Kinetics and Mechanisms of Redox Reactions in Aqueous Solution. Part 9.[1] Permanganate Oxidation of Phosphorous Acid in Perchlorate Solution

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The reaction between phosphorous acid and permanganate exhibits a first-order dependence both on $[Mn^{VII}]$ and $[H_3PO_3]$ and the dependence of $k_{obs.}$ on $[H^+]$ is of the form (i) at constant ionic strength;

$$k_{obs.} = a + b[H^+] \qquad \text{(i)}$$

$k_{obs.}$ is independent of ionic strength. The most probable mechanism in which the 'inactive' form of phosphorous acid, $H{-}P{=}O(OH)_2$, is the reactive species is discussed and the values of the rate-limiting constants together with their associated thermodynamic parameters are reported. The duality of H^+ catalysis is also discussed in an alternative mechanism.

The oxidation of phosphorous acid by several metal [2-7] and non-metal ions [8-11] has been studied. All these oxidations could be classified in two broad groups: those first order with respect to oxidant concentration and those with a zero-order dependence on the oxidant. The latter dependence is invariably explained by assuming that the rate-limiting step involves the transformation of the 'inactive form' into the 'active form' which then reacts rapidly with the oxidant.

It is surprising that the oxidation of phosphorous acid by permanganate ion has not yet been reported. The present study is thus an attempt to characterise the kinetics of this reaction, to suggest the most probable mechanism, and to discuss the nature of the reactive tautomer of phosphorous acid, a problem which has not been tackled well in most previous studies.

Experimental

Fluka puriss grade phosphorous acid was used as received. The stock solution was standardised against vanadium(v)[2] at higher temperatures (*ca.* 60 °C) to a stable end-point, using barium *p*-(phenylamino)benzenesulphonate as the indicator. In a few cases these titrations were carried out in the presence of Ag^I as catalyst.

The stock solution of perchloric acid was prepared by suitable dilution of the sample received (70%, E. Merck) and standardised against a standard alkali solution. Anhydrous sodium perchlorate (G. F. Smith) was used for the preparation of a stock solution, and standardised gravimetrically.

Old solutions of potassium permanganate were not used. The solid (B.D.H., AnalaR) was dissolved in hot distilled water which had previously been degassed with pure commercial nitrogen. The hot solution was left overnight then filtered and stored in the dark. Solutions were discarded if slight turbidity due to manganese dioxide was observed. In general, solutions older than 72 h were not used. As a further safeguard, the concentration of permanganate solutions was checked daily against the absorbance at 525 nm.[12]

Stoicheiometry.—Mixtures of phosphorous acid and potassium permanganate of different concentrations and at various acidities (0.2—2 mol dm^{-3} perchloric acid) were prepared. They were kept at room temperature (30 °C) for sufficiently long times to ensure completion of the reaction. In cases where permanganate ion was in excess, the unreacted permanganate was estimated from its absorbance at 525 nm. When phosphorous acid was in excess, the unreacted acid was estimated with vanadium(v) in the presence of Ag^I, or iodometrically.[4] The results of these estimations indicated that the reaction proceeded according to equation (1).

$$2Mn^{VII} + 3H_3PO_3 + 3H_2O \longrightarrow 2Mn^{IV} + 3H_3PO_4 + 6H^+ \qquad (1)$$

Quantitative estimation of the phosphoric acid product could not be carried out because there seems to be no method available for its determination in the presence of phosphorous acid. However, the absence of phosphorous acid in reaction mixtures containing excess of permanganate ion could be shown by the usual method.[13] It may be pointed out that manganese dioxide is the normal end product of permanganate oxidation except in strongly alkaline solution and in certain oxidations in acidic solution, notably with oxalic acid where it is reduced to manganese(II).[14] Manganese dioxide is known to precipitate slowly in the presence of phosphate ions.[14]

Rate Measurements.—The rates were measured under pseudo-first-order conditions, H_3PO_3 being present in excess over MnO_4^- in the reaction mixtures. The ionic strength, kept constant at 2 mol dm^{-3} with sodium perchlorate, was calculated by assuming that potassium permanganate was completely dissociated whereas phosphorous acid did not dissociate under the experimental conditions. (Even if it did at lower $[H^+]$, the overall ionic strength of 2 mol dm^{-3} would not be significantly affected.)

