Kinetics of Oxidation of Hypophosphite Ion by Alkaline Hexacyanoferrate(III) Catalysed by Os(VIII)

KALYAN K. SENGUPTA & BISWANATH BASU

Department of Chemistry, Jadavpur University, Calcutta 700032

The reaction between hypophosphite ion, $H_2PO_2^-$ and hexacyanoferrate(III) in the presence of Os(VIII) catalyst has been studied at different temperatures. The reaction is first order in each $[H_2PO_2^-]$, $[Os(VIII)]$ and $[OH^-]$. The rate constant is 30 ± 1.2 (M^{-1} sec^{-1}) at 25°. The energy of activation is 9.0 ± 1.0 kcal $mole^{-1}$ and entropy is -21.5 ± 3.0 e.u. Hypophosphite is oxidized to phosphite stage and further oxidation of phosphite is too slow. Though free radical mechanism cannot be excluded, as has been observed by earlier workers, it could not be substantiated in the present study. Various mechanisms have been considered but the one which involves the formation of a 1:1 complex between hypophosphite and Os(VIII) and its decomposition in the rate-determining step appears to explain the results.

THOUGH oxidation of phosphorus compounds by various oxidants has been the subject of a number of investigations[1-3], mechanism of oxidation of phosphorus(III) compound by hexacyanoferrate(III) has not received attention so far. Further kinetics of oxidation of some inorganic and organic compounds by alkaline hexacyanoferrate(III) have been studied[4-8]. The kinetics of oxidation of hypophosphite ion ($H_2PO_2^-$) by hexacyanoferrate-(III) has now been investigated. The results have been compared with those for the oxidation of phosphite (HPO_3^{2-}) ion by the same oxidant. The reactions are extremely slow in the absence of added catalyst and hence have been carried out in the presence of Os(VIII) catalyst.

Materials and Methods

Reagents — All inorganic materials except osmium(VIII) were of the highest purity available. A standard solution of hexacyanoferrate(III) was prepared by weighing and its actual strength was checked by usual titration procedure. Hypophosphite ion was estimated by the method of Jones and Swift[6]. The solution of osmium tetroxide (Johnson & Matthey) was prepared by dissolving it in potassium hydroxide solution.

Procedure — The rate of disappearance of hexacyanoferrate(III) was followed spectrophotometrically in a Beckman DU spectrophotometer at 240 nm using a cell of path length 1 cm. Other species were transparent at this wavelength. The reactions were carried out under the conditions, when $[Substrate] \gg [Fe(CN)_6^{3-}]$. The initiation of reaction was carried out by mixing the requisite quantity of substrate maintained at a constant temperature with the solution of oxidant, alkali and catalyst. The observed initial rate (dD/dt) was calculated from the slope of optical density (D) vs time plots. The corrected initial rate (dc/dt) [hereafter referred to as k_0] was obtained by dividing the observed rate by extinction coefficient (ϵ) of hexacyanoferrate-(III) which is $1060 \pm 10M$ litre $mole^{-1}$ cm^{-1} at 420 nm. The reproducibility was better than $\pm 3\%$.

The rate of loss of initial hexacyanoferrate(III) was followed up to 80% and 50% conversion of initial oxidant for the oxidations of hypophosphite and phosphite ions respectively.

Results

Effect of varying reactant concentration — The plot of absorbances against time are linear for various initial [oxidant]. These studies have been made at constant substrate, OH^- and Os(VIII) concentrations. It has been observed that the rate is independent of initial hexacyanoferrate(III). The initial rates at different [substrate] are directly proportional to the [substrate] at constant initial hexacyanoferrate(III), OH^- and osmium(VIII) concentrations (Table 1).

Effect of varying OH^- ion concentration — The effect of added $[OH^-]$ on the initial rate was studied at constant reactant as well as catalyst concentrations. The reactions were studied over a wide range of $[OH^-]$. The values of initial rates at various $[OH^-]$ are recorded in Table 2. The $k_0/[OH^-]$ values indicate that the rate is directly proportional to the initial $[OH^-]$ for hypophosphite

TABLE 1 — EFFECT OF VARYING
SUBSTRATE CONCENTRATIONS ON INITIAL RATE

[(a) [Hexacyanoferrate(III)] = $5.26 \times 10^{-4}M$, [Os(VIII)] = $5 \times 10^{-5}M$, $[OH^-]$ = $1.5 \times 10^{-1}M$, temp. = 23.5°. (b) [Hexacyanoferrate(III)] = $5.67 \times 10^{-4}M$, [Os(VIII)] = $5 \times 10^{-5}M$, $[OH^-]$ = $7.5 \times 10^{-2}M$, temp. = 33.5°]

