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Oxidation of phosphorous acid and ethyl phosphonates by permanganate

Éva Záhonyi-Budó and László I. Simándi
Central Research Institute for Chemistry, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest (Hungary)

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Abstract

The kinetics of the permanganate oxidation of P(III) compounds (phosphorous acid, mono- and diethyl phosphonate and their anions) have been investigated at pH 0–8.3 and pH > 12. Results indicate that attack of the oxidant on the P–H bond is rate-determining for all substrates in both acidic and basic solutions. Deprotonation of the P–H bond prior to oxidation does not take place with the exception of diethyl phosphonate at pH > 7, where the reaction proceeds via two parallel pathways. Although the products of the reaction do vary with pH, they can all be derived from the same Mn(V) intermediate. There is evidence to suggest that mixed anhydride formation of the type Mn^{V}–O–P^{III} may play an essential role in the formation of the final products.

Introduction

In previous papers we have proposed that the oxidation of hypophosphorous acid by permanganate [1] and the induced oxidation of phosphorous acid in the Mn(VII)–As(III)–P(III) system [2] involves the formation of the same Mn^{V}–O–P^{III} intermediate which can be regarded as a mixed anhydride of hypomanganous and phosphorous acids. We have now extended studies to the permanganate oxidation of various P(III) compounds which differ in their ability for anhydride formation. We have chosen phosphorous (phosphonic) acid, $HP(O)(OH)_2$, and its ethyl esters as substrates. They are known to be oxidized by permanganate ion [3], but kinetic studies on these reactions have not yet been reported, except for H_3PO_3 in strongly acidic solution [4].

Experimental

Kinetic measurements were carried out by recording successive UV–Vis spectra on a Hewlett-Packard 8452A diode array spectrophotometer, which was combined with a Hi-Tech Scientific stopped flow type accessory for fast runs.

Analytical grade chemicals and doubly distilled water were used throughout. Diethyl phosphonate was purified by vacuum distillation. Aqueous solution of monoethyl phosphonate was prepared from the diethyl ester.

Reactions were run in buffered solutions, and in the presence of pyrophosphate in at least a ten-fold excess over Mn(VII) to avoid disproportionation of the Mn(III) formed. Ionic strength was kept constant. The stable manganese products: Mn(III), Mn(IV) (in a soluble or colloidal form) and Mn(VI) were identified spectrophotometrically and by redox titrations. Immediate MnO_2 deposition between pH 8.3 and 12 precluded kinetic measurements in this pH region.

Results and discussion

Reaction of phosphorous acid and phosphites with permanganate

The stoichiometry of the reaction between MnO_4^- and the phosphorous acid/phosphites system depends on the pH. The following three limiting cases can be identified by spectrophotometric titration.

In the pH range of 0–7.2, in the presence of pyrophosphate (pyr), phosphorous acid and phosphites reduce permanganate to Mn(III)

$$\mathrm{Mn(VII)} + 2\mathrm{P(III)} \xrightarrow[\mathrm{pyr}]{\mathrm{pH}\ 0\text{–}7.2} \mathrm{Mn(III)} + 2\mathrm{P(V)} \qquad (1)$$

where P(III) is the sum of H_3PO_3, $H_2PO_3^-$ and HPO_3^{2-}, Mn(III) is the pyrophosphatomanganese(III) and P(V) is phosphoric acid or its ionized forms.

At pH ~ 8 the formation of Mn(IV), whereas at pH > 12 that of Mn(VI) is predominant

$$2\mathrm{Mn(VII)} + 3\mathrm{P(III)} \xrightarrow{\mathrm{pH} \sim 8} 2\mathrm{Mn(IV)} + 3\mathrm{P(V)} \qquad (2)$$

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$$2\mathrm{Mn(VII)} + \mathrm{P(III)} \xrightarrow{\mathrm{pH}>12} 2\mathrm{Mn(VI)} + \mathrm{P(V)} \quad (3)$$

Kinetic investigation of this reaction was carried out by following the disappearance of Mn(VII) under pseudo-first-order conditions, at a 50–200-fold excess of P(III). The rate law was found to be first order with respect to both Mn(VII) and P(III), as demonstrated by the data in Table 1

$$w = -\frac{d[\mathrm{Mn(VII)}]}{dt} = k_{\mathrm{obs}}[\mathrm{Mn(VII)}]$$

$$= nk[\mathrm{P(III)}]_0[\mathrm{Mn(VII)}] \quad (4)$$

where n is a stoichiometric factor.

