Kinetics and Mechanism of Oxidation of Hypophosphite by Hexacyanoferrate(III) Ion in Alkaline Solution

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Hypophosphite is oxidised to phosphlte by hexacyanoferrate(III) in alkaline solution according to equation (i).

$$[H_2PO_2]^- + 2[Fe(CN)_6]^{3-} + OH^- \longrightarrow H_3PO_3 + 2[Fe(CN)_6]^{4-} \qquad (i)$$

The rate law at 55.7 °C is (ii) where $k' = (2.80 \pm 0.08) \times 10^{-4}$ l^2 mol^{-2} s^{-1} at $I = 4.7$M. The ionic-strength

$$-d[Fe(CN)_6{}^{3-}]/dt = k'[Fe(CN)_6{}^{3-}][H_2PO_2{}^-][OH^-] \qquad (ii)$$

dependence and entropy of activation show that ion-pair species are more reactive in this reaction.

OXIDATIONS of hypophosphorous acid have been characterised [1] by an equilibrium involving active and normal forms and these have been represented [2] as $HP(OH)_2$ and $H_2PO(OH)$ respectively. Another important fact is that the rates of reaction become independent of larger concentrations of the oxidants listed in ref. 1 (Cl_2, Br_2, I_2, $[IO_3]^-$, $CuCl_2$, $HgCl_2$, and $Ag[NO_3]$). Our interest in oxidation studies of hypophosphorous acid accrued on account of these observations and several papers [3-5] have appeared from this laboratory. Hexacyanoferrate(III) ion as oxidant was particularly chosen for such a study because in the oxidations of hexoses [6] and disaccharides [7] the rate of reaction is independent of the concentration of $[Fe(CN)_6]^{3-}$ ion. Another advantage of $[Fe(CN)_6]^{3-}$ is that it is inert to substitution and as such there can be no possibility of complex formation between iron(III) and hypophosphite. Thus complications arising out of complex formation, as reported in oxidations by thallium(III),[3] cerium(IV),[4] chromium(VI),[8] *etc.*, are likely to be absent in oxidations by $[Fe(CN)_6]^{3-}$. The reaction between $[Fe(CN)_6]^{3-}$ and hypophosphorous acid is quite slow at ordinary temperatures and hence the study was made at 55.7 °C in an alkaline medium. Under these conditions hypophosphite is oxidised to phosphite and further oxidation of the latter does not occur.

EXPERIMENTAL

Sodium hypophosphite ($Na[H_2PO_2]$), potassium hexacyanoferrate(III), sodium hydroxide, sodium chloride, potassium chloride, and sodium sulphate were obtained from B.D.H. (AnalaR). Sodium perchlorate solution was prepared by neutralizing perchloric acid with sodium hydrogencarbonate to pH 7. It was boiled to remove CO_2 and cooled before use. All solutions were prepared in redistilled water (second distillation from permanganate). All glass vessels were from Corning. Solutions of $[Fe(CN)_6]^{3-}$ were stored in the dark and solutions older than 48 h were not used. The concentration was checked iodometrically.[9]

Kinetic Procedure.—Measured quantities of sodium hypophosphite and sodium hydroxide in a stoppered conical flask were placed in a thermostatted water-bath at 55.7 ± 0.1 °C unless mentioned otherwise. The reaction was started by adding equilibrated $K_3[Fe(CN)_6]$ solution. Aliquot portions (5 cm^3) withdrawn at intervals were added to an ice-cold acid solution of such concentration that the resulting overall concentration of the acid was *ca.* 0.05N. The unused $[Fe(CN)_6]^{3-}$ was then determined iodometrically. A slow reaction of iodine with hypophosphorous acid and phosphorous acid has been reported,[10] but the acid conditions and the low temperature eliminated this possibility and the iodometric determination of $[Fe(CN)_6]^{3-}$ was free from interference.

Concentrations of sodium hydroxide employed in the investigation were large compared to those of the main reactants and hence the pH and the ionic strength remained practically constant. The maximum error in titration of the aliquot portions was ± 0.02 cm^3 of thiosulphate, which introduced a maximum error of $\pm 10\%$ depending on the volume of the titrant but in general the individual observations were within $\pm 6\%$. In most cases duplicate measurements were reproducible to $\pm 5\%$.

The decomposition of $[Fe(CN)_6]^{3-}$ was studied in 1.0 and

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[1] A. D. Mitchell, *J. Chem. Soc.*, 1920, **117**, 1920, 1322; 1921, **119**, 1266; 1922, **121**, 1624; 1923, **123**, 629; R. O. Griffith and A. Micheown, *Trans. Faraday Soc.*, 1934, **30**, 530; 1940, **36**, 752; P. Hayword and D. M. Yost, *J. Amer. Chem. Soc.*, 1949, **71**, 915.

