Copper(II)-catalysed Oxidation of Hypophosphite by Peroxydisulphate in Perchloric Acid Solution

By **Ratan Swaroop** and **Y. K. Gupta,*** Department of Chemistry, University of Rajasthan, Jaipur, India

The copper(II)-catalysed oxidation of hypophosphite by peroxydisulphate in aqueous perchloric acid solution was measured in the presence of varying amounts of Cu^{II} (1×10^{-4}—4×10^{-3}M) in the range of hydrogen-ion concentration of 0·01—0·8M and at temperatures of 28, 35, and 40 °C. The rate law is (i) where K_d is the dissociation

$$-\frac{d[S_2O_8^{2-}]}{dt} = \frac{kK[Cu^{II}][S_2O_8^{2-}][H_3PO_2]}{[H^+] + K_d + K[H_3PO_2]} \qquad (i)$$

constant for hypophosphorous acid and k and K were found to be 54·8 ± 2·4 (average) l mol^{-1} min^{-1} and 3·6 respectively at 35 °C and μ = 0·2M. Complex formation between Cu^{++} and H_3PO_2 is suggested. Mn^{II} decreases the rate of reaction and a limiting rate is obtained by increasing the concentration of Mn^{II}. Sulphate ion is without any effect, but hydrogen sulphate decreases the rate. The overall energy of activation was found to be 10·7 kcal mol^{-1}. A chain mechanism has been suggested. The rate constant at 35 °C and energy of activation for the chain-initiating step were found to be 2·80 l mol^{-1} min^{-1} and 13·4 kcal mol^{-1} respectively.

ALTHOUGH Ag^I appears to be an universal catalyst [1] in

flask and placed in a thermostatted water bath at 35 ±

RESULTS

Stoicheiometry.—Hypophosphite, copper sulphate, and peroxydisulphate in perchloric acid solutions of different concentrations were kept at room temperature for 5—6 h.

with an intercept would be obtained. From the slope and the intercept of the line, K_a can be calculated. Such plots at different temperatures are shown in Figure 3. The

TABLE 1

Pseudo-first-order (k') and related (k) constants for the reaction between $S_2O_8^{2-}$ and H_3PO_2 in the presence of Cu^{II} with $\mu = 0{\cdot}25$M and $[NaHSO_4] = 0{\cdot}05$M

$10^3[S_2O_8^{2-}]$/M	$10^2[NaH_2PO_2]$/M	$10^3[Cu^{II}]$/M	$10^2[H^+]$/M	$\frac{10^3k'}{min^{-1}}$	$\frac{k'([H^+] + K_d + K[H_3PO_2])}{K[Cu^{II}][H_3PO_2]}$ l mol^{-1} min^{-1}
			28 °C		
2·5	4·0	1·0	5·5	15·4	36·6
2·5	3·0	1·0	5·5	13·1	36·9
2·5	2·0	1·0	5·5	9·67	36·3
2·5	5·0	1·0	5·5	16·8	35·3
2·5	4·0	1·0	57·0	5·5	33·9
2·5	4·0	1·0	47·2	6·33	34·4
2·5	4·0	1·0	37·3	7·48	35·3
2·5	4·0	1·0	27·6	8·97	35·9
2·5	4·0	1·0	18·4	10·4	34·5
					Av. 35·4 ± 0·8
			35 °C		
3·0	4·0	4·5	5·5	120	59·8
3·0	4·0	4·0	5·5	106	59·4
3·0	4·0	3·5	5·5	89·8	57·5
3·0	4·0	2·0	5·5	52·9	59·3
3·0	4·0	0·8	5·5	20·7	58·1
3·0	4·0	0·4	5·5	9·80	55·5
3·0	4·0	0·25	5·5	6·51	58·4
3·0	4·0	0·15	5·5	3·85	53·7
3·0	4·0	0·10	5·5	2·60	58·3
2·5	4·0	4·0	5·5	106	59·4
2·5	4·0	3·0	5·5	79·3	59·2
2·5	4·0	2·0	5·5	52·9	59·3
2·5	4·0	1·0	5·5	25·3	56·6
2·5	4·0	0·5	5·5	11·8	52·4
2·5	4·0	0·3	5·5	7·70	57·6
2·5	4·0	0·2	5·5	4·61	51·7
2·5	4·0	0·1	5·5	2·53	56·7
2·5	5·0	1·0	37·3	15·3	57·6
2·5	4·0	1·0	37·3	12·2	54·4
2·5	3·0	1·0	37·3	9·89	54·2
2·5	2·0	1·0	37·3	6·91	54·6

sociation of hydrogen sulphate[16] ion and association[17] of $H_2PO_2^-$ and H^+. A plot of $1/k'$ against $1/[H_3PO_2]$ was also made at different hydrogen-ion concentrations and from this the values of K_a were found to be 16·7, 10·0, and 6·7 at 0·05, 0·20, and 0·38M-[$HClO_4$] respectively. Table 1 shows all these results.

