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OXIDATIONS OF BIFUNCTIONAL SUBSTRATES WITH SOLUBLE MANGANESE(IV) PHOSPHATE

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Abstract—Water-soluble manganese(IV) phosphate which is capable of auto-catalytic oxidation of compounds containing two functional groups, was prepared in 3 M phosphoric acid. The reaction was studied with an ethylene glycol–glycollic aldehyde–glycollic acid–glyoxylic acid sequence of compounds, and a reaction mechanism is proposed. The autocatalytic effect is due to manganese(III), which is in itself much less reactive to these substrates. The reaction order of 0.5 related to manganese(IV) can be explained by the existence of binuclear complexes.

In our previous papers[1,2] we reported the preparation of soluble manganese(IV) phosphate. It can be generally stated that the oxidation mechanism of manganese(IV) has not been fully clarified. It may be expected that the investigations performed under homogeneous conditions might be adapted under heterogeneous conditions as well, which may contribute to the elucidation of the oxidation mechanism of useful oxidants, such as solid MnO_2. At the same time, manganese(IV) generally appears in permanganate oxidations. According to the studies of Freeman[3,4] and Perez-Benito,[5–10] it is present in colloidal form (at *ca* pH 6–7), stabilized by the phosphate anion applied as a buffer. At the moment of formation, however, manganese(IV) must appear in molecular dispersion, therefore, knowledge of the behaviour of dissolved manganese(IV) is also essential for the elucidation of the complete mechanism of permanganate reactions.

Manganese(IV) phosphate was found to be non-colloidal according to ultracentrifugal and electron microscope examinations.[1] It cannot be definitely stated that manganese(IV) has molecular dispersity in this case, but particle size was definitely under 2 nm. However, by monitoring the concentration spectrophotometrically we could observe first-order kinetics in several oxidation reactions. This points to the existence of mono- or multinuclear complexes, or chain-like associates, at most, where every Mn atom can participate in light absorption.[2]

Manganese(IV) phosphate is a strong oxidizing agent, which can react according to two types of mechanisms. It oxidizes simple substrates, such as formaldehyde, formic acid and α,β-unsaturated alcohols according to first-order kinetics. On the other hand, it autocatalytically oxidizes substrates that are able to form chelate complexes.[1] For example, it does not attack single hydroxyl groups, but it does oxidize glycols. However, it does not oxidize 1,4-butanediol, because owing to the great distance no chelate complex can be formed. The same can be observed for carboxylic acids. The situation is similar in the case of carbonyl compounds, since, although their monofunctional derivatives can be oxidized, bifunctional derivatives show a considerable increase in reactivity. The present paper deals with the latter mechanism in the sequence of compounds ethylene glycol–glycollic aldehyde–glycollic acid–glyoxylic acid.

EXPERIMENTAL

All substrates were Fluka purest grade and phosphoric acid was Rudipont electronic grade. In order to obtain manganese(IV) phosphate, we dissolved MnO_2 freshly prepared by reduction of permanganate with sodium formate in H_3PO_4 (3 M), then filtered it on a glass filter of G5 porosity, as previously given in detail.[1] The brown coloured solution strictly obeyed the Beer's law.

The substrates were also dissolved in H_3PO_4 (3 M) in order to maintain phosphoric acid concentration at 3 M after the mixing of reactants. Mn^{III} was produced *in situ* by the reaction of Mn^{2+} with Mn^{IV}.

Kinetic measurements were performed on a Hewlett–Packard (8452A) spectrophotometer, connected to a stopped-flow device developed in our laboratory. Another Hewlett–Packard 9000-300 computer directly coupled to the spectrophotometer was used for the calculations. Each value was the average of at least five individual measurements.

RESULTS AND DISCUSSION

The following notations have been introduced. Manganese(IV) phosphate is denoted as Mn^{IV}; manganese(III), which should also be present in some form of phosphate complex [otherwise it would undergo disproportionation at this pH value (pH 0.78)], is designated as Mn^{III}.

Kinetic experiments were carried out in H_3PO_4 (3 M) in the presence of the substrate in great excess. The decay of Mn^{IV} was followed spectrophotometrically at 390 nm. Sigmoid-shaped kinetic curves were detected: the reaction accelerated after a slow stage. The reduction product of Mn^{IV} was Mn^{III}, which reacted rather slowly.

