

Kinetics & Mechanism of Osmium(VIII) Oxidation of Phosphite in Aqueous Alkaline Medium

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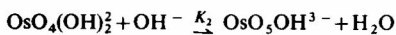
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Received 13 October 1983; revised and accepted 9 February 1984

The title reaction has been followed colorimetrically at 400 nm in $0.5 \text{ mol dm}^{-3} [\text{OH}^-]$ and the kinetic results conform to the rate law

$$-d[\text{Os(VIII)}]/dt = kK_3[\text{Os(VIII)}][\text{HPO}_3^{2-}]/(1 + K_2[\text{OH}^-] + K_3[\text{HPO}_3^{2-}] + K_2K_4[\text{OH}^-] \times [\text{HPO}_3^{2-}])$$

where k is the decomposition rate constant of the complex formed from $\text{OsO}_4(\text{OH})_2^{2-}$ and HPO_3^{2-} with a formation constant of K_3 , and K_4 is another formation constant for the unreactive complex, $\text{OsO}_5(\text{PO}_3)^{5-}$. K_2 is defined by equilibrium



The values of k , K_2 , K_3 and K_4 have been found to be $(1.3 \pm 0.1) \times 10^{-2} \text{ s}^{-1}$, $(6.8 \pm 0.6) \text{ mol dm}^{-3}$, $(175 \pm 30) \text{ mol dm}^{-3}$ and $(18 \pm 3) \text{ mol dm}^{-3}$ respectively at 50° and $I = 2.5 \text{ mol dm}^{-3}$.

Osmium(VIII) is a very effective catalyst in hexacyanoferrate(III) oxidations of a variety of reductants and the rate is independent of [oxidant] in a large number of reactions^{1,2}. The rate-controlling step is the reaction between osmium(VIII) and the reductant. Recently we studied² the osmium(VIII) catalyzed oxidation of phosphite with chloramine-T in alkaline solution. The rate was found to depend on the concentrations of both, the oxidant and the reductant, and this necessitated a direct study of the reaction between osmium(VIII) and phosphite. Incidentally redox studies involving osmium(VIII) seem to be few and one such study deals with the oxidation of thiourea³ in perchloric acid solution.

Materials and Methods

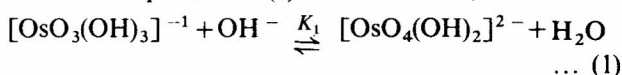
Stock solution of osmium(VIII), prepared by dissolving osmic acid (Johnson-Mattley) in 0.5 mol dm^{-3} NaOH solution, was standardized iodometrically and kept in a cool and dark place. Aqueous solution of sodium phosphite (BDH, AR) was prepared and standardized iodometrically. All other chemicals used were of either AR (BDH) or GR (E. Merck) quality. Doubly distilled conductivity water was employed for preparing the solutions.

The solutions of phosphite, hydroxide and other reactants were mixed and equilibrated at $(50 \pm 0.1)^\circ$. Osmium(VIII) solution was also equilibrated separately at this temperature unless mentioned otherwise. The reaction was initiated by adding a known quantity of osmium(VIII) solution to the phosphite mixture. Aliquots (5 or 10 cm^3) were withdrawn at suitable time intervals, quenched in ice cold water and analyzed for the unreacted osmium(VIII) colorimetrically by noting the absor-

bance at 400 nm on an ECIL junior spectrophotometer. Osmium(VI), which was one of the products, and other reactants and phosphate were transparent at this wavelength. Initial rates were determined by the plane mirror method. Pseudo-first order plots were also made wherever possible, reaction being first order in Os(VIII). The results were reproducible within $\pm 8\%$.

Since the absorbance of Os(VIII) depends on $[\text{OH}^-]$ the molar extinction coefficients were determined for all the concentrations of $[\text{OH}^-]$ employed and appropriate values were used at each $[\text{OH}^-]$ for calculating $[\text{Os(VIII)}]$. There was no change in the absorbance of Os(VIII) in the presence of phosphite.

