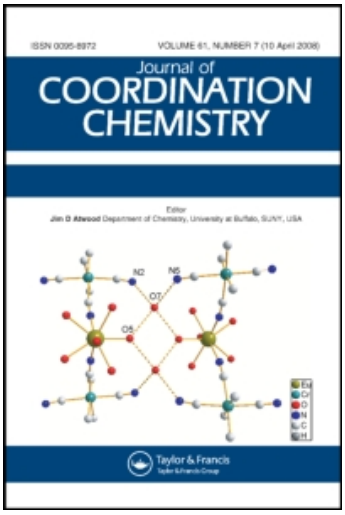


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Kinetics and Mechanism of Aquachromium(III) Anation by *L*-Arginine

Kabir-Ud-Din[a]; Ghulam Jilani Khan[a]
[a] Department of Chemistry, Aligarh Muslim University, Aligarh, India

To cite this Article Kabir-Ud-Din and Khan, Ghulam Jilani(1992) 'Kinetics and Mechanism of Aquachromium(III) Anation by *L*-Arginine', Journal of Coordination Chemistry, 26: 4, 351 — 355
To link to this Article: DOI: 10.1080/00958979209407938
URL: http://dx.doi.org/10.1080/00958979209407938

J. Coord. Chem. 1992, Vol. 26. pp. 351–355
Reprints available directly from the publisher
Photocopying permitted by license only

NOTE

KINETICS AND MECHANISM OF AQUACHROMIUM(III) ANATION BY *L*-ARGININE

KABIR-UD-DIN* and GHULAM JILANI KHAN

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

(*Received February 18 1992*)

Following Mertz's[1a] remarkable discovery of GTF's (*G*lucose *T*olerance *F*actor, a low-molecular-weight Cr(III) complex[1b]) insulin potentiating activity, reports on various aspects of Cr(III) complexation with biologically important ligands have appeared.[2] In order to further clarify the substrate behaviour of aqueous Cr(III), we report the kinetics of the reaction of $Cr(H_2O)_6^{3+}/Cr(H_2O)_5OH^{2+}$ with *L*-arginine.

The progress of the reaction was monitored spectrophotometrically at 550 nm (in all sets $[arginine]_T \geqslant 10[Cr(III)]_T$; other details are given elsehwere[2g]). Variation of *pseudo*-first-order rate constants (k_{obs}), obtained as a function of $[arginine]_T$, $[H^+]$, %EtOH and T was similar to earlier results.[2g] These results, along with the nature of the dependence of k_{obs} on $[arginine]_T$ (Figure 1 shows saturation of k_{obs} at high [ligand]), are consistent with the following mechanism where an ion-pairing precedes the rate-limiting loss of a coordinated water molecule.

$$H_3L^{2+} \rightleftharpoons K_a \rightleftharpoons H_2L^+ + H^+ \qquad (1)$$

$$Cr(H_2O)_6^{3+} \rightleftharpoons K_h \rightleftharpoons Cr(H_2O)_5OH^{2+} + H^+ \qquad (2)$$

$$Cr(H_2O)_6^{3+} + H_2L^+ \rightleftharpoons K_{OS1} \rightleftharpoons OSC1 \qquad (3)$$

$$Cr(H_2O)_5OH^{2+} + H_2L^+ \rightleftharpoons K_{OS2} \rightleftharpoons OSC2 \qquad (4)$$

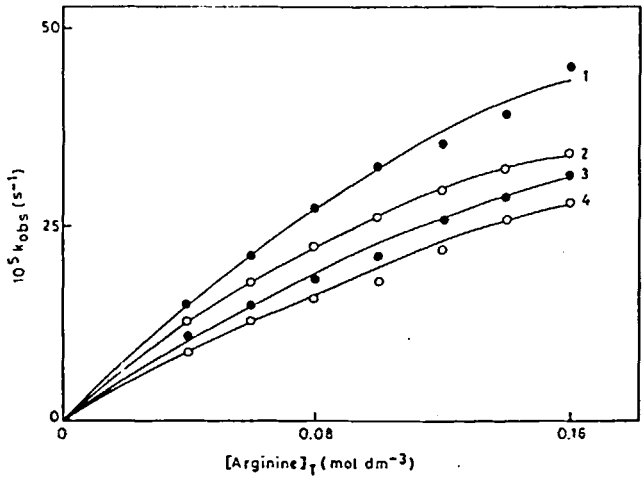
$$OSC1 \xrightarrow{k_1} [Cr(H_2O)_5LH_2^+]^{3+} + H_2O \qquad (5)$$