However, when Mn^{III} was previously added to the system, the auto-catalytic character decreased and practically ceased at $[Mn^{III}]_0 = 5[Mn^{IV}]_0$. Thus, the catalytic effect was exerted by Mn^{III}. Under such conditions, the $[Mn^{IV}]^{1/2}$ vs t plots gave straight lines, indicating that the reaction was 0.5 order with respect to Mn^{IV}.

Manganese(IV) is known to have several water soluble complexes.[11-21] Shilov[14] also observed 0.5 order in his kinetic investigations, which he explained by the dissociation of the binuclear complex into reactive mononuclear complexes. If the equilibrium is strongly shifted to the left, then:

$$(Mn^{IV})_2 \xleftrightarrow{K_1} 2\,Mn^{IV}$$

$$K_1 = \frac{[Mn^{IV}]^2}{[(Mn^{IV})_2]} = \frac{[Mn^{IV}]^2}{\dfrac{[Mn^{IV}]_T}{2} - [Mn^{IV}]} \approx \frac{[Mn^{IV}]^2}{\dfrac{[Mn^{IV}]_T}{2}} \tag{1}$$

and we obtain

$$[Mn^{IV}] = \sqrt{\frac{K_1}{2}}\,[Mn^{IV}]_T^{1/2}, \tag{2}$$

where $(Mn^{IV})_2$ denotes the dimer, while $[Mn^{IV}]_T$ is the total concentration of Mn^{IV} measured spectrophotometrically (or iodometrically), that is:

$$[Mn^{IV}]_T = 2[(Mn^{IV})_2] + [Mn^{IV}].$$

It should be noted that the same 0.5 order could also be obtained when Mn^{IV} formed longer chains. Denoting this with $(Mn^{IV})_n$:

$$(Mn^{IV})_n \xleftrightarrow{K'_1} (Mn^{IV})_{n-1} + Mn^{IV}$$

$$K'_1 = \frac{[(Mn^{IV})_{n-1}][Mn^{IV}]}{[(Mn^{IV})_n]} = \frac{[Mn^{IV}]^2}{\dfrac{[Mn^{IV}]_T}{n} - [Mn^{IV}]} \approx \frac{[Mn^{IV}]^2}{\dfrac{[Mn^{IV}]_T}{n}},$$

while $[(Mn^{IV})_{n-1}] = [Mn^{IV}]$;

consequently:

$$[Mn^{IV}] = \sqrt{\frac{K'_1}{n}}\,[Mn^{IV}]_T^{1/2}$$

was obtained again.

Considering the strong complex-forming tendency of manganese(III) towards bidentate ligands,[22] it seemed plausible that it would also rapidly form complexes with the substrates studied by us. Let us denote this complex with $(Mn^{III}\cdot S)$. Then, the following mechanism is obtained for the binuclear $(Mn^{IV})_2$ complex:

$$(Mn^{IV})_2 \xleftrightarrow{K_1} 2Mn^{IV} \tag{3}$$

$$Mn^{IV} + S \xrightarrow{W_1} Mn^{2+} + P \tag{4}$$

or

$$(Mn^{IV})_2 + S \xrightarrow{W_1} 2Mn^{III} + P \tag{4a}$$

$$Mn^{IV} + Mn^{2+} \xrightarrow{\text{fast}} 2Mn^{III} \tag{5}$$

or

$$(Mn^{IV})_2 + 2Mn^{2+} \xrightarrow{\text{fast}} 4Mn^{III} \tag{5a}$$

$$Mn^{III} + S \xleftrightarrow{K_2} (Mn^{III}\cdot S) \tag{6}$$

$$\mathrm{Mn^{IV}} + (\mathrm{Mn^{III}} \cdot \mathrm{S}) \xrightarrow{k_e} \mathrm{Mn^{2+}} + \mathrm{Mn^{III}} + \mathrm{P} \tag{7}$$

and (5) or (5a), again.

