Kinetics of Anation of Hexaaquochromium(III) Ion by Serine in Aqueous-Acidic Medium

IQRAR A KHAN, MOHAMMAD SHAHID & KABIR-UD-DIN*

Department of Chemistry, Aligarh Muslim University, Aligarh 202001

Chromium(III) forms 1:3 complex (metal-ligand) with serine. The rates of formation of Cr(III)-serine complex from hexaaquochromium(III) ion and serine in aqueous-acidic medium have been studied spectrophotometrically at different [serine] and [H$^+$] in the temperature range 39.5-55°C. The rates have been found to be insensitive towards the change in ionic strength from 0.2 to 1.0 mol dm^{-3} of the medium. The results are in accord with a mechanism involving ion-pair formation between hexaaquochromium(III) ion and serine in the zwitterionic form. The activation and thermodynamic parameters for anation rate constant, k_{an} and ion-pair equilibrium constant, K_{IP}, have been calculated by using Eyring equation. These and other data provide evidence for an associative interchange (I_a) mechanism.

Recent studies[1-6] on the substitution reactions of hexaaquochromium(III) ion have revealed that these reactions proceed via an associative interchange process. In continuation of our previous studies[7-9] on the substitution reactions of hexaaquochromium(III), we report herein the results of studies on the kinetics of anation of hexaaquochromium(III) ion by serine in aqueous-acidic medium. A comparison with literature data has also been made.

Materials and Methods

DL-Serine (BDH) was used as such. Stock solutions of chromium nitrate, potassium nitrate, sodium hydroxide (all AnalaR grade) were prepared in doubly distilled air-free water. Chromium nitrate solution was standardized by ion-exchange method, using Dowex 50W-8X (H$^+$-form) resin, as described by Banerjea and Duttachaudhuri[10].

All spectral measurements were done with a Bausch and Lomb spectronic-20 spectrophotometer.

Composition of chromium(III)-serine complex was determined spectrophotometrically at 540 nm, using Job's method of continuous variations. For this, a series of solutions containing different metal-ligand ratios were prepared, boiled and equilibrated at 50°C for 24 hr. Absorbances were measured at 540 nm after bringing the solutions to room temperature.

Kinetics of substitution of aquo-ligand by serine was followed spectrophotometrically by recording change in the absorbance at 540 nm, the λ_{max}, at which the molar extinction coefficient of $Cr(H_2O)_6^{3+}$-serine complex is 92.5 dm^{3}mol^{-1}cm^{-1}. In all kinetic runs the concentration of chromium nitrate was 0.004 mol dm^{-3} whereas the concentration of serine was varied from 0.04 to 0.22 mol dm^{-3}. The pH of experimental solutions were adjusted by adding NaOH/HNO$_3$. Ionic strength of solutions was kept constant at 1.0 mol dm^{-3} (KNO$_3$), except where the ionic strength effect was studied.

Details of the kinetic procedure were the same as those given in our earlier publications[7-9].

Under pseudo-first order conditions, the rate constants, k_{obs}, were obtained from the plots of log(A$_\infty$-A$_t$) versus t. The plots were linear for at least two half-lives.

All the calculations were done on a VAX-11/780 computer.

Results and Discussion

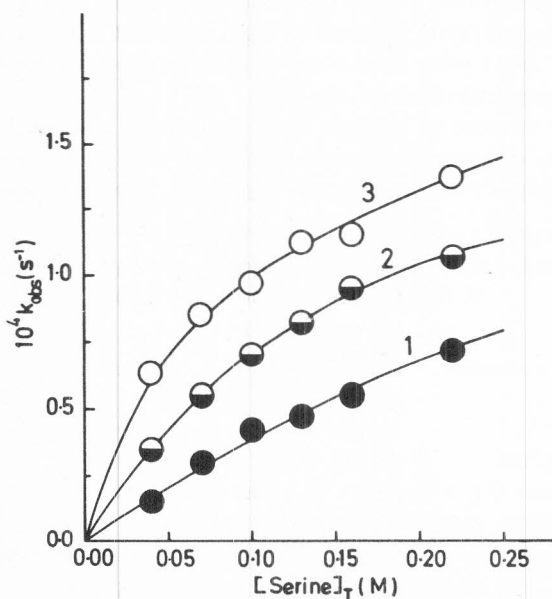Hexaaquochromium(III) ion forms 1:3 (metal-ligand) complex with serine.

