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Kinetics and Mechanism of the Silver Catalysed Oxidation of Malic Acid by Potassium Peroxydisulphate

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Preliminary experiments showed that the reaction between malic acid and potassium peroxydisulphate is very slow. The reaction rate becomes a measurable value at 25°C by introducing the Ag^+ ion as a catalyst. The total order of the reaction has been found to be nearly unity. The effect of the concentration of catalyst and malic acid has been studied. The temperature coefficient of the reaction between the temperature range of 30 and 45°C is 1.76 and the mean value of the energy of activation is 10.9 kcal. The frequency factor and entropy of activation are 16.8×10^5 sec^{-1} and -41.1 e.u. respectively. The probable mechanism for the reaction has been suggested.

The reaction between potassium peroxydisulphate and several reducing ions such as oxalate, formate, *etc.*, has been studied by a number of workers and various mechanisms have been suggested to explain the reactions in each case. Ghosh and co-workers[1)] following the work of King[2)] and Howell[3)] studied the catalysed and uncatalysed reaction between oxalic acid and potassium peroxydisulphate. Allen[4)] studied the copper catalysed reaction between potassium formate and potassium peroxydisulphate. The kinetics of the reaction between potassium formate and potassium peroxydisulphate also formed a topic of study of Ghosh *et al.*[5)] Saxena and Singhal[6)] have studied the reduction of peroxydisulphate with tartaric acid.

A study of literature (*loc. cit.*) showed that the reaction between malic acid and potassium peroxydisulphate has not been studied so far. The authors have therefore taken up the study of this in order to arrive at the general mechanism of the reaction.

Preliminary experiments showed that the reaction in the absence of any catalyst is very slow. However, the rate is enhanced by the introduction of Ag^+ ion as a catalyst.

Experimental

All the chemicals used were that of purest quality available. Solutions were prepared in redistilled water. Calculated amounts of malic acid and silver nitrate solutions were taken in a reaction vessel kept in a Townson and Mercer, Croydan Thermostat (adjustable upto ±0.1°C). The flask containing potassium peroxydisulphate was also kept in the thermostat to attain the temperature of the bath. After attaining the required temperature in the bath, the two solutions were mixed in order to initiate the reaction. At suitable intervals of time, 10 m*l* of the reaction mixture were withdrawn and added to 10 m*l* of an ice cold solution of 10% potassium iodide in order to estimate the unreacted potassium peroxydisulphate. The flask was allowed to remain for five minutes in order to liberate the iodine. The liberated iodine was titrated by a standard solution of sodium thiosulphate using starch as an indicator.

Results

Order of Reaction. The total order of the reaction was calculated employing the isolation method. The data of experiments are recorded in Tables 1 and 2. Column 1 gives the time in minutes, colum 2 volume of sodium thiosulphate used to titrate the liberated iodine at various time intervals and column 3 the values of k. "a" is the volume of sodium thiosulphate at the start of the reaction and $a-x$ is the volume of sodium thiosulphate at different time. Since k exhibits satisfactory consistency, the order with respect to potassium peroxydisulphate must be unity.

By making a run at each of two different initial concentrations of any one component, the other concentrations remaining constant, the data will enable the determination of the order of the reac-

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1) S. P. Srivastava and S. Ghosh, *Z. Physik Chem.*, **202**, 191 (1953); **205**, 332 (1956).

2) C. V. King, *J. Amer. Chem. Soc.*, **49**, 2869 (1927); **50**, 2089 (1928).

3) W. J. Howells, *ibid.*, **61**, 463 (1939).

4) T. L. Allen, *ibid.*, **73**, 3589 (1951).

5) S. P. Srivastava and S. Ghosh, *Z. Physik Chem.*, **202**, 198 (1953); **207**, 161, 1957.

6) L. K. Saxena and C. P. Singhal, *J. Ind. Chem. Soc.*, **38**, 346 (1961); *J. Phys. Chem.*, **211**, 161 (1959); *ibid.*, **214**, 179 (1960).

