



Effect of acid and ionic strength on the kinetics of electron transfer reaction of n-(2-hydroxy-ethyl) ethylenediamine-n, n', n'-triacetatocobaltate (ii) complex with hypochlorite ion in aqueous acidic medium

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Abstract

The influence of acid and ionic strength on the rate of electron transfer reaction of N-(2-hydroxy-ethyl)ethylenediamine-N,N',N'-triacetatocobaltate(II)(hereafter, $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$) complex with Hypochlorite ion in aqueous nitric acid medium have been studied at $I = 0.2 \text{ mol dm}^{-3}(\text{NaNO}_3)$, $[\text{H}^+] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $T = 300 \pm 1 \text{ K}$ and $\lambda_{\text{max}} = 525 \text{ nm}$. Stoichiometric study showed 1:1 mole ratio. The rate law derived from the kinetic study under pseudo first order condition is $\frac{d[\text{Co(III)HEDTA(OH}_2\text{)}]}{dt} = k_2[\text{Co(II)HEDTA}^-][\text{ClO}^-]$. The rate constant of reaction, k_2 varies inversely with acid concentration, $[\text{H}^+]$. The overall rate law is therefore represented as: $\frac{d[\text{Co(III)HEDTA(OH}_2\text{)}]}{dt} = 2.28 \times 10^{-4}[\text{H}^+]^{-1}[\text{Co(II)HEDTA(OH}_2\text{)}^-][\text{ClO}^-]$. The reaction displayed positive salt effect which suggests the activated complex was made up of similar charged species. The reaction was catalysed by addition of formate, HCOO^- and potassium, K^+ ions and the Michaelis-Menten's plot gave zero intercept indicating the absence of intermediate complex. A reaction mechanism via an outer-sphere pathway is proposed for this reaction.

Keywords: Aminocarboxylate; Electron Transfer Reaction; Hypochlorite; Ionic Strength; Kinetics.

1. Introduction

Aminopolycarboxylic acids form strong complexes with metal ions when its acidic protons are lost (Anderegg et al., 2005). This property makes it useful complexone in a wide variety of chemical, environmental and medical applications (Michihiko and Sakayu, 1999; Vuckovic et. al., 2011 and Onu et al., 2009, 2011, and 2015). Metal amino carboxylate complexes are used to study phenomenon of the structure, stability, magnetic properties and non-covalent interactions, molecular recognition and regulation of biochemical processes (Vuckovic et. al., 2011). These properties play an important role in metalloenzyme catalyzed reactions. Typical example of the complexes is N-(2-hydroxy-ethyl) ethylenediamine-N, N', N'-triacetatocobaltate (II) ion. Despite the applications of these important complexes, there is a paucity of information on the kinetics of electron transfer reaction of aminocarboxylatocobalt (II) with oxyanions such as hypochlorite ion, ClO^- though, other researchers (Onu et al., 2008, 2009, 2015 and 2016; Naik et al., 2007 and 2010 and Mansour, 2003) have carried out the study using different oxidants. Both inner-sphere and outer-sphere have been reported in these works. Moreover, ClO^- ion is the strongest oxidizing agent of the chlorine oxyanions (Mohammed et al., 2010), thus its reaction with this complex will give us more insight on the mechanism of oxidation of the complex. The kinetic study of these complexes may be used as a model in understanding the mechanism of oxygen transport and metalloenzyme reactions in biological systems (Vuckovic et al., 2011). Also, the study will be used as simple models to understanding or to mimic the biochemical pathways of some metabolic processes which involve the use of co-enzymes.

The interest in this research is to study the influence of acid and ionic strength on the rate of electron transfer reaction of N-(2-hydroxy-ethyl) ethylenediamine-N, N',N'-triacetatocobaltate(II) complex with hypochlorite ion in aqueous nitric acid medium with hope the study will complement much needed kinetic information in the field and highlight more on the pathway of the reaction.

