Kinetics and Mechanism of the Oxidation of Phosphite with Chloramine T † catalyzed by Osmium(VIII) in Alkaline Solutions

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The osmium(VIII)-catalyzed oxidation of phosphite by chloramine T was studied by determining chloramine T (cat) iodometrically. The rate law (i) holds for $[OH^-] = 0.05$—0.5 mol dm^{-3} and $[HPO_3^{2-}] = 0.005$—0.05 mol dm^{-3}, where K_1 is defined by equation (ii); K_2 and K_3 are the

$$-d[cat]/dt = \frac{k_1K_2[cat][Os^{VIII}][HPO_3^{2-}]}{1 + K_1[OH^-] + K_2[HPO_3^{2-}] + K_1K_3[HPO_3^{2-}][OH^-]} \quad (i)$$

$$[OsO_4(OH)_2]^{2-} + OH^- \overset{K_1}{\rightleftharpoons} [OsO_5(OH)]^{3-} + H_2O \quad (ii)$$

equilibrium constants of formation of complexes between $[OsO_4(OH)_2]^{2-}$ and HPO_3^{2-} and $[OsO_5(OH)]^{3-}$ and HPO_3^{2-} respectively. The former complex reacts with cat. The values of k_1, K_1, K_2, and K_3 were found to be 4.0 dm^3 mol^{-1} s^{-1}, 5 dm^3 mol^{-1}, 300 dm^3 mol^{-1}, and 60 dm^3 mol^{-1} respectively at 70 °C.

The use of osmium(VIII) in oxidations with the sodium salt of *N*-chlorotoluene-*p*-sulphonamide, commonly known as chloramine T or cat, is well known. However, only a few kinetic studies [1-4] of such systems have been made. The cycle Os^{VIII}/Os^{VI} is said to operate in the oxidation of primary alcohols [4] since the rate is independent of the concentration of cat. In other cases [1-3] there is no evidence for this cycle. The $[OH^-]$ dependence of the rate and its correlation with cat species are still uncertain. Such aspects of the mechanism require further investigation. Phosphite was considered a suitable reducing substance for such an investigation since the system would be free of side reactions and phosphite would have no $[OH^-]$ dependence in the alkaline solutions employed.

We recently reported [5] the uncatalyzed oxidation of H_3PO_2 with cat in an acidic medium in which the product, H_3PO_3, was slow to react further at 35 °C. Oxidation [6] of H_3PO_3 has been carried out at a higher temperature (70 °C) and the rate was found to increase and then decrease with increasing pH from 3 to 7. The reaction at higher pH occurs only when catalyzed with Os^{VIII}. Osmium(VIII)-catalyzed oxidation [7] of phosphite with hexacyanoferrate has also been studied. Catalysis by Os^{VIII} in hexacyanoferrate(III) oxidations is well known.[8]

Experimental

Chloramine T (E.Merck) solution was prepared by direct weighing and was standardized iodometrically.[9,10] Sodium hydroxide was from E.Merck. Sodium phosphite was of BDH AnalaR grade. A stock solution of osmium(VIII) was prepared by dissolving Johnson Matthey OsO_4 in about 0.5 mol dm^{-3} NaOH. All other chemicals were of BDH AnalaR quality. Doubly distilled water was employed for preparing solutions and in the reaction mixtures.

The progress of the reactions was followed by determining chloramine T iodometrically [9,10] in aliquots withdrawn after suitable intervals of time. The iodine liberated by Os^{VIII} was taken into account. Since iodine reacts [11] slowly with phosphite in dilute acidic media, the aliquots were adjusted to about 2.0 mol dm^{-3} in $HClO_4$ before the addition of KI. The reactions were initiated by the addition of chloramine T solution to the other reagents, although the order of addition had no effect on the rate. The studies were made in a thermostat at 70 ± 0.1 °C. The rates were reproducible to ±5%.

Spectrophotometric work was done on a Toshniwal u.v. spectrophotometer with 1-cm cells. An alkaline solution of Os^{VIII} shows a broad maximum between 320 and 360 nm. There is no change in the absorbance upon variation of $[OH^-]$ from 0.1 to 1.0 mol dm^{-3}. Similarly, there was no change in the spectrum in the presence of chloramine T. A complex of cat and Os^{VIII} has been reported,[1-3] but without any supporting evidence. Spectrophotometric studies of complex formation were made in view of a report [12] of a complex between copper(II) and cat. Although we have no evidence for such a complex with Os^{VIII}, it is possible that weak complexing does occur in the presence of phosphite.

