

Fig. 3. Variation of the distribution ratio for Zn(II), Cd(II) and Hg(II) tracers in 0.1 M oxalate solution as a function of amine concentration in chloroform. Graphs: A, Zn(II); B, Cd(II); C, Hg(II). Curves: 1, Aliquat 336; 2, Primene JM-T.

Acknowledgements—The financial assistance of University Grants Commission, New Delhi (India) is gratefully acknowledged. We also thank Rohm and Haas Co (U.S.A.) and General Mills Inc. (U.S.A.) for supplying research quantities of the amines as gifts.

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REFERENCES

1. C. F. Coleman, C. A. Blake, Jr. and K. B. Brown, *Talanta* 9, 297 (1962).
2. H. Green, *Talanta* 11, 1561 (1964).
3. H. Green, *Talanta* 20, 139 (1973).
4. S. E. Bryan and M. L. Good, *J. Inorg. Nucl. Chem.* 21, 339 (1961).
5. J. M. Singh and S. N. Tandon, Unpublished work.

Kinetics and mechanism of Cu(II) catalysed oxidation of malic acid by the peroxydisulphate ion

(Received 25 May 1978; received for publication 10 November 1979)

Catalysis by copper (II) in peroxydisulphate oxidation has been reported for many systems[1-12]. Insufficient kinetic data do not provide evidence for the mechanism of the catalytic action[13]. Kinetics of Cu(II) catalysed oxidation of malic acid by the peroxydisulphate ion have been studied in order to elucidate the catalytic role of Cu(II).

EXPERIMENTAL

All chemicals used were either BDH "AnalaR" or E. Merck G.R. samples and reactants solutions were prepared in double-distilled water. Kinetics were followed by estimating residual peroxydisulphate iodometrically at different intervals of time[14].

The $S_2O_8^{2-}$ equivalents of Cu(II) concentration ($\geq 5 \times 10^{-4}$ M) in terms of titre volume (of 0.04 N) have been subtracted from the observed titre volume to obtain $(a-x)$. (At lower Cu(II) concentrations it was not necessary). Table 1 shows how the first order rate constants (k_1) were calculated; data reported in different tables were similarly evaluated.

RESULTS

Stoichiometry. One molecule of malic acid reacts with two molecules of peroxydisulphate.

The rate law. Table 1 gives the results of the kinetic run at 60°C.

The first order rate constant value increases with time for an initial period of 900-3600 sec, whereafter a fair constancy is obtained. The later slight increase is due to further consumption of $S_2O_8^{2-}$ by the reaction product which proceeds slowly. The concentration time curve (Fig. 1) is somewhat "S" shaped, typical of autocatalytic reactions. Such kinetic features are reproduced at other reactant concentrations. To explain this disturbed autocatalytic nature of the first order constant it is presumed that the reaction starts as an uncatalysed one and that after a period a catalysed reaction starts; after about an hour both reactions occur simultaneously. This view is supported by results obtained with uncatalysed oxidation under identical conditions. The value of first order rate constant for the uncatalysed reaction was

Table 1. (Malic acid)₀ = (K₂S₂O₈)₀ = 0.02 M, (CuSO₄)₀ = 0.0005 M, Temp. 60°C

Time (sec)	Vol. of 0.04 N Na ₂ S ₂ O ₃	(a - x)	(S ₂ O ₈ ²⁻) _t mole/l	10 ⁴ k (sec ⁻¹)
0	5.06	5.00	0.0200	—
900	4.89	4.83	0.0193	0.4
1800	4.51	4.45	0.0178	0.7
2700	4.02	3.96	0.0158	0.9
3600	3.54	3.48	0.139	1.0*
4500	3.12	3.06	0.0122	1.1
5400	2.78	2.72	0.0109	1.1
7200	2.24	2.18	0.0087	1.2
9000	1.80	1.74	0.0070	1.2
10800	1.40	1.34	0.0054	1.2
12600	1.12	1.06	0.0042	1.2
14400	0.90	0.84	0.0034	1.2
Average value				1.2
Slope value				1.1

*Mean calculated hereafter.

