

KINETIC AND MECHANISTIC STUDY ON THE SUBSTITUTION REACTION OF AQUO-LIGANDS FROM CIS-DIAQUO-BIS (BIGUANIDE) CHROMIUM(III) ION WITH IMINODIACETIC ACID IN AQUEOUS MEDIUM

A. K. GANGOPADHYAY and G. S. DE

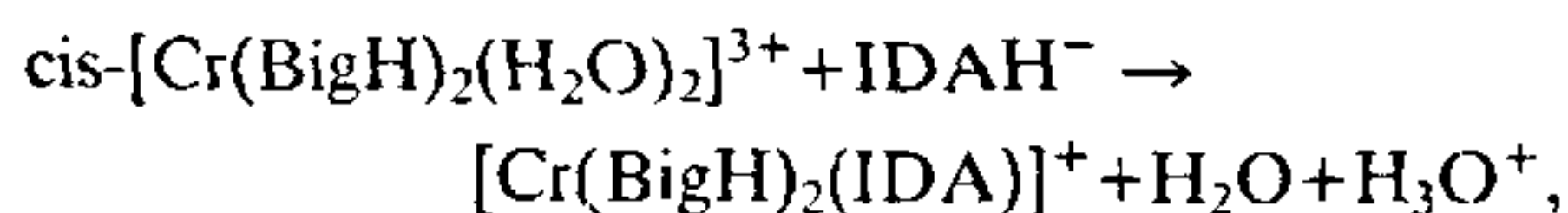
Department of Chemistry, University of Burdwan, Burdwan 713 104, India.

ABSTRACT

The kinetics of substitution of aquo ligands from cis-diaquo-bis (biguanide) chromium(III) ion by iminodiacetic acid in aqueous medium has been studied spectrophotometrically and a rate law has been established. The reaction rate is pH-dependent in the range 3.6 to 4.5. From the values of rate constants at four different temperatures, values of activation parameters, ΔH^\ddagger and ΔS^\ddagger have been evaluated. The results are consistent with a mechanism involving outer sphere association of the reactants followed by associative interchange of this outer sphere complex into the product.

INTRODUCTION

MANY studies¹⁻⁵ on ligand substitution reactions in octahedral complexes indicate that the reactions of Co(III) and Cr(III) systems proceed through I_d and I_a path respectively. However exceptions⁶⁻¹¹ are not rare. Experimental evidence has been adduced that depending on the nature of the system, I_d or I_a mechanism may operate both for Co(III) and Cr(III). Banerjee and coworkers⁸ studied base hydrolyses of $[M(NH_3)_5NCS]^{2+}$ [$M = Co(III), Cr(III)$ and $Rh(III)$] in aqueous organic mixed solvents and observed a significant difference in the relative degree of M-NCS bond breaking [significantly higher for Cr(III)] and M-OH bond making considerably more pronounced for Co(III) and Rh(III) in the three different cases studied. Chatterjee and coworkers¹⁰ studied base hydrolysis of $[Cr(NH_3)_5N_3]^{2+}$ and suggested dissociative mechanism whereas Banerjee and coworkers¹¹ studied base hydrolysis of $[Co(NH_3)_5(S_2O_3)]^+$ and suggested associative character of the reaction. It was therefore thought worthwhile to study the anation reactions of similar aquo complexes of Co(III) and Cr(III). We selected the systems like cis- $[M(BigH)_2(H_2O)_2]^{3+}$ and cis- $[M(DMg)_2(H_2O)_2]^{3+}$ (where $M = Co(III), Cr(III)$) with incoming ligands, such as pyridine carboxylic acids and a series of amino acids for anation reactions. The present paper relates to the reaction



where $IDAH^-$ is the anionic form of iminodiacetic acid.

MATERIALS AND METHODS

cis- $[Cr(BigH)_2(H_2O)_2](ClO_4)_3$ [Complex-I] was prepared *in situ* by the methods described earlier¹²⁻¹⁴. Absorption spectrum of a 0.005 M solution of [complex-I] was taken in a UVISPEK spectrophotometer and the values of λ_{max} were found to be at 385 nm and at 490 nm. The values are identical with those reported earlier¹⁵. The absorption spectra of 1:1, 1:2 and 1:3 mixtures thermostated at 50°C for 48 hr at pH 4.0 and fixed complex concentration of 0.005 M were taken and it was observed that all the solutions had λ_{max} at 490 nm (figure 1).