The pseudo-first order rate constants, k_{obs}, for the anation of hexaaquochromium(III) by serine are listed in Table 1. The plots of k_{obs} versus [Serine] at 45°C, μ = 1.0 mol dm^{-3} and at different acidities were non-linear (Fig. 1). The deviations from linearity were more pronounced at higher acidity range which may be explained on the basis of strong ionic association of the reactant species. Similar plots were obtained for other temperatures also.

It is generally believed that in the amino acid-metal complex formation only the anion of the ligand is the reactive species although other forms do exist at high concentrations[11]. It is well known that, depending on the pH of the solution, serine can exist either as an anion, or zwitterion or cation[12].

Under our experimental conditions (pH = 2.9-3.85) the major species are cation, H$_2$L$^+$, and zwitterion, HL. That this is indeed the case and the concentration of anionic form is very low, is clearly shown by the data plotted in Fig. 2. The zwitterion has negative charge on the carboxylate part and can undergo ion-pairing with
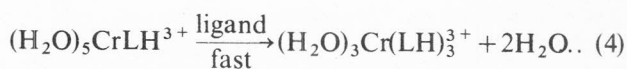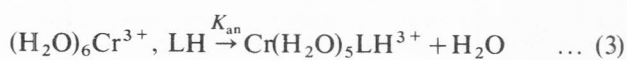
Table 1—Dependence of Pseudo-First Order Rate Constants (k_{obs}) on [Serine]$_T$, [H$^+$] and Ionic Strength at Different Temperatures

$\{ [Cr(H_2O)_6^{3+}] + 4.0 \times 10^{-3}\,mol\,dm^{-3};\ [Serine]_T \geqslant 10\,[Cr(H_2O)_6^{3+}] \}$

Temp. ($^\circ$C)	μ (mol dm^{-3})	$10^4 \times$[H$^+$] (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1}) at [Serine] (mol dm^{-3})					
			0.04	0.07	0.10	0.13	0.16	0.22
39.5	1.0	12.590	0.076	0.145	0.182	0.250	0.298	0.380
	1.0	4.467	0.150	0.241	0.298	0.385	0.408	0.476
	1.0	1.413	0.208	0.296	0.395	0.490	0.532	0.588
45	1.0	12.590	0.185	0.30	0.43	0.48	0.56	0.72
	1.0	4.467	0.36	0.56	0.70	0.82	0.96	1.08
	0.8	4.467			0.66			1.03
	0.6	4.467			0.70			1.65
	0.4	4.467			0.70			1.06
	0.2	4.467			0.69			1.08
	1.0	1.413	0.46	0.85	0.965	1.13	1.60	1.38
50	1.0	12.590	0.32	0.52	0.61	0.84	0.90	1.18
	1.0	4.467	0.58	0.88	1.10	1.25	1.38	1.66
	1.0	1.413	1.52	1.85	2.08	2.13	2.20	2.56
55	1.0	12.590	0.50	0.81	1.18	1.34	1.45	1.95
	1.0	4.467	1.075	1.58	1.80	2.05	2.55	3.35

