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Kinetics of Silver(I) Ion Catalysed Oxidation of Glycine by Peroxodisulphate Ion

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The kinetics of Ag(I) ion catalysed oxidation of glycine by peroxodisulphate in aqueous medium has been studied. The reaction is found to be first order in peroxodisulphate and Ag(I) ions and almost independent of glycine concentration. The rate constant is found to decrease with the increase in the concentration of peroxodisulphate ion. Addition of neutral salts shows a retarding effect. A suitable mechanism has been proposed and a theoretical rate law has been derived to account for the results.

The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation-reduction potential for the reaction

$$2SO_4^{2-}\ (\text{aq.}) \longrightarrow S_2O_8^{2-}\ (\text{aq.}) + 2e^-$$

is estimated to be -2.01 V.[10] The reactions involving this ion are generally very slow in the absence of suitable catalysts.[2] The most thoroughly investigated catalyst is Ag(I) ion although reactions involving Cu(II) and Fe(III) ions also have been studied.[3]

Only a very few kinetic studies have been made so far on organic nitrogen compounds. The kinetics of oxidation of urea and acetamide[4] has been studied by Agarwal and Mushran. Ag(I) ion catalysed oxidation of formamide[5] by peroxodisulphate was also investigated by the above authors. Recently Bacon and his co-workers[6] studied certain aspects of Ag(I) ion oxidation of primary aliphatic amines and α-amino acids.

This paper deals with the kenetics of Ag(I) catalysed oxidation of glycine by peroxodisulphate. A mechanism has been proposed and a theoretical rate law has been derived to account for the kinetic data.

Experimental and Results

Potassium peroxodisulphate of G.R.E. Merck quality, glycine and silver nitrate A.R. B.D.H. quality were dissolved in redistilled water for preparing standard solutions. All other chemicals used were also of analytical grade. Potassium peroxodisulphate solution was always prepared fresh. The standard solutions were stored in Jena glass bottles and the same solutions were used throughout the course of investigation.

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[5] M. C. Agarwal and S.P. Mushran, *Chim. Anal.*, **50**, 310 (1968).

[6] a) R. G. R. Bacon and D. Stewart, *J. Chem. Soc., C*, **1966**, 1384. b) R. G. R. Bacon, W. J. W. Hanna, and D. Stewart, *ibid.*, **1966**, 1388.

Table 1
Glycine=0.01 M, $AgNO_3$=0.0005M, Temp.=35°C

Time in min	$K_2S_2O_8$=0.005M		$K_2S_2O_8$=0.01M		$K_2S_2O_8$=0.02M	
	$Na_2S_2O_3$ ml	$k/2.303\times10^3$ min^{-1}	$Na_2S_2O_3$ ml	$k/2.303\times10^3$ min^{-1}	$Na_2S_2O_3$ ml	$k/2.303\times10^3$ min^{-1}
0	5.00	—	5.00	—	10.00	—
10	3.89	10.91[a)]	3.90	10.79[a)]	9.06	4.29[a)]
20	3.16	9.97	3.56	7.38	8.42	3.74
30	2.51	9.97	3.05	7.16	7.68	3.82
40	2.01	9.89	2.61	7.06	7.00	3.87
50	1.60	9.90	2.16	7.29	6.41	3.86
60	1.29	9.81	1.80	7.04	6.09	3.59
70	1.04	9.74	1.67	6.80	5.67	3.52
80	0.84	9.68	1.42	6.83	5.18	3.57
90	0.63	9.98	1.21	6.85	4.78	3.56
	Average	9.87		7.05		3.68

a) neglected

All reactions were carried out in pyrex conical flasks coated outside with black japan. Calculated volumes of silver nitrate and glycine were taken in a reaction vessel and were put in a thermostat maintained at 35±0.1°C. To start the reaction the calculated quantities of potassium peroxodisulphate solution were added to the reaction flasks. The progress of the reaction was studied by estimating the remaining peroxodisulphate iodometrically by a slightly modified method of Bartlett and Cotman[7)] adopted by Saxena and Singhal.[8)] First order rate constants with respect to peroxodisulphate were calculated and the order with respect to glycine was obtained by changing the concentration of glycine keeping the concentrations of other reactants constant.

