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LETTER

Induced oxidation of phosphorus(III) by a short-lived manganate(V) intermediate in the permanganate oxidation of arsenite(III)

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Manganese(V) intermediates have long been assumed to be involved in the oxidation of organic and inorganic compounds by permanganate ion [1–5], but they have escaped direct detection except in the oxidation of sulfite ion [6, 7]. Owing to this uncertainty, information about Mn(V) transients is of considerable importance due to mechanistic implications for an extensive family of redox reactions.

In a previous paper on the oxidation of hypophosphorous acid by permanganate ion [8] we suggested the involvement of a reactive manganese(V) intermediate of the type Mn^V–O–P^{III}, which can be regarded as a mixed anhydride of hypomanganous and phosphorous acid. Theoretically, such an anhydride may also be formed from manganese(V) and phosphorus(III). In an attempt to examine this possibility, we designed a system in which the putative manganese(V) intermediate was generated by the very fast reduction of permanganate with arsenite(III) in the presence of phosphorus(III). We anticipated, and searched for, some indication that an interaction took place between Mn(V) and P(III).

We have found that if the known fast oxidation of arsenious acid, H_3AsO_3, is carried out in the presence of phosphorous acid, H_3PO_3, and pyrophosphate (for binding Mn(III) to prevent its disproportionation), permanganate is consumed in excess of the amount used up by As(III) when no P(III) is present. According to kinetic measurements, direct oxidation of P(III) by MnO_4^- is negligible under these conditions during the time intervals involved. Thus the overconsumption of MnO_4^- we encounter here is due to an induced oxidation of phosphorus(III), involving an intermediate of the permanganate–As(III) reaction.

Induced reactions can be characterized by the induction factor, I_f. In our case I_f is the ratio of oxidation equivalents consumed by the acceptor, P(III), and the inductor, As(III). The induction factors determined in the presence of increasing amounts of P(III) (0.0–0.04 M) at fixed initial concentrations of the other reactants are listed in Table 1 for different pHs. Permanganate ion was used in excess over As(III), ensuring that the latter was fully consumed in all cases. The reactions were carried out by mixing aqueous solutions of permanganate (containing pyrophosphate) with As(III) + P(III) in a High-Tech Scientific stopped-flow device. Residual permanganate was measured using a Hewlett-Packard 8452A diode array UV–Vis spectrophotometer.

According to Table 1, I_f depends not only on the ratio of reactant concentrations, but also on the pH. The induction factor approaches the limiting value of 1.0 with increasing P(III) concentration at pH 0–4. Above this pH, I_f rapidly decreases and around pH 8 no induced oxidation can be observed.

In the absence of P(III), As(III) reduces permanganate very rapidly to a mixture of Mn(III) and Mn(IV). With P(III) present, it is reduced mainly to Mn(III). We have found that direct reduction of Mn(IV) by P(III) does not occur under these conditions. Also, if P(III) is added to the solution after complete oxidation of As(III), no induced reaction can be detected.

TABLE 1. Induction factors (I_f) in the As(III)–P(III)–Mn(VII) system ($[MnO_4]_0 = 4.0 \times 10^{-4}$ M; $[pyr]_0^a = 80 \times 10^{-4}$ M; $T = 25$ °C; $\mu = 1.0$ M)

pH	$[As(III)]_0$ $\times 10^4$ (M)	$\frac{[P(III)]_0}{[As(III)]_0}$	Oxidation equivalents consumed $\times 10^4$	I_f^b
0.0	4.0	0.0	8.0	0.0
		25.0	13.6	0.70
		100.0	15.26	0.91
3.8	4.0	0.0	8.0	0.0
		5.0	11.17	0.40
		12.5	12.19	0.52
		25.0	12.89	0.61
		50.0	14.42	0.80
		100.0	14.98	0.87
	2.0	200.0	7.89	0.97
5.8	4.0	0.0	8.0	0.0
		25.0	11.58	0.45
		100.0	13.17	0.65
6.8	4.0	0.0	8.0	0.0
		100.0	9.96	0.25
	2.0	200.0	5.89	0.47
8.6	4.0	0.0	8.0	0.0
		25.0	8.0	0.0
		100.0	8.44	0.06

[a] pyr = pyrophosphate. [b] $I_f = \frac{\text{equiv. consumed by P(III)}}{\text{equiv. consumed by As(III)}}$.

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The observed behavior can be explained by the formation of a reactive Mn(V) intermediate in the reaction of As(III) with MnO_4^-, which is further reduced to Mn(III) either by As(III) or P(III), or may undergo disproportionation. With increasing concentration of P(III), reaction (3) gradually becomes predominant and I_f approaches a limiting value of unity. This corresponds to an overall reaction described by eqns. (1) and (3).

$$\mathrm{Mn(VII)} + \mathrm{As(III)} \longrightarrow \mathrm{Mn(V)} + \mathrm{As(V)} \qquad (1)$$

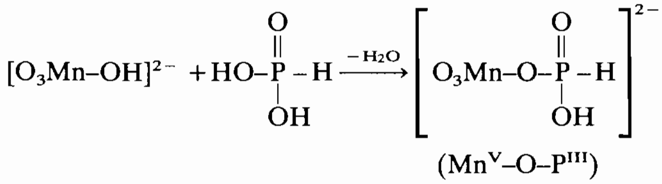
$$\mathrm{Mn(V)} + \mathrm{As(III)} \longrightarrow \mathrm{Mn(III)} + \mathrm{As(V)} \qquad (2)$$

$$\mathrm{Mn(V)} + \mathrm{P(III)} \longrightarrow \mathrm{Mn(III)} + \mathrm{P(V)} \qquad (3)$$

$$3\mathrm{Mn(V)} \longrightarrow 2\mathrm{Mn(IV)} + \mathrm{Mn(VII)} \qquad (4)$$

Under these conditions phosphorus(III) selectively reduces the transient manganese(V), thereby providing a means of detection of this elusive intermediate. This specific and high reactivity is somewhat surprising in view of the generally slow oxidation of phosphorous acid and phosphites [9, 10], a consequence of the cleavage of the strong P–H bond.

Apparently, oxidation by Mn(V) may occur by electron transfer via the oxo-bridge of the anhydride intermediate postulated before [8] (eqns. (5) and (6)).



$$[\mathrm{O_3Mn{-}OH}]^{2-} + \mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}H} \xrightarrow{-\mathrm{H_2O}} \left[\mathrm{O_3Mn{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}H}\right]^{2-}$$

$(\mathrm{Mn^V{-}O{-}P^{III}})$

(5)

$$(\mathrm{Mn^V{-}O{-}P^{III}}) \xrightarrow{\text{fast}} \mathrm{Mn(III)} + \mathrm{P(V)} \qquad (6)$$

The reason why short-lived Mn(V) is selectively reduced by P(III) in the presence of MnO_4^- seems to be its ability to form the anhydride $\mathrm{Mn^V{-}O{-}P^{III}}$ in which electron transfer via the oxo-bridge may readily occur. Similar anhydride formation followed by oxidation has been reported to occur between P(III) and Cr(VI) [9].

For anhydride formation to take place, at least one OH group should be available in both the P(III) and the Mn(V) species. This is possible because MnO_4^{3-} is a stronger base than MnO_4^-. At higher pH, when only HPO_3^{2-} is present, the induced oxidation is suppressed, owing to the lack of an OH group at the phosphorus(III).

Further work is in progress on the utilization of the title reaction for the detection of manganese(V) transients.

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