2. Experimental

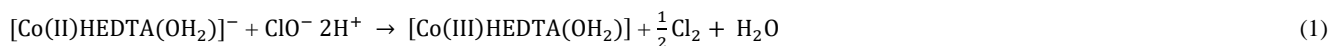
All chemicals and reagents used were of analar grade and distilled water was used in preparing the solutions. While sodium nitrate was used to maintain and investigate the influence of ionic strength of the reaction medium, Nitric acid was used for the investigation of effect of hydrogen ion on the reaction rate. N-(2-hydroxy-ethyl)ethylenediamine-N, N', N'-triacetatecobalt(II) complex (hereafter, $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$) and sodium hypochlorite (NaClO^-) were the reductant and oxidant respectively. The $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$ was prepared according to the method adopted by Onu et al., (2015). This gave λ_{max} of 526 nm after characterization using Cary series 300 Uv-Vis spectrophotometre in the wavelength range of 400 – 800 nm. Stock solution of various reagents were prepared by dissolving accurately weighed amounts of each in a known volume of distilled water.

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method (Onu et al., 2009, 2010, and 2015). The concentration of $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$ was kept constant at $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ while that of ClO^- was varied from 4 folds below and above. The reactions were allowed to go to completion at constant $[\text{H}^+]$ ($\text{HNO}_3 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$), ionic strength ($\text{NaNO}_3 = 0.1 \text{ mol dm}^{-3}$), $\lambda_{\text{max}} = 525 \text{ nm}$ $T = 300 \pm 1 \text{ K}$. The stoichiometry (indicated by the point of inflexion) of the reaction was determined from the plot of absorbance against mole ratio $[\text{ClO}^-]/[\text{Co(II)HEDTA(OH}_2\text{)}]^-$

The rate of the reaction was monitored by recording the change in absorbance at 525 nm on a Sherwood Colorimeter 254. The kinetic study was carried out under pseudo-first order conditions with the concentration of $[\text{Co(II)HEDTA(OH}_2\text{)}]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ and that of the oxidant, ClO^- in at least 12-fold excess over the reductant at temperature of $300 \pm 1 \text{ K}$, ionic strength of 0.5 mol dm^{-3} and $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$. Pseudo-first order rate constants (k_{obs}) for the reactions were obtained from slope of the plots of $\log(A_\infty - A_t)$ versus time. Where A_∞ is the absorbance at infinity and A_t is the absorbance at time t. The order with respect to the oxidant concentration ($[\text{ClO}^-]$) was determined from the slope of the plots of $\log k_{\text{obs}}$ versus $\log [\text{ClO}^-]$. The second order rate constants, k_2 were obtained from k_{obs} as $k_{\text{obs}}/[\text{ClO}^-]$ and the results are presented in Table 1. The effects of change in acid concentration, ionic strength on the reaction rate were studied under the reaction condition stated in Table 2 and 3 respectively. Effect of added ions is investigated and reported in Table 4 to help us assign the mechanistic pathway for the reaction. Likely presence of free radical species was tested by the addition of 5.0 cm^3 of acrylamide to a partially oxidized reaction mixture.

3. Result and discussions

The result of spectrophotometric titration showed that one mole of the reductant was oxidised by one mole of the oxidant. This is in conformity with stoichiometric equation presented in Equation 1:



This stoichiometry (1:1) may be attributed to the fact that, one mole of electron was transferred in the reaction of complex to form Co (III) complex. Similar results have been reported in converting Mn(III) to Mn(V) during the Jacobsen epoxidation reaction and in the conversion of Ce^{3+} to Ce^{4+} (Perumareddi et al., 2003) which involved hypochlorite ion. The spectrum of the reaction product showed two maxima at 381 and 534 nm using Carey series 300 Uv-Vis spectrophotometre in the wavelength range of 400 – 800 nm. This is typical spectrum of Co (III) (Abdel-Khalek et al., 1993; Mansur, 2003; Perveen et al., 2013 and Onu et al., 2009, 2015 and 2016).

