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KINETICS OF ANATION OF AQUACHROMIUM(III) IONS BY *L*-LEUCINE

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The kinetics of the reaction of chromium(III) and *L*-leucine have been investigated under varying conditions of $[\text{chromium(III)}]_T$, $[\text{ligand}]_T$, $[H^+]$, ionic-strength, %EtOH and temperature by spectrophotometry. The observed pseudo-first order rate constants were found to be expressed by the following equation

$$k_{obs} = \frac{(k_1 K_a K_{OS_1}[H^+] + k_2 K_a K_h K_{OS_2})[\text{Leucine}]_T}{[H^+]^2 + [H^+]K_a + [H^+]K_h + K_a K_h + (K_a K_{OS_1}[H^+] + K_a K_h K_{OS_2})[\text{Leucine}]_T}$$

A mechanism has been proposed and the anation rate constants (k_1, k_2) and outer-sphere association constants (K_{OS_1}, K_{OS_2}) have been calculated.

The reaction of $[Cr(H_2O)_6]^{3+}$ follows an associative (I_a) path whereas that of $[Cr(H_2O)_5OH]^{2+}$ follows a dissociative (I_d) path.

Key Words: Kinetics; Anation; Aquachromium(III) Ions; Amino Acid; *L*-Leucine

Introduction

Though a large body of work is available on substitution reactions of $[M(N)_5X]^{n+}$ (M = Co, Cr or Rh; N = primary, secondary, tertiary amine or water; X = anionic ligand or water)[1,2], those containing chromium(III) are still a lively issue because of mechanistic implications[3-7] and as a result of Mertz's[8] experiments showing GTF's insulin potentiating activity (GTF = glucose tolerance factor—a chromium(III) complex of low-molecular-weight). Literature concerned with structural and equilibrium studies is abundant but only limited kinetic data are available on chromium(III)-amino acid systems[3-7]. Furthermore, lability of both the free metal and its monohydroxy species have been considered by few workers only[4,6].

The work reported here deals with the kinetics and mechanism of the chromium(III)-L-leucine system in aqueous-acid where the experiments were performed in such an acidity range that predominant leucine species were $leuH_2^+$ and leuH and that of chromium(III) were $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5OH]^{2+}$.

Materials and Methods

L-leucine (E. Merck, India, chromatographically homogeneous) was used without further purification. Other chemicals used were of reagent grade. H_2O was redistilled from alkaline $KMnO_4$ solution in an all glass still. EtOH was dis-

tilled once. The stock solution of $Cr(NO_3)_3.9H_2O$ was standardised by literature method[3].

A solution of *L*-leucine and required amount of HNO_3/NaOH solution (for maintaining the required *p*H) were taken in a two-necked flask together with KNO_3 (to adjust ionic-strength). A separate $Cr(NO_3)_3.9H_2O$ solution was thermostated with the above solution under bubbling nitrogen gas at the desired temperature. After mixing, the reaction was followed at 540nm (Fig. 1). The conditions were pseudo-first order (an excess of leucine) and the rate constants, k_{obs}, were evaluated from the slopes of the plots of log $(A_\infty - A_0)/(A_\infty - A_t)$ *vs* time (t) where A denotes measured absorbance and subscripts have the usual meaning. Such plots were linear for at least three half-lives. The reported rate constants represent the average of two kinetic runs.

The spectrophotometer used was a Bausch and Lomb Spectronic-20 and the pH meter was an ELICO model LI-120. Data analysis was performed on a VAX-11/780 Computer.

The other experimental details and data evaluation methods were the same as described in earlier publications[5,6].

Results and Discussion

L-Leucine Complex of Chromium(III)

The solutions of L-leucine give upon addition of $Cr(NO_3)_3$ in acidic solution an increase of absorption in the visible range. The absorption spectra of mixtures in different molar ratios exhibited maxima different from a solution of $Cr(NO_3)_3$ (see, for example, Fig. 1 for 1 : 9 molar ratio). Two *d-d* transitions were observed for each solution with absorption maxima at 400 and 540nm. As chelation is not a favoured process when the amino group of an amino acid

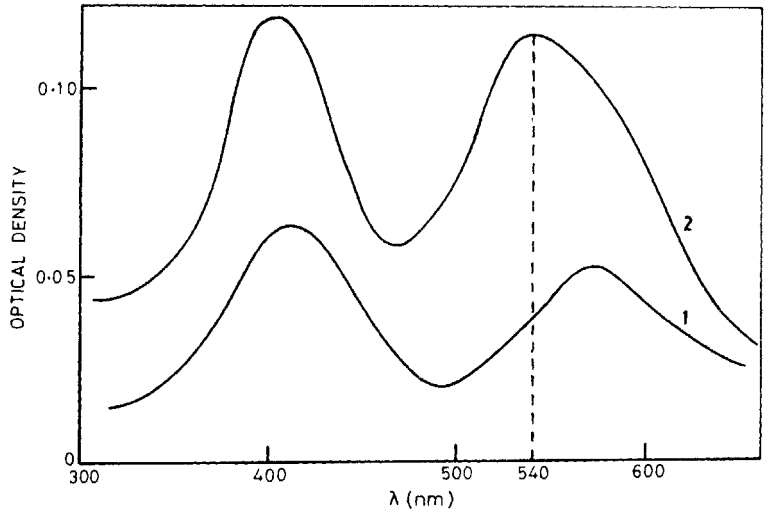


Fig 1 Absorption curves of $Cr(NO_3)_3 \cdot 9H_2O$ and its L-leucine complex; (1) 10^3 $[Cr(III)]_T$ = 2.0 mol dm^{-3}; (2) 10^2 $[Cr(III)]_T = 10^2$ $[Leucine]_T$ = 2.0 mol dm^{-3} (1 : 9 molar ratio).

