Kinetics of Substitution of Aquo Ligands from Hexaaquochromium(III) Ion by 1,10-Phenanthroline in Water-Ethanol Mixture

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The kinetics of substitution of aquo ligands from hexaaquochromium(III) by 1,10-phenanthroline in water-ethanol mixture has been studied spectrophotometrically. The following rate law has been established:

\[ \text{Rate} = k_2 [\text{Cr} \, (\text{H}_2\text{O})_6] \, [\text{Phen}] \]

The reaction for substitution is found to be pH dependent in the range 3.5 to 5.0. Above pH 5.2 precipitation of chromium hydroxide occurs and below pH 3.5 the reaction rate is extremely slow at 45°. The reaction is independent of ionic strength. Activation parameters for the reaction path \((SN_2)\) have been calculated and compared with the water exchange rate and with the reaction between hexaaquochromium(III) and 2,2'-dipyridyl. A probable mechanism has been suggested.

The anation reactions of \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\) are very interesting as they do not follow any single mechanism and the reaction path depends on several factors. Thus Hamm and coworkers\(^3\) observed that the anation reactions of \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\) with different ligands such as oxalate-malonate, citrate, acetate and o-phthalate, follows an \(S_N1\) mechanism. Their observation was supported by Ardon's experiment\(^4\) on replacement of F by Cl in \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\). However, Banerjea and collaborators observed that anation reactions of \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\) with oxalate\(^\delta\) and malonate\(^\delta\) proceed through outer-sphere association and the transformation of outer-sphere complex into the product is an essentially dissociative process in which loss of a water molecule from the hexaaquochromium(III) ion is only significant bond formation by the incoming ligand. But for the corresponding reaction with glycine\(^\delta\), they suggested an associative character of the process. In view of the conflicting mechanisms proposed so far, we decided to study the kinetics of substitution of aquo ligands of \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\) by o-phenanthroline in water-ethanol mixture in the hope that these studies will further enrich this area. Further we like to record here that the studies on substitution of aquo ligands from