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Substitution of Aquo - Ligands from Hexaaquochromoium(III) Ion by Cysteine. A Kinetic and Mechanistic Study

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Abstract: Substitution of aquo - ligands from hexaaquochromoium(III) ion by cysteine (HCys) has been studied kinetically at $[H^+]$ of 1.0×10^{-2} mol dm^{-3}. The calculated activation parameters (ΔH^* and ΔS^*) have been compared with those of water - exchange and related anation reactions of haxaaquochromium (III) ion. The obtained results support an associative path (S_N2)

Key Words: Anation, Association, Chromium(III), Cysteine, Substitution

Introduction

Ligand substitution reactions in octahedral complexes have been extensively studied. Aside from Co^{III}, the most-studied metal ion has been Cr^{III}. According to the ligand-field model, Cr^{III} is subjected to a large loss in LFSE on going from six to either five- or seven-coordinate species. Thus, Cr^{III} complexes can react with either dissociative or associative activation with the latter being most common.

Gaswick and Malinak (1993) suggested an I_d mechanism for the anation of $[Cr(NH_3)_5H_2O]^{3+}$ by entering ligands such as NCS^-, $HC_2O_4^-$, $C_2O_4^{2-}$, H_3PO_4 , $H_2PO_4^-$ and $[Cr(CN)_6]^{3-}$. Gonzalez and Martinez (1995) also proposed a dissociative shift of the mechanism of the anation of substituted pentaamine-chromium(III) and -rhodium(III) complexes on crowding the $[M(RNH_2)_5H_2O]^{3+}$ (M = Rh, R = H, Me, Et, Pr; M = Cr, R = H, Me, Pr) for the entering ligands $H_3PO_4/H_2PO_4^-$, $H_3PO_3/ H_2PO_3^-$, CF_3COO^-, Br^-, Cl^- and SCN^-. The anation of cis-$[Cr(OX)_2(H_2O)_2)^-$ followed an associative path for glycine (Mazumdar and DE, 1991); bipyridine and o-phenanthroline (Banerjea and Roy, 1973); oxalate (Kelm and Harris, 1967); picolinate, dipicolinate, and quinolinate (Mazumdar and DE, 1987a, 1986 and 1987b). Anation of $[Cr(H_2O)_6)^{3+}$ also has been reported as both associative and dissociative depending on the entering ligand. De and De (1987); Banerjea and Chatterjee (1969); Postmus and King (1995) reported associative mechanisms for glutamic acid, glycine and NCS^- entering ligands respectively. However, Hamm *et al.*, (1958) did report a dissociative mechanism for oxalate, malonate, citrate ... *etc.* as entering ligands.

Cysteine (HCys) is an amino acid that plays a very important rule in several iron-sulfur proteins that participate in all major pathways of electron transport, photosynthesis, respiration, hydroxylation and bacterial hydrogen and nitrogen fixation. Besides, sulfhdryl groups of cysteine residue do participate in the catalytic mechanism of a variety of enzymes. The present work concerns with the substitution of aquo - ligands from $[Cr(H_2O)_6]^{3+}$ by this important amino acid.

Materials and Methods

The hexaaquochromoium(III) perchlorate was prepared according to Postmus and King(1995). The complex showed maximum absorbance at 410 and 750 nm with ε values of 14.2 and 17.0 respectively. Cysteine (HCys) and $[Cr(H_2)_6]^{3+}$, of desired concentrations, were prepared in double distilled water and the $[H^+]$ maintained constant by $NaOH/HClO_4$, as required, using a pH-meter from Hanna Instruments, Model 8521. The product of the reaction between $[Cr(H_2O)_6]^{3+}$ and HCys was prepared by mixing the two reactants in different molar ratio, *viz.* 1:1, 1:2, 1:3, 1:4, 1:5 and 1:10 at 318 K for about three days. All mixtures exhibited similar λ_{max} at 410 and 560 nm. The composition of the product in solution was determined by Job's method of continuous variation. The product revealed a metal to ligand ratio of 1:2.

Kinetic Runs: The course of the reaction was followed spectrophotometrically by measuring absorbance at 560 nm (product does not interfere) using UV-2 Unicam uv/vis Spectrometer. All experiments were carried under large excess of HCys and at constant ionic strength (μ), maintained by $NaClO_4$. The pseudo-first order rate constants (k_{obs}) were determined graphically. The rate constant values were reproducible within ± 5%.