We measured the rates of reactions (5) or (5a) and indeed obtained[2] a high value of 970 $\mathrm{M^{-1}\ s^{-1}}$ for the rate constant. Considering that:

$$K_2 = \frac{[(\mathrm{Mn^{III}} \cdot \mathrm{S})]}{[\mathrm{Mn^{III}}][\mathrm{S}]} = \frac{[(\mathrm{Mn^{III}} \cdot \mathrm{S})]}{\{[\mathrm{Mn^{III}}]_{\mathrm{T}} - [(\mathrm{Mn^{III}} \cdot \mathrm{S})]\}[\mathrm{S}]},$$

and from this

$$[(\mathrm{Mn^{III}} \cdot \mathrm{S})] = \frac{K_2[\mathrm{S}]}{K_2[\mathrm{S}]+1}[\mathrm{Mn^{III}}]_{\mathrm{T}} \tag{8}$$

where $[\mathrm{Mn^{III}}]_{\mathrm{T}}$ is the total concentration of $\mathrm{Mn^{III}}$, the kinetic equation is:

$$-\frac{\mathrm{d}[\mathrm{Mn^{IV}}]_{\mathrm{T}}}{\mathrm{d}t} = W_{\mathrm{i}} + 2k_{\mathrm{e}}\sqrt{\frac{K_1}{2}}\frac{K_2[\mathrm{S}]}{K_2[\mathrm{S}]+1} \times [\mathrm{Mn^{III}}]_{\mathrm{T}}[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2}. \tag{9}$$

If $\mathrm{Mn^{III}}$ was previously added to the system, its concentration at any moment was $[\mathrm{Mn^{III}}]_{\mathrm{T}} = [\mathrm{Mn^{III}}]_{\mathrm{To}} + [\mathrm{Mn^{IV}}]_{\mathrm{To}} - [\mathrm{Mn^{IV}}]_{\mathrm{T}}$ and thus, eq. (9) assumes the form:

$$-\frac{\mathrm{d}[\mathrm{Mn^{IV}}]_{\mathrm{T}}}{\mathrm{d}t} = W_{\mathrm{i}} + k\frac{K_2[\mathrm{S}]}{K_2[\mathrm{S}]+1}(C[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2} + [\mathrm{Mn^{IV}}]_{\mathrm{T}}^{3/2}), \tag{10}$$

where the subscript o relates to initial concentrations:

$$C = [\mathrm{Mn^{III}}]_{\mathrm{To}} + [\mathrm{Mn^{IV}}]_{\mathrm{To}} \quad \text{and} \quad k = 2k_{\mathrm{e}}\sqrt{\frac{K_1}{2}}.$$

In our experience, if $[\mathrm{Mn^{III}}]_{\mathrm{To}} \geqslant 2[\mathrm{Mn^{IV}}]_{\mathrm{To}}$, then W_{i} can be neglected, thus, in accordance with Perez-Benito[23] the integrated form of (10) is:

$$\sqrt{C}k\frac{K_2[\mathrm{S}]}{K_2[\mathrm{S}]+1}t = \ln\frac{\sqrt{C}+[\mathrm{Mn^{IV}}]_{\mathrm{To}}^{1/2}}{\sqrt{C}-[\mathrm{Mn^{IV}}]_{\mathrm{To}}^{1/2}} - \ln\frac{\sqrt{C}+[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2}}{\sqrt{C}-[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2}}. \tag{11}$$

If the measurements were performed with different $[\mathrm{Mn^{III}}]_{\mathrm{To}}$ and [S] concentrations, the plots:

$$\frac{1}{\sqrt{C}}\ln\frac{\sqrt{C}+[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2}}{\sqrt{C}-[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2}} \quad \text{vs} \quad t \tag{12}$$

always gave straight lines, the slopes of which are denoted as m_s. As can be seen from eq. (11):

$$-m_s = k\frac{K_2[\mathrm{S}]}{K_2[\mathrm{S}]+1}. \tag{13}$$

The m_s values obtained at initial concentrations of $[\mathrm{Mn^{IV}}]_{\mathrm{To}} = 1 \times 10^{-3}$ M and $[\mathrm{Mn^{III}}]_{\mathrm{To}} = 2 \times 10^{-3}$ M are listed in Table 1.

