

# KINETICS AND MECHANISM OF FORMATION OF CHROMIUM(III)-*TRANS*-1,2-DIAMINECYCLOHEXANE TETRAACETATE COMPLEX FROM TRIS(ETHYLENEDIAMINE)-CHROMIUM(III) ION AND *TRANS*-1,2-DIAMINECYCLOHEXANE-N,N,N',N'-TETRAACETIC ACID IN ALKALINE MEDIA

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Kinetics of formation of chromium(III)*trans*-1,2-diaminecyclohexane N,N,N',N'-tetracetate (Cr(III)-CDTA) from *tris*(ethylenediamine)chromium(III) ion  $[\text{Cr}(\text{en})_3]^{3+}$  and *trans*-1,2-diaminecyclohexane-N,N,N',N'-tetra acetic acid (CDTA) has been studied spectrophotometrically under different conditions. The following rate law has been established

$$\text{Rate} = [k_1 + k_2[\text{CDTA}]][\text{Cr}(\text{en})_3^{3+}]$$

An increase in *pH* decreases the observed rate constant value ( $K_{\text{obs}}$ ) but the rate of formation is found to increase with [CDTA]. Corresponding activation parameters have also been evaluated. A suitable reaction scheme, consistent with our kinetic data has been proposed.

**Key Words:** Kinetics; Formation; Substitution; Spectrophotometer; Rate Constant and Rate Law

## Introduction

The substitution reactions of octahedral complexes of Co(III) and Cr(III) are very interesting as they do not follow any single mechanism<sup>1-10</sup>. Experimental evidences piled up over the years indicate that reaction path depends on the nature of the substrate complex as well as the substituting ligands. Though a fairly large work has been carried out to study the kinetics of the complex formation and substitution, little attention has, as yet been, given to the reactions involving the substitution of chelating ligands by a multidentate ligand. It was therefore thought worthwhile to study the kinetics and mechanistic aspects of the title reaction which involves the substitution of a chelating agent by a multidentate ligand.

## Materials and Method

All the reagents used were of highest available grade. Chromic chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) (BDH, London) and *trans*-1,2-diamino cyclohexanetetraacetic acid (Aldrich) were used.

$[\text{Cr}(\text{en})_3]^{3+}$  (Complex-I) was prepared by the method as outlined in literature<sup>11</sup> and characterised by elemental analysis and IR spectral data. Absorption

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spectra of (Complex-I) solution ( $2 \times 10^{-3} \text{ mol dm}^{-3}$ ) in water was recorded by a CECIL Ultraviolet Double Beam Spectrophotometer exhibits  $\lambda_{\text{max}}$  at 460nm which is consistent with reported in literature<sup>3</sup>. The composition of the product complex (Complex-II) was determined by recording the spectra of three different solutions thermally equilibrated to 338.15K for 24h in which the concentration of Complex-I and CDTA were maintained at 1:1, 1:2 and 1:3 ratios. All the three compositions exhibited identical spectra having maximum absorption at 390 and 550nm. The 1:1 metal ligand composition of the product (Complex-II) was verified by Job's method of continuous variation.

Spectral changes with time associated with the product complex (Complex-II) (Fig. 1) showed two clear isobestic points at 438 and 480nm throughout the period in which the data were recorded. These isobestic points indicate the existence of an intermediate  $[\text{Cr}(\text{en})_3]^{3+} \text{-----} \text{CDTA}^{4-}$  as  $[\text{Cr}(\text{en})_3]^{3+}$  shows very little absorbance at these wavelengths while final product shows maximum absorbance at 550nm.