The pH-dependence of rate constant k is shown in Fig. 1. Between pH 0 and 7.2 the observed behaviour is consistent with a mechanism involving two fast protonation equilibria (5) and (6) of the dibasic phosphorous acid (for pK_as, see Table 2), followed by rate-determining reduction of Mn(VII) by each of the three P(III) species, as given by eqns. (7)–(9).

TABLE 1. Kinetic data for phosphorous acid oxidation ($[\mathrm{Mn(VII)}]_0 = 4.0\times10^{-4}$ M, $\mu = 1.0$ M, $t = 22$ °C)

No.	pH	$[\mathrm{P(III)}]_0\times10^2$ (M)	$k_{\mathrm{obs}}\times10^{3\,a}$ ($\mathrm{s^{-1}}$)	n	k^a ($\mathrm{M^{-1}\ s^{-1}}$)
1	3.64^b	2.00	2.78	1	0.139
2		4.00	5.43	1	0.136
3		6.00	7.84	1	0.131
4		8.00	10.53	1	0.132
5	12.36	2.00	31.9	2	0.798
6		3.00	47.4	2	0.790
7		6.00	94.8	2	0.790
8		8.00	125.0	2	0.781

^{a}Pseudo-first-order rate constant, $k_{\mathrm{obs}} = nk\ [\mathrm{P(III)}]_0$, determined from the integrated form of eqn. (4). ^{b}[pyr] $= 8\times10^{-3}$ M.

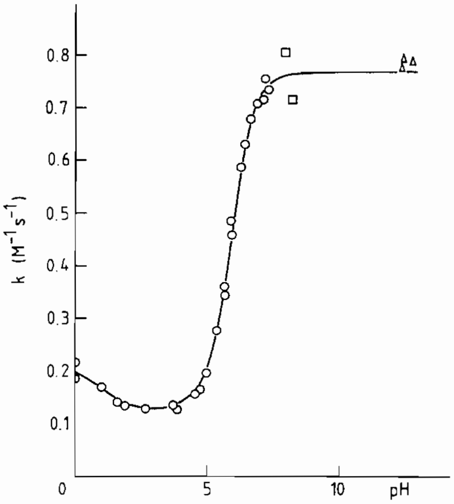


Fig. 1. pH dependence of the second-order rate constant (k) in the oxidation of phosphorous acid by permanganate ($[\mathrm{Mn(VII)}]_0 = 4\times10^{-4}$ M, $[\mathrm{P(III)}]_0 = 0.04$ M; [pyr] $= 8\times10^{-3}$ M). The curve was calculated from eqn. (10), using the values in Table 2 for the rate and dissociation constants and $n = 1$ (○), 2/3 (□), 2 (△).

$$\mathrm{H_3PO_3} \overset{K_1}{\rightleftharpoons} \mathrm{H_2PO_3^-} + \mathrm{H^+} \quad (5)$$

$$\mathrm{H_2PO_3} \overset{K_2}{\rightleftharpoons} \mathrm{HPO_3^{2-}} + \mathrm{H^+} \quad (6)$$

fast equilibria

$$\mathrm{H_3PO_3} + \mathrm{Mn(VII)} \xrightarrow{k_1} \mathrm{Mn(V)} + \mathrm{P(V)} \quad (7)$$

$$\mathrm{H_2PO_2^-} + \mathrm{Mn(VII)} \xrightarrow{k_2} \mathrm{Mn(V)} + \mathrm{P(V)} \quad (8)$$

$$\mathrm{HPO_3^{2-}} + \mathrm{Mn(VII)} \xrightarrow{k_3} \mathrm{Mn(V)} + \mathrm{P(V)} \quad (9)$$

rate determining steps

Protonation of the permanganate ion ($\mathrm{p}K_{\mathrm{HMnO_4}} = -2.25$ [7]) is not likely to influence the rate at the acidities used in this work. If mechanism (5)–(9) is valid, by the usual treatment one can derive eqn. (10) for the dependence of k on the H$^+$-ion concentration.

