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LETTER

Oxidation of hypophosphorous acid by permanganate ion

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The kinetics of redox reactions between permanganate ion and oxo anions/acids have been studied in only a few cases, viz. nitrite [1] and sulfite [2, 3] ion, and phosphorous acid [4]. Recent reports on the existence of oscillating reactions involving permanganate ion [5] and the rapid progress in that general field with special reference to quantitative description and design of systems raise interest in rate constants for redox reactions between oxo anions and other (mostly inorganic) species. We report here a kinetic analysis of the oxidation of hypophosphorous acid (H_3PO_2) and hypophosphite ion $H_2PO_2^-$ by permanganate ion in aqueous solution.

Experimental

Successive UV–Vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer in combination with a Hi-Tech Scientific stopped-flow type rapid kinetics accessory. This setup permits measurement of half-lives in excess of *c.* 500 ms. In slower runs ($\tau_{1/2}>30$ s) the reacting solutions were injected from syringes into the spectrophotometric cell. The kinetic data were evaluated using the instrument software. Curve-fitting was done by least-squares procedures.

Analytical grade chemicals were used throughout. The 50% aqueous solution of H_3PO_2 (Fluka) was found to contain less than 1% of H_3PO_3 [6]. Reactions were run in buffered solutions, in the presence of an at least ten-fold excess of pyrophosphate to avoid disproportionation of manganese(III).

Results and discussion

Stoichiometry

In acidic solution, permanganate ion oxidizes hypophosphorous acid to phosphoric acid. The reaction is slow: quantitative transformation can only be achieved by using permanganate in excess and KBr as catalyst [7]. Rapid quantitative reaction between H_3PO_2 and MnO_4^-, yielding H_3PO_3 and Mn(III) stabilized as MnF_4^- has also been reported [8]. These observations as well as the known kinetic data for H_3PO_3 oxidation [4] suggest a very significant difference in the reactivities of H_3PO_3 toward permanganate. We have found that in the presence of pyrophosphate, the stoichiometric factor defined as

$$n=\frac{\Delta[H_3PO_2]}{\Delta[MnO_4^-]} \qquad (1)$$

is very close to 1.0 and remains constant between pH 1 and 6, despite a further slow reaction observed at higher pH. The value of *n* was determined by spectrophotometric estimation of unreacted permanganate when the latter was used in excess, and by kinetic analysis providing both *n* and the rate constant (see below). Between pH 0 and *c.* 2, permanganate ion is reduced to manganese(III), as demonstrated by comparison of the spectra of product solutions with those of pyrophosphatomanganese(III) prepared from authentic manganese(III) acetate:

$$\mathrm{Mn(VII)}+\mathrm{P(I)}\xrightarrow{\text{pyr}}\mathrm{Mn(III)}+\mathrm{P(V)} \qquad (2)$$

where Mn(VII) is permanganate ion, P(I) is the sum of H_3PO_2 and $H_2PO_2^-$ (p*K* of monobasic H_3PO_2 1.2 [9]), pyr is pyrophosphate, Mn(III) is the pyrophosphatomanganese(III) and P(V) phosphoric acid and/or its ionized forms.

The spectral changes accompanying the reaction at pH 1.03 are shown in Fig. 1. The isosbestic point at *c.* 300 nm supports the presence of two absorbing

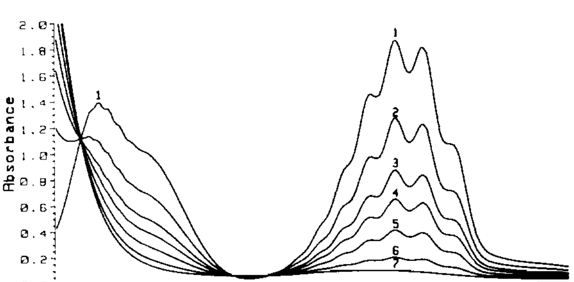

Fig. 1. Time evolution of the spectra at pH 1.03 ($[MnO_4^-]_0=8.0\times10^{-4}$ M; $[H_3PO_2]_0=16.0\times10^{-4}$ M; $[\text{pyrophosphate}]_0=80.0\times10^{-4}$ M; $I=1.0$ M; $t=25$ °C). Times after mixing of the reactants: 1, immediately; 2, 5 s; 3, 15 s; 4, 25 s; 5, 45 s; 6, 95 s; 7, 250 s.