Results

The stoicheiometry of the reaction was determined by estimating the excess of cat after about 2 h at 70 °C in the presence of 0.5 mol dm^{-3} NaOH and 5×10^{-5} mol dm^{-3} Os^{VIII}, the concentrations of the main reactants being in the range 0.5×10^{-3}—3×10^{-3} mol dm^{-3}. The reaction occurs according to equation (1) where R = p-$MeC_6H_4SO_2$.

$$RNCl^- + HPO_3^{2-} + H_2O \longrightarrow RNH_2 + Cl^- + HPO_4^{2-} \quad (1)$$

Chloramine T and Osmium(VIII) *Dependences*.—The concentration of chloramine T was varied from 5.0×10^{-4} to 4.0×10^{-3} mol dm^{-3} at fixed concentrations of the other reagents. The reaction is first order in [cat] from the initial rates. Pseudo-first-order plots gave straight lines. The results are shown in Table 1.

The concentration of Os^{VIII} was varied from 0.1×10^{-4} to 1.0×10^{-4} mol dm^{-3} under the conditions shown in Table 1. The pseudo-first-order rate constants (k') when plotted against

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† Sodium salt of *N*-chlorotoluene-*p*-sulphonamide.

Table 1. Pseudo-first-order rate constants (k') and second-order rate constants (k_0) for different concentrations of chloramine T and Os^{VIII}. $[OH^-] = 0.1$ mol dm^{-3}, 70 °C

10^3[cat]	$10^4[Os^{VIII}]$	$10^2[HPO_3^{2-}]$	$10^4k'/s^{-1}$	k_0/dm^3 mol^{-1} s^{-1}
	mol dm^{-3}			
0.5	1.3	5.0	6.0	4.6
1.0	1.3	5.0	6.1	4.7
1.5	1.3	5.0	6.4	4.9
2.0	1.3	5.0	6.6	5.1
2.5	1.3	5.0	6.5	5.0
3.0	1.3	5.0	6.1	4.7
3.5	1.3	5.0	5.4	4.2
4.0	1.3	5.0	5.4	4.2
4.0	0.2	5.0	0.9	4.5
4.0	0.4	5.0	1.8	4.5
4.0	0.6	5.0	2.7	4.5
4.0	0.8	5.0	4.0	5.0
4.0	1.0	5.0	4.6	4.6
				Av. 4.7 ± 0.2
2.0	0.8	2.5	3.2	4.0
2.5	0.8	2.5	3.0	3.75
3.0	0.8	2.5	3.0	3.75
3.5	0.8	2.5	3.0	3.75
4.0	0.8	2.5	2.8	3.5
2.5	0.1	2.5	0.36	3.6
2.5	0.2	2.5	0.76	3.8
2.5	0.4	2.5	1.5	3.75
2.5	0.6	2.5	2.2	3.7
2.5	0.8	2.5	3.2	4.0
2.5	1.0	2.5	4.0	4.0
				Av. 3.8 ± 0.1

$[Os^{VIII}]$ yielded a straight line passing through the origin. These constants and second-order rate constants (k_0) are also shown in Table 1.

Phosphite Dependence.—The concentration of phosphite was varied from 0.005 to 0.05 mol dm^{-3} at fixed concentrations of the other reactants. The results at three hydroxide concentrations are given in Table 2. The rate constant k_0 increases and tends to a limiting value with increasing $[HPO_3^{2-}]$. A double reciprocal plot of the rate constant *versus* $[HPO_3^{2-}]$ yielded a straight line conforming to the rate equation (2) where A and B are constants.

$$k' = \frac{A[HPO_3^{2-}][Os^{VIII}]}{1 + B[HPO_3^{2-}]} \tag{2}$$

Hydroxide Dependence.—Hydroxide was varied in the range 0.05—0.5 mol dm^{-3} at three concentrations of phosphite and fixed concentrations of the other reactants. The results are given in Table 2. A plot of the reciprocal of the rate constant *versus* $[OH^-]$ yields a straight line with non-zero intercept, conforming to the rate equation (3) where A' and B' are constants.

$$k' = \frac{A'[HPO_3^{2-}][Os^{VIII}]}{1 + B'[OH^-]} \tag{3}$$

*Effects of Toluene-*p*-sulphonamide and Ionic Strength.*—The concentration of toluene-*p*-sulphonamide was varied from 0.001 to 0.01 mol dm^{-3}, but there was no effect on the rate. Similarly, a variation of ionic strength from 0.1 to 1.0 mol dm^{-3} using $NaNO_3$ had no effect on the rate.