Effect of Ionic Strength, Chloride, Hydrogen Sulphate, Sulphate, and Phosphite.—Ionic strength was varied with sodium perchlorate and there appeared to be no change in the rate. This also shows that perchlorate ion has no specific effect. The effect of sodium chloride was studied in view of its reported inhibiting effect in the oxidations of As^{III} [6] and Sb^{III} [7] and its accelerating effect in case of hydrazine,[2] but no such effect was found in the present investigation. An increase in the concentration of hydrogen sulphate decreases the rate as shown in Table 2. Variation of sulphate ion from 10^{-3} to 0·2M had no effect. Addition of sulphate ion results in the decrease of hydrogen ion and an increase of hydrogen sulphate ion. Although the two factors have opposing kinetic effects, their magnitudes are different and hence the effect of hydrogen sulphate ion remains unexplained. Phosphorous acid in the concentration range 0·001—0·01M had no effect on the rate.

TABLE 2

Effect of hydrogen sulphate ion on the reaction between $S_2O_8^{2-}$ and H_3PO_2 in the presence of Cu^{II}; $[S_2O_8^{2-}] = 3 \times 10^{-3}$M; $[NaH_2PO_2] = 0{\cdot}04$M; $[Cu^{II}] = 1 \times 10^{-3}$M; $[HClO_4] = 0{\cdot}05$M; $t = 35$ °C

$10^2[NaHSO_4]$/M	0·10	0·50	1·0	2·5	5·0
$10^4k'$/min^{-1}	3·34	3·27	2·95	2·53	2·37

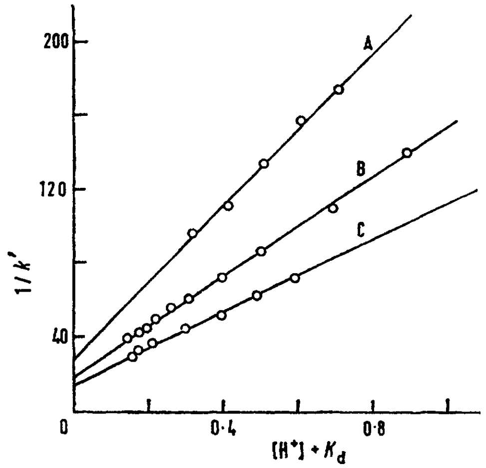

FIGURE 4 Hydrogen-ion dependence of the rate at different temperatures; $[S_2O_8^{2-}] = 2{\cdot}5 \times 10^{-3}$M; $[NaH_2PO_2] = 0{\cdot}04$M; $[Cu^{II}] = 0{\cdot}001$M; $[NaHSO_4] = 0{\cdot}05$M; A, 28 °C, $K_d = 0{\cdot}132$; B, 35 °C, $K_d = 0{\cdot}124$; C, 40 °C, $K_d = 0{\cdot}119$

Effect of Mn^{II}.—Mn^{II} has been reported to be an anticatalyst in most oxidations by peroxydisulphate, both catalysed[6,7,18] and uncatalysed.[19,20] The rate decreases in the present case too. A plot of k' against $1/[Mn^{II}]$ yields a straight line with an intercept as shown in Figure 5.

