

KINETICS OF SUBSTITUTION OF AQUO LIGANDS FROM CIS DIAQUO BIS OXALATO CHROMIUM[III] ION BY DIPICOLINIC ACID IN WATER-ETHANOL MIXTURE

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ABSTRACT

The kinetic behaviour of $cis-[Cr(Ox)_2(H_2O)_2]^-$ with dipicolinic acid as a function of temperature, pH and dipicolinic acid concentration has been studied spectrophotometrically at pH 4. The following rate law has been established: Rate = k_2 [complex] [dipicH⁻], where k_2 is the second order rate constant. The rate is slow at low pH around 3.8, increases with increase of pH and reaches a maximum at pH 6.0, then again decreases with further increase of pH. Values of activation parameters ΔH_2^\ddagger and ΔS_2^\ddagger have been evaluated and a reaction mechanism involving S_N2 path has been suggested.

INTRODUCTION

ANATION reactions of various chromium(III) aquo complexes were studied extensively by various workers. Some studies¹⁻⁴ showed that the reaction rates are independent of the concentration of entering anions and proposed S_N1 mechanism, others⁵⁻¹⁴ interpreted their results implying that bond-making plays a significant role in anation reaction as evidenced by the small but definite dependence of the formation rates on nature and concentration of ligands. Some of them⁹⁻¹⁴ also showed that substitution proceeds through the formation of ion-pair association. Thus, the ligand substitution reactions in the case of Cr(III) complexes do not follow any single mechanism, and the reaction path depends on the nature of the incoming ligand and the experimental conditions. This prompted us to study the kinetics of substitution of aquo ligands from $cis-[Cr(Ox)_2(H_2O)_2]^-$ by a series of pyridine carboxylic acids in water ethanol mixture. The present study relates to anation of $cis-[Cr(Ox)_2(H_2O)_2]^-$ by dipicolinate ion.

MATERIALS AND METHODS

Cis-K[Cr(C₂O₄)₂(H₂O)₂].2H₂O [complex I] was prepared following the literature method¹⁵ and its purity was checked by analysis. The prepared complex showed maximum absorbance at 416 and 562 nm and agrees with literature values¹⁶. The ϵ values at the two wavelengths were experimentally determined and found to be 67.25 and 50.0 as compared with literature values of 68.5 and 51.0 respectively. Chromium and oxalate found experimentally were 14.84% (calcd. 15.34%) and 50.9% (calc. 51.9%). Solutions of dipicolinic acid and the complex of desired concentration

were prepared by dissolving the calculated amounts in 30% ethanol. The pH values of the reaction mixtures were adjusted with perchloric acid and sodium hydroxide. All chemicals used were of analar grade. An Elico pH meter of model LI10T was used to measure pH and a Beckman D.B.G. spectrophotometer was used for absorbance measurements.

Due to high solubility it was not possible to isolate the product (complex II) of the reaction between $cis-[Cr(Ox)_2(H_2O)_2]^-$ and dipicolinic acid in pure crystalline form. However, the formation of product in solution was indicated by following the absorbance of the reaction mixtures, thermostated at 65°C for 24 hrs, containing complex I and ligand in ratios 1:1, 1:2, 1:3 and 1:5. These solutions show absorbance maxima at 550 nm ($\epsilon = 148$). Shifting of λ_{max} (from that of complex I) towards lower wavelengths and higher value of extinction coefficient indicate the formation of a hetero chelate by dipicolinic acid in solution. Composition of the product (1:1) in solution was confirmed by Job's method of continuous variation.

The temperature for any set of experiments was thermostatically controlled to within $\pm 0.1^\circ C$. The rate of reaction was followed spectro-photometrically at 530 nm where the molar extinction coefficient of the product and reacting complex differ appreciably (figure 1). Dipicolinic acid has no absorbance at this wavelength. The reaction medium was 30% aqueous ethanol.

