Steps (1) and (2) of Scheme 1 have been proposed by a large number of workers[7-12] and the hydrogen abstraction from the organic substrate to yield the radical is considered to be the next possible step[13]. The formation of bivalent silver ion in peroxydisulphate redox processes has been shown by McMillan and Smaller[14] and the existence of SO_4^{-} and ·OH in the peroxydisulphate redox reactions have recently been proved by the ESR studies[15].

It can safely be assumed that the next stage, namely the oxidation of hydroxyaldehyde to the corresponding hydroxy acid, follows a similar mechanism.

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References

1. Menghani, G. D. & Bakore, G. V., *Curr. Sci.*, **37** (1968), 641.
2. Szabo, Z. G., Csanyi, L. & Galiba, H., *Z. anal. Chem.*, **135** (1952), 269.
3. Khulbe, K. C. & Srivastava, S. P., *Agra Univ. J. Res.* (*Sci.*), **9** (1960), 177; **14** (1965), 85.
4. Vogel, Arthur I., *Textbook of practical organic chemistry* (ELBS & Longmans, London), 1957, 1061.
5. Das, K. G. & James, E. P., *Organic mass spectrometry* (Oxford & IBH Publishers, New Delhi), 1976, 100.
6. Friedel, R. A., Shultz, J. L. & Sharkey, A. G., *Analyt. Chem.*, **28** (1956), 926.
7. Srivastava, S. P. & Ghosh, S., *Proc. natn. Acad. Sci.* (*India*), **22A** (1953), 91; **23A** (1954), 44.
8. Bawn, C. E. H. & Margerison, D., *Trans. Faraday Soc.*, **51** (1955), 925.
9. Bhakuni, R. S. & Srivastava, S. P., *Z. phys. Chem.*, **210** (1959), 246.
10. Khulbe, C. P. & Srivastava, S. P., *Agra Univ. J. Res.* (*Sci.*), **15** (1966), 27.
11. Khan, M. M. & Srivastava, S. P., *J. Indian chem. Soc.*, **46** (1969), 574.
12. Srivastava, S. P. & Singhal, S. K., *J. Indian chem. Soc.*, **46** (1969), 705.
13. Srivastava, S. P., Singh, Hambir & Kumar, Anil, *J. Indian chem. Soc.*, **52** (1975), 404.
14. McMillan, J. A. & Smaller, B., *J. chem. Phys.*, **35** (1961), 1698.
15. Chawla, Om P. & Richard, W. Fessenden, *J. phys. Chem.*, **79** (1975), 2693.

Kinetics & Mechanism of Ag^{+}–catalysed Oxidation of Dicarboxylic Acids by Potassium Peroxydisulphate

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Kinetics of oxidation of saturated dicarboxylic acids by potassium peroxydisulphate catalysed by Ag^{+} is reported under varying acidities, [substrate] and [Ag^{+}]. The results indicate that these oxidations are first order in [oxidant] and [Ag^{+}] but show zero order dependence on the [substrate]. Catalytic influence of Cu^{2+} and Hg^{2+} in H_2SO_4, $HClO_4$ and HCl media have also been investigated. A mechanism and rate law consistent with the results obtained is postulated.

THE kinetics of peroxydisulphate oxidations, both Ag^{+} catalysed[1-6] and uncatalysed[7], of a large number of organic substrates including dicarboxylic acids have been reported. We have recently reported the oxidation of saturated dicarboxylic acids by Ce^{4+} catalysed by Ag^{+} (ref. 8). In continuation of this work, the kinetics of Ag^{+}-catalysed oxidation of succinic, adipic, pimelic, suberic and sebacic acids by peroxydisulphate under varying conditions are reported in this note.

Standard solution of recrystallized potassium peroxydisulphate was always prepared fresh and standardized by iodometric method. Standard solutions of recrystallized dicarboxylic acids (AR) were prepared by direct weighing. The reaction was carried out by running a calculated volume of $K_2S_2O_8$ solution into the thermostated ($\pm 0{\cdot}1°$) reaction vessel containing the substrate and estimating the unreacted $K_2S_2O_8$ by the iodometric method. The decomposition of peroxydisulphate was followed separately and necessary corrections have been made in computing the rate constants. The rate constants have been computed by the usual tangential method.

