Kinetics and Mechanism of Oxidations by Peroxodiphosphate Ions. Part 3.† Oxidation of Hypophosphite in Aquous Perchloric Acid by the Hydrolytic Product Peroxomonophosphate in a Consecutive Reaction

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Oxidation of hypophosphite by peroxodiphosphate in perchloric acid solution is a consecutive reaction, (i) and (ii),

$$H_4P_2O_8 + H_2O \xrightarrow{k_h} H_3PO_5 + H_3PO_4 \qquad \text{(i)}$$

$$H_3PO_5 + H_3PO_2 \xrightarrow{k_2} H_3PO_4 + H_3PO_3 \qquad \text{(ii)}$$

and a plot of $[H_3PO_5]$ against time for the reaction exhibits a maximum. In a separate study, the rate law for reaction (ii) has been found to be (iii), where K_1 and K_2 are the acid-ionization constants of H_3PO_2 and H_3PO_5

$$-d[H_3PO_5]/dt = k_2[H_3PO_5]_T[H_3PO_2]_T[H^+]^2/([H^+] + K_1)([H^+] + K_2) \qquad \text{(iii)}$$

respectively; k_2 was $(1.2 \pm 0.08) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at $[H^+] = 0.50$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, and 45 °C. An estimated value of K_2 is 0.15 mol dm^{-3} at 35 °C and $I = 1.0$ mol dm^{-3}. Maximum concentrations of H_3PO_5 and the times at which they are built up have been calculated using the values of k_h and k_2, and these are in good agreement with the observed values.

A SYSTEMATIC study of the oxidations by peroxodiphosphate has been recently started in this laboratory and the oxidations of As^{III},[1] Sb^{III},[2] and bromide[3] have been found to have essentially a hydrolytic mechanism in which the rate is independent of the concentration of the reductant. The rates of these reactions were found to be similar to those observed in previous hydrolytic studies.[4] Peroxodiphosphate hydrolyzes to peroxomonophosphate and the latter oxidizes the reductant in a fast step. Hypophosphite oxidations in general are slow and it would be particularly interesting to study its oxidation by peroxodiphosphate in order to determine whether this reaction has the same mechanism as those studied earlier.[1-3] In case of hypophosphite the above two steps have comparable rates and the reaction is a typical consecutive one. A quantitative treatment of this reaction was made possible by studying separately the hydrolysis of peroxodiphosphate and the oxidation of hypophosphite by peroxomonophosphate.

EXPERIMENTAL

Tetrapotassium peroxodiphosphate $K_4[P_2O_8]$ was a gift from FMC Corporation, U.S.A. Its solution and other solutions were prepared and standardized as described earlier.[1] Perchloric acid was used for varying the hydrogen-ion concentration, and sodium perchlorate, prepared as described,[1] was employed for adjusting the ionic strength. Sodium hypophosphite was May and Baker quality and its cerimetric assay[5] was not less than 99%. All the solutions were prepared in doubly distilled water, the second distillation being from potassium permanganate.

Peroxomonophosphoric acid was prepared by hydrolysis of peroxodiphosphate in 0.5 mol dm^{-3} $HClO_4$ at 45 °C. Venturini *et al.*[6] used 1.0 mol dm^{-3} $HClO_4$ at 25 °C in 4 h. In our case the conversion was >99% complete in 1 h.

$$H_4P_2O_8 + H_2O \longrightarrow H_3PO_5 + H_3PO_4 \qquad (1)$$

Kinetic Procedure.—Oxidation of hypophosphite by peroxodiphosphate. Appropriate quantities of hypophosphite, $HClO_4$, and $Na[ClO_4]$ in a stoppered bottle and of peroxodiphosphate in a second bottle were equilibrated in a thermostat at 45 ± 0.1 °C. The reaction was initiated by adding the requisite quantity of peroxodiphosphate. The kinetics were followed by determining the intermediate product, peroxomonophosphate, iodimetrically in acetate buffer as described earlier.[1] Slow reactions between I_2 and hypophosphite,[7] and between I_2 and phosphite,[8] have been reported, but no reaction appeared to take place in our case in the acid solutions employed and during the time of the titration.

