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Kinetics of Oxidation of Pinacol by Peroxydisulphate Catalysed by Silver Ions

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The kinetics of the reaction between peroxydisulphate and piancol catalysed by silver ions (Ag^+) has been studied. The rate of peroxydisulphate disappearance was found to be dependent (i) on [$S_2O_8^{2-}$] (ii) on (Ag^+). The rate is independent of the concentration of pinacol. Effects of [H^+], temperature on the rate were studied. *ΔE, Pz, ΔS, ΔF, etc.* were evaluated. Mechanism of oxidation of pinacol based on the formation of reactive [Ag^{2+}] is postulated.

Kinetic studies on oxidation of a variety of substrates, both organic and inorganic by peroxydisulphate were reviewed recently by House[1] and Wilmarth and Haim.[2] The reactions involving peroxydisulphate ion are generally slow at ordinary temperature and the oxidation does not proceed at a convenient rate at room temperature unless a catalyst is present. The most thoroughly investigated catalyst is silver(I) ion, although cupric ion (Cu^{2+}) has also been studied.

A review of literature on the oxidation by peroxydisulphate shows that oxidation of diols by peroxydisulphate has not received any attention. This investigation, has therefore been undertaken. The present work summarizes the results obtained in the oxidation of pinacol by peroxydisulphate, catalysed by silver(I) ions.

Experimental

Material. Pinacol (B. D. H. A. R.) and potassium peroxydisulphate E. Merck were used. All other chemicals were chemically pure.

Kinetic Method. Reactions were carried out in bottles at constant temperature (±0.03°C). Reaction mixture containing the requisite quantities of diol, Ag^+ was prepared in reaction vessel. The reaction mixture and peroxydisulphate solution were thermostated for about 20 min to attain experimental temperature (48.5°C). A known volume of peroxydisulphate solution was then transferred to the reaction mixture and aliquots were removed and analysed from time to time. The rate at which peroxydisulphate was consumed was estimated by the method of BARTLETT and COTMAN.[3]

Results

The rate at which the peroxydisulphate was consumed follows first order rate laws. The first order rate constants at different peroxydisulphate concentrations are summarised in Table 1.

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3) P. D. Bartlett and J. D. Cotman, *J. Am. Chem. Soc.*, **71**, 1419 (1949).

TABLE 1. VARIATION OF RATE CONSTANT WITH CONCENTRATION OF PEROXYDISULPHATE

[Pinacol]=4.90×10^{-2} M Temp. 48.5°C
[Ag^+]=5.30×10^{-4} M

[$S_2O_8^{2-}$]$\times10^3$ mol/l	$k_1\times10^3$ sec^{-1}
0.98	1.81
1.96	1.70
2.94	1.34
3.92	1.18
4.90	1.08

The first order rate constants are expected to be independent of initial concentration of peroxydisulphate, however, results show a small decrease with increase in concentration of the oxidant. This decrease may be ascribed to specific inhibitory effect of potassium ions, as reported in the oxidation of oxalate[4] also.

TABLE 2. VARIATION OF RATE CONSTANT WITH CONCENTRATION OF PINACOL

[$S_2O_8^{2-}$]=1.96×10^{-3} M Temp. 48.5°C
[Ag^+]=5.30×10^{-4} M

Pinacol$\times10^2$ mol/l	$k_1\times10^4$ sec^{-1}
0.981	15.3
1.96	15.1
2.94	15.2
3.92	16.0
4.90	15.1

TABLE 3. VARIATION OF RATE CONSTANT WITH CONCENTRATION OF SILVER(I) IONS

[Pinacol]=4.90×10^{-2} M Temp. 48.°C
[$S_2O_8^{2-}$]=4.90×10^{-3} M

[Ag^+]$\times10^4$ mol/l	$k_1\times10^4$ sec^{-1}	k_1/[Ag^+]
2.65	7.21	2.71
5.30	15.5	2.92
7.95	22.0	2.76
10.6	29.7	2.81
13.25	36.9	2.79
15.9	46.1	2.89

TABLE 4. EFFECT OF H^+ IONS CONCENTRATION ON THE RATE OF REACTION KEEPING CONCENTRATION OF SULPHATE ION CONSTANT

[Pinacol]=4.90×10^{-2} M [Ag^+]=5.3×10^{-4} M
[$S_2O_8^{2-}$]=4.90×10^{-3} M [SO_4^{2-}]=0.245 M
Temp. 48.5°C

[H^+]$\times10^2$ mol/l	$k_1\times10^4$ sec^{-1}
0.0	15.67
4.90	3.07
9.81	2.82
14.7	3.13
18.7	3.99

The results show that the rate is independent of the concentration of pinacol.