Table I

Effect of chromium concentration, ionic strength and %EtOH on k_{obs} (10^4 [H^+] = 11.5 mol dm^{-3}, (t = 45°C)

10^3 [Cr(III)]$_T$ (mol dm^{-3})	μ (mol dm^{-3})	% EtOH (v/v)	10^4 k_{obs} (s^{-1})
			10^2 [Leucine]$_T$ = 4.0 mol dm^{-3}
2.0	1.0	0	0.29
3.0	1.0	0	0.34
4.0	0.3	0	0.35
4.0	0.5	0	0.37
4.0	0.7	0	0.39
4.0	0.9	0	0.42
4.0	1.0	0	0.45
4.0	1.0	10	0.72
4.0	1.0	15	1.02
4.0	1.0	20	1.32
4.0	1.0	25	1.80
			10^3 [Leucine]$_T$ = 4.0 mol dm^{-3}
20.0	1.0	0	0.20
30.0	1.0	0	0.24
40.0	1.0	0	0.19
50.0	1.0	0	0.17

is protonated[9] the ligands bind to chromium(III) only through carboxylate oxygen. This is in confirmity with previous findings of Shuttleworth and Sykes[10] where they reported complex formation with coordination of the carboxylate group taking place at *p*H value less than 4 and coordination of the amino group only taking place at pH value greater than 7.0. This coordination mode is well known for some other metal ions (e.g., Co(III)[11], Pt(II)[12]) but to a lesser extent for Cr(III)[13].

The composition of the complex formed, as determined by Job's method, was found to be 1 : 3 which is in confirmity with the previously reported observations[14].

Chromium(III) Concentration Dependence of the Reaction Rate

The first set of experiments were performed with varying [Cr(III)]$_T$ at fixed [Leucine]$_T$, ionic-strength, *p*H and temperature. The results (Table I) show that the rate of reaction is first order in total chromium(III) concentration and the rate law would be:

$$d[\text{complex}]/dt = -d[\text{Cr(III)}]_T/dt = k_{obs}[\text{Cr(III)}]_T \quad \ldots (1)$$

pH Dependence of the Reaction Rate

The chromium(III)-leucine reaction was studied as a function of *p*H between 2.75 and 3.8 at $[\text{Cr(III)}]_T = 0.004$ mol dm^{-3} and at various fixed $[\text{Leucine}]_T$. Data at several constant temperatures are given in Table II which show that the k_{obs} increases with increasing *p*H.

To explain the *p*H dependence of the rate the following equilibrium is considered necessary:

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H^+ \quad \ldots (2)$$
$$(pK_h = 4.1, \text{ambient}^{15})$$

For this equilibrium we can write:

$$4.1 = pH + \log \frac{[Cr(H_2O)_6^{3+}]}{[Cr(H_2O)_5OH^{2+}]} \quad \ldots (3)$$

At lower *p*H mainly $[Cr(H_2O)_6]^{3+}$ exists and, as *p*H increases, the percentage of $[Cr(H_2O)_5OH]^{2+}$ increases which, in turn, increases the reaction rate. The presence of OH^- ligand in the hydroxoaqua species in several cases, even if not in general, has caused increased liabilities (due to its π-bonding ability) and therefore increased rates are found in the case of, for example, Al(III)[16], Ga(III)[17], Mn(III)[18], Fe(III)[19] or Cr(III)[6,7,20]. In the case of Cr(III), the OH^- ligand increases by about 2 orders of magnitude the rate of water exchange of the unhydrolysed metal and gives a dissociative character to the metal centre[21].

The ligand, on the other hand, also participates in acid-base equilibria:

$$\text{leuH}_2^+ \overset{K_{a_1}}{\rightleftharpoons} \text{leuH} + H^+ \quad (pK_{a_1} = 2.36) \quad \ldots (4)$$

and

$$\text{leuH} \overset{K_{a_2}}{\rightleftharpoons} \text{leu}^- + H^+ \quad (pK_{a_2} = 9.60), \quad \ldots (5)$$

where leuH_2^+ represent the cationic, $(Me)_2CHCH_2CH(H_3N^+)(CO_2H)$, leuH the zwitterionic, $(Me)_2CHCH_2CH(H_3N^+)(CO_2^-)$, and leu^- the anionic, $(Me)_2CHCH_2CH(H_2N)(CO_2^-)$, forms of the amino acid. From the K_a values one can ascertain that, under our experimental conditions of *p*H 2.75-3.8, the monopositive and zwitterionic species exist in significant concentrations (Fig. 2).

The most widely accepted first step of anation reactions is the formation of outer-sphere complexes (OSC's). The monopositive species of L-leucine being the unlikely partner (as it carries a net positive charge), it is the zwitterionic species which can undergo outer-sphere complexation with multivalent cations (though the net charge is zero, they carry a separated negative charge on the carboxylate part which provides the binding site for the final product).