$$k = \frac{k_1[\mathrm{H^+}]^2 + k_2K_1[\mathrm{H^+}] + k_3K_1K_2}{K_1K_2 + K_1[\mathrm{H^+}] + [\mathrm{H^+}]^2} \quad (10)$$

Least-squares fitting of eqn. (10) to the kinetic results shown in Fig. 1 was carried out by fixing k_2 at 0.130 $\mathrm{M^{-1}\ s^{-1}}$ (which is the average of k at pH 2–4) and using the reported value of $K_1 = 0.107$ M [5]. The values of k_1, k_3 and K_2 were allowed to vary. The resolved rate and equilibrium constants are listed in Table 2. Significantly, K_2 determined kinetically is in good agreement with the literature value. Calculation of the pH-profile using eqn. (10) and these values (solid line in Fig. 1) demonstrates consistency with the proposed mechanism.

The fate of the Mn(V) intermediate depends on the pH, as shown by the observed products of permanganate reduction. It seems to disappear rapidly via the following three routes, whose contributions are governed by the pH.

TABLE 2. Second-order rate constants for oxidations by permanganate ion and pK_a values for the P(III) compounds discussed in the paper ($t = 22$ °C, $\mu = 1.0$ M)

Species	Rate constant of oxidation ($\mathrm{M^{-1}\ s^{-1}}$)	pK_a	Reference for pKa
$\mathrm{H_3PO_3}$	$k_1 = 0.20$	p$K_1 = 0.97$	5
$\mathrm{H_2PO_3^-}$	$k_2 = 0.13$	p$K_2 = 5.90$	this work
		6.01	6
$\mathrm{HPO_3^{2-}}$	$k_3 = 0.77$	38	10
HPO(OEt)(OH)	0.50	0.8	9
HPO(OEt)(O$^-$)	0.27	26	10
$\mathrm{HPO(OEt)_2}$	$k_4 = 1.80$	13	10
$:\mathrm{P(O^-)(OEt)_2}$	$k_5 = 2.4\times10^6$		

$$\mathrm{Mn(V)+H_3PO_3\ (or\ H_2PO_3^-)\xrightarrow{pH\ 0\text{–}7.2}Mn(III)+P(V)\ (fast)} \quad (11)$$

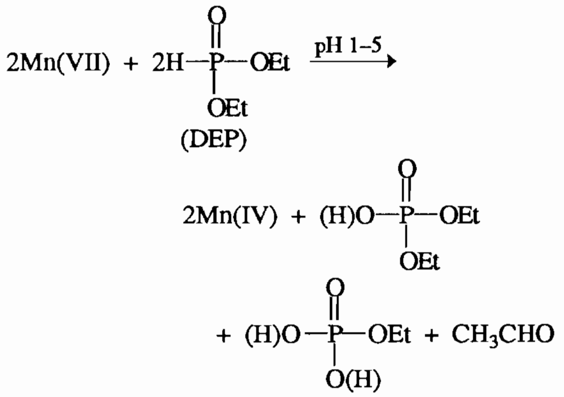
$$\mathrm{3Mn(V)\xrightarrow{pH\sim 8}2Mn(IV)+Mn(VII)\ (fast)} \quad (12)$$

$$\mathrm{Mn(V)+Mn(VII)\xrightarrow{pH>12}2Mn(VI)\ (fast)} \quad (13)$$

Up to about pH 7.2 reaction (11) is predominant and rate constant k, obtained from pseudo-first-order plots, follows the course predicted by eqn. (10). Above that pH the stoichiometry switches to eqn. (12), which implies that in the kinetic eqn. (4) $n=2/3$. Upon further increase of the pH above 12, stoichiometry (13) becomes valid, which in turn requires that $n=2$. Indeed, these factors place the experimental value of rate constants on the pH profile in Fig. 1, which supports that step (9) remains rate-determining also in the pH range of 7–13.

