Kinetics of the Reaction between Citrate and Aqueous Iodine in Presence of Mn(III)

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With 1 Figure

Abstract

The reaction between citrate and aqueous iodine is accelerated by the presence of tripositive manganese. The reaction is of first order with respect to iodine and increase in concentration of Citrate suppresses the rate of reaction. Increase in the concentration of Mn(III) enhances the reaction rate. pH has a marked influence on the rate of reaction, the reaction being fastest at pH 4.25. The temperature coefficient is of the order of 3. The manganous ions lower the rate of reaction at pH higher than 3.30 while no such effect is noted below this pH. A suitable mechanism has been suggested.

Introduction

The kinetics of the reaction between sodium citrate and iodine was first investigated by Mukerji and Dhar[1]). These authors reported that the reaction in the dark is bimolecular with respect to sodium citrate and unimolecular with respect to iodine. This reaction was also studied by Qureshi and Veeraih[2]) who reported that this reaction is not appreciably affected by sunlight. In the present paper citrate—iodine reaction in dark has been investigated in presence of very low concentrations of trivalent manganese using citrate solutions at different pH. The effect of concentration of citrate solution and also that of Mn(III) on the rate of reaction have been investigated.

Experimental

All the chemicals used were either B. D. H., A. R. quality or E. Merck extra pure quality. Stock solutions of 0.125 M citric acid, 0.125 M potassium citrate, 0.01 M potassium permanganate, 0.04 M manganous sulphate were prepared and standardised by usual volumetric and gravimetric methods. Iodine solution was prepared by shaking crystals of iodine with water (with no added KI) for about an hour and ca 0.002 N iodine solution could thus be obtained. Citrate—citri cacid mixtures of the following composition were prepared so that

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1) B. K. Mukerji and N. R. Dhar, J. physic. Chem. **33**, 850 (1929).

2) M. Qureshi and K. Veeraih, Current Sci. **15**, 132 (1946).

these gave the same concentration of citrate but different hydrogen ion concentrations. The pH of these mixtures were measured with Leeds and Northrup pH meter.

A measured volume of the citrate solution was kept in a constant temperature bath maintaining a temperature of $\pm$ 0.1 °C and trivalent manganese was formed in this citrate solution as a citrate complex by the interaction of calculated amounts of manganous sulphate with potassium permanganate according to the following reaction.

$$Mn(VII) + 4\,Mn(II) \rightarrow 5\,Mn(III).$$
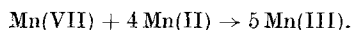
The formation of manganicitrate complex was practically instantaneous as was visually seen by the quick change of the pink colour of permanganate to yellow colour of the citrate complex. The λ_{max} of the complex formed was determined with a spectrophotometer and the value of 430 mμ was found to tally with that

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	95	5	6.38
B	80	20	5.68
C	60	40	4.86
D	40	60	4.14
E	20	80	3.30
F	0	100	2.28

Table 2

Effect of concentration of Mn(III) on the Rate of Reaction

Citrate = 0.05 M (pH = 6.38); Iodine = 0.001 N; Temp. = 20 °C

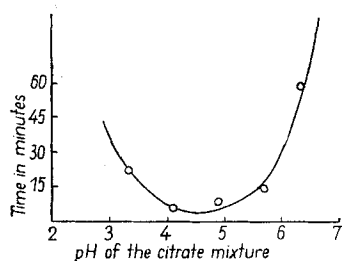| Mn(III) Time (min)	0.0002 M $k_1/2.303$ (min^{-1})	0.0003 M $k_1/2.303$ (min^{-1})	0.0004 M $k_1/2.303$ (min^{-1})
1	—	—	—
5	0.00110	0.00220	0.00280
15	0.00284	0.00346	0.00475
30	0.00288	0.00423	0.00681
40	0.00291	0.00483	0.00722
50	0.00297	0.00525	0.00575
60	0.00295	0.00507	0.00710
70	0.00291	0.00506	—

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

recorted by DUKE[3]). A measured volume of aqueous iodine was added to it atonce. The rate of consumption of iodine was noted by estimating iodine in 5 ml of the reaction mixture at different intervals of time. For comparison the rate of reaction between citrate and iodine was also studied in the absence of Mn(III).

