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Kinetics and Mechanism of Ru(III) Catalysed Oxidation of Sodium Thioglycollate by Alkaline Hexacyanoferrate(III) Ion

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Kinetic data on Ru(III) catalysed oxidation of sodium thioglycollate by alkaline solution of hexacyanoferrate(III) has been reported. The reaction follows zero-order kinetics in hexacyanoferrate(III) while first order dependence on each sodium thioglycollate, OH and Ru(III) was observed. A suitable mechanism consistent with kinetics data has been proposed.

INTRODUCTION

Earlier, some work[1, 2] on the role of Ru(III) as catalyst has been reported. The present investigation communicates the investigation on kinetics and mechanism of sodium thioglycollate by alkaline hexacyanoferrate(III) in the presence of ruthenium(III) chloride as catalyst. Mechanistic details are discussed.

EXPERIMENTAL

E. Merck grade of sodium thioglycollate and hexacyanoferrate(III) of GR (S. Merck) were used. All other reagents were of AR grade. Ruthenium(III) chloride (Johnson and Matthey Ltd.) sample was dissolved in dilute hydrochloric acid and its strength was checked. Bidistilled water was used throughout the investigation. Calculated amount of sodium thioglycollate solution was added to the already equilibrated mixture containing hexacyanoferrate(III), sodium hydroxide, ruthenium(III) chloride solution to initiate the reaction. The kinetics of the reactions were followed by examining[3] aliquot portions of the mixture at different intervals of time for hexacyanoferrate(III) produced by standard solution of ceric sulphate using ferroin as redox indicator. The reaction gave reproducible results.

RESULTS AND DISCUSSION

The values of zero-order rate constants recorded in Table 1 at several initial concentrations of hexacyanoferrate(III) indicate that the reaction follows zero-order kinetics with respect to hexacyanoferrate(III). The value of zero-order rate constant (k_s) increases linearly with the increase in sodium thioglycollate concentration, indicating first-order dependence on sodium thioglycollate (Table 1). First order dependence of the reaction on sodium hydroxide and ruthenium (III) was obvious from the constant values of k_1 which are obtained on dividing zero-order rate constant, values with different concentrations of either sodium hydroxide or ruthenium(III) chloride. The reaction has been studied in the temperature range 25°C to 40°C and from the rate measurements at these temperatures, the value of energy of activation was calculated and was found as 14.96 kcals/mole.

TABLE 1

KINETIC DATA SHOWING EFFECT OF VARIATION OF [REACTANT] ON RATE OF THE REACTION AT 35°C

[NaOH] = 0.50 M, [Ru(III)] = 1.00×10^{-6} M

[Hexacyanoferrate (III)] $\times 10^3$ M	[STG] $\times 10^2$ M	$k_s \times 10^6$ mol l^{-1} min^{-1}	$10^4 k_1 = \frac{k_s}{[STG]}$ min^{-1}
1.44	1.00	7.12	—
1.60	1.00	6.68	—
2.00	1.00	7.03	—
2.20	1.00	7.44	—
2.70	1.00	7.03	—
3.34	1.00	7.10	—
2.00	0.80	5.48	6.85
2.00	1.00	7.03	7.03
2.00	1.25	8.52	6.82
2.00	2.00	13.52	6.76
2.00	2.40	16.22	6.75
2.00	4.00	27.38	6.85
2.00	1.00	4.56[a]	—
2.00	1.00	9.19[b]	—
2.00	1.00	14.13[c]	—

STG—Sodiun thioglycollate a—30° b—40° and c—45°

Before proposing the reaction mechanism, it is worthwhile and appropriate first to discuss the real reactive species of ruthenium(III) chloride in alkaline solution. It has already been well established[4, 5] under the similar condition of experiments that $[Ru(H_2O)_5OH]^{2+}$ is the real reactive species of ruthenium(III).

The experimental results obtained in the present investigation and above statement clearly suggest that the reaction follows the following routes. For the sake of simplicity Ru(III) as such has been used as real reactive species and S has been for the reducing substrate.

$$S + OH^- \overset{K_1}{\rightleftharpoons} S^- + H_2O \qquad \text{(i)}$$

$$\underset{C_1}{Ru(III)} + S^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{\substack{C_2 \\ \text{complex}}}{[Ru(III) \ldots S^-]} \qquad \text{(ii)}$$

$$C_2 \xrightarrow[\text{Slow}]{K_2} \text{Ru(III) hydride + Products} \qquad \text{(iii)}$$

$$\text{Ru(III) hydride} + 2OH^- + 2Fe(CN)_6^{3-} \xrightarrow[\text{Fast}]{} 2\,Fe(CN)_6^{4-} + H_2O + \text{Ru(III)} \qquad \text{(iv)}$$

On considering above steps, the following rate law is obtained in terms of loss of hexacyanoferrate(III) concentration.

$$\frac{-d[Fe(CN)_6]^{3-}}{dt} = k[Ru(III)]_T[S][OH^-]$$

where
$$k = \frac{k_1k_2K_1}{(k_{-1} + k_2)[H_2O]}$$

The above rate law accords well with the observed kinetics *i.e.* the reaction is zero-order in hexacyanoferrate(III), first order in sodium thioglycollate, sodium hydroxide and ruthenium(III) chloride. Hence the proposed mechanism is valid.

TABLE 2
EFFECT OF [Ru(III)] and [NaOH] ON REACTION RATE AT 35°C [STG] = 1.00×10^{-2} M, [HEXACYANOFERRATE(III)] = 1.60×10^{-3} M

[NaOH] × 10 M	[Ru(III)] × 10^6 M	$k_s \times 10^6$ mol l^{-1} min^{-1}	$k_l = \frac{k_s}{[STG] \text{ or } [Ru(III)]}$ min^{-1}
1.00	1.00	1.33	1.33×10^5
2.00	1.00	2.64	1.32×10^5
3.00	1.00	4.02	1.34×10^5
4.00	1.00	5.25	1.31×10^5
5.00	1.00	6.88	1.34×10^5
7.50	1.00	9.96	1.33×10^5
0.50	0.40	3.14	7.85*
0.50	0.75	5.21	6.95*
0.50	1.00	7.03	7.03*
0.50	1.50	10.17	6.78*
0.50	2.00	13.45	6.72*
0.50	2.50	16.76	6.70*

* [Hexacyanoferrate(III)] = 2.00×10^{-3} M STG—Sodium thioglycollate

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