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Anticatalytic Effect of Mn(II) in the Silver Catalyzed Oxidations by Peroxydisulphate

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Mn(II) has been found to be an anticatalyst in the silver catalyzed oxidations of oxalate, citrate, tartrate, malonate and arsenious acid and the limiting value of the rate constants in each case is about 0.4 *l*/mol·min at 35°C which is very much comparable to the rate constant for the separate silver catalyzed oxidation of Mn(II), H_2O, Ce(III), N_2H_4 and vanadyl ion. A mechanism has been proposed in which the simultaneous oxidation of Mn(II) and the organic substrate or arsenious acid takes place and when sufficiently large concentration of Mn(II) is present, the latter oxidation is almost completely suppressed. The oxidations of citrate and tartrate are consecutive reactions. The first faster reaction is followed by the second slower reaction.

Mn(II) has been reported to be an anticatalyst in the silver catalyzed oxidations of As(III)[1] and oxalate[2] by peroxydisulphate, but no mechanism to explain its action has been proposed so far. We have made a systematic relevant study in the oxidations of arsenious, malonic, oxalic, tartaric,

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[1] Y. K. Gupta and D. D. Mishra, This Bulletin, **32**, 1306 (1959).

[2] E. Ben-zvi and T. L. Allen, *J. Am. Chem. Soc.*, **83**, 4352 (1961).

citric, acetic and formic acids. The kinetics have been followed by estimating peroxydisulphate iodometrically by the method of Szabo, Csanyi and Galiba.³⁾ The detailed kinetic study of the oxidation of malonic, tartaric and citric acids has not been made in the past and nor we intend to report such results in the present paper. We have considered their oxidations only with reference to the effect of Mn(II).

Experimental

All chemicals used were either B. D. H. Analar or E. Merck G. R. quality. Manganous sulphate was used for Mn(II). Water used was doubly distilled in pyrex glass vessels. Potassium peroxydisulphate was freshly prepared by direct weighing and its concentration checked by any known method.

Calculated quantities of perchloric acid, substrate (arsenious, malonic, citric, tartaric, acetic, oxalic or formic acid), silver nitrate, manganous sulphate and water were taken in the reaction vessel placed in a thermostat at 35°C. Peroxydisulphate solution was separately thermostated. Calculated quantity of peroxydisulphate was then added to the reaction vessel to initiate the reaction. Total reaction mixture was 100 m*l*. After suitable intervals 5 m*l* of the reaction mixture was pipetted out and determined for peroxydisulphate.⁴⁾ For this aliquots were transferred to a beaker containing 2.5 m*l* of 60% KI (added in the last), 2.5 m*l* of conc. HCl, 5 m*l* of water and 1 m*l* of the catalyst. The catalyst was prepared by dissolving 2.59 g of ferrous ammonium sulphate and 9.52 g of copper sulphate in 500 m*l* of water. A drop or two of conc. H_2SO_4 was added to make the solution clear.

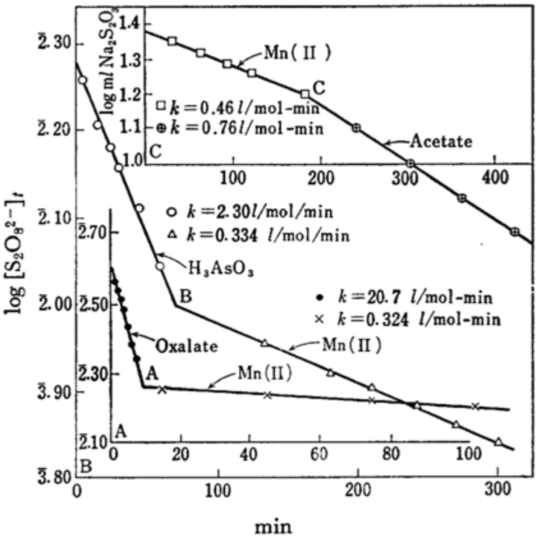

Fig. 1. First order plots showing the oxidation of Mn(II) only when that of oxalate or arsenious acid is complete, or before the oxidation of acetate starts.