Reaction of diethyl phosphonate (DEP) with permanganate

Diethyl phosphonate reduces permanganate to Mn(IV) in both acidic and neutral solutions. However, the reaction shows a variable stoichiometry. Under the conditions of excess permanganate we have found that, up to about pH 5, one mole of the substrate consumes about 3 oxidation equivalents. Oxidation of the ethylate moiety produces acetaldehyde, whose formation can be detected (sodium nitroprusside/morpholine test) even if DEP is in excess over the oxidant. We have found that the hydrolysis of DEP and the oxidation of ethanol by permanganate are both very slow under the conditions used, consequently, acetaldehyde formation cannot be accounted for by the oxidation of hydrolysis products. Therefore, we suppose that acetaldehyde is formed in the main reaction, which can be written as



$$\mathrm{2Mn(VII)+2H{-}P(=O)(OEt){-}OEt\ (DEP)\xrightarrow{pH\ 1\text{–}5}2Mn(IV)+(H)O{-}P(=O)(OEt){-}OEt+(H)O{-}P(=O)(O(H)){-}OEt+CH_3CHO} \quad (14)$$

As acetaldehyde is less reactive than DEP, its further oxidation by excess permanganate becomes noticeable only at the very end of the main reaction (14) and it is certainly negligible when the substrate is used in excess.

In more basic solutions DEP is oxidized by 2 equiv. (with the OEt groups remaining intact):

$$\mathrm{2Mn(VII)+3HPO(OEt)_2\xrightarrow{pH\ 7\text{–}8.3}2Mn(IV)+3HO\text{–}PO(OEt)_2} \quad (15)$$

The rate of reaction (14) is first order in both reactants and independent of the H^+-ion concentration (Table 3, entries 1–14).

$$w=-\frac{d[\mathrm{Mn(VII)}]}{dt}=k_4[\mathrm{Mn(VII)}][\mathrm{DEP}] \quad (16)$$

This suggests that the rate-controlling step is similar to that of phosphorous acid oxidation

$$\mathrm{Mn(VII)+HPO(OEt)_2\xrightarrow{k_4}Mn(V)+HO\text{–}PO(OEt)_2} \quad (17)$$

The stoichiometry of the reaction can be rationalized by assuming the fast oxidation of an EtO^- group in diethyl phosphate by the Mn(V) intermediate

$$\mathrm{2Mn(V)+HO\text{–}PO(OEt)_2\xrightarrow{pH\ 1\text{–}5}2Mn(IV)+(HO)_2PO(OEt)+CH_3CHO} \quad (18)$$

Evidence for reaction (18) arises from the observation that added phosphorous acid can prevent acetaldehyde formation by 'trapping' Mn(V) by the fast reaction (11).

At higher pH, oxidation of DEP becomes more rapid. The increase in rate can achieve several orders of magnitude: at pH 12 the reaction is too fast to measure using our stopped-flow accessory. Kinetic measurements carried out in the pH range of 7.5–8.3 indicate that the pH-dependent reaction runs in parallel to reaction (17) and is first order in the substrate concentration (entries 27–30 in Table 3), but changes over from a first-order to a zero-order dependence on Mn(VII) concentration (entries 19–26 and Fig. 2).

