Kinetics and Mechanism of Oxidations by Peroxodiphosphate Ions. Part I. Oxidation of Arsenic(III) in Aqueous Perchloric Acid

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Peroxodiphosphate, $[P_2O_8]^{4-}$, oxidises arsenious acid in perchloric acid medium according to equation (i). The

$$H_4P_2O_8 + H_3AsO_3 + H_2O \longrightarrow 2H_3PO_4 + H_3AsO_4 \qquad \text{(i)}$$

mechanism essentially involves hydrolysis of the species $[H_2P_2O_8]^{2-}$, $[H_3P_2O_8]^-$, and $H_4P_2O_8$, and the rate of the redox reaction is independent of the arsenic(III) concentration. The rate law when $2.5 > [HClO_4] > 0.1$ mol dm^{-3} is as in (ii), and the values of k_2 and k_3 are $(2.7 \pm 0.2) \times 10^{-4}$ and $(8.65 \pm 0.3) \times 10^{-3}$ s^{-1} respectively at 45 °C.

$$-d[P_2O_8]/dt = k_2[H_3P_2O_8^-] + k_3[H_4P_2O_8] \qquad \text{(ii)}$$

The rate of reaction is independent of the ionic strength. Acrylamide, F^-, Cu^{2+}, Mn^{2+}, Fe^{2+}, and phosphate have no effect on the reaction, but Ag^+ catalyzes the reaction.

Little is known about the chemistry of peroxodiphosphate, $[P_2O_8]^{4-}$, and much less about the kinetics of its oxidations. Interest in its kinetics is of recent origin and most of the work has been done by Edwards and his co-workers.[1] The study on the kinetics of hydrolysis seems to be exhaustive.[2] Studies on the oxidation of iodide [3] and vanadyl ion [4] have also been made. Interest in peroxodiphosphate oxidations arises from three facts: (*i*) $H_4P_2O_8$ is isoelectronic and isostructural with $H_2S_2O_8$, and perhaps the oxidation potential is also similar (a comparative study therefore can be made); (*ii*) the oxidations of iron(II) complexes [5,6] are independent of the concentration of $[P_2O_8]^{4-}$ and the rate is governed by the dissociation of the complex which results in loss of one ligand group (it may be worthwhile to investigate whether the same mechanism operates in other cases); (*iii*) little work has been done in this field. Systematic studies of the kinetics of peroxodiphosphate reactions are therefore desirable, and we have carried out the oxidation of arsenious acid in aqueous perchloric acid.

EXPERIMENTAL

Materials.—Tetrapotassium peroxodiphosphate, $K_4[P_2O_8]$, was a gift from FMC Corporation of U.S.A. It contained potassium phosphate and potassium fluoride as impurities. However, the preliminary work showed that these impurities had little effect on the kinetics and hence the sample was used as such. All other chemicals were B.D.H. (AnalaR) or E. Merck quality. Doubly distilled water was employed, the second distillation being from potassium permanganate. Perchloric acid was 70% AnalaR (Riedel). Sodium perchlorate (E. Merck) was used as such or prepared by neutralizing perchloric acid with sodium hydrogencarbonate to pH 6.7. The solution of $[P_2O_8]^{4-}$ was prepared by direct weighing and was standardized cerimetrically [7] and iodimetrically.[8] The results were similar. A stock solution of 0.1 mol dm^{-3} arsenious acid, H_3AsO_3, was prepared. For this an amount of arsenious oxide sufficient to give a little more than 0.1 mol dm^{-3} acid was dissolved by boiling in distilled water. After allowing the solution to cool, it was filtered and standardized against permanganate.[9] The hydrogen-ion concentration was varied with perchloric acid, and the ionic strength was adjusted with sodium perchlorate.

Kinetic Procedure.—Requisite quantities of arsenious acid, perchloric acid, sodium perchlorate, and other reagents were thermostatted in a reaction vessel in a water-bath at 45 ± 0.1 °C unless otherwise stated. Tetrapotassium peroxodiphosphate, separately equilibrated, was added to the reaction vessel to initiate the reaction. Aliquot portions

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(5 cm^3) were analyzed cerimetrically[7] at intervals for $[P_2O_8]^{4-}$. In some cases the kinetics were followed by determining arsenite iodimetrically in hydrogencarbonate medium by titrating against a potassium iodide solution containing iodine. The results were similar in both cases.