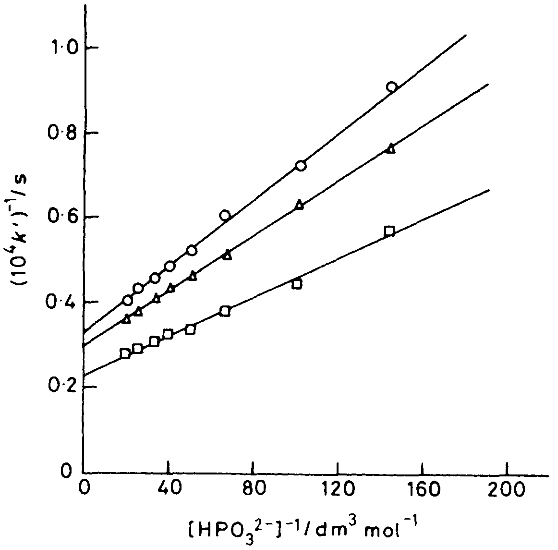

Figure 1. Plot of $(k')^{-1}$ *vs.* $[HPO_3^{2-}]^{-1}$ at different $[OH^-]$ at 70 °C, [cat] = 2.5 × 10^{-3} mol dm^{-3} and $[Os^{VIII}] = 1.0 \times 10^{-4}$ mol dm^{-3}. $[OH^-] = 0.4$ (○), 0.3 (△), or 0.2 mol dm^{-3} (□)

Discussion

A number of species of cat are said to exist [13-16] in acidic and alkaline solutions. Considering the various equilibria [13] and the magnitudes of the equilibrium constants, and the fact that the rate of the present reaction is unaffected by NH_2R, the anion of cat, $RNCl^-$, appears to be the predominant and reactive species. The same species has been reported to be reactive in the oxidation of anilines.[17]

The ion HPO_3^{2-} is regarded as the reactive phosphite species since the first [18] and second [19] acid-dissociation constants are reported to be 0.107 and 7 × 10^{-7} mol dm^{-3} respectively at 25 °C and the acid is only dibasic. Any hydroxide-ion dependence would thus not be connected with HPO_3^{2-}.

A number of species of Os^{VIII} are said to exist [20,21] in alkaline solutions, and a red solution of $[OsO_4(OH)_2]^{2-}$ has been reported [21] in dilute alkaline solutions; OsO_4 is almost completely converted into $[OsO_4(OH)_2]^{2-}$ in alkaline solutions (*ca.* 0.1 mol dm^{-3}) through equation (4) since K would be

$$[OsO_3(OH)_3]^- + OH^- \overset{K}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \tag{4}$$

more than 80 dm^3 mol^{-1} at 70 °C on the basis of its values [7] of 24, 30, and 42.5 dm^3 mol^{-1} at 25, 35, and 45 °C respectively. Since the rate of the present reaction is not constant at $[OH^-] > 0.10$ mol dm^{-3} (it decreases), another species of Os^{VIII} appears to be formed through equilibrium (5). We cannot be

$$[OsO_4(OH)_2]^{2-} + OH^- \overset{K_1}{\rightleftharpoons} [OsO_5(OH)]^{3-} + H_2O \tag{5}$$

sure of the structures of the osmium(VIII) species in solution, but can be reasonably sure of equilibria of the types (4) and (5) on the basis of the observed hydroxide-ion dependence.

It has already been mentioned that the phosphite dependence is typical of complex formation. Complexing is possible only with Os^{VIII} in the present system. Complexing of phosphite with metal ions is well known.[22] A direct reaction [23] between Os^{VIII} and HPO_3^{2-} has also yielded kinetic evidence for complex formation.