In all cases first order constants have been calculated, as the reaction is found to follow this order more closely than any other order. The results are tabulated. The concentrations recorded in the tables are overall concentrations.

3) F. R. DUKE, J. Amer. Chem. Soc. 69, 2885 (1947).

For comparison the reaction between citrate and iodine in the absence of Mn(III) was also carried out. The reaction at pH 6.38 of the citrate solution was found to be very slow and the average value of $k_1/2.303$ was found to be 0.000672 min^{-1}.

From the above Table 4, a graph (vide fig. 1) has been plotted showing the effect of pH on the time of half reduction of iodine. It has been observed that decrease in pH decreases the time of half reduction and becomes minimum at pH 4.25. However, when pH is further decreased the time of half reduction suddenly increases. The rate of loss of iodine is maximum when the time of half reduction is minimum. Hence it can be said that the rate of reaction is maximum at pH 4.25 of the citrate solution.

Table 3
Effect of Concentration of Citrate on the Rate of Reaction
Mn(III) = 0.0002 M; Iodine = 0.001 N; Temp. = 20 °C; pH of the citrate solution = 5.65

Concentration of Citrate solution Time (min)	(a) 0.05 M $k_1/2.303$ (min^{-1})	(b) 0.025 M $k_1/2.303$ (min^{-1})
1	—	—
4	0.00802	0.0120
10	0.00991	0.0117
15	0.01106	0.0126
20	0.01009	0.0134
25	0.01012	0.0127
35	0.00781	0.0099

Effect of Bivalent Maganese on the Rate of Reaction

Effect of 0.002 M manganous sulphate was studied on the rate of reaction employing citrate solutions at different pH using 0.05 M citrate, 0.001 N iodine and 0.0004 Mn (III).

It was observed that manganous sulphate lowers the accelerating effect of Mn(III) towards the reaction between citrate and iodine. This effect of manganous sulphate was found to decrease with decrease in pH of the citrate solution used, so much so, that when citrate solution of pH 3.30 or below were used the depressing effect of manganous sulphate on the rate of reaction completely disappeared.

Table 4
Effect of pH on the Rate of Reaction
Citrate = 0.05 M; Iodine = 0.001 N; Mn(III) = 0.0004 M; Temp. = 20 °C.

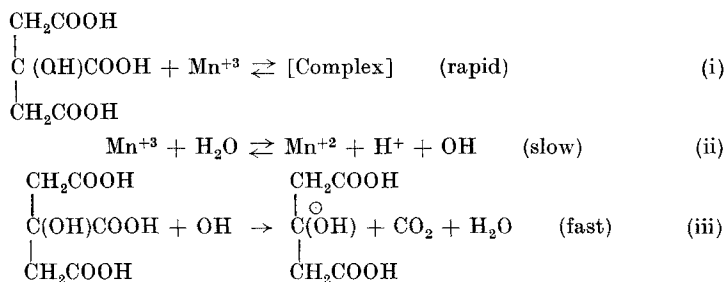| pH of the citrate mixture	Time for half reduction of iodine
6.38	59 min. 0 sec.
5.68	14 min. 0 sec.
4.86	8 min. 0 sec.
4.14	5 min. 30 sec.
3.30	22 min. 0 sec.
2.28	Infinity

Discussion

The experimental results described in the paper show that the reaction between citrate and iodine in dark is accelerated by Mn(III). (The increase in the concentration of Mn(III) increases the rate of reaction (vide table 2). It

Table 5
Effect of Temperature on the Rate of Reaction
Citrate = 0.05 M (pH = 6.38); Iodine = 0.001 N; Mn(III) = 0.0002 M