The total peroxomonophosphate was determined from hydrolytic studies using the same concentrations of peroxodiphosphate and $HClO_4$ as employed in the oxidation of hypophosphite. The details have been described earlier.[1] The concentration of peroxomonophosphate at any time could be known from a plot of concentration against time.

Oxidation of hypophosphite by peroxomonophosphate. The kinetics of the oxidation were studied by adding a calculated amount of equilibrated hypophosphite to peroxomonophosphate in a suitable acid medium. The kinetics were followed by determining the peroxomonophosphate by iodimetry. The results were reproducible to ±8%. Under the conditions employed, $[HPO_3]^{2-}$ is not oxidized by peroxomonophosphate or the peroxodiphosphate.

RESULTS AND DISCUSSION

Stoicheiometry.—Sodium hypophosphite and tetrapotassium peroxodiphosphate of different concentrations in suitable acid media were kept for 8—10 h and the excess of peroxodiphosphate was determined cerimetrically.[9] One mol of hypophosphite required 1.02 ± 0.03 mol of peroxodiphosphate for conversion into phosphite.

$$H_4P_2O_8 + H_3PO_2 + H_2O \longrightarrow 2H_3PO_4 + H_3PO_3 \qquad (2)$$

Reaction between Hypophosphite and Peroxomono-

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† Part 2 is ref. 3.

[1] Surinder Kapoor and Y. K. Gupta, *J.C.S. Dalton*, 1976, 473.

[2] Surinder Kapoor and Y. K. Gupta, unpublished work.

[3] L. M. Bharadwaj, D. N. Sharma, and Y. K. Gupta, *Inorg. Chem.*, 1976, **15**, 1695.

[4] M. M. Crutchfield, ' Peroxydiphosphoric Acid in Peroxide Reaction Mechanism,' ed. J. O. Edwards, Interscience, New York, 1961, p. 41.

[5] D. N. Bernhart, *Analyt. Chem.*, 1954, **26**, 1798.

[6] M. Venturini, A. Indelli, and G. Raspi, *Electroanalyt. Chem. Interfac. Electrochem.*, 1971, **33**, 99.

[7] A. D. Mitchell, *J. Chem. Soc.*, 1920, **117**, 1322; R. T. Jones and E. H. Swift, *Analyt. Chem.*, 1953, **25**, 1272.

[8] A. D. Mitchell, *J. Chem. Soc.*, 1923, **123**, 2241.

[9] I. M. Kolthoff and R. Belcher, ' Volumetric Analysis,' Interscience, New York, 1957, vol. 3, p. 44.

phosphate.—The concentration of peroxomonophosphate was varied in the range 1.72×10^{-3}—1.36×10^{-2} mol dm^{-3} at constant [H$^+$] and hypophosphite. The order of reaction with respect to the concentration of peroxomonophosphate was found to be 0.91 from the log-log plot of the initial rate and concentration of the peroxomonophosphate. Good straight lines were also obtained by plotting log [peroxomonophosphate] against time when excess of hypophosphite was used. The initial rates and pseudo-first-order rate constants are given in Table 1. The order with respect to hypophosphite was also one and the second-order rate constants are also given in Table 1.

TABLE 1

Pseudo-first-order and second-order rate constants for the reaction between peroxomonophosphate and hypophosphite at $[H^+] = 0.50$ mol dm^{-3}, 45 °C, and $I = 1.0$ mol dm^{-3}