Leucine Concentration Dependence of the Reaction Rate

The effect of varying the entering leucine concentration [0.04-0.09 mol dm^{-3}] on the reaction rate was studied at various fixed $[H^+]$ and at $[Cr(III)]_T = 0.004$ mol dm^{-3} and $\mu = 1.0$ mol dm^{-3}. The results are given in Table II

Table II

Variation of k_{obs} *with* $[Leucine]_T$ *and* $[H^+]$ *at different temperatures* (°C). (10^3 $[Cr(III)]_T = 4.0$ mol dm^{-3} dm, $\mu = 1.0$ mol dm^{-3})

10^4 $[H^+]$ (mol dm^{-3})	10^2 $[Leucine]_T$ (mol dm^{-3})	10^4 k_{obs} (s^{-1})			
		40	45	50	55
20.4	4.0	0.28	0.38	0.49	0.68
	5.0	0.28	0.43	0.59	0.82
	6.0	0.39	0.53	0.67	0.98
	7.0	0.41	0.59	0.75	1.02
	8.0	0.46	0.61	0.80	1.12
	9.0	0.49	0.64	0.89	1.20
11.5	4.0	0.35	0.46	0.65	0.97
	5.0	0.42	0.52	0.76	1.17
	6.0	0.49	0.63	0.88	1.31
	7.0	0.52	0.67	0.92	1.54
	8.0	0.57	0.70	1.02	1.54
	9.0	0.60	0.77	1.08	1.64
7.2	4.0	0.44	0.58	0.82	1.20
	5.0	0.50	0.69	0.99	1.39
	6.0	0.55	0.75	1.06	1.49
	7.0	0.62	0.78	1.16	1.69
	8.0	0.66	0.86	1.22	1.78
	9.0	0.70	0.92	1.30	1.85
4.6	4.0	0.56	0.76	1.12	1.56
	5.0	0.60	0.89	1.25	1.75
	6.0	0.68	0.94	1.33	1.82
	7.0	0.73	0.96	1.49	2.08
	8.0	0.79	1.04	1.51	2.04
	9.0	0.81	1.10	1.61	2.22
1.8	4.0	0.71	1.00	1.28	2.22
	5.0	0.83	1.22	1.47	2.50
	6.0	0.96	1.35	1.72	3.12
	7.0	1.11	1.61	2.08	3.22
	8.0	1.11	1.52	2.63	3.57
	9.0	1.16	1.78	2.63	3.57

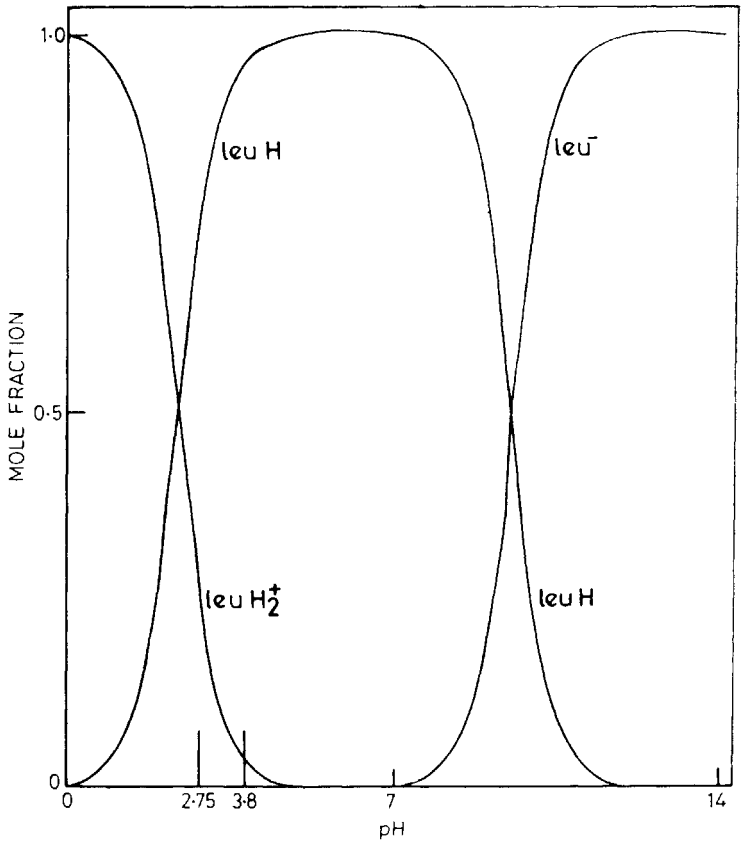
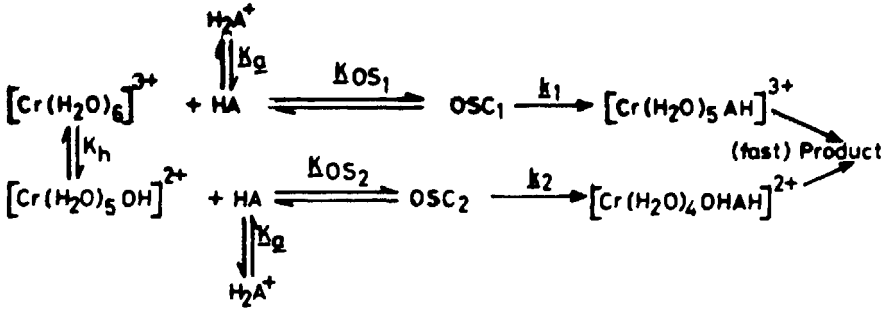


Fig 2 Concentration profile of the species of L-leucine over the *p*H range 1-14

and representative plots of the dependence of k_{obs} on $[Leucine]_T$ are illustrated in Fig. 3. The remaining data in Table II produced similar plots. It is observed that as $[Leucine]_T$ increases, k_{obs} increases but non-linearly. A marked curvature is observed in all the cases which becomes more pronounced at higher *p*H. Such behaviour is indicative of outersphere complexation between the reactive species[22].