[2] W. A. Jenkins and D. M. Yost, *J. Inorg. Nuclear Chem.*, 1959, **11**, 308.

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

[4] S. K. Mishra and Y. K. Gupta, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1643.

[5] Ratan Swaroop and Y. K. Gupta, *J.C.S. Dalton*, 1972, 851.

[6] N. Nath and M. P. Singh, *J. Phys. Chem.*, 1965, **69**, 2038.

[7] R. K. Srivastava, N. Nath, and M. P. Singh, *Tetrahedron*, 1967, **23**, 1189.

[8] J. H. Espenson and D. E. Binau, *Inorg. Chem.*, 1966, **5**, 1365.

[9] I. M. Kolthoff and R. Bechler, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3, p. 344.

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

4.0M-NaOH colorimetrically and iodometrically. No decomposition (from 0.001 to 0.1M) was observed in 1.0M-NaOH in 2 h.* In 4.0M-NaOH there was 6—10% decomposition in 2 h for lower concentrations (0.001 and 0.002M) of $[Fe(CN)_6]^{3-}$. No decomposition was observed for concentrations of $[Fe(CN)_6]^{3-}$ larger than 0.003M even in 4.0M-NaOH. The colorimetric and iodometric results were similar.

TABLE 1

Pseudo-first- and second-order rate constants for the reaction between $[Fe(CN)_6]^{3-}$ and hypophosphite at $[NaOH] = 4.0$ and $I = 4.7$M

θ_c/°C	$10[NaH_2PO_2]$/M	$10^2[K_3Fe(CN)_6]$/M	10^4k_1/s^{-1}	10^3k_2/l mol^{-1} s^{-1}
55.7	2.0	0.1	2.24	1.12
	2.0	0.2	2.18	1.19
	2.0	0.3	2.20	1.10
	2.0	0.6	2.24	1.12
	2.0	0.8	2.28	1.14
	2.0	1.0	2.26	1.08
	0.5	0.2	5.55	1.11
	0.5	0.4	5.75	1.15
	0.5	0.6	5.40	1.08
	0.5	0.8	5.70	1.14
	0.5	0.5	5.94	1.19
	0.6	0.5	6.59	1.10
	0.7	0.5	7.99	1.14
	0.8	0.5	9.27	1.16
	0.9	0.5	10.1	1.12
	1.0	0.5	11.4	1.14
	2.5	0.5	27.6	1.10
	3.0	0.5	32.1	1.07
	4.0	0.5	46.3	1.16
	1.0	1.0	12.0	1.20
	3.0	1.0	33.6	1.12
	5.0	1.0	56.2	1.12
	0.3	10.0		1.12
	0.6	10.0		1.11
	1.2	10.0		1.05
	1.0	5.0		1.09
	1.0	10.0		1.10
	1.0	15.0		1.10
	1.0	20.0		1.09
	0.25	5.0		1.10
	0.50	10.0		1.08
				Av. 1.12 ± 0.03 $k' = 2.80 \pm 0.08$ l^2 mol^{-2} s^{-1}
50	0.40	0.5		0.59
	1.0	0.5		0.60
	1.5	0.5		0.58
	2.0	0.5		0.58
	4.0	0.5		0.61
				Av. 0.59
45	0.40	0.5		0.33
	1.0	0.5		0.31
	1.5	0.5		0.33
	2.0	0.5		0.32
	4.0	0.5		0.36
				Av. 0.33
35	0.40	0.5		0.11
	1.0	0.5		0.10
	2.0	0.5		0.10
	4.0	0.5		0.11
				Av. 0.105

RESULTS

Stoicheiometry.—Mixtures were allowed to react at 55 °C for *ca.* 6—8 h. Excess of hypophosphite was determined cerimetrically [11] after precipitating [9] out $[Fe(CN)_6]^{4-}$ on adding zinc sulphate solution. Excess of $[Fe(CN)_6]^{3-}$ was determined iodometrically. Hexacyanoferrate(II) was determined cerimetrically. With excess of $[Fe(CN)_6]^{3-}$ 1 mol of hypophosphite required 2.06 ± 0.06 mol of $[Fe(CN)_6]^{3-}$. With excess of hypophosphite the stoicheiometry was 1.95 ± 0.04 : 1.

Hexacyanoferrate(III) *and Hypophosphite Dependences.*—The concentration of $[Fe(CN)_6]^{3-}$ was varied from 1×10^{-3} to 1×10^{-1}M and that of hyphophosphite from 2.5×10^{-2} to

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* 1M = 1 mol dm^{-3}, 1 cal = 4.184 J.