While determining $[P_2O_8]^{4-}$ cerimetrically, particularly in the lower range of concentrations, the results appeared to be irregular at the beginning of the experiments. In the cerimetric estimation the reaction mixture was added to a solution of Fe^{II} and Fe^{III} was formed. It appears that a slow reaction[10] between Fe^{III} and arsenite occurs, thus vitiating the determinations. When phosphate is initially added to complex[11] the Fe^{III}, no such difficulty was encountered. The results were consistent towards the end of reaction, even in the absence of added phosphate, because phosphate is produced in the reaction. Thus all reactions were carried out in the presence of 0.05 mol dm^{-3} sodium dihydrogenphosphate.

A kinetic study of the hydrolysis was necessitated since it was found that this was relevant to the redox study. A few experiments under identical conditions were therefore planned for hydrolytic studies. The reaction was again initiated by the addition of $[P_2O_8]^{4-}$ to a mixture of requisite quantities of perchloric acid and sodium perchlorate, but not containing arsenious acid. Aliquot portions were analyzed iodimetrically[12] in an acetate buffer of pH 4—5 in the presence of trace amounts of ammonium molybdate. Aliquot portions of reaction mixtures were added to requisite quantities of acetate, acetic acid, or sodium hydroxide (to neutralize excess of perchloric acid in the reaction mixture), yielding the buffer. Potassium iodide was added and the resulting iodine was titrated against thiosulphate using starch as indicator. Since $[P_2O_8]^{4-}$ slowly hydrolyzes, even at pH 4—5, the first disappearance of the blue colour was noted. Peroxodiphosphate hydrolyzes[13] to peroxomonophosphoric acid, H_3PO_5, and then to hydrogen peroxide. At pH 4—5, $[P_2O_8]^{4-}$ does not liberate iodine from iodide, although H_3PO_5 does so readily and H_2O_2 does so slowly. However, the reaction of H_2O_2 with $[I]^-$ is strongly catalyzed by trace amounts of ammonium molybdate, and thus $H_3PO_5 + H_2O_2$ could be estimated.

In most cases duplicate rate measurements were reproducible to ±5%. The rates were measured by the plane-mirror method. First-order rate constants could also be calculated from a plot of log $[P_2O_8{}^{4-}]$ against time under all conditions because the rate was independent of arsenite concentration. The maximum individual deviation from the mean value of the first-order rate constant was not more than 5—6%.

pH Measurements were made on a Expand 821 pH meter from the Electronic Corporation.

RESULTS

Stoicheiometry.—Different amounts of $[P_2O_8]^{4-}$ and H_3AsO_3 were mixed in 0.5 mol dm^{-3} $HClO_4$ and kept for *ca.* 96 h. Excess of arsenite was estimated with permanganate,[9] and excess of $[P_2O_8]^{4-}$ was determined cerimetrically.[7] The results with $[K_4P_2O_8] = 4 \times 10^{-3}$—$2 \times 10^{-2}$ mol dm^{-3} and $[As^{III}] = 5 \times 10^{-5}$—0.1 mol dm^{-3} showed that 1.00 ± 0.02 mol of $[P_2O_8]^{4-}$ is consumed per mol of As^{III}.

Peroxodiphosphate Dependence.—The concentration of $[P_2O_8]^{4-}$ was varied in the range 1.80×10^{-3}—10.82×10^{-3} mol dm^{-3}; plots of log $[P_2O_8{}^{4-}]$ against time yielded straight lines, from which first-order rate constants were calculated from the gradients. Such rate constants could be also calculated from the initial rates. An average value was 7.2 ± 0.2 s^{-1} at 45 °C, I = 0.5 mol dm^{-3}, and $[HClO_4]$ = 0.5 mol dm^{-3}.

Arsenite Dependence.—The concentration of H_3AsO_3 was varied in the range 0.002—0.1 mol dm^{-3} and it had no effect on the rate. These results, together with those for the $[P_2O_8{}^{4-}]$ dependence, are shown in Table 1. All peroxodiphosphate species have been indicated by $[P_2O_8]$ and all arsenic species by $[As^{III}]$.