The reaction was initiated by the quick addition of permanganate solution to the rest of the reaction mixture having the required concentrations of phosphorous acid and other reagents. The two solutions were first thermally equilibrated in a water-bath maintained at the desired temperature (±0.1 °C).

The progress of the reaction was monitored at 525 nm (disappearance of MnO_4^-) by using a Spectrochem spectrophotometer. The rate constant was estimated from the slope of plots of $\ln (A_t - A_\infty)$ against time which were linear up to three half-lives except at low $[H^+]$. Even in the latter cases the plots were linear beyond one half-life. The $k_{obs.}$ values given in the Tables are average values from two or more determinations. The deviations were reasonably small, suggesting that the estimations of the slopes were reasonably accurate.

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Table 1. Dependence of $k_{obs.}$ on initial [NaF] at 27 °C, $[KMnO_4] = 0.0004$, $[H_3PO_3] = 0.0136$, $[HClO_4] = 2.0$, and $I = 2.1$ mol dm^{-3}

[NaF]/mol dm^{-3}	0.004	0.01	0.02	0.04	0.06	0.076
$10^3 k_{obs.}$/s^{-1}	4.44	4.53	4.39	4.31	4.67	4.60

Average $10^3 k_{obs.} = 4.49 \pm 0.13$ s^{-1}

Table 2. Dependence of $k_{obs.}$ on $[H_3PO_3]$ at $[KMnO_4] = 0.0004$, $[HClO_4] = 2.0$, and $I = 2.1$ mol dm^{-3} at 27 °C

(*a*) In the presence of 0.01 mol dm^{-3} NaF

$[H_3PO_3]$/ mol dm^{-3}	0.0027	0.0068	0.0136	0.0204	0.0272	0.0408	0.0544
$10^3 k_{obs.}$/s^{-1}	0.817	2.13	4.49	6.56	8.66	13.4	17.6

(*b*) In the absence of NaF

$[H_3PO_3]$/ mol dm^{-3}	0.0027	0.0068	0.0136	0.0204	0.0272	0.0408	0.0544
$10^3 k_{obs.}$/s^{-1}	0.833	2.19	4.36	6.94	8.84	13.4	17.9

The linearity of the first-order plots ($r > 0.999$) suggested the absence of appreciable formation of intermediates. In acid solution, Mn^{VI} is quite unstable and the absorbance of Mn^{V} is negligible [15] at 525 nm. The absorbance A_∞ (which remained constant until MnO_2 finally precipitated) is presumably due to the Mn^{IV} which remained in the dissolved state.

A Test for Free Radical.—Acrylonitrile was added to the partially oxidised reaction mixtures to determine if free radicals were generated as the reaction proceeded to completion. The reaction mixtures were previously degassed with nitrogen and kept under a nitrogen atmosphere. The monomer did not show any sign of polymerisation, at least for the first 10 min. The free radical $\dot{P}(O)(OH)_2$ is expected if the permanganate ion oxidises phosphorous acid through a one-electron change: $Mn^{VII} + HP(O)(OH)_2 \longrightarrow Mn^{VI} + H^+ + \dot{P}(O)(OH)_2$.

Results and Discussion

In the initial stages of the study fluoride ions were included in the reaction mixtures with a view to avoiding any contribution from Mn^{III} (having a redox potential of 1.51 V *vs.* n.h.e.) [16] by removing it as a stable $[MnF_4]^-$ complex.[17] The results in Table 1 indicate that F$^-$ did not affect the observed rate, a retardation in the rate would have been expected if Mn^{III} had participated in the reaction. Commenting on this observation one of the referees suggested that the independence of $k_{obs.}$ on [F$^-$] may be an artifact of the high [H$^+$] or at best that Mn^{III} occurred, if at all, only after the rate-limiting step.

