

Kinetics and Mechanism of the Reaction between Trivalent Manganese
and Carboxylic Acids in Aqueous Solution. I

Reduction of Trivalent Manganese by Tartrate

By H. L. KALRA and S. GHOSH

Abstract

The kinetics of the reduction of trivalent manganese by tartrate in aqueous solution has been studied. The reaction is catalysed by H^+ -ions and retarded by the presence of Mn^{2+} . Increase in the concentration of tartrate lowers the rate of reduction of manganese (III). The temperature coefficient of the reaction which is first order, is 3.97 between 30° and 40° .

Introduction

The importance of the role of Mn(III) in the oxidation of oxalate by various oxidising agents has been shown by GHOSH et al.¹⁻⁴), MACMOHAN et al.⁵), TAUBE⁶)⁷) and others. It has been established that free radicals like $C_2O_4^-$ and OH are formed by the reaction between Mn(III) and oxalate and subsequently these free radicals influence the rate of reaction between oxalate and the oxidising agents. The catalytic role of Mn(II) in the oxalate-permanganate reaction has also been attributed to the formation of Mn(III) by GHOSH et al.⁸). In most of these reactions Mn(III) is reduced to the bivalent state and is not regenerated. With a view to understand the role of Mn(III) in these reactions, the reaction between Mn(III) and oxalate has been studied by LAUNER⁹), LIDWELL and BELL¹⁰), BRADLEY and

¹) D. N. CHAKRAVARTY and S. GHOSH, *J. Ind. Chem. Soc.* **34**, 841 (1957).

²) Y. K. GUPTA and S. GHOSH, *J. Ind. Chem. Soc.* **36**, 237 (1959).

³) B. D. BANERJI, A. K. DEY and S. GHOSH, *Z. phys. Chem.* **202**, 261 (1953).

⁴) B. D. BANERJI, A. K. DEY and S. GHOSH, *Z. phys. Chem.* **202**, 269 (1953).

⁵) P. S. MACMOHAN and B. B. LAL, *J. Ind. Chem. Soc.* **20**, 307, 1943.

⁶) H. TAUBE, *J. Amer. chem. Soc.* **69**, 1418 (1947).

⁷) H. TAUBE, *J. Amer. chem. Soc.* **70**, 3928 (1948).

⁸) Y. K. GUPTA and S. GHOSH, *Z. phys. Chem.* **210**, 1 (1959).

⁹) H. F. LAUNER, *J. Amer. chem. Soc.* **54**, 2597 (1932).

¹⁰) O. M. LIDWELL and R. P. BELL, *J. Chem. Soc.* 1303 (1935).

VAN PRAAGE¹¹⁾ and more recently by TAUBE¹²⁾ and also by GHOSH and CHAKRAVARTY¹³⁾. The authors¹⁴⁾ have already observed the catalytic influence of Mn(III) on the reaction between some carboxylic acids and iodine.

It was thought to be of interest to study the reduction of tripositive manganese by carboxylic acids and in the present paper reduction of Mn(III) by tartrate has been described.

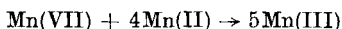
Experimental

Standard solution of 0.02 M potassium permanganate, 0.25 M sodium tartrate, 0.25 tartaric acid and 0.08 M manganous sulphate were prepared in the boiled and cooled distilled water. The chemicals used were either of B. D. H., A. R., or E. MERCK extra pure quality. Different solutions of tartrate and tartaric acid mixtures were prepared so that these gave the same concentration of tartrate but different hydrogen ion concentrations in the reaction mixtures. pH of these mixtures were measured by a pH meter using glass-calomel electrodes.

Table 1
pH of Mixtures of Sodium Tartrate
and Tartaric Acid

Solution	Mixture		pH
	0.25 M Sodium tartrate	0.25 M Tartaric acid	
A	0	100	2.30
B	20	80	3.05
C	40	60	3.50
D	60	40	4.00
E	80	20	4.50
F	90	10	4.90

The solutions of tartrate, permanganate and manganous sulphate were kept in an electrically regulated thermostat to acquire a constant temperature. Trivalent manganese was prepared as a tartrate complex by the interaction of calculated amounts of manganous sulphate with potassium permanganate according to the following reaction



in a tartrate solution. The formation of Mn(III) in the tartrate solution was practically instantaneous.

The rate of reduction of Mn(III) was investigated by pipetting out 5 ml. of the reaction mixture at different intervals of time and adding it instantaneously to an acidified 7% KI solution. The liberated iodine was titrated against sodium thiosulphate using a microburette

¹¹⁾ J. BRADLEY and G. V. PRAAGE, *J. Chem. Soc.* 1624 (1938).