TABLE 1

First-order rate constants for the $[P_2O_8]^{4-} + H_3AsO_3$ reaction at $[HClO_4]$ = 0.5 mol dm^{-3}, 45 °C, $[H_2PO_4{}^-]$ = 0.05 mol dm^{-3}, and $I \approx 0.5$ mol dm^{-3}

Experiment no.	$10^3[P_2O_8]$/mol dm^{-3}	$10^2[As^{III}]$/mol dm^{-3}	10^4k/s^{-1}
1	1.81	4.0	6.9
2	2.68	4.0	6.9
3	3.62	4.0	6.9
4	4.46	4.0	6.9
5	1.81	5.0	6.9
6	2.68	5.0	6.9
7	3.62	5.0	6.9
8	4.46	5.0	6.9
9	5.54	5.0	6.9
10	6.42	5.0	6.9
11	1.81	6.0	7.6
12	2.68	6.0	7.3
13	3.62	6.0	7.3
14	4.46	6.0	7.5
15	5.54	6.0	7.3
16	6.42	6.0	7.3
17	8.30	0.5	7.3
18	8.30	1.0	7.6
19	8.30	3.0	6.9
20	8.30	6.0	7.1
21	8.30	7.0	7.2
22	8.30	8.0	7.3
23	8.30	9.0	7.6
24	8.30	10.0	7.6
25	10.8	0.5	7.6
26	9.10	0.5	7.6
27	7.28	0.5	7.0
28	5.46	0.5	7.6
29	3.64	0.5	7.1
30	8.30	1.0	7.3
31	9.10	0.2	6.9
32	9.10	0.3	7.0
33	9.10	0.4	7.0
34	9.10	0.5	6.9
35	9.10	0.6	6.9
36	9.10	0.7	7.2
37	9.10	0.8	7.3
38	9.10	0.9	7.6
39	9.10	1.0	7.1
40	9.10	2.0	6.9
41	9.10	3.0	7.3
42	9.10	4.0	7.3
43	9.10	7.0	7.6
44	9.10	9.0	7.2
		Average	7.2 ± 0.2

Reactions (1)—(24) were followed by determining $[P_2O_8]^{4-}$ cerimetrically, and reactions (25)—(44) were followed by determining As^{III} iodimetrically.

Hydrogen-ion Dependence.—The hydrogen-ion concentration was varied with perchloric acid in the range 0.1—2.5

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[12] I. M. Kolthoff, *Z. Analyt. Chem.*, 1921, **60**, 400.

[13] Ref. 2, p. 59.

mol dm^{-3} and the ionic strength was adjusted with sodium perchlorate. The first-order rate constants increased significantly with increasing [H$^+$]. Results at four temperatures are given in Table 2.

TABLE 2

First-order rate constants for the $[P_2O_8]^{4-} + H_3AsO_3$ reaction at different [HClO$_4$]. $I = 2.5$ mol dm^{-3}, $[P_2O_8] = 4.55 \times 10^{-3}$ mol dm^{-3}, $[As^{III}] = 1.0 \times 10^{-2}$ mol dm^{-3}, and $[H_2PO_4^-] = 5 \times 10^{-2}$ mol dm^{-3}

	10^4 k/s^{-1}			
[HClO$_4$]/mol dm^{-3}	30	35	45	55 °C
0.1			0.61	0.97
0.2			1.8	4.9
0.3			3.3	8.8
0.5	1.2	2.5	7.2	17
0.8	2.8	5.7	14.3	30
1.0	4.1	6.8	20.3	46
1.2	5.3	8.0	26	54
1.5	7.0	10.3	32	60
1.8	7.3	13.0	38	69
2.0	8.0		40	81
2.2	8.5	15.3	42	
2.5	9.2	16.0	47	92

Ionic-strength Effect.—The ionic strength of the medium was varied with sodium perchlorate from 0.5 to 2.5 mol dm^{-3} at [HClO$_4$] = 0.5 mol dm^{-3} and there was no change in the rate.

Effects of Other Ions and Compounds.—Fluoride ion, Cu^{2+}, Fe^{2+}, Mn^{2+}, and H_3PO_4 had no effect in the concentration range 4×10^{-5}—1×10^{-2} mol dm^{-3}. Acrylamide had no effect on the rate. The reaction was catalyzed by Ag^I, the rate constant, k, at 45 °C being more than doubled in the presence of 5×10^{-4} mol dm^{-3} Ag[NO$_3$]. In the presence of 0.05 mol dm^{-3} $Na_4[P_2O_7]$ or $Na_2[HAsO_4]$ the rate constant was reduced to almost half its value. The rate decreased in the presence of $\geqslant 1.0$ mol dm^{-3} $Na[H_2PO_4]$. The decrease in rate caused by these three salts can be ascribed to the decrease in hydrogen-ion concentration.

Activation Energy and Entropy.—The first-order rate constants at 25, 35, 45, and 55 °C and at [HClO$_4$] = 0.5 mol dm^{-3} were 1.2×10^{-4}, 2.5×10^{-4}, 7.2×10^{-4}, and 17×10^{-4} s^{-1} respectively. The overall energy of activation from a plot of log k against $1/T$ was 82 ± 1 kJ mol^{-1}. The entropy of activation was estimated to be -55 ± 4 J K^{-1} mol^{-1}.