A: $[S_2O_8^{2-}]=0.0199$ M; $[Na_2C_2O_4]=0.01$ M
B: $[S_2O_8^{2-}]=0.0093$ M; $[H_3AsO_3]=0.005$ M
C: $[S_2O_8^{2-}]=0.05$ M; $[CH_3COONa]=0.10$ M
$[HClO_4]=0.182$ M, $[Mn(II)]=0.01$ M, $[Ag^+]=0.005$ M

The liberated iodine was titrated against a standard solution of thiosulphate from a burette using starch as indicator. A blank was also run with the catalyst and all other reactants except the peroxydisulphate and this was subtracted from all observed readings of the burette.

The results of experiments referred to Fig. 1 were also obtained in a similar way. The fortunate circumstance is that in any run Mn(II) and the substrate are not oxidized simultaneously, at least apparently. In case of oxalate, citrate, tartarate, malonate, As(III), *etc.*, these are first oxidized and no Mn(III) or MnO_2 is seen or found in the system. Mn(III) or MnO_2 could be found only when the substrate was completely oxidized. In case of acetate Mn(II) is first oxidized to MnO_2, and when this is complete, only then acetate is oxidized. It was possible to make a check on this conclusion in case of acetate. MnO_2 formed was separated by centrifuging the reaction mixture, and the precipitate and the liquid were separately analyzed for MnO_2 and peroxydisulphate respectively iodometrically. It was found that the decrease in peroxydisulphate was exactly equal to MnO_2 formed and hence it was concluded that acetate was not oxidized till there was any Mn(II) in the system. In other cases (oxalic, citric acid, *etc.*) there appeared no MnO_2 in the system till there was any substrate. The reduction of peroxydisulphate, therefore, takes palce in two parts with two different rates as shown in Fig. 1.

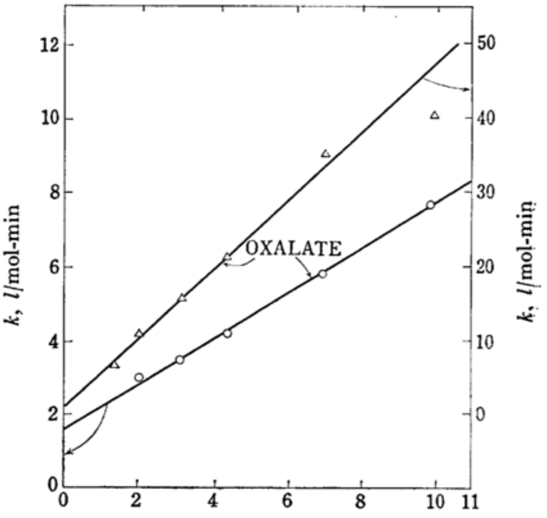

Fig. 2. Effect of manganous ion on the oxidation of oxalate by peroxydisulphate.
$[S_2O_8]=0.02$ M;
○: [oxalate]=0.10 M, $[AgNO_3]=0.0005$ M $[HClO_4]=0.91$ M;
△: [oxalate]=0.01 M, $[AgNO_3]=0.002$ M $[HClO_4]=0.182$ M

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3) Z. G. Szabo, L. Csanyi and H. Galiba, *Z. anal. Chem.*, **135**, 269 (1952).

4) Y. K. Gupta and S. Ghosh, *J. Inorg. Nucl. Chem.*, **11**, 320 (1959).

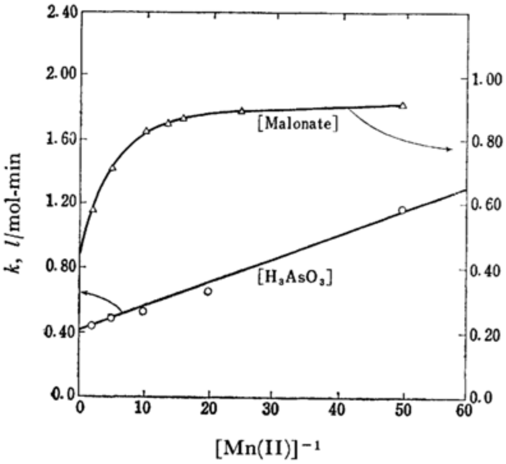

Fig. 3. Effect of manganous sulphate on the oxidation of arsenious and malonic acids by peroxydisulphate.
$[S_2O_8^{2-}]=0.02$ M; $[H_3AsO_3$ or $CH_2(COOH)_2]=0.02$ M; $[HClO_4]=0.182$ M; $[NaClO_4]=0.50$ M; $[AgNO_3]=0.002$ M