$[H_3PO_2]$/mol dm^{-3}	$10^3[H_3PO_5]$/mol dm^{-3}	10^3k_1/s^{-1}	10^6 Initial rate/mol dm^{-3} s^{-1}	10^2k_2/dm^3 mol^{-1} s^{-1}
0.20	3.4	2.24		1.12
0.18	3.4	1.95		1.06
0.15	3.4	1.72		1.15
0.12	3.4	1.55		1.30
1.10	3.4	1.28		1.28
0.08	3.4	1.03		1.29
0.05	3.4	0.64		1.28
0.05	1.72	0.64		1.28
0.05	1.72		1.1	1.28
0.05	5.35	0.575		1.15
0.05	5.35		3.0	1.12
0.05	6.2		3.4	1.10
0.05	7.8		4.3	1.10
0.05	9.6		4.9	1.01
0.05	13.6		6.9	1.01
0.03	3.4		1.2	1.25
0.01	3.4		0.41	1.21
0.008	3.4		0.33	1.21
0.005	3.4		0.20	1.18
0.002	3.4		0.083	1.22
			Average:	1.2 ± 0.08

TABLE 2

Pseudo-first-order rate constants (k_1) at different [H$^+$] in the reaction between peroxomonophosphate and hypophosphite. $[H_3PO_5]_T = 3.4 \times 10^{-3}$, $[H_3PO_2]_T = 0.05$, and $I = 2.5$ mol dm^{-3}

[H$^+$]/mol dm^{-3}	10^4k_1/s^{-1} at 35	45	55 °C
0.10	0.76	1.7	2.7
0.13			5.0
0.16			6.2
0.20	1.52	3.64	7.7
0.30	2.00	4.8	9.6
0.40	2.45	5.4	10.5
0.50	3.00	6.5	11.5
0.60	3.40	7.6	13.9
0.70	3.83	7.7	14.8
0.80	4.0	7.8	15.3
0.90	4.1	8.1	16.1
1.00	4.2	9.2	16.3
1.5		10.3	20.7
2.0		10.3	21.0
2.5		10.6	21.4

The hydrogen-ion concentration was varied from 0.1 to 2.5 mol dm^{-3} (at constant $I = 2.5$ mol dm^{-3} adjusted with Na[ClO$_4$]) at three temperatures. The results are given in Table 2. The rate constants tended to a limiting value with increasing hydrogen-ion concentration at the three temperatures. The hydrogen-ion concentration may be correlated with the ionization equilibria (3) and (4) which are important under the acid conditions employed. One or more of the following reactions can occur in the present system: (*i*) $H_3PO_2 + H_3PO_3$; (*ii*) $[H_2PO_2]^- + [H_2PO_5]^-$; (*iii*) $H_3PO_2 + [H_2PO_5]^-$; and (*iv*) $[H_2PO_2]^- + H_3PO_5$.

$$H_3PO_2 \overset{K_1}{\rightleftharpoons} [H_2PO_2]^- + H^+ \qquad (3)$$

$$H_3PO_5 \overset{K_2}{\rightleftharpoons} [H_2PO_5]^- + H^+ \qquad (4)$$

If k_1 is the pseudo-first-order rate constant and k_2 the second-order rate constant, the rate law for case (*i*) would be (5) or (6). Relation (6) is in accordance with the hydrogen-ion dependence observed, and a plot of $[H^+]^2/k_1([H^+] + K_1)$ against [H$^+$] was linear, K_2 being calculated from the gradient and intercept. Values of K_1 at 35, 45, and 55 °C were calculated from the value[10] (K_1) of 0.135 mol dm^{-3} at $I = 1.0$ mol dm^{-3} and 25 °C and from $\Delta H = 1.6$ kcal mol^{-1} for reaction (3).[11] The plots yielded values of K_2 of 0.15, 0.20, and 0.26 mol dm^{-3} at 35, 45, and 55 °C respectively ($I = 1.0$ mol dm^{-3}). Battaglia and Edwards[12] obtained a spectrophotometric value of 0.089 mol dm^{-3} at $I = 0.2$ mol dm^{-3} and 25 °C. The two values of K_2 are in reasonable agreement, given the difference in ionic strength involved. That the reaction may be between neutral species[13] is supported by the fact that the rate constants do not vary by more than 10% for a four-fold variation in ionic strength. The observed hydrogen-ion dependence can also be explained by assuming a reaction between one protonated acid and one anionic species as in (7) or (8). The rate law would have one additional constant K in the numerator of (5) and the salt effect on these mechanisms would be identical with that for two neutral molecules.