The effect of $[H_3PO_3]$ on the observed rate constant was investigated both in the presence [Table 2(*a*)] and absence [Table 2(*b*)] of fluoride ions. In each case the plot between $k_{obs.}$ and $[H_3PO_3]$ passed through the origin and the slopes, 0.327 and 0.330 dm^3 mol^{-1} s^{-1} respectively, once again confirmed that $k_{obs.}$ was not affected by the presence of fluoride ions. Subsequently, fluoride ions were excluded from the reaction mixtures.

That permanganate ion was reduced to manganese dioxide was confirmed by measuring the rate of appearance of Mn^{IV} at 400 nm.[18] The $k_{obs.}$ thus calculated had a value 4.96×10^{-3} s^{-1} which compared well with the value 5.03×10^{-3} s^{-1} obtained by following the disappearance of permanganate ion under identical conditions ($[KMnO_4] = 0.0004$, $[H_3PO_3] = 0.0136$, $[HClO_4] = 0.1$, and $I = 2.0$ mol dm^{-3} at 32 °C).

Table 3. Dependence of $10^3 k_{obs.}$/s^{-1} on $[HClO_4]$ at different temperatures; $[KMnO_4] = 0.0004$, $[H_3PO_3] = 0.0136$, and $I = 2.0$ mol dm^{-3}

	[H$^+$]/mol dm^{-3}							
θ$_c$/°C	0.1	0.2	0.4	0.7	1.0	1.3	1.6	2.0
27	—	3.79	3.86	3.95	4.06	4.15	4.21	4.36
32	5.03	5.08	5.18	5.34	5.50	5.64	5.80	6.00
39	7.61	7.74	7.95	8.21	8.55	8.82	9.16	9.54
42	8.66	8.74	9.10	9.48	9.80	10.2	10.6	11.1
47	11.0	11.2	11.7	12.3	12.9	13.5	14.1	15.1

The invariance of $k_{obs.}$ over an eight-fold variation in the initial $[MnO_4^-]$ (0.0004—0.0034 mol dm^{-3}) confirmed the first-order dependence on permanganate concentration. The mean $10^3 k_{obs.}$ was 13.4 ± 0.2 s^{-1} at 27 °C ($[HClO_4] = 2.0$, $[H_3PO_3] = 0.041$, and $I = 2.1$ mol dm^{-3} and 525 nm).

A plot of $k_{obs.}$ against [H$^+$] was linear with an intercept on the rate ordinate. The results of rate measurements at different temperatures are given in Table 3.

The value of $k_{obs.}$ was independent of ionic strength when varied with sodium perchlorate, indicating that the reaction involved either an ion and a molecule or molecular species.

The initial addition of Mn^{II} (as $MnSO_4$) considerably increased the reaction velocity, *viz.* 0.1 mol dm^{-3} at 37 °C decreased the absorbance at 525 nm of the reaction mixture ($[MnO_4^-] = 0.0004$, $[HClO_4] = 2.0$, $[H_3PO_3] = 0.015$, and $I = 2.0$ mol dm^{-3}) to *ca.* 0.09 after 1 min. This is rationalised by considering either or both of reactions (2) and (3) which are followed by the appropriate reactions (14) and (15) (see below).