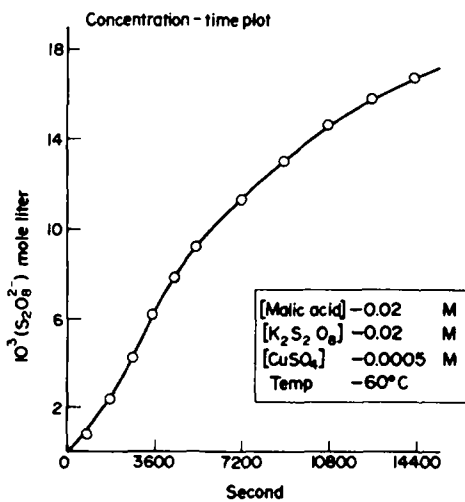


Fig. 1.

$0.5 \times 10^{-4} \text{ sec}^{-1}$, in good agreement with the value $0.4 \times 10^{-4} \text{ sec}^{-1}$ obtained at the initial stage of the catalysed reaction.

The pH changes quasi-linearly during the reaction as shown in Table 2.

Table 2. Variation of pH during the course of the reaction conditions same as Table 1

Time (sec)	0	600	1200	1800	2700	3600	5400	7200
pH	2.6	2.5	2.4	2.2	2.1	2.0	1.7	1.8

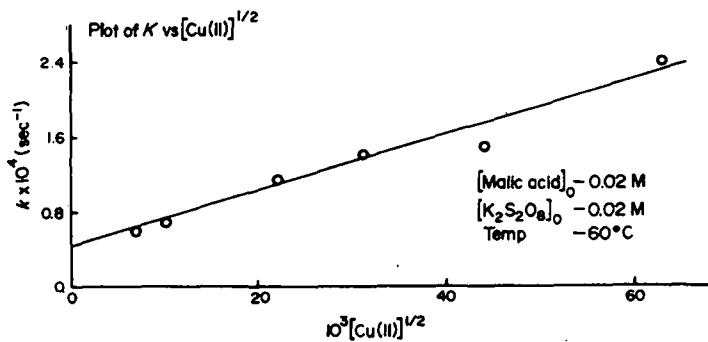


Fig. 2.

Peroxydisulphate dependence. Table 3 includes the results of runs obtained with different initial concentrations of peroxydisulphate and constant malic acid and catalyst concentrations.

Table 3. (Malic acid)₀ = 0.02 M, (CuSO₄)₀ = 0.0005 M. Temp. 60°C

(K ₂ S ₂ O ₈) M	0.005	0.01	0.015	0.02	0.03	0.04
10 ⁴ k (sec ⁻¹)	1.4	1.3	1.2	1.1	1.0	0.9

The slight decrease in the value of k with increase in S₂O₈²⁻ is due to the inhibition by K⁺ ions which is characteristic of most peroxydisulphate oxidations [15].

Malic acid dependence. Table 4 shows the results of the kinetic runs at 60°C, in which the concentration of peroxydisulphate was kept constant and the concentration of malic acid was varied over an eight-fold range (the catalyst concentration was fixed).

Table 4. (K₂S₂O₈)₀ = 0.02 M, (CuSO₄)₀ = 0.0005 M Temp. = 60°C

(Malic acid) ₀	0.005	0.01	0.015	0.02	0.03	0.04
10 ⁴ k (sec ⁻¹)	1.1	1.2	1.1	1.1	1.1	1.2

Copper (II) dependence. A plot of rate constant against [Cu(II)]^{1/2} (Fig. 2) gives a straight line not passing through origin, indicating again that the uncatalysed reaction occurs simultaneously with the catalysed reaction. The first order rate constants obtained experimentally are governed by the expression

$$k = 5 \times 10^{-5} + 2.5 \times 10^{-3} [\text{Cu(II)}]^{1/2}$$

at 60°C.

This expression supports the view that if the reaction starts by an uncatalysed pathway the second term is absent at the initial stage.

Temperature dependence. The effect of temperature on k is shown in Table 5.

Table 5. (K₂S₂O₈)₀ = (Malic acid)₀ = 0.02 M, (CuSO₄)₀ = 0.0005 M

Temp. (°C)	50	55	60	65
10 ⁴ k (sec ⁻¹)	0.3	0.7	1.1	2.0

The Arrhenius plot is linear and gives $k = 2.2 \times 10^{12} \exp(-25/RT) \text{ sec}^{-1}$. The entropy of activation is $0.3 \text{ cal deg}^{-1} \text{ mole}^{-1}$.

Influence of acids, salts and gases. The reaction is retarded by acids, K₂SO₄ and KCl while sodium acetate accelerates it; oxygen gas is observed to inhibit the reaction.