The results show that rate of oxidation is proportional to the first power of the concentration of silver(I) ions. The effect of H^+ ion concentration on the rate of oxidation was studied by adding sulphuric acid, at the same time adjusting the concentration of sulphate to a constant value by adding potassium sulphate. It is found that when the sulphate ion concentration is kept constant, addition of small quantities of acid decreases the rate constant appreciably, but further addition of acid does not produce any change in the rate of oxidation. The effect of ionic strength on the rate of reaction has been summarised in Table 5. The effect of ionic strength was studied by adding potassium sulphate and potassium nitrate. It is observed that change in ionic strength produced by either K_2SO_4 or KNO_3 has more or less the same effect on rate.

As shown in Fig. 1 a plot of log$K$ against $\sqrt{\mu}$ in case of K_2SO_4 and KNO_3 gives a straight line with

TABLE 5. EFFECT OF IONIC STRENGTH ON RATE OF REACTION

[Pinacol]=4.90×10^{-2} M Temp. 48.5°C
[Ag^+]=5.23×10^{-4} M [$S_2O_8^{2-}$]=4.90×10^{-3} M

$\sqrt{\mu}$, M	K_2SO_4		KNO_3	
	$k_1\times10^4$ sec^{-1}	K, l mol^{-1} sec^{-1}	$k_1\times10^4$ sec^{-1}	K, l mol^{-1} sec^{-1}
0.0	17.7	3.38	17.7	3.38
0.336	—	—	10.1	1.93
0.358	8.2	1.56	—	—
0.402	6.56	1.25	7.39	1.41
0.459	5.91	1.13	7.56	1.45
0.561	5.05	0.97	—	—
0.562	—	—	5.54	1.06
0.632	4.45	0.85	4.30	0.82
0.675	4.04	0.77	4.94	0.94
0.777	3.05	0.58	3.57	0.68

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[4] Y. K. Gupta and S. Ghosh, *J. Inorg. and Nuclear Chem.*, **1**, 178 (1959).

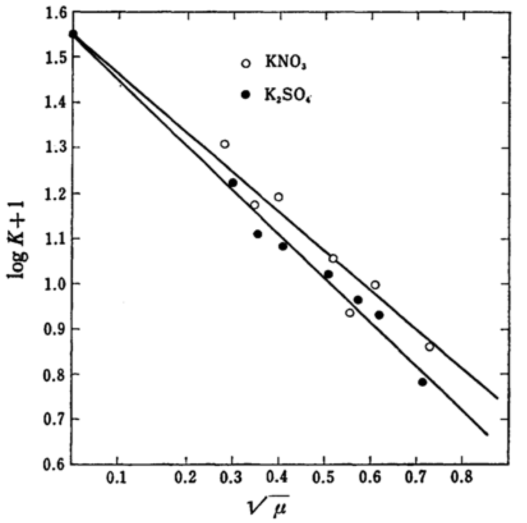

Fig. 1. Effect of addition of K_2SO_4 and KNO_3 on rate of oxidation of pinacol. *cf.* Table 5.

Table 6. Effect of temperature
[Pinacol]$=4.90\times10^{-2}$ M [Ag$^+$]$=5.30\times10^{-4}$ M
[$S_2O_8^{2-}$]$=4.90\times10^{-3}$ M

Temp. °C	$k_1\times10^4$ sec^{-1}	K, l mol^{-1} sec^{-1}
28.5	5.42	1.03
40.0	10.6	2.0
48.5	15.6	2.96
54.0	24.6	4.46

Table 7

Specific rate constant at 48.5°C	2.96
Frequency factor, l mol^{-1} sec^{-1}	8.28×10^7
ΔE, kcal/mol	10.87
ΔS, e. u.	−23.1
ΔF, kcals	18.3

slope equal to 0.97 and 0.82 respectively. The reaction was studied at 28.5, 40.0, 48.5 and 54.0°C. The specific rate constant (K) was obtained by dividing the first order rate constant by the concentration of silver ions. A plot of $\log k_1$ against inverse of absolute temperature gives a straight line. This show that Arrhenius equation is valid. The energy of activation was estimated from the slope of the straight line obtained by plotting $\log k_1$ against the inverse of T. The energy of activation comes out to be 10.87 kcal mol^{-1}. The frequency factor and entropy of activation, free energy of activation were estimated from data in Table 6 and have been summarised in Table 7.

Discussion

The reaction between pinacol and peroxydisulphate in absence of silver(I) ions is extremely slow. The rate of (Ag$^+$) ions catalysed reaction is proportional to the concentration of (Ag$^+$) ions and of peroxydisulphate but independent of the concentration of pinacol. Since the uncatalysed reaction between peroxydisulphate and pinacol is extremely slow, it therefore suggests that peroxydisulphate or sulphate radical ions do not react with pinacol. However, to explain the increased rate of disapprearance of peroxydisulphate on addition of substrate, it is necessary to postulate that reactive silver species and pinacol react to produce a radical. The radical so produced from the substrate further induces peroxydisulphate decomposition.