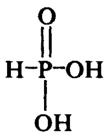
$$Mn^{VII} + Mn^{II} \longrightarrow Mn^{VI} + Mn^{III} \tag{2}$$

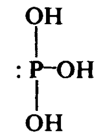
$$Mn^{VII} + 2Mn^{II} \longrightarrow Mn^{V} + 2Mn^{III} \tag{3}$$

The first dissociation constant of phosphorous acid has been reported.[11,19-22] All of these values are sufficiently small to allow the assumption that phosphorous acid exists in the undissociated state at [H$^+$] > 0.5 mol dm^{-3} and as such will be the reactive species. However, there may be significant amounts of the dissociated species, $H_2PO_3^-$, that might well be the reactive species at [H$^+$] < 0.5 mol dm^{-3}. In view of the fact that the plot between $k_{obs.}$ and [H$^+$] did not show any deviation from linearity at low [H$^+$], it may not be unreasonable to assume that both H_3PO_3 and $H_2PO_3^-$ have compensatory reactivities towards oxidising species in the acidic solutions considered.

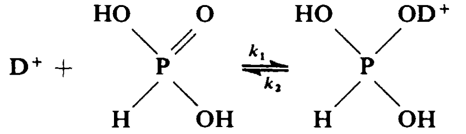
The oxidation of phosphorous acid by vanadium(V),[2,3] chromium(VI),[4] cerium(IV),[5] thallium(III),[7] and peroxodisulphate ions [9] is generally a slow process and in most of the cases the kinetics were studied at high temperatures. In contrast, the present one is considerably faster. A comparison of redox potentials, expressed in volts *vs.* n.h.e., Mn^{VII}–Mn^{IV} (1.51),[14] Cr^{VI}–Cr^{III} (1.33),[16] Ce^{IV}–Ce^{III} (1.61),[16] $S_2O_8^{2-}$–$2SO_4^{2-}$ (2.0),[16] and V^{V}–V^{IV} (1.0),[23] indicated that the present comparatively faster rate of oxidation is certainly not related to the redox potential.

The structure of phosphorous acid has been the subject of several studies because of the two possible alternatives, the 'inactive' form (A) and the 'active' form (B). *X*-Ray,[24] n.m.r.,[25] and u.v. data [26] for phosphorous acid and its salts indicated that these have structure (A). The hydrolysis of phosphorous tribromide at pH 5.7 and low temperatures, however, indicated structure (B) in high concentration.[27] Further support for (B) was provided by the


(A)


(B)

kinetics of oxidation of phosphorous acid by Ag^{II},[6] mercury(II) chloride,[8] and iodine.[10] It is significant that in all these cases the order with respect to oxidant concentration was zero. The H^+-catalysed isotopic exchange of hydrogen bound to phosphorous with deuterium [28,29] proceeding through the mechanism in equations (4)—(7) also provides support for structure (B). The reactions (4)—(7) lead to the rate law (8)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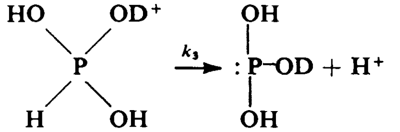
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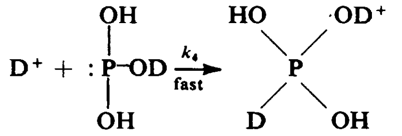
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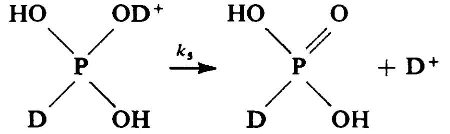
(7)

$$\frac{-d[H-P=O(OH)_2]}{dt} = \frac{d[D-P=O(OH)_2]}{dt} = \frac{k_1k_3[H-P=O(OH)_2][D^+]}{k_2 + k_3} \qquad (8)$$

which is consistent with the first-order dependence in phosphorous acid concentration. Since the plot of the observed first-order rate constant for deuterium exchange, k_{exch}, against $[D^+]$ had an intercept on the rate ordinate, equation (9) was proposed where k_H is the acid catalysis constant and

$$k_{exch} = k_H[D^+] + k_w \qquad (9)$$

k_w the specific rate of the acid-independent exchange of the unprotonated phosphorous acid of structure (A). The values of k_H and k_w are 3.0×10^{-5} dm^3 mol^{-1} s^{-1} and 8.3×10^{-6} s^{-1} respectively at 80 °C.[30,31] From equations (8) and (9), expression (10) is obtained. A further discussion of the k_H and k_w

$$k_H = \frac{k_1k_3}{k_2 + k_3} \qquad (10)$$

values in relation to the reactivities of the structures (A) and (B) is deferred to a later stage.