Table 2. Observed and calculated * values of k_0 in the Os^{VIII}-catalyzed oxidation of phosphite with cat. [cat] = 2.5×10^{-3}, $[Os^{VIII}] = 1.0 \times 10^{-4}$ mol dm^{-3}, 70 °C

(*a*) $[OH^-] = 0.4$ mol dm^{-3}									
$10^2[HPO_3^{2-}]$/mol dm^{-3}	0.5	0.7	1.0	1.5	2.0	2.5	3.0	4.0	5.0
k_0(obs.)/dm^3 mol^{-1} s^{-1}	1.07	1.09	1.37	1.63	1.90	2.05	2.17	2.30	2.50
k_0(calc.)/dm^3 mol^{-1} s^{-1}	1.17	1.42	1.66	1.93	2.00	2.22	2.31	2.24	2.50
(*b*) $[OH^-] = 0.3$ mol dm^{-3}									
$10^2[HPO_3^{2-}]$/mol dm^{-3}	0.5	0.7	1.0	1.5	2.0	2.5	3.0	4.0	5.0
k_0(obs.)/dm^3 mol^{-1} s^{-1}	1.20	1.30	1.58	1.95	2.15	2.30	2.46	2.61	2.76
k_0(calc.)/dm^3 mol^{-1} s^{-1}	1.35	1.60	1.80	2.10	2.33	2.45	2.53	2.65	2.73
(*c*) $[OH^-] = 0.2$ mol dm^{-3}									
$10^2[HPO_3^{2-}]$/mol dm^{-3}	0.5	0.7	1.0	1.5	2.0	2.5	3.0	4.0	5.0
k_0(obs.)/dm^3 mol^{-1} s^{-1}	1.58	1.75	2.22	2.58	2.95	3.07	3.22	3.40	3.55
k_0(calc.)/dm^3 mol^{-1} s^{-1}	1.60	2.02	2.14	2.43	2.61	2.74	2.81	2.93	3.0
(*d*) $[HPO_3^{2-}] = 0.0050$ mol dm^{-3}									
$[OH^-]$/mol dm^{-3}	0.05	0.1	0.15	0.2	0.25	0.30	0.35	0.40	0.50
k_0(obs.)/dm^3 mol^{-1} s^{-1}	—	1.90	1.65	1.50	1.37	1.23	1.16	1.10	0.95
k_0(calc.)/dm^3 mol^{-1} s^{-1}	—	1.90	1.73	1.60	1.45	1.35	1.25	1.18	1.04
(*e*) $[HPO_3^{2-}] = 0.004$ mol dm^{-3}									
$[OH^-]$/mol dm^{-3}	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.40	0.50
k_0(obs.)/dm^3 mol^{-1} s^{-1}	2.00	1.70	1.48	1.36	1.22	1.10	1.04	0.97	0.85
k_0(calc.)/dm^3 mol^{-1} s^{-1}	1.90	1.70	1.53	1.40	1.28	1.18	1.10	1.02	0.91
(*f*) $[HPO_3^{2-}] = 0.003$ mol dm^{-3}									
$[OH^-]$/mol dm^{-3}	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50
k_0(obs.)/dm^3 mol^{-1} s^{-1}	1.62	1.45	1.27	1.18	1.07	0.94	0.90	0.82	0.72
k_0(calc.)/dm^3 mol^{-1} s^{-1}	1.64	1.45	1.29	1.17	1.07	0.98	0.91	0.85	0.74

* k_0 values were calculated from equation (12) with k_1 = 4.0 dm^3 mol^{-1} s^{-1}, K_1 = 5 dm^3 mol^{-1}, K_2 = 300 dm^3 mol^{-1}, and K_3 = 60 dm^3 mol^{-1}.