DISCUSSION

Since the rate of reaction is independent of the arsenite concentration, the only interest from the mechanistic point of view lies in the hydrogen-ion dependence. The peroxodiphosphate anion has a charge of 4− and the third and fourth acid-dissociation constants [14] are reported to be 6.6×10^{-6} and 2.1×10^{-8} mol dm^{-3} respectively. It is obvious therefore that the salt would be converted into $[H_2P_2O_8]^{2-}$. However, further association with H$^+$ is also possible according to equations (1) and (2), and the forms $[H_3P_2O_8]^-$and $H_4P_2O_8$ are likely to be present under the acid conditions employed in the investigation. It was not possible to determine the values of K_1 and K_2, but they have been estimated [14] by extrapolation of the corresponding values for $H_4P_2O_7$ and $H_4P_2O_6$, and are *ca.* 3.33 and 0.5 dm^3 mol^{-1} respectively. The amounts of the various species present on the basis of these values and as a function of pH have already been given.[15]

$$[H_2P_2O_8]^{2-} + H^+ \overset{K_1}{\rightleftharpoons} [H_3P_2O_8]^- \qquad (1)$$

$$[H_3P_2O_8]^- + H^+ \overset{K_2}{\rightleftharpoons} H_4P_2O_8 \qquad (2)$$

If all the species are considered to contribute to the rate, expression (3) can be obtained since the rate is independent of arsenite concentration. However, a plot

$$-d[P_2O_8]/dt = k_1[H_2P_2O_8{}^{2-}] + k_2[H_3P_2O_8{}^-] + k_3[H_4P_2O_8]$$

$$= \frac{[P_2O_8](k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2)}{1 + k_1[H^+] + K_1K_2[H^+]^2}$$

$$\text{or} \qquad k = (k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2)/(1 + K_1[H^+] + K_1K_2[H^+]^2) \qquad (3)$$

of $k(1 + K_1[H^+] + K_1K_2[H^+]^2)$ against $[H^+]^2$ yielded a straight line with almost zero intercept. Plots of other functions of [H$^+$] were also attempted, but no straight lines were obtained. The values of the rate constant k_3 obtained from such plots at four temperatures are shown in Table 3. It appears that, by and large, $H_4P_2O_8$ is the species which contributes to the rate when $[H^+] > 1.0$ mol dm^{-3}. Further, the plots for $[H^+] <$ 1.0 mol dm^{-3} were not straight lines. It is obvious that at low [H$^+$], $[H_3P_2O_8]^-$ also contributes to the rate. The hydrogen-ion concentration for such reactions was calculated from the pH measurements, and from this the concentrations of various species were calculated. With the values of k_3 obtained from the above plots, k_2 could also be estimated. Thus under the acid conditions employed, although all the three species $[H_2P_2O_8]^{2-}$, $[H_3P_2O_8]^-$, and $H_4P_2O_8$ exist, only $[H_3P_2O_8]^-$ and $H_4P_2O_8$ contribute to the rate. However, much reliance cannot be placed on the absolute values of the individual rate constants because of uncertainty in the values of K_1 and K_2.

TABLE 3

Rate constants k, k_2, and k_3 for the reaction between $[P_2O_8]^{4-}$ and H_3AsO_3 and their comparison with the corresponding rate constants for the hydrolysis reaction

θ_c/°C	[HClO$_4$]/mol dm^{-3}	I/mol dm^{-3}	10^4k/s^{-1}	10^4k_2/s^{-1}	10^3k_3/s^{-1}	Ref.
25	1.0	1.1	2.45	1.0	9.0	*a*
25	0.1	0.1		0.6		3
30	0.5	2.5	1.2		1.85 ± 0.1	*b*
30		3.0		0.58	0.7	17
35	0.5	2.5	2.5		2.8 ± 0.3	*b*
45	0.5	2.5	7.2	2.7 ± 0.2	8.65 ± 0.3	*b*
49.9		1.0		1.4	3.0	17
50	0.39	0.5	12.6			*a*
55	0.5	2.5	17	12 ± 1	15.5 ± 0.4	*b*

[a] Ref. 1, p. 391. [b] This work.

The observed first-order rate constants of 7.2×10^{-4} s^{-1} at 45 °C and 17×10^{-4} s^{-1} at 55 °C compare well with the hydrolysis rate constant [16] of 12.6×10^{-4} s^{-1} at 50 °C.