(a)

$[H_2PO_2^-] \times 10^3 M$	2.5	3.75	5.00	6.25	7.5
$k_0 \times 10^7$ (mole sec^{-1})	5.13	7.49	10.00	12.4	15.00
$k_0/[H_2PO_2^-] \times 10^4$ (sec^{-1})	2.05	1.99	2.00	1.98	2.00

(b)

$[HPO_3^{2-}] \times 10^2 M$	2.42	4.85	9.69	14.54	19.38
$k_0 \times 10^7$ (mole sec^{-1})	1.35	2.70	5.50	8.17	11.25
$k_0/[HPO_3^{2-}] \times 10^6$ (sec^{-1})	5.58	5.58	5.68	5.62	5.70

TABLE 2 — VARIATION OF RATE WITH HYDROXYL ION CONCENTRATIONS

[(a) $[H_2PO_2] = 2\cdot5\times10^{-3}M$, [Hexacyanoferrate(III)] = $5\cdot26 \times10^{-4}M$, [Os(VIII)] = $5\cdot0\times10^{-5}M$, temp.= 25°. (b) $[HPO_3^{2-}]$ = $2\cdot42\times10^{-2}M$, [Hexacyanoferrate(III)] = $5\cdot67\times10^{-4}M$, [Os(VIII)] = $1\cdot0\times10^{-4}M$, temp.= 33·5°]

(a)

$[OH^-]\times10M$	1·50	2·25	3·00	3·75	4·5	5·25
$k_0\times10^7$ (mole sec^{-1})	5·66	8·49	11·63	13·83	16·66	19·92
$k_0/[OH^-]\times10^6$ (sec^{-1})	3·77	3·77	3·88	3·69	3·70	3·79

(b)

$[OH^-]\times10^2M$	7·50	10·00	12·5	15·00	17·50	20·00
$k_0\times10^7$(mole sec^{-1})	2·66	3·35	3·62	3·67	3·85	4·38
$k_0/[OH^-]\times10^6$ (sec^{-1})	3·55	3·35	2·90	2·50	2·20	2·19

TABLE 3 — EFFECT OF VARYING OSMIUM(VIII) CONCENTRATION ON INITIAL RATE

[(a) $[H_2PO_2^-] = 2\cdot5\times10^{-3}M$, [Hexacyanoferrate(III)] = $5\cdot26 \times10^{-4}M$, $[OH^-]$ = $1\cdot5\times10^{-1}M$, temp.= 25°. (b) $[HPO_3^{2-}]$ = $2\cdot42\times10^{-2}M$, [Hexacyanoferrate(III)] = $5\cdot67\times10M^{-4}$, $[OH^-]$ = $7\cdot5\times10^{-2}M$, temp.= 30·3]

(a)

$[Os(VIII)]\times10^5M$	1·00	2·00	3·00	4·00	5·00
$k_0\times10^7$ (mole sec^{-1})	1·14	2·28	3·40	4·51	5·64
$k_0/[Os(VIII)]\times10^2$ (sec^{-1})	1·14	1·14	1·13	1·13	1·13

(b)

$[Os(VIII)]\times10\ M^5$	5·00	10·00	15·00	20·00	25·00
$k_0\times10^7$ (mole sec^{-1})	1·07	2·20	3·21	4·31	5·25
$k_0/[Os(VIII)]\times10^3$ (sec^{-1})	2·14	2·20	2·15	2·16	2·10

oxidation whereas the order with respect to $[OH^-]$ is significantly less than unity (0·5) for the other reaction. Moreover, the above increase in rate was mainly due to the increase in $[OH^-]$ and not due to increase in ionic strength since the addition of various concentrations of sodium perchlorate ($2\cdot5$-$12\cdot5\times10^{-2}M$) had no effect on the rate.

Effect of varying Os(VIII) concentration — The rate of reactions increased with the increase in [catalyst]. The results show that the initial rate is directly proportional to [Os(VIII)] in both these reactions (Table 3).