The reactions are first order in peroxydisulphate as seen by the linear plots of log $(a-x)$ versus time. The reactions are independent of the nature of the substrate and [substrate], indicating zero order dependence on the substrate (Tables 1 and 2). Though there appears to be very slight deviation in rate constants with increasing [substrate] the order with respect to substrate comes to be 0·08 which can be taken as zero order.

For a threefold increase in the [acid] there is a slight decrease in the rate (Table 1) which may be due to the increase in ionic strength. Such slight decrease was observed earlier by Gupta and Sengar[9] in the reaction between persulphate and silver ion. Surprisingly the reactions are accelerated at *p*H 4·5 (Table 2). Further in the absence of Ag^{+}, the reactions in H_2SO_4 medium are very sluggish, whereas the uncatalysed reactions in the presence of HCl proceed fairly well and first order rate constants are reported in Table 3. Even in HCl medium and in the absence of catalyst the reactions are zero order with respect to the [substrate].

An increase in [Ag^{+}] increases the rate and a plot of log k vs log [Ag^{+}] is linear with unit slope establishing the order as unity with respect to [Ag^{+}]. It was thought worth while to study the catalytic effect of Cu^{2+} and Hg^{2+}. Surprisingly there was no reaction in presence of Cu^{2+} and Hg^{2+} in H_2SO_4 or $HClO_4$ media. But in HCl medium though there is no positive catalytic effect due to Hg^{2+} and Cu^{2+} the reactions are facile as compared to H_2SO_4 and $HClO_4$ media. Further, there is no dramatic catalysis in presence of Ag^{+} in $HClO_4$ medium as in the Ce^{4+} oxidations of saturated dicarboxylic acids in $HClO_4$ medium reported earlier.

Mechanism — Present evidences in literature point to the fact that in aqueous acid solutions it is more likely that Ag^{2+} ions exist rather than Ag^{3+} ions. Allen and his associates have shown that the equilibrium $2Ag^{2+} \rightleftharpoons Ag^{+}+Ag^{3+}$ lies far to the left. The fraction of Ag^{3+} (likely to exist as AgO^{+} in solution) has been estimated to be 0·03% of Ag^{2+}. Further, Yost has shown that Ag^{3+} may be formed by a direct interaction of Ag^{+} and $S_2O_8^{2-}$ followed by a rapid reaction of Ag^{3+} with water

TABLE 1 — EFFECT OF VARYING [SUBSTRATE], [ACIDITY] AND $[Ag^+]$ ON THE RATE CONSTANT

[Peroxydisulphate conc. = 0·004*M*; temp. = 50°]

[Substrate] *M*	$[H^+]$ *M*	$[Ag^+]$ *M*	$k \times 10^4$ min^{-1}
SUCCINIC ACID			
0·05	0·5	0·001	14·03
0·10	0·5	0·001	15·75
0·15	0·5	0·001	14·78
0·20	0·5	0·001	14·33
0·05	0·5	0·00075	8·72
0·05	0·5	0·0015	18·61
0·05	0·5	0·002	23·62
0·05	1·0	0·001	10·59
0·05	1·5	0·001	11·45
ADIPIC ACID			
0·015	0·5	0·001	13·01
0·025	0·5	0·001	13·23
0·035	0·5	0·001	13·96
0·05	0·5	0·001	13·71
0·05	0·5	0·00075	10·13
0·05	0·5	0·0015	16·69
0·05	0·5	0·002	21·94
0·05	0·25	0·001	13·96
0·05	1·0	0·001	11·81
0·05	1·5	0·001	11·29
PIMELIC ACID			
0·005	0·5	0·001	11·63
0·005	0·5	0·0015	17·45
0·005	0·5	0·002	21·32
0·005	0·25	0·001	14·77
0·005	1·0	0·001	13·01
0·005	1·5	0·001	12·59
SUBERIC ACID			
0·005	0·5	0·001	12·79
0·005	0·5	0·0015	17·06
0·005	0·5	0·002	22·58
0·005	1·0	0·001	13·23
0·005	1·5	0·001	13·01
0·0025	0·5	0·001	11·46
SEBACIC ACID			
0·001	0·5	0·001	10·66
0·001	0·5	0·0015	14·77
0·001	0·5	0·002	19·68
0·001	1·0	0·001	9·48
0·001	1·5	0·001	10·10