Effect of Peroxodisulphate Concentration. The results obtained at three different initial concentrations of $K_2S_2O_8$ on the oxidation of glycine are shown in Table 1. First order rate constants were calculated and found to be fairly constant.

The rate constants k calculated from the Table 1 for three different concentrations of $K_2S_2O_8$ *viz.* 0.005M, 0.01M, and 0.02M are 22.70×10^{-3}, 16.22×10^{-3}, and 8.49×10^{-3} min^{-1}, respectively.

It is evident that the reaction is first order in peroxodisulphate at all concentrations of peroxodisulphate. However, as the concentration of $K_2S_2O_8$ is increased, the value of the first order rate constant decreases due to the specific inhibitory effect of K^+ ion.[4,9)]

From the data shown in the last row of the 6th column of Table 1 it may be concluded that the equimolecular consumption of $S_2O_8^{2-}$ and glycine takes place. The stoichiometry can be given as

$$S_2O_8^{2-} + NH_2CH_2COO^- + H_2O \xrightarrow{Ag^+} CO_2 + HCHO + NH_3 + SO_4^{2-} + HSO_4^-$$

Effect of Changing Glycine Concentration. Results showing the effect of the change of initial concentrations of glycine on reaction rate are shown in Table 2.

Table 2
$K_2S_2O_8$=0.01M, $AgNO_3$=0.0005M, Temp.=35°C

Initial concentration of glycine (M)	Rate constant $k\times10^3$ min^{-1}
0.005	16.22
0.010	16.22
0.015	16.01
0.020	15.91
0.025	15.98

We see that the rate is uneffected by a chang in glycine concentration and that the reaction is zero order with respect to glycine concentration because the total order is one at equimolecular concentrations of the reactants.

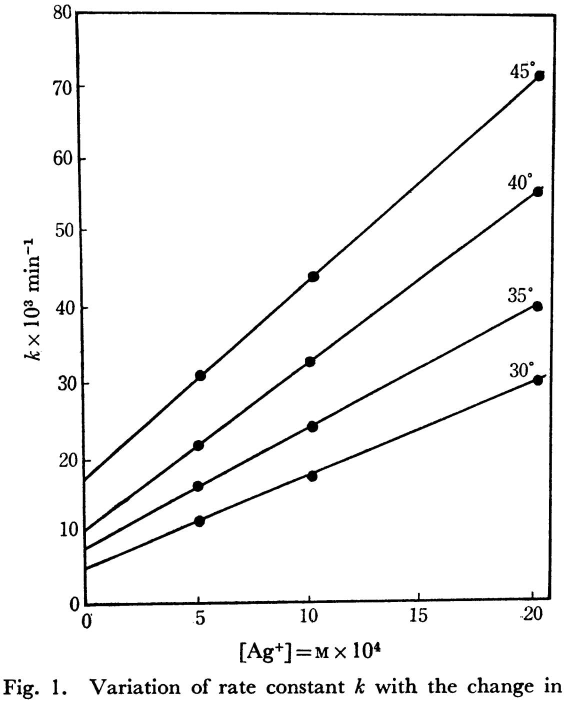

Fig. 1. Variation of rate constant k with the change in the concentration of Ag(I) ion at different temperatures. $K_2S_2O_8$=0.01 M Glycine=0.01 M

[7)] P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **71** 1419 (1949).

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Effect of Ag(I) Ion Concentration. The reaction is carried out with different initial concentrations of silver nitrate (the concentrations of other reactants are kept constant) to find the order of reaction with respect to silver ion. In order to show the catalytic activity a graph is plotted between the concentrations of silver ion and rate constants at different temperatures. The plots obtained are straight lines showing direct dependence of reaction rate on silver ion concentration (Fig. 1). As these strainght lines do not pass through origin, it is evident that the uncatalysed oxidation of glycine by peroxodisulphate is also possible. It has been observed that the reaction is slower in absence of Ag(I) ion.

The reaction has also been studied at various temperatures to obtain energy of activation, entropy of activation, frequency factor, *etc.* The results are given in Table 3.