Mechanism.—The present data are not sufficiently precise to differentiate between inner- and outer-sphere mechanisms.

Table 4. Values of k_6 and k_7K_1 at different temperatures and the corresponding activation parameters

θ_c/°C	27	32	39	42	47	80
k_6/dm^3 mol^{-1} s^{-1}	0.137	0.183	0.277	0.314	0.397	1.83
k_7K_1/dm^6 mol^{-2} s^{-1}	0.0114	0.0188	0.0371	0.0474	0.0776	1.112

$\Delta H^‡(k_6) = 42 \pm 3$ kJ mol^{-1}, $\Delta H(k_7K_1) = 74 \pm 4$ kJ mol^{-1}
$\Delta S^‡(k_6) = -122 \pm 5$ J K^{-1} mol^{-1}, $\Delta S(k_7K_1) = -34 \pm 6$ J K^{-1} mol^{-1}

$$H^+ + MnO_4^- \overset{K_1}{\rightleftharpoons} HMnO_4 \qquad (11)$$

$$MnO_4^- + H_3PO_3 + H_2O \xrightarrow{k_6} H_3PO_4 + Mn^V + 2H^+ \qquad (12)$$

$$HMnO_4 + H_3PO_3 + H_2O \xrightarrow{k_7} H_3PO_4 + Mn^V + 3H^+ \qquad (13)$$

$$Mn^{VII} + Mn^V \xrightarrow{\text{fast}} 2Mn^{VI} \qquad (14)$$

$$2Mn^{VI} + 2H_3PO_3 + 2H_2O \xrightarrow{\text{fast}} 2Mn^{IV} + 2H_3PO_4 + 4H^+ \qquad (15)$$

$$\frac{-d[MnO_4^-]}{dt} = \frac{2(k_6 + k_7K_1[H^+])[H_3PO_3][MnO_4^-]}{1 + K_1[H^+]} \qquad (16)$$

$$k_{obs.} = 2(k_6 + k_7K_1[H^+])[H_3PO_3] \qquad (17)$$

While an outer-sphere mechanism is more consistent with the data, the possibility of an inner-sphere mechanism cannot be completely ruled out. Support or otherwise for an inner-sphere mechanism could have been provided by use of the stopped-flow technique where the change in absorbance of permanganate ion could be registered soon after its mixing with phosphorous acid.

The increased activity of MnO_4^- in solutions of strong acids [32] is due to its protonation, reaction (11).[33] The protonation equilibrium constant K_1 is calculated to have a value of 5.6×10^{-3} dm^3 mol^{-1} from the known pK_a = −2.25 for permanganic acid.[34] The rate of disappearance of permanganate ion in terms of reactions (11)—(15) is given by equation (16). Since the value of K_1 is *ca.* 10^{-3} dm^3 mol^{-1}, it is clear that $1 \gg K_1[H^+]$ whence equation (16) reduces to (17) which is the observed rate equation for the reaction. Values of k_6 and k_7K_1 at different temperatures and the corresponding activation parameters are given in Table 4.