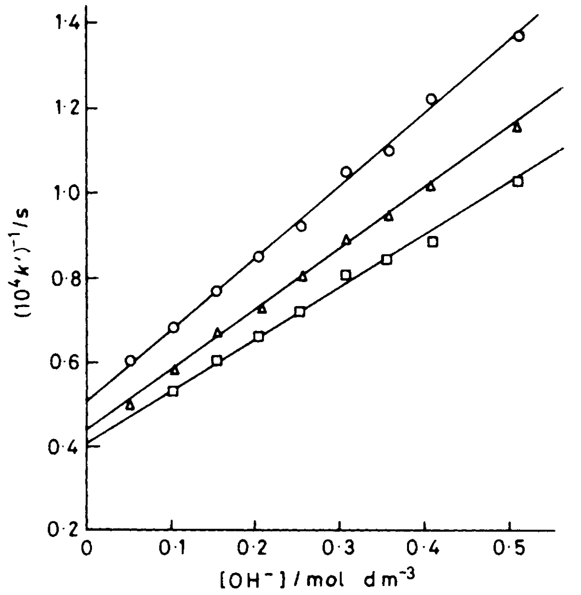

Figure 2. Plot of $(k')^{-1}$ *vs.* $[OH^-]$ at different $[HPO_3^{2-}]$ at 70 °C, [cat] = 2.5×10^{-3} mol dm^{-3} and $[Os^{VIII}] = 1.0 \times 10^{-4}$ mol dm^{-3}. $[HPO_3^{2-}]$ = 0.003 (○), 0.004 (△), and 0.005 mol dm^{-3} (□)

Since the rate of the present reaction is not independent of the concentration of cat, the Os^{VIII}/Os^{VI} cycle does not operate in this system. Also, since the rate depends on $[HPO_3^{2-}]$, any direct redox reaction between Os^{VIII} and cat can be ruled out. In other words, the cycle Os^{VIII}/higher valent Os does not operate but it is obvious that cat has a definite role in the formation of the activated complex. There is no evidence for a complex between cat and Os^{VIII} in the present investigation or in other studies. In all probability the complex of Os^{VIII} and HPO_3^{2-} reacts with cat in a bimolecular step. The com-

$$[OsO_4(OH)_2]^{2-} + OH^- \overset{K_1}{\rightleftharpoons} [OsO_5(OH)]^{3-} + H_2O \tag{5}$$

$$[OsO_4(OH)_2]^{2-} + HPO_3^{2-} \overset{K_2}{\rightleftharpoons} \text{complex } C_1 + H_2O \tag{6}$$

$$[OsO_5(OH)]^{3-} + HPO_3^{2-} \overset{K_3}{\rightleftharpoons} \text{complex } C_2 + H_2O \tag{7}$$

$$\text{Complex } C_1 + \text{cat} \xrightarrow{k_1} \text{products} \tag{8}$$

$$\text{Complex } C_2 + \text{cat} \xrightarrow{k_2} \text{products} \tag{9}$$

$$-\mathrm{d}[\text{cat}]/\mathrm{d}t = \frac{[\text{cat}][Os^{VIII}][HPO_3^{2-}](k_1K_2 + k_2K_1K_3[OH^-])}{1 + K_1[OH^-] + K_2[HPO_3^{2-}] + K_1K_3[OH^-][HPO_3^{2-}]} \tag{10}$$

$$k' = \frac{k_1K_2[Os^{VIII}][HPO_3^{2-}]}{1 + K_1[OH^-] + K_2[HPO_3^{2-}] + K_1K_3[OH^-][HPO_3^{2-}]} \tag{11}$$

$$k_0 = \frac{k_1K_2[HPO_3^{2-}]}{1 + K_1[OH^-] + K_2[HPO_3^{2-}] + K_1K_3[OH^-][HPO_3^{2-}]} \tag{12}$$

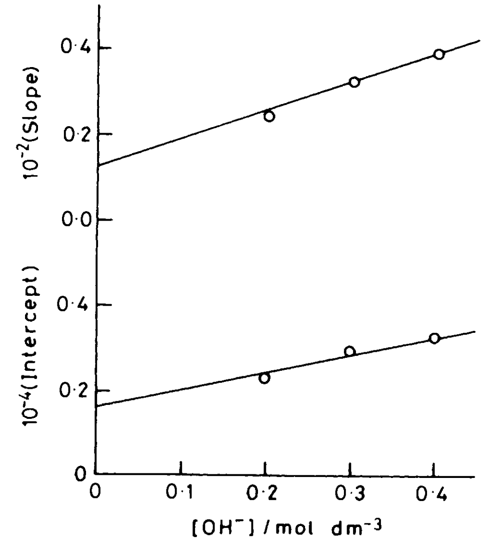

Figure 3. Plots of intercepts and slopes (from Figure 1) *vs.* [OH⁻]

plete mechanism is postulated to comprise steps (5)—(9) which yield the rate law (10).