$$OSC2 \xrightarrow{k_2} [Cr(H_2O)_4OHLH_2^+]^{2+} + H_2O \qquad (6)$$

$$\left.\begin{array}{l} [Cr(H_2O)_5LH_2^+]^{3+} \xrightarrow{ligand} \\ [Cr(H_2O)_4OHLH_2^+]^{2+} \xrightarrow{ligand} \end{array}\right\} \text{product} \qquad (7)$$

(Arginine has a separated negative charge on the carboxyl group but can take part in reactions as charges far from the reaction centre have been found to have no influence on reaction rate;[3] the extra positive charge on the protonated N atom of

* Author for correspondence.



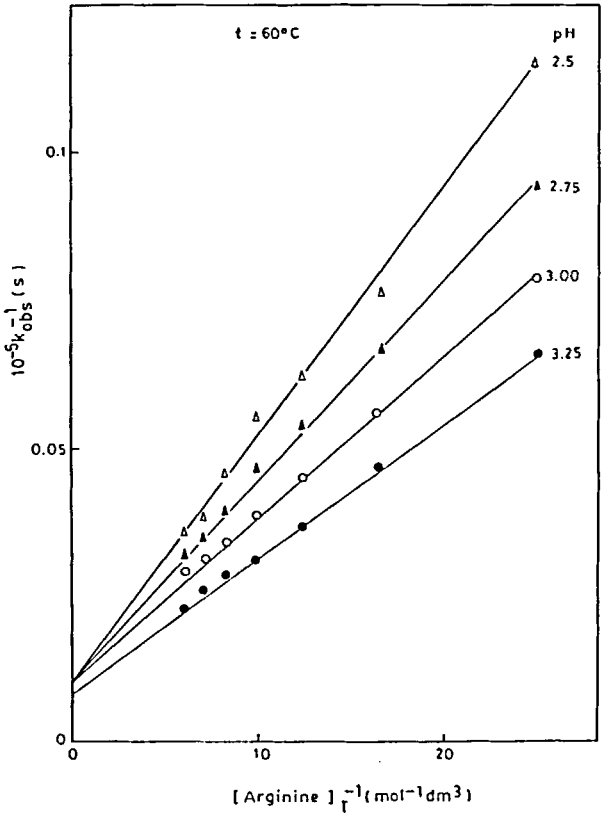


FIGURE 1 (Upper) dependence of k_{obs} on pH and $[Arginine]_T$; $[Cr(III)]_T = 4.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3}, T = 60°C, pH = 3.25(1), 3.00(2), 2.75(3), 2.50(4). (Lower) linear dependence of k_{obs}^{-1} on $[Arginine]_T^{-1}$ (see (*9*) and (*10*)); details as above.

TABLE I
Determined k_i and K_{OS} values for the anation of aquachromium(III) by *L*-arginine.

T (°C)	$10^4 k_1$ (s^{-1})	$10^3 k_2$ (s^{-1})	K_{OS1} ($mol^{-1}\,dm^3$)	K_{OS2} ($mol^{-1}\,dm^3$)
45	1.5		8.4	
50	3.3		5.6	
55	5.7	3.7	4.5	0.9
60	10.0	9.6	4.1	2.3
ΔH‡	100 kJ mol^{-1}			
ΔS‡	−23 $JK^{-1}\,mol^{-1}$			

the guanidine function in *L*-arginine can be ignored; OSC1 = $\{Cr(H_2O)_6^{3+} \cdot LH_2^+\}$; OSC2 = $\{Cr(H_2O)_5OH^{2+} \cdot LH_2^+\}$).

