Kinetics and Mechanism of the Silver(I) Catalyzed Oxidation of Water with Peroxodiphosphate in Acetate Buffers

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A kinetic study of the title reaction (i) was made by estimating peroxodiphosphate (pdp) iodometrically.

$$K_4P_2O_8 + H_2O \xrightarrow{Ag^I} 2\ K_2HPO_4 + 0.5\ O_2 \qquad \text{(i)}$$

Two species of pdp, $H_2P_2O_8^{2-}$ and $HP_2O_8^{3-}$, and two species of Ag^I, Ag^+ and $Ag(O_2CMe)$, participate in the reaction. The rate law (ii) holds, where K_3 is the acid dissociation constant of

$$-\frac{d[pdp]}{dt} = \frac{(k_3[H^+] + K_3k_4 + k_3'K[H^+][^-O_2CMe] + k_4'KK_3[^-O_2CMe])[Ag^I][pdp]}{(K_3 + [H^-])(1 + K[^-O_2CMe])} \qquad \text{(ii)}$$

$H_2P_2O_8^{2-}$ and K the complex formation constant of $Ag(O_2CMe)$. The values of k_3, $k_{3'}$, k_4, and $k_{4'}$ are 0.04, 0.0935, 0.19, and 0.42 $dm^3\ mol^{-1}\ s^{-1}$ respectively at 50 °C and $I = 1.0$ mol dm^{-3}. A comparison of this reaction with that of $S_2O_8^{2-}$ with Ag^I is made.

Most of the oxidations[1–6] with peroxodiphosphate (pdp) involve a hydrolytic rate-determining step producing peroxomonophosphate which is the potential oxidising species. It seems that direct reaction of peroxodiphosphate with the reducing substances is quite slow and that catalysis by silver(I) may be of help in these cases. This is expected in view of the universal application of silver(I) catalysis[7] in peroxodisulphate (pds) oxidations and the fact that peroxodiphosphate and peroxodisulphate are isoelectronic and isostructural.

A literature survey revealed that investigations into silver(I) catalysis in peroxodiphosphate reactions have not been made although the former is known to oxidize the latter at a convenient rate.[8,9] Preliminary investigations indicated that silver(I) is an efficient catalyst for several pdp oxidations. It was, therefore, considered desirable to study the kinetics of the silver(I)–pdp reaction first, as a sequel to the study of the mechanism of silver(I) catalysis. Silver(II) and/or silver(III) are expected to be the products of the oxidation of silver(I) as found in case of the Ag^I–pds reaction.[7] Since it is known that silver(II) and/or silver(III) readily oxidize[10,11] water in the absence of any reducing substance and similarly in the case of peroxodiphosphate, the reaction of Ag^I–pdp may be appropriately regarded as the silver(I) catalysed oxidation of water with peroxodiphosphate. The aim of the present investigation, therefore, is to study the kinetics and mechanism of the reaction for comparison with those of the peroxodisulphate reaction. There is one report of the Ag^I–pdp reaction by Maruthamuthu and Santappa[12] in 0.5 mol dm^{-3} acid in the temperature range of 30—60 °C. However, this study does not lead to clear-cut results and mechanism since it is complicated by the hydrolysis of peroxodiphosphate to peroxomonophosphate in the acid solutions employed, and the subsequent oxidation[13] of silver(I) with peroxomonophosphate. The present study has been carried out under such conditions of acidity that there is no significant hydrolysis and the results exclusively pertain to the Ag^I–pdp system.

Experimental

Tetrapotassium peroxodiphosphate was a gift sample from FMC Corporation, U.S.A. and was used without further purification. It was standardized iodometrically.[14] All other chemicals were of either BDH, AnalaR, or E. Merck G.R. quality. Doubly distilled water was employed for preparing the solutions and in the reaction mixture, the second distillation being from potassium permanganate. All glass vessels were either Corning or Pyrex.

Acetate buffers were employed for maintaining the medium at the desired constant pH, and sodium nitrate was employed to vary the ionic strength. The pH was varied by changing the concentrations of acetic acid at a fixed concentration of acetate. It was found that the rate was independent of acetate ion concentration above a particular concentration (different for different pH); hence the acetate concentration was varied by mixing acetic acid and acetate buffer solutions of various (but equal) concentrations in a fixed ratio. By this procedure there was no change in the pH of the system, but the concentration of acetate ion could be varied. The pH of the reaction mixture was measured at the beginning and end of the reaction. The change was within ±0.01 unit. All pH measurements were made on a ECL Digital pH meter.