Procedure for kinetic study: Equal volumes of solutions of dipicolinic acid and the complex of desired concentration were taken in reaction vessels after adjusting pH and ionic strength by dropwise addition of HClO₄ and NaClO₄ solution, and kept at the

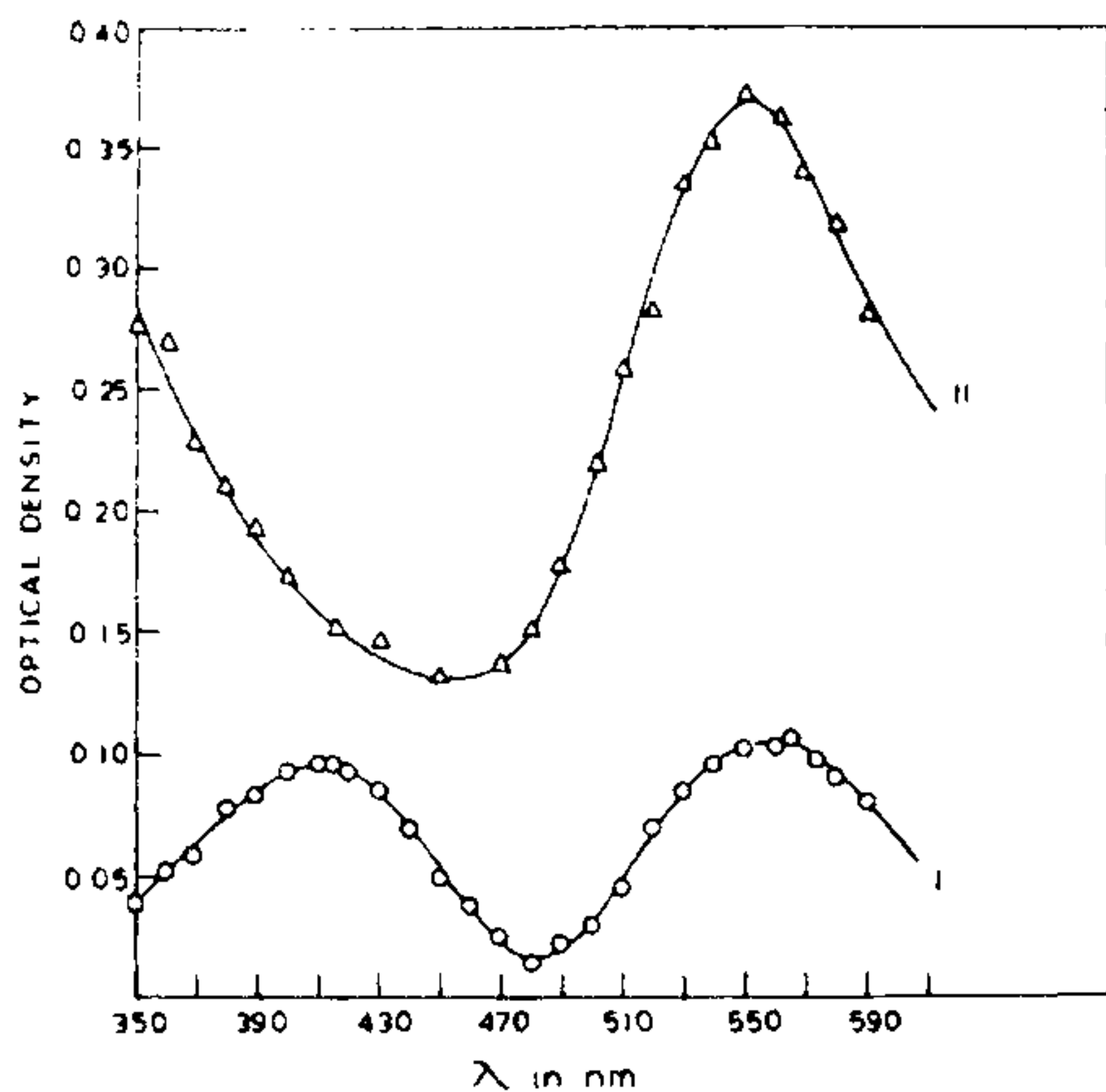


FIG 1

Figure 1. Absorption spectra

(I) $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$, 0.0025 M, pH = 4.0
 (II) $[\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]^-$, 0.0025 M, Dipicolinic acid 0.025 M, pH = 4.0, spectra recorded after keeping the mixture at 60°C for 24 hr.