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

4×10^{-1}M. With excess (20 times or more) of hypophosphite plots of log $[Fe(CN)_6{}^{3-}]_t$ against time were linear showing a first-order dependence in $[Fe(CN)_6{}^{3-}]$. The pseudo-first-order rate constants were calculated from the gradients of these plots. With comparable concentrations of the reactants good second-order plots were obtained and the rate constants were similar to those derived from the pseudo-first-order rate constants. These results are given in Table 1.

Hydroxide Dependence.—The concentration of sodium hydroxide was varied from 0.25 to 3.0M at constant ionic strength of 3.23M adjusted with sodium perchlorate and assuming complete ion pairing between K^+ and $[Fe(CN)_6]^{3-}$ as $K[Fe(CN)_6]^{2-}$. In any case the change in the ionic strength due to the latter is small. The first-order dependence on hydroxide-ion concentration is obvious from Table 2. It is interesting to note that the rate of the oxidation of sulphite[12] by $[Fe(CN)_6]^{3-}$ is independent of $[OH^-]$.

TABLE 2

Effect of sodium hydroxide concentration on the reaction between $[Fe(CN)_6]^{3-}$ and hypophosphite at 55.7 °C, $[NaH_2PO_2] = 0.2$, $[K_3Fe(CN)_6] = 0.01$, and $I = 3.53$M

[NaOH]/M	10^4k_2/l mol^{-1} s^{-1}	$10^4k_2[OH^-]^{-1}$/l^2 mol^{-2} s^{-1}
0.5	0.66	1.32
1.0	1.23	1.23
1.5	1.79	1.20
2.0	2.40	1.20
2.5	3.25	1.30
3.0	4.20	1.40

Product Dependences.—The concentration of $[Fe(CN)_6]^{4-}$ was varied from 0.001 to 0.1M at 4.0M-NaOH. Ionic strength was adjusted to 5.0M with sodium perchlorate taking into account the extensive ion pairing[13] of K^+ and $[Fe(CN)_6]^{4-}$ to yield $K[Fe(CN)_6]^{3-}$. The concentrations of $[Fe(CN)_6]^{3-}$ and hyphophosphite were 0.01 and 0.2M respectively. The reaction was very slow in 1.0M-NaOH and hence lower concentrations could not be employed. The concentration of the other product, phosphite, was varied from 0.01 to 0.1M at $I = 4.1$M. No effect was observed with either product.

Ionic-strength Dependence.—The effect of ionic strength on the rate was studied by varying the concentration of sodium perchlorate and potassium chloride. The rate increased with increasing concentration of these salts (Table 3). Lanthanum and bivalent salts of Ba^{2+}, *etc.*, could not be employed because of precipitation of the hydroxides.

TABLE 3

Effect of ionic strength on the rate of reaction between $[Fe(CN)_6]^{3-}$ and hypophosphite at $[K_3Fe(CN)_6] = 5 \times 10^{-3}$, $[Na_2PO_2] = 0{\cdot}1$M, and 55·7 °C

(*a*) [NaOH] = 2.0M

I/M	2.63	3.13	3.63	4.13	4.52
10^4k_2/l mol^{-1} s^{-1}	0.702	1.23	2.43	4.51	5.79

(*b*) [NaOH] = 4.0M

[KCl]/M	0.02	0.1	0.5	1.0	2.0
I/M	4.13	4.21	4.61	5.11	6.11
10^4k_2/l mol^{-1} s^{-1}	9.8	10.5	14.4	22.2	37.4

Energy and Entropy of Activation.—The reaction was studied at three more temperatures, *i.e.* 35, 45, and 50 ° C. The overall energy and entropy of activation were 23 ± 1 kcal mol^{-1} and −5.4 ± 4 cal K^{-1} mol^{-1} (based on the pseudo-second-order rate constant, k_2) respectively.

DISCUSSION

Not much is known about the alkaline chemistry of hypophosphite. Since hypophosphorous acid is monobasic, the likely species of hypophosphite is $[H_2PO_2]^-$ in alkaline solutions. Since the rate of reaction depends on the concentration of hydroxide ion, the latter is also involved in the activated complex with hypophosphite and $[Fe(CN)_6]^{3-}$. So far no reaction of $[Fe(CN)_6]^{3-}$ and hydroxide ion has been reported and in all probability the involvement of hydroxide ion in the activated complex is through a reactive adduct of hypophosphite and hydroxide ion. The mechanism in equations (1)—(3) is suggested. Species like $[H_3PO_3]^{2-}$ or $[HPO_2]^{2-}$ have been suggested recently in the oxidation[14] of hypophosphite by perruthenate in alkaline medium. From the above mechanism, rate law (4) follows. It has been assumed that K_1 is small.