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[14] M. M. Crutchfield and J. O. Edwards, *J. Amer. Chem. Soc.*, 1960, **82**, 3533.

[15] Ref. 2, p. 56.

[16] Ref. 2, p. 53.

This, and the fact the reaction rate is independent of arsenite concentration, suggested that the reaction is essentially one of hydrolysis and led us to make a study of the hydrolysis reaction. The results at different $[H^+]$ are given in Table 4. These observations compare well with those of the redox reactions in Table 2. However, the results of a study of the hydrolysis made by Goh *et al.*,[17] and by Indelli and Bonora,[3] when compared to our results, vary by a factor of two to five. The results of the previous studies are also not in agreement.

TABLE 4

First-order rate constants for the hydrolysis reaction of $[P_2O_8]^{4-}$ at different $[HClO_4]$, and $[P_2O_8] = 4.375 \times 10^{-3}$ mol dm^{-3} and $I = 2.5$ mol dm^{-3}

	10^4k/s^{-1}		
$[HClO_4]$/mol dm^{-3}	35	45	55 °C
0.1	0.23	0.66	1.9
0.2	0.52	2.50	2.87
0.3	1.04	4.2	
0.4	2.3	5.0	12.7
0.5	3.4	8.4	19.1
0.8	6.1	13.6	30.6
1.0	8.6	17.8	43
1.2	9.8	20.4	53
1.5	12.6	32.6	54
1.8	15.3	38	70
2.0	17.6	44	77
2.2	18.2	46	96
2.5	20	54	103

Thus the following mechanism may be suggested for the oxidation of As^{III} by peroxodiphosphate, where

$$[H_nP_2O_8]^{(4-n)-} + H^+ \overset{K}{\rightleftharpoons} [H_{n+1}P_2O_8]^{(3-n)-} \qquad (4)$$

$$[H_mP_2O_8]^{(4-m)-} + H_2O \overset{k}{\rightleftharpoons} [H_{m-1}PO_5]^{(4-m)-} + H_3PO_4 \qquad (5)$$

$$[H_{m-1}PO_5]^{(4-m)-} + As^{III} \longrightarrow \text{Products (fast)} \qquad (6)$$

$n = 2$ or 3 and $m = 2$—4. Another redox system[18] involving $[P_2O_8]^{4-}$ and having an essentially hydrolytic mechanism is that of the oxidation of bromide. Bromide is oxidized in a fast step by the hydrolytic products and not by $[P_2O_8]^{4-}$. It is interesting to note that the oxidation of iodide studied by Indelli and Bonora[3] is dependent to some extent on the concentration of iodide, whereas that of bromide is not. However, the range of $[H^+]$ studied by the previous workers was less than 0.04 mol dm^{-3} ($HClO_4$) and it may be worthwhile to study the oxidation at greater hydrogen-ion concentrations.

Our results differ from those of Goh *et al.*[17] in that the additional step (7) is included by the previous workers.

$$H_4P_2O_8 + H^+ \longrightarrow [H_5P_2O_8]^+ \qquad (7)$$

Our results on the hydrogen-ion dependence do not merit this. Thus on the basis of the above mechanism the composition of the three activated complexes would be $([H_2P_2O_8]^{2-}\cdot H_2O)$, $([H_2P_2O_8]^{2-}\cdot H^+\cdot H_2O)$, and $([H_2P_2O_8]^{2-}\cdot 2H^+\cdot H_2O)$, but under our acid conditions the contribution[19] to the rate from step (8) would be greater than

$$H_4P_2O_8 + H_2O \xrightarrow{k_3} H_3PO_5 + H_3PO_4 \qquad (8)$$

98%. The overall effect of ionic strength would be determined by steps (1), (2), and (8). Although a decrease in rate on increasing ionic strength is predicted for steps (1) and (2), these steps do not seem to be important, probably because the effect of ionic strength on the equilibria is small. Since the rate-determining step (8) does not involve any ionic species, there is no effect of ionic strength.

Although $H_4P_2O_8$ is isoelectronic and isostructural with $H_4S_2O_8$, there appears to be no resemblance with regard to their oxidizing behaviour. Since the present reaction is not affected by acrylamide, Cu^{II}, Mn^{II}, and Fe^{II}, the mechanism is probably not free radical in nature in contrast to the peroxodisulphate oxidations.[20] Even in the oxidation of propan-2-ol,[21] where organic free radicals are likely to be formed, there is no evidence for free radicals from peroxodiphosphate ions. However, some more peroxodiphosphate systems must be studied before the absence of a free-radical mechanism can be established.

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