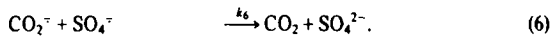
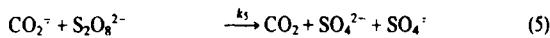
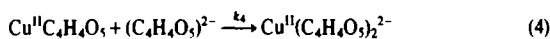
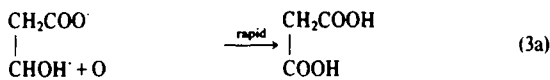
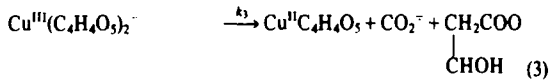
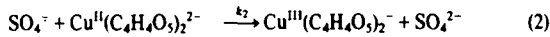
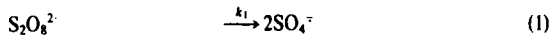
DISCUSSION

For the interpretation of the kinetic data any proposed mechanism must incorporate (a) the first order dependence on

peroxydisulphate (b) independence on malic acid and (c) linear dependence in $[\text{Cu(II)}]^{1/2}$.

It is therefore obvious that the rate determining step involves peroxydisulphate and not malic acid. Moreover, the formation of copper complexes now seems to be well founded [16-19].

Since a bimolecular reaction between oxidant and the catalyst is ruled out on kinetic grounds [20], a reasonable mechanism which accounts for the faster oxidation rate in the presence of Cu(II) ($k \text{ Cu(II)-cat}/k \text{ uncat}$ is 3.25) may involve:-



Reaction (2) is rate determining as it does not involve malate ion directly but in a complex state; this is in accordance with the view of Kovats[21]. The Cu(III) state is postulated in the mechanism, which is well established [22-26, 28]. Moreover, it is also reported that the metal ion after forming a complex with the organic substrate decays to produce the $\text{CO}_2^{\cdot-}$ radical [27-29].

Alternatively reactions (2) and (3) may be combined in a single concerted step. This change avoids a Cu(III) complex.

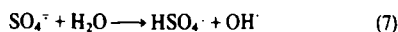
With the production of the $\text{CO}_2^{\cdot-}$ radical-ion the higher decomposition rate of $\text{S}_2\text{O}_8^{2-}$ is explained (reaction 6). That $\text{CO}_2^{\cdot-}$ is produced is evident from the fact that the system reduces Hg(II) chloride [27] and oxygen inhibits the reaction rate. Reaction with peroxydisulphate ion (step 5) regenerates $\text{SO}_4^{\cdot-}$. Thus $\text{CO}_2^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ act as chain carrier to control the mechanism of reduction of $\text{S}_2\text{O}_8^{2-}$. Step [6] is chain terminating.

With the limitations that step (3a) is instantaneous and $4K_2k_5(\text{Cu}^{\text{II}}(\text{C}_4\text{H}_4\text{O}_5)_2^{2-}) \gg k_1k_6$, the following rate expression is obtained:-

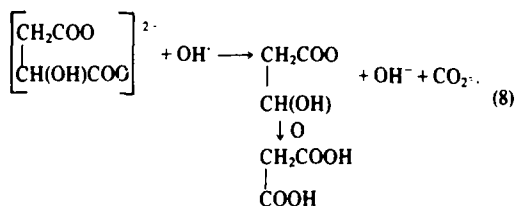
$$-d(\text{S}_2\text{O}_8^{2-})/dt = \frac{k_1k_2k_3}{k_6}(\text{S}_2\text{O}_8^{2-})(\text{Cu}^{\text{II}}(\text{C}_4\text{H}_4\text{O}_5)_2^{2-})^{1/2} \quad (A)$$

The derived rate law is first order in peroxydisulphate and shows a linear order dependence on $(\text{Cu}^{\text{II}}(\text{C}_4\text{H}_4\text{O}_5)_2^{2-})^{1/2}$ (which can be taken as representing Cu(II) concentration).

Experimental results suggest that an uncatalysed mechanism is also operative [12, 30]. In this mechanism $\text{SO}_4^{\cdot-}$ generate OH radicals as follows:



which react with uncomplexed malate ion to yield products in the following manner.



In this, steps (2) and (3) of the previous mechanism are replaced

by (7) and (8). These are much more likely than (2) and (3) because the concentrations of H_2O and malate ions are quite large in comparison to the Cu(II) malate complex. Therefore, it can be assumed that in the initial stages the reaction is uncatalysed.

Steady state treatment of this mechanism gives:-

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k_1(\text{S}_2\text{O}_8^{2-}) + k'k_5(\text{S}_2\text{O}_8^{2-}) \quad (B)$$

where $k' = k_{1/2} + (k_1^2/4 + 4k_1k_7k_5/k_6 \times (\text{H}_2\text{O}))^{1/2}/2k_5$.

