

Kinetics and mechanism of anation of *cis*-diaquo-*bis*-oxalatochromate(III) ion by DL-alanine in ethanol–water mixtures of varying dielectric constant

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Abstract. The kinetics of the anation reaction of *cis*-diaquo-*bis*-oxalatochromate(III) ion by DL-alanine has been studied spectrophotometrically in the pH range 3.8 to 7.3, where DL-alanine remains in zwitterionic form. A second-order rate law has been established. Reaction rates in three different ethanol–water mixtures were measured. In each solvent medium the anation rate is higher as compared to water exchange reaction at a particular temperature. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) in different ethanol–water mixtures were obtained from Eyring plots. ΔG^\ddagger ($\Delta H^\ddagger - T\Delta S^\ddagger$) values were calculated in each solvent medium and compared with that of the isotopic water exchange process. A reaction mechanism involving the S_N2 path has been suggested.

Keywords. Anation; *bis*-oxalato-diaquo-chromate(III) ion; amino acid; associative mechanism.

1. Introduction

Extensive study on substitution of aquo-ligands from *cis*-diaquo-*bis*-oxalatochromate(III) ion has not been undertaken so far though a few reports were found in literature. Banerjee and Roy (1973) studied the reaction of *cis*-[Cr(Ox)₂(H₂O)₂][−] with bipyridine and *o*-phenanthroline, and suggested two concurrent paths of the reaction, one independent of the reagent, and the other dependent on the reagent. Kelm and Harris (1967) studied the substitution reactions of *bis*-oxalato-diaquochromate(III) ion with the oxalato species and suggested an associative interchange mechanism for the substitution reactions. However, anation of the *cis*-[Cr(Ox)₂(H₂O)₂][−] ion by picolinate (Mazumdar and De 1987), dipicolinate (Mazumdar and De 1986) and quinolate (Mitra and De 1987) takes place via an S_N2 path. The present study relates to the substitution of aquo ligands from *cis*-diaquo-*bis*-oxalatochromate(III) ion by a bidentate zwitterionic ligand DL-alanine.

2. Materials and methods

cis-K[Cr(Ox)₂(H₂O)₂]2H₂O (complex I) was prepared in the laboratory following the method found in literature (Palmer 1954) and its purity checked by analysis. The prepared complex showed maximum absorbance at 416 and 562 nm which is consistent with the literature values (Krishnamurthy and Harris 1961). ϵ values at the

two wavelengths were experimentally determined to be 67.25 and 50.0 mol⁻¹ cm⁻¹ respectively (literature values 68.5 and 51.0 mol⁻¹ cm⁻¹). Chromium and oxalate as determined experimentally were 14.84% (calcd. 15.34%) and 50.9% (calcd. 51.9%). Solutions of DL-alanine and the complexes of the desired concentrations, were prepared by dissolving calculated amounts in three different ethanol-water mixtures (20, 30 and 40% v/v). The pH values of the reaction mixtures were adjusted with perchloric acid and sodium hydroxide.

The product of the reaction between **I** and DL-alanine at pH 5.0 was prepared by mixing the aqueous solutions of the two and refluxing this on a water bath for several hours. It was finally evaporated on a water bath and the solid obtained recrystallised from 40% ethanol. Elemental analysis (found Cr 14.57, N 3.85%; calcd. Cr 14.59, N 3.93%) of the product complex, K₂H[Cr(Ox)₂Ala] (complex **II**), revealed that the composition is 1:1 (M:L). The product shows λ_{max} at 405 nm (ε = 58.5) and 545 nm (ε = 67.0). Composition of **II** in solution was further checked by Job's method of continuous variation. In all experiments A.R. chemicals and double distilled water were used throughout. An Elico pH-meter (model LI10T) was used to measure pH and a Beckman D.B.G. spectrophotometer was used for the absorbance measurements.