Gupta and Ghosh[4] have proposed a mechanism involving an equilibrium which is followed by a termolecular rate determining step:

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^- \text{ (rapid)} \quad (1)$$

$$2SO_4^- + Ag^+ \rightarrow 2SO_4^{2-} + Ag^{3+} \text{ (slow)} \quad (2)$$

The break down of peroxydisulphate into sulphate free radicals appears to be irreversible, as it seems likely that sulphate free radicals would exchange electrons with sulphate ions at a rate comparable with their recombination to perxoydisulphate. However no exchange has been observed under the conditions of the kinetic experiments.[5-8] Thus postulation of termolecular rate determining step introduces difficulties and consequently any proposed mechanism of decomposition involving equilibrium between peroxydisulphate and sulphate ion radicals—step (i) is probably incorrect.

Alternatively catalytic effects of silver ions may be explained by considering the following initial steps:

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^- + SO_4^{2-} \quad (3)$$

$$Ag^+ + SO_4^- \rightarrow Ag^{2+} + SO_4^{2-} \quad (4)$$

The nature of the silver intermediate in the oxidations by peroxydisulphate is uncertain. Both Ag^{2+} and Ag^{3+} ions have been postulated as intermediates.[4,9-13] The postulation of Ag^{2+} and SO$_4^-$ as the reactive species accords with the observations of Subbaraman and Santappa,[14] Higgenison and Marshall[15] that one electron transfer is more likely in oxidation-reduction system between a transition

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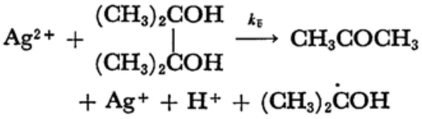
metal ion and an ion derived from a non transition element. In view of the above consideration we are led to suggest the following mechanism:

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k_3} Ag^{2+} + SO_4^- + SO_4^{2-} \quad (3)$$

$$Ag^+ + SO_4^- \xrightarrow{k_4} Ag^{2+} + SO_4^{2-} \quad (4)$$



$$Ag^{2+} + \begin{array}{c}(CH_3)_2COH\\ | \\ (CH_3)_2COH\end{array} \xrightarrow{k_5} CH_3COCH_3 + Ag^+ + H^+ + (CH_3)_2\dot{C}OH \quad (5)$$

$$(CH_3)_2\dot{C}OH + S_2O_8^{2-} \xrightarrow{k_6} (CH_3)_2CO + H^+ + SO_4^{2-} + SO_4^- \quad (6)$$

$$(CH_3)_2\dot{C}OH + SO_4^- \xrightarrow{k_7} (CH_3)_2CO + H^+ + SO_4^{2-} \quad (7)$$

Application of steady state condition gives:

$$\frac{d[Ag^{2+}]}{dt} = k_3[Ag^+][S_2O_8^{2-}] + k_4[Ag^+][SO_4^-] - k_5[Ag^{2+}][(CH_3)_2COHCOH(CH_3)_2] = 0 \quad (I)$$

$$\frac{d[(CH_3)_2\dot{C}OH]}{dt} = k_5[Ag^{2+}]\begin{bmatrix}(CH_3)_2COH\\ | \\ (CH_3)_2COH\end{bmatrix} - k_6[(CH_3)_2\dot{C}OH][S_2O_8^{2-}] - k_7[(CH_3)_2\dot{C}OH][SO_4^-] = 0 \quad (II)$$

$$\frac{d[SO_4^-]}{dt} = k_3[Ag^+][S_2O_8^{2-}] + k_6[(CH_3)_2\dot{C}OH][S_2O_8^{2-}] - k_4[Ag^+][SO_4^-] - k_7[(CH_3)_2\dot{C}OH][SO_4^-] = 0 \quad (III)$$

From I, II and III following relationship follows:

$$[k_3[Ag^+] - k_6[(CH_3)_2\dot{C}OH]][S_2O_8^{2-}] = [k_7[(CH_3)_2\dot{C}OH] - k_4[Ag^+]][SO_4^-]$$

$$[k_3[Ag^+] + k_6[(CH_3)_2\dot{C}OH]][S_2O_8^{2-}] = [k_7[(CH_3)_2\dot{C}OH] + k_4[Ag^+]][SO_4^-]$$

and

$$[(CH_3)_2\dot{C}OH] = \left\{\frac{k_3k_4}{k_6k_7}\right\}^{1/2}[Ag^+]$$

The rate at which peroxydisulphate disproportionates is given by:

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_3[Ag^+][S_2O_8^{2-}] + k_6[(CH_3)_2\dot{C}OH][S_2O_8^{2-}] = \left[k_3 + k_6\left\{\frac{k_3k_4}{k_6k_7}\right\}^{1/2}\right][Ag^+][S_2O_8^{2-}] = K[Ag^+][S_2O_8^{2-}]$$

Where $K = \left[k_3 + k_6\left\{\frac{k_3k_4}{k_6k_7}\right\}^{1/2}\right]$

This mechanism leads to correct rate laws and explains the dependence of rate constant on the first power of silver(I) ion concentration. The product of the oxidation of pinacol as confirmed by its usual tests has been found to be Acetone.