Activation parameters of the oxidation of hypophosphite ion — The plot of log k

$$\left(k = \frac{k_0}{[H_2PO_2^-][OH^-][Os(VIII)]}\right) \text{ against } \frac{1}{T}$$

is linear. The thermodynamic parameters have been calculated as described earlier[7]. The energy and entropy of activations have been calculated to be $9\cdot0\pm1\cdot0$ kcal mole^{-1} and $-21\cdot5\pm3\cdot0$ e.u. respectively.
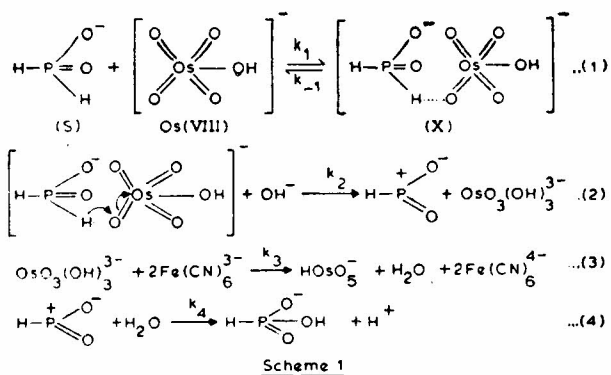
Discussion

Hypophosphite is oxidized to phosphite stage. Following evidences can be cited in support of this. It has been observed that the rate of reduction of oxidant by HPO_3^{2-} is slow as compared with the reduction by $H_2PO_2^-$. Analysis of reaction mixture by the method of Jones and Swift[6] indicated the consumption of 2 moles of oxidant per mole of $H_2PO_2^-$. After the complete oxidation of $H_2PO_2^-$ ammonium molybdate was added to the reaction mixture when no precipitation resulted. On the other hand, when $[HPO_3^{2-}]$ is around $10^{-2}M$, the oxidation of HPO_3^{2-} takes place slowly. The quotients $k_0/[H_2PO_2^-]$ and $k_0'[HPO_3^{2-}]$ were calculated to be $1\cdot02\times10^{-4}$ and $5\cdot63\times10^{-6}$ sec^{-1} at 23·5° and 33·5°C and at constant [Os(VIII)] and $[OH^-]$ of $5\cdot04\times10^{-2}M$ and $7\cdot5\times10^{-2}M$ respectively. Moreover, striking dissimilarities between these two reactions have been observed. All these indicate that further oxidation of phosphite is insignificant under the conditions at which $H_2PO_2^-$ is oxidized. However, it has been proposed[9] earlier that reaction between

α-hydroxy acid and $OsO_4(OH)_2^{2-}$ takes place through the formation of intermediate complex. The exact composition of perosmic acid is not known which possibly exists[10,11] as OsO_5H^- and $OsO_4(OH)_2^{2-}$ in potassium hydroxide solution. The first and second dissociation constants of the parent acid are $\sim10^{-10}$ and $\sim10^{-15}$ respectively. It is likely, therefore, that OsO_5H^- may attack the substrate to give initial 1:1 complex as $H_2PO_2^-$: Os(VIII) which finally decomposes in the presence of OH^-. In some of the metal ions, the higher valency states are stabilized with maximum coordination number and this explains why the 2:1 complex as $H_2PO_2^-$: Os(VIII) (if formed) do not undergo decomposition whereas those of lower coordination number, i.e. 1:1 complex undergo decomposition. However, the formation of free radical in the present study cannot be totally excluded since free radicals involving phosphorus in the +3 oxidation state are well known.[12] The best authenticated radical reaction involving phosphorus derivative is the reduction of diazonium ion by hypophosphorous and phosphorous acids studied by Kornblum[13]. In either case, the oxidation has been affected by the formation of radical intermediate. Benzvi[15] also suggested that hypophosphite radical is involved in the oxidation of $H_2PO_2^-$ by peroxydisulphate. Although free radical mechanism cannot be excluded, it could not be substantiated since the addition of acrylonitrile failed to give any precipitate. Moreover, there is no evidence to date for the existence of Os(VII) species[14]. The complex therefore, decomposes in the presence of OH^- to give $H-P^+\!\!\leqslant^{O^-}_{O}$ and Os(VI). The reaction mixture containing substrate, Os(VIII) and OH^- was stored, acidified and then titrated against Ce(IV) solution. It was found that 2 moles of substrate are consumed per mole of Os(VIII) indicating that Os(VIII) is reduced to Os(VI). The intermediate $H-P^+\!\!\leqslant^{O^-}_{O}$ finally reacts

with water to give stable compound $H-P\!\leqslant^{O^-}_{O}$ with OH attached.

Scheme 1

Scheme 2

followed by step (4).

