevant temperatures. The value of the rate-limiting constant

TABLE 3

Values ($dm^3\ mol^{-1}\ s^{-1}$) of the rate-limiting constant k_2 (or k_1K_1) for various substrates at different temperatures, $[Mn^{III}] = 0.002\ mol\ dm^{-3}$, $[HClO_4] = 3\ mol\ dm^{-3}$, and $I = 4\ mol\ dm^{-3}$

	$\theta_c/°C$			
	20	25	30	35
Substrate	$10^4k_2/dm^3\ mol^{-1}\ s^{-1}$			
3-Methoxybutan-1-ol	18.25 ± 0.20	28.48 ± 0.21	49.86 ± 0.66	76.78 ± 0.36
Butane-1,4-diol	7.56 ± 0.38	12.19 ± 0.49	20.22 ± 0.36	33.77 ± 0.49
Hexane-1,6-diol	4.12 ± 0.10	7.12 ± 0.19	13.05 ± 0.11	23.20 ± 0.46
Pentane-1,5-diol	2.80 ± 0.10	4.88 ± 0.13	9.52 ± 0.18	16.61 ± 0.10

k_2 was then calculated from the known values of the second-order rate constant k'' reported in Table 1.

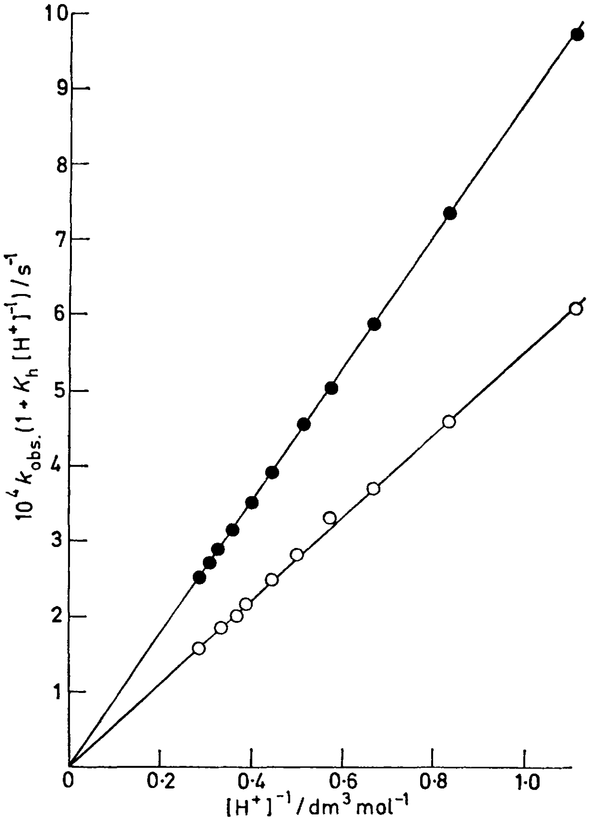

FIGURE 3 Plot of $k_{obs.}(1 + K_h[H^+]^{-1})$ against $[H^+]^{-1}$ at $[Mn^{III}] = 0.002\ mol\ dm^{-3}$; $[Substrate] = 0.2\ mol\ dm^{-3}$, $I = 4\ mol\ dm^{-3}$, and 30 °C. Substrates; (○) butane-1,4-diol; (●) hexane-1,6-diol

These values of k_2 are in Table 3, and values of the thermodynamic parameters calculated from k_2 are in Table 4.