At $[\text{OH}^-] > 0.2 \text{ mol dm}^{-3}$, Os(VIII) showed maximum absorbance at 400 nm. At lower $[\text{OH}^-]$ in which the equilibrium (1) is said to exist,



K_1 was found to be (22 ± 3) by a method recommended by Ramette⁴. This value is similar to the one reported earlier by Mohan and Gupta⁵ at 25° .

Results

The results of the kinetic investigation can be summarised as follows:

(i) Stoichiometric runs with 0.0005 to $0.001 \text{ mol dm}^{-3}$ of Os(VIII) in which $[\text{Os(VIII)}]$ was determined after 10 hr, both colorimetrically and iodometrically, revealed that 1 mol of Os(VIII) oxidised one mol of phosphite giving Os(VI) and HPO_4^{2-} .

(ii) The order in Os(VIII) was found to be one from the linear plot of initial rate (ir) versus Os(VIII) passing through the origin with unit slope. In these experiments $[\text{osmium(VIII)}]$ was varied in the range

3.1×10^{-4} to 1.4×10^{-3} mol dm $^{-3}$ for $[\text{HPO}_3^{2-}] = 5.0 \times 10^{-3}$ mol dm $^{-3}$ and $[\text{OH}^-] = 0.5$ mol dm $^{-3}$, at 50° and $I \approx 0.5$ mol dm $^{-3}$.

(iii) The concentration of phosphite was varied in the range (0.001 to 0.02 mol dm $^{-3}$) at three different temperatures and three $[\text{OH}^-]$. The rate increased and tended to attain limiting value with the increase in $[\text{HPO}_3^{2-}]$ (Table 1). The results conform to the rate law (2)

$$-d[\text{Os(VIII)}]/dt = A[\text{Os(VIII)}][\text{HPO}_3^{2-}]/(B + [\text{HPO}_3^{2-}]) \quad \dots (2)$$

where A is a rate constant and B is another constant involving $[\text{OH}^-]$.

(iv) The $[\text{OH}^-]$ was varied in the range 0.05 to 0.5 mol dm $^{-3}$ at three different concentrations of phosphite and at $I = 2.5$ mol dm $^{-3}$ adjusted with NaNO_3 . These results are given in Table 2. The rate decreased with the increase in $[\text{OH}^-]$. At constant $[\text{HPO}_3^{2-}]$ a plot of $(ir)^{-1}$ versus $[\text{OH}^-]$ was linear with an intercept, conforming to the rate law (3).

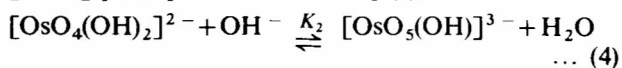
$$-d[\text{Os(VIII)}]/dt = A'[\text{Os(VIII)}]/(B' + [\text{OH}^-]) \quad \dots (3)$$

where A' is a rate constant and B' is a constant, both involving HPO_3^{2-} .

(v) The rate increased significantly with the increase in ionic strength. For example, under the conditions $[\text{Os(VIII)}] = 3 \times 10^{-4}$ mol dm $^{-3}$; $[\text{HPO}_3^{2-}] = 5.0 \times 10^{-3}$ mol dm $^{-3}$ and $[\text{OH}^-] = 0.5$ mol dm $^{-3}$ $10^6(ir)$ increased from 0.64 to 2.3 mol dm $^{-3}$ s $^{-1}$ when I was varied from 0.5 to 3.0 mol dm $^{-3}$.

Discussion

A number of species of Os(VIII) are said to exist in alkaline solutions in equilibrium^{6,7} and a red solution of complex $[\text{OsO}_4(\text{OH})_2]^{2-}$ is reported⁷ in dilute alkaline solution. In alkaline solutions employed in the investigation osmium(VIII) is completely converted⁸ into $[\text{OsO}_4(\text{OH})_2]^{2-}$ through equilibrium (1). Although the absorption of Os(VIII) becomes constant in $[\text{OH}^-]$ larger than 0.2 mol dm $^{-3}$ indicating no change in the species of Os(VIII), the rate of reaction decreases with the increase in $[\text{OH}^-]$ showing that the species of Os(VIII) further changes, with the increase in $[\text{OH}^-]$ perhaps as shown in Eq. (4).



but this is not indicated spectrophotometrically.