Sodium nitrate was used to maintain the ionic strength of the reaction medium and the pH of the system was adjusted (Systronic digital pH meter, 335) with the

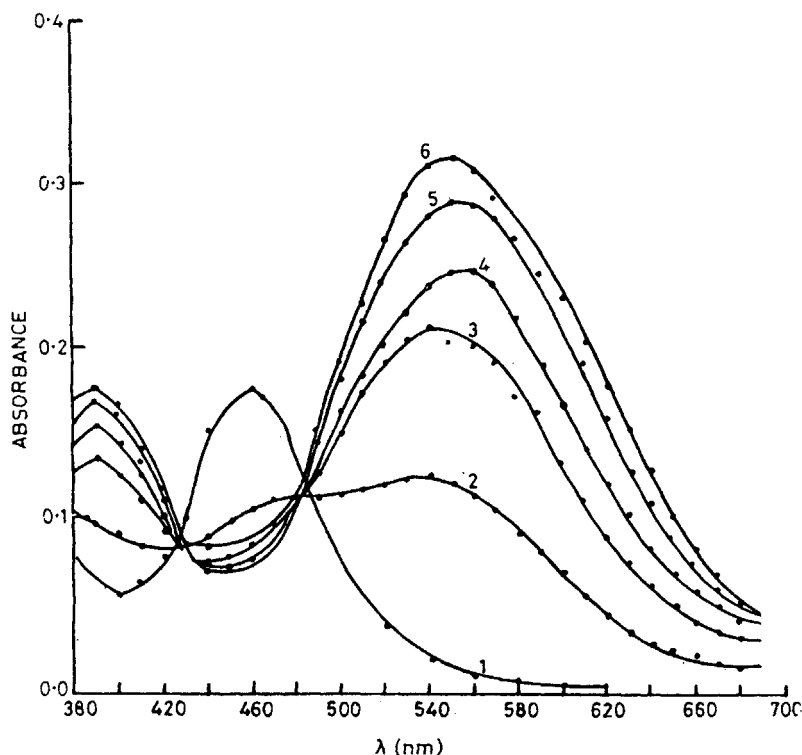


Fig. 1 Repetitive scan of the reaction mixture during a typical kinetic run:  $([\text{Cr}(\text{en})_3]^{3+} + \text{CDTA} \text{ system})$   $[\text{Cr}(\text{en})_3]^{3+} = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{CDTA}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ , pH 8.0,  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ) and temp. = 338.15K (Curves 1-6 were obtained after time intervals of 0, 15, 20, 30, 60 and 120 min, respectively)

addition of  $\text{HNO}_3/\text{NaOH}$ . Freshly prepared solutions of the substituting ligand were employed throughout the experiment. All kinetic experiments were carried out spectrophotometrically by a CECIL Ultraviolet double beam spectrophotometer at 550nm where a substantial difference existed between the absorption of Complex-I and Complex-II as a function of time. The concentration of the substituting ligand, CDTA, was always high so that pseudo-first order rate law could be applied. The pseudo-first order rate constant ( $k_{\text{obs}}$ ) were evaluated graphically from the slope of the linear plot of  $\log(A_\infty - A_0)/(A_\infty - A_t)$  versus time ( $t$ ), where  $A_\infty$ ,  $A_t$  and  $A_0$  were the absorbance at infinite time at an arbitrary time ' $t$ ' and at the beginning of the reaction, respectively. The temperature was controlled with in  $\pm 0.1$  °C. The reported  $K_{\text{obs}}$  values represent an average of three replicate runs and all values were reproducible within  $\pm 3\%$  error limits.

## Results and Discussion

### *Effect of Varying [Complex-I] on Rate Constant*

At fixed  $[\text{CDTA}] = 0.02 \text{ mol dm}^{-3}$ ,  $\text{pH } 8.0$ , ionic strength ( $\mu$ ) =  $0.25 \text{ mol dm}^{-3}$ , temperature  $338.15\text{K}$  and at five different  $[\text{complex-I}]$  ( $0.001, 0.002, 0.003, 0.004$  and  $0.005 \text{ mol dm}^{-3}$ ) the  $10^4 \times K_{\text{obs}}$  values were  $5.76, 5.80, 5.78, 5.80$  and  $5.80 \text{ s}^{-1}$ , respectively. The data indicate that the reaction is first order in  $[\text{complex-I}]$ . The rate law may be represented as