Fig. 1—Dependence of k_{obs} on [Serine]$_T$ for the reaction of Cr(H$_2$O)$_6^{3+}$ with serine at 45°C, $\mu = 1.0$ mol dm^{-3} (KNO$_3$); [H$^+$] = 12.590 $\times$ 10^{-4} mol dm^{-3}(1), 4.467 $\times$ 10^{-4} mol dm^{-3}(2) and 1.413 $\times$ 10^{-4} mol dm^{-3}(3)
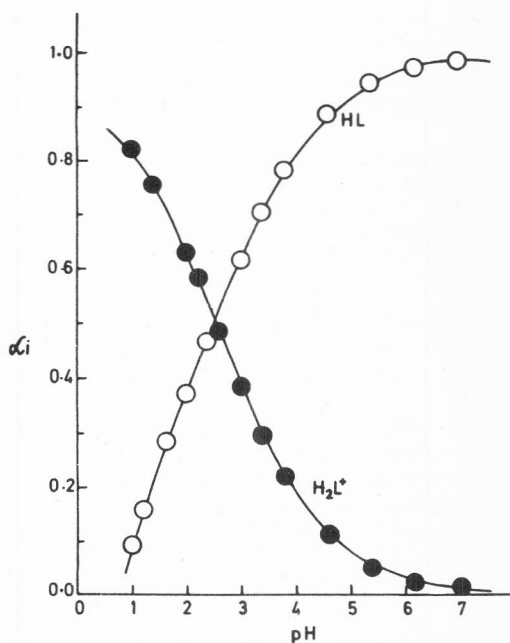
Fig. 2—Variation with pH of the distributions (given as α_i) of several species in aqueous solution of serine

multivalent cations; but, the net charge being zero, value of ion-pair formation constant should be smaller than that of the complexes with anionic ligands.

The lack of dependence of rate on ionic strength clearly excludes the participation of either L$^-$ or H$_2$L$^+$ ions as a reactive species in the anation process. Hence, the overall reaction is best accounted for by an ion-pair equilibrium involving zwitterion followed by slow interchange of the bound water and the entering ligand in the ion-pair (Scheme 1)

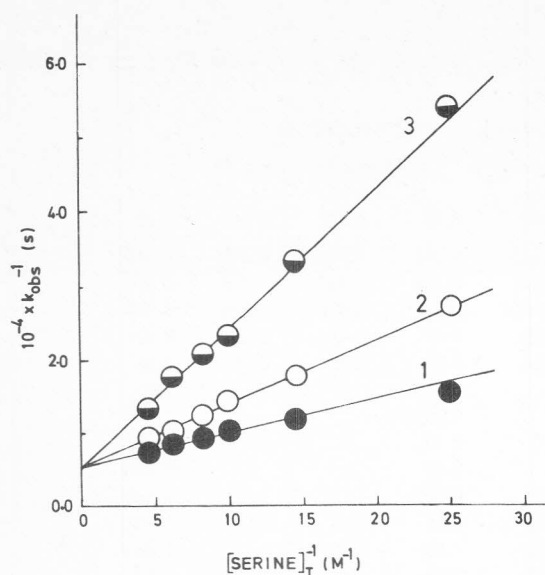$$H_2L^+ \overset{K_a}{\rightleftharpoons} HL + H^+ \qquad \ldots (1)$$

$$(H_2O)_6Cr^{3+} + HL \overset{K_{IP}}{\rightleftharpoons} (H_2O)_6Cr^{3+},\,LH \qquad \ldots (2)$$

$$(H_2O)_6Cr^{3+},\,LH \overset{K_{an}}{\to} Cr(H_2O)_5LH^{3+} + H_2O \qquad \ldots (3)$$

$$(H_2O)_5CrLH^{3+} \xrightarrow[\text{fast}]{\text{ligand}} (H_2O)_3Cr(LH)_3^{3+} + 2H_2O \ldots (4)$$

