

## Kinetics and mechanism of anation of hydroxopenta-aquo chromium(III) ion by DL-alanine in aqueous solution

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**Abstract.** The kinetics of substitution of aquo-ligand from hydroxopenta-aquo chromium(III) by DL-alanine in aqueous medium has been studied spectrophotometrically. The rate law involving the formation of ion-pair has been established in the pH range 4.5–5.4. The reaction rate is higher compared to water exchange and other substitution reactions of hydroxopenta-aquo chromium(III) ion. Activation parameters have been evaluated. A lower  $\Delta H^\ddagger$  value for the reaction suggests that both bond-breaking and bond making are equally important in the transition state.

**Keywords.** Anation; hydroxopenta-aquo chromium(III) ion; amino acid; ion-pair; hydrogen-bonding; associative interchange.

### 1. Introduction

Anation reactions of hexaaquo chromium(III) ion and hydroxopenta-aquo chromium(III) ion by different ligands have been studied extensively (Hamm *et al* 1958; Banerjea and Chatterjee 1969; Banerjea and Sarkar 1972; Bhattacharya and De 1981; Mandal and De 1980; Postmus and King 1955; Phatak *et al* 1970, 1976) and some generalisations have been made regarding the reaction mechanism. Anation rate constants for  $\text{Cr}(\text{H}_2\text{O})_5\text{OH}^{2+}$  with  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$  and  $\text{NCS}^-$  at  $25^\circ\text{C}$  span a range of  $0.26\text{--}8.5 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$  (Espenson 1969; Thusius 1971) and for  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , with the aforementioned anions at  $25^\circ\text{C}$  cover a range of  $0.08\text{--}73 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$ . This result has been interpreted as implying that bond-making plays a significant role in these reactions as evidenced by the small but definite dependence of the formation rates on the nature of the ligand. The difference in the range of rates spanned by  $\text{Cr}(\text{H}_2\text{O})_5\text{OH}^{2+}$  is smaller as compared to that by  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  with the same anions. This may be explained on the basis that coordinated  $\text{OH}^-$  facilitates a dissociative mechanism through its  $\pi$ -bonding ability. Anation of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  by glycine has been reported (Banerjea and Dutta Choudhuri 1968) to proceed 10 times faster than the water exchange rate. On this basis Banerjea and Dutta Choudhuri 1968 have advanced an associative interchange (Ia) mechanism. However, Hartley suggested a dissociative mechanism for the anation of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  by  $\text{COO}^-$  in wool. Thus despite the large amount of work done on chromium(III) complexes, controversy regarding its mechanism persists. Further the aquo-ligand substitution in hexa-aquo chromium(III) ion by amino acids except glycine has not been studied so far and similar substitution in hydroxopenta-aquo chromium(III) ion has not received any

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attention. Hydroxopenta-aquo chromium(III) complex is distinctly different from hexa-aquo complex. Hydroxide ion is not only a strong  $\sigma$ -bonding ligand but is a strong  $\pi$ -donor as well. It is therefore planned to study the kinetics of substitution of aquo ligands in  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  by alanine,  $\beta$ -alanine, phenylalanine, aspartic acid and other related amino acid ligands. In this paper the results on alanine are presented.

## 2. Materials and methods

Analar quality chemicals were used. The reactant  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$  was prepared by the method of Moor and Basolo (1965);  $\lambda_{\text{max}}$  410 nm (log  $\epsilon$ , 1.52), 572 nm (log  $\epsilon$ , 1.20). The solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  (Complex-I) was prepared *in situ* from  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$  by adjusting pH to 5:  $\text{pK}_a$  of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  being 3.8, a solution of this at pH 5 with  $\lambda_{\text{max}}$  430 nm (log  $\epsilon$ , 1.44) and 590 nm (log  $\epsilon$ , 1.24), represents complex (I) (figure 1). DL-alanine ( $\text{pK}_1$  2.34 due to the dissociation of  $-\text{COOH}$ , and  $\text{pK}_2$  9.69 due to dissociation of  $-\text{NH}_3^+$ ), at pH 5 remains in the Zwitter ionic form,  $\text{H}_3\text{N}^+ - \text{CH}(\text{CH}_3) - \text{COO}^-$  (PI, isoelectric point being 6) (Fox and Foster 1957). The product of the reaction between  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  and alanine was prepared by mixing them in different molar ratios of 1:1, 1:2, 1:3 and 1:5 at pH 5. The deep red (maroon) coloured solution when placed over concentrated  $\text{H}_2\text{SO}_4$  gave a product with the composition  $[\text{Cr}(\text{Alanine})_2(\text{OH})\text{H}_2\text{O}]$ , complex-II. The composition of the complex (1:2) formed in the reaction mixtures was checked by the Jobs' method of continuous variation which was confirmed by the studies of Green and Ang (1955). The values of  $\lambda_{\text{max}}$  400 nm (log  $\epsilon$ , 1.53) and 540 nm (log  $\epsilon$ , 1.61) (figure 1) of our product is nearly identical with that of Green and Ang.

