# Autocatalytic Oxidation of Propane-1,2-diol by Soluble Manganese(IV) in Aqueous Phosphoric Acid

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Mechanistic studies on permanganate ion oxidations of unsaturated carboxylic acids in acidic media have revealed that soluble forms of manganese(IV) may in some cases be encountered as intermediates [1–4]. In weakly alkaline solutions, where permanganate oxidations lead to $MnO_2$ formation, yellow solutions of considerable stability often precede the precipitation of this solid [5–8]. There are several reports on soluble manganese(IV) species [9–14], but its oxidation properties have not been investigated. We now report a kinetic study of the oxidation of propane-1,2-diol (PD) by soluble manganese(IV) in phosphoric acid, with special reference to the autocatalytic nature of the process and the effect of added manganese(III).

Manganese(IV) solutions were prepared by shaking freshly precipitated $MnO(OH)_2$ with 3 M phosphoric acid for 30 min, followed by filtering through a G5 glass frit. The brown solutions obtained obey Beer's law and can be analyzed by iodometry. The visible spectrum of soluble manganese(IV) reveals an increasing absorbance [2, 4] with decreasing wavelength from about 550 nm, but no peak is discernible. The treatment of a manganese(IV) solution with an equivalent amount of manganese(II) sulfate in 3 M phosphoric acid results in the quantitative formation of manganese(III), as witnessed by the spectrum with a wide band at 505 nm ($\epsilon$ = 90 $dm^3$ $mol^{-1}$ $cm^{-1}$). The solutions show no light scattering or any other apparent sign of being colloidal in nature.

The organic products of oxidation were determined by analyzing the precipitate obtained upon adding 2,4-dinitrophenylhydrazine in 30% perchloric acid. Thin-layer chromatography (Merck DC-Alufolien Cellulose) with n-hexane or cyclohexane (both saturated with DMSO) gave two major products, which were shown to be the 2,4-dinitrophenylhydrazones of formaldehyde and acetaldehyde. Mass spectroscopy of the precipitate revealed the expected molecular ions 210 and 224. The same products were identified by $^1H$-NMR spectroscopy of the precipitate dissolved in DMSO-$d_6$. The minor component was found to be the osazone derived from either hydroxyacetone or lactic aldehyde (mass spectroscopy). These compounds give identical osazones.

The kinetics of PD oxidation were followed spectrophotometrically, monitoring the disappearance of manganese(IV) at 390 nm, where manganese(III) effectively does not absorb. The reduction of manganese(IV) leads to manganese(III), whose accumulation was measured at 505 nm. Kinetic runs were carried out in excess PD in 3 M $H_3PO_4$. Initial rates were utilized throughout.

Typical absorbance *vs.* time curves for the reaction of manganese(IV) with PD are displayed in Fig. 1, illustrating the effect of added manganese(III). In the absence of Mn(III), the Mn(IV) concentration decreases according to a sigmoid curve with a considerable induction period, followed by an autocatalytic increase in the rate. Increasing concentrations of added Mn(III) gradually eliminate the induction period (curves 2–9).

This would seem to imply that the active oxidant is in fact Mn(III) formed slowly from the initial Mn(IV). Surprisingly, PD is practically unreactive on