¹²⁾ H. TAUBE, *J. Amer. chem. Soc.* **70**, 1216 (1948).

¹³⁾ D. N. CHAKRAVARTY and S. GHOSH, *Z. phys. Chem.* **207**, 392 (1957).

¹⁴⁾ H. L. KALRA and S. GHOSH, communicated.

reading upto 0.02 ml. The reaction, were always carried out in Jena bottles coated from outside with black Japan and further wrapped in black opaque linen to avoid the effect of light.

In all cases the first order constants have been calculated, as the velocity constants calculated for other orders give continuously more falling or rising values. The concentrations recorded in the tables are overall concentrations.

Table 2

	(a)	(b)	(c)
Concentration of tartaric acid	0.05 M	0.1 M	0.2 M
Time (min)	$k_1/2.303$ (min ⁻¹)	$k_1/2.303$ (min ⁻¹)	$k_1/2.303$ (min ⁻¹)
1	—	—	—
5	0.0956	0.0635	0.0390
10	0.0863	0.0669	0.0473
15	0.0713	0.0693	0.0494
20	—	—	0.0530
Average $k_1/2.303$	0.0844	0.0693	0.0472

Table 4

Effect of Mn(II) on the Rate of Reaction

Table 3
Effect of pH of the Tartrate Solution on the Rate of Reaction

Tartrate = 0.1 M; Mn(III) = 0.005 M;
Temperature = 30°C

pH of the tartrate mixture	Average $k_1/2.303$
2.30	0.0666
3.05	0.0290
3.50	0.0217
4.00	0.0157
4.50	0.0133
4.90	0.0097

Table 4 shows the results obtained by the study of the reaction in presence of 0.020 M manganous sulphate, concentration of other reactants being the same as in table 2 (Column b)

Time (min)	$k_1/2.303$ (min ⁻¹)
1	—
5	0.0345
10	0.0375
15	0.0363
20	0.0438
25	0.0463
Average $k_1/2.303$ =	0.0397

Results and Discussion

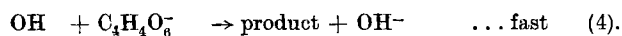
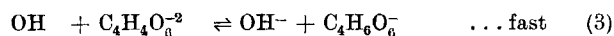
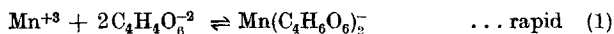
The experimental results show that the rate of reaction is of first order with respect to Mn(III), though these constants are found to vary in certain cases. The rate of reaction is highly influenced by the variation of pH of the

Table 5
Effect of Temperature on the Rate of Reaction

Table 5. Summarises the effect of temperature on the rate of reaction at pH 4.90

Temperature	Average $k_1/2.303$	$k_1 35^\circ/k_1 30^\circ$	$k_1 40^\circ/k_1 35^\circ$	$k_1 40^\circ/k_1 30^\circ$
30°C	0.00972			
35°C	0.02007	2.05	1.92	3.97
40°C	0.03860			

tartrate solution. Increase in the concentration of tartrate solution as well as the presence of Mn(II) lowers the rate of reaction. Based on the above observations the following mechanism may be suggested.



The formation of manganitartrate complex by the interaction of manganese sulphate and potassium permanganate in presence of the tartrate solution has been found to be instantaneous. The complex has the composition $\text{Mn}(\text{C}_4\text{H}_6\text{O}_6)_2^-$ as reported by GARCIA¹⁵).

The reactions given in (3) and (4) involve free radicals and are expected to be fast. The rate of reaction therefore, depends upon (2). The concentration of trivalent manganese depends on the stability constant of manganitartrate ion. Hence larger concentrations of tartrate depress the dissociation of the complex anion and therefore, the amount of trivalent manganese available for the production of OH decreases. This explains the decrease in the reaction rate with the increase in the concentration of tartrate. Effect of Mn(II) in decreasing the rate of reaction is also clear from (2). Hydrogen ions are known to decrease the stability of manganitartrate complex. Hence decrease in pH increases the concentration of Mn^{+3} ions available for the production of OH radicals. The opposing effect of hydrogen ions on (2) has not been observed experimentally. It appears that the catalysing effect of

¹⁵) H. S. GARCIA, *Anales real Soc. espan fis. Y. quim (Madrid)* 49 B, 187 (1953).

hydrogen ions on (1) is much greater as compared to its retarding effect on step (2). The nett result is the overall increase in the reaction rate with increase in H^+ ion concentration.

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