## 3. Kinetic run

The temperature-equilibrated solution of DL-alanine and complex (I), prepared in

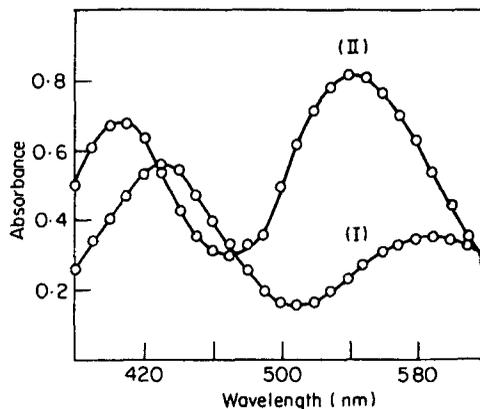


Figure 1. Absorption spectra. (I)  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , 0.01 M, pH = 5. (II)  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , 0.01 M, alanine 0.1 M, pH = 5. Spectrum recorded after keeping the mixture at  $40^\circ\text{C}$  for 24 hr.

solution at pH 5 of desired concentrations were mixed in the reaction vessels and its optical density measured (Hilger UVISPEK spectrophotometer), at 540 nm, and there was a substantial difference in the spectra of the complexes  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  and  $[\text{Cr}(\text{alanine})_2\text{OH}\cdot\text{H}_2\text{O}]$ . DL-alanine does not absorb at this wavelength. The assumption that only hydroxopentaaquo chromium(III) is involved in the reaction is reasonable since under the experimental condition (pH 5) the percentage of hexa-aquo chromium(III) is very small. The pseudo-first order rate constants for the substitution reaction were obtained by plotting  $\log (D_a - D_o)/(D_a - D_t)$  against time where  $D_a$ ,  $D_o$  and  $D_t$  are the optical density values at infinite time, at the beginning and end of time  $t$  respectively. The pseudo-first order plots were linear (figure 2). However the rate constants were calculated on the basis of the least square method were reproducible within  $\pm 3\%$ .

#### 4. Results and discussion

##### 4.1 Effect of varying concentration of complex (I)

In the first set of experiments the concentration of  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , (complex I) was varied at a fixed concentration (0.15 M) of alanine. The ionic strength (0.06 M), and pH (5) was also kept constant. The value of  $k_{\text{obs}} (\times 10^5)$  was found to be 15.2, 15.4, 15.82 and 15.9  $\text{sec}^{-1}$  at varied concentrations of [complex I] 0.005, 0.0075, 0.01 and 0.015 M respectively at a temperature of 35°C. The reaction rate is of first order with respect to [complex I] i.e.

$$d[\text{complex-II}]/dt = k[\text{complex-I}]$$

##### 4.2 Effect of varying pH on rate constant

At fixed [complex I] (0.01 M), [alanine] (0.15 M) and  $\mu = 0.03$  M the values of pseudo-first order rate constant ( $k_{\text{obs}} (\times 10^5)$ ) at 35°C were 6.9, 12.4, 15.5, 25.6 and 40.2  $\text{sec}^{-1}$  at pH 4.5, 4.8, 5, 5.2 and 5.4 respectively (figure 5). The pH dependence of rate constant indicates that the rate constant decreases with decreasing pH. To explain the effect of