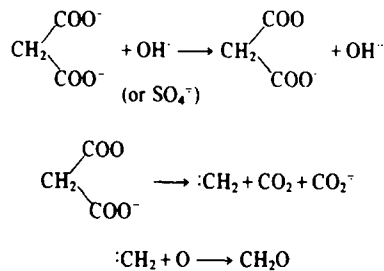
The first term of the right hand side is the thermal decomposition of peroxydisulphate which is quite small and, therefore, negligible. Thus the rate expression for the uncatalysed path reduces to,

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k'k_5(\text{S}_2\text{O}_8^{2-}) \quad (C)$$

since both (catalysed and uncatalysed) reactions later occur simultaneously, the overall rate of disappearance of peroxydisulphate can be given by the expression,

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k'k_5(\text{S}_2\text{O}_8^{2-}) + (k_1k_2k_3/k_6)^{1/2}(\text{S}_2\text{O}_8^{2-})(\text{Cu}^{\text{II}}(\text{C}_4\text{H}_4\text{O}_5)_2^{2-})^{1/2} \quad (D)$$

Product analysis. The main reaction product malonic acid was identified by spot tests [31]. However, C_1 -products (formaldehyde and formic acid) were also obtained in traces, which signifies the successive breakdown of malonic acid. Vasudeva and Wasif [32] reported the formation of C_1 products in the uncatalysed oxidation. It has been established that the breakdown of malonic acid is very slow and in the present investigation the percentage cleavage represents only 5% of the oxidation pathway. The steps accounting the formation of C_1 -products may be:



Acknowledgement—We are grateful to Dr. L.K. Saxena for his help.

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REFERENCES

1. L. B. Morgan, *Trans. Faraday Soc.* **42**, 169 (1946).
2. C. V. King and O. F. Steinback, *J. Am. Chem. Soc.* **52**, 4779 (1931).
3. E. Ben-Zvi and T. L. Allen, *J. Am. Chem. Soc.* **83**, 4352, 1961.
4. Y. K. Gupta and S. Ghosh, *J. Inorg. Nucl. Chem.* **11**, 62 (1959).
5. A. P. Bhargava, Y. K. Gupta and K. S. Gupta, *J. Inorg. Nucl. Chem.* **31**, 777 (1969).

6. A. P. Bhargava, R. Swaroop and Y. K. Gupta, *J. Chem. Soc.* 2183 (1970).
7. H. S. Samant and S. P. Srivastava, *Proc. Natl. Acad. Sci. (India)* 27, 282 (1958).
8. D. L. Ball, M. M. Crutchfield and J. O. Edwards, *J. Org. Chem.* 25, 1599 (1960).
9. J. O. Edwards and A. P. Gallopo, *J. Org. Chem.* 36, 4089 (1971).
10. A. G. Khachatryan, N. M. Beileryan and O. A. Chaltykyan, *Dobl. Akad. Nauk. Arm. S.S.P.* 54, 249 (1972).
11. K. Kumar and L. K. Saxena, *J. Inorg. Nucl. Chem.* 13, 2491 (1971).
12. S. C. Agarwal and L. K. Saxena, *Ind. J. Chem.* 16A, 602 (1978).
13. (i) W. K. Wilmoth and A. Haim, *Mechanism of Oxidation by Peroxodisulphate Ion (Peroxide Reaction Mechanism)* by J. O. Edwards, p. 175. Conference, Rhode Island (1960); (ii) D. A. House, *Chem. Rev.* 62, 105 (1962).
14. L. K. Saxena and C. P. Singhal, *Agra Univ. J. Res. (Sci)* 6, 43 (1957).
15. (a) G. Chandra and S. N. Srivastava, *J. Inorg. Nucl. Chem.* 34, 197 (1972). (b) R. L. Eagar and C. A. Winkler, *Can. J. Res.* 268, 527 (1948). (c) M. C. Agarwal & S. P. Mushran, *J. Ind. Chem. Soc.* 42, 629 (1965); *ibid.* 43, 343 (1966).
16. J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava and I. D. Smith, *J. Chem. Soc. (A)*, 94 (1969).
17. S. Ramamourty and M. Santappa, *J. Inorg. Nucl. Chem.* 30, 185 (1968).
18. Jean Zefebvre, *J. Chim. Phys.* 54, 581 (1957).
19. Jean Zefebvre and Pierre Souchay, *Compt. Rend* 243, 1416 (1956).
20. S. C. Agarwal and L. K. Saxena, *Agra Univ. J. Res. (Sci)* 23, 53 (1974).
21. Z. Kovats, *Magyar Kem Folyoirat* 66, 181 (1960).
22. Kimura Misaru, *J. Phys. Chem.* 77, 1265 (1973).
23. H. S. Samant and S. P. Srivastava, *Proc. Natl. Acad. Sci. (India)* 27, 282 (1958).
24. K. Kumar and L. K. Saxena, *J. Inorg. Nucl. Chem.* 33, 2491 (1971).
25. Monk, *Trans Faraday Soc.* 47, 297 (1951); *ibid.* 47, 285 (1951).
26. L. K. Saxena and C. P. Singhal, *J. Ind. Chem. Soc.* 31, 405 (1960); 38, 863 (1961); K. Kumar and L. K. Saxena, *J. Inorg. Nucl. Chem.* 31, 280 (1969); K. Kumar and L. K. Saxena, *Bull. Chem. Soc. Japan.* 42, 3148 (1969); K. Kumar and L. K. Saxena, *J. Ind. Chem. Soc.* 45, 669 (1969); K. P. Sarabhai and L. K. Saxena, *J. Inorg. Nucl. Chem.* 34, 2563 (1972).
27. T. L. Allen, *J. Am. Chem. Soc.* 73, 3589 (1951).
28. W. A. Waters, *Mechanism of Oxidation of Organic Compounds*, pp. 55-56 (1964).
29. W. C. Vasudeva, M. F. Taha and S. Wasif, *J. Inorg. Nucl. Chem.* 34, 3159 (1972), *Carb. Res.* 2, 175 (1966).
30. Fritz Eiegl, *Spot Tests in Organic Analysis*, 6th Edn (1960).
31. W. C. Vasudeva and Saad Wasif, *J. Inorg. Nucl. Chem.* 34, 3153 (1972).