The phosphite dependence found in the present investigation is typical of complex formation and thus a complex of osmium(VIII) with phosphite is possible. Osmium(VIII) is well known to form complexes on account of the available vacant d -orbitals. Complex formation of phosphite with other metal ions has also been reported, such as in its oxidations with Ti(III) ⁹, Cr(VI) ¹⁰, Mn(III) ¹¹ and Ce(IV) ¹². Thus equilibria (5)

Table 1—Initial rates (ir) of the reaction of Osmium(VIII) with Phosphite in alkaline solutions at different $[\text{HPO}_3^{2-}]$ $[\text{Os(VIII)}] = 6.4 \times 10^{-4}$ mol dm $^{-3}$; $I \approx 2.5$ mol dm $^{-3}$

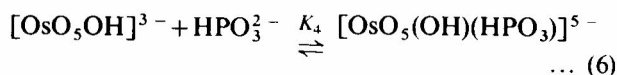
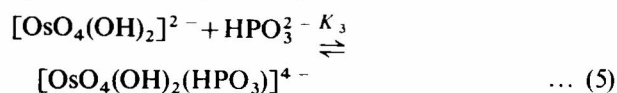
$10^2[\text{HPO}_3^{2-}]$ mol dm $^{-3}$	$10^6(ir)/\text{mol dm}^{-3}\text{s}^{-1}$ at $[\text{OH}^-](\text{mol dm}^{-3})$				
	0.1*	0.3*	0.5 at		
			40°	50°	60°
0.1			0.13	0.22	0.35
0.2	1.6	0.70	0.26	0.63	0.69
0.4	2.9	1.9	0.57	1.4	1.7
0.5	—	2.2	—	—	—
0.6	—	—	0.78	1.8	2.25
0.8	4.0	3.0	0.93	2.2	2.9
1.0	4.6	3.5	1.2	2.6	3.25
1.5	4.9	—	1.5	3.0	4.0
2.0	5.2	4.5	1.8	3.25	4.7

* Values at 50°C

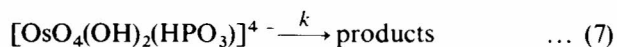
Table 2—Effect of Varying $[\text{OH}^-]$ at Three Different $[\text{HPO}_3^{2-}]$ in the Reaction of Os(VIII) with HPO_3^{2-} $[\text{Os(VIII)}] = 5.0 \times 10^{-4}$ mol dm $^{-3}$; $I = 2.5$ mol dm $^{-3}$; temp = 50°

$[\text{OH}^-]$ mol dm $^{-3}$	$10^3k_1(\text{s}^{-1})$ at $[\text{HPO}_3^{2-}](\text{mol dm}^{-3})$		
	0.005	0.01	0.02
0.05	5.4	8.2	—
0.10	4.8	7.6	9.5
0.20	4.0	6.1	8.3
0.30	3.3	5.3	7.7
0.40	2.9	—	7.1
0.50	2.5	4.25	6.5

and (6) involving complex formation are likely to be operative in the present system.



The complex so formed may decompose to yield the products.



HPO_3^{2-} has been used for the phosphite species since the first¹³ and second¹⁴ acid dissociation constants are reported to be 0.107 and 7×10^{-7} mol dm $^{-3}$ respectively at 25° and the acid is only dibasic. Hence hydroxide dependence would not be connected with HPO_3^{2-} .

From the inverse rate dependence of $[\text{OH}^-]$, and if Eq. (4) is the only one involving OH^- dependence, it is obvious that the rate law would not have $[\text{OH}^-]$ in the numerator and thus complex $[\text{OsO}_5(\text{OH})\text{HPO}_3]^{5-}$

does not appear to be reactive. The above discussion leads to rate law (8).

$$-d[\text{Os(VIII)}]/dt = \frac{kK_3[\text{HPO}_3^{2-}][\text{Os(VIII)}]}{1 + K_2[\text{OH}^-] + K_3[\text{HPO}_3^{2-}] + K_2K_4[\text{OH}^-][\text{HPO}_3^{2-}]} \quad \dots (8)$$

where k is the decomposition constant of the complex $[\text{OsO}_4(\text{OH})_2\text{HPO}_3]^{4-}$. If k_1 is the pseudo-first order rate constant, Eq. (9) easily follows from Eq. (8)

$$k_1 = \frac{kK_3[\text{HPO}_3^{2-}]}{1 + K_2[\text{OH}^-] + K_3[\text{HPO}_3^{2-}] + K_2K_4[\text{OH}^-][\text{HPO}_3^{2-}]} \quad \dots (9)$$