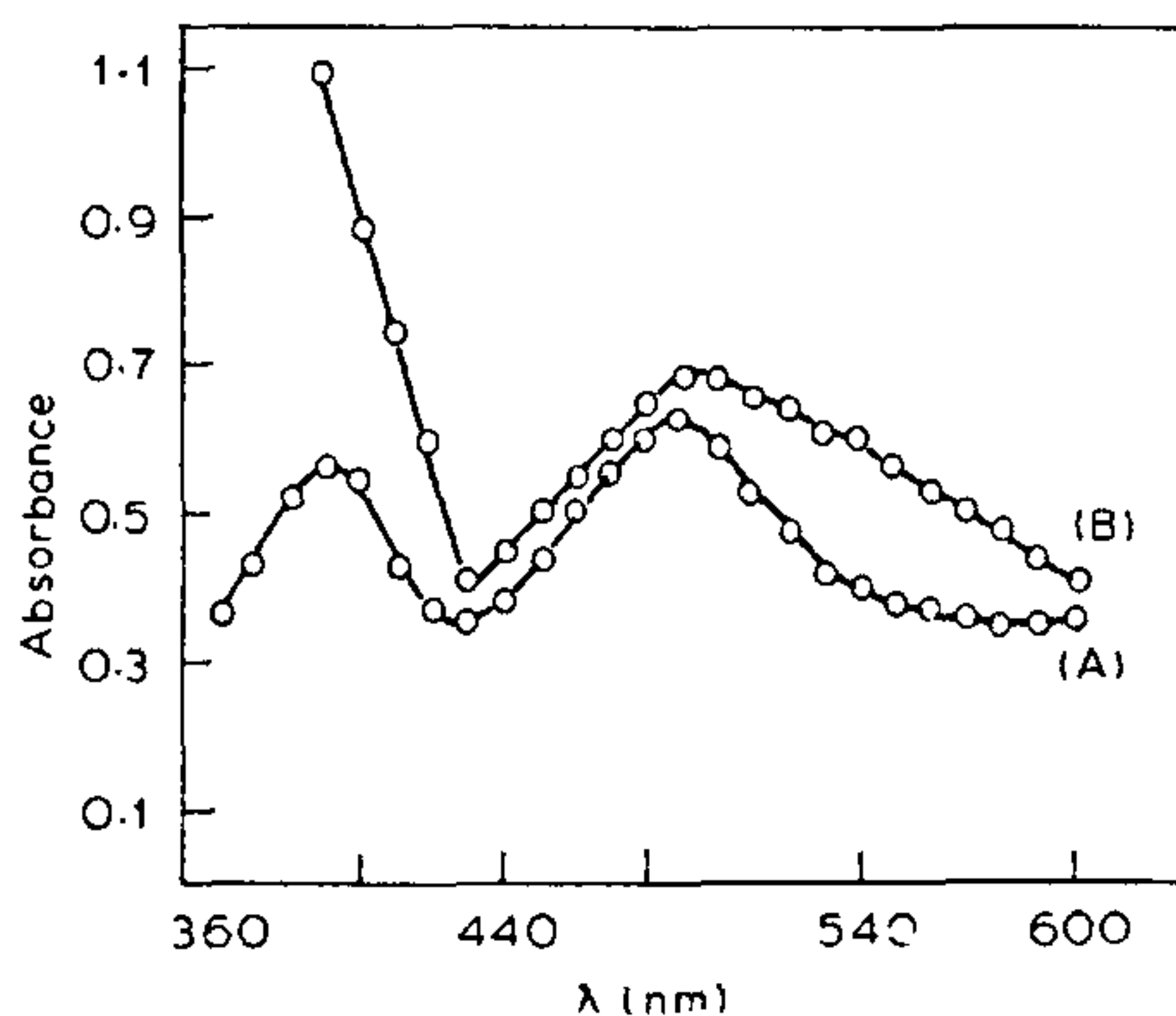


Figure 1. (A) Spectra of 0.005 M $[Cr(BigH)_2(H_2O)_2](ClO_4)_3$ at pH 4.0; (B) Spectra of 0.005 M $[Cr(BigH)_2(IDA)](ClO_4)$ at pH 4.0.