$$\frac{d[\text{complex-II}]}{dt} = k_{\text{obs}} [\text{complex-I}]$$

### *Effect of Varying Ionic Strength on Rate Constant*

In these experiments  $[\text{complex-I}]$  and  $[\text{CDTA}]$  were kept constant at  $0.002$  and  $0.02 \text{ mol dm}^{-3}$ , respectively. The  $10^4 \times K_{\text{obs}} \text{ s}^{-1}$  values were  $5.80, 4.86, 2.40, 1.65, 1.37$  and  $1.23$  at  $0.25, 0.50, 1.00, 1.50, 2.00$  and  $2.50 \text{ mol dm}^{-3}$  ionic strength at  $338.15\text{K}$  and  $\text{pH } 8.0$ . The decrease in the rate constant values with ionic strength is in agreement for a reaction between ions having opposite charges. The value of  $Z_A \cdot Z_B$  was  $1.42$ , which is smaller than the expected value if only the reactants were  $[\text{Cr}(\text{en})_3]^{3+}$  and  $\text{CDTA}^{4-}$ . The factor which appears to affect the value of  $Z_A \cdot Z_B$  may be possible formation of ion pairs of  $[\text{Cr}(\text{en})_3]^{3+}$  and  $\text{CDTA}^{4-}$  with  $\text{N}_q^+$  present in sufficient concentration in the reaction medium.

A series of runs at  $\text{pH } 8.0$  to study the effect of different inert electrolytes ( $\text{NaNO}_3, \text{KNO}_3, \text{KCl}, \text{NaCl}$  and  $\text{NaClO}_4$ ) on the rate constant at fixed  $[\text{complex-I}]$  ( $0.002 \text{ mol dm}^{-3}$ ),  $[\text{CDTA}]$  ( $0.02 \text{ mol dm}^{-3}$ ) and temperature  $338.15\text{K}$  indicated that the  $K_{\text{obs}}$  values increased on changing  $\text{Na}^+$  to  $\text{K}^+$  at a particular ionic strength. Similar trend for the substitution reactions has already been reported<sup>12,13</sup>.

### *Effect of Varying pH on Rate Constant*

The  $K_{\text{obs}}$  values at fixed  $[\text{complex-I}]$  ( $0.002 \text{ mol dm}^{-3}$ ), ionic strength ( $0.25 \text{ mol dm}^{-3}$ ) and  $[\text{CDTA}]$  ( $0.02 \text{ mol dm}^{-3}$ ) at five different temperatures ( $318.15, 323.15, 328.15, 333.15$  and  $338.15\text{K}$ ) and at  $\text{pH}$  values ranging from  $7.0$

**Table I**  
*Variation of rate constant with pH at different temperatures*

$[\text{Cr}(\text{en})_3]^{3+} = 0.002 \text{ mol dm}^{-3}; [\text{CDTA}] = 0.02 \text{ mol dm}^{-3}; \mu = 0.25 \text{ mol dm}^{-3}$					
pH	$K_{\text{obs}} \times 10^5 \text{ s}^{-1}$				
	318.15K	323.15K	328.15K	333.15K	338.15K
7.00	9.34	17.60	29.50	52.50	71.40
7.50	8.56	16.08	27.60	48.08	64.46
8.00	7.68	14.70	25.40	43.20	58.00
8.50	6.45	13.25	22.26	38.30	51.28
9.00	5.69	11.80	19.80	33.30	44.90
9.50	4.30	10.35	17.38	28.78	37.78
10.00	3.02	8.60	14.60	23.80	31.50
10.50	2.34	7.18	12.45	19.42	25.43