The following scheme can be proposed to explain the data obtained:



where $OSC_1 = \{[Cr(H_2O)_6]^{3+}.AH\}$, $OSC_2 = \{[Cr(H_2O)_5OH]^{2+}.AH\}$, and $A = leu^-$.

The reaction sequence is given as:

$$[Cr(H_2O)_6]^{3+} \overset{K_h}{\rightleftharpoons} [Cr(H_2O)_5OH]^{2+} + H^+ \quad \ldots (6)$$

$$H_2A^+ \overset{K_a}{\rightleftharpoons} HA + H^+ \quad \ldots (7)$$

$$[Cr(H_2O)_6]^{3+} + HA \overset{K_{OS_1}}{\rightleftharpoons} OSC_1 \quad \ldots (8)$$

$$[Cr(H_2O)_5OH]^{2+} + HA \overset{K_{OS_2}}{\rightleftharpoons} OSC_2 \quad \ldots (9)$$

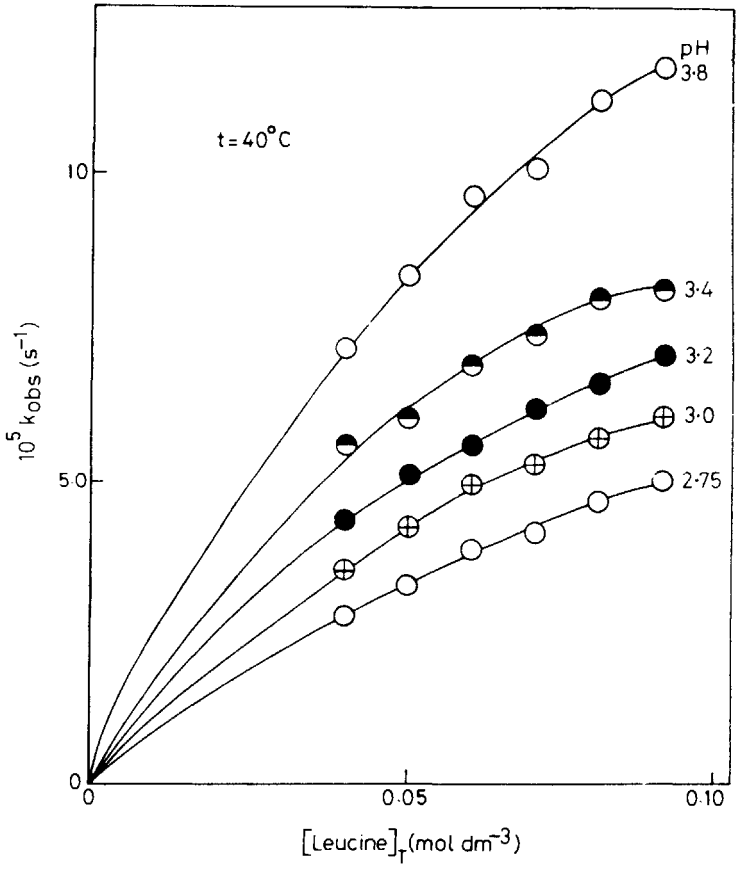


Fig 3 Dependence of k_{obs} on [Leucine]$_t$. 10^3[Cr(III)]$_t$ = 4.0 mol dm^{-3}, μ = 1.0 mol dm

$$OSC_1 \xrightarrow{k_1} \{[Cr(H_2O)_5AH]^{3+} + H_2O \quad \ldots (10)$$

$$OSC_2 \xrightarrow{k_2} [Cr(H_2O)_4OHAH]^{2+} + H_2O \quad \ldots (11)$$

$$\left.\begin{array}{l} [Cr(H_2O)_5AH]^{3+} \xrightarrow[\text{ligand}]{\text{fast}} \\ \\ [Cr(H_2O)_4OHAH]^{2+} \xrightarrow[\text{ligand}]{\text{fast}} \end{array}\right\} \text{Product} \quad \ldots (12)$$

The proposed mechanism is identical with the so-called 'Eigen-Tamm'[23] mechanism for anation reactions of labile aqua complexes involving (*i*) free ions ⇌ outer-sphere complex, and (*ii*) outer-sphere complex ⇌ inner-sphere complex with a difference that the contribution of the reverse reaction of step (*ii*) is very small (in fact, zero, as the plots of k_{obs} *vs* $[Leucine]_T$ have zero intercepts). According to the proposed mechanism, the rate of exchange of first water molecule in the inner-coordination sphere of the metal centre is slow and rate-determining. As soon as one molecule of AH enters into the inner-coordination sphere and $[Cr(H_2O)_5AH]^{3+}$/$[Cr(H_2O)_4OHAH]^{2+}$ complex is formed, the electron density on the chromium(III) centre is increased (owing to the inductive effect). As a result, the remaining water ligands are labilized easily and subsequent substitutions are fast.

The rate law corresponding to the above scheme can be expressed as:

$$\text{rate} = d[\text{complex}]/dt = k_1[OSC_1] + k_2[OSC_2] \quad \ldots (13)$$

Using the usual expressions for K_h, K_{OS1}, K_{OS2} (rapid establishment of these equilibria are assumed) and the mass balance equation for Cr(III) the rate law (14) is obtained:

$$d[\text{complex}]/dt = \frac{(k_1K_aK_{OS_1}[H^+] + k_2K_aK_hK_{OS_2})[Cr(III)]_T[Leucine]_T}{[H^+]^2 + [H^+]K_a + [H^+]K_h + K_aK_h + (K_aK_{OS_1}[H^+] + K_aK_hK_{OS_2})[Leucine]_T} \quad \ldots (14)$$