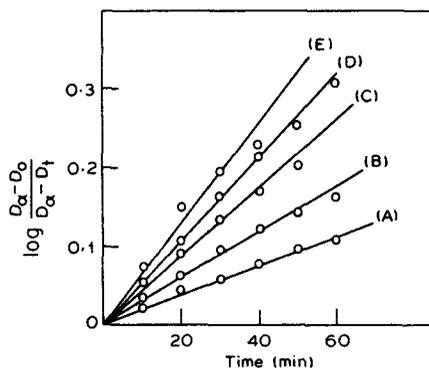
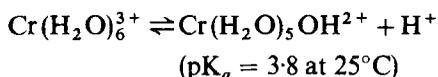
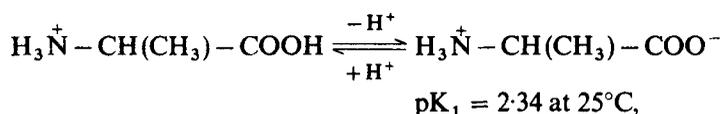


Figure 2. Graphical presentation of  $k_{\text{obs}}$  (35°C),  $\mu = 0.03$  alanine variation:  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ , 0.01 M, pH = 5. [alanine], 0.05 (A), 0.1 (B), 0.15 (C), 0.2 (D) and 0.25 M (E).

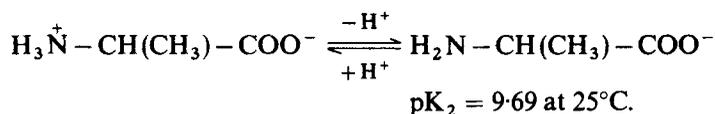
pH variation the following equilibrium is considered necessary (Basolo and Pearson 1967)



As the pH of the reaction medium decreases the ratio of [hydroxopenta-aquo chromium(III)]: [hexa-aquo chromium(III)] decreases which in turn decreases the reaction rate. Hydroxopenta-aquo complex due to its π-bonding ability is a very reactive species compared to hexa-aquo complex. Alanine, an α-amino mono-carboxylic acid, at pH ≤ 2 has two dissociable groups H<sub>3</sub>N<sup>+</sup>–CH(CH<sub>3</sub>)–COOH, one uncharged in the carboxylic acid (–COOH) and the other in the cationic form (–NH<sub>3</sub><sup>+</sup>). With the pH range (4.5 to 5.4) studied the following equilibria are also significant



and



It can be assumed that within the pH range studied for the substitution reaction the ligand alanine exists in the dipolar (Zwitter ionic) form NH<sub>3</sub><sup>+</sup>–CH(CH<sub>3</sub>)–COO<sup>–</sup>. Thus the effect of pH on the reaction rate is solely due to the change in the ratio of [hydroxopenta-aquo chromium(III)]: [hexa-aquo chromium(III)] ion.

### 4.3 Effect of varying alanine concentration

The concentration of alanine ( $\bar{\text{O}}\text{OC}\cdot\text{CH}(\text{CH}_3)\text{--}\overset{+}{\text{N}}\text{H}_3$ ) was varied in the range 0.05 to 0.25 M at a fixed [complex-I] (0.01 M). In these experiments the ionic strength and pH were kept constant at 0.03 M and 5 respectively. The results in table 1, show that the rate increases with increasing alanine concentration and at high concentration a limiting rate is reached (figure 3), which invokes a completion of the ion-pair formation.

The following reaction scheme can be proposed to explain the variation of rate due to

**Table 1.** Variation of rate constant *k*<sub>obs</sub> with [alanine] at different temperatures (°C). [Cr(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup> = 0.01 M, ionic strength μ = 0.03 M, pH = 5.

[Alanine] (M)	<i>k</i> <sub>obs</sub> (× 10 <sup>5</sup> sec <sup>–1</sup> )				
	25	30	35	40	45
0.05	6.01	6.42	7.29	9.38	18.9
0.10	10.01	10.42	11.05	14.87	29.9
0.125				17.72	33.9
0.15	13.14	13.96	15.52	20.52	38.6
0.20	15.17	17.14	19.81		
0.25			22.06		



From (6), (4) and (1) we get

$$\frac{d[B]}{dt} = \frac{k \cdot k_E [A]_{\text{total}} [L]}{1 + K_E [L]}, \quad (7)$$

i.e.

$$\begin{aligned} \frac{d[\text{Cr}(\text{alanine})_2\text{OH} \cdot \text{H}_2\text{O}]}{dt} &= \frac{k \cdot K_E [\text{Cr}(\text{H}_2\text{O})_5\text{OH}]_{\text{total}}^2 [\text{alanine}]}{1 + K_E [\text{alanine}]} \\ &= k_{\text{obs}} [\text{Cr}(\text{H}_2\text{O})_5\text{OH}]_{\text{total}}^2, \end{aligned} \quad (8)$$

