

Study of effect of pH on ligand exchange reaction between Ni₂EGTA and cyanide ion

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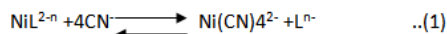
Abstract

The kinetics of ligand substitution reaction of binuclear nickel (II) chelate, Ni₂L, Where L is EGTA ((ethylenedioxy) diethylenedinitrilo tetraacetic acid) with cyanide ion has been investigated spectrophotometrically. The reaction conditions are pH=11.0± 0.1, I=0.1M (NaClO₄) and temp.=25±0.1°C. The formation of Ni(CN)₄²⁻ is first order in Ni₂L and first order in cyanide in a large range of cyanide concentration. However, at low cyanide concentration i.e., below 10⁻³ M, the reaction becomes zero order in cyanide. These results indicate the presence of a slow dissociation step in which Ni₂L dissociates to give NiL²⁻ⁿ and Ni²⁺(aquo) at low cyanide concentration and a cyanide assisted rapid dissociation of Ni₂L to produce NiL(CN)^{2-2-n-x} and Ni²⁺(aquo) at higher cyanide concentration. These species react with excess cyanide finally producing Ni(CN)₄²⁻. A five step mechanism has been proposed and the rate determining step has been identified. In this present paper, we studied the effect of pH on the reaction of cyanide ion with Ni₂EGTA.

Keywords: Ligand exchange reaction, pH value, Ni₂EGTA, Cyanide ion

INTRODUCTION

A considerable amount of data is now available on the formation of tetracyanonicklate (II) from mononuclear nickel (II) complexes of aminocarboxylates¹⁻¹⁰, polyamines^{11,12} as well as aquonickel (II)¹³⁻¹⁵. Cyanide ions react with mono (aminocarboxylato) complexes of nickel (II) to form Ni(CN)₄²⁻ complex releasing the aminocarboxylate ligand according to the equation



But the kinetic and mechanistic studies on the binuclear complexes of nickel (II) have attracted little attention so far¹⁶⁻¹⁸. We had occasion to reinvestigate the reaction between Ni₂TTHA and cyanide, earlier reported by Stara and Kopanica¹⁶, and to disprove their mechanism^{17,18}. We also undertook the study of Ni₂DTPA-CN⁻ reaction to gain further understanding of the reaction pathways of binuclear complexes in substitution processes.

In this work the kinetics and mechanism of the substitution reaction of another binuclear complex of nickel(II) viz. Ni₂EGTA with cyanide ion has been investigated and interpreted in further support of the mechanism proposed by us¹⁸.

EXPERIMENTAL SECTION

EGTA was obtained through the courtesy of Geigy chemical company (Switzerland) and was recrystallised twice by dissolving the acid in hot water with the aid of sodium hydroxide and precipitating

the same by adjusting the pH of solution to 2 with dilute HClO₄. The recrystallised acid was dried in an oven at 110°C. It was standardised by potentiometric titration against CO₂ free NaOH. Nickel perchlorate, supplied by alpha Inorganics, was recrystallised before use. A stock solution of Ni(ClO₄)₂ was standardized against EDTA by complexometric titration¹⁹. A solution of Ni₂EGTA was prepared by adding a slight excess of Ni ion over stoichiometric amount of EGTA and removing excess Ni as Ni(OH)₂ at pH 10 by Millipore filtration using 0.45 micrometer filter. The clear solution of Ni₂EGTA was standardized by the addition of a fifty fold excess of NaCN at pH 11.0. All other chemicals were of AR grade and were used without further purification. All solutions were prepared in double distilled water. All pH measurements were made on an Elico digital pH meter model LI-120.

RESULT AND DISCUSSION

The pH dependence of the forward reaction is given in figure 1.1 and Table 1.1. Under the condition where order dependence in cyanide is one. It was seen that the rate remains almost constant in the pH range 9.5-11.0. But it decreases below pH 9.0. As found also in our earlier studies¹⁸ on Ni₂TTHA and Ni₂DTPA reactions. This is due to the formation of less reactive species HCN below pH 9.0. The initial linear portion of the plot of log k_f vs -log [H⁺], (K_f=K_{obsd}/[CN⁻]_T) gives a slope equal to one (fig.1.1). This value indicates that one HCN is involved in addition to two cyanides up to the rate determining step below pH 9.0.

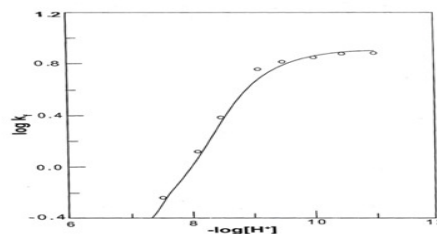


Fig 1.1 Effect of pH on the reaction of cyanide ion with Ni₂EGTA.

Received: July 01, 2012; Revised: Aug 20, 2012; Accepted: Sept 25, 2012.

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Table 1.1. Hydrogen ion dependence of the forward rate constant $[Ni_2EGTA]=2.58 \times 10^{-6}M$; $[CN^-]=2.0 \times 10^{-3}M$; $I=0.1M$ ($NaClO_4$); $temp.=25 \pm 0.1^\circ C$.

$-\log [H^+]$	$K_{obsd} S^{-1}$	$K_f = K_{obsd} / [CN^-]_T, M^{-1} S^{-1}$
7.5	1.15×10^{-3}	0.57
8.1	2.40×10^{-3}	1.20
8.5	4.50×10^{-3}	2.25
9.1	11.50×10^{-3}	5.75
9.5	12.90×10^{-3}	6.47
10.0	13.83×10^{-3}	6.92
10.5	14.48×10^{-3}	7.24
10.7	14.72×10^{-3}	7.36
10.9	14.83×10^{-3}	7.41

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