Comparison of Eq. (14) with (1) gives Eq. (15) which can be re-written as eq. (16) with $Y = k_1K_aK_{OS1}[H^+] + k_2K_aK_hK_{OS2}$.

$$k_{obs} = \frac{(k_1K_aK_{OS_1}[H^+] + k_2K_aK_hK_{OS_2})[Leucine]_T}{[H^+]^2 + [H^+]K_a + [H^+]K_h + K_aK_h + (K_aK_{OS_1}[H^+] + K_aK_hK_{OS_2})[Leucine]_T} \quad \ldots (15)$$

$$1/k_{obs} = \frac{K_a K_{OS_1}[H^+] + K_a K_h K_{OS_2}}{Y} + \frac{[H^+]^2 + [H^+]K_a + [H^+]K_h + K_a K_h}{Y} \cdot \frac{1}{[\text{Leucine}]_T} \quad \ldots (16)$$

Plots of $1/k_{obs}$ *vs* $1/[\text{Leucine}]_T$, at each acidity, show the expected linear relationship (Fig. 4). The intercepts of these plots are dependent on $[H^+]$ [as envisaged by Eq. (16)], but only upto 10^4 $[H^+] \approx 2$ mol dm^{-3}. The straight lines converge above this $[H^+]$ and give a common intercept. Thus, above this hydrogen ion concentration the intercepts become independent of $[H^+]$. At the low *p*H range, as $K_h \approx 10^{-4}$ mol dm^{-3} and $K_{OS_1} > K_{OS_2}$, $K_a K_h K_{OS_2}$ and

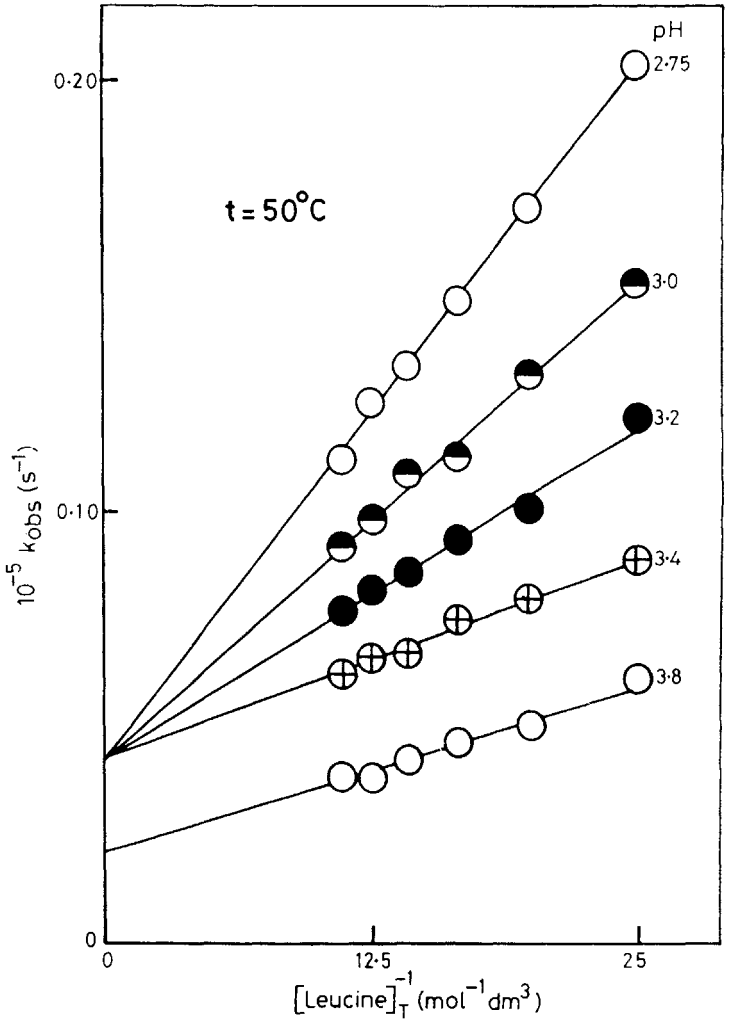


Fig 4 k_{obs}^{-1} *vs* $[\text{Leucine}]_T^{-1}$ plots (conditions were the same as in Fig 3)

$k_2K_aK_hK_{OS2}$ can be neglected in comparison with $K_aK_{OS1}[H^+]$ and $k_1K_aK_{OS1}[H^+]$, respectively, and also $[H^+]K_h + K_aK_h$ as compared to $[H^+]^2 + [H^+]K_a$. Introducing these approximations, Eq. (16) simplifies to Eq. (17):

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{[H^+] + K_a}{k_1 K_a K_{OS_1}} \cdot \frac{1}{[\text{Leucine}]_T} \quad \ldots (17)$$

Again, under these conditions, a linear plot will be obtained on plotting $1/k_{obs}$ *vs* $1/[\text{Leucine}]_T$ at a given $[H^+]$. This is also confirmed by the plots of Fig. 4 (upper lines) having intercepts independent of $[H^+]$. Eq. (17) may also be derived independently if the interactions with $[Cr(H_2O)_5OH]^{2+}$ are neglected in the scheme[5].

The values of k_1 and K_{OS1} were obtained from plots producing convergent straight lines (according to Eq. (17)). With the knowledge of k_1 and K_{OS1}, k_2 and K_{OS2} were determined from the plots of $1/k_{obs}$ *vs* $1/[\text{Leucine}]_T$ obtained at higher *p*H values. The results are given in Table III.