to 10.50 are given in Table I. The data indicate that  $K_{\text{obs}}$  values decrease with pH at each temperature. The predominant species of CDTA in the studied pH range are  $\text{HCDTA}^{3-}$  and  $\text{CDTA}^{4-}$  in varying proportions. The  $\text{pK}_1$  and  $\text{pK}_2$  values for CDTA are 11.78 and 6.20 at 293.15K. The donor capacity of the substituting ligand decreases at lower pH values since the CDTA anionic species  $\text{HCDTA}^{3-}$  and  $\text{CDTA}^{4-}$  have a tendency for protonation of carboxylate ion. At higher pH values, CDTA mainly exists as  $\text{CDTA}^{4-}$ , the donor capacity increases but  $K_{\text{obs}}$  values have been found to decrease. This is probably due to that at higher pH,  $\text{OH}^-$  ion having smaller size enters the inner periphery of the solvation layer of  $[\text{Cr}(\text{en})_3]^{3+}$  and forms an ion pair of high degree of stability with strong electrostatic interactions and hydrogen bonding, whereas  $\text{CDTA}^{4-}$  being bulky in size does not favour solvation and also interacts by much weaker electrostatic interactions through the intervening anionic and cationic solvation shells (Grothius Transfer Mechanism). Thus both the species  $\text{HCDTA}^{3-}$  and  $\text{CDTA}^{4-}$  with their negative charges distributed over the carboxylate groups can only be expected to form ion pairs with  $[\text{Cr}(\text{en})_3]^{3+}$  which are much less stable than the one formed with  $\text{OH}^-$  ions.

#### *Effect of Varying CDTA on Rate Constant*

At fixed  $[\text{CDTA}]$  ( $0.002 \text{ mol dm}^{-3}$ ), ionic strength ( $0.25 \text{ mol dm}^{-3}$ ) and pH 8.0, the  $[\text{CDTA}]$  was varied in the range 0.01 to  $0.06 \text{ mol dm}^{-3}$  at five temperatures (318.15, 323.15, 328.15, 333.15 and 338.15K). In each case the  $K_{\text{obs}}$  values were found to increase with  $[\text{CDTA}]$  at each temperature. A plot of  $K_{\text{obs}}$  versus  $[\text{CDTA}]$  was linear at all the temperatures with an intercept (Fig. 2). The values of  $K_{\text{obs}}$  have been given in Table II.

The reaction was found to obey Arrhenius temperature dependence. Activation parameters  $\Delta H^*$  and  $\Delta S^*$  have been evaluated for the gross rate constants  $k_1$  and  $k_2$  using Eyring plots (Fig. 3).