Results and Discussion

Effect of Varying $[Cr(H_2O)_6^{3+}]$ on Reaction Rate: The concentration of $[Cr(H_2O)_6]^{3+}$ was varied from 2.0×10^{-3} to 5.0×10^{-3} mol dm^{-3} at a fixed excess concentration of HCys (5.0×10^{-2} mol dm^{-3}), constant ionic strength ($\mu = 3.0 \times 10^{-2}$ mol dm^{-3}), constant $[H^+]$ (1.0×10^{-2} mol dm^{-3}) and constant temperature (313 K). The experimental data indicate that the reaction rate is first order with respect to $[Cr(H_2O)_6^{3+}]$ as indicated by the constant value of k_{obs} ,

$$-d[Cr(H_2O)_6^{3+}] / dt = k_{obs} [Cr(H_2O)_6]^{3+}]$$

Effect of Varying $[H^+]$ on Rate Constant: $[H^+]$ was varied from 1.0×10^{-5} to 1.0×10^{-2} mol dm^{-3} at fixed temperature, μ, $[Cr(H_2O)_6^{3+}]$, and [HCys]. The reaction rate was dependent on $[H^+]$ as the rate constant values (k_{obs}) decreased markedly with increasing $[H^+]$ (Table 1). This could be explained, in part, due to the

Table 1: Variation of Rate Constant (k_{obs}) with $[H^+]$

$[H^+]$ mol dm^{-3}	10^4 k_{obs} (s^{-1})
1.0×10^{-5}	2.73
1.0×10^{-4}	2.18
1.0×10^{-3}	1.65
1.0×10^{-2}	1.16

$[Cr(H_2O)_6]^{3+}] = 2.0 \times 10^{-3}$ mol dm^{-3}, [HCys]$= 5.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 3.0 \times 10^{-2}$ mol dm^{-3}, T = 313K

successive acid dissociation constants of the amino acid, cysteine: K_1 (-COOH) = 1.1 x 10^{-2}, K_2 (-SH) = 6.6 x 10^{-9} and K_3 (-NH_3^+) = 5.2 x 10^{-11} (White *et al.*, 1973). Increasing the $[H^+]$ is expected to enhance the formation of the cationic form of cysteine $\{HSCH_2CH(NH_3^+)COOH\}$ over the zwitterionic form $\{HSCH_2CH(NH_3^+)COO^-\}$. The donor ability of the latter is higher compared to that of the cationic form and thus the rate is reduced upon increasing $[H^+]$. The effect of $[H^+]$ on k_{obs} has to do also with the variation of the nature of $[Cr(H_2O)_6]^{3+}$ with varying $[H^+]$:

$$[Cr(H_2O)_6]^{3+} \overset{K}{\longleftrightarrow} [Cr(H_2O)_5OH]^{2+} + H^+ \quad (1)$$

Where K = 1.6 x 10^{-4}

The Cr^{III} complex - ion exists in two forms depending on the acidity of the medium; the hexaaquo- ion and the less positively charged hydroxopentaaquo- ion. The latter is more labile to substitution than the former due to the electronic effect of the hydroxo group (strong *pi* donor) on the chromium atom. At $[H^+]$ = 1.6 x 10^{-4} mol dm^{-3}, the concentration of the two forms are comparable, however at $[H^+ > 1.6 \times 10^{-4}$ mol dm^{-3} the hexaaquo- form becomes dominant and thus a decrease in rate constant value is observed with increasing the concentration of hydronium ion.

Effect of Varying the [HCys] on Rate Constant: The [HCys] was varied in the range 1.0 x 10^{-2} - 5.0 x 10^{-2} mol dm^{-3} at 313, 318, 323 and 328 K keeping $[Cr(H_2O)_6^{3+}]$, μ and $[H^+]$ constant. The values of k_{obs} increased with increasing [HCys], as shown in Table 2

Table 2: Variation of k_{obs} with [HCys] at Different Temperatures

10^2[HCys] mol dm^{-3}	$10^5 k_{obs}$ (s^{-1})			
	313 K	318 K	323 K	328 K
2	5.00	7.40	9.10	11.30
3	7.50	10.80	13.20	16.15
4	9.50	14.30	18.00	23.90
5	11.70	18.20	22.20	27.30

$[Cr(H_2O)_6^{3+}]$ = 2.0 x 10^{-3} mol dm^{-3}, $[H^+]$ = 1.0 x 10^{-2} mol dm^{-3}, μ = 3.0 x 10^{-2} mol dm^{-3}

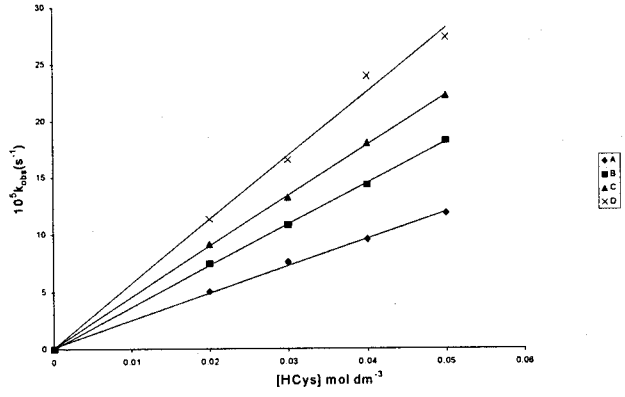

Fig.1: Dependence of k_{obs} on the Concentration of Cysteine at Different Temperatures: (A) 313 K, (B) 318 K, (C) 323 K and (D) 328 K