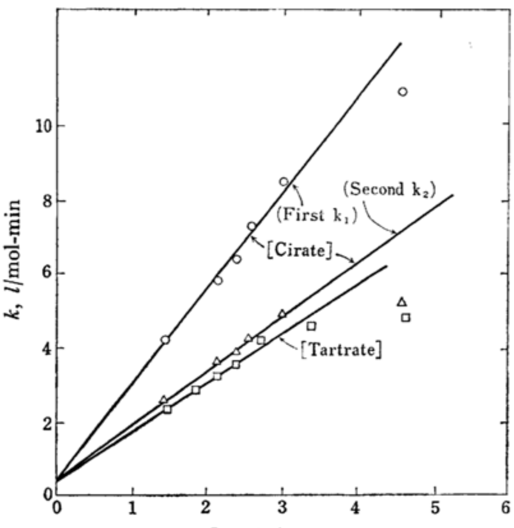

Fig. 4. Effect of manganous sulphate on the oxidation of citrate and tartrate by peroxydisulphate.
$[S_2O_8^{2-}]=0.02$ M; [citraie or tartrate]$=0.02$ M; $[HClO_4]=0.182$ M; $[NaClO_4]=1.0$ M; $[AgNO_3]=0.002$ M.

Results and Discussion

All the reactions are first order with respect to peroxydisulphate and the first order catalytic constants, k were calculated[5] from the following equation:

$$k=\frac{2.303\times \text{slope}}{[Ag^+]}$$

where the slope refers to that of the straight line obtained by plotting the logarithm of the concentration of peroxydisulphate at different intervals of time, against time. The effect of Mn(II) on all these acids is shown in Figs. 2, 3 and 4 and a comparison of the rate for one concentration of Mn(II) has been made in Table 1.

A particular function of the concentration of

Table 1
$[S_2O_8^{2-}]=0.02$ M; $[Ag^+]=0.002$ M; $[HClO_4]=0.182$ M

Reducing substance	k, l/mol-min		Limiting value of k	Other conditions
	In absence of Mn(II)	In presence of 0.1 M Mn(II)		
Oxalate, 0.01 M	153.5	16.16	1.5	Induction period
0.1 M	35.44	3.57	1.6	Induction period
As(III),* 0.02 M	23.03	0.55	0.42	$HClO_4=0.91$ M
Malonic acid, 0.02 M	0.98	0.83	0.41—0.43	
Citric acid, 0.02 M				
First reaction	12.25	5.87	0.45	1 M $NaClO_4$
Second reaction	3.90	3.65	0.40	
Tartaric acid, 0.02 M				
First reaction	17.42	3.70	0.40	1 M $NaClO_4$
Second reaction	3.83	4.65	—	
Acetic acid, 0.02 M	1.36	0.44	—	0.5 M $NaClO_4$

* Arsenious acid solution was prepared by boiling arsenious oxide with water as detailed in an earlier paper.[6]

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[5] H. G. S. Sengar and Y. K. Gupta, *J. Indian Chem. Soc.*, **43**, 223 (1966).

[6] Y. K. Gupta and S. Ghosh, *J. Inorg. Nucl. Chem.*, **11**, 62 (1959).

Mn(II) has been selected for a graphical plot to obtain a limiting value of k in presence of infinite amount of Mn(II). The dependency of the pseudo-first order rate constants upon Mn(II) concentration is of varying nature in different cases. Only complete kinetic studies of the oxidation of organic acids by Mn(III) can give an explanation for this curious behaviour. However, we are concerned here only with the mechanism of the reduction of peroxydisulphate in presence of Mn(II) and the limiting value of the rate constant and not with the mechanism of the oxidation of the organic acids by Mn(III) or MnO_2. Nevertheless, this curious dependency on Mn(II) appears to be connected in some way with the complex formation of Mn(III) with the organic acids.

A look at the figures of Table 1 will indicate that in all cases except one, the limiting value of k is about 0.4—0.5 l/mol-min which is the same as for the oxidations of Mn(II),⁽⁷,⁸⁾ Tl(I),⁽⁵⁾ Ce(III),⁽⁹⁾ H_2O,⁽¹⁰⁾ *etc.* These results can be explained on the basis of the following general mechanism which has already been advanced by the previous workers.