desired temperature for appropriate time. The composition of the experimental solution was such that the first order rate law was applicable and pseudo first order rate constant (k_{obs}) for each experiment was evaluated graphically by plotting $\log(D_x - D_0)/(D_x - D_t)$ vs time, where D_0 , D_t and D_x are respectively the initial optical density values, the values after time t and after completion of the reaction. The pseudo first order plots were linear. However, the rate constants were calculated on the basis of the least square method and were reproducible within $\pm 3\%$.

RESULTS AND DISCUSSION

(a) *Effect of variation of complex concentration on rate constant:* In this set of experiment the concentration of complex I was varied in the range 0.001 to 0.0025 M at a constant excess concentration 0.025 (M) of dipicolinic acid. Ionic strength (0.04 M), pH (4.0) and temperature (60°C) were also kept constant. At pH 4.0, $\text{cis-}[\text{Cr}(\text{Ox})_2(\text{H}_2\text{O})_2]^-$ and dipicH^- are the reacting species. It was observed that the rate of reaction is first order with respect to [complex I] i.e.

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

(b) *Effect of varying dipicolinic acid concentration on*

the rate constant: In these experiments the complex concentration was kept constant at 0.001 M and dipicolinic acid concentration was varied over the range 0.01 M to 0.03 M at 50°, 55°, 60° and 65°C. The pH was kept constant at pH 4.0 and the ionic strength is kept 0.04 M. The effect of ligand concentration on the rate constant is shown in table 1.

At constant pH 4.0 the rate constant increases with increase in $[\text{DipicH}^-]$ at each temperature (table 1) according to the rate law

$$\begin{aligned} \text{Rate} &= k_2[\text{Complex I}][\text{DipicH}^-] \\ &= k_{\text{obs}}[\text{Complex I}], \end{aligned}$$

where k_2 is the second order rate constant and k_{obs} is the pseudo first order rate constant. From the slope of linear plot k_{obs} vs $[\text{DipicH}^-]$ the value of k_2 can be calculated. The values of k_2 are shown in table 2. The linear dependence of $[\text{DipicH}^-]$ on rate suggests that the reaction proceeds through associative path.

(c) *Effect of variation of pH on rate constant:* In this set of experiments the concentration of complex and dipicolinic acid was kept constant at 0.0025 M and 0.025 M respectively and pH was varied from 3.8 to 7.3. The pH dependence of rate constants (table 3) indicates that the rate constant values pass through a maximum around pH 6.0. To explain the effect of pH variation on the rate constant, the equilibria (1) and (2) for dipicolinic acid and equilibria (3), (4) for *cis-*

Table 1 Variation of rate constant (k_{obs}) with concentration of dipicolinic acid

[DipicH ⁻] (M)	$k_{\text{obs}} \times 10^3 \text{ min}^{-1}$			
	50°C	55°C	60°C	65°C
0.010	1.79	2.42	4.03	5.80
0.015	2.67	3.64	5.73	8.20
0.020	3.40	4.95	7.74	11.60
0.025	4.34	5.90	10.05	14.12
0.030	5.30	7.00	11.78	16.50