The zero-order dependence on MnO_4^- is consistent with deprotonation of the P–H bond in the rate-limiting step, producing an intermediate with a lone pair of electrons on the phosphorus atom, which then reacts rapidly with permanganate ion

$$\mathrm{OH^-+HPO(OEt)_2\underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}}:P(O^-)(OEt)_2+H_2O} \quad (19)$$

$$\mathrm{:P(O^-)(OEt)_2+Mn(VII)\xrightarrow{k_5}Mn(V)+O{=}P(O^-)(OEt)_2} \quad (20)$$

(Similar deprotonation steps may also occur with other bases present in the system. Under the experimental conditions used, the effect of OH^- ion is predominant.)

Considering stoichiometric eqn. (15), and applying a steady-state approximation for $P(O^-)(OEt)_2$, the following kinetic law for the overall reaction at pH 7–8.3 can be derived

TABLE 3. Kinetic data for the oxidation of diethyl phosphonate (DEP) ($t=22$ °C, $\mu=1.0$ M, $[\text{pyr}]=5.0\times10^{-3}$ M)

No.	pH	$[\text{DEP}]_0\times10^4$ (M)	$[\text{Mn(VII)}]_0\times10^4$ (M)	$k_{\text{obs}}\times10^{3}$ [a] (s^{-1})	$w_0\times10^{6}$ [b] (Ms^{-1})	k [c] ($M^{-1}\,s^{-1}$)	$k_5\times10^{-6}$ [d]
1	0.96	388	20.0	73.3		1.89	
2	3.80	39	20.0	6.8		1.75	
3		78	20.0	14.6		1.87	
4		116	20.0	20.4		1.76	
5		388	20.0	70.4		1.82	
6		582	20.0	108		1.86	
7		2.5	10.0		0.437	1.75	
8		5.0	10.0		0.902	1.80	
9		7.5	10.0		1.304	1.74	
10		10.0	10.0		1.730	1.73	
11		7.5	8.0		1.074	1.79	
12		7.5	6.0		0.784	1.74	
13		7.5	4.0		0.556	1.85	
14	5.02	40.0	10.0		7.520	1.88	
15	7.51	40.0	2.0		3.36	4.20	2.05
16		40.0	10.0		10.22	2.56	
17	7.80	40.0	2.0		5.92	7.40	2.62
18		40.0	10.0		14.38	3.60	
19	8.02	40.0	0.8		4.26	13.3	2.39
20		40.0	1.2		5.96	12.4	
21		40.0	1.6		7.15	11.2	
22		40.0	2.0		8.23	10.3	
23		40.0	4.1		12.4	7.56	
24		40.0	6.1		15.3	6.27	
25		40.0	8.1		17.4	5.37	
26		40.0	10.0		18.8	4.70	
27	8.00	20.0	10.0		9.07	4.53	
28		40.0	10.0		17.5	4.37	
29		60.0	10.0		27.0	4.50	
30		80.0	10.0		35.9	4.49	
31	8.30	40.0	2.0		13.7	17.2	2.33
32		40.0	10.0		29.7	7.43	
						Average:	2.35

[a] Pseudo-first-order rate constant, $k_{\text{obs}}=k[\text{DEP}]_0$, determined from the integrated form of eqn. (16). [b] Initial rate, $w_0=(\text{d}[\text{Mn(VII)}]/\text{d}t)_0$. [c] At pH⩽5: $k=k_4=k_{\text{obs}}/[\text{DEP}]_0$ (entries 1–6) or $k=k_4=w_0/[\text{DEP}]_0[\text{Mn(VII)}]_0$ (entries 7–14); at pH>7: $k=k_{\text{eff}}=w_0/[\text{DEP}]_0[\text{Mn(VII)}]_0$. [d] From the slopes in Fig. 3 (see eqn. (21)).

$$\frac{3}{2}w=-\frac{3}{2}\frac{\text{d}[\text{Mn(VII)}]}{\text{d}t}=\frac{\text{d}[\text{DEP}]}{\text{d}t}$$
$$=k_4[\text{Mn(VII)}][\text{DEP}]$$
$$+\frac{k_5k_b[\text{OH}^-][\text{Mn(VII)}][\text{DEP}]}{k_{-b}+k_5[\text{Mn(VII)}]} \qquad (21)$$

The observed dependence of the rate on $[\text{OH}^-]$ is in line with base catalysis reported for both iodine oxidation [8] and H–D exchange of DEP [9].