The pseudo – first order plots was linear to more than 70% extent of the reaction which suggests a first order dependence of rate on $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$. The slope obtained from the logarithmic plot of k_{obs} versus $[\text{ClO}^-]$ was 1.03 indicating first order dependence with respect to $[\text{ClO}^-]$. The reaction is second order overall at constant $[\text{H}^+]$ concentrations. Therefore the rate equation for the reaction is

$$\frac{d[\text{Co(III)HEDTA(OH}_2\text{)}]}{dt} = k_2[\text{Co(II)HEDTA(OH}_2\text{)}]^{-}[\text{ClO}^-] \quad (2)$$

Where $k_2 = (3.13 \pm 0.09) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Variation in hydrogen ion concentration showed that the reaction rate decreased with increase in $[\text{H}^+]$ within the concentration range investigated. This inverse relationship implies that there is deprotonation pre-equilibrium step and the rate determining step involves both the deprotonated and undeprotonated species (Wilkins, 2002 and Onu et al., 2009, 2015 and 2016).

Similar inverse dependence on the acid has been reported (Onu et al., 2009, 2015 and 2016) for reaction involving this complex with oxyanions. The slope obtained from the plot of $\log k_1$ vs $[\text{H}^+]$ was -0.70, indicating negative first order with respect to acid concentration. Also plot of k_2 vs $[\text{H}^+]^{-1}$ was linear with zero intercept. The overall rate equation showing acid dependence effect is represented in Equation 3:

$$\frac{d[\text{Co(III)HEDTA}]}{dt} = (a[\text{H}^+]^{-1})[\text{Co(II)HEDTA}^{-}][\text{ClO}^-] \quad (3)$$

Where $a = 2.280 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

The observed first order dependence of the reaction rates on both [reductants] and $[\text{ClO}^-]$ is a common feature of hypochlorite ion reactions (Jiann-Kuo, 1987; Idris et al., 2015).

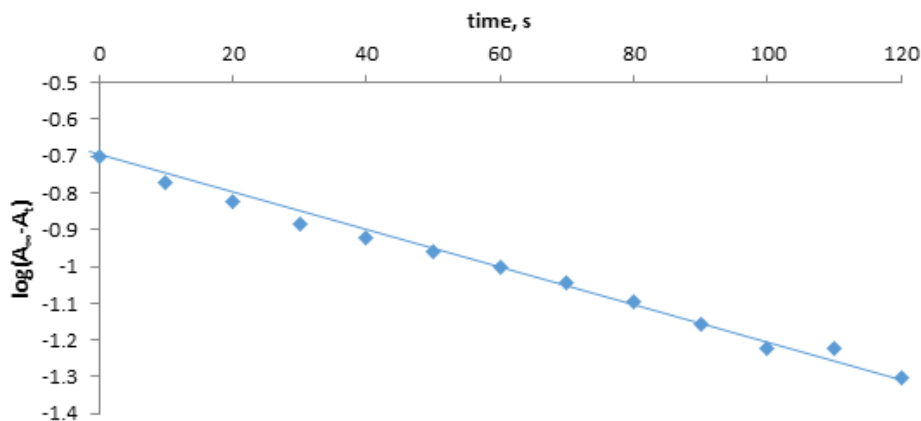


Fig. 1: Typical Pseudo-First Order Plot for the Reaction.

Table 1: The Pseudo-First Order And Reaction Rate Constants for the Reaction of $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^-$ and ClO^- at $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol Dm}^{-3}$, $T = 300 \pm 1\text{K}$ and $\Lambda_{\text{max}} = 525 \text{ Nm}$

$10^3 [\text{ClO}^-]$, mol dm^{-3}	$10^3 [\text{H}^+]$ mol dm^{-3}	10 I mol dm^{-3}	$10^3 k_{\text{obs}}$ S^{-1}	$10^2 k_2$ $\text{dm}^3 \text{mol}^{-1} \text{S}^{-1}$
50	10	2.0	1.6	3.2
60	10	2.0	1.8	3.0
70	10	2.0	2.1	3.0
80	10	2.0	2.5	3.2
90	10	2.0	2.8	3.1
100	10	2.0	3.2	3.2
110	10	2.0	3.5	3.2
120	10	2.0	3.7	3.1