[Complex I] = 0.001 M, Ionic strength = 0.04 M and pH = 4.0

Table 2 Values of k_2 at different temperatures

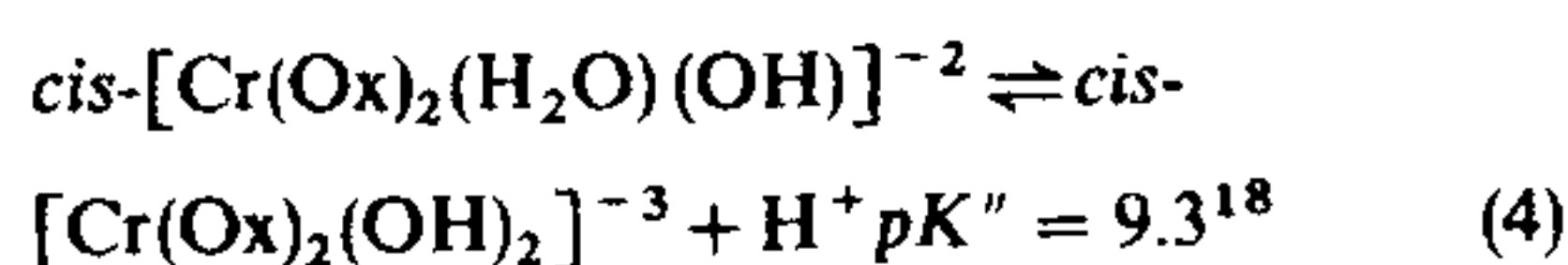
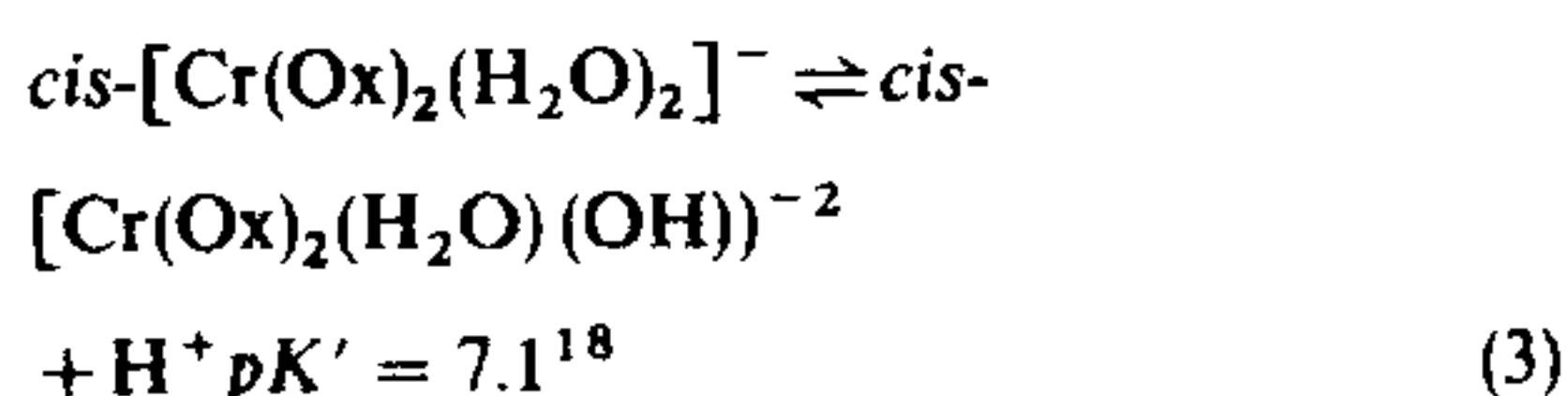
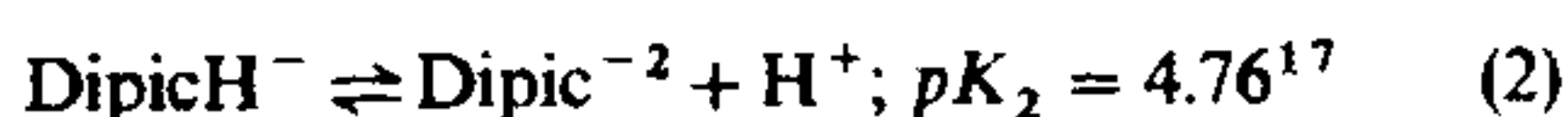
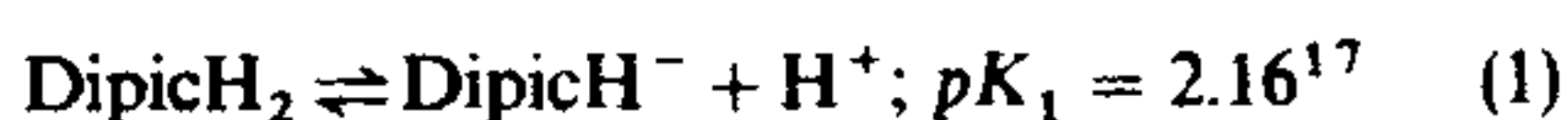
Temp.(°C)	50	55	60	65
$k_2 \times 10^2$ ($\text{min}^{-1} \text{ mol}^{-1}$)	17.37	24.25	39.26	56.47