The solution of peroxodiphosphate together with requisite amounts of acetate buffer and other chemicals was allowed to attain the temperature (50 ± 0.1 °C) of a thermostat waterbath. The reaction was initiated by mixing the solution of silver nitrate pre-equilibrated to the same temperature. The aliquots of 5 or 10 cm^3 were taken out at suitable time intervals and analysed iodometrically.[1–6] The kinetic data were initially treated for the calculation of the initial rates by the plane mirror method[15] for the determination of the order with respect to pdp and this was found to be equal to one. Subsequent pseudo-first-order plots were made since the concentration of silver(I) as a catalyst remains constant during a run. The results were reproducible to ±3%. Different samples of peroxodiphosphate yielded similar results within the limits of error mentioned and the irreproducibility found earlier in the oxidation[16] of hexacyanoferrate(II) was not encountered. Thus the trace amounts of metal ions present as impurities have no role in the present reaction.

Preliminary Investigations.—When a solution of silver nitrate is added to peroxodiphosphate, a brown to black precipitate [possibly silver(II) peroxodiphosphate] is formed which decomposes giving oxygen and silver(I) phosphate. Stoicheiometric experiments with different concentrations of peroxodiphosphate yielded oxygen which corresponded

Table 1. The values of $k_{obs.}$ at different peroxodiphosphate, silver(I) concentrations, and ionic strength at 50 °C

$10^3[P_2O_8^{4-}]_T$/ mol dm^{-3}	$10^3[Ag^I]$/ mol dm^{-3}	$[NaNO_3]$/ mol dm^{-3}	pH	$10^5k'$*/s^{-1}	$10^2k_{obs.}$/ dm^3 mol^{-1} s^{-1}
2.0	2.0	1.0	3.42	9.6	4.80
4.0	2.0	1.0	3.42	9.5	4.75
6.0	2.0	1.0	3.42	9.6	4.80
10.0	2.0	1.0	3.42	9.5	4.75
2.0	4.0	1.0	3.42	20.4	5.08
2.0	6.0	1.0	3.42	30.7	5.11
2.0	8.0	1.0	3.42	40.9	5.11
2.0	10.0	1.0	3.42	53.7	5.37
2.0	5.0	0.04	3.42	51.8	10.36
2.0	5.0	0.08	3.42	49.7	9.94
2.0	5.0	0.10	3.42	39.2	7.84
2.0	5.0	0.30	3.42	30.1	6.12
2.0	5.0	0.60	3.42	28.0	5.60
2.0	5.0	0.20	4.99	75.4	15.1
2.0	5.0	0.40	4.99	59.4	11.9
2.0	5.0	0.60	4.99	52.4	10.5
2.0	5.0	0.80	4.99	46.0	9.2
2.0	5.0	1.00	4.99	33.8	6.7

* k' = Pseudo-first-order rate constant.

approximately (±10%) to half the number of moles of initial pdp, as shown in equation (1). Since 2,2′-bipyridyl is known to form [17] a golden yellow complex with silver(II), an attempt to determine the stoicheiometry of equation (1) was made by

$$K_4P_2O_8 + H_2O \xrightarrow{Ag^I} 2\,K_2HPO_4 + 0.5\,O_2 \qquad (1)$$

precipitating silver(II). We did detect formation of Ag^{II}, but it soon decomposed yielding silver(I) and hence the stoicheiometry could not be determined by estimating silver(II). The situation is similar to that obtained in the silver(I) catalyzed oxidation of water with cerium(IV) in an attempt to study the equilibrium (2).[18]

$$Ce^{IV} + Ag^I \rightleftharpoons Ce^{III} + Ag^{II} \qquad (2)$$

Preliminary experiments indicated that insignificant hydrolysis occurs above pH 3 and the reaction becomes too fast for experimental study above pH 5.5. Moreover, phosphate which is one of the products precipitates silver(I) as silver phosphate above pH 6. Hence the hydrogen ion concentration was varied within the pH range 3—5.5.