The following rate equation was deduced,

$$k_{obs} = \{k_1K_aK_{OS1}[H^+] + k_2K_aK_hK_{OS2}\}[\text{arginine}]_T \div \{[H^+]^2 + [H^+]K_a + [H^+]K_h + K_aK_h + (K_aK_{OS1}[H^+] + K_aK_hK_{OS2})[\text{arginine}]_T\} \quad (8)$$

$$k_{obs}^{-1} = A/C + B/C[\text{arginine}]_T^{-1} \quad (9)$$

with $A = K_aK_{OS1}[H^+] + K_aK_hK_{OS2}$, $B = [H^+]^2 + [H^+]K_a + [H^+]K_h + K_aK_h$, and $C = k_1K_aK_{OS1}[H^+] + k_2K_aK_hK_{OS2}$.

The mechanism was confirmed by plotting k_{obs}^{-1} *vs* $[\text{arginine}]_T$ at different acidities (Figure 1). In the low pH range (where the part played by the conjugate base, $Cr(H_2O)_5OH^{2+}$, can be omitted), (*9*) simplifies to

$$k_{obs}^{-1} = 1/k_1 + B'/C'[\text{arginine}]_T^{-1} \quad (10)$$

which envisages a common intercept (see upper plots in Figure 1, $B' = [H^+] + K_a$, $C' = k_1K_aK_{OS1}$).

Straight line plots (according to (*9*) and (*10*)) were employed to evaluate k_1, k_2, K_{OS1} and K_{OS2} (Table I).

The question remaining unanswered is whether the interchange mechanism of $Cr(H_2O)_6^{3+}/Cr(H_2O)_5OH^{2+}$ is I_a or I_d. An answer is to be found on examining criteria of assigning the I_d (as opposed to I_a) mechanism to anations of Co(III). No appreciable change in k on changing the nature of entering ligand was found (the k span was only *ca* half an order of magnitude[4] for anation of $Co(NH_3)_5H_2O^{3+}$ whereas k values are almost constant for anations of *cis*-$Co(en)_2(H_2O)_2^{3+}$ and *cis*-*β*-$Co(trien)(H_2O)_2^{3+}$, Table II). Values of k and k_{ex} (for solvent water) are comparable and the volume of activation, ΔV‡, for water exchange is positive (+1.2 $cm^3\,mol^{-1}$)[6] for $Co(NH_3)_5H_2O^{3+}$. Once these criteria are applied to anations of $Cr(H_2O)_6^{3+}/Cr(H_2O)_5OH^{2+}$ by amino acids, we find that (see Table II) k_1 and k_2 spans are, respectively, $(0.8–7.8) \times 10^{-4}$ and $(0.17–3.7) \times 10^{-3}\,s^{-1}$, k_1 is always $> k_{ex}$ whereas k_2 is comparable with k'_{ex}, and ΔV‡ for water exchange at $Cr(H_2O)_6^{3+}$ is negative (−9.6 $cm^3\,mol^{-1}$) but at $Cr(H_2O)_5OH^{2+}$ is positive (+2.7 $cm^3\,mol^{-1}$). It is seen that on all counts the favoured mechanism is I_a for the anation of $Cr(H_2O)_6^{3+}$ and I_d for $Cr(H_2O)_5OH^{2+}$ by *L*-arginine.

TABLE II
Comparison of anation rate constants (k_1) for Cr(III) and Co(III) species.[a]