Ionic-Strength Dependence of the Reaction Rate

In these experiments the $[Cr(III)]_T$, $[\text{Leucine}]_T$ and *p*H were kept constant and ionic-strength was varied by the addition of requisite amount of KNO_3. The pseudo-first order rate constants obtained at constant temperature are given in Table I. It is observed that the reaction rate increases with increase in ionic-strength which indicates easy removal of coordinated water molecule from outer-sphere complexes. These results in the light of Bronsted-Bjerrum-Christiansen-Scatchard theory[24], corroborate the proposed ion-dipole outer-sphere complexation mechanism. On the addition of excess nitrate, the water molecules which are coordinated in the outer-sphere complex, reorient considerably around nitrate ions through hydrogen bonding. As a result, NO_3 ions, though inert, thus facilitate the metal ion-water ligand bond fission. Labilization of this water catalyzes the entry of outer-sphere ligand and its subsequent coordination to the metal. The water molecules are then engaged in the nitrate ions solvation.

Alcohol Percentage Dependence of the Reaction Rate

In order to see the influence of dielectric constant of the medium on reaction rate the anation reaction was studied in ethanol-water mixed solvent also. An increase in k_{obs} value was obtained with decrease in the dielectric constant of the medium (Table I). The plot of log k_{obs} *vs* $1/D$ was linear with positive slope supporting that the reaction under study is of ion-dipole type (Fig. 5). Obviously, the values of K_{OS1} and K_{OS2} will increase with decrease in D of the medium and, therefore, outer-sphere complexations are enhanced with a consequent increase in the rate.

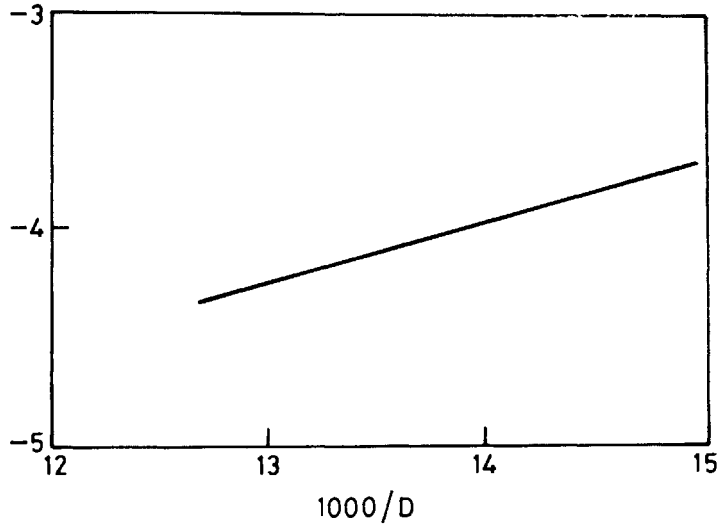


Fig 5 A plot of log k_{obs} against the reciprocal of the dielectric constant (D)

Table III

Anation and outer-sphere association constants of Cr(III) + L-leucine reaction at $\mu = 1.0$ mol dm^{-3}

Temperature (°C)	$10^4 k_1$ (s^{-1})	K_{OS_1} (mol^{-1} dm^3)	$10^3 k_2$ (s^{-1})	K_{OS_2} (mol^{-1} dm^3)	$10^3 K_a^a$ (mol^{-1} dm^3)
40	1.33	11.38	0.34	9.52	4.73
45	1.69	11.50	0.43	10.30	4.69
50	2.32	12.10	0.54	10.86	4.64
55	3.12	14.20	0.69	12.02	4.54

[a] P R Smith, A C Taylor and E R B Smith *J biol Chem* **122** (1937-38) 109; values were calculated by Harned and Embree's equation: $pK = pK_{max} + p(t - \theta)^2$ with $pK_{max} = 2.324$, $p = 5 \times 10^{-5}$ and $\theta = 35.4$.

Temperature Dependence of the Reaction Rate

The temperature dependence of the reaction rate was studied for different $[Leucine]_T$ and $[H^+]$ at $\mu = 1.0$ mol dm^{-3}. The k_{obs} values are given in Table II and the k_1 and K_{OS} in Table III.

Activation parameters collected in Table IV (along with some previously studied related systems) were calculated by the least-squares method using Eyring plots of the temperature dependence of k_1 and k_2.

Mechanism

It is generally accepted[26] that complex formation reaction of metal ions proceed by a mechanism in which the rate-determining step is the reaction from the outer-sphere complex to the inner-sphere complex, preceded by formation of the outer-sphere complex between metal ion and ligand. It has al-

Table IV

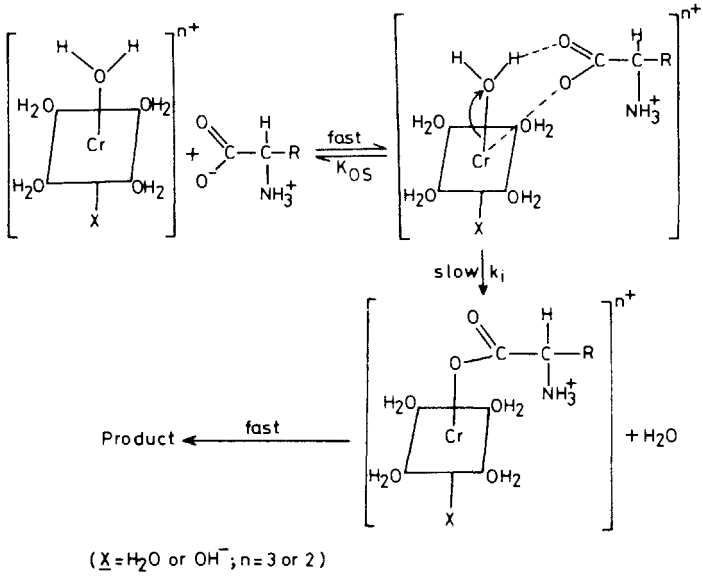
Comparison of rate-constants, k_1 and k_2, and their activation parameters for the anation of $[Cr(H_2O)_6]^{3+}$ an $[Cr(H_2O)_5OH]^{2+}$ at $\mu = 1.0$ mol dm^{-3}