The composition of the product in the reaction mixture was checked by Job's method of continuous variation and had a 1:1 metal ligand ratio in the product. The product of the reaction between $[\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ and iminodiacetic acid was prepared by mixing these in the molar ratio of 1:1 and refluxed for 48 hr on a water bath. The reaction mixture was then concentrated and treated with ether whereupon the solid product was separated. Analyses of the isolated product revealed the composition as $[\text{Cr}(\text{BigH})_2(\text{IDA})]^+$ [complex-II]. Absorption spectrum of the isolated product was taken which also shows λ_{max} at 490 nm. IDA can behave as a tridentate ligand but here it functions as a bidentate one. Hence donation may take place via O,O donor (carboxyl oxygens) or N,O donor centres. In the case of O,O donation a chelate with eight member ring should be produced where a large strain must be operative. So it may easily be concluded that the donation here occurs through N,O donor centres producing a stable five membered ring.

In all the experiments A.R. grade chemicals and distilled water were used.

Kinetic run

All kinetic runs were made on a Hilger UVISPEK spectrophotometer at 540 nm where the absorption of the reacting complex and the complex formed as product differs appreciably. Temperature-equilibrated solutions of iminodiacetic acid and the Complex-I were mixed and the concentrations of the reactants in the experimental solutions were such that the first order rate law was applicable and the pseudo-first order rate constant, k_{obs} , for each experiment was evaluated graphically by plotting $\log (D_\infty - D_0 / D_\infty - D_t)$ vs time t , where D_∞ , D_0 and D_t are the absorbances at infinite time, at the beginning and after time t respectively.

RESULTS AND DISCUSSION

Effect of variation of [complex-I] on rate constant

In experiments at temperature 45°C the substrate [complex-I] was varied from 0.005 M to 0.0075 M at constant excess concentration of 0.1 M iminodiacetic acid. The pseudo-first order rate constants (k_{obs}) were found to be $1.05 \times 10^{-4} \text{ sec}^{-1}$, $1.08 \times 10^{-4} \text{ sec}^{-1}$ and $1.10 \times 10^{-4} \text{ sec}^{-1}$ at [complex-I] concentrations 0.005 M, 0.006 M and 0.0075 M respectively at 45°C and ligand iminodiacetic acid concentration 0.1 M and pH = 4.0.

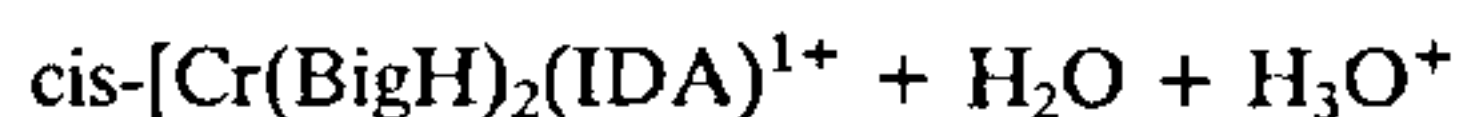
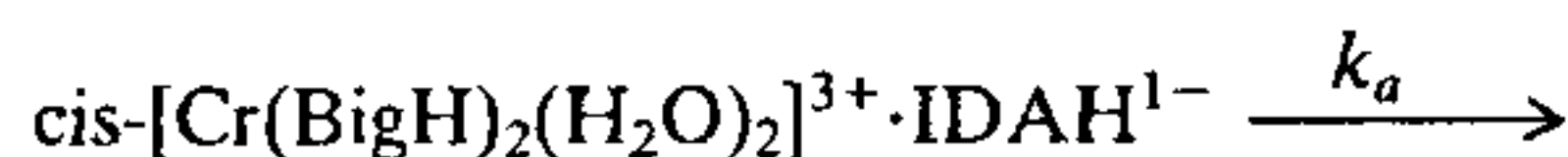
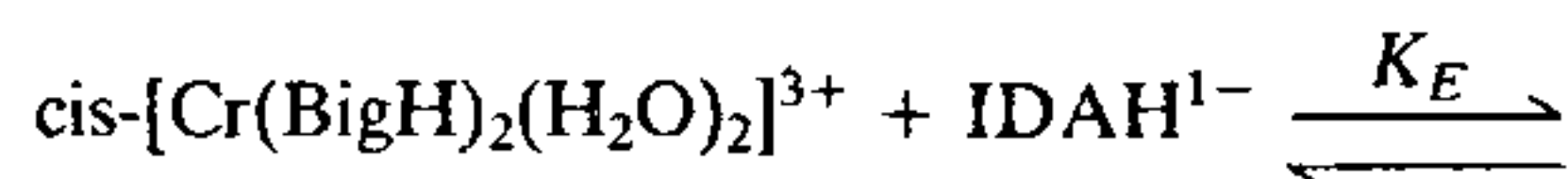
The ionic strength of the medium was fixed at 0.5 M. The values of k_{obs} were in good agreement with the first order rate law:

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

Effect of varying iminodiacetic acid concentration on rate constant

The concentration of iminodiacetic acid $[\text{IDAH}^{1-}]$ was varied in the range 0.05 to 0.15 M at a fixed [complex-I] 0.005 M, pH = 4.0 and ionic strength, μ , 0.05 M. The results presented in table 1 show that the rates increase with increasing $[\text{IDAH}^{1-}]$ attaining a limiting rate at higher [IDAH] and this happens due to completion of ion pair formation at higher $[\text{IDAH}^{1-}]$ ¹⁶.

The following scheme may be proposed to explain the variation of rate at varying concentrations of incoming ligand.



$$\frac{d[\text{Cr}(\text{BigH})_2(\text{IDA})]^{1+}}{dt} = \frac{k_a K_E [\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}]_{\text{total}} [\text{IDAH}]^{1-}}{1 + K_E [\text{IDAH}^{1-}]} \quad (1)$$

$$= k_{\text{obs}} [\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}]_{\text{total}} \quad (2)$$

Table 1 Variation of rate constant (k_{obs}) with $[\text{IDAH}^{1-}]$ at different temperatures $[\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}] = 0.005 \text{ M}$, pH = 4.0

[Iminodiacetic acid] (M)	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$			
	40°C	45°C	50°C	55°C
0.05	0.40	0.62	1.05	3.07
0.075	0.57	0.83	1.43	4.10
0.10	0.72	1.05	1.90	5.30
0.125	0.83	1.25	2.10	6.10
0.15	0.96	1.40	2.30	6.70

where K_E is the ion pair equilibrium constant and k_a the rate constant for conversion of outer sphere complex to inner sphere complex. Therefore,

$$k_{\text{obs}} = \frac{K_a K_E [\text{IDAH}^{1-}]}{1 + K_E [\text{IDAH}^{1-}]} \quad (3)$$

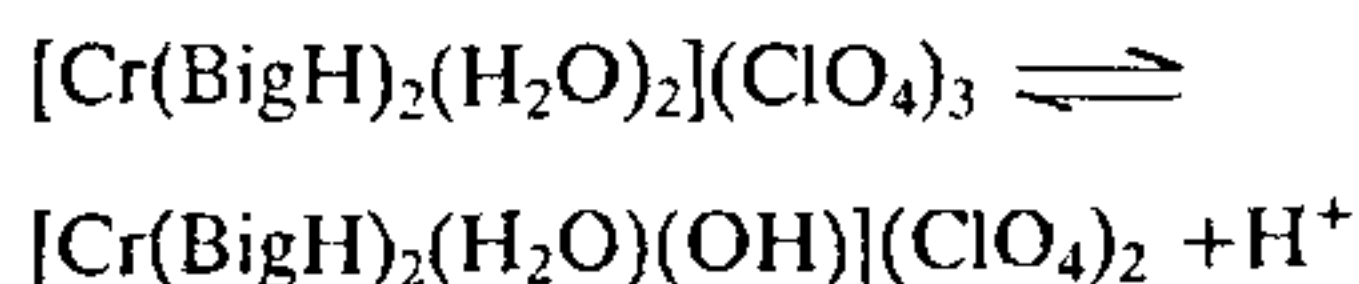
or

$$1/k_{\text{obs}} = 1/K_a + 1/K_a K_E [\text{IDAH}^{1-}]. \quad (4)$$

From (4) it is seen that the plot of $1/k_{\text{obs}}$ vs $1/[\text{IDAH}^{1-}]$ should be a straight line and this was confirmed by figure 2. From such straight lines, the values of k_a (table 2) and K_E were obtained from the intercept ($1/k_a$) and slope ($1/k_a K_E$) respectively. The K_E values are almost constant in the range 1.7 to 3.7 at four different temperatures.