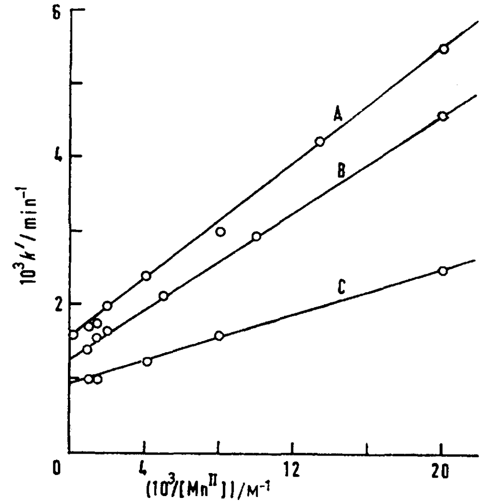

FIGURE 5 Effect of Mn^{II} on the rate; $[S_2O_8^{2-}] = 0{\cdot}003$M; $[NaH_2PO_2] = 0{\cdot}04$M; $[Cu^{II}] = 0{\cdot}001$M; $[NaHSO_4] = 0{\cdot}05$M; $[HClO_4] = 0{\cdot}05$M; A, 40 °C; B, 35 °C; C, 30·5 °C

Effect of Scavengers.—Allyl acetate and acrylamide are effective scavangers[21-23] for free radicals. The reaction was almost completely arrested by *ca.* 0·2M-acrylamide or allyl acetate. Any possibility of a non-chain reaction is thus excluded.

DISCUSSION

An appreciable concentration of hypophosphorous acid would exist as $H_2PO_2^-$. Because the present investigation was made at lower acidities (0·05—0·8M-$HClO_4$), account has to be made for the dissociation equilibrium (3). Espenson and Dustin[16] have reported a value of

$$H_3PO_2 \overset{K_d}{\rightleftharpoons} H_2PO_2^- + H^+ \qquad (3)$$

0·135M for K_d at 25 °C. The values at 28, 35, and 40 °C were calculated on the basis of $\Delta H = 1{\cdot}6$ kcal mol^{-1} [24] and found to be 0·132, 0·124, and 0·119M respectively.

A literature survey reveals that Cu^{II} forms complexes with a number of reducing substances such as hydrazine,[2] thiosulphate,[3] oxalate,[5] and As^{III} [6] in the Cu^{II}-catalysed oxidations by peroxydisulphate. Although the existence of a Cu^{II}–H_3PO_2 complex is not certain in the absence of any circumstantial evidence, a probability for it exists in view of the ligand properties of hypophosphite exhibited with other metal ions. Tl^{III} [25] and

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Ce^{IV} [26] are said to form complexes with H_3PO_2. A chromium(III) [27] complex has also been characterised and the kinetics studied. Banerjee [28] reported a complex formation between Fe^{III} and hypophosphite ion. Hypophosphorous acid is a monobasic acid of the formula $HOPH_2O$, in which the co-ordination number four for phosphorous is preserved. Considerable kinetic evidence has been noted for a second and more reactive form of the acid which plays an important role in a number of oxidation reactions [29] of hypophosphorous acid and also in exchange reaction.[30] The rate-determining step in these reactions involves only hypophosphorous acid in which the structural rearrangement (4) is presumed. The complex with cupric ion may have the structures

$$HOPH_2O \rightleftharpoons (HO)_2PH \qquad (4)$$

$(H_2O)_3Cu^{II}(OPHOH)^+$ or $(H_2O)_3Cu^{II}(OPH_2O)^+$ but since there is no specific evidence for one, a non-committal form $[Cu^{II}H_2PO_2]^+$ has been used.

The nature of hypophosphite-dependence shows that a complex of Cu^{II} and H_3PO_2 is the reactive species which undergoes oxidation. The chain mechanism (5)—(10) can be suggested in view of the observed orders with respect to the different reactants. From the scheme

$$Cu^{++} + H_3PO_2 \overset{K}{\rightleftharpoons} CuH_2PO_2^+ + H^+ \qquad (5)$$

$$CuH_2PO_2^+ + S_2O_8^{2-} \xrightarrow{k_6} Cu^{II} + H_2PO_2\cdot + SO_4^{-}\cdot + SO_4^{2-} \qquad (6)$$

$$H_2PO_2\cdot + S_2O_8^{2-} \xrightarrow{k_7} H_2PO_2^+ + SO_4^{-}\cdot + SO_4^{2-} \qquad (7)$$

$$(H_2PO_2^+ + H_2O \xrightarrow{\text{fast}} H_3PO_3 + H^+) \qquad (8)$$

$$CuH_2PO_2^+ + SO_4^{-}\cdot \xrightarrow{k_9} Cu^{II} + SO_4^{2-} + H_2PO_2\cdot \qquad (9)$$