3. Kinetic run

The course of the reaction was followed by measuring the absorbance at 530 nm where substantial difference exists in absorption of **I** and the product. The pseudo first-order

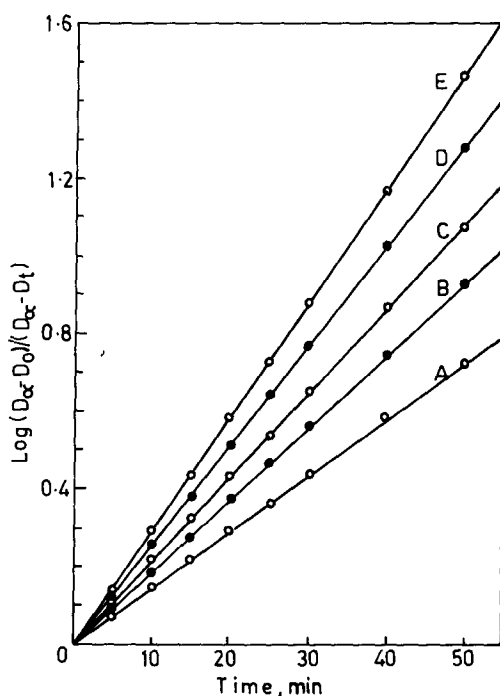
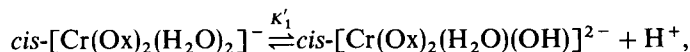


Figure 1. Graphical presentation of k_{obs} at 60°C in 30% (v/v) EtOH/H₂O mixture. [**I**], 0.01 M, pH = 5.0; [DL-alanine], 0.1 M (A), 0.125 M (B), 0.15 M (C), 0.175 M (D), 0.2 M (E).

with increase of pH, the rate of substitution increases slowly upto pH 6.0. Again, the acid dissociation equilibrium of substrate complex can be represented as follows,



where the pK'_1 value (Schenk *et al* 1972) is 7.1 at 25°C.

Now considering the above equilibrium, the effect of pH on the observed rate constant can be expressed as follows:

$$k_{\text{obs}} = k' + k'' K_1 [\text{H}^+]^{-1}, \quad (1)$$

where k' is the observed rate constant, when the reacting species is the diaquo complex, and k'' is the observed rate constant for the hydroxoquo complex. It is seen from (1) that the increase in pH i.e. decrease in hydrogen ion concentration increases the reaction rate. A plot of k_{obs} vs $1/[\text{H}^+]$ gives a good straight line and departure from linearity starts at higher pH. As the pH of the medium is raised above pH 6.0, the proportion of monohydroxy species increases. The hydroxoquo complex, due to its π -bonding ability, facilitates the replacement of water molecules in the reaction, and is thus much more reactive than the diaquo complex. Thus the rapid increase in rate with increase of pH above 6.0 can be explained.

4.3 Effect of ionic strength on rate constant

The ionic strength of the reaction mixture was adjusted with sodium perchlorate, considering the net charge on DL-alanine to be zero (isoelectric nature). The concentrations of I and DL-alanine were kept constant at 0.01 and 0.1 M respectively at pH 5.0 and 50°C in a 30% (v/v) ethanol-water mixture, while the ionic strength was varied. The rate of reaction increases with increase of μ . The pseudo first-order rate constants were 1.74, 2.24, 2.43 and $2.59 \times 10^{-4} \text{ s}^{-1}$ at ionic strength 0.1, 0.5, 0.8 and 1.0 M, respectively. A similar effect of ionic strength has been observed by Hamm *et al* (1958) in their study of the substitution reaction between $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and different organic acid anions.

4.4 Effect of varying DL-alanine concentration on rate constant

$[\text{AlaH}]$ was varied in the range 0.1 to 0.2 M at a fixed $[\text{I}]$ (0.01 M) and at a fixed pH (5.0) and ionic strength (0.5 M). The effect of variation of $[\text{AlaH}]$ on reaction rate was studied at four different temperatures 45, 50, 55 and 60°C in 30% (v/v) ethanol-water. The same experiment was repeated at 50, 55 and 60°C in two solvent media (20% and 30% v/v ethanol-water). In each case k_{obs} (table 2) increases linearly with increase of $[\text{AlaH}]$ at a particular temperature in each solvent (figure 2). In order to explain such a variation in rate with change in $[\text{AlaH}]$, the following reaction scheme is proposed