Table 3 Effect of variation of pH on the rate constant

pH	$k_{\text{obs}} \times 10^3$ (min ⁻¹)	pH	$k_{\text{obs}} \times 10^3$ (min ⁻¹)
3.80	3.70	5.6	10.8
4.00	4.34	6.0	12.8
4.30	5.60	6.3	11.9
4.65	6.80	6.8	10.1
5.25	8.00	7.3	6.1

[DipicH₂] = 0.025 M, [Complex I] = 0.0025 M, Ionic strength = 0.04 M, Temp. = 50°C.

[Cr(Ox)₂(H₂O)₂]⁻¹ should be considered.



At lower pH values, where the complex remains in diaquo form, the reaction is slow due to protonation of carboxylate ion of the ligand. The lower the pH, higher is the protonation of dipicolinate anion, automatically the donor capability of the ligand decreases and as a result pseudo first order rate constant (k_{obs}) decreases. At pH 5.8 and above, dipicolinic acid exists mainly as its anionic form. The experimental results show that at pH 6.0, k_{obs} is maximum and again it decreases with increase of pH. The substrate complex remains mainly in diaquo form at and below pH 6; as pH increases above 6 the substrate complex is converted into hydroxo complex. The hydroxide ion in hydroxo complex exert electromeric effect which increases electron density on chromium and reduces the possibility of nucleophilic attack by dipicolinate ion on reaction site. So rate constants should decrease with increase in pH above pH 6.0.

Thus, in the pH range 3.8–7.3, the pseudo first order rate constant of the reaction increases at first with increase of pH, reaches a maximum around 6.0 and then decreases.

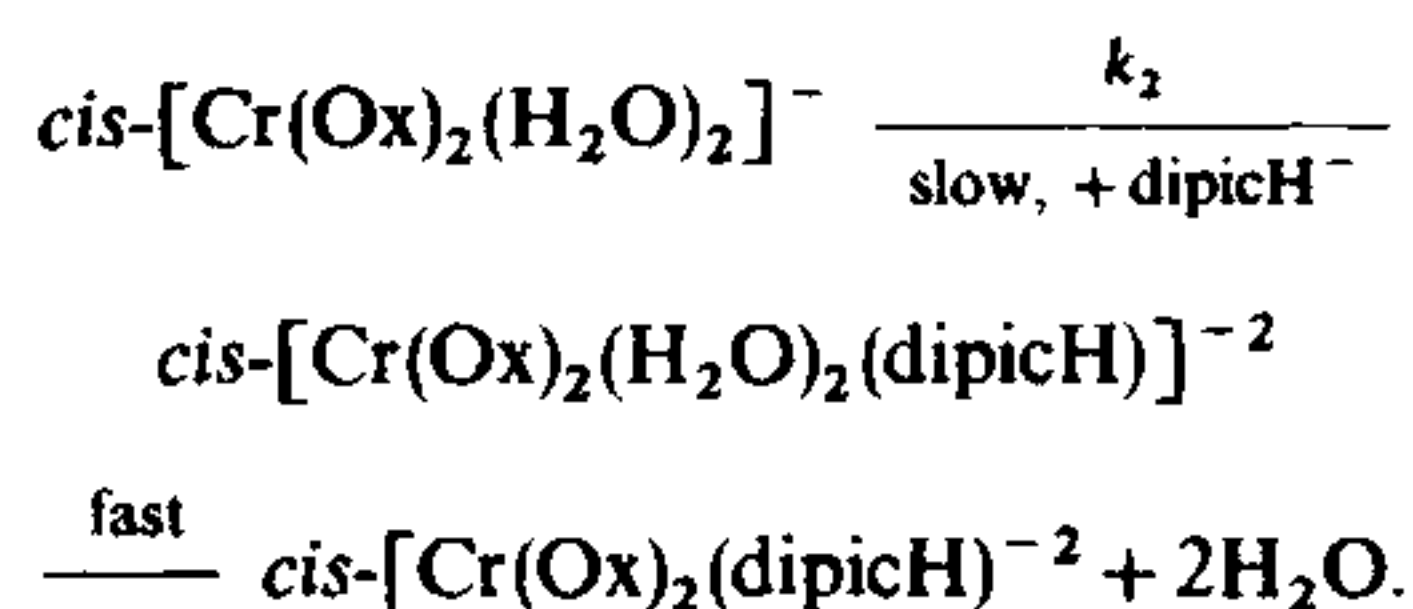
(d) *Effect of ionic strength on the rate constant:* In this set of experiments performed at pH 4.0 and 50°C the concentrations of complex I and dipicolinic acid were kept constant at 0.0025 (M) and 0.025 (M) respectively and ionic strength was varied by the addition of desired