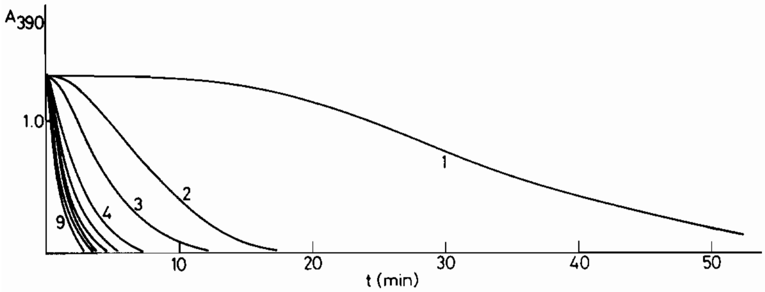

Fig. 1. Decrease of absorbance in time at 390 n. $[Mn(IV)]_0$ = 1.00 × $10^{-3}$ mol $dm^{-3}$; $[PD]_0$ = 0.10 mol $dm^{-3}$; $[H_3PO_4]$ = 3.0 mol $dm^{-3}$; T = 25 °C. Curves 1 through 9 correspond to initial manganese(III) concentrations of zero, 1, 2, 3, 4, 5, 6, 7 and 8 mmol $dm^{-3}$, respectively.

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this time scale toward Mn(III). Formaldehyde and acetaldehyde, the first products of Pd oxidation, were found to be unreactive (under comparable conditions) toward both manganese(IV) and manganese(III). This excludes the possibility of formation of a more reactive (oxidized) substrate as the source of autocatalysis.

The kinetic curves of Fig. 1, which bear no induction period (greater than 4-fold excess of Mn(III)), yield straight lines upon plotting $[Mn(IV)]^{1/2}$ against time (Fig. 2) whereas attempted first order plots are definitely curved. The rate equation for PD oxidation can thus be written as

$$-\frac{d[Mn(IV)]}{dt} = w_0 + k[Mn(IV)]^{1/2}[Mn(III)]^n[PD]^m \qquad (1)$$

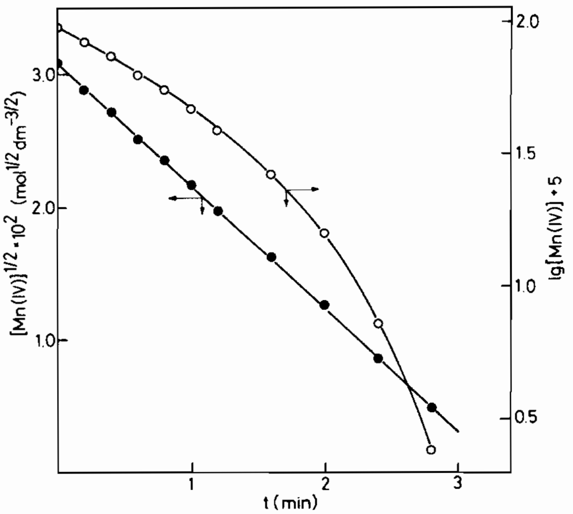


Fig. 2. Plot of lg[Mn(IV)] and $[Mn(IV)]^{1/2}$ *versus* time. $[Mn(IV)]_0 = 1.00 \times 10^{-3}$ mol dm$^{-3}$; $[Mn(III)]_0 = 5.0 \times 10^{-3}$ mol dm$^{-3}$; $[PD]_0 = 0.10$ mol dm$^{-3}$; T = 25 °C.

where $w_0$ is the initial rate in the absence of Mn(III), and $n$ and $m$ are constants to be determined experimentally. In the absence of an induction period, $w_0$ can be neglected, and eqn. (1) integrates to

$$[Mn(IV)]_0^{1/2} - [Mn(IV)]^{1/2} = \frac{k}{2}[Mn(III)]^n[PD]^m \qquad (2)$$

Taking finite difference with respect to time yields

$$\frac{\Delta[Mn(IV)]^{1/2}}{\Delta t} = \frac{k}{2}[Mn(III)]^n[PD]^m \qquad (3)$$

Plots of the left-hand side of eqn. (3) against the concentration of Mn(III) and PD yielded straight lines with zero intercepts, thus $n = m = 1$. From the slopes of these lines $k = 34 \pm 0.5$ dm$^{2/3}$ mol$^{-2/3}$ min$^{-1}$.