$$\frac{-d[H_3PO_5]_T}{dt} = \frac{k_2[H_3PO_5]_T[H_3PO_2]_T[H^+]^2}{([H^+] + K_1)([H^+] + K_2)} \qquad (5)$$

$$k_1 = \frac{k_2[H_3PO_2]_T[H^+]^2}{([H^+] + K_1)([H^+] + K_2)} \qquad (6)$$

$$H^+ + H_3PO_5 \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [H_4PO_5]^+ \xrightarrow[\text{slow}]{[H_2PO_2]^-} \text{products} \qquad (7)$$

$$H^+ + H_3PO_2 \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [H_4PO_2]^+ \xrightarrow[\text{slow}]{[H_2PO_5]^-} \text{products} \qquad (8)$$

Hydrolysis of Peroxodiphosphate.—An exhaustive study of the hydrolysis was made by Edwards and Crutchfield[4] and by Goh *et al*.[14] We recently reported[1]

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[10] J. H. Espenson and D. F. Dustin, *Inorg. Chem.*, 1969, **8**, 1760.

[11] W. H. Dumbaugh, jun., Thesis, Pennsylvania State University, 1959.

[12] C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, 1965, **4**, 552.

[13] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., John Wiley, New York, 1961, p. 152.

[14] S. H. Goh, R. B. Heslop, and J. W. Lethbridge, *J. Chem. Soc.* (*A*), 1966, 1302.

some more results. We thus carried out only those reactions which are relevant to the present investigation. The first-order hydrolysis rate constants (k_h) at $I = 2.5$ mol dm^{-3}, 45 °C, and $[H^+] = 0.5, 0.8, 1.0, 1.5, 2.0$, and 2.5 mol dm^{-3} were found to be 0.98×10^{-3}, 1.57×10^{-3}, 1.96×10^{-3}, 3.02×10^{-3}, 4.9×10^{-3}, and 5.75×10^{-3} s^{-1} respectively.

Oxidation of Hypophosphite by Peroxodiphosphate.—As mentioned earlier, the oxidation of hypophosphite by peroxodiphosphate does not occur directly. It occurs through peroxomonophosphate, the hydrolytic product [equations (1) and (9)]. Since k_2 is not very large

$$H_3PO_5 + H_3PO_2 \xrightarrow{k_2} H_3PO_4 + H_3PO_3 \qquad (9)$$

compared to k_h, a concentration of H_3PO_5 will be built up in the system, depending on the concentrations of H^+ and hypophosphite. Thus the concentration of peroxomonophosphate will pass through a maximum (Figure 1). The peroxomonophosphate determined in the main reaction and in the separate hydrolytic study enables one to calculate the amount of peroxomonophosphate used in the oxidation of hypophosphite. Thus the concentrations of all the species in the system are known. The maximum concentration of peroxomonophosphate and the time at which it reaches a maximum are given [15] by equations (10) and (11), where

$$[H_3PO_5]_{max.} = a\left(\frac{k_2[H_3PO_2]}{k_h}\right)^{k_2[H_3PO_2]/(k_h - k_2[H_3PO_2])} \qquad (10)$$

$$t_{max.} = \frac{2.303 \log(k_h/k_2[H_3PO_2])}{(k_h - k_2[H_3PO_2])} \qquad (11)$$

a is the initial concentration of peroxodiphosphate. The agreement between the observed and calculated values (Table 3) is satisfactory and confirms the consecutive nature of the reaction of peroxodiphosphate with hypophosphite.