Ligands	$10^4 k_1$ (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	$10^3 k_2$ (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	Reference
H_2O^{18}	0.10 (35°C, k_{ex})	108.6	+11.6	0.76 (35°C, k_{ex}')	111.0	+55.6	a, 21
Glycine	6.80 (35°C)	51.9	−42.7	—	—	—	3
Glycine[b]	3.34 (35°C)	58.0	−129.2	—	—	—	5
Sarcosine	3.57 (40°C)	54.7	−136.6	1.23 (50°C)	—	—	6
Alanine$_h$	0.58 (35°C)	64.9	−113.6	0.46 (45°C)	77.0	−68.0	6
Alanine	—	—	—	0.40 (35°C)[c]	34.1	−201.8	7
Valine	2.35 (35°C)	90.4	−21.0	—	—	—	5
Leucine	1.33 (40°C)	46.4	−171.0	0.34 (40°C)	37.5	−192.0	This work
Serine[b]	0.62 (35°C)	78.0	−72.5	—	—	—	5
H_2asp	1.80 (35°C)	81.0	−54.0	—	—	—	5
Hasp	1.30 (35°C)	50.0	−157.0	0.74 (35°C)[d]	45.4	−144.9	5, 7
Glutamine	1.81 (40°C)	52.0	−150.6	0.46 (40°C)	43.7	−161.1	e
Methionine	2.22 (35°C)	61.1	−116.3	0.36 (35°C)	83.4	−48.2	f
Methionine[g]	—	—	—	0.80 (35°C)	59.8	−97.0	7
Phenylalanine	1.85 (35°C)	53.6	−141.7	0.71 (45°C)	—	—	6
Phenylalanine[h]	—	—	—	0.32 (35°C)	53.9	−136.0	7
Hydroxyproline	1.00 (40°C)	72.9	−98.2	0.21 (40°C)	63.2	−114.1	6
Tryptophan	1.17 (40°C)	65.6	−112.4	0.25 (40°C)	85.0	−44.8	6

[a] $\mu = 0.7$ mol dm^{-3}, [b] Extrapolated values, [c] $\mu = 0.03$ mol dm^{-3}, [d] $\mu = 0.065$ mol dm^{-3}, [e] Kabir-ud-din, I A Khan and M Shahid *Indian J Chem* **32A** (1993) 171. [f] I A Khan, M Shahid and Kabir-ud-Din *Transition Met Chem* **16** (1991). 18, [g] $\mu = 0.0075$ mol dm^{-3}, water-ethanol medium, [h] $\mu = 0.0075$ mol dm^{-3}.

ready been established that the reactions under study are of ion-dipole type. From the ionic-strength and dielectric constant effects it can be suggested that the reactions are between a positive ion and dipole.

The reaction mechanism can be given as follows:—



The reactions of the aquachromium(III) complexes are assumed to occur *via* outer-sphere associations which are stabilized by hydrogen bonding. The carboxylate moiety of the amino acid forms a weak bond in the reaction of hexaaquachromium(III) complex and a more weak bond in the reaction of hydroxopentaaqua complex.

In order to decide whether the interchange mechanism of $[Cr(H_2O)_6]^{3+}$/ $[Cr(H_2O)_5OH]^{2+}$ complex is I_a or I_d, we can utilize the following three criteria which have been used in assigning I_d (as opposed to I_a) mechanism to substitution reactions of $[Co(NH_3)_5H_2O]^{3+}$:

(*a*) in k_i no appreciable change is obtained on changing the nature of the entering ligand (earlier[27], examination of second-order rate constant $k_f (= k_i K_{OS})$ were used to characterize anation reactions of metal ions but this has been proved faulty as K_{OS} values depend not only on the charge of the entering ligand but also on its nature).

(*b*) k_1 is always less than k_{ex} for solvent water[2].

(*c*) The volume of activation, $\Delta V^{\ddagger}$, (this parameter has been regarded to possess definite mechanistic discriminating ability; $\Delta V^{\ddagger}$ is positive for I_d and negative for I_a mechanism) for water-exchange is positive for $[Co(NH_3)_5H_2O]^{3+}$ (ref. 28).

Applying these criteria to substitution reactions of $[Cr(H_2O)_6]^{3+}$/ $[Cr(H_2O)_5OH]^{2+}$, we have:

(*a*) Spans of k_1 and k_2 are $(0.58\text{-}6.80)\times 10^{-4}$ (35-40°C) and $(0.21\text{-}1.23)\times 10^{-3}\ s^{-1}$ (35-50°C), respectively.