TABLE 2 — FIRST ORDER RATE CONSTANTS IN THE CATALYSED OXIDATION OF DICARBOXYLIC ACIDS STUDIED

{Substrate = 0·001*M*; $S_2O_8^{2-}$ = 0·005*M*; H_2SO_4 = 0·5*M*; $[Ag^+]$ = 0·001*M*; temp. = 50°}

Substrate	$k \times 10^4$ min^{-1} (H_2SO_4 = 0·5*M*)	$k \times 10^4$ min^{-1} (*p*H 4·5)
Succinic acid	10·96	31·99
Adipic acid	10·38	26·47
Pimelic acid	11·13	22·75
Suberic acid	10·81	22·75
Sebacic acid	10·66	25·60

TABLE 3 — RATE CONSTANTS IN THE UNCATALYSED OXIDATIONS OF DICARBOXYLIC ACIDS IN HCl MEDIUM

[Peroxydisulphate = 0·005*M*; HCl = 0·5*M*; temp. = 50°]

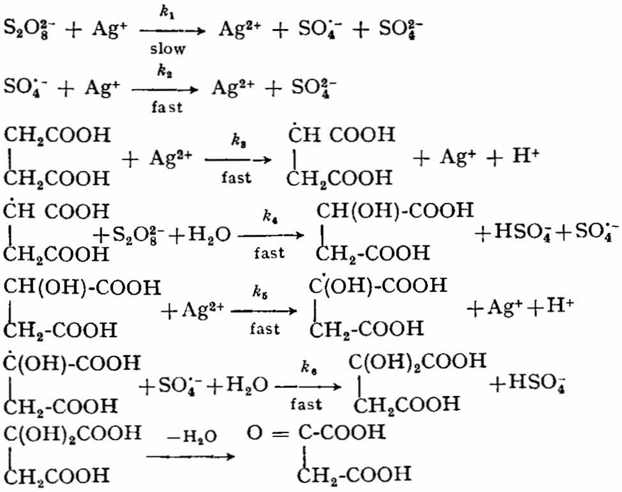
Substrate	Conc.	$k \times 10^4$ min^{-1}
Succinic acid	0·05	4·07
Adipic acid	0·05	5·61
Pimelic acid	0·001	5·05
Suberic acid	0·001	5·05
Sebacic acid	0·001	5·25

to give OH radicals and Ag^{2+} ions formed in equilibrium (1) may also react with water to give hydroxyl radical (Eq. 2).

$$Ag^{3+} + H_2O \longrightarrow Ag^{2+} + OH^{\cdot} + H^+ \qquad \ldots(1)$$

$$Ag^{2+} + H_2O \longrightarrow Ag^{+} + OH^{\cdot} + H^+ \qquad \ldots(2)$$

Although it is difficult to decide conclusively about the nature of the silver species, the observed kinetic picture is indicative of a free radical mechanism proceeding via Ag^{2+} ion. The peroxydisulphate reacts with Ag^+ in a rate limiting step to produce Ag^{2+}, $SO_4^{\cdot-}$ and SO_4^{2-} as shown in Scheme 1.