Results

Peroxodiphosphate and Silver(I) *Dependences.*—The concentration of the peroxodiphosphate was varied in the range (2.0×10^{-3}—1.0×10^{-2}) mol dm^{-3} at fixed $[Ag^I] = 2.0 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, and pH = 3.42. The concentration of silver(I) was varied in the range (2.0×10^{-3}—1.0×10^{-2}) mol dm^{-3} at fixed [pdp] = 2.0×10^{-3} mol dm^{-3} and other similar conditions as mentioned above. The order from the initial rates with respect to each reactant was found to be one and the rate law at constant pH is described by equation (3). During any run the concentration of silver(I)

$$-d[pdp]/dt = k[pdp][Ag^I] \qquad (3)$$

remained constant since it is reformed *in situ* from the higher valent silver (produced by the oxidation with peroxodiphosphate). These results are given in Table 1.

Ionic Strength Dependence.—The ionic strength was varied with the aid of sodium nitrate in the concentration range 0.04—1.0 mol dm^{-3} at pH 3.42 and 4.99 and other fixed conditions. The pseudo-first-order rate constants decreased with increasing ionic strength. The data are given in Table 1.

Acetate Ion Dependence.—The acetate ion concentration was varied from 0.0117 to 0.0672 mol dm^{-3} with the help of sodium acetate in the manner described in the Experimental section, at constant pH and other conditions. It was found that the pseudo-first-order rate constants increased and tended to attain a limiting value with the increase of acetate ion concentration. These results at pH 3.42, 4.05, and 4.99 are given in Table 2.

Hydrogen Ion Dependence.—The pH of the reaction mixture was varied from 3.33 to 5.30 by changing the ratio of 3.0 mol dm^{-3} acetic acid and 3.0 mol dm^{-3} sodium acetate at a total acetate ion concentration of 0.045 mol dm^{-3} and $I = 1.0$ mol dm^{-3}. In the range of pH employed the lower limit avoided hydrolysis of peroxodiphosphate and the upper limit avoided precipitation of silver(I) phosphate. The rate increased with increasing pH and the results are given in Table 2.

Effect of Methyl Methacrylate.—The reaction was carried out in the presence of 0.1 mol dm^{-3} methyl methacrylate to ascertain whether there is any formation of an intermediate free radical. A white turbidity appeared within 3—4 min and a transparent sheet of polymer-like material appeared after *ca.* 10 min. This indicates the formation of free radicals. Both pdp or Ag^I when present alone, failed to initiate the polymerization of methyl methacrylate.

Discussion

Peroxodiphosphate in aqueous solution exists in several forms differing in the number of protons and is governed by the equilibrium (4).[19] The values of K_3 (acid dissociation constant

$$[H_nP_2O_8]^{n-4} \rightleftharpoons [H_{n-1}P_2O_8]^{n-5} + H^+ \qquad (4)$$

of $H_2P_2O_8^{2-}$) and K_4 have been found to be $(6.6 \pm 0.3) \times 10^{-6}$ and $(2.1 \pm 0.1) \times 10^{-8}$ mol dm^{-3} respectively. The values K_1 and K_2 could not be determined but were estimated to be *ca.* 2 and *ca.* 0.3 respectively by Crutchfield and Edwards.[19] Later, however, Venturini *et al.*[20] and then Gupta and co-workers [4]

Table 2. Values of $k_{obs.}$ and $k_{calc.}$ at different pH and acetate ion concentrations at 50 °C and I = 1.0 mol dm^{-3}