The rate law (9) is a combination of Eqs (2) and (3) satisfying the rate dependence on $[\text{OH}^-]$ and $[\text{HPO}_3^{2-}]$. Plots of (initial rate) $^{-1}$ versus $[\text{HPO}_3^{2-}]$ are linear with non-zero intercepts (Fig. 1). Intercepts and slopes of such plots give the values of $(K_3 + K_2K_4[\text{OH}^-])/kK_3[\text{Os(VIII)}]$ and $(1 + K_2[\text{OH}^-])/kK_3[\text{Os(VIII)}]$ respectively. From the plots of the values of intercepts and slopes of plots in Fig. 1 versus $[\text{OH}^-]$ (Fig. 2) the values of k , K_2 and K_2K_4/K_3 are found to be $1.2 \times 10^{-2} \text{ s}^{-1}$, 6.8 mol dm^{-3} and $0.8 \text{ dm}^3 \text{ mol}^{-1}$ respectively at 50° and $I = 2.5 \text{ mol dm}^{-3}$. Similarly plots of $(k_1)^{-1}$ versus $[\text{OH}^-]^{-1}$ at three $[\text{HPO}_3^{2-}]$ are linear with non-zero intercepts (Fig. 3). Different intercepts and slopes in both the cases (Figs 1 and 3) justify the terms in the denominator of Eq. (9). Plots of the values of intercepts and slopes of the linear plots in Fig. 3 versus

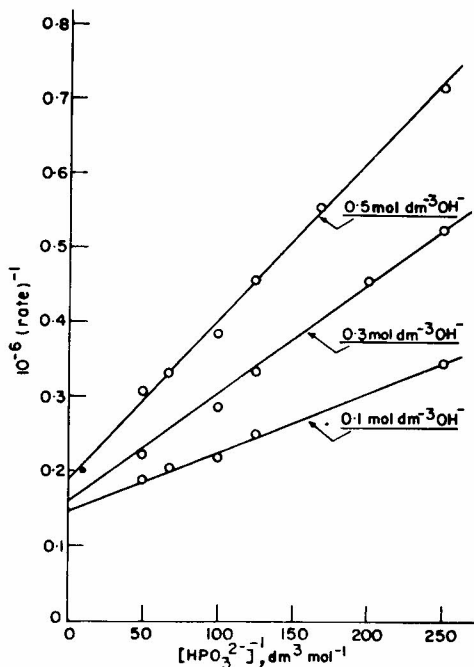


Fig. 1—Plots of (rate) $^{-1}$ versus $[\text{HPO}_3^{2-}]^{-1}$ at 50° , $[\text{Os(VIII)}] = 6.4 \times 10^{-4} \text{ mol dm}^{-3}$; $I \approx 2.5 \text{ mol dm}^{-3}$.

$[\text{HPO}_3^{2-}]^{-1}$ (Fig. 4) yield the values of K_3 and K_4 equal to $175 \text{ dm}^3 \text{ mol}^{-1}$ and 18 respectively. The value of k is found to be $1.4 \times 10^{-2} \text{ s}^{-1}$ from Fig. 4. The value of K_2K_4/K_3 calculated from the separate values of K_2 , K_3 and K_4 , is found to be 0.7 which is comparable to the one (0.8) obtained from Fig. 2.

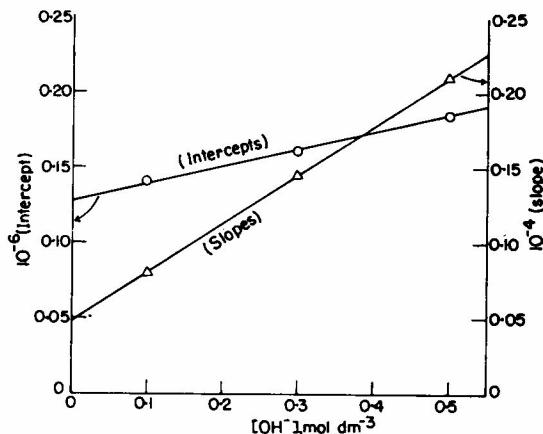


Fig. 2—Plots of intercepts (O) and slopes (Δ) from Fig. 1 versus $[\text{OH}^-]$.