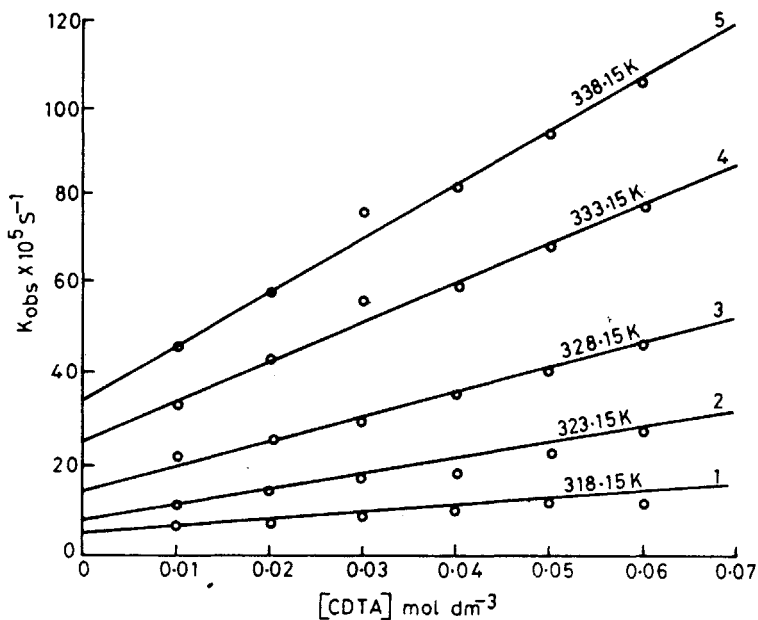


Fig. 2 Effect of CDTA concentration on rate constant of  $[\text{Cr}(\text{en})_3]^{3+} + \text{CDTA}$  system:  $[\text{Cr}(\text{en})_3]^{3+} = 2 \times 10^{-3} \text{ mol dm}^{-3}$  and  $\mu = 0.25 \text{ mol dm}^{-3}$

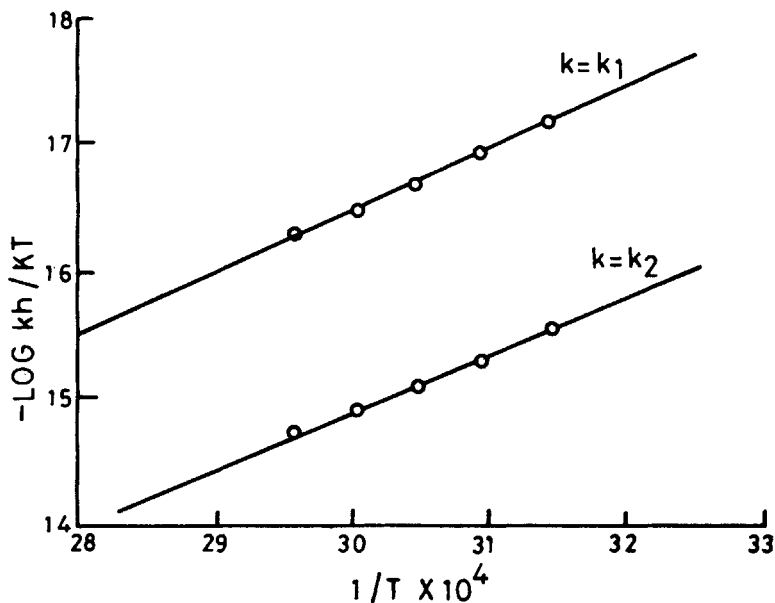
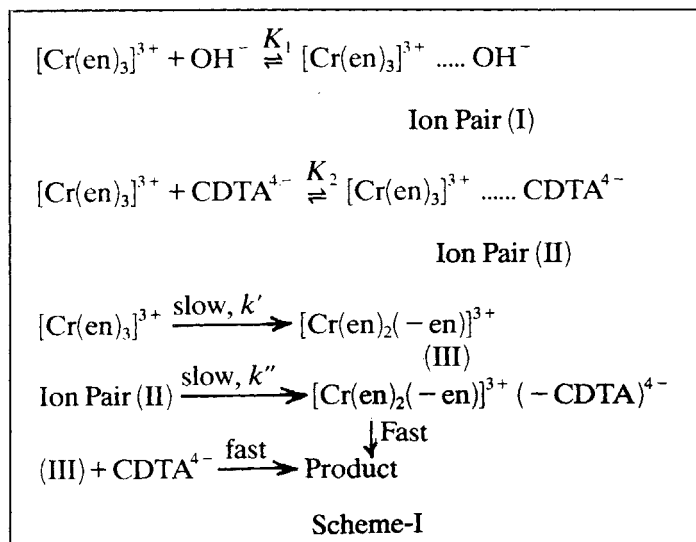


Fig. 3 Eyring plot for  $[\text{Cr}(\text{en})_3]^{3+} + \text{CDTA}$  system

Based on the results Scheme-I may be proposed to explain the variation in rate with [CDTA] and pH.