$$S_2O_8^{2-} + Ag^+ \xrightarrow[\text{slow}]{k_1} Ag^{2+} + SO_4^{\cdot-} + SO_4^{2-}$$

$$SO_4^{\cdot-} + Ag^+ \xrightarrow[\text{fast}]{k_2} Ag^{2+} + SO_4^{2-}$$

$$\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array} + Ag^{2+} \xrightarrow[\text{fast}]{k_3} \begin{array}{l}\dot{C}H\ COOH\\ |\\ CH_2COOH\end{array} + Ag^+ + H^+$$

$$\begin{array}{l}\dot{C}H\ COOH\\ |\\ CH_2COOH\end{array} + S_2O_8^{2-} + H_2O \xrightarrow[\text{fast}]{k_4} \begin{array}{l}CH(OH)\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{array} + HSO_4^- + SO_4^{\cdot-}$$

$$\begin{array}{l}CH(OH)\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{array} + Ag^{2+} \xrightarrow[\text{fast}]{k_5} \begin{array}{l}\dot{C}(OH)\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{array} + Ag^+ + H^+$$

$$\begin{array}{l}\dot{C}(OH)\text{-}COOH\\ |\\ CH_2\text{-}COOH\end{array} + SO_4^{\cdot-} + H_2O \xrightarrow[\text{fast}]{k_6} \begin{array}{l}C(OH)_2COOH\\ |\\ CH_2COOH\end{array} + HSO_4^-$$

$$\begin{array}{l}C(OH)_2COOH\\ |\\ CH_2COOH\end{array} \xrightarrow{-H_2O} \begin{array}{l}O = C\text{-}COOH\\ \quad |\\ \quad CH_2\text{-}COOH\end{array}$$

Scheme 1

Thus the rate of disappearance of peroxydisulphate may be given by Eq. (3)

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}][Ag^+] + k_4\begin{bmatrix}\dot{C}H-COOH\\ |\\ CH_2COOH\end{bmatrix}[S_2O_8^{2-}] \qquad \ldots(3)$$

Considering the steady state conditions,

$$\begin{bmatrix}\dot{C}H-COOH\\ |\\ CH_2COOH\end{bmatrix} = \left(\frac{k_1k_2}{k_4k_6}\right)^{\frac{1}{2}}[Ag^+]$$

and substituting the value of $\begin{bmatrix}\dot{C}H-COOH\\ |\\ CH_2COOH\end{bmatrix}$ in Eq. (3), we get

$$-\frac{d[S_2O_8^{2-}]}{dt} = K_r\,(S_2O_8^{2-})[Ag^+] \qquad \ldots(4)$$

where $K_r = \{k_1 + k_4(k_1k_2/k_4k_6)\}^{\frac{1}{2}}$.

The rate expression (4) is in accordance with the experimental observations.

References

1. House, D. A., *Chem. Rev.*, **62** (1962), 185.
2. Wilmarth, W. H. & Harim, A., *Mechanism of oxidation by peroxydisulphate ions in peroxide reaction mechanism*, edited by J. O. Edwards (John Wiley, New York), 1962, 175.
3. Sabesan, A. & Venkatasubramanian, N., *Indian J. Chem.*, **9** (1971), 942.
4. Sabesan, A. & Venkatasubramanian, N., *Indian J. Chem.*, **8** (1970), 251.
5. Srivastava, S. P., Maheswari, G. L. & Singhal, S. K., *J. Indian chem. Soc.*, **49** (1972), 235.
6. Srivastava, S. P. & Singhal, S. K., *J. Indian chem. Soc.*, **46** (1969), 705.
7. Santappa, M. & Padma, S., *Proc. Indian Acad. Sci.*, (1969), 7.
8. Radhakrishna Murti, P. S. & Swamy, B. R. K., *Indian J. Chem.*, (in press).
9. Gupta, Y. K. & Sengar, H. G. S., *J. Indian chem. Soc.*, **44** (1967), 769.

Kinetics & Mechanism of Ag^+-catalysed Oxidation of Glyoxal & Glyoxalic Acid by Peroxydisulphate in Aqueous Medium

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Silver(I) ion-catalysed peroxydisulphate oxidations of glyoxal and glyoxalic acid follow first order kinetics with respect to peroxydisulphate and zero order with respect to each substrate. A direct proportionality of the reaction velocity on $[Ag^+]$ is observed. The addition of some inorganic salts decreases the reaction rate. On the basis of the results, a probable mechanism has been proposed.