Effect of varying pH on rate constant

Maintaining a constant [complex-I] 0.005 M, [IDAH¹⁻] 0.075 M, ionic strength 0.5 M, the pH of the medium was varied in the range 3.63 to 4.50 [pH was adjusted by adding NaOH and HClO₄]. It was observed that at 45°C the pseudo-first order rate constant k_{obs} were 0.73×10^{-4} , 0.79×10^{-4} , 0.83×10^{-4} , 0.92×10^{-4} and $0.99 \times 10^{-4} \text{ sec}^{-1}$ at pH 3.63, 3.79, 4.0, 4.2 and 4.5 respectively. The small increase in k_{obs} values can be explained in the following manner. The pK of the following equilibrium



determined by pH metric titration was 8.0 at 35°C. So in the above pH range complex-I remains in the diaquo form. The ligand iminodiacetic acid undergoes the following type of dissociation

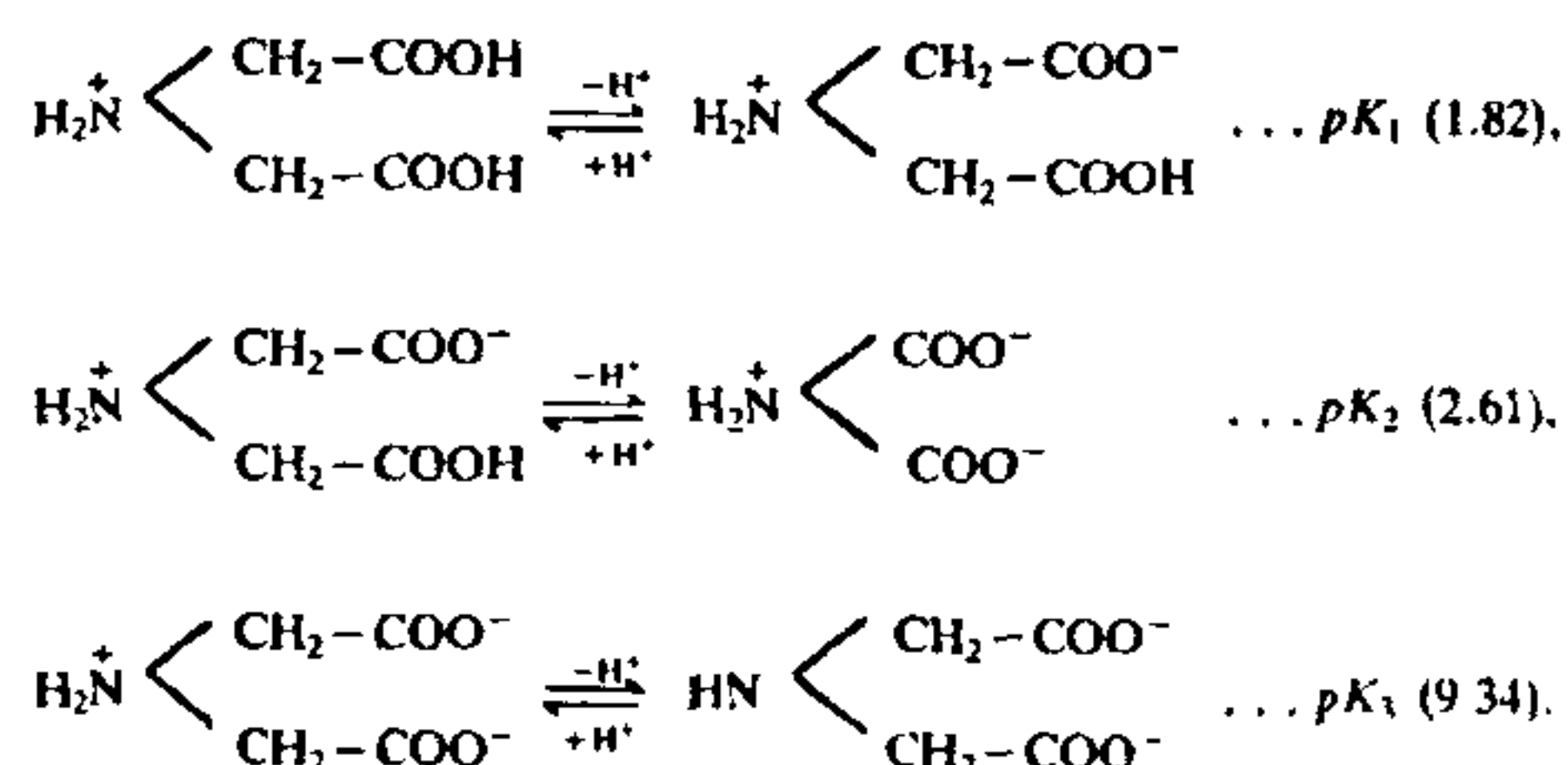


Table 2 Values of k_a for the anation of $[\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2]^{3+}$ by iminodiacetic acid at different temperatures