and Fig. 1. The dependence of rate on [HCys] was also confirmed by the linear plot of $1/k_{obs}$ versus 1/[HCys} (Fig. 2). This variation of k_{obs} with change in [HCys] could be explained by considering the following reaction scheme,

$$[Cr(H_2O)_6^{3+}] + HCys \xrightarrow{k_2\ (slow)} [(H_2O)_5H_2O\text{---}Cr\text{...}CysH]^{3+} \quad (2)$$

$$[(H_2O)_5H_2O\text{---}Cr\text{...}CysH]^{3+} + H_2O + H_3O^+ \xrightarrow{fast} [Cr(H_2O)_4\ Cys]^{2+} \quad (3)$$

$$[Cr(H_2O)_4\ Cys]^{2+} + CysH + H_2O + H_3O^+ \xrightarrow{fast} [Cr(H_2O)_2\ (Cys)_2]^+ + \quad (4)$$

The rate law for the proposed mechanism is

$$d[Cr(H_2O)_2\ (Cys)_2]^+/dt = k_2[[Cr(H_2O)_6^{3+}][HCys] = k_{obs}[[Cr(H_2O)_6^{3+}]$$

or, $k_{obs} = k_2[HCys]$

Where k_2 is the second order rate constant and its values, at different temperatures, were calculated from Fig. 1 and are shown in Table 3.

Table 3: Values of k_2 at Different Temperatures

Temperature (K)	$10^3 k_2$ (mol^{-1} s^{-1})
313	2.63
318	3.70
323	4.55
328	5.56

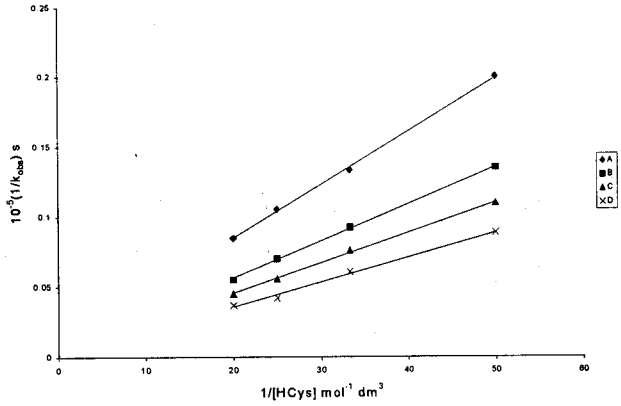

Fig.2: $1/k_{obs}$ Versus 1/[HCys] at Different Temperatures: (A) 313 K, (B) 318 K, (C) 323 K and (D) 328 K

Effect of Varying Ionic Strength on Rate Constant: Using $NaClO_4$, the ionic strength of the medium was varied at constant $[Cr(H_2O)_6^{3+}]$ (0.002 mole dm^{-3}); [HCys] (0.05mol dm^{-3}); and $[H_3O^+]$ (0.01mol dm^{-3}) and constant temperature (313K). The obtained k_{obs} values were in the range 2.75 x 10^{-4} to 2.78 x 10^{-3} s^{-1} for μ = 0.310 to 0.620 mol dm^{-3}. This indicates a negligible effect of ionic strength on substitution rate, as expected for such systems that involve metal-ligand interaction of cationic-zwitterionic type.

Effect of Temperature on Reaction Rate: The activation parameters were calculated from the linear Wynne-Jones and Eyring plot of $\ln(k_2/T)$ versus 1/T.

The values of ΔH^*, ΔS^* and ΔG^* are 40.63 (kJ mol^{-1}), -177.53 (J mol^{-1} K^{-1}) and 96.20 (kJ mol^{-1}) respectively (Table 4).

Table 4: Comparison of k_2 and Activation Parameters of Substitution of Aquo-ligands from $[Cr(H_2O)_6]^{3+}$ by Different Entering Ligands

Entering ligand	k_2 (s^{-1} mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
Isotopic water exchange[14]	4.10×10^{-6} [a]	109.2	11.70
Glutamic acid[11]	8.09×10^{-5} [b]	73.5	-86.10
Glycine[15]	1.20×10^{-3} [b]	52.08	42.84
Oxalate[15]	8.97×20^{-2} [b]	121.80	59.22
Malonate[10]	3.70×10^{-3} [b]	102.48	-0.55
Cysteine[*]	2.63×10^{-3} [b]		

[a] at 308K, [b] at 3313K, [*]present work

Conclusion

Comparing the present results with some related reactions (Table 4) indicates a definite dependence of substitution rate on the nature of entering ligand, thus bond-making is important. The anation rate of present reaction is faster than that of water exchange which, as a sufficient though not necessary condition, also suggests that bond formation is an important step in the mechanism. Rapid increase in anation rate with decreasing $[H^+]$, which was explained earlier as a result of OH^- pi- donor ability, suggests that bond-breaking has an influence on rate-determining step. Further, it can be seen that ΔS^* for cysteine substitution is negative as expected for an association process. Thus in the present work, both bond-breaking and bond-making are important which support an association (S_N2) mechanism.

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