Scheme 1

383

Fig. 3—Dependence of k_{obs}^{-1} on $[Serine]_T^{-1}$ at $45^\circ C$, $[Cr^{3+}] = 4.0 \times 10^{-3} \, mol \, dm^{-3}$, $\mu = 1.0 \, mol \, dm^{-3}$, $[H^+] = 1.413 \times 10^{-4} \, mol \, dm^{-3}(1)$, $4.467 \times 10^{-4} \, mol \, dm^{-3}(2)$ and $12.590 \times 10^{-4} \, mol \, dm^{-3}(3)$

On the basis of the above mechanism the rate law is given by Eq. (5)

$$k_{obs} = \frac{k_{an}K_aK_{IP}[Serine]_T}{[H^+] + K_a + K_aK_{IP}[Serine]_T} \quad \ldots (5)$$

where $[Serine]_T$ is the total concentration of serine added. Equation(5) can be rearranged to Eq. (6)

$$\frac{1}{k_{obs}} = \frac{1}{k_{an}} + \frac{[H^+] + K_a}{k_{an}K_aK_{IP}[Serine]_T} \quad \ldots (6)$$

Equation (6) envisages that a plot of k_{obs}^{-1} against $[Serine]_T^{-1}$ should be linear. Furthermore, such plots at different $[H^+]$ would be linear with a common intercept, $1/k_{an}$. The experimental results confirm these two criteria (Fig. 3).

The rate parameters, k_{an} and K_{IP}, used in Eq. (5) were evaluated by linear-least squares regression analysis of the data and are listed in Table 2. Enthalpies of activation ($\Delta H\ddagger$) and entropies of activation ($\Delta S\ddagger$) for anation rate constant, k_{an}, were obtained from the plots of $\log k_{an}/T$ against $1/T$. Thermodynamic parameters for ion-pair formation constant, K_{IP}, were evaluated from the plots of $\log K_{IP}$ against $1/T$ (Table 3). Errors were determined in all the cases by least-squares treatment of the data.

A number of workers have studied the anation kinetics of hexaaquochromium(III) ion with a variety of ligands—both organic and inorganic. The data were

Table 2—Rate Parameters Used in Equation(5) for Anation of Hexaaquochromium(III) Ion by Serine

$[H^+] = 4.467 \times 10^{-4} \, mol \, dm^{-3}$; $\mu = 1.0 \, mol \, dm^{-3}(KNO_3)$;
$[Cr(H_2O)_6^{3+}] = 4.0 \times 10^{-3} \, mol \, dm^{-3}$

Temp. ($^\circ C$)	$k_{an} \times 10^4$ (s^{-1})	K_{IP} ($dm^3 mol^{-1}$)	$K_a^* \times 10^3$ ($dm^{-3} mol$)	R.m.s.† $\times 10^5$
39.5	0.98 ± 0.07	4.83 ± 0.12	7.12 ± 0.005	0.120
45	1.92 ± 0.06	6.18 ± 0.05	7.24 ± 0.060	0.148
50	2.68 ± 0.08	7.34 ± 0.11	7.28 ± 0.090	0.245
55	4.43 ± 0.65	8.63 ± 0.75	7.40 ± 0.190	2.619

* Extrapolated values from the data of Smith P K, Gorham A T & Smith E R B, *J biol Chem*, 144 (1942) 737.
† Root-mean-square deviation between the observed and calculated values of pseudo-first order rate constants.

Table 3—Activation Parameters for k_{an} and K_{IP} for Anation of Hexaaquochromium(III) by Serine

$\mu = 1.0 \, mol \, dm^{-3}$ (KNO_3)

Rate parameters	$\Delta H\ddagger(kJ \, mol^{-1})$	$\Delta S\ddagger(J \, mol^{-1}K^{-1})$
$k_{ex}(s^{-1})$	109.62[a]	$+1.25$[b]
$k_{an}(s^{-1})$	$78.00 + 3.05$	-72.51 ± 9.54
$K_{IP}(dm^3mol^{-1})$	30.20 ± 1.13	-110.00 ± 3.51

[a] Stranks D R & Swaddle T W, *J Am chem Soc*, 93 (1971) 2783.
[b] Exchange of one ligand only.