TABLE 3

$K_2S_2O_8$=0.01M, Glycine=0.01M, $AgNO_3$=0.0005M

$k_{35}\times10^3$ min^{-1}	$k_{45}\times10^3$ min^{-1}	Temp. Coeff.	E kcal	A sec^{-1}	S e.u.
16.22	31.32	1.93	12.76	3.27×10^5	−33.45

The entropy of activation is negative. This can be explained on the basis of reaction sequence (5) of the proposed reaction scheme, where a water molecule is incorporated. This will decrease the entropy of activation.[10] A graph showing linear relationship between log k and $1/T$ has been plotted (Fig. 2).

Effect of Various Neutral Salts. The results of the addition of various neutral salts on the reaction rate are shown in Table 4.

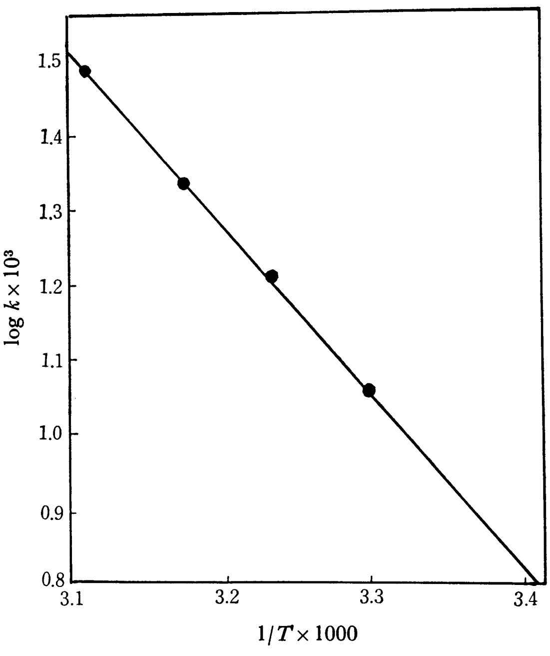

Fig. 2. Linear relationship between log k and $1/T$. $K_2S_2O_8$=0.01M, Glycine=0.01M, $AgNO_3$=0.0005M

TABLE 4

$K_2S_2O_8$=0.01M, Glycine=0.01M, $AgNO_3$=0.0005M, Temp.=35°C

Neutral salt	Concentration M×10^3	Ionic strength contributed $\mu\times10^3$	Rate constant $k\times10^3$ min^{-1}
NH_4NO_3	1.0	1.0	16.12
	2.0	2.0	16.01
	4.0	4.0	15.82
KNO_3	1.0	1.0	16.07
	2.0	2.0	15.92
	4.0	4.0	15.71
K_2SO_4	1.0	3.0	15.12
	2.0	6.0	14.75
	4.0	12.0	14.12
$Al(NO_3)_3$	1.0	6.0	15.53
	2.0	12.0	15.31
	4.0	24.0	14.89

This shows the retarding effect of some ions on the reaction rate of Ag(I) ion catalysed oxidation of glycine by peroxodisulphate. The rate constants in the presence of 4×10^{-3}M NH_4NO_3, K_2SO_4, and $Al(NO_3)_3$ are 15.82, 14.12, and 14.89×10^{-3} min^{-1}, respectively, and the ionic strength contributed by these salts are 4.0, 12.0, and $24.0\times10^{-3}\mu$, respectively. The decrease in the rate constant is not strictly related to the increase in ionic strength and evidently there is a considerable specific effect of the ions. Similar observations have been obtained by Levitt and Malinowski,[11] and Bartlett and Cotman.[7]

Discussion

Peroxodisulphate oxidation of some organic and inorganic compounds has been reported.[12] It was suggested by Bartlett and Cotman that the initial step in peroxodisulphate oxidation is the formation of two sulphate free radical ions as follows:

$$S_2O_8^{2-} = 2SO_4^-$$

The decomposition may be initiated by dust or impurities present in the solution.