Table 1

(Temperature 25°C)

Reaction mixture	Overall concentration
Malic acid	0.0330M (C_2')
Potassium peroxydisulphate	0.0066M
Silver nitrate	0.00066M

Time (min)	Volume of $Na_2S_2O_3$ (ml)	$k\times10^{-2}=2.303/t\log\frac{a}{a-x}$
1	13.10	—
5	12.00	1.75
10	10.80	1.93
15	9.90	1.87
20	8.90	1.93
25	8.00	1.97
30	7.00	2.10
40	5.95	1.98
		Mean value 1.93

Table 2

(Temperature 25°C)

Reaction mixture	Overall concentration
Malic acid	0.0660M (C_2'')
Potassium peroxydisulphate	0.0066M
Silver nitrate	0.00066M

Time (min)	Volume of $Na_2S_2O_3$ (ml)	$k\times10^{-2}=2.303/t\log\frac{a}{a-x}$
1	13.00	—
5	12.00	1.60
10	11.00	1.67
15	10.20	1.67
20	9.40	1.62
25	8.70	1.61
30	8.00	1.62
35	7.65	1.52
40	7.15	1.50
45	6.50	1.54
50	6.00	1.55
		Mean value 1.59

Table 3

[$K_2S_2O_8$]=0.0066M, [$AgNO_3$]=0.00066M

Temperature	[Malic acid]	$k\times10^{-2}$ (min^{-1})	
25°C	0.0330M	1.93	$n=-0.27$
25°C	0.0660M	1.59	
30°C	0.1330M	1.57	
35°C	0.1638M	1.50	$n=-0.32$
35°C	0.3276M	1.21	

tion with respect to that component.[7] Using the data given in Tables 1, 2 and 3, the order of reaction with respect to malic acid was determined by means of the equation

$$n=\frac{\log\frac{k_1'}{k_2''}}{\log\frac{C_2'}{C_2''}}$$

where k_1' and k_2'' are the first order rate constants obtained at two different concentrations of malic acid C_2' and C_2''. The value of n is -0.3 which suggests that the rates of reaction are slightly dependent on the concentration of reducing ions. Thus the total order of the reaction is 0.7 which may be taken as unity *i. e.* the velocity at any instant is dependent on the peroxydisulphate concentration only.

Effect of Malic Acid. Different sets of experiments were carried out at different concentrations of malic acid in order to study is behaviour on the reaction rates. The results are tabulated in Table 3.

A perusal of the above table shows that the value of the first order rate constant decreases with simultaneous increase in malic acid concentration and temperature. The effect can be seen clearly that even increase in temperature has little effect on the rate indicating the important role of malic acid concentration on the reaction mechanism.

Effect of Silver Nitrate Concentration. In order to decide the role of silver nitrate as catalyst on the kinetics of the reaction, the study was carried out using different concentration of $AgNO_3$. The observations are given below:

Table 4

(Temperature 25°C)

[$K_2S_2O_8$]=0.0066M, [Malic acid]=0.0660M

[Silver nitrate]	$k\times10^{-2}$ (unimolecular)
0.00066M	1.57
0.00100M	2.28
0.00133M	3.16

The above data indicates that the rate is dependent on the catalyst concentration. When a graph is plotted between $AgNO_3$ concentration and the rate constant, a linear curve is obtained indicating that the rate is linearly related to $AgNO_3$ concentration *i. e.* $dx/dt\propto[Ag^+]$ (Fig. 1)

Temperature Coefficient. The reaction velocities were measured at four different temperatures. All the four experiments were performed at the identical concentration of the reactants. The values of temperature coefficient calculated are given in Table 5.

Energy and Entropy of Activation. The average value of energy of activation (E) was found to be 10.9 kcal. The value of E is also calculated graphically by plotting $1/T$ *vs.* log k and is found

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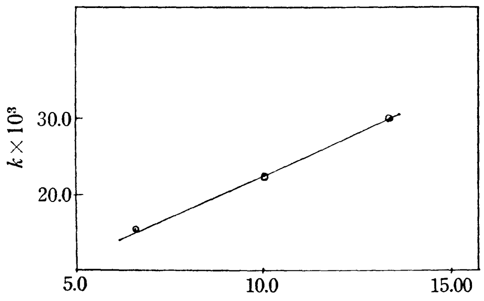
[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley, New York (1961), p. 45.