TABLE 4

Activation parameters calculated from the rate-limiting constant for various substrates

Substrate	$\Delta H^‡/kJ\ mol^{-1}$	$\Delta S^‡/J\ K^{-1}\ mol^{-1}$
3-Methoxybutan-1-ol	73 ± 4	−58 ± 13
Butane-1,4-diol	79 ± 3	−45 ± 10
Hexane-1,6-diol	90 ± 3	−13 ± 11
Pentane-1,5-diol	92 ± 2	−8 ± 6

An alternative mechanism might also be suggested on the basis that the complexes formed in reactions (6) and (7) disproportionate in the rate-limiting steps. However, it might be pointed out here that the inclusion of reaction (14) in this mechanism has been avoided in view

$$[Mn\{HOCH_2(CH_2)_nR\}]^{3+}(aq) \longrightarrow Mn^{II} + O\dot{C}H_2[CH_2]_nR + H^+ \quad (14)$$

of the observed dependence of the observed rate constant $k_{obs.}$ on $[H^+]$, as explained earlier. These reactions give

$$Mn^{3+}(aq) + H_2O \xrightleftharpoons{K_h} [Mn(OH)]^{2+}(aq) + H^+ \quad (5)$$

$$Mn^{3+}(aq) + S \xrightleftharpoons{\beta_1} [Mn\{HOCH_2(CH_2)_nR\}]^{3+}(aq) \quad (6)$$

$$[Mn(OH)]^{2+} + S \xrightleftharpoons{K_1} [Mn\{OCH_2(CH_2)_nR\}]^{2+}(aq) + H_2O \quad (7)$$

$$[Mn\{HOCH_2(CH_2)_nR\}]^{3+}(aq) \xrightleftharpoons{K_2} [Mn\{OCH_2(CH_2)_nR\}]^{2+}(aq) + H^+ \quad (15)$$

$$[Mn\{OCH_2(CH_2)_nR\}]^{2+}(aq) \xrightarrow{k_1} Mn^{II} + O\dot{C}H_2[CH_2]_nR + H^+ \quad (16)$$

$$Mn^{III} + O\dot{C}H_2[CH_2]_nR \xrightarrow{\text{fast}} Mn^{II} + HOC[CH_2]_nR + H^+ \quad (10)$$

the rate equation (17).

$$k_{obs.} = \frac{2k_1K_1K_h[H^+]^{-1}[Substrate]}{1 + K_h[H^+]^{-1} + (\beta_1 + K_1K_h[H^+]^{-1})[Substrate]} \quad (17)$$

In view of the comment above that $(1 + K_h[H^+]^{-1}) \gg (\beta_1 + K_1K_h[H^+]^{-1})[S]$, equation (17) reduces to (18) which is identical with (4) where $A = 2k_1K_1K_h$ and $B = K_h$. Comparison of equation (18) with (13) indicates that $k_2 = k_1K_1$. The rate-limiting constant k_1 and the equilibrium formation constant K_1, however, remain inseparable. In view of the rate-limiting reaction (16) which involves an electron transfer within the complex

$$k_{obs.} = \frac{2k_1K_1K_h[H^+]^{-1}[Substrate]}{1 + K_h[H^+]^{-1}} \quad (18)$$

$[Mn\{OCH_2(CH_2)_nR\}]^{2+}(aq)$, there is ambiguity as to its formation. It could be formed through the equilibrium reactions (6) and (15) from $Mn^{3+}(aq)$ or *via* reaction (7) from $[Mn(OH)]^{2+}(aq)$ ion, or by both routes simultaneously. It should be noted that because of the identity $K_1K_h = \beta_1K_2$ a kinetic distinction between the two alternative routes is not possible. This problem, however, could be solved by carrying out careful rate measurements in the period preceding the establishment of the equilibria shown in (6) and (7).

Further perusal of Table 3 indicates that the rate of oxidation of various substrates is in the order: 3-methoxybutan-1-ol > butane-1,4-diol > hexane-1,6-diol > pentane-1,5-diol. However, the energy and entropy of activation (Table 4) follow the opposite sequence: pentane-1,5-diol > hexane-1,6-diol > butane-1,4-diol > 3-methoxybutan-1-ol. A plot of ΔH against $T\Delta S$ was found to be linear which among other things indicates that all the substrates are being oxidised in one fashion and the rate is governed by changes both in the enthalpy and the entropy of activation. Since 3-methoxybutan-1-ol could only act as a unidentate ligand with manganese(III) ion, it must be assumed that the other substrates are also oxidised through the formation of an intermediate in which they act as unidentate ligands.

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