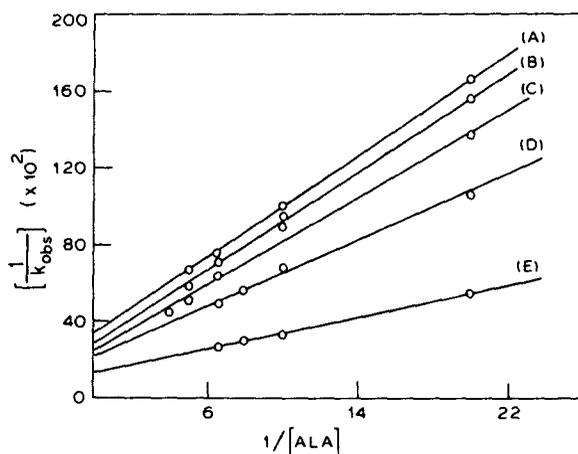
and

$$k_{\text{obs}} = \frac{k \cdot K_E [\text{alanine}]}{1 + K_E [\text{alanine}]}, \quad (9)$$

or,

$$1/k_{\text{obs}} = 1/k + 1/k \cdot K_E [\text{alanine}]. \quad (10)$$

From (10) the plot of  $1/k_{\text{obs}}$  vs  $1/[\text{alanine}]$  should be linear with an intercept,  $1/k$  and slope,  $1/k \cdot K_E$  (figure 4). The values of  $k$  ( $\times 10^5$ ) and  $K_E$  thus obtained are given in table 2. The  $K_E$  values remain almost constant at all temperatures. The  $k$  values (anation rate constant) are much greater than the rate constant for isotopic water exchange under identical experimental condition [ $< 10 \times 10^{-5} \text{ sec}^{-1}$  at  $25^\circ\text{C}$ , Thusius 1971].



**Figure 4.** Plot of  $1/k_{\text{obs}}$  vs  $1/\text{ligand concentration}$  at various temperatures (A) 25, (B) 30, (C) 35, (D) 40 and (E)  $45^\circ\text{C}$ .

**Table 2.** Values of  $k$  ( $\times 10^5$ )  $\text{sec}^{-1}$  and  $K_E$  for the anation of  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  by alanine at different temperatures.

Temperature ( $^\circ\text{C}$ )	$k$ ( $\times 10^5$ ) $\text{sec}^{-1}$	$K_E$
25	30.18	4.78
30	34.93	4.46
35	39.90	4.35
40	44.74	5.26
45	75.86	6.60

#### 4.4 Effect of ionic strength on reaction rate

The ionic strength of the reaction mixture was adjusted by adding sodium perchlorate, considering the net charge of alanine to be zero (isoelectronic nature). The pseudo-first order rate constants ( $\times 10^5$ ) at  $35^\circ\text{C}$  are found to be 11.05, 15.9, 19.84 and 22.69  $\text{sec}^{-1}$  at ionic strengths of 0.03, 0.15, 0.3 and 0.45 M respectively at  $[\text{complex-I}] = 0.01 \text{ M}$  and  $[\text{alanine}] = 0.1 \text{ M}$  (figure 6). The increase in rate,  $k_{\text{obs}}$  with increase in ionic concentration indicates the easy removal of coordinated water molecule from the ion pair.

#### 4.5 Effect of temperature on reaction rate

The temperature effect on the reaction rate was studied at five different temperatures for different ligand concentrations. The values for anation rate constants ( $k$ ) are calculated by the least square method and are given in table 2.

Activation parameters are also calculated by the least square method using the Eyring plot of  $\log k$  vs  $1/T$ . A much lower  $\Delta H^\ddagger$  amounting to 8.14 kcal/mol and  $\Delta S^\ddagger$ ,  $-48.23 \text{ e.u.}$  was obtained.

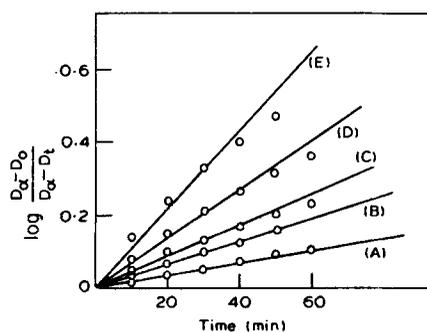


Figure 5. Effect of pH on reaction rate: pH for curve (A) 4.5, (B) 4.8, (C) 5, (D) 5.2 and (E) 5.4.