Temp. (°C)	$k_a \times 10^4 \text{ sec}^{-1}$
40	5.0
45	8.3
50	13.3
55	22.2

Hence at the pH range of 3.6 to 4.5 the major portion of the ligand remains in the mononegative ionic form i.e. (IDAH¹⁻). But at the lower pH range, the percentage of the Zwitterionic form (IDAH) is also not negligible. The ligand capability is always higher with larger negative charge on the ligands. Thus at higher pH the percentage of anionic form goes on increasing, thereby increasing the rate.

Effect of ionic strength on reaction rate

The ionic strength of the medium was adjusted by the addition of sodium perchlorate. The pseudo-first order rate constants at 50°C were 1.43×10^{-4} , 1.24×10^{-4} , and $1.19 \times 10^{-4} \text{ sec}^{-1}$ at ionic strengths 0.5 M, 0.7 M and 1.0 M respectively at [complex-I] 0.005 M, [ligand] 0.075 M and pH = 4.0. The rates decrease with increasing ionic strength of the medium supporting the theory given by Bronsted, Bjerrum, Christiansen and Scatchard for ionic reactions in solutions. However, when the ionic strength of the medium was varied in the range 0.5 M to 1.0 M by the addition of NaNO₃ and [complex-I] 0.005 M, [IDAH¹⁻] 0.075 M and pH