The catalytic activity of silver(I) ion is due to the formation of higher valent silver species. In the case of peroxodisulphate oxidation of oxalate ion catalysed by Ag(I) Allen and Kalb[13] have proposed the formation of bivalent silver. In silver catalysed oxidation of several organic compounds the active species is trivalent silver.[14] However, single electron change in oxidation state of silver ion as catalyst is known.[15,16]

There is a first order dependence of reaction rates with respect to both silver(I) ion and peroxodisulphate concentrations and zero order dependence on glycine. Thus the rate determining step seems to be bimolecular

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but gives first order rate constant at constant Ag(I) concentration. The following scheme has been proposed.

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k_1} Ag^{2+} + SO_4^- + SO_4^{2-} \qquad (1)$$

The sulphate free radical further reacts with silver ion to produce higher valent silver[17] as follows:

$$SO_4^- + Ag^+ \xrightarrow{k_2} Ag^{2+} + SO_4^{2-} \qquad (2)$$

The bivalent silver reacts with glycine and regenerates Ag(I)

$$Ag^{2+} + NH_2CH_2COO^- \xrightarrow{k_3} Ag^+ + NH_2CH_2COO\cdot \qquad (3)$$

Like similar radicals[18] $NH_2CH_2COO\cdot$ also decomposes and evolves carbon dioxide

$$NH_2CH_2COO\cdot \xrightarrow{k_4} NH_2\dot{C}H_2 + CO_2 \qquad (4)$$

followed by

$$NH_2\dot{C}H_2 + H_2O \xrightarrow{k_5} NH_3 + CH_2O + H\cdot \qquad (5)$$

Hydrogen free atom reacts with $S_2O_8^{2-}$ as follows:

$$S_2O_8^{2-} + H\cdot \xrightarrow{k_6} HSO_4^- + SO_4^- \qquad (6)$$

The chain terminating step may be

$$SO_4^- + H\cdot \xrightarrow{k_7} HSO_4^- \qquad (7)$$

From the foregoing mechanism the rate law is given by equation

$$-\frac{d}{dt}[S_2O_8^{2-}] = k_1[S_2O_8^{2-}][Ag^+] + k_6[H\cdot][S_2O_8^{2-}] \qquad (8)$$

Applying the steady state to Eqs. (1)—(7) the following equation can be derived:

$$[H\cdot] = (k_1k_2/k_6k_7)^{1/2}[Ag^+] \qquad (9)$$

Substituting this value of $[H\cdot]$ into Eq. (8) we obtain the final rate expression:

$$-\frac{d}{dt}[S_2O_8^{2-}] = \{k_1 + (k_1k_2/k_6k_7)^{1/2}\cdot k_6\}[Ag^+][S_2O_8^{2-}] \qquad (10)$$

which is a satisfactory representation of the kinetic rate law, for it explains the observed first order kinetics of peroxodisulphate and zero order dependence on glycine concentration. It is also evident that there is a linear relationship between silver ion concentration and reaction rate when the concentrations of other reactants are kept constant.

Reaction sequence (6) is also supported by the observed increase in the reaction rate caused by the addition of reductant (glycine). Furthermore, the reaction rate is also increased by 20% in N_2 medium. This difference in reaction rate may be explained on the basis of the formation of peroxo radical in presence of air[19] as follows:

$$H\cdot + O_2 = HO_2$$

In this case Eqs. (6) and (7) take the following forms, and k_6' and k_7' will be different from k_6 and k_7.

$$S_2O_8^{2-} + HO_2 \xrightarrow{k_6'} SO_4^- + HSO_4^- + O_2$$

$$SO_4^- + HO_2 \xrightarrow{k_7'} HSO_4^- + O_2$$

Deamination is characteristic of amino acids. Kovats[20] has oxidatively deaminated glycine in the presence of KOH and Cu, the oxidant being KIO_4. The kinetics of reaction between glycine and $KMnO_4$ has been investigated by Pokrovskya.[21] The products were NH_3 and HCN. However, in the present investigation the evolution of CO_2 indicates the degradation of glycine. Identification of formaldehyde was not successful probably because of the reaction with NH_3. However, in the presence of NaOH, formaldehyde has been identified by preparing 2,4-dinitrophenyl hydrazone and determining its melting point.

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