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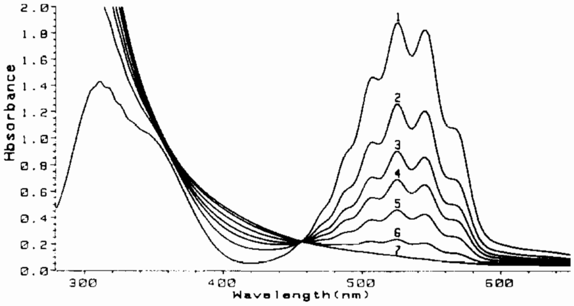

Fig. 2. Time evolution of the spectra at pH 6.24 (conditions and numbering are the same as in Fig. 1).

species, viz. MnO_4^- and Mn(III). At higher pHs, increasing amounts of soluble manganese(IV), a species observed in various permanganate oxidations [2, 3, 10] are formed. This modifies the successive spectra to the set shown in Fig. 2 for pH 6.24. That means increasing contributions by the stoichiometry

$$2\mathrm{Mn(VII)} + 2\mathrm{P(I)} \longrightarrow 2\mathrm{Mn(IV)} + \mathrm{P(V)} + \mathrm{P(III)} \quad (3)$$

Both eqns. (2) and (3) correspond to a consumption ratio of 1.0, but reaction (3) produces P(III) too. At pH 1, at equal reactant concentrations only reaction (2) took place, whereas at 6.5, the contribution of (3) was *c.* 50%, as determined via oxidation of P(III) by I_2 [6].

As for side reactions, tests have shown that H_3PO_3 is oxidized by MnO_4^- 250 times slower than H_3PO_2, and Mn(IV) oxidizes H_3PO_2 only very slowly.

Kinetic measurements

The successive spectra recorded under pseudo-first order conditions (ten-fold or greater excess of H_3PO_2) or at comparable reactant concentrations ($[P(I)]_0/[Mn(VII)]_0 = 0.25$–$2.0$) were used as sources of absorbance versus time curves at various wavelengths, with the objective to analyze the kinetic behaviour. The reaction was found to be first order in both MnO_4^- and total phosphorus(I)

$$-\frac{d[MnO_4^-]}{dt} = k[MnO_4^-][P(I)]_T \quad (4)$$

A least-squares procedure was used to fit the corresponding integrated kinetic equation to the rate data, treating k and the stoichiometric factor n defined by eqn. (1) as parameters. Factor n was included in the balance equations required for integration of rate law (4). From a total of 15 kinetic curves, the best-fit value of n was found to be 1.05 ± 0.03.

The rate coefficients k obtained from the fitting of eqn. (4) to the kinetic curves are listed in Table 1 as a function of the pH.

TABLE 1. Rate constant k and consumption ratio n as a function of pH[a] ($[MnO_4^-]_0 = 2.0 \times 10^{-4}$ M; $[H_3PO_2]_0 = 40 \times 10^{-4}$ M; $[pyr]_0 = 80 \times 10^{-4}$ M; $t = 24$ °C; ionic strength $I = 1.0$ M; chloroacetate, acetate or phosphate buffer)

pH	k (M^{-1} s^{-1})
0.0	76.4
0.5	69.8
1.02[b]	57.5
2.01	54.2
2.22	53.5
2.28	52.3
2.43	50.9
3.66	48.8
3.96[c]	47.4
3.96[d]	33.1
3.96[e]	59.5
4.27	47.9
4.45	48.9
5.04	50.8
5.42	48.2
5.42	10.4[f]
5.93	47.1
6.23[g]	48.8

[a] Each result is the average of 5 runs reproducible to within ±3%. [b] $n = 1.06$. [c] $n = 1.07$. [d] $I = 0.2$ M. [e] $I = 2.0$ M. [f] Oxidation of $D_2PO_2^-$ in D_2O. [g] $n = 1.05$.

We have found that the oxidation of deuterated hypophosphorous acid produces a kinetic isotope effect of $k_H/k_D = 4.6$ (pH 5.42), indicating that the P–H bond is cleaved in the rate-determining step. The similarity of k_1 and k_2 indicates that the single ionizable OH group of H_3PO_2 is not involved in the rate-determining step. This and the kinetic isotope effect point to hydride ion abstraction probably via a bridged transition state, leading to an intermediate (X) with simultaneous ejection of a proton.

The observed kinetic behaviour is consistent with the following mechanism

$$MnO_4^- + H_3PO_2\ (\text{or } H_2PO_2^-) \xrightarrow[\text{slow}]{k_1\ (\text{or } k_2)} [^-O_3MnO..H..PH(O)(OH)]^{\neq} \xrightarrow[\text{fast}]{-H^+} \underset{(X)}{[O_3Mn^{V}\text{–}O\text{–}P^{III}H(O)(OH)]^{2-}} \quad (5)$$

$$X \begin{cases} \xrightarrow{\text{fast}} \mathrm{Mn(III)} + \mathrm{P(V)} & (6) \\ \xrightarrow[+X]{\text{fast}} 2\mathrm{Mn(IV)} + \mathrm{P(III)} + \mathrm{P(V)} & (7) \end{cases}$$

Intermediate X is required by the facts that while the ratio n remains constant, the amounts of both Mn(IV) and P(III) increase upon going from pH 1 to about 6. The further consumption of excess permanganate (above pH 3) after all of the P(I) had been used up is due to the slow oxidation of P(III) produced in reaction (7). The best-fit rate constants accounting for the slight acceleration with increasing acidity are $k_1 = 80$ M^{-1} s^{-1} and $k_2 = 48.5$ M^{-1} s^{-1}. The first dissociation constant of H_3PO_2 is $K = 0.158$ M, as compared with the reported value of 6.31×10^{-2} M (p$K = 1.2$) [9].

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