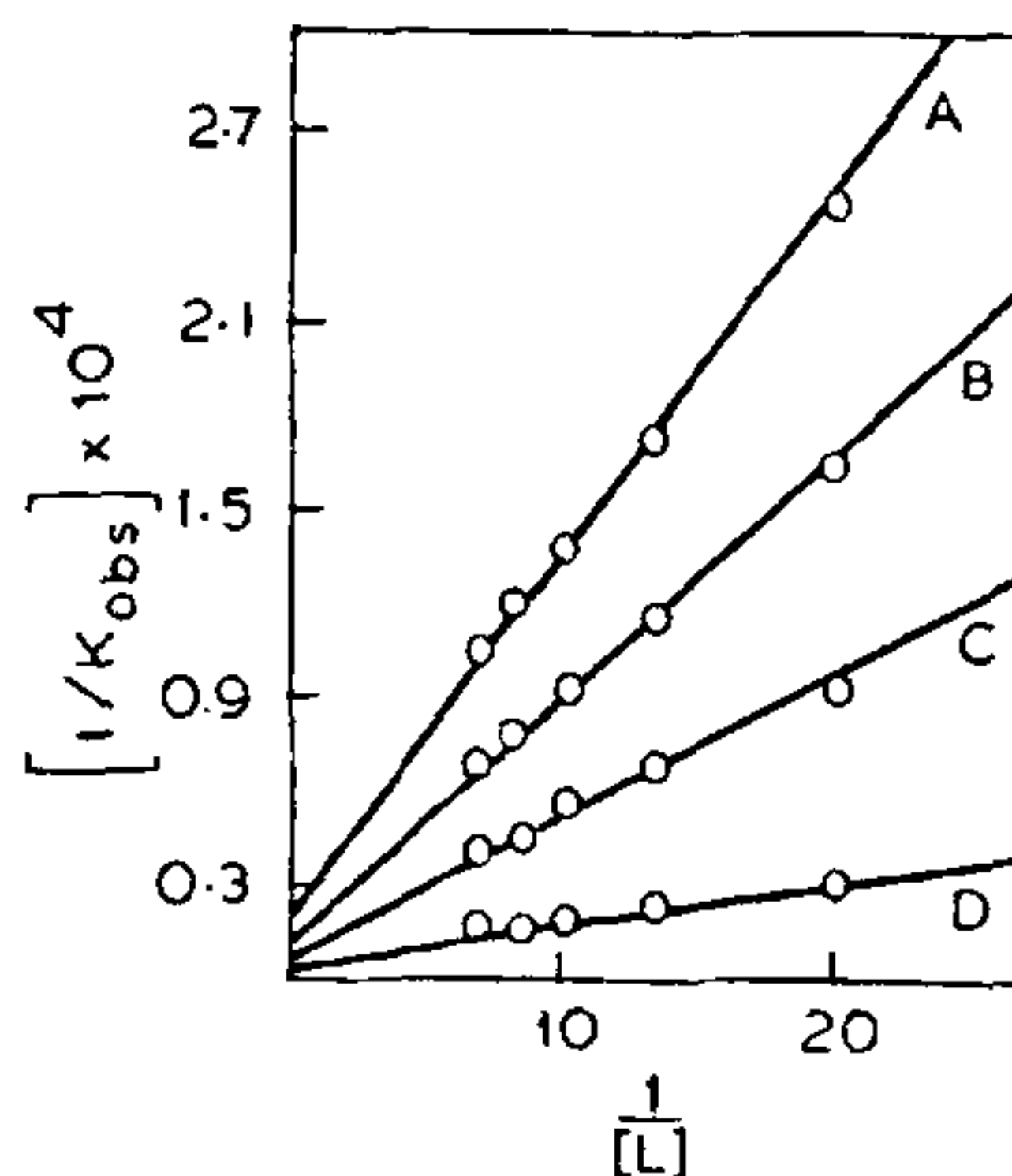


Figure 2. Plot of $1/k_{\text{obs}}$ vs $1/[\text{ligand}]$ at: (A) 40°C, (B) 45°C, (C) 50°C, and (D) 55°C.