Table 4—A Comparison of Anation Rate Constants[a], k_{an}, and Activation Parameters of Analogous Systems

System	$k_{an}(s^{-1})$	$\Delta H\ddagger(kJ \, mol^{-1})$	$\Delta S\ddagger(J \, mol^{-1}K^{-1})$	Ref.
$Cr(H_2O)_6^{3+}$-18 OH_2	4.17×10^{-6}	109.62	$+11.74$	20
$Cr(H_2O)_6^{3+}$-Glycine[b]	3.34×10^{-4}	58.00	-129.16	7
$Cr(H_2O)_6^{3+}$-Glycine	6.80×10^{-4}	51.88	-42.67	10
$Cr(H_2O)_6^{3+}$-Alanine[b]	0.58×10^{-4}	64.89	-113.60	8
$Cr(H_2O)_6^{3+}$-Valine	2.35×10^{-4}	91.88	-24.89	9
$Cr(H_2O)_6^{3+}$-Serine[b]	0.62×10^{-4}	78.00	-72.51	this work
$Cr(H_2O)_6^{3+}$-Anthranilic acid	4.66×10^{-4}	94.90	-0.58	c
$Cr(H_2O)_6^{3+}$-Nitrilotriacetic acid	1.67×10^{-4}	86.44	-36.82	d
$Cr(H_2O)_6^{3+}$-Salicylic Acid	17.82×10^{-4}	74.48	-60.49	e

[a] All values at $35^\circ C$ and $\mu = 1.0 \, mol \, dm^{-3}$, except where otherwise stated.
[b] Extrapolated values from 39.5°, 45°, 50° and $55^\circ C$.
[c] From Tyagi S C & Khan A Aziz, *Indian J Chem*, 16A (1978) 657.
[d] Ref. 5; $\mu = 0.25 \, mol \, dm^{-3}$, water-ethanol medium (30%, v/v).
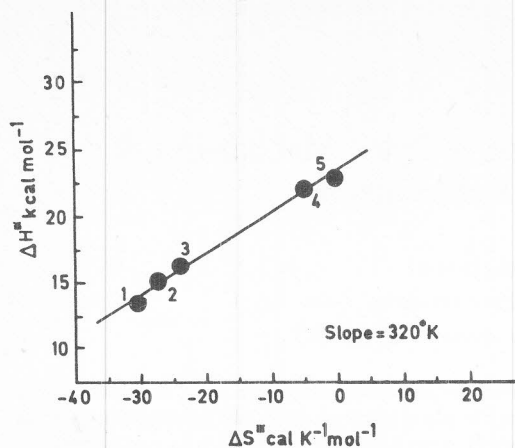[e] From Tyagi S C & Khan A Aziz, *J inorg nucl Chem*, 40 (1978) 1899.

Fig. 4—Isokinetic plot for the anation of $Cr(H_2O)_6^{3+}$ by (1) Glycine, (2) Alanine, (3) Serine, (4) Valine and (5) Anthranilic acid

discussed in terms of dissociative interchange $(I_d)^{13-17}$ and associative interchange $(I_a)^{5,6,10}$ mechanisms. Swaddle[18] has reviewed the activation parameters and mechanisms of octahedral substitutions and has concluded that an I_a mechanism is operative for octahedral cationic complexes of all trivalent transition metal ions [except Co(III)] having an ionic radii greater than 60 pm; but an I_d mechanism is operative for very large tripositive ions where charge-to-radius ratio is again small, as for divalent ions. The field free ionic radius of Cr^{3+} is 68-69 pm[19].

A comparison of water-exchange rate, k_{ex}, with that of anation rate constant, k_{an}, has been utilized as a significant tool for distinguishing an associative mechanism from a dissociative interchange mechanism. For an I_d process, k_{an} should be less than k_{ex} and insensitive to the nature of incoming ligand, X^-, whereas for an I_a process k_{an} should vary markedly with the nucleophilic power of incoming ligand towards M^{n+}, and where this power is high it actually exceeds k_{ex}.