Ligand	$Cr(H_2O)_6^{3+}$ 10^4k_1 (s^{-1}, at 45°C)	$Cr(H_2O)_5OH^{2+}$ 10^3k_2 (s^{-1}, at 45°C)	*cis*-$Co(en)_2(H_2O)_2^{3+}$ 10^4k (s^{-1}, at 45°C)[b]	*cis*-β-$Co(trien)(H_2O)_2^{3+}$ 10^4k (s^{-1}, at 45°C)[c]
$H_2^{18}O$[d]	36.1×10^{-2} (k_{ex})	3.26 (k'_{ex})		
$\Delta H^{\ddagger}$ (kJ mol^{-1})	108.6	111.0		
$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	+11.6	+55.6		
D,L-alanine	0.8	0.17	2.01 2.12 (β-alanine)	1.92
L-hydroxyproline	1.3	0.42		
D,L-tryptophan	1.3	0.27		
L-arginine	1.5	3.7 (55°C)		
D,L-serine	1.9			2.01 (*L*-serine)
D,L-threonine	2.0	0.71		
L-lysine	2.4	0.29		
D,L-aspartic acid	2.5			
L-phenylalanine	3.2	0.70		
L-isoleucine	3.3	0.70		
L-proline	4.0			2.13
D,L-aspartate	5.1			
D,L-methionine	5.1	0.99		
Sarcosine	5.3	1.23 (50°C)		
L-histidine	5.6	1.54		
D,L-valine	7.3		2.01	1.82
Glycine	7.8		1.33 (40°C)	2.22

[a] From sources cited in Ref. 2g; $\mu = 1.0$ mol dm^{-3}.
[b] From sources cited in Ref. 5b; $\mu = 0.03$ mol dm^{-3}, 30% EtOH (v/v).
[c] Ref. 5c; $\mu = 0.5$ mol dm^{-3}, 30% EtOH (v/v).
[d] Ref. 5a; $\mu = 0.7$ mol dm^{-3}.

Furthermore, a lower $\Delta H\ddagger$ (than for $H_2^{18}O$ exchange) and a negative value of $\Delta S\ddagger$ are suggestive of a more pronounced participation of the incoming ligand in the transition state and confirm the associative character of the reaction involving $Cr(H_2O)_6^{3+}$ species.

The labilizing effect of hydroxide is once again seen in the conjugate base. By virtue of its lone-pair of electrons, the hydroxide ion (adjacent to the leaving water molecule) exerts a strong electromeric effect and facilitates the loss of the H_2O ligand.

REFERENCES

1. (a) W. Mertz and K. Schwarz, *Amer. J. Physiol.*, **196**, 614 (1959); (b) E. W. Toepfer, W. Mertz, M. M. Polansky, E. E. Roginski and W. R. Wolf, *J. Agric. Food Chem.*, **25**, 162 (1977).
2. (a) E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, M. Sabat and J. A. Ibers, *Inorg. Chim. Acta*, **66**, 115 (1982); (b) J. V. McArdle, E. de Laubenfels, A. L. Shorter and H. L. Ammon, *Polyhedron*, **1**, 471 (1982); (c) D. R. Prasad, T. Ramasami, D. Ramaswamy and M. Santappa, *Inorg. Chem.*, **21**, 850 (1982); (d) L. E. Gerdom and H. M. Goff, *Inorg. Chem.*, **21**, 3847 (1982); (e) J. A. Cooper, L. F. Blackwell and P. D. Buckley, *Inorg. Chim. Acta*, **92**, 23 (1984); and references therein; (f) K. Govindaraju, T. Ramasami and D. Ramaswamy, *J. Inorg. Biochem.*, **35**, 127, 137 (1989); (g) M. Shahid, I. A. Khan and Kabir-ud-Din, *J. Chem. Soc. Dalton Trans.*, 3007 (1990), and references therein.
3. (a) E. Mentasti and G. Saini, *Atti Accad. Sci. Torino*, **106**, 561 (1972); (b) B. Perlmutter-Hayman and R. Shinar, *Inorg. Chem.*, **15**, 2932 (1976).
4. J. M. Coronas, R. Vicente and M. Ferrer, *Inorg. Chim. Acta*, **49**, 259 (1981).
5. (a) F. C. Xu, H. R. Krouse and T. W. Swaddle, *Inorg. Chem.*, **24**, 267 (1985); (b) D. Chatterjee and G. S. De, *Bull. Chem. Soc. Jpn.*, **61**, 2623 (1988); (c) D. Chatterjee, D. Mallick and G. S. De, *Bull. Soc. Chem. Jpn.*, **63**, 3058 (1990).
6. H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).