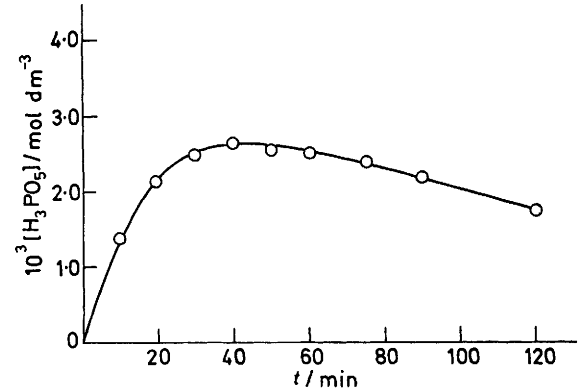

FIGURE 1 Oxidation of H_3PO_2 by $H_4P_2O_8$ in a consecutive reaction. Plot of concentration of intermediate product against time at $[H_4P_2O_8] = 3.4 \times 10^{-3}$, $[H_3PO_2] = 8.0 \times 10^{-3}$, and $[HClO_4] = 0.5$ mol dm^{-3} and 45 °C

The consecutive nature of the reaction can also be verified as follows. From equations (10) and (11), equation (12) is easily obtained and plots of log

$$\log [H_3PO_5]_{max.} = \log a - (k_2[H_3PO_2]t_{max.}/2.303) \qquad (12)$$

$[H_3PO_5]_{max.}$ against $t_{max.}$ for different $[H^+]$ and at three fixed concentrations of H_3PO_2 yielded straight lines (Figure 2). Values of k_2 calculated from the gradients of the three lines are 1.46×10^{-2}, 1.54×10^{-2}, and 1.42×10^{-2} dm^3 mol^{-1} s^{-1}. The average value of k_2 in the separate reactions studied (Table 1) is 1.20×10^{-2} dm^3 mol^{-1} s^{-1}. All the three series have nearly the

TABLE 3

Values of $[H_3PO_5]_{max.}$ and $t_{max.}$ in the reaction between peroxodiphosphate and hypophosphite at 45 °C and $[H_4P_2O_8]_T = 3.4 \times 10^{-3}$ mol dm^{-3}

$[H_3PO_2]$/mol dm^{-3}	$[H^+]$/mol dm^{-3}	$10^3[H_3PO_5]_{max.}$/mol dm^{-3}		$t_{max.}$/min	
		Calc.	Obs.	Calc.	Obs.
0.03	0.5	1.79	1.75	27.0	25
0.03	0.8	2.02	1.85	18.1	20
0.03	1.0	2.05	2.00	14.8	17
0.03	1.5	2.24	2.30	11.1	13
0.03	2.0	2.51	2.50	8.0	9
0.03	2.5	2.59	2.60	7.2	8
0.05	0.5	1.48	1.45	21.6	20
0.05	0.8	1.69	1.62	14.6	15
0.05	1.0	1.72	1.70	12.0	12.5
0.05	1.5	1.94	1.90	8.9	11
0.05	2.0	2.23	2.20	6.6	7
0.05	2.5	2.33	2.35	6.0	6.5
0.10	0.5	1.07	0.925	15.3	15
0.10	1.0	1.28	1.25	8.6	10
0.10	1.5	1.48	1.45	6.6	8
0.10	2.0	1.80	1.80	5.0	6
0.10	2.5	1.90	1.95	4.6	5.5
0.03	0.5	1.79	1.75	27.0	25
0.05	0.5	1.48	1.45	21.6	20
0.08	0.5	1.16	1.25	17.2	15
0.10	0.5	1.07	0.925	15.3	15

The values were calculated from equations (10) and (11); *a* was 3.4×10^{-3} mol dm^{-3}. Values of 10^4k_h and of 10^3k_2 at $[H^+] = 0.5, 0.8, 1.0, 1.5, 2.0$, and 2.5 mol dm^{-3} determined and used were 9.8, 15.7, 19.6, 30.2, 49, and 57.5 s^{-1} and 11.9, 16.0, 19.0, 21.0, and 21.0 s^{-1} respectively.