At Mn(VII) concentrations in the range of $(0.4\text{–}10.0)\times10^{-4}$ M, k_{-b} and $k_5[\text{Mn(VII)}]$ are comparable in magnitude so that the second term in the right-hand side of eqn. (21) cannot be simplified. The individual rate constants can be determined by plotting the left-hand side of eqn. (22) against $[\text{Mn(VII)}]^{-1}$. The resulting straight lines are shown in Fig. 3.

$$\frac{1}{\frac{3}{2}\frac{w}{[\text{DEP}]}-k_4[\text{Mn(VII)}]}=\frac{1}{k_b[\text{OH}^-]}$$
$$+\frac{k_{-b}}{k_5k_b[\text{OH}^-]}\frac{1}{[\text{Mn(VII)}]} \qquad (22)$$

The slopes of the graphs give $k_5=2.4\times10^6$ M^{-1} s^{-1} (Table 3) if we use the value of 10^{-13} M for the acid dissociation constant $K_a=K_wk_b/k_{-b}$ [10]. (Estimation of the pK_a of DEP in ref. 10 is based on thermodynamic data, as direct measurement is not possible owing to rapid hydrolysis of the ester). The intercepts provide values of k_b at different pHs. As expected, k_b agrees

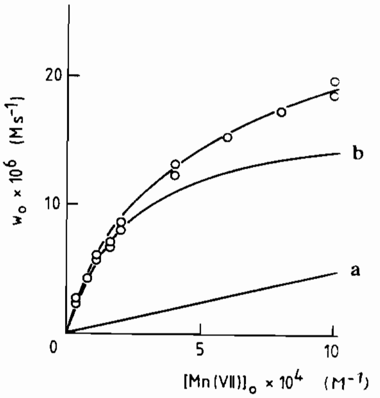


Fig. 2. Dependence of the initial rates on permanganate concentration in the oxidation of diethyl phosphonate at pH = 8.02. ($[DEP]_0 = 0.004$ M). (a) pH-independent reaction; (b) base-assisted reaction.

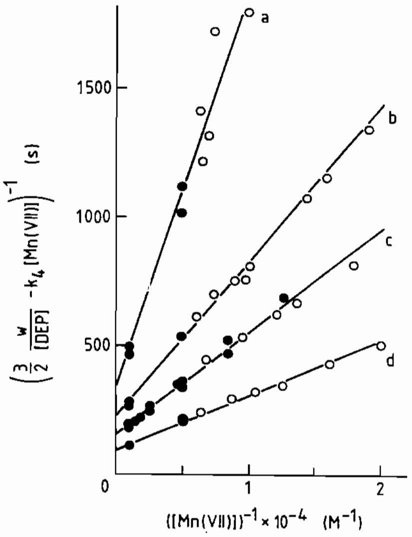


Fig. 3. Plot of eqn. (22). Data are derived from initial rates (●) and from the slopes of single kinetic curves ($[Mn(VII)]_0 = 2 \times 10^{-4}$ M) at various times (○); ($[DEP] = 4 \times 10^{-3}$ M); pH: 7.51 (a); 7.80 (b); 8.02 (c) and 8.30 (d).

well with the rate constant of the first-order reaction between iodine and DEP (rate is independent of iodine concentration) if both are determined in the same buffer solution.

Figure 3 also shows that hydrolysis of DEP must be negligible compared with its oxidation: the data obtained from initial rates and those derived from later stages of the kinetic runs are on the same straight line within experimental error.