Table 2: Effect of Acid on the Reaction Rate for the Reaction of $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^-$ and ClO^- at $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol Dm}^{-3}$, $T = 300 \pm 1\text{K}$ and $\Lambda_{\text{max}} = 525 \text{ Nm}$

$10^3 [\text{ClO}^-]$, mol dm^{-3}	$10^3 [\text{H}^+]$ mol dm^{-3}	10 I mol dm^{-3}	$10^3 k_{\text{obs}}$ S^{-1}	$10^2 k_2$ $\text{dm}^3 \text{mol}^{-1} \text{S}^{-1}$
90	6.0	2.0	4.0	4.4
90	8.0	2.0	3.4	3.8
90	10	2.0	2.7	3.0
90	12	2.0	2.4	2.6
90	14	2.0	2.1	2.4
90	16	2.0	1.8	2.0

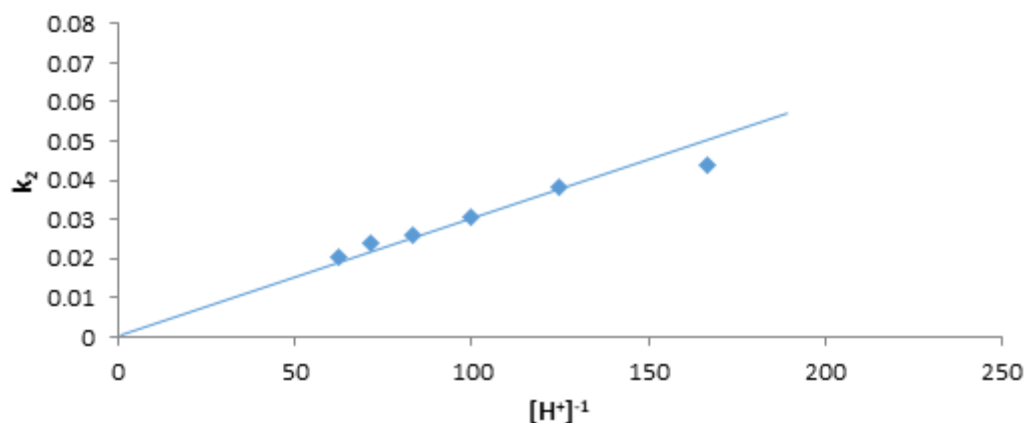


Fig. 2: Plot Of k_2 Versus $[\text{H}^+]^{-1}$ for the Reaction at $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol Dm}^{-3}$, $\text{ClO}^- = 9.0 \times 10^{-2} \text{ mol Dm}^{-3}$, $I = 0.2 \text{ Mol}$.

Table 3: Effect of Ionic Strength of the Medium on the Reaction Rate for the Reaction of $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^-$ and ClO^- at $[\text{Co}^{\text{II}}\text{hedta}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol Dm}^{-3}$, $T = 300 \pm 1\text{K}$ and $\Lambda_{\text{max}} = 525 \text{ Nm}$

$10^3 [\text{ClO}^-]$, mol dm^{-3}	$10^3 [\text{H}^+]$ mol dm^{-3}	10 I mol dm^{-3}	$10^3 k_{\text{obs}}$ S^{-1}	$10^2 k_2$ $\text{dm}^3 \text{mol}^{-1} \text{S}^{-1}$
90	10	2.0	2.9	3.2
90	10	3.0	3.2	3.6
90	10	4.0	3.8	4.2
90	10	5.0	3.9	4.4
90	10	6.0	4.0	4.5
90	10	7.0	4.3	4.8
90	10	8.0	4.8	5.3