Scheme 3

Scheme 1 satisfactorily explain the mechanism of oxidation of $H_2PO_2^-$

The rate of formation of complex is

$$\frac{d[X]}{dt} = k_1[S][Os(VIII)] - k_{-1}[X] - k_2[X][OH^-] \quad ...(5)$$

Applying steady state approximation and substituting the concentration of the complex the rate of disappearance of hexacyanoferrate(III) may be expressed as

$$-\frac{d[Fe(CN)_6^{-3}]}{dt} = \frac{2k_1k_2[S][Os(VIII)][CH^-]}{k_{-1} + k_2[OH^-]} \quad ...(6)$$

when $k_{-1} \gg k_2[OH^-]$, the Eq. (6) reduces to Eq. (7)

$$-\frac{d[Fe(CN)_6^{-3}]}{dt} = k[S][Os(VIII)][OH^-] \quad ...(7)$$

where $k = \dfrac{2k_1k_2}{k_{-1}}$
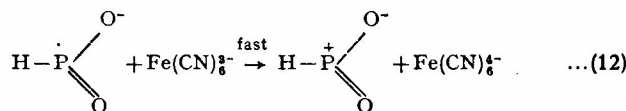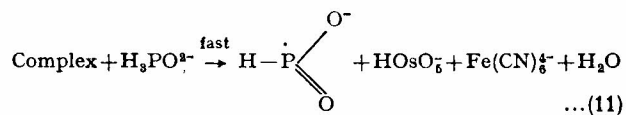
The rate constant k (average of 10 determinations) for the oxidation of $H_2PO_2^-$ has been calculated to be 30 ± 1.2 $(M^{-2} \text{ sec}^{-1})$ at $25°$. In the oxidation of hypophosphite by RuO_4^- in alkaline solution, Paton and Brubaker[16] have suggested a mechanism which involves a rapid reaction between OH^- and $H_2PO_2^-$ to give $H_3PO_3^{2-}$ followed by the reaction of the latter with RuO_4^- to form a complex in the rate determining step. Alternatively, the reaction of $H_3PO_3^{2-}$ with Os(VIII) giving a complex in the rate determining step followed by the decomposition of the same cannot be totally ruled out in the present study (Scheme 2). Step (9) is followed by steps (3) and (4) in Scheme 1.

$HOsO_5^-$ may also react with hexacyanoferrate (III) to give reversible formation of a complex in the rate determining step. The complex may further react with $H_2PO_2^-$ to give free radical and regenerating osmium(VIII). The free radical is converted to $H-P^+\!\!\leqslant^{O^-}_O$ by reacting rapidly with another hexacyanoferrate(III) as shown in Scheme 3.

However, if the reaction proceeded according to Scheme 3, it would demand first order dependence on hexacyanoferrate(III) and zero order in $H_2PO_2^-$ which is contrary to the observation made in this study. Again, the activation energy obtained in the oxidation of $H_2PO_2^-$ by RuO_4^- was very low $(2.46 \text{ kcal mole}^{-1})$. The low value has been explained to be due to the non-involvement of inactive-active tautomeric species[16]. The higher activation energy obtained in the oxidation of hypophosphite ion further indicates that oxidation via Schemes 2 and 3 may not take place.

Acknowledgement

Thanks are due to Prof. M. N. Das for providing laboratory facilities and constant encouragement.

References

1. Speakman, P. J. & Waters, W. A., J. chem. Soc., (1955), 40.
2. Kolthoff, I. M., Meehan, E. J., Tsao, M. S. & Choi, Q. W., J. phys. Chem., 66 (1962), 1233.
3. Meehan, E. J., Kolthoff, I. M. & Kakuichi, H., J. phys. Chem., 66 (1962), 1238.
4. Bridgart, G., Waters, W. A. & Wilson, I. R., J. chem. Soc. Dalton, (1972), 1582.
5. Bridgart, G., Fuller, M. W. & Wilson, I. R., J. chem. Soc. Dalton, (1973), 1274.
6. Jones, R. T. & Swift, E. H., Analyt. Chem., 25 (1953), 1272.
7. Sengupta, K. K., Pal, B. B. & Mukherjee, D. C., J. chem. Soc. Dalton, (1974), 229.
8. Sengupta, K. K., Pal, B. B. & Mukherjee, D. C., J. chem. Soc. Perkin II, (1973), 926.
9. Singh, M. P., Singh, H. S., Singh, V. N. & Lal, V., Indian J. Chem., 10 (1972), 392.
10. Krauss, F. & Wilken, D., Z. anorg. allg. Chem., 145 (1925), 151.
11. Sanerbrunn, R. D. & Sandel, E. B., J. Am. chem. Soc., 75 (1953), 4171.
12. Griffith, E. J. & Grayson, M., Topics in phosphorous chemistry, Vol. 3 (Interscience, New York), 1966, 42.
13. Kornblum, N., Kelley, A. E. & Cooper, G. D., J. Am. chem. Soc., 74 (1952), 3074.
14. Cotton, F. A. & Wilkinson, G., Advanced inorganic chemistry (John Wiley, New York), 1962, 828.
15. Benzvi, E., J. phys. Chem., 67 (1963), 2649.
16. Patton, S. J. & Brubaker, H. C., Inorg. Chem., 12 (1973), 140.