$$[H_2PO_2]^- + OH^- \overset{K_1}{\rightleftharpoons} [H_3PO_3]^{2-} \qquad (1)$$

$$[H_3PO_3]^{2-} + [Fe(CN)_6]^{3-} \xrightarrow{k} [H_3PO_3]^- + [Fe(CN)_6]^{4-} \qquad (2)$$

$$[H_3PO_3]^- + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} H_3PO_3 + [Fe(CN)_6]^{4-} \qquad (3)$$

$$\begin{aligned}-d[Fe(CN)_6{}^{3-}]/dt &= 2kK_1[Fe(CN)_6{}^{3-}][H_2PO_2{}^-][OH^-] \\ &= k'[Fe(CN)_6{}^{3-}][H_2PO_2{}^-][OH^-] \\ &= k_2[Fe(CN)_6{}^{3-}][H_2PO_2{}^-] \text{ (at constant } [OH^-]) \\ &= k_1[Fe(CN)_6{}^{3-}] \text{ (at constant } [H_2PO_2{}^-] \text{ and } [OH^-])\end{aligned}$$

Ion pairing between K^+ and $[Fe(CN)_6]^{3-}$ is well known,[14] but not between Na^+ and $[Fe(CN)_6]^{3-}$. This is in conformity with the fact[15] that association or ion pairing decreases with cation size. Since there is a large concentration of sodium ions, the possibility of its ion pairing with $[Fe(CN)_6]^{3-}$ does exist. Experiments were also carried out by replacing Na^+ with Li^+ at constant total $[ClO_4{}^-] = 2.0$M. No change in rate was observed. No spectrophotometric evidence for ion pairing was obtained even in the presence of 2.0M-$Na[ClO_4]$ or KCl with 0.005M-$[Fe(CN)_6]^{3-}$. It is possible that $[H_2PO_2]^-$ may also form ion pairs, probably of the form[16] B^--H_2OA^+ in which the cation and anion are separated by a water molecule. A different interpretation[17] follows if the cation modifies the hydration shell of the anion in such a way as to increase the rate of reaction. However, no kinetic evidence for ion pairing was obtained and therefore no such step has been shown in the mechanism.

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[12] J. H. Swinehart, *J. Inorg. Nuclear Chem.*, 1967, **27**, 2315.

[13] R. W. Chlebek and M. W. Lister, *Canad. J. Chem.*, 1966, **44**, 437 and ref. 13 therein.

[14] S. J. Paton and C. H. Brubaker, jun., *Inorg. Chem.*, 1973, **12**, 1402.

[15] Apurba K. Ray and M. N. Das, *J. Chem. Soc.*, 1970, 464.

[16] R. A. Robinson and H. S. Harned, *Chem. Rev.*, 1941, **28**, 419.

[17] B. Perlmutter Hayman and G. Stein, *J. Phys. Chem.*, 1964, **40**, 848.

The ionic strength range is too large for the Davies equation[18] to hold, but since the rate increases with increasing ionic strength a qualitative inference that the reaction is between similarly charged ions is probably justified. The concentration of ion pairs $Na[Fe(CN)_6]^{2-}$ and $Na[H_3PO_3]^-$ will increase with increasing ionic strength and if it is assumed that these ion pairs are more reactive than the corresponding species $[Fe(CN)_6]^{3-}$ and $[H_3PO_3]^{2-}$ part of the increase in rate of reaction can be explained by the decreased electrostatic repulsion between $Na[Fe(CN)_3]^{2-}$ and $Na[H_3PO_3]^-$. Specific-ionic effects[19] are likely to be observed in the presence of large concentrations of cations, but in the present investigation either this tendency is masked by the hydroxide-ion dependence or not shown at all.

On the basis of the charge on the reacting species in equations (2) and (5)[20] a large entropy decrease (*ca.* 60 cal K^{-1} mol^{-1}) is expected for step (2). Entropy will decrease for step (1) also. Hence a large entropy decrease should occur for the overall reaction. The fact

$$\Delta S^{\ddagger} = -10Z_AZ_B \qquad (5)$$

that the entropy change is near the normal value of -12 cal K^{-1} mol^{-1} for a bimolecular reaction suggests the occurrence of one or more intermediate steps like (6) and (7) for which there would be an entropy increase.[21]

$$Na^+ + [Fe(CN)_6]^{3-} \rightleftharpoons Na[Fe(CN)_6]^{2-} \qquad (6)$$

$$Na^+ + [H_3PO_3]^{2-} \rightleftharpoons Na[H_3PO_3]^- \qquad (7)$$

This fact compensates the decrease in entropy in steps (1) and (2) and thus the experimentally determined entropy change is normal. Thus entropy considerations also support ion-pair formation.

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[18] C. W. Davies, ' Ion Association,' Butterworths, London, 1962.

[19] Y. A. Majid and K. E. Howlett, *J. Chem. Soc.* (*A*), 1968, 679.

[20] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, p. 145.

[21] Ref. 20, p. 143.