Temperature	Average $k_1/2.303$	Temp. coeff. (k_1 30 °C/k_1 20 °C)
20 °C	0.00291	
30 °C	0.00849	2.92

may be noted that the values of the first order velocity constants have a tendency to change regularly with time, showing that the reactions are complicated and cannot be expressed by a definite equation. Hence, for comparison of the rates, the time required for half reduction of Mn(III) at different pH have been computed and it has been found that reaction is fastest at pH 4.25 (vide fig. 1). Increase in the concentration of the citrate solution lowers the rate of reaction. Mn(II) depresses the rate of reaction when citrate solutions of higher pH are employed while when citrate solutions of pH 3.30 or below are used, Mn(II) does not lower the rate of reaction.

WATERS et al.[4])[5]) have shown that in the oxidation of carboxylic acids by manganic pyrophosphate, complexes of these acids are formed with Mn(III) which break down to give free radicals. These free radicals have been detected by their ability to initiate vinyl polymerisation. The increase in the rate of reaction has been attributed to the production of free radicals in the citrate solution by its interaction with Mn(III). The authors have already shown similar effect of Mn(III) on the oxalate-iodine[6]) and tartrate-iodine[7]) reactions which they have attributed to be due to the free oxalate and tartrate radicals. The citrate free radicals may be produced in the solution according to the following scheme.

$$
\begin{array}{l}
CH_2COOH \\
| \\
C\,(OH)COOH + Mn^{+3} \rightleftarrows [Complex] \qquad (rapid) \qquad\qquad (i) \\
| \\
CH_2COOH
\end{array}
$$

$$
Mn^{+3} + H_2O \rightleftarrows Mn^{+2} + H^+ + OH \qquad (slow) \qquad\qquad (ii)
$$

$$
\begin{array}{l}
CH_2COOH \qquad\qquad CH_2COOH \\
| \qquad\qquad\qquad\quad | \overset{\ominus}{} \\
C(OH)COOH + OH \rightarrow C(OH) + CO_2 + H_2O \qquad (fast) \qquad (iii) \\
| \qquad\qquad\qquad\qquad | \\
CH_2COOH \qquad\qquad CH_2COOH
\end{array}
$$

Increase in the concentration of Mn^{+3} increases the concentration of OH radicals and hence the concentration of $[HOOCCH_2C(OH)-CH_2COOH]$ radicals. These radicals are expected to react with iodine at a much faster rate than citrate radicals due to their greater chemical reactivity. When concentration of the citrate solution is increased the concentration of Mn^{+3} in solution decreases according to equation (i). The concentration of OH free radicals which are produced by the interaction of water and Mn^{+3} therefore decrease and consequently the concentration of $[HOOC-CH_2-C(OH)-CH_2COOH]$ radicals fall. The stability of manganicitrate complex is known

[4]) A. Y. DRUMMOND and W. A. WATERS, J. chem. Soc. London **1954**, 2456; **1955**, 497.

[5]) P. LAVESLEY and W. A. WATERS, J. chem. Soc. London **1955**, 217.

[6]) K. L. KALRA and S. GHOSH, Communicated.

[7]) H. L. KALRA and S. GHOSH, Communicated.

to decrease with increase in acidity. It is likely to increase the concentration of Mn^{+3} ion in the uncomplexed form and hence the concentration of OH radicals will increase but from equation (ii) it is expected that increase in hydrogen ion concentration will decrease the formation of OH radicals. Thus the two factors appear with the increase in hydrogen ion concentration and have opposing effects. Hence there will be optimum pH at which the concentration of OH radicals will be maximum, which in turn produce organic free radicals. It is therefore evident that the rate of reaction is guided by the production of free radicals of the organic acid in the reaction mixture and that the catalytic activity of citrate solution in presence of Mn(III) is due to these free radicals.

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