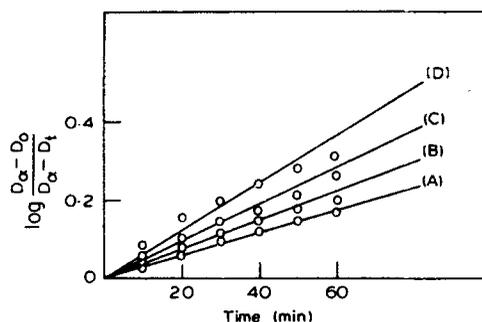


Figure 6. Effect of ionic strength on reaction rate: (A)  $\mu = 0.03$ , (B) 0.15, (C) 0.3 and (D) 0.45 M.

## 5. Mechanism and conclusion

The reaction between  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  and alanine (in Zwitter ionic form) involves outersphere association between the two reacting species followed by an associative interchange process in which both bond-breaking and bond-making are equally important. The following mechanism (figure 7) can be proposed to explain the rate data and activation parameters of alanine substitution in  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ .

Ligand  $\text{OH}^-$  which is electron donating facilitates the loss of a water ligand in the *trans* position by increasing the electron density in the chromium(III)  $d_{2z}$  orbital. Further the activated complex formation through outersphere association is stabilized by hydrogen bonding. In this activated complex, carboxylate ion of alanine is able to form a weak bond. These assumptions are supported by the rate data and activation parameters. The rate of anation by alanine is much faster than that of isotopic water exchange and other anation processes (Thusius 1971). Further the aquo ligand substitution in  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  by alanine is much faster than that in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  by glycine. The presence of  $\text{OH}^-$  in the complex facilitates the easy rupture of Cr(III)– $\text{OH}_2$  bond. Activation parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) of the present system are evaluated from the Eyring plot. A lower  $\Delta H^\ddagger$  value as compared to other anation reactions of  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  suggests significant associative character of the interchange process. In the associative interchange process the rupture of the Cr(III)– $\text{OH}_2$  bond already present and formation of new Cr(III)–L bond are equally important in the activated state. In this process positive enthalpy change due to rupture of Cr(III)– $\text{OH}_2$  bond is partially compensated by negative enthalpy change due to the bond formation by the incoming ligand.

The high rate of alanine substitution in  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  over the rate of water exchange and other substitution reactions of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is due to the presence of  $\text{OH}^-$  in  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  which facilitates the cleavage of Cr(III)– $\text{OH}_2$  bond. This in turn favours the entry of outersphere ligand and its subsequent coordination to chromium(III).

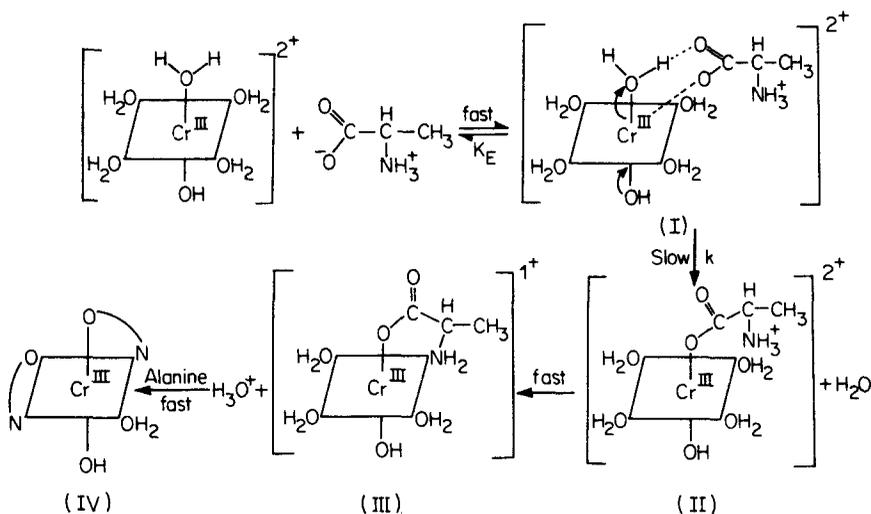


Figure 7. Probable mechanism for the anation process.

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