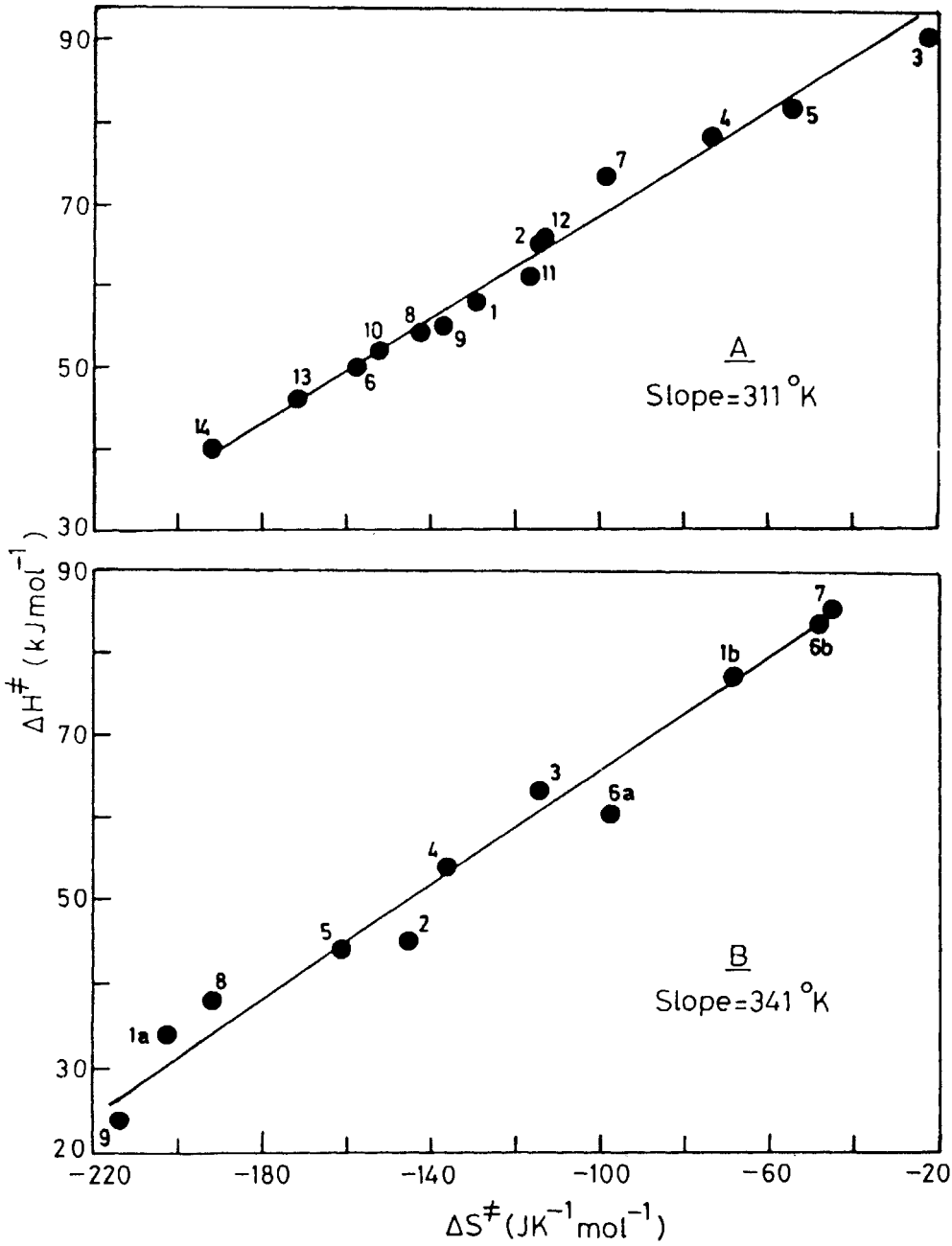


Fig 6 Isokinetic relationship, $\Delta H^{\ddagger}$ *vs* $\Delta S^{\ddagger}$, for amino acid anations of (A) $[Cr(H_2O)_6]^{3+}$ by (1) glycine, (2) alanine, (3) valine, (4) serine, (5) H_2asp, (6) $Hasp^-$, (7) hydroxyproline, (8) phenylalanine, (9) sarcosine, (10) glutamine, (11) methionine, (12) tryptophan, (13) leucine, (14) cysteine, and (b) $[Cr(H_2O)_5OH]^{2+}$ by (1) alanine, (2) $Hasp^-$, (3) hydroxyproline, (4) phenylalanine, (5) glutamine, (6) methionine, (7) tryptophan, (8) leucine, (9) cysteine

(*b*) For all the systems investigated k_1 is always greater than the value of k_{ex} (water exchange of $[Cr(H_2O)_6]^{3+}$) whereas k_2 values are comparable with k_{ex}' (water exchange of $[Cr(H_2O)_5OH]^{2+}$) (Table IV). Due to the labilization effect of hydroxide, this latter result is in accord with the expectations.
(*c*) $\Delta V^{\ddagger}$ for water exchange of $[Cr(H_2O)_6]^{3+}$ has a negative value (-9.6 cm^3 mol^{-1}) but for $[Cr(H_2O)_5OH]^{2+}$ it is positive ($+2.7$ cm^3 mol^{-1})[21].

We see that on all counts the favoured mechanism for the anation reaction of $[Cr(H_2O)_6]^{3+}$ is an associative interchange (I_a) and dissociative interchange (I_d) for $[Cr(H_2O)_5OH]^{2+}$.

A comparison of the activation parameters for anation reactions of Cr(III) (Table IV) also support the above assignments[2,27].

The isokinetic plots of $\Delta H^{\ddagger}$ *vs* $\Delta S^{\ddagger}$ for the interaction of aquachromium(III) species with various amino acids are linear (Fig. 6) (slopes = 308 and 334 K, which are well within the experimental temperature range). This indicates that similar transition states are formed and, therefore, similar mechanisms are operating in all such anation reactions; namely, I_a for reactions involving $[Cr(H_2O)_6]^{3+}$ and I_d involving $[Cr(H_2O)_5OH]^{2+}$.

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