An alternative mechanism [equation (18)—(20)] that can

$$H^+ + H_2PO_3^- \overset{K_2}{\rightleftharpoons} H_3PO_3 \qquad (18)$$

$$MnO_4^- + H_2PO_3^- + H_2O \xrightarrow{k_8} Mn^V + H_2PO_4^- + 2H^+ \qquad (19)$$

$$MnO_4^- + H_3PO_3 + H_2O \xrightarrow{k_9} Mn^V + H_3PO_4 + 2H^+ \qquad (20)$$

also explain the experimental results has been suggested by a referee. Here reaction (20) is followed by reactions (14) and (15). The disappearance of permanganate ion will now be

Table 5. Values of k_8 and k_9 at different temperatures and the corresponding activation parameters

θ_c/°C	27	32	39	42	47	80
k_8/dm^3 mol^{-1} s^{-1}	0.0028	0.0039	0.0049	0.0049	0.0040	—
k_9/dm^3 mol^{-1} s^{-1}	0.1529	0.2051	0.3202	0.3688	0.4860	2.51

$\Delta H(k_9)^\ddagger = 43 \pm 4$ kJ mol^{-1}, $\Delta S(k_9)^\ddagger = -110 \pm 6$ J K^{-1} mol^{-1}

given by the rate law (21). If the first dissociation constant

$$\frac{-d[MnO_4^-]}{dt} = \frac{2(k_8 + k_9K_2[H^+])[MnO_4^-][H_3PO_3]}{1 + K_2[H^+]} \qquad (21)$$

K_{a1} of phosphorous acid is accepted to have a value of 0.107 mol dm^{-3} at 25 °C [22] (the highest value giving the maximum amount of $H_2PO_3^-$) then K_2 has a value of 9.35 dm^3 mol^{-1} and therefore $K_2[H^+]$ cannot be neglected in comparison to 1 even at $[H^+]$ as low as 0.03 mol dm^{-3}. Hence equation (21) is written as (22) and a plot of the left-hand side against $[H^+]$

$$\frac{k_{obs.}(1 + K_2[H^+])}{2[H_3PO_3]} = k_8 + k_9K_2[H^+] \qquad (22)$$

should be linear with an intercept on the rate ordinate. The linearity ($r = 0.999$) of such plots was however restricted to 1 mol dm^{-3} perchloric acid. The values of k_8 and k_9 are given in Table 5 from which it is seen that k_8 acquired a limiting value at about 30 °C but k_9 increased with temperature as predicted by the Arrhenius equation. The value of K_2 at different temperatures was obtained from calculated values of K_{a1} which was itself calculated at each temperature by using $\Delta H(K_{a1}) = -22.6$ kJ mol^{-1} obtained from the values of K_{a1} at two temperatures.[11]

It is interesting that the values of the rate constants k_6 (Table 4) and k_9 (Table 5) agree within experimental error. These rate constants refer to a common reaction in the two mechanisms. The ambiguity about the exact role of H^+ thus cannot be resolved by the kinetics.

One- vs. *Two-electron Transfer*.—If the free radical, $\dot{P}(O)(OH)_2$, produced as a result of a one-electron transfer is more reactive towards other species than with the monomer, acrylonitrile, then there will be no induced polymerisation of the monomer. Hence, the failure of the present system to induce polymerisation of the monomer does not constitute evidence against a possible one-electron transfer. However, by analogy with arsenious acid which is resistant to oxidation by one-electron oxidants, a two-electron transfer in the initial oxidation step seems to be more probable because the oxidation rate in the present case is faster than that observed with one-electron oxidants.[2,3,5,6]

Reactive Form of Phosphorous Acid.—The question which of the two tautomeric forms (A) or (B) is involved in the redox process is answered by comparing the rate constants for the rate-limiting oxidation steps with the rate constants k_H and k_W for the formation of the active form (B). It is, however, essential for this purpose to convert $k_{obs.}$ into a rate constant corresponding to the disappearance of phosphorous acid in the redox process. In terms of the stoicheiometric equation (1) this relation is given in equation (23).

$$3\left(\frac{-d[Mn^{VII}]}{dt}\right) = 2\left(\frac{-d[H_3PO_3]}{dt}\right) \qquad (23)$$