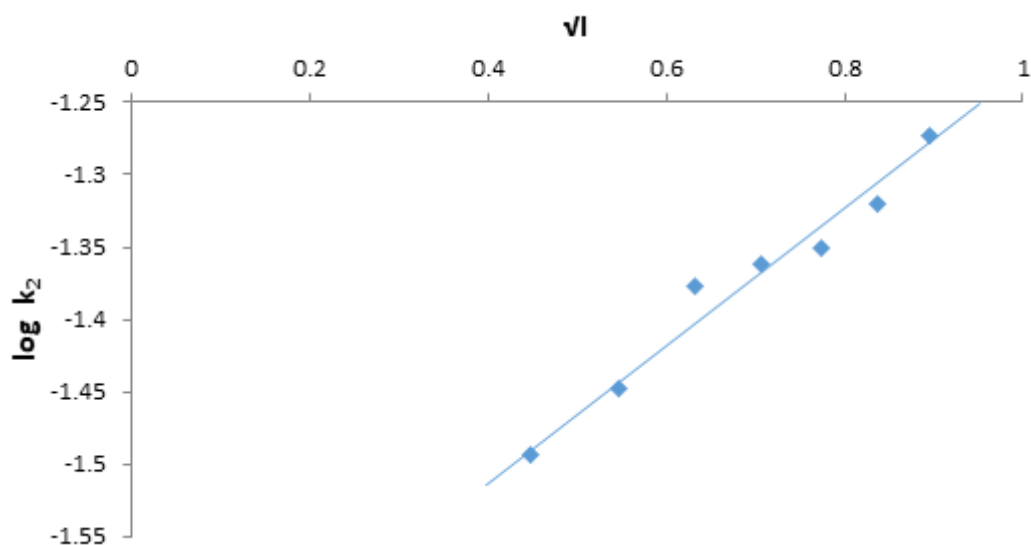


Fig. 3: Plot of Log k_2 versus \sqrt{I} for the Reaction.

Table 4: Effect of Added Anions on the Reaction Rate of $[\text{Co}(\text{II})\text{HEDTA}(\text{OH}_2)]^-$ with ClO^- at $[\text{Co}(\text{II})\text{HEDTA}(\text{OH}_2)] = 5.0 \times 10^{-3} \text{ mol Dm}^{-3}$, $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol Dm}^{-3}$, $I = 0.2 \text{ Mol Dm}^{-3}$, $T = 299 \pm 1\text{K}$ and $\Lambda_{\text{max}} = 525 \text{ Nm}$

X	$10^2 [\text{X}], \text{ mol dm}^{-3}$	$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10^2 k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
HCOO ⁻	0.0	2.76	3.07
	1.0	2.70	3.00
	2.0	2.63	2.92
	3.0	3.02	3.36
	4.0	2.84	3.16
	5.0	2.58	2.87
K ⁺	0.0	2.76	3.07
	1.0	2.78	3.09
	2.0	3.03	3.36
	3.0	2.46	2.74
	4.0	3.13	3.48
	5.0	3.22	3.58