**Table II**

*Variation of rate constant with [CDTA] at different temperatures*

$[\text{Cr}(\text{en})_3]^{3+} = 0.002 \text{ mol dm}^{-3}$ ;  $\mu = 0.25 \text{ mol dm}^{-3}$ ; and  $\text{pH} = 8.0$

[CDTA] $\times 10^2$ mol dm <sup>-3</sup>	$K_{\text{obs}} \times 10^5 \text{ s}^{-1}$				
	318.15K	323.15K	328.15K	333.15K	338.15K
1.0	6.53	10.80	21.70	33.10	45.30
2.0	7.68	14.70	25.40	43.20	58.00
3.0	9.20	17.50	29.40	56.10	76.80
4.0	10.70	18.20	35.60	59.40	81.90
5.0	11.90	23.50	41.40	68.90	94.30
6.0	13.10	27.80	46.90	78.20	106.80

The reaction Scheme-I leads to the rate law

$$K_{\text{obs}} = \frac{k' [\text{H}^+]}{K_1 \cdot K_w} + \frac{k'' \cdot K_2}{K_1 \cdot K_w} [\text{H}^+] [\text{CDTA}]$$

and

$$k' [\text{H}^+] / K_1 \cdot K_w = k_1;$$

Table III

Gross rate constants  $k_1$  and  $k_2$  at different temperatures

Temp. (K)	$k_1 \times 10^5 \text{ s}^{-1}$	$k_2 \times 10^3 \text{ mol S}^{-1}$
318.15	4.3	1.74
323.15	7.4	3.48
328.15	14.1	5.39
333.15	23.0	8.94
338.15	32.5	12.27

Table IV

Thermodynamic parameters of Cr-N complexes

Complex	$\text{mol}^n \text{ dm}^{-3}$	Temp. (K)	$\Delta H_1^*$ (KJ mol <sup>-1</sup> )	$\Delta H_2^*$ (KJ mol <sup>-1</sup> )	$\Delta S_1^*$ (JK <sup>-1</sup> )	$\Delta S_2^*$ (JK <sup>-1</sup> )	Reference
Cr-en-CDTA	0.25	338.15	41.5	37.9	-12.1	-10.0	This work
Cr-en-EDTA	3.00	328.15	168.0	29.6	194.5	221.7	4
Cr(BiSH)-EDTA	0.25	318.15	41.0	140.0	-133.4	159.8	5

$$k'' \cdot K_2[\text{H}^+]/K_1 \cdot K_w = k_2$$

so

$$K_{\text{obs}} = k_1 + k_2[\text{CDTA}^{4-}]$$

where  $k_1$  and  $k_2$  are the gross rate constants evaluated from the intercept and slope, respectively, of the linear plot of  $K_{\text{obs}}$  versus  $[\text{CDTA}]$  (Fig. 2). The values of  $k_1$  and  $k_2$  are given in Table-III.

The above proposed reaction scheme proves to be the most probable because the rate law derived from these steps is similar to that derived based upon the experimental observations. The existence of ion pair mechanism may also be explained as there was a decrease of conductance of  $[\text{Cr}(\text{en})_3]^{3+}$  and CDTA (sodium salt) mixture as compared to CDTA (sodium salt) and  $[\text{Cr}(\text{en})_3]^{3+}$  alone. The thermodynamic parameters  $\Delta H^*$  and  $\Delta S^*$  suggest that the reaction between  $[\text{Cr}(\text{en})_3]^{3+}$  and CDTA involves association followed by an associative interchange process. A higher value of  $\Delta H_1^*$  corresponds to the process in which bond breaking (single ended dissociation of a stable chelate ring) is primarily important and a lower values of  $\Delta H_2^*$  (corresponding to  $k_2$ ), suggest an ion-pair mechanism in which bond breaking is synchronous with bond making. The entropies of activation  $\Delta S^*$  for CDTA substitution are also negative which are expected for an asso-

ciating interchange process. Table IV illustrates the thermodynamic parameters obtained in which Cr-N is broken and multidentate chelate ring is formed by ion pair mechanism.

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