Hence, we obtain expressions (24) and (25). Now if k_H equals

$$\frac{-d[H{-}P{=}O(OH)_2]_{redox}}{dt} = 3(k_6 + k_7K_1[H^+])[Mn^{VII}][H_3PO_3] \qquad (24)$$

$$\text{or } 3(k_8 + k_9K_2[H^+])[Mn^{VII}][H_3PO_3] \qquad (24a)$$

$$\frac{-d[H{-}P{=}O(OH)_2]_{taut}}{dt} = (k_w + k_H[H^+])[H_3PO_3] \qquad (25)$$

either $3k_7K_1[Mn^{VII}]$ or $3k_9K_2[Mn^{VII}]$ and k_w equals $3k_6[Mn^{VII}]$ or $3k_8[Mn^{VII}]$, the rate-limiting step in each case is the transformation of the inactive form (A) into the active form (B). Under these conditions the order with respect to oxidant concentration is expected to be zero as was the case in the corresponding oxidations by silver(II),[6] mercury(II) chloride,[8] and iodine.[10] However, if $k_H/3k_7K_1[Mn^{VII}] \gg 1$ and similarly $k_w/3k_6[Mn^{VII}] \gg 1$, then the situation becomes complicated because under these conditions both tautomeric forms will be present in the system and each of these will have different reactivities. The situation when $3k_7K_1[Mn^{VII}]/k_H \gg 1$ and also $3k_6[Mn^{VII}]/k_w \gg 1$ is more simple. The tautomeric form (A) will only be oxidised because the rate of formation of (B) is much less than that of oxidation.

The values of k_H and k_w are, unfortunately, known only at 80 °C.[30,31] Hence values of k_7K_1 (or k_9) and k_6 at this temperature were obtained by extrapolation of the linear plots between ln k_7K_1 or ln k_6 and $1/T$. The values so obtained are given in the Tables. The fact that $3k_6[Mn^{VII}]/k_w = 265$ and $3k_7K_1[Mn^{VII}]/k_H = 44$ or $3k_9K_2[Mn^{VII}]/k_H = 3.9 \times 10^3$ establishes that phosphorous acid is oxidised (by permanganate ion) in its inactive form (A). Support for this conclusion can be obtained by comparing the values of $3k_7[Mn^{VII}]$ or $3k_9[Mn^{VII}]$ with that of k_1 which is, however, not known, but a useful guess could be made from equation (10) by making the following assumptions: (*a*) when $k_2 \approx k_3$ then $k_1 = 2k_H$; (*b*) when $k_2 \ll k_3$ then $k_1 = k_H$. The value of $k_7 \approx 1.98 \times 10^2$ dm^3 mol^{-1} s^{-1} at 80 °C was calculated with the assumption that the value of K_1 will not materially change (at least in order of magnitude) with temperature. In either case, $3k_7[Mn^{VII}]/k_1 \approx 10^3$ mol dm^{-3} or $3k_9[Mn^{VII}]/k_1 \approx 100$ mol dm^{-3} indicated that the rate of oxidation is much more than the rate of protonation of phosphorous acid in form (A).

Additional evidence against the active form as the reactive species can be obtained by comparing the rates of oxidation of arsenious acid and hydrogensulphite ion or H_2SO_3. The rates of oxidation of these compounds are so large that rapid mixing techniques are required to study the kinetics, as is evident from the fact that these compounds can be directly titrated against permanganate at room temperature. Both arsenious acid and sulphurous acid have a pair of electrons available on the As and S atoms like the one available on the P atom in the active form of phosphorous acid. Since the rate of oxidation of phosphorous acid is slower than of these compounds, it is reasonable to conclude that the active form (B) is not the reactive species.

Acknowledgements

Thanks are due to C.S.I.R. and U.G.C., New Delhi, for financial support, Miss Purnima for assistance with the experimental work, and a referee for suggesting an alternative mechanism.

