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

Reduction of Trivalent Manganese by Citrate

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With 1 Figure

Abstract

The kinetics of the reduction of trivalent manganese by citrate in aqueous solution has been studied. The reaction is optimum at pH 3.30 of the citrate solution and is retarded by the presence of Mn^{2+} for the citrate solution of pH 3.30 or higher. Increase in the concentration of citrate lowers the rate of reduction of Mn(III). The temperature coefficient of the reaction is 1.83 between 20 °C and 30 °C.

Introduction

In a previous communication[1]) the kinetics of the reduction of trivalent manganese by tartrate has been described in detail. It was shown that the reaction is catalysed by H^+ ions and retarded by the presence of Mn^{2+}. Increase in the concentration of tartrate solution was found to lower the rate of reduction of Mn(III). In the present investigation, the reduction of Mn(III) by citrate solution has been studied.

Experimental

The experimental procedure in this case is similar to that already described[1]). In the present case 0.125 M potassium citrate and 0.125 M citric acid were mixed in different proportions to give solution of the same concentration of citrate but different hydrogen ion concentration, as shown below.

Trivalent manganese was prepared in the citrate solution by the interaction of manganous sulphate and potassium permanganate in equivalent proportions. The reactions were carried out in dark at a constant temperature. The rate of reduction of Mn(III) was investigated by pipetting out 5 ml of the reaction mixture at suitable intervals and determining trivalent manganese iodometrically. As mentioned earlier, the reactions follow first order more closely than any other order. The concentrations recorded are the overall ones.

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¹) H. L. KALRA and S. GHOSH, J. prakt. Chem. 28, 108 (1965).

From the above table a curve (vide fig. 1) has been plotted showing the effect of pH of the citrate solution on the time of half reduction of Mn(III). It has been observed that decrease in pH decreases the time of half reduction of Mn(III) and becomes minimum at pH 3.30. However, when pH is further decreased, the time of half reduction suddenly increases. Rate of loss of Mn(III) is maximum when the time of half reduction is minimum and hence the rate reduction of Mn(III) is maximum at pH 3.30.

Effect of Temperature on the Rate of Reaction

Effect of temperature was studied on the rate of reaction, employing citrate solution at pH 5.68. In view of the inconsistency of the values of velocity constants at this pH we have chosen the highest values of the velocity constants for calculating the temperature coefficient.

Effect of Bivalent Manganese on the Rate of Reaction

Effect of 0.02 M manganous sulphate was studied on the rate of reaction employing citrate solutions at different pH using 0.05 M citrate and 0.005 M Mn(III) solutions. It was observed that bivalent manganese lowers the rate of reaction. The effect of lowering the rate of reaction decreases with the decrease in pH of the citrate solution so much so that when citrate solutions of pH 3.30 or below were employed the depressing effect of manganous sulphate on the rate of reaction completely disappeared.

Discussion

The results presented in this paper show that the rate of reaction is of first

Table 1

pH of the Potassium Citrate—Citric Acid Mixtures

| Solution | Mixture | | pH |
	0.125 M Potassium citrate (ml)	0.125 M Citric acid (ml)	
A	80	20	5.68
B	60	40	4.86
C	40	60	4.14
D	20	80	3.30
E	0	100	2.28

Table 2

Effect of change in the concentration of Citric Acid on the rate of Reaction

Mn(III) = 0.005 M   Temperature = 25 °C

| Conc. of citric acid | 0.05 M | 0.1 M |
Time (min) (min)	$k_1/2.303$ (min^{-1})	$k_1/2.303$ (min^{-1})
1	—	—
5	0.0442	0.0418
10	0.0471	0.0428
15	0.0514	0.0456
20	0.0526	0.0462
30	0.0528	0.0476

Table 3

Effect of pH of the Citrate solution on the Rate of Reaction

Citrate = 0.05 M; Mn(III) = 0.0005 M; Temp. = 25 °C

pH of the citrate solution	Time of half reduction of Mn(III)
5.68	14 min. 30 sec.
4.86	8 min. 30 sec.
4.14	6 min. 0 sec.
3.30	4 min. 0 sec.
2.28	7 min. 30 sec.