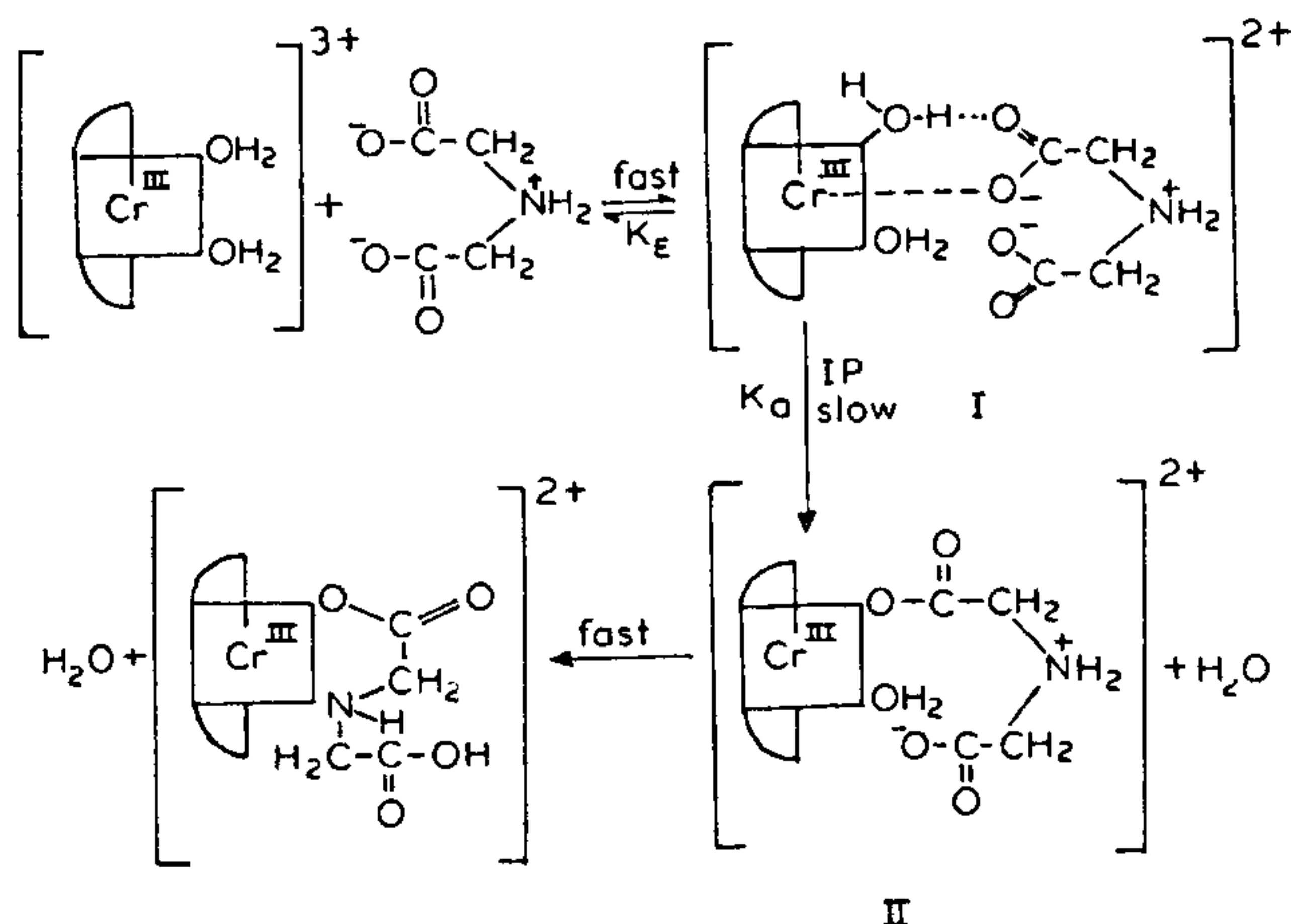


Figure 3. Probable mechanism for the anation process.

4.0 at 50°C, the values of k_{obs} (table 3) increase with increasing ionic strength. This typical effect of ionic strength can be explained by the fact that the nonsubstituting nitrate ion facilitates metal ion water ligand bond cleavage through specific attack on the coordinated water molecule.

Effect of temperature on reaction rate

The reaction was studied at four different temperatures for different [ligands] and the values of the rate constants for the interchange process are shown in table 1.

Table 3 Variation of rate constant (k_{obs}) with ionic strength (μ) at 50°C [$\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}$] = 0.005 M, pH = 4.0, [ligand] = 0.075 M

Ionic strength (M)	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$
0.5	2.303
0.7	2.490
1.0	2.780

Table 4 Activation parameters

System	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (e.u.)	Ref.
cis- $\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}$ + iminodiacetic acid	20.4	-9.76	Present work

Activation parameters (ΔH^\ddagger and ΔS^\ddagger) of the system are evaluated from the linear Eyring plot of $\log k_a$ vs $1/T$. A lower ΔH^\ddagger value (20.4 kcal/mol) and a negative ΔS^\ddagger (-9.76 e.u.) were obtained.

MECHANISM AND CONCLUSION

The results suggest that the reaction between the title complex and iminodiacetic acid (uninegative form) occurs by an associative interchange process via ion pair formation. In an associative interchange process both bond-breaking and bond-making are equally important. The energy of the bond-breaking is thus partially compensated by the energy released due to the bond formation by the incoming ligand in the transition state. In the present system such a mechanism is well reflected from the low ΔH^\ddagger value as compared to the other ligand substitution in Cr(III) centre. The probable scheme of the reaction is drawn in figure 3. A compact associated transition state is produced by the ion pair formation between complex-I and ligand by hydrogen bonding as shown in the figure. The negative ΔS^\ddagger value can also be accounted for by the formation of such transition state.

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ANNOUNCEMENT

NEW SUPERCONDUCTOR APPLICATIONS CLOSER WITH ELECTRICAL CONTACTS DISCOVERY

The new contact method developed by Dr Jack W. Ekin of the NBS Center for Electronics and Electrical Engineering and Dr Armand J. Panson of the Westinghouse Research and Development Center, has achieved contact surface resistivities of less than 10 micro-ohm-cm², using bulk samples of the new yttrium-barium-copper-oxide ceramic superconductor (YBa₂Cu₃O₇), a typical high-temperature superconductor. This level of performance for the "super contacts" was achieved while operating the superconductor at the relatively high temperature of liquid nitrogen—77 kelvins (−320°F). Even lower contact resistances are expected when the technique is refined and with superconducting films, which are

less granular.

The method for producing the contacts is carried out at room temperature. It should be directly applicable to making connections to thin films for computer applications as well as bulk samples for fabricating magnets such as those used in motors and generators.

Further particulars may be had from: Dr Jack W. Ekin, NBS Center for Electronics and Electrical Engineering, National Bureau of Standards, Boulder, Colorado, USA, or United States Department of Commerce, Attn: Collier Smith, Gaithersburg, MD 20899).