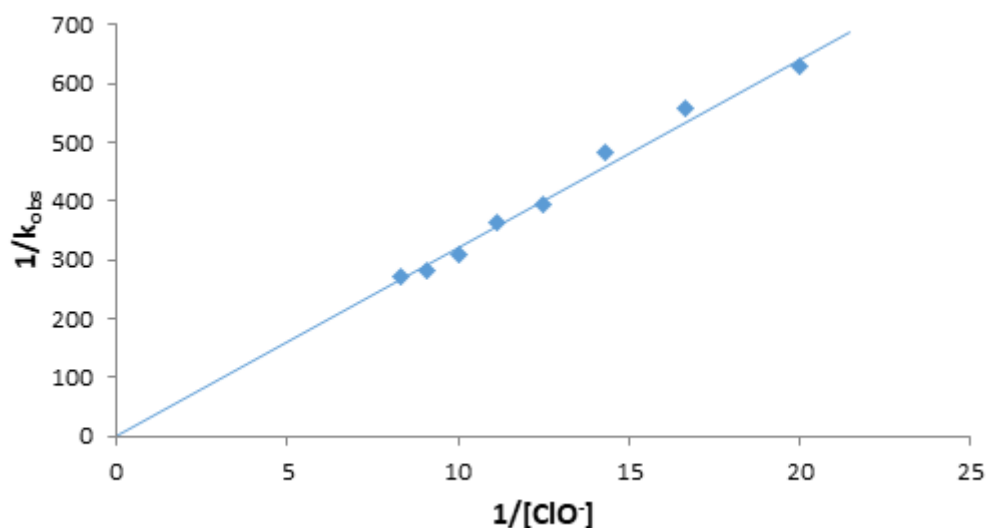
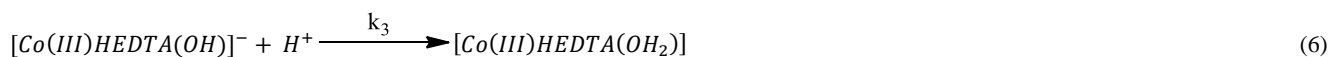
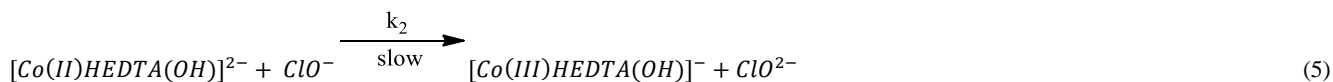
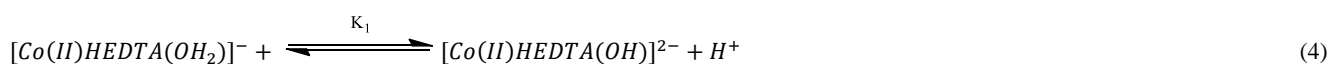


Fig. 4: Michaelis-Menten Plot for the Reaction.

The rate of the reaction increased with increase in ionic strength of the reaction medium in the concentration range investigated (Table 3) suggesting positive Bronsted-Debye salt effect (Benson, 1969). This shows that there may be the presence of similar charged species during the formation of activated complex (Atkins and de Paula, 2002) for the reaction. Positive value of the slope of plot of $\log k_2$ versus \sqrt{I} (Figure 3.0) supported the presence of two similar charged species at the rate determining step.

The rate of reaction was found to decrease by the addition of formate ion and increase with addition K^+ ion. The result is presented in Table 4. This showed that the reaction is catalysed by the presence of both added cation and anion which implies that an outer-sphere mechanism is likely to be in operation. This may be supported by the Michaelis - Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{ClO}^-]$ which had zero intercept suggesting the absence of an intermediate in the rate determining step, thus, an outer-sphere mechanism is likely to be in operation. The free radical species was not detected as the reaction progresses evidenced by absent of gel formation upon addition 5.0 cm^3 of acrylamide.

In view of the above results obtained and discussions, the following reaction mechanism is hereby proposed via an outer-sphere pathways:



$$\frac{d[Co(III)HEDTA(OH_2)]}{dt} = k_2[Co(II)HEDTA(OH)]^{2-}[ClO^-] \quad (8)$$

$$\text{But } [Co(II)HEDTA(OH)]^{2-} = \frac{K_1[Co(II)HEDTA(OH_2)]^-}{[H^+]} \quad (9)$$

$$\text{Hence, } \frac{d[Co(III)HEDTA(OH_2)]}{dt} = \frac{K_1 k_2}{[H^+]} [Co(II)HEDTA(OH_2)]^- [ClO^-] \quad (10)$$

This is analogous to Eq. 3, where $a = K_1 k_2$

4. Conclusion

The influence of acid and ionic strength on the rate of electron transfer reaction of N-(2-hydroxy-ethyl)ethylenediamine-N, N', N'-triacetatecobaltate(II) complex with hypochlorite ion in aqueous nitric acid medium was carried out. While the rate of the reaction was found to increase with increase in ionic strength of the reaction medium, the rate was inversely dependent on acid concentration, $[H^+]$. The experimental data showed that, the electron transfer reaction proceeds through outer-sphere mechanism and a plausible mechanistic pathway which explained the data was proposed for the reaction.

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