<div align="center">Table 4</div>
<div align="center">Citrate = 0.1 M (pH = 5.68); Mn(III) = 0.005 M</div>

Temperature	$k_1/2.303$	k_1 25 °C/k 20 °C	k_1 30 °C/k_1 25 °C	k_1 30 °C/k_1 20 °C
20 °C	0.0211			
25 °C	0.0281	1.33	1.37	1.83
30 °C	0.0386			

order with respect to Mn(III). Increase in the concentration of citrate solution lowers the rate of reaction. The rate of reduction depends upon the pH of the citrate solution and has been found to pass through maximum at pH 3.30 (vide fig. 1). Bivalent manganese lowers the rate of reaction at higher pH of the citrate solutions. The following mechanism for the reaction may be suggested to explain the above observations.
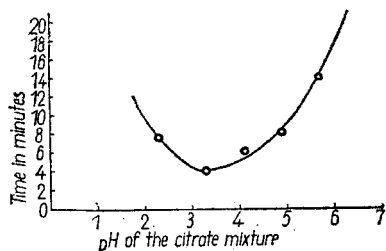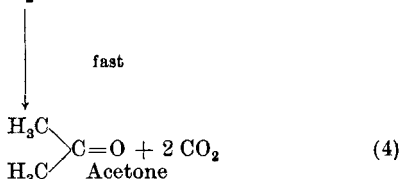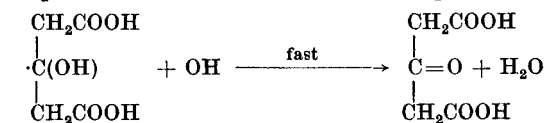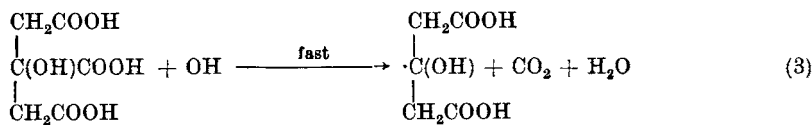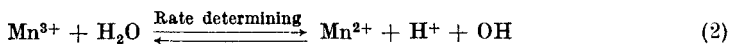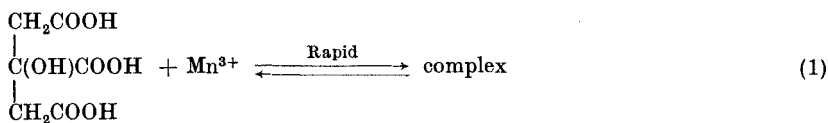

Fig. 1. Variation of the time of half reduction of Mn(III) with pH

The formation of mangani-citrate complex by the interaction of bivalent and heptavalent manganese in citrate solution has been found to be instantaneous. The λ_{max} of the complex formed was determined with a spectrophotometer and the value of 430 mμ was found to tally with that recorded by DUKE[2]).

$$
\begin{array}{c}
CH_2COOH \\
| \\
C(OH)COOH + Mn^{3+} \xrightleftharpoons{\text{Rapid}} \text{complex} \\
| \\
CH_2COOH
\end{array}
\tag{1}
$$

$$
Mn^{3+} + H_2O \xrightleftharpoons{\text{Rate determining}} Mn^{2+} + H^+ + OH \tag{2}
$$

$$
\begin{array}{c}
CH_2COOH \\
| \\
C(OH)COOH + OH \xrightarrow{\text{fast}} \cdot C(OH) + CO_2 + H_2O \\
| \\
CH_2COOH
\end{array}
\qquad
\begin{array}{c}
CH_2COOH \\
| \\
\\
| \\
CH_2COOH
\end{array}
\tag{3}
$$

$$
\begin{array}{c}
CH_2COOH \\
| \\
\cdot C(OH) + OH \xrightarrow{\text{fast}} \\
| \\
CH_2COOH
\end{array}
\qquad
\begin{array}{c}
CH_2COOH \\
| \\
C=O + H_2O \\
| \\
CH_2COOH
\end{array}
$$

$$
\downarrow \text{fast}
$$

$$
\begin{array}{c}
H_3C \\
\diagdown \\
C=O + 2 CO_2 \\
\diagup \quad \text{Acetone} \\
H_3C
\end{array}
\tag{4}
$$

²) F. R. DUKE, J. Amer. chem. Soc. 69, 2885 (1947).

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 in the free state i. e. Mn^{3+} depends upon the stability constant of the manganicitrate complex. Hence larger concentrations of citrate depress the dissociation of the complex and therefore, the amount of Mn^{3+} available for the production of OH radicals decreases. This explains the decrease in the reaction rate with the increase in the concentration of citrate solution. The stability of manganicitrate complex is known to decrease with increase in acidity. It is likely to increase the concentration of Mn^{3+} ions and hence the concentration of OH radicals increases, but from equation (2) it is expected that increase in hydrogen ion concentration decreases the formation of OH radicals, an important species in the production of free radicals of the organic anion. Thus the two factors appear with the increase in the hydrogen ion concentration and have opposing effects This explains why there is an optimum pH at which the rate of reaction is maximum. Effect of Mn(II) in decreasing the rate of reaction is clear from equation (2).

The presence of acetone in the reaction mixture was confirmed by the usual tests.

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