Reaction of monoethyl phosphonate (MEP) with permanganate

TABLE 4. Kinetic data for the oxidation of monoethyl phosphonate (MEP) ($t = 22$ °C, $\mu = 1.0$ M, $[Mn(VII)]_0 = 2 \times 10^{-4}$ M, $[pyr] = 5.0 \times 10^{-3}$ M)

pH	$[MEP]_0$	$k_{obs} \times 10^{3a}$ (s^{-1})	k (M^{-1} s^{-1})
0.0	0.20	100.0	0.501
1.36	0.20	73.2	0.366
3.08	0.20	57.5	0.287
4.00	0.02	5.80	0.290
	0.04	11.0	0.275
	0.10	27.7	0.277
	0.20	58.7^{b}	0.294
5.75	0.20	58.3^{b}	0.291
6.69	0.20	56.1^{b}	0.280
7.47	0.20	45.8^{b}	
8.08	0.20	40.9^{b}	0.307^{c}
8.30	0.20	34.7^{b}	0.260^{c}
12.16^{e}	0.04	23.1	0.289^{d}
	0.20	111.0	0.278^{d}

$^{a}k_{obs} = nk[MEP]_0$. ^{b}Determined from initial rates. $^{c}n = 2/3$. $^{d}n = 2$. ^{e}No pyrophosphate added.

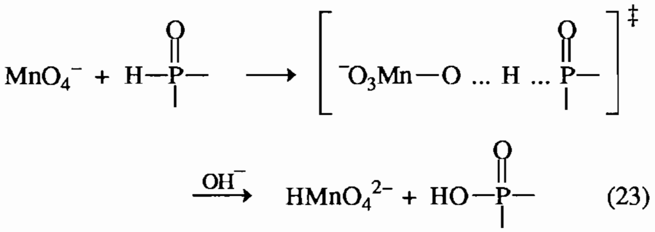
This reaction was found to be first order with respect to both Mn(VII) and MEP in both acidic and basic solutions (Table 4). The pH dependence of the second-order rate constant can be ascribed to deprotonation equilibrium of the single OH group in acidic media and to a change of the oxidant to substrate consumption ratio from 1:1 to 2:3 around pH 7, and again to 2:1 at pH > 12.

In slightly acidic solutions, the reaction can be described analogously to eqn. (14), if Mn(VII) is in excess over MEP: the ethoxy group will be partially oxidized and Mn(IV) will be produced. However, when the substrate is used in increasing excess, more and more Mn(III) will also be formed. This is probably caused by phosphorous acid resulting from MEP hydrolysis. (If the starting MEP contains as little as 2% of added H_3PO_3, then under the conditions shown in Table 4, Mn(VII) will be reduced nearly completely to Mn(III), whereas the rate constant remains unchanged).

Mechanism of oxidative cleavage of the P–H bond

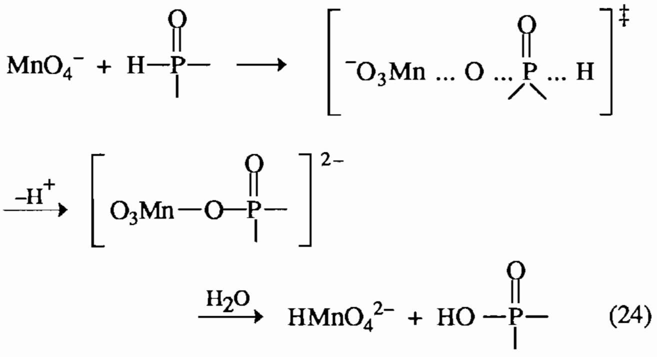
Kinetic data show that the base-assisted reaction path described in eqns. (19) and (20) is significant only in the oxidation of DEP. This is in accordance with the fact that ionization of the P–H bond in the other P(III) species is not favorable. (The estimated pK_a values are given in Table 2.)