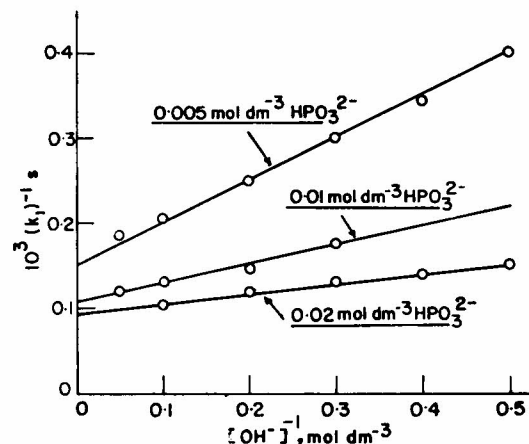


Fig. 3—Plots $(k_1)^{-1}$ versus $[\text{OH}^-]^{-1}$, $[\text{Os(VIII)}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $I \approx 2.5 \text{ mol dm}^{-3}$.

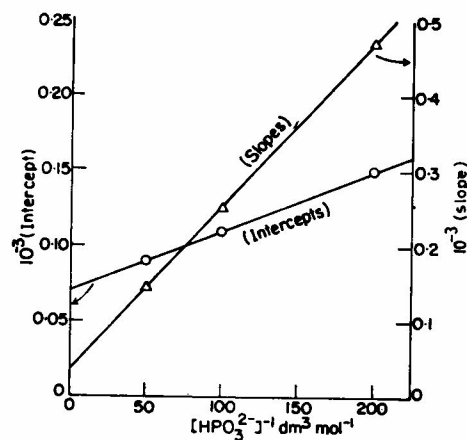


Fig. 4—Plots of intercepts (O) and slopes (Δ) from Fig. 3 versus $[\text{HPO}_3^{2-}]^{-1}$.

The significant increase in the rate with increase in ionic strength can be understood on the basis of reactions (4) and (5) between similarly charged ions.

The earlier work⁵ on the Os(VIII) catalyzed oxidation of phosphite with $\text{Fe}(\text{CN})_6^{3-}$ is essentially the oxidation of phosphite with Os(VIII) since the rate is independent of $\text{Fe}(\text{CN})_6^{3-}$. Thus the present work and the previous work should have given similar results, which is not the case. The main points of differences are: (i) absence of evidence for complex formation between Os(VIII) and HPO_3^{2-} in the previous work, and (ii) the opposite role of OH^- in the previous work⁵; the rate increases and tends to be limiting with the increase in $[\text{OH}^-]$. The difference in the $[\text{OH}^-]$ dependence can be understood since the previous work was carried out mainly at $[\text{OH}^-] = 0.05 \text{ mol dm}^{-3}$ and the present work has been carried out at $[\text{OH}^-] = 0.5 \text{ mol dm}^{-3}$. The $[\text{OH}^-]$ dependence is governed by equilibrium (1) in the previous work⁵ and by equilibrium (4) in the present work. In both the cases $[\text{OsO}_4(\text{OH})_2]^{2-}$ is the reactive species. It is difficult to say why the results of the two studies differ so far as complex formation is concerned. It may be due to the presence of $\text{Fe}(\text{CN})_6^{3-}$. It is not unexpected since in the Os(VIII) catalyzed oxidation of phosphite with chloramine-T, the rate is not independent of the oxidant. It seems that the answer to the problem cannot be had unless a few more redox reactions with Os(VIII) as oxidant have been studied.

There are several characteristics common in this study and the Os(VIII) catalyzed oxidation of phosphite by chloramine-T. Both show decrease in rate with the increase in $[\text{OH}^-]$, and a complex formation between Os(VIII) and HPO_3^{2-} . However, the results are quantitatively different perhaps on account of the presence of chloramine-T which is reported to form a complex with Os(VIII).

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