In the present case, the values of k_{an} are far greater than the value of k_{ex} $(=4.2 \times 10^{-6}s^{-1})$ (ref. 20), suggesting a ligand assisted anation and hence an I_a path. The values of the activation parameters (Table 3) also support the I_a mechanism.

For comparison, k_{an} values and those reported in literature for the anation of $Cr(H_2O)_6^{3+}$ by different anionic and neutral ligands are presented in Table 4. Anation rate constants for different ligands show a significant dependence on the nature of the incoming ligand which strongly suggests an associative interchange (S_N2) mechanism.

The associative nature of the reaction of $Cr(H_2O)_6^{3+}$ with serine is further supported by the isokinetic plot (Fig. 4) for the interaction of hexaaquochromium(III) with various monoaminomonocarboxylic acid ligands. The plot gives the same isokinetic temperature (slope).

The possibility of the ion-pairing of the zwitterion with the hydroxy species of $Cr(H_2O)_6^{3+}$ $(pK_a = 4.1)^{21}$ is ruled out on the basis of the observed values of K_{IP} which are in fair agreement with those calculated by Nor and Sykes[22] for the process where the part played by hydroxy species is negligible. Also, on the basis of the unfavourable charge factor, ion-pairing of the H_2L^+ with $Cr(H_2O)_6^{3+}$ and the subsequent reactions are assumed to be insignificant.

Acknowledgement

References

1 Schenk C, Steiger H & Kelm H, *Coord Chem*, **2** (1972) 71.
2 Kornev V I & Valyaeva V A, *Zh Fiz Khim*, **51** (1977) 1669.
3 Ohashi K, Suzuki K, Kubo K & Yamamoto K, *Nippon Kagaku Kaishi*, **7** (1977) 978.
4 Kimura M & Shirai J, *J inorg nucl Chem*, **40** (1978) 1085.
5 Mandal J N &De G S, *Indian J Chem*, **19A** (1980) 25.
6 Tyagi S C & Khan A Aziz, *J chem Soc Dalton*, (1979) 420.
7 Khan I A & Kabir-Ud-Din, *J inorg nucl Chem*, **43** (1981) 1082.
8 Khan I A & Kabir-Ud-Din, *Inorg Chem*, (Communicated).
9 Khan I A & Kabir-Ud-Din, *Int J chem Kinet*, (Communicated).
10 Banerjea D & Duttachaudhuri S, *J inorg nucl Chem*, **30** (1968) 871.
11 Lin C T & Rorabacher B D, *Inorg Chem*, **12** (1973) 2402. and the references contained therein.
12 McGilvery R W, *Biochemistry, a fundamental approach* (Saunders W B Co, London) 1970. Chap 28.
13 Hamm R E & Davis R E, *J Am chem Soc*, **75** (1953) 3085.
14 Hamm R E & Perkins R H, *J Am chem Soc*, **77** (1955) 2083.
15 Hamm R E, Johnson R L, Perkins R H & Davis R E, *J Am chem Soc*, **80** (1958) 4469.
16 Banerjea D & Duttachaudhuri S, *J inorg nucl Chem*, **32** (1970) 1617.
17 Banerjea D & Chatterjee C, *J inorg nucl Chem*, **31** (1969) 3845.
18 Swaddle T W, *Coord Chem*, **14** (1974) 217.
19 Shannon R D & Prewitt C R, *Acta Crystallogr*, Sect B, **25** (1969) 925; **26** (1970) 1046.
20 Plane R A & Taube H, *J phys Chem*, **56** (1952) 33.
21 Sasaki Y & Sykes A G, *J chem Soc Dalton*, (1975) 1048.
22 Nor O & Sykes A G, *J chem Soc*, A (1973) 1232.