Thallium isotope exchange in Tl_4Cl_6

(Received 30 August 1978; received for publication 14 November 1978)

In a recent paper Fernandez Valverde, Duplâtre and Maddock have described the exchange of ^{204}Tl between the $Tl(I)$ and $Tl(III)$ fractions in Tl_4Cl_6 [1]. A striking dependence of the extent and rate of exchange on the condition of the Tl_4Cl_6 was reported.

We have made similar observations on samples of this compound prepared and analyzed in a different way.

Inactive Tl_4Cl_6 was prepared by adding three equivalents of $TlCl$ to a solution of $TlCl_3$ in dilute nitric acid and boiling the mixture. The Tl_4Cl_6 was then recrystallized from 0.01 N HCl containing some ^{204}Tl .

The two thallium fractions were separated by treating the Tl_4Cl_6 with methanol for a number of hours. This dissolved the $TlCl_3$ together with a smaller part of the $TlCl$, leaving most of the

$TlCl$ as an insoluble residue. After washing with methanol the $TlCl$ was dried and its specific activity compared to that of the original Tl_4Cl_6 by measuring the mercury K-line.

A serious difficulty occurred in that we were unable to combine preparation and analysis in such a way as to give zero exchange for the unannealed samples. At 300°C the exchange process has reached equilibrium distribution within a few minutes. At 200°C the exchange does not seem to be the same for the samples A, C and D.

Two activations of inactive Tl_4Cl_6 were performed with fast neutrons. The activity distribution of the product of the $^{203}Tl(n, 2n) ^{202}Tl$ reaction was not very different from equilibrium distribution, 21.3 and 21.0% of the ^{202}Tl being found in the $(TlCl_6)^{3-}$ -ion.

Table 1. Annealing $^{204}Tl_3$ ($TlCl_6$) per cent activity in the $Tl(Cl_6)^{3-}$ -ion

Sample	A	B	C	C	D	D
Annealing temp.	200°	300°	100°	200°	200°	300°
Duration annealing unannealed	4	13.5	10.2 ± 0.3	10.2 ± 0.3	6.5 ± 0.3	6.5 ± 0.3
3 min					14.0 ± 1.6	24.0
10 min					11.1 ± 1.0	23.4
30 min					10.6 ± 1.5	23.5
2 hr				21.7		
3 hr		24.5	11.7 ± 1.7			
4 hr	12.5			18.6		
6 hr	13	23.0	13.8 ± 1.6	22.7		