amount of NaClO₄ in the reaction mixture. Solubility of dipicolinic acid is low in the reaction medium and difficulty arises during this study at higher ionic strength. In the lower range of ionic strength (0.03–0.05 M) the rate constant values indicate that the reaction is insensitive to ionic strength.

(e) *Effect of temperature on rate constant:* The activation parameters have been calculated from the plot of $\log k_2$ vs $1/T$. The results are found to be: $\Delta H_2^\ddagger = 17.07$ kcal/mol, $\Delta S_2^\ddagger = -17.60$ e.u.,

Mechanism: The above results suggest that under the experimental conditions employed the reaction proceeds through the following mechanism:

S_N2 path:



The above mechanism is supported by comparison of rate constant and activation parameters of dipicolinic acid substitution with the corresponding parameter for water exchange process in $\text{cis-[Cr(Ox)}_2\text{(H}_2\text{O)}_2\text{]}^-$ (table 4).

It appears from table 4 that rate constant of dipicolinic acid substitution is much faster than isotopic water exchange rate constant at a common temperature. The activation enthalpy for dipicolinic acid substitution is lower than the corresponding parameter for water exchange process. These data indicate an associative character of the substitution process.

Associative mechanism for the dipicolinic acid substitution is further supported by the effect of pH on reaction rate. At lower pH values, where the complex remains in diaquo form, the reaction is slow due to protonation of carboxylate ion of the ligand. The rate increases with increase of pH from 4 to 6 due to increased donor capability of dipicolinate anion. This phenomenon indicates that the dipicolinate anion takes part in the rate determining step. Above pH 6.0 the rate constant again decreases with increase of pH, due to formation of hydroxo aquo species. The hydroxide ion in hydroxo aquo complex forms π bond and increases the electron density on chromium centre which reduces the possibility of nucleophilic attack by

Table 4 Comparison of activation parameters of analogous systems

System	Rate constant at 25°C	ΔH_2 (kcal/mol)	ΔS_2 (e.u.)	Ref.
$cis-[Cr(Ox)_2(H_2O)_2]^-$ + dipicolinic acid	$3.27 \times 10^{-4} \text{ sec}^{-1}$ mol^{-1*}	17.07	-17.6	Present work
$cis-[Cr(Ox)_2(H_2O)_2]^-$ + H ₂ O (isotopic water exchange)	$7.78 \times 10^{-6} \text{ sec}^{-1}$	18.00	-21.6	19

* Extrapolated value from Eyring plot

dipicolinate ion on reaction site. Thus the rate decreases.

Thus we can conclude that aquoligand substitution in $cis-[Cr(Ox)_2(H_2O)_2]^-$ by dipicolinate anion involves the formation of new metal-ligand bond in transition state and the mechanism is associative in nature.

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