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^- \qquad \text{(i)}$$

$$2SO_4^- + Ag^+ \rightarrow 2SO_4^{2-} + Ag^{3+} \qquad \text{(ii)}$$

(1)

$$Ag^{3+} + IS \rightarrow \text{Products}$$

$$Ag^{3+} + Mn(II) \rightarrow Ag^+ + Mn(III) \text{ or } MnO_2 \qquad \text{(iiia)}$$

(2)

$$Ag^{3+} + S \rightarrow Ag^+ + R_1 \qquad \text{(iiib)}$$

$$S_2O_8^{2-} + R_1 \rightarrow SO_4^- + SO_4^{2-} + \text{products}$$

$$SO_4^- + R_1 \rightarrow SO_4^= + \text{products}$$

$$2R_1 \rightarrow \text{products}$$

Steps (iiia) and (iiib) are faster than (ii). Mechanism (I) refers to the oxidation of inorganic substrate (IS) and hence, is independent of the concentration of the latter giving overall catalytic rate constant of 0.4—0.5 l/mol-min (or the observed rate constant of $8—10\times10^{-4}$/min). Mechanism (2) involving the organic substrate is a chain mechanism. This mechanism and hence the overall rate constant would slightly change (the chain breaking step in particular) depending on the species being oxidized.

It appears that in presence of Mn(II), both mechanisms (I) and (2) occur simultaneously. Mn(II) competes with S in reaction with Ag^{3+}. Mn(II) is oxidized to Mn(III) or MnO_2 and the latter in acid medium quickly reacts with S. In previous studies of oxidations of tartarate,⁽¹¹⁾ citrate,⁽¹²⁾ malonate⁽¹³⁾ and oxalate⁽¹⁴⁾ by MnO_2, the first order rate constants were found to be of the order of $5\times10^{-2}—1\times10^{-1}$/min which are about a hundred times higher than the observed rate constant of the present study. Hence the reaction of MnO_2 with S is fast, but this process may not be an efficient chain mechanism. Although S is oxidized by both mechanisms, the chain process becomes less significant in competition with the reaction with MnO_2 and the rate decreases. In the limit when sufficient Mn(II) is present, the chain mechanism (2) may not work at all and S is oxidized only through mechanism (1). The rate, therefore, falls to the limiting value of 0.4—0.5 l/mol-min. The limiting value in case of oxalate is slightly higher, but is by no means very different than 0.5. The probable reason for this higher value is that the reaction of Mn(III) with oxalate itself is a free radical reaction involving chains as reported by Taube⁽¹⁵⁾ and Alder and Noyes⁽¹⁶⁾.

The results with acetate are a little different. The catalytic rate constant was found to be about 1.1 to 1.5 l/mol-min depending on the ionic strength, and in absence of Mn(II). In presence of any concentration of Mn(II), the rate constant was 0.44 l/mol-min. Mn(II) is oxidized to MnO_2, but the latter does not react with acetate and hence accumulates in the system. (The peroxydisulphate was estimated after separating MnO_2 by centrifuging the reaction mixture.) Acetate, however, was not oxidized by the independent path (mechanism (2)) also and it was oxidized only when the oxidation of Mn(II) was complete. There are two distinct oxidations as is apparent from Fig. 1. This was proved by the fact that the rate of decrease of peroxydisulphate was exactly equal to the rate of formation of MnO_2, and acetate had absolutely no effect, *i. e.,* it was neither oxidized nor it affected the oxidation of Mn(II). This may indicate that the step (iiib) is too slow as compared to step (iiia), although the former is quite fast as compared to step (i) or step (ii). The situation is similar to the oxidation of water⁽¹⁰⁾ in absence of any reducing substance, which takes place at the same rate at which Mn(II), if present, is oxidized and in that case water is not at all oxidized so long any Mn(II) is present. Another point of mechanistic interest

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7) Y. K. Gupta and S. Ghosh, *ibid.,* **9**, 178 (1959).

8) A. O. Dekker, H. A. Levy and D. M. Yost, *J. Am. Chem. Soc.,* **59**, 2129 (1937).

9) W. H. Cone, *ibid.,* **67**, 78 (1945).

10) H. C. S. Sengar and Y. K. Gupta, *J. Indian Chem. Soc.,* **44**, 769 (1967).

11) Y. K. Gupta and S. Ghosh, *Proc. Natl. Acad. Sci., India,* **28A**, 214 (1959).

12) Y. K. Gupta and S. Ghosh, *ibid.,* **29A**, 331 (1960).

13) Y. K. Gupta and R. Dutta, *Bull. Acad. polon. Sci.,* **7**, 821 (1959).