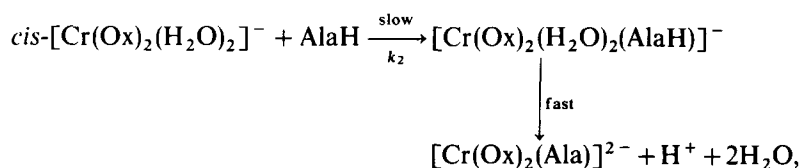
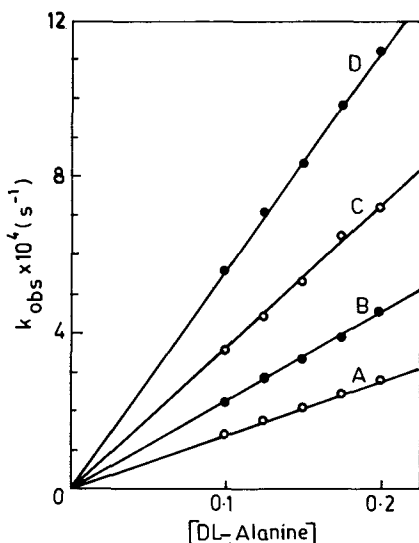


Table 2. Values of k_{obs} at various [AlaH] in different ethanol-water mixtures at different temperatures.pH = 5.0, [I] = 0.01 M, $\mu = 0.5$ M

[AlaH] (M)	$k_{\text{obs}} \times 10^4 \text{ s}^{-1}$									
	45°C		50°C		55°C			60°C		
	(30)*	(20)	(30)	(40)	(20)	(30)	(40)	(20)	(30)	(40)
0.100	1.38	1.65	2.44	3.20	2.70	3.54	4.66	4.41	5.56	7.12
0.125	1.76	2.06	2.78	4.02	3.39	4.41	4.83	5.52	7.16	8.84
0.150	2.08	2.42	3.30	4.82	4.075	5.33	7.00	6.56	8.31	10.60
0.175	2.40	2.88	3.89	5.63	4.73	6.59	8.17	7.65	9.88	12.34
0.200	2.76	3.29	4.51	6.43	5.43	7.21	9.33	8.83	11.28	14.23

* Values in parentheses refer to the percentage of ethanol present in the mixture (v/v).

**Figure 2.** Dependence of k_{obs} on DL-alanine concentration. Solvent – 30% (v/v) EtOH/H₂O mixture. [I], 0.01 M, pH = 5.0; 45°C (A), 50°C (B), 55°C (C), 60°C (D).

where k_2 is the second order rate constant.

Values of k_2 (table 3) at different temperatures and in different media were evaluated from the slopes of the straight lines obtained by plotting k_{obs} versus [AlaH].

4.5 Effect of dielectric constant on rate constant

The reaction was studied in three different ethanol-water mixtures (20, 30 and 40% v/v) and at four different temperatures. k_2 values increased with the increase in concentration of the organic component at a particular temperature as shown in table 3. Association between the charged substrate complex and the zwitterionic ligand DL-alanine, through its negative end, is favoured in a medium of low dielectric constant (D). For each particular temperature, a plot of $\log k_2$ versus $1/D$ is linear and

Table 3. Values of k_2 ($\text{s}^{-1} \text{mol}^{-1}$) at different ethanol–water concentrations and temperatures.

Ethanol (% v/v)	45°C		50°C		55°C		60°C	
	D	$k_2 \times 10^3$	D	$k_2 \times 10^3$	D	$k_2 \times 10^3$	D	$k_2 \times 10^3$
20			61.24	1.65	60.28	2.72	59.33	4.40
30	58.14	1.39	56.72	2.25	55.33	3.59	53.93	5.65
40			52.25	3.22	50.77	4.67	49.29	7.17

Table 4. Comparison of activation parameters at different ethanol–water concentrations with the water exchange process.

System	Ethanol (% v/v)	$k_2 \times 10^4$ ($\text{s}^{-1} \text{mol}^{-1}$) at 25°C	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	ΔG ($\Delta H^\ddagger - T\Delta S^\ddagger$) (kJ mol^{-1}) at 25°C
<i>cis</i> -[Cr(Ox) ₂ (H ₂ O) ₂] ⁻ + DL-AlaH	20	1.08	84.57 ± 2.5	-37.26 ± 7.5	95.67
	30	1.88	76.20 ± 2.5	-59.87 ± 7.5	94.35
	40	3.09	71.59 ± 2.5	-72.10 ± 7.5	93.08
<i>cis</i> -[Cr(Ox) ₂ (H ₂ O) ₂] ⁻ + H ₂ O (isotopic water exchange)		7.78 × 10 ⁻⁶	75.36	-90.43	102.31

