

Mechanism of Rh(III) Catalysis in Oxidation of Glutamic Acid by Alkaline Solution of Hexacyanoferrate(III)

BIRENDRA KUMAR SINGH AND R. P. SINGH*

Department of Chemistry, A. M. College, Gaya, 823 001 India

Kinetics of Rh(III) catalysed hexacyanoferrate(III) oxidation of glutamic acid in alkaline medium have been studied. The reaction showed zero-order dependence on hexacyanoferrate(III) and OH⁻ ion and first order kinetics with respect to both glutamic acid and Rh(III). Insignificant effect of variation of ionic strength of the medium was observed. A suitable mechanism consistent with kinetic data is proposed.

INTRODUCTION

Although kinetic studies on hexacyanoferrate(III) oxidation of amino acid in the presence of Ru(III)^{1,2} have been reported, but kinetic investigation on Rh(III) catalysed oxidation of amino acids by alkaline hexacyanoferrate(III) has not been reported. This prompted us to study the kinetics and mechanism of oxidation of glutamic acid by alkaline hexacyanoferrate(III) involving Rh(III) as catalyst.

EXPERIMENTAL

The solution of rhodium(III) chloride (Johnson and Matthey) was prepared by dissolving the sample in HCl of known strength. All other reagents used were of A.R. grade except glutamic acid (Fluka), sodium perchlorate (Riedel) and ferroin indicator (E. Merck).

The reaction was followed by quenching the reaction mixture in H₂SO₄ and estimating the ferrocyanide formed volumetrically against standard ceric sulphate solution.

RESULTS AND DISCUSSION

Variation of hexacyanoferrate(III) concentration shows zero-order dependence on hexacyanoferrate(III). The rate of oxidation follows first-order kinetics with respect to glutamic acid (Table 1). The reaction rate is directly proportional to [Rh(III) chloride] showing first order dependence on [Rh(III)]. Insignificant effect of variation of [OH⁻] and ionic strength of the medium on reaction rate was observed (Table 2). The value of energy of activation (ΔE) was calculated from rate measurements in the temperature range 30-45°C (Table 1) and was found to be 17.70 Kcal/mole.

Rhodium(III) chloride is reported³⁻⁵ to exist as Rh(OH)₃ in low concentration of sodium hydroxide. Thus Rh(OH)₃ has been assumed to be active species of ruthenium(III) chloride in the alkaline medium. First order kinetics with respect to ruthenium(III) chloride and glutamic acid

TABLE 1

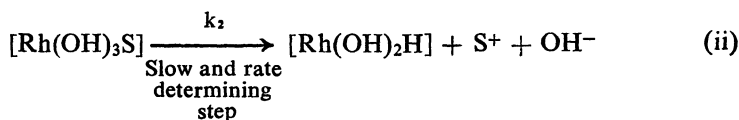
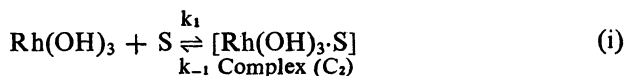
A	$[K_3Fe(CN)_6] \times 10^3$ M	1.00	1.25	1.67	2.00	2.50	4.00
	$k_0 \times 10^7$ ML ⁻¹ Sec ⁻¹	3.04	3.08	2.98	3.08	3.02	3.10
A → [Glutamic acid] = 0.50×10^{-2} M, [NaOH] = 0.75×10^{-2} M, [Rh(III)] = 8.00×10^{-6} M, Temp. 30°C and ionic strength (μ) = 3.15×10^{-2} M							
B	[Glutamic acid] $\times 10^2$ M	0.50	0.75	1.00	1.50	2.00	2.50
	$k_1 \times 10^5$ sec ⁻¹	6.08	6.08	6.24	6.24	5.80	5.84
B → $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, [NaOH] = 0.75×10^{-2} M, [Rh(III)] = 8.00×10^{-6} M, Temp. 30°C and ionic strength (μ) = 1.50×10^{-2} M							
C	Temp. °C	30	35	40	45		
	$k_0 \times 10^7$ ML ⁻¹ sec ⁻¹	3.08	4.62	7.58	11.46		
C → $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, [NaOH] = 0.75×10^{-3} M, [Rh(III)] = 8.00×10^{-6} M and [Glutamic acid] = 0.50×10^{-2} M and ionic strength (μ) = 1.50×10^{-2} M							

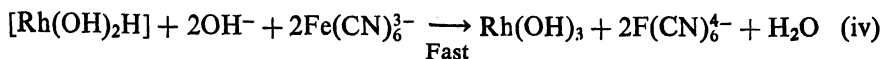
TABLE 2

$[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, Temp. 30°C

A	[Rh(III)] $\times 10^6$ M	1.00	2.00	4.00	8.00	10.00	12.00
	$k_1 \times 10^{-2}$ sec ⁻¹	8.00	8.20	8.18	7.80	7.48	7.85
A → [NaOH] = 0.75×10^{-2} M, [Glutamic acid] = 1.00×10^{-2} M, ionic strength (μ) = 1.50×10^{-2} M							
B	[NaOH] $\times 10^2$ M	0.50	0.75	1.00	1.50	2.00	2.50
	$k_0 \times 10^7$ ML ⁻¹ sec ⁻¹	3.08	3.08	3.06	3.10	3.04	3.08
B → [Rh(III)] = 8.00×10^{-6} M, [Glutamic acid] = 0.50×10^{-2} M, ionic strength (μ) = 3.25×10^{-2} M							
C	Ionic strength (μ) $\times 10^2$ M	1.50	3.00	4.50	6.00	7.50	10.00
	$k_0 \times 10^7$ ML ⁻¹ sec ⁻¹	3.08	3.17	3.04	3.06	3.00	3.02
C → [Rh(III)] = 8.00×10^{-6} M, [Glutamic acid] = 0.50×10^{-2} M, [NaOH] = 0.75×10^{-2} M							

suggests an interaction between ruthenium(III) chloride species and glutamic acid(S) as a primary step. Zero order dependence on hexacyanoferrate(III) suggests its involvement in fast step. Following steps are proposed for the title reaction.





It is clear from the above steps that complex formed, between Rh(III) species and glutamic acid disproportionate in a slow and rate determining step (II) forming hydride of ruthenium which on interaction with hexacyanoferrate(III) in a fast step regenerates Rh(OH)₃ for recycling. The carbonium ion formed as a result of abstraction of hydride ion from α -carbon atom of glutamic acid in step (II) further reacts with OH⁻ rapidly to form keto acid and ammonia.

The rate law of the reaction in terms of loss of [hexacyanoferrate(III)] has been derived on the basis of above reaction route as given below:

$$\frac{-d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = k_2[\text{C}_2] \quad (1)$$

The total concentration of Rh(III), *i.e.* [Rh(III)]_T may be expressed as Eqn. (2)

$$[\text{Rh}(\text{III})_T] = [\text{C}_1] + [\text{C}_2] \quad (2)$$

Application of steady state treatment to [C₂] on considering the inequality $k \gg (S)$ the final rate law may be written with the help of Eqn. (1) and (2) as Eqn. (3)

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

where $k = \frac{k_2}{k_1}$ and $k_1 = \frac{(k_2 + k_{-1})}{k_1}$.

The rate law (3) fully explains all the observed kinetics. The mechanism proposed is also in agreement with negligible effect of ionic strength proving involvement of a dipole in the rate controlling step.

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[Received: 15 November 1990; Accepted: 10 March 1971]

AJC-305