THE kinetics of Ag^+-catalysed peroxydisulphate oxidations of several organic substrates have been extensively investigated[1-9]. The kinetic results pertaining to the Ag(I)-catalysed oxidation of glyoxal and glyoxalic acid by peroxydisulphate, hitherto not reported, are presented in this note and a mechanism for the oxidation reaction has been proposed.

All the chemicals except glyoxal (40% solution, Riedel) were of either AR (BDH) or GR (E. Merck) grade. Their solutions were prepared in redistilled water. The stock solution of peroxydisulphate was always prepared fresh.

The kinetics was followed[10] by estimating the amount of unconsumed peroxydisulphate at definite intervals of time iodometrically[11]. Self-decomposition of peroxydisulphate in the presence of silver(I) ion and absence of the substrate has also been observed.

The reaction is first order with respect to [peroxydisulphate] (Table 1). In Table 1 k_a represents first order velocity constant, k_d gives the first order velocity constant for the decomposition of peroxydisulphate itself and $k = (k_a - k_d)$ represents the velocity constant for the oxidation process. The first order velocity constants were calculated from the slope of the plots made between logarithm of the volume of thiosulphate solution consumed (which is proportional to the concentration of $S_2O_8^{2-}$) and time.

A close examination of the data in Table 2 clearly substantiates the direct proportionality of the reaction rate on [Ag(I)]. The rate constant is independent of the concentrations of glyoxal and glyoxalic acid (Table 3).

The kinetic study has also been performed at different temperatures and the energy of activation (E_a) for the oxidation of glyoxal (14·6 kcal mole^{-1}) and glyoxalic acid (12·3 kcal mole^{-1}) have also been calculated from the slope of the Arrhenius plot.

The addition of inorganic salts such as KNO_3 and K_2SO_4 into the reaction vessel decreases the rate of reaction (negative salt effect).

Mechanism — Thus on the basis of the observed kinetic results, the rate law (1) is suggested for the

Table 1 — Effect of Varying the Concentration of Peroxydisulphate in the Ag(I)-catalysed Oxidation of Glyoxal and Glyoxalic Acid

$[S_2O_8^{2-}] \times 10^2$ M	$k_a \times 10^2$ min^{-1}	$k_d \times 10^3$ min^{-1}	$k \times 10^2$ min^{-1}
[GA] = 0·048M; $[Ag^+]$ = 1·0×10^{-3}M; temp. = 35° ± 0·1°			
0·50	4·61	1·33	4·48
0·75	3·76	1·28	3·63
1·00	4·35	1·21	4·23
1·50	4·08	1·07	3·97
2·00	4·30	0·97	4·20
[G] = 0·03M; $[Ag^+]$ = 1·0×10^{-3}M; temp. = 35° ± 0·1°			
0·50	3·21	1·33	3·08
0·70	2·93	1·28	2·80
1·00	3·06	1·21	2·94
1·50	3·02	1·07	2·91
2·00	2·88	0·97	2·78

GA = glyoxalic acid; and G = glyoxal.

Table 2 — Effect of Varying $[Ag^+]$ on the Rate Constant for the Oxidation of Glyoxal and Glyoxalic Acid by Peroxydisulphate

{$[S_2O_8^{2-}]$ = 0·01M; temp. = 35° ± 0·1°}

$[Ag^+] \times 10^3$ M	$k_a \times 10^2$ min^{-1}	$k_d \times 10^3$ min^{-1}	$k \times 10^2$ min^{-1}	$k/[Ag^+]$ M^{-1} min^{-1}
[GA] = 0·048M				
0·25	1·42	0·32	1·39	5·55
0·50	2·28	0·67	2·21	4·43
0·75	2·98	0·92	2·89	3·85
1·00	4·35	1·21	4·23	4·23
1·50	6·35	1·82	6·17	4·11
[G] = 0·03M				
0·50	2·19	0·67	2·12	4·25
1·00	3·06	1·21	2·94	2·94
1·25	3·68	1·54	3·53	2·82
1·50	4·67	1·82	4·49	2·99
1·75	5·30	2·16	5·08	2·90
2·00	5·76	2·57	5·50	2·75

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