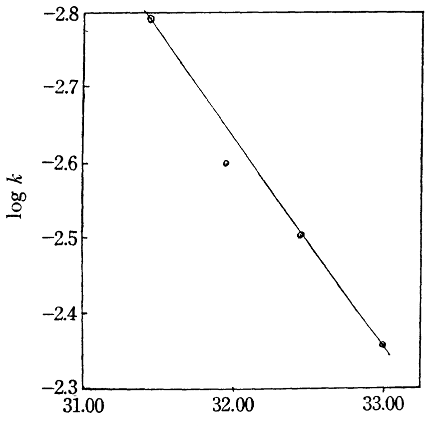
$[AgNO_3]\times10^4$M

Fig. 1. Concentration of $AgNO_3$ *vs.* *K*.

TABLE 5

$[K_2S_2O_8]$=0.0066M, [Malic acid]=0.0660M
$[AgNO_3]$=0.00066M

Temperature	$k\times10^{-2}$ (in units)	Temperature coefficient
30°C	2.28	$k(t+10)/k(t)$
40°C	4.12	1.81 (30—40°C)
35°C	3.64	1.70 (35—45°C)
45°C	6.12	
	Average value	1.76



$1/T\times10^4$

Fig. 2. Plot of log *k* *vs.* $1/T$.

to be 11.4 kcal (Fig. 2). The value of frequency factor with E=10.9 kcal at 40°C is 16.8×10^5 sec^{-1} and entropy of activation at 40°C is −41.1 e. u.

Discussion

The total order of the reaction between potassium peroxydisulphate and malic acid in presence of Ag^+ ion as a catalyst comes out near unity. Then the observed rate equation is

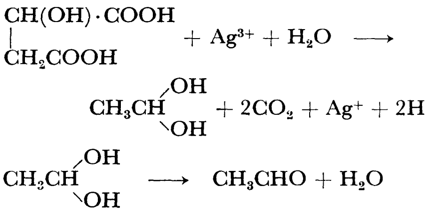
$$-\frac{d(S_2O_8{}^{2-})}{dt}=k(S_2O_8{}^{2-})\ (\text{malic acid})^{-0.3}\ (Ag^+)$$

which represents that velocity at any instant is largely proportional to the peroxydisulphate concentration.

Since the rate of reactions catalysed by silver ions are very much independent of the reductant concentrations, it has been suggested[8] that these reactions have a common rate determining step

$$Ag^+ + S_2O_8{}^{2-} \longrightarrow Ag^{3+} + 2SO_4{}^{2-} \qquad (1)$$

If we take this reaction as a rate determining step, then Ag^{3+} formed reacts with malic acid:



$$\begin{array}{l}CH(OH)\cdot COOH\\ |\\ CH_2COOH\end{array} + Ag^{3+} + H_2O \longrightarrow$$

$$CH_3CH\begin{array}{l}\diagup OH\\ \diagdown OH\end{array} + 2CO_2 + Ag^+ + 2H^+ \qquad (2)$$

$$CH_3CH\begin{array}{l}\diagup OH\\ \diagdown OH\end{array} \longrightarrow CH_3CHO + H_2O \qquad (3)$$

The presence of acetaldehyde in the reaction mixture after completion of the reaction has been confirmed by the spot test method.[9]

It has also been observed that the rate of reaction decreases with an increase in the concentration of malic acid. Decrease in the rate might be due to the complex formation between Ag^{3+} ion and malic acid. If this is the case, part of the trivalent silver will be used to form complex compound and thus the concentration of silver will be reduced in the reaction mixture. Since the rate is linearly related to the catalyst concentration, a decrease in the rate constant is observed with increasing concentration of malic acid

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[8] D. A. House, *Chem. Rev.*, **62**, 185 (1962).

[9] F. Feigle, "Spot Test in Organic Analysis," Elsevier Publishing Company, New York (1956) p. 208.