Since no limiting rates even at high [OH⁻] (employed in the investigation) are obtained, the contribution of the second term in the numerator to the rate appears to be insignificant in the [OH⁻] range employed. Thus, either $k_1 \gg k_2$ or [complex C_2] $\ll$ [complex C_1]. If k' and k_0 are the pseudo-first-order and second-order rate constants respectively, equation (10) reduces to (11) and (12). The above equations incorporate the characteristics of both equations (2) and (3). A plot of $(k')^{-1}$ *versus* $[HPO_3^{2-}]^{-1}$ should yield a straight line (Figure 1) with non-zero intercept and slope $(K_2 + K_1K_3[OH^-])/k_1K_2[Os^{VIII}]$ and $(1 + K_1[OH^-])/k_1K_2[Os^{VIII}]$ respectively. Plots of intercepts *versus* [OH⁻] and slope *versus* [OH⁻] can also be made as shown in Figure 3 and from these the values of k_1, K_1, and K_1K_3/K_2 were found to be 6.0 dm^3 mol^{-1} s^{-1}, 5 dm^3 mol^{-1}, and 1.7 dm^3 mol^{-1} respectively at 70 °C. Similarly, a plot of $(k')^{-1}$ *versus* [OH⁻] at three different concentrations of HPO_3^{2-} can be made (Figure 2), the intercepts and slopes of which would be equal to $(1 + K_2[HPO_3^{2-}])/k_1K_2[Os^{VIII}][HPO_3^{2-}]$ and $(K_1 + K_1K_3[HPO_3^{2-}])/k_1K_2[Os^{VIII}][HPO_3^{2-}]$ respectively. Plots of the intercepts *versus* $[HPO_3^{2-}]^{-1}$ and of the slopes *versus* $[HPO_3^{2-}]^{-1}$ (Figure 4) yield the values of k_1, K_2, and K_3 equal to 4.0 dm^3 mol^{-1} s^{-1}, 300 dm^3 mol^{-1}, and 60 dm^3 mol^{-1} respectively. The calculated values of k_0 as shown in Table 2 are in fair agreement with the observed values.

There is evidence for steps similar to (5)—(7) in the direct reaction [23] between Os^{VIII} and HPO_3^{2-}, but the values of the equilibrium constants are not similar (K_1, K_2, and K_3 were 6.8, 175, and 18 dm^3 mol^{-1} respectively). In the catalyzed reaction there is no evidence for a step independent of [cat]. These facts show that the two reactions differ in mechanism. In the catalyzed reaction it is probably a complex of cat, Os^{VIII}, and HPO_3^{2-} which undergoes intramolecular redox reaction.

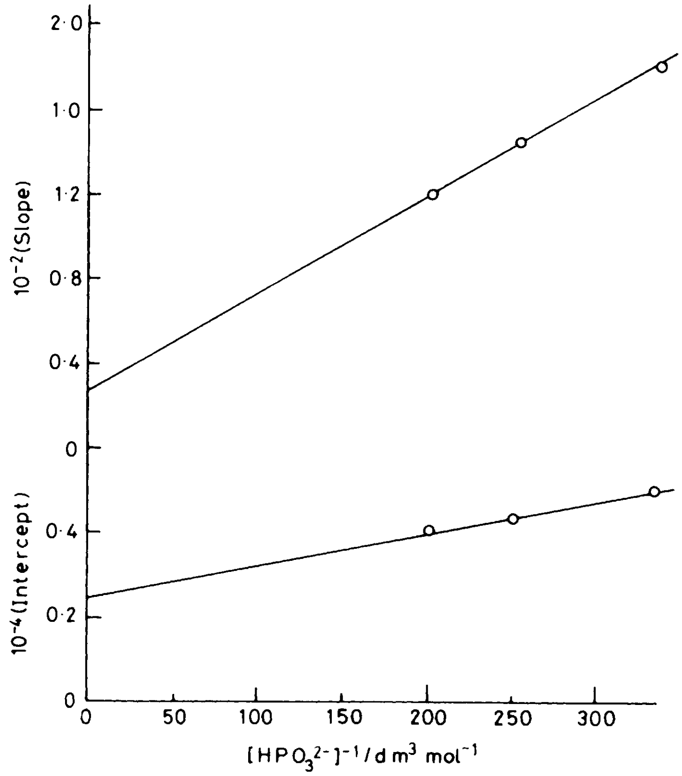

Figure 4. Plots of intercepts and slopes (from Figure 2) *vs.* $[HPO_3^{2-}]^{-1}$

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