has a positive slope. As temperature increases, the magnitude of the slope decreases. All these facts can be explained by the simplified Laidler–Eyring equation (Laidler and Eyring 1940) for the effect of dielectric constant on reaction rates. The equation is

$$\frac{d \ln k_2}{d(1/D)} = \frac{z^2 e^2}{2kT} \left(\frac{1}{r} - \frac{1}{r^*} \right)$$

where D is the dielectric constant of the medium, ze is the ionic charge of one of the reactants, while the ionic charge of the other reactant is zero, r is the effective radius of the charged reactant, r^* is the radius of the activated species and k is the Boltzmann constant. The positive slope of the lines drawn by plotting $\log k_2$ versus $1/D$, indicates that $r^* > r$, i.e. the rate-determining step is associative in nature.

4.6 Effect of temperature on the anation rate constant

Activation parameters were calculated from the Eyring plot and the data obtained were checked by the least squares method. Table 4 shows that the ΔH^\ddagger and ΔS^\ddagger values decrease as the dielectric constant of the medium decreases. For the associative process ΔH^\ddagger should decrease as the concentration of organic component in the medium increases. An increase in the organic component affects the solvation of activated species and ground state of the reacting species. An isokinetic plot of ΔH^\ddagger versus ΔS^\ddagger is linear and it may be inferred that similar transition states are formed in the studied range of composition of the solvent pair.

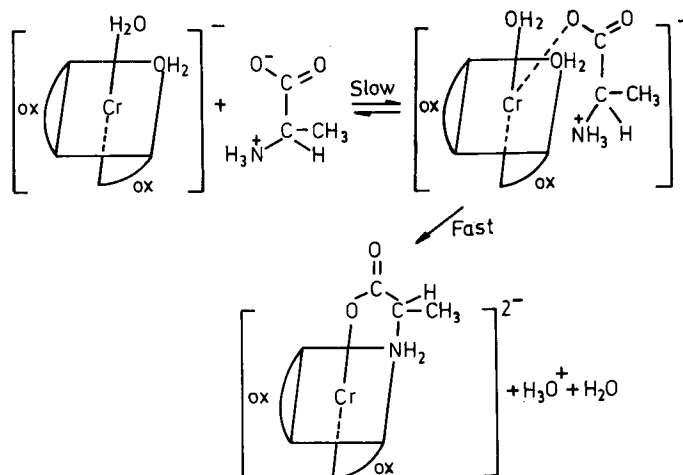


Figure 3. Probable mechanism for the anation process.

5. Mechanism and conclusion

Anation reaction of $\text{cis-}[\text{Cr}(\text{Ox})_2(\text{H}_2\text{O})_2]^-$ with DL-alanine in zwitterionic form involves association between the complex anion and the negative end of the ligand zwitterion. In the rate-determining step both bond-making and bond-breaking are important. The anation rate is much faster (table 4) than the isotopic water exchange rate (Stieger *et al* 1970) of **I**, hence the bond-making is important. Rapid increase in the anation rate above pH 6.0 can be explained thus: $\text{cis-}[\text{Cr}(\text{Ox})_2(\text{H}_2\text{O})(\text{OH})]^{2-}$ is formed above pH 6.0, and the ligand OH^- being a strong π -donor facilitates the loss of the coordinated water ligand. Thus bond-breaking has also an influence on the rate-determining step. Table 4 also indicates that the ΔG^\ddagger ($\Delta H^\ddagger - T\Delta S^\ddagger$) values of the anation reaction are less than that of the water exchange reaction; thus the associative path is favoured.

The above conclusion is supported by the results obtained for the variation of dielectric constant. The positive slope of the linear plot of $\log k_2$ versus $1/D$ indicates that, the radius of the activated species is greater than the radius of the charged reactant (**I**), according to the Laidler–Eyring equation. Moreover, the small decrease in ΔH^\ddagger with increase in the dielectric constant of the medium can be explained on the basis that a medium with higher dielectric constant lowers the possibility of association between the **I** and the negative end of the reactive DL-alanine molecule and automatically needs some higher energy of activation. Thus, in the present system, ligand substitution occurs by a process of association (S_N2) where both bond-breaking and bond-making have their importance. A model for the activated state is depicted in figure 3.

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