pH	10^3[pdp]/ mol dm^{-3}	10^3[Ag^I]/ mol dm^{-3}	$[^-O_2CMe]_T$ [a]/ mol dm^{-3}	$10^4k'$/ s^{-1}	$10^2k_{obs.}$/ dm^3 mol^{-1} s^{-1}	$10^2k_{calc.}$ [b]/ dm^3 mol^{-1} s^{-1}
3.42	2.0	4.0	0.0117	1.89	4.7	4.6
3.42	2.0	4.0	0.0176	1.91	4.8	4.8
3.42	2.0	4.0	0.0235	1.97	4.9	4.9
3.42	2.0	4.0	0.0412	2.07	5.2	5.3
3.42	2.0	4.0	0.0471	2.07	5.2	5.4
4.05	2.0	4.0	0.02	2.30	5.75	6.1
4.05	2.0	4.0	0.044	2.81	7.0	6.9
4.05	2.0	4.0	0.068	2.94	7.35	7.4
4.05	2.0	4.0	0.092	3.16	7.9	7.9
4.05	2.0	4.0	0.164	3.76	9.4	8.8
4.05	2.0	4.0	0.188	3.76	9.4	9.0
4.99	2.0	4.0	0.126	5.76	14.4	11.0
4.99	2.0	4.0	0.252	6.14	15.3	13.1
4.99	2.0	4.0	0.336	6.37	15.9	14.5
4.99	2.0	4.0	0.588	6.64	16.6	16.7
4.99	2.0	4.0	0.672	6.71	16.8	17.2
3.33	2.0	5.0	0.018	2.13	4.25	4.7
3.36	2.0	5.0	0.045	2.30	4.60	5.3
3.76	2.0	5.0	0.09	3.37	6.75	6.5
4.06	2.0	5.0	0.18	4.60	9.2	8.3
4.35	2.0	5.0	0.27	6.52	13.0	10.5
4.99	2.0	5.0	0.36	6.90	13.8	12.1
4.675	2.0	5.0	0.45	7.67	15.3	14.3
4.86	2.0	5.0	0.54	8.90	17.8	17.1
5.05	2.0	5.0	0.63	9.21	18.4	20.3
5.30	2.0	5.0	0.72	10.30	20.6	24.8
3.16	2.0	2.0	0.045	1.02	5.1	5.2
3.46	2.0	2.0	0.045	1.26	6.3	5.4
3.87	2.0	2.0	0.045	1.40	7.0	5.9
4.03	2.0	2.0	0.045	1.53	7.65	6.26
4.26	2.0	2.0	0.045	1.66	8.3	7.0
4.54	2.0	2.0	0.045	1.69	8.45	8.47
4.76	2.0	2.0	0.045	2.04	10.2	10.3

[a] Free concentration of acetate ion. [b] Calculated from equation (12) with the values $k_3 = 0.04$, $k_{3'} = 0.0935$, $k_4 = 0.19$, and $k_{4'} = 0.42$ dm^3 mol^{-1} s^{-1}, $K_3 = 6.6 \times 10^{-6}$ mol dm^{-3}, and $K = 5.4$ dm^3 mol^{-1}.

estimated them to be about twenty times larger. It is obvious therefore that under the pH conditions employed in the investigation, only two species $H_2P_2O_8^{2-}$ and $HP_2O_8^{3-}$ would predominate.

As far as silver(I) species are concerned, they are likely to be Ag^+ and $Ag(O_2CMe)$ since a complex of Ag^+ with acetate ion with a formation constant [21] of 5.4 has been reported. Thus with four species in the system, the following steps of reaction are possible [equations (6)—(10)]. These are followed by a number of fast steps in which the radical ions react to give the final products. Formation of the $PO_4^{\cdot 2-}$ radical ion has been involved in several other reactions.[9,22] Our observation with methyl methacrylate also indicates this. In the acid catalyzed self-decomposition of peroxodiphosphate the initiation of vinyl polymerization has been adduced as evidence for the formation of this ion radical.[23] These steps lead to the rate law (11), where [Ag^I] and [pdp] represent the analytical concentrations of silver(I) and pdp respectively and $[^-O_2CMe]$ represents the equilibrium free concentration of the acetate ions. Equation (11) can be written in the form of equation (12).

$$H_2P_2O_8^{2-} \overset{K_3}{\rightleftharpoons} HP_2O_8^{3-} + H^+ \tag{5}$$

$$Ag^+ + MeCO_2^- \overset{K}{\rightleftharpoons} Ag(O_2CMe) \tag{6}$$

$$H_2P_2O_8^{2-} + Ag^+ \overset{k_3}{\rightleftharpoons} Ag^{II} + PO_4^{\cdot 2-} + H_2PO_4^- \tag{7}$$

$$H_2P_2O_8^{2-} + Ag(O_2CMe) \xrightarrow{k_{3'}} Ag^{II} + MeCO_2^- + PO_4^{\cdot 2-} + H_2PO_4^- \tag{8}$$

$$HP_2O_8^{3-} + Ag^+ \xrightarrow{k_4} Ag^{II} + PO_4^{\cdot 2-} + HPO_4^{2-} \tag{9}$$

$$HP_2O_8^{3-} + Ag(O_2CMe) \xrightarrow{k_{4'}} Ag^{II} + MeCO_2^- + PO_4^{\cdot 2-} + HPO_4^{2-} \tag{10}$$