Kinetic law (1) is consistent also with the fact that the rate of Mn(IV) consumption measured at the first half-life, $w_{1/2}$, depends on the initial Mn(IV) concentration, provided that no manganese(III) has been added. Neglected $w_0$, and using the condition

$$[Mn(IV)] = [Mn(III)] = C_0/2 \qquad (4)$$

we have

$$w_{1/2} = \frac{k}{2^{3/2}}[PD]C_0^{3/2} \qquad (5)$$

Equation (5) was found to be valid at initial Mn(IV) concentrations of (0.5–6.0) × $10^{-3}$ mol dm$^{-3}$, which provides additional proof for rate law (1).

The observed kinetic behaviour requires a mechanism that is capable of accounting for the crucial rate-enhancing effect of Mn(III), and the kinetic order of 1/2 with respect to Mn(IV). The following set of reactions is consistent with the available kinetic information:

$$[Mn(IV)]_2 \overset{K_a}{\rightleftharpoons} 2Mn(IV) \qquad (a)$$

$$Mn(IV) + PD \xrightarrow[+H_2O]{w_0} CH_2(OH)_2 + CH_3CHO + Mn(II) + 2H^+ \qquad (b)$$

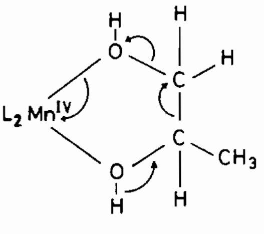
$$Mn(IV) + Mn(II) \xrightarrow{fast} 2Mn(III) \qquad (c)$$

$$Mn(III) + PD \overset{K_d}{\rightleftharpoons} Mn(III)PD \qquad (d)$$

$$Mn(III)PD + Mn(IV) \xrightarrow{k_e} Mn(IV)PD + Mn(III) \qquad (e)$$

$$Mn(IV)PD \xrightarrow{H_2O} CH_2(OH)_2 + CH_3CHO + Mn(II) + 2H^+ \qquad (f)$$

where Mn(IV) PD is



$L = HPO_4^{2-}$

Manganese(IV), which is predominantly dimeric in solution [13, 15, 16] should first dissociate to a reactive monomeric species, which then reacts either with free PD in a slow process (rate $w_0$) or, in the presence of Mn(III), with the [Mn(III)PD] chelate, step (e). If the oxidation of [Mn(III)PD] by Mn(IV) is faster than reaction (b), then the rate should increase in an autocatalytic fashion from $w_0$ (Fig. 1, curve 1). Added Mn(III) eliminates this behaviour, as [Mn(III)-PD] is already present initially (curves 2–9). Any Mn(II) formed undergoes rapid conproportionation with Mn(IV), step (c).

If the concentration of monomeric Mn(IV) and of [Mn(III)PD] are small, the rate law corresponding to the proposed mechanism is

$$-\frac{d[\mathrm{Mn(IV)}]}{dt} = w_0 + k_e K_a^{1/2} K_d [\mathrm{Mn(IV)}]^{1/2} [\mathrm{Mn(III)}][\mathrm{PD}] \qquad (6)$$

in agreement with the experimental kinetic eqn. (1), in which $k = k_e K_a^{1/2} K_d$.

The key to the observed pattern seems to be the difference in the lability of manganese(IV) and manganese(III), a $d^3$ and $d^4$ system, respectively. Oxidative C–C cleavage of PD, as in the well-known oxalate system [17], requires prior complexation to the oxidant. This occurs readily with the labile Mn(III), step (d), but is very slow with the inert Mn(IV), first step of process (b). However, C–C cleavage in the Mn(III)PD complex is apparently very slow, therefore the central ion is first converted to Mn(IV) via outer-sphere electron transfer, (e), followed by a 2-electron step yielding the products (f).

The exact identity of the dimeric manganese(IV) species is not known at present. It is likely to be a $\mu_2$-oxo- or $\mu_2$-hydroxo-bridged dinuclear phosphato complex of the type described with 1,10-phenanthroline ligands [13].

Work is in progress on the nature of other oxidations with soluble manganese(IV) species.

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