$$H_2PO_2\cdot + SO_4^{-}\cdot \xrightarrow{k_{10}} H_2PO_2^+ + SO_4^{2-} \qquad (10)$$

of reactions (5)—(10) rate law (11) can be deduced,

$$-[S_2O_8^{2-}]/dt = \left[k_6 + \left(\frac{k_6k_7k_9}{k_{10}}\right)^{\frac{1}{2}}\right] \frac{K[S_2O_8^{2-}][Cu^{II}]_T[H_3PO_2]_T}{[H^+] + K_d + K[H_3PO_2]_T} \qquad (11)$$

where $[Cu^{II}]_T$ and $[H_3PO_2]_T$ are given by (12) and (13).

$$[Cu^{II}]_T = [Cu^{2+}] + [CuH_2PO_2^+] \qquad (12)$$

$$[H_3PO_2]_T = [H_3PO_2]_{free} + [H_2PO_2^-] \qquad (13)$$

The concentration of $CuOH^+$ would be too small [31,32] and is not considered in (12). Similarly $CuH_2PO_2^+$ can be neglected in comparison with H_3PO_2 and $H_2PO_2^-$ in equation (13). $[Cu^{II}]$ and $[H_3PO_2]$ of equation (2a) refer to the total analytical concentrations. A comparison would show that k is given by equation (14) and K_a by (15). Although copper catalysis is not apparent from the above

$$k = k_6 + \left(\frac{k_6k_7k_9}{k_{10}}\right)^{\frac{1}{2}} \qquad (14)$$

$$K_a = \frac{K}{[H^+] + K_d} \qquad (15)$$

mechanism, the idea is implicit in equation (6). Copper(II) may first oxidize H_3PO_2 with the formation of Cu^I which is subsequently quickly oxidized by peroxydisulphate to Cu^{II}. The mechanism is similar to one postulated by Kornblum *et al.*[33] in the copper-catalysed oxidation of hypophosphorous acid by diazonium salts. Cu^{II} catalysis may also be explained by a Cu^I–Cu^{II} cycle in which Cu^{II} acts as an oxidant for a transient radical as suggested in copper-catalysed reactions of peroxidic compounds.[34] Both these mechanisms are incorporated in a single step (6).

The complex may also be formed by the interaction of Cu^{2+} and $H_2PO_2^-$ as shown in (16).

$$Cu^{2+} + H_2PO_2^- \overset{K_{16}}{\rightleftharpoons} CuH_2PO_2^+ \qquad (16)$$

The rate law (17) easily follows and it is of the same form as (11) except that $K = K_{16}K_d$. The rate law (11)

$$-d[S_2O_8^{2-}]/dt = \frac{kK_{16}K_d[Cu^{II}]_T[S_2O_8^{2-}][H_3PO_2]_T}{[H^+] + K_d + K_{16}K_d[H_3PO_2]_T} \qquad (17)$$

indicates that a plot of $1/k'$ against $1/[H_3PO_2]$ would be a straight line of slope equal to $([H^+] + K_d)/(kK[Cu^{II}])$ and with intercept equal to $1/k[Cu^{II}]$. Such plots at different hydrogen-ion concentrations show the straight lines passing through the same point on the $1/k'$ axis, thus indicating that probably one type of complex is predominantly formed. The ratio of intercept to slope gives the values of K_a as in (18), where K is true equilibrium constant for the complex formation between Cu^{++}

$$K_a = \frac{K}{[H^+] + K_d} \qquad (18)$$

and H_3PO_2. Again a plot of $1/K_a$ against $[H^+]$ results in a straight line yielding $K = 3·6$ and $K_d = 0·157$. K_d is somewhat larger than reported,[16] but the order of magnitude is the same. A plot of $1/k'$ against $[H^+] + K_d$ also gives a straight line with an intercept (Figure 4) in

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conformity with the rate expression (11). The fair constancy of column 6 of Table 1 at constant temperature and ionic strength strongly supports the suggested rate law.

The values of k calculated from Figures 3 or 4 were found to be 36, 59, and 71 l mol^{-1} min^{-1} at 28, 35, and

process. It is noteworthy that for the copper chloride–hypophosphite reaction (only with large concentrations of the reactants) also Mitchell[14] suggested a mechanism involving a complex formation between the reactants before the redox reaction.

The role of Mn^{II} in peroxydisulphate oxidations has