References

1 Part 8, Sharad K. Vajpai, Raj N. Mehrotra, and R. C. Kapoor, *J. Chem. Soc., Dalton Trans.*, 1984, 999.
2 Raj N. Mehrotra, *J. Chem. Soc., Dalton Trans.*, 1978, 681.
3 K. K. Sengupta, B. B. Pal, and D. C. Mukherjee, *J. Chem. Soc., Dalton Trans.*, 1974, 226.
4 G. P. Haight, M. Rose, and J. Preer, *J. Am. Chem. Soc.*, 1968, **90**, 4809.
5 S. K. Misra, P. D. Sharma, and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1845.
6 A. Viste, D. A. Holme, P. L. Wang, and G. D. Veith, *Inorg. Chem.*, 1971, **10**, 631.
7 K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. A*, 1971, 1180.
8 G. A. Linehart and E. Adams, *J. Am. Chem. Soc.*, 1917, **39**, 948.
9 E. Ben-Zvi, *J. Phys. Chem.*, 1963, **67**, 2968.
10 A. D. Mitchell, *J. Chem. Soc.*, 1923, 2241.
11 R. O. Griffiths and A. McKeown, *Trans. Faraday Soc.*, 1940, **36**, 766.
12 M. Jaky and L. I. Simandi, *J. Chem. Soc., Perkin Trans. 2*, 1976, 939.
13 A. I. Vogel, 'A Textbook of Qualitative Inorganic Analysis,' 2nd edn., Longmans, London, 1951, p. 499.
14 R. Stewart, in 'Oxidation in Organic Chemistry,' Part A, ed. K. B. Wiberg, Academic Press, New York, 1965, p. 1.
15 K. B. Wiberg and R. D. Greer, *J. Am. Chem. Soc.*, 1966, **88**, 5827.
16 R. Clarke, A. Kuhn, and E. Okoh, *Chem. Brit.*, 1975, **11**, 59.
17 H. F. Launer, *J. Am. Chem. Soc.*, 1932, **54**, 2597.
18 F. Freeman, C. O. Fuselier, C. R. Armstead, C. E. Dalton, P. A. Davidson, E. M. Karchesfski, D. E. Krochman, M. N. Johnson, and N. K. Jones, *J. Am. Chem. Soc.*, 1981, **103**, 1154.
19 E. Blanc, *J. Chim. Phys.*, 1920, **18**, 28.
20 K. Takahase and N. Yul, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1941, **20**, 521.
21 A. D. F. Troy, in 'Comprehensive Inorganic Chemistry,' ed. A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973, vol. 2, p. 473.
22 J. H. Espenson and D. F. Dustin, *Inorg. Chem.*, 1969, **8**, 1760.
23 R. J. H. Clark, in 'Comprehensive Inorganic Chemistry,' ed. A. F. Trotman-Dickenson, Pergamon Press, Oxford, vol. 3, 1973.
24 S. Furberg and P. Land Mark, *Acta Chem. Scand.*, 1957, **11**, 1505.
25 J. R. Van Wazer, C. F. Callis, J. N. Schoolery, and R. C. Jones, *J. Am. Chem. Soc.*, 1956, **78**, 5715.
26 J. L. de Hauss, *Chem. Anal.*, 1952, **34**, 248.
27 J. H. Kolitowska, *Rocz. Chem.*, 1953, **27**, 191.
28 R. B. Martin, *J. Am. Chem. Soc.*, 1959, **81**, 1574.
29 B. Silver and Z. Luz, *J. Phys. Chem.*, 1962, **66**, 1356.
30 D. Samuel and B. L. Silver, quoted in ref. 31.
31 J. Reuben, D. Samuel, and B. L. Silver, *J. Am. Chem. Soc.*, 1963, **85**, 3093.
32 R. Stewart and J. A. MacPhee, *J. Am. Chem. Soc.*, 1971, **93**, 4271.
33 D. Benson, 'Mechanisms of Oxidation by Metal Ions,' Elsevier, Amsterdam, 1976, p. 153.
34 N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 1960, 290.

Received 19th *April* 1983; *Paper* 3/626