14) Y. K. Gupta and S. Ghosh, *Z. physik. Chem.,* **208**, 368 (1957).

15) H. Taube, *J. Am. Chem. Soc.,* **70**, 1216 (1948).

16) S. J. Alder and R. M. Noyes, *ibid.,* **77**, 2036 (1955).

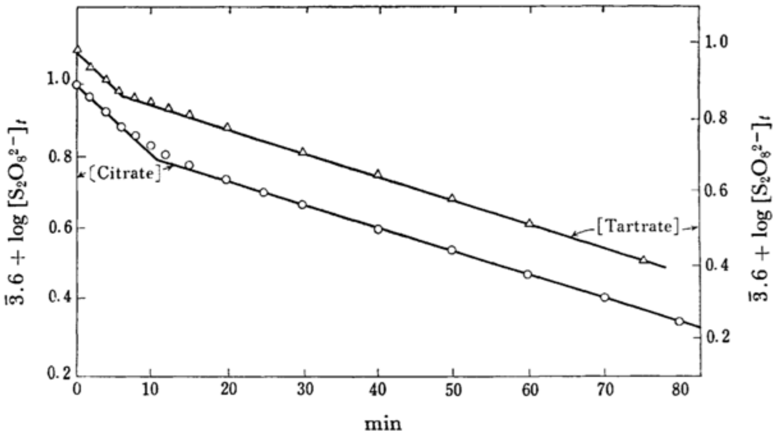

Fig. 5. First order plots for the oxidation of citrate and tartrate by peroxydisulphate, each one of them showing two reactions, one after the other.
$[S_2O_8^{2-}]=0.02$ M; [citrate]=[tartrate]=0.02 M; $[Ag^+]=0.005$ M; $[HClO_4]=0.182$ M; $[NaClO_4]=0.50$ M

found was that the rate of decrease of peroxydisulphate or the rate of oxidation of acetate (in absence of Mn(II)) was always about three times that of the oxidation of Mn(II).

A reverse behaviour is seen with the pair oxalate-Mn(II) or As(III)-Mn(II). So long any oxalate or arsenious acid is present in the system, Mn(II) is apparently not oxidized, and MnO_2 begins to form only after the oxidation of oxalate or arsenious acid is complete. Figure 1 shows these results. In fact Mn(II) is definitely oxidized as stated earlier, but Mn(III) formed reacts with oxalate or arsenious acid. The reaction is almost instantaneous in high acid medium.

In the oxidation of formic acid in presence of Mn(II), MnO_2 is formed as in the case of acetate, but the results show that the formic acid is also oxidized because the rate of decrease of peroxydisulphate is more than the rate of formation of MnO_2. In fact the rate of formation of MnO_2 is less than even the value of 0.4—0.5. A plot of $\log[MnO_2]$ *vs.* time also does not give a straight line. It appears that MnO_2 is further oxidized to permanganate which then slowly reacts with the formic acid. In this process more of peroxydisulphate is used up and some quantity of MnO_2 is also consumed. The overall observed first order rate constant, therefore, is more (0.51) than 0.4 (for Mn(II) alone). However, this constant is much less than the rate constant for the oxidation of formic acid alone in absence of Mn(II) which was found[17] to be 8—10 *l*/mol-min. The reaction mixtures were found to turn pink, obviously due to the formation of permanganate which subsequently slowly reacted with the formic acid forming back Mn(II). Mn(II), therefore, is never completely oxidized to MnO_2 in such a case till any formic acid is present. However, in case of acetate, permanganate even if formed does not react with the acetate.

We thus find that Mn(II) retards the rate in the silver catalyzed peroxydisulphate oxidations which go by a chain mechanism and this it does by reacting with the chain propagating free radical in competition with the substance being oxidized.

Oxidation studies of citrate and tartrate revealed another interesting fact though not relevant to the present paper. Both reactions seem to involve two consecutive reactions and that the first faster reaction is followed by the second slower reaction almost after when the former is complete (Fig. 5). First and second of Fig. 4 refer to these first and second reactions. In case of tartarate the first reaction is retarded and the second accelerated in presence of Mn(II). A detailed study of this reaction is being made to explain such behaviour of Mn(II). In case of citrate both the reactions are retarded in presence of Mn(II) and the limiting value in each case is 0.4 *l*/mol-min.

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[17] R. K. Nigam and Y. K. Gupta, *J. Indian Chem. Soc.*, **37**, 125 (1960).