Thus a plot of $k_{obs.}(K_3 + [H^+])(1 + K[^-O_2CMe])$ *versus* $[^-O_2CMe]$ would yield a straight line with an intercept at pH 3.42, 4.05, and 4.99 as shown in Figure 1. The intercept and slope would be equal to $(k_3[H^+] + k_4K_3)$ and $(k_{3'}K[H^+] + k_{4'}KK_3)$ respectively. Now, if plots of intercept *versus* $[H^+]$ and those of slopes *versus* $[H^+]$ are made, again straight lines with intercepts would be obtained. These are given in Figure 2. From these plots and using the values of $K_3 = 6.6 \times 10^{-6}$ mol dm^{-3} and $K = 5.4$ dm^3 mol^{-1}, k_3, $k_{3'}$, k_4, and $k_{4'}$ were found to be

$$-\frac{d[pdp]}{dt} = \frac{(k_3[H^+] + K_3k_4 + k_{3'}K[H^+][^-O_2CMe] + k_{4'}KK_3[^-O_2CMe])[Ag^I][pdp]}{(K_3 + [H^+])(1 + K[^-O_2CMe])} \tag{11}$$

$$k_{obs.} = \frac{k_3[H^+] + K_3k_4 + k_{3'}K[H^+][^-O_2CMe] + k_{4'}KK_3[^-O_2CMe]}{(K_3 + [H^+])(1 + K[^-O_2CMe])} \tag{12}$$

0.04, 0.0935, 0.19, and 0.42 $dm^3 mol^{-1} s^{-1}$ respectively at 50 °C and $I = 1.0$ mol dm^{-3}. These values were utilized to calculate the value of $k_{obs.}$ given by rate law, (11). It can be seen from Table 2 that the values of $k_{obs.}$ and $k_{calc.}$ are in satisfactory agreement within ±20%.

It is noteworthy that the acetatosilver(I) complex is nearly twice as reactive as Ag^+. In the Ag^I–N_2H_4 reaction[24] the acetato- and sulphato-complexes are reported to be more reactive than the aqua-ion. It appears that the presence of an acetate group bound to Ag^+ in the transition state helps in the formation of Ag^{II}, since acetate is likely to stabilize Ag^{II} by forming a stronger complex than with silver(I). Although a complex of Ag^{II} with acetate ion has not been reported so far, it is likely in view of the existence of nitrate[25,26] and sulphate[27] complexes of silver(II).

The reaction of peroxodisulphate and silver(I) proceeds according to equation (13), with a rate shown by equation (14).

$$S_2O_8^{2-} + Ag^I \xrightarrow{k} SO_4^- + SO_4^{2-} + Ag^{II} \quad (13)$$

$$-d[S_2O_8^{2-}]/dt = [S_2O_8^{2-}][Ag^I] \quad (14)$$

The present reaction therefore occurs by the same mechanism, and the rate law for this reaction at constant $[H^+]$ and $[^-O_2CMe]$ would be similar to (14). Incidentally, the second-order rate constants in the two cases are also similar. The value * of k in equation (14) is 3.6 × 10^{-2} $dm^3 mol^{-1} s^{-1}$ at 50 °C and $I = 1.0$ mol dm^{-3} as compared to the values of 4.0 × 10^{-2} and 9.35 × 10^{-2} $dm^3 mol^{-1} s^{-1}$ for k_3 and $k_{3'}$ respectively at the same temperature and ionic strength. This is not unexpected since the oxidation potentials of both the peroxo-compounds are nearly the same.[8] However, in spite of this similarity the reactions of these two oxidants with Os^{II} [28] and Fe^{II} [29] complexes have quite different mechanisms.

Peroxodiphosphate is reported to react with metal ions through the formation of inner-sphere complexes.[28] Although in the present investigation there is no kinetic evidence, a possibility for it does exist since the formation of weak complexes with Li^+, Na^+, and K^+ are known.[19] It should be pointed out that the species $P_2O_8^{4-}$ is more complexing[19] than the protonated species $HP_2O_8^{3-}$ and hence $HP_2O_8^{3-}$ in turn is likely to be more complexing than $H_2P_2O_8^{2-}$. This could be the reason for the greater reactivity of the species $HP_2O_8^{3-}$ than $H_2P_2O_8^{2-}$. It is therefore logical to include one more step [equation (15)] for the weak complexing of Ag^I with $H_2P_2O_8^{2-}$ and $HP_2O_8^{3-}$ in the mechanism preceding the rate-determining step. However, it should be noted that so far there is no kinetic evidence, not even spectrophotometic, for this complex.