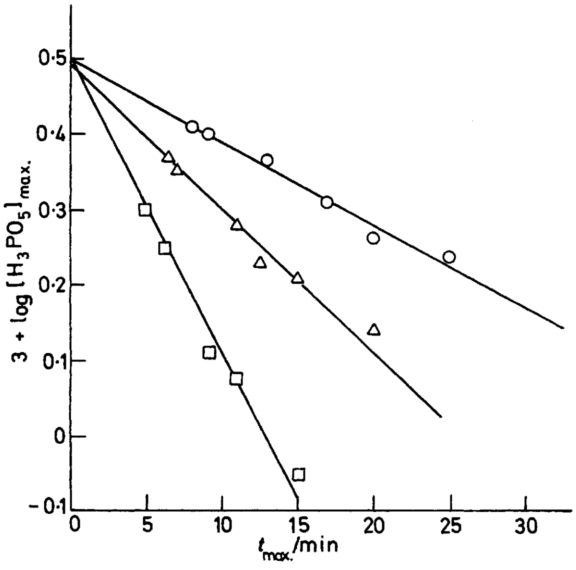

FIGURE 2 Plot of $\log [H_3PO_5]_{max.}$ against $t_{max.}$ at $[H_4P_2O_8] = 3.4 \times 10^{-3}$ mol dm^{-3} and 45 °C. $[H_3PO_2] = 0.1$ (□), 0.03 (○), and 0.05 mol dm^{-3} (△)

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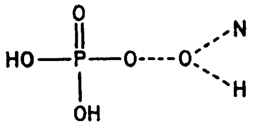
[15] S. Glasstone, ' Textbook of Physical Chemistry,' MacMillan, London, 1948, p. 1077.

same intercept, which gives the initial concentration of peroxodiphosphate as 3.16×10^{-3} mol dm^{-3}.

Our main aim was to study the oxidation by peroxodiphosphate, but it became necessary to study the oxidation by peroxomonophosphate owing to the consecutive nature of the former reaction. Although this limited purpose has been achieved, it may be worthwhile to compare the results of the latter reaction with those from other reactions. In general, hypophosphite oxidations are slower than those of As^{III}. The second-order rate constants for thallium(III) oxidations of arsenic(III) [16] and hypophosphite [17] are 88 and 15 dm^3 mol^{-1} s^{-1} respectively. A similar comparison for Ce^{IV} gives *ca.* 4×10^{-3} (at 12.7 °C) [18] and 2×10^{-5} dm^3 mol^{-1} s^{-1} at 25 °C.[19] In the case of peroxodisulphate, which is isoelectronic and isostructural with peroxodiphosphate, the comparison is difficult owing to much different rate laws. The first-order rate constant in the oxidation of As^{III} was found [20] to be 4.5×10^{-5} s^{-1} at 45 °C and the rate was independent of the concentration of As^{III}. With hypophosphite [21] the second-order rate constant is *ca.* 2×10^{-6} dm^3 mol^{-1} s^{-1} at 45 °C.

The oxidations by peroxomonophosphoric acid are said to take place by nucleophilic displacement of the peroxide oxygen and the activated complex may be represented as below where N is the nucleophile.



Oxidations of As^{III},[1] bromide,[3] nitrite, and hydrazine [2] by H_3PO_5 are much faster than that of hypophosphite. This shows that hypophosphite is less reactive than these as a nucleophile with peroxide oxygen. An active form of H_3PO_2 has been suggested [22] in many of its oxidations and exchange reaction. No evidence was found in the present investigation, but there seems to be no doubt that the active form, which may be $\dot{\,}P(OH)_2H$, is a better electron donor and hence more reactive than the normal form $PO(OH)H_2$.

[6/1307 *Received, 6th July, 1976*]

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[16] P. D. Sharma and Y. K. Gupta, *J.C.S. Dalton*, 1972, 52.

[17] K. S. Gupta and Y. K. Gupta, *J. Chem. Soc.* (*A*), 1970, 256.

[18] K. G. Everett and D. A. Skoog, *Analyt. Chem.*, 1971, **43**, 1541.

[19] R. L. Carrol and L. B. Thomas, *J. Amer. Chem. Soc.*, 1966, **88**, 137.

[20] Y. K. Gupta and S. Ghosh, *J. Inorg. Nuclear Chem.*, 1959, **11**, 62.

[21] E. Ben-Zvi, *Inorg. Chem.*, 1967, **6**, 1143.

[22] W. A. Jenkins and D. M. Yost, *J. Inorg. Nuclear Chem.*, 1959, **11**, 297.