The other route of oxidation, not catalyzed by acid or base, seems to be common in the case of each P(III) compound discussed in this paper. Relevant to the nature of the rate-determining step is that the oxidation of phosphites produces a kinetic isotope effect of $k_H/k_D = 4.3 \pm 0.2$ (determined at pH 2.2, 7.1 and 12.3), if H is replaced by D in the P–H bond. It appears that permanganate attacks the substrate directly, the P–H bond being broken in the rate-determining step. The slow steps may consist of hydride-ion transfer to the oxidant



$$MnO_4^- + H-\underset{|}{\overset{\overset{O}{\|}}{P}}- \longrightarrow \left[{}^-O_3Mn-O\ \ldots\ H\ \ldots\ \underset{|}{\overset{\overset{O}{\|}}{P}}-\right]^{\ddagger} \xrightarrow{OH^-} HMnO_4^{2-} + HO-\underset{|}{\overset{\overset{O}{\|}}{P}}- \qquad (23)$$

Attack of MnO_4^- on the phosphorous atom to form an oxygen bridge with five-coordinate P is another possibility. The transfer of an electron pair through the bridge occurs with concomitant proton transfer to the solvent



$$MnO_4^- + H-\underset{|}{\overset{\overset{O}{\|}}{P}}- \longrightarrow \left[{}^-O_3Mn\ \ldots\ O\ \ldots\ \underset{/\backslash}{\overset{\overset{O}{\|}}{P}}\ \ldots\ H\right]^{\ddagger} \xrightarrow{-H^+} \left[O_3Mn-O-\underset{|}{\overset{\overset{O}{\|}}{P}}-\right]^{2-} \xrightarrow{H_2O} HMnO_4^{2-} + HO-\underset{|}{\overset{\overset{O}{\|}}{P}}- \qquad (24)$$

Mechanism of the fast steps

Our kinetic results are consistent with the assumption that in neutral and basic solutions the manganese(V) intermediate decomposes without being reduced by the substrate (reactions (12) and (13)). However, in acidic solutions the Mn(V) intermediate will react with the substrate, yielding Mn(III) or Mn(IV) (eqns. (11) and (18)). Our earlier observation [2] that induced oxidation of H_3PO_3 takes place in the Mn(VII)–As(III)–P(III) system has demonstrated the fast oxidation of phosphorous acid by the Mn(V) intermediate.

$$\mathrm{Mn(VII)} + \mathrm{As(III)} \longrightarrow \mathrm{Mn(V)} + \mathrm{As(V)} \qquad (25)$$

$$\mathrm{Mn(V)} + \mathrm{P(III)} \longrightarrow \mathrm{Mn(III)} + \mathrm{P(V)} \qquad (26)$$

In excess permanganate, As(III) is fully consumed. Since reaction (25) is very fast, the Mn(VII)–P(III) reaction can be neglected. As As(III) and P(III) compete for Mn(V), the product ratio depends on their relative concentration. Reactions (25) and (26) represent the limiting case when all the reduction of Mn(V) is done by P(III).

In this work we have repeated the experiments described in ref. 2, but used phosphonate esters (MEP and DEP) instead of H_3PO_3. We have found that diethyl phosphonate and the anion of monoethyl phosphonate, $HPO(OEt)(O^-)$ have no effect on the oxidation of As(III), i.e. permanganate consumption is the same as that in the absence of P(III). In contrast to this, induced oxidation of the protonated monoester, HPO(OEt)(OH), does readily take place in acidic solution, which is required for its formation. This supports our previous assumption that the high reactivity of P(III) towards Mn(V) can be attributed to its ability to form an anhydride of the Mn^V–O–P^{III} type in which the binding O atom offers a bridge for electron transfer. If the protons in phosphorous acid are removed or replaced by ethyl groups, anhydride formation is not possible and oxidation by Mn(V) is inhibited.

A different type of mechanism must apply in the reduction of Mn(V) by diethyl phosphate, reaction (18), which may be a sequence of two one-equivalent steps, involving the formation of an ethoxyl radical. Alternatively, the Mn(V) species initially formed in reaction (24), which is a mixed anhydride with diethyl phosphate, may undergo disproportionation prior to hydrolysis. In the resulting Mn^{VI}–O–$PO(OEt)_2$, one of the ethoxy groups could be oxidized to acetaldehyde via an intramolecular path.

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