$$Ag^I + H_nP_2O_8^{n-4} \rightleftharpoons Ag^IH_nP_2O_8^{n-4} \quad (15)$$

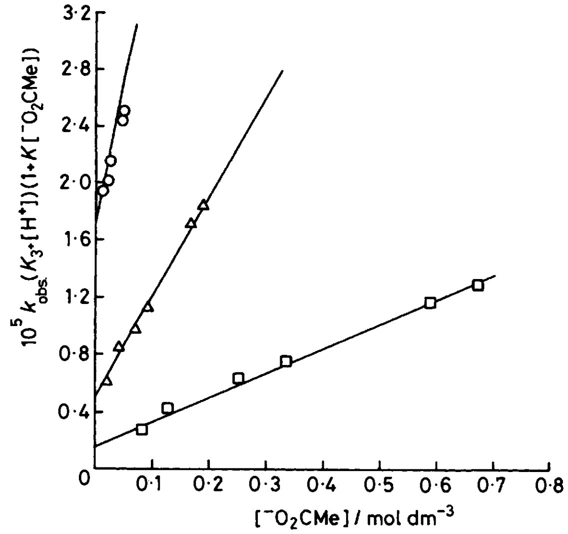

Figure 1. Plot of $[^-O_2CMe]$ *versus* $k_{obs.}$ $(K_3 + [H^+])(1 + K[^-O_2CMe])$ at pH 3.42 (○); 4.05 (△); and 4.99 (□). [pdp] = 2.0 × 10^{-3} mol dm^{-3}, $[Ag^I]$ = 4.0 × 10^{-3} mol dm^{-3}, and I = 1.0 mol dm^{-3} at 50 °C

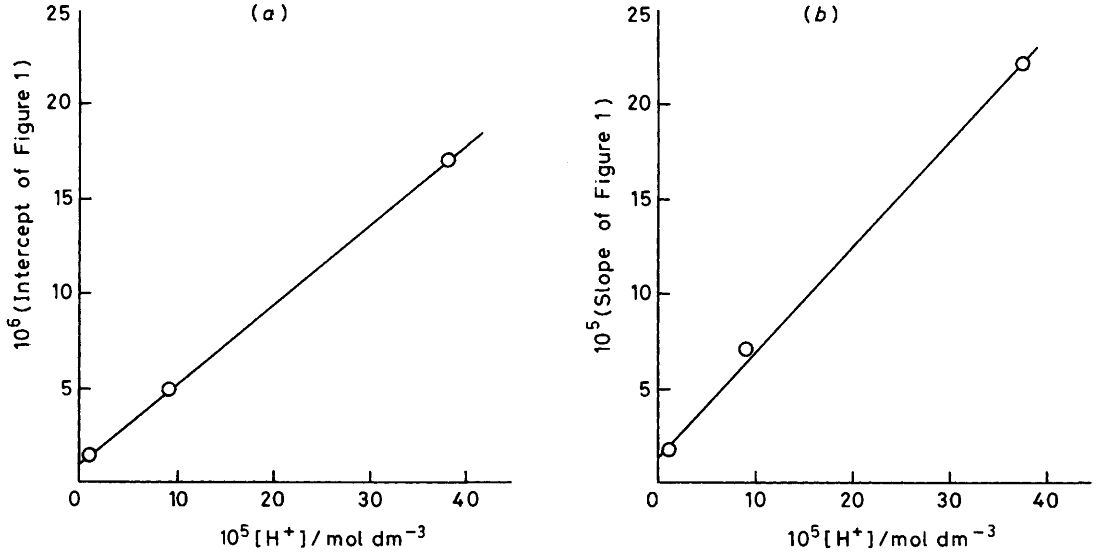

Figure 2. (*a*) Plot of intercept of Figure 1 *versus* $[H^+]$ at 50 °C, I = 1.0 mol dm^{-3}. (*b*) Plot of slope of Figure 1 *versus* $[H^+]$ at 50 °C, I = 1.0 mol dm^{-3}

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* Calculated at 50 °C from the value given at 40 °C in ref. 10, using E = 54.2 kJ.

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