At $[\mathrm{Mn^{III}}]_{\mathrm{To}} = 3 \times 10^{-3}$ M and 5×10^{-3} M initial concentrations, eq. (12) also gave straight lines with the same slopes, verifying again the validity of first-order with respect to $\mathrm{Mn^{III}}$.

The reciprocal value of (13) is:

$$-\frac{1}{m_s} = \frac{1}{kK_2}\frac{1}{[\mathrm{S}]} + \frac{1}{k} \tag{14}$$

i.e. the $1/m_s$ vs 1/[S] plot gave a straight line for each substrate, and from the intercept and slope of this plot k and K_2 can be calculated. Naturally, the same results were obtained by the direct fitting of (13). The values obtained are listed in Table 2.

We must add the following supplements and explanations to the above observations.

(a) Equilibrium of (3) and (6) are assumed to set in rapidly.

(b) The difference between the absorption coefficients of monomer $\mathrm{Mn^{IV}}$ and dimer $(\mathrm{Mn^{IV}})_2$ may be considered negligible.[13,17]

(c) Similarly, one may neglect the difference between the absorption coefficients of $\mathrm{Mn^{III}}$ and $(\mathrm{Mn^{III}} \cdot \mathrm{S})$. This is justified by the observation that when mixing the substrates with the solution of $\mathrm{Mn^{III}}$ we could see no change in the absorbance at the initial moment.

(d) The contribution of W_{i} to the consumption of $\mathrm{Mn^{IV}}$ is below 1% if $[\mathrm{Mn^{III}}]_{\mathrm{To}} \geqslant 2 \times 10^{-3}$. Although we do not deal here with this initial reaction, it should be noted that both processes (4) and (4a) seem to proceed, since a 0.8 order dependence on $[\mathrm{Mn^{IV}}]$ was observed.

(e) In the case of high $[\mathrm{Mn^{III}}]_{\mathrm{To}}$ eq. (11) assumes the form of:

$$[\mathrm{Mn^{IV}}]_{\mathrm{To}}^{1/2} - [\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2} = \frac{k}{2}\frac{K_2[\mathrm{S}]}{K_2[\mathrm{S}]+1}t, \tag{15}$$

which means that the $[\mathrm{Mn^{IV}}]_{\mathrm{T}}^{1/2}$ vs t plot gives a straight line. Actually, in the case of $[\mathrm{Mn^{III}}]_{\mathrm{To}} = 5[\mathrm{Mn^{IV}}]_{\mathrm{To}}$, the difference of m_s slopes obtained according to (11) and (15) was 6%.

(f) The present publication does not deal with the oxidation of oxalic acid, the final member of the sequence, owing to the several anomalies emerged in connection with this reaction. It could be stated that oxalic acid reacted more slowly than glyoxylic acid, therefore, it did not interfere within limits of error with the kinetic behaviour of the latter compound.

Table 1. Dependence of $1/m_s$ values on 1/[Substrate], see eqs (13) and (14); $[H_3PO_4] = 3.0$ M; $[\text{Mn}^{\text{IV}}]_{\text{T}_0} = 1.0 \times 10^{-3}$ M; $[\text{Mn}^{\text{III}}]_{\text{T}_0} = 2.0 \times 10^{-3}$ M; 25°C

[Substrate] (mol dm^{-3})	1/[Substrate]	$1/m_s$ Ethylene glycol	Glycollic aldehyde	Glycollic acid	Glyoxylic acid
0.025	40	—	25.6	—	1.10
0.050	20	147	13.3	19.3	0.68
0.075	13.33	105	9.2	14.9	0.58
0.10	10	81.8	7.6	13.0	0.519
0.20	5	42.1	4.2	9.2	0.375
0.40	2.5	24.3	2.9	6.67	0.335
0.60	1.67	19.1	2.29	6.33	0.313
0.80	1.25	16.0	2.07	5.81	0.302
1.00	1.0	13.8	2.00	5.71	0.292

(g) In the reaction of ethylene glycol, the intermediate product glycollic aldehyde reacted further at a higher rate, but, owing to the concentration ratios, this reaction practically did not affect the kinetic picture of ethylene glycol. This holds for the glycollic acid–glyoxylic acid pair as well.

(h) The reaction of Mn^{III} with ethylene glycol and glycollic acid was very slow, but in the case of glycollic aldehyde and glyoxylic acid the reaction proceeded at a measurable rate. After reaching equilibrium (6), the complex broke apart oxidatively:

$$[(\text{Mn}^{\text{III}} \cdot \text{S})] \xrightarrow{k_3} \text{Mn}^{2+} + \text{S}\cdot \quad (16)$$

$$\text{Mn}^{\text{III}} + \text{S}\cdot \xrightarrow{\text{fast}} \text{Mn}^{2+} + \text{P}. \quad (17)$$

Consequently:

$$-\frac{\text{d}[\text{Mn}^{\text{III}}]_{\text{T}}}{\text{d}t} = 2k_3 \frac{K_2[\text{S}]}{K_2[\text{S}]+1}[\text{Mn}^{\text{III}}]_{\text{T}}. \quad (18)$$

On plotting the integrated form of eq. (18) we found that:

$$\tfrac{1}{2}\ln[\text{Mn}^{\text{III}}]_{\text{T}} \quad \text{vs} \quad t$$

indeed gave straight lines. From the dependence of the slopes on [S], k_3 and K_2 could be calculated similarly to (13) and (14).

The value of K_2 was found to be identical within limits of error with the value obtained with the oxidation of Mn^{IV}, which further supports the mechanism for Mn^{IV} given by eqs (3)–(7). The k_3 values, also listed in Table 2, are by orders of magnitude lower than the corresponding k values, therefore, the kinetics of oxidation with Mn^{IV} was affected by reactions (16) and (17) only to a negligible degree.

(i) As can be seen from the data of Table 2, the K_2 values vary within a relatively small interval. Upon the effect of the carboxylic group, the stability constant naturally increases. At the same time, both glycollic aldehyde and glyoxylic acid are known to be present in hydrated form in aqueous solution,[24–26] thus, in the case of ethylene glycol–glycollic aldehyde and glycollic acid–glyoxylic acid pairs, the higher stability constant of a geminal glycol is reflected by the increase of K_2.

In summary, it can be established that Mn^{IV} oxidizes bifunctional substrates. In all these cases, oxidation proceeds autocatalytically with the intervention of Mn^{III}, although Mn^{III} is much less reactive to these substrates.

As can be seen from the literature,[11–21] most water-soluble manganese(IV) compounds exist in the form of $\text{Mn}^{\text{IV,IV}}$ or $\text{Mn}^{\text{IV,III}}$ bis-μ-oxo binuclear complexes. Sarneski *et al.*[20,21] studied in detail the disproportionation of the mixed bipyridyl phosphate complex in aqueous phosphoric acid and the related structural changes, and established that only the Mn^{III} complex was mononuclear. It seems obvious that any other bidentate ligand can form mixed complexes of the same structure with a lower value of stability constant (K_2). In analogy with Sarneski:

Table 2. The stability constants of $(\text{Mn}^{\text{III}} \cdot \text{S})$ complex [see eq. (6)] and the rate constants [see eqs (10) and (16)]

	K_2 (M^{-1})	k (M$^{-1/2}$ s^{-1})	$10^3 k_3$ (s^{-1})
Ethylene glycol	0.92	0.15	~0
Glycollic aldehyde	2.3	0.73	2.4
Glycollic acid	6.6	0.20	~0
Glyoxylic acid	12.7	3.65	46

Estimated accuracy ±5%.

the ($Mn^{III}\cdot S$) complex may appear as $Mn^{III}(S)(HPO_4)(H_2PO_4)$ and the $(Mn^{IV})_2$ as $[Mn_2^{IV}(\mu\text{-}O)_2(\mu_2\text{-}HPO_4)(H_2PO_4)_2]$

Regarding the actual oxidation step we must rely on assumptions. By all means, the 0.5 order dependence on $[Mn^{IV}]_T$ points to the appearance of Mn^{IV} in mononuclear form. The interaction of the latter with ($Mn^{III}\cdot S$) may produce a binuclear complex, such as $(H_2PO_4)(S)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(H_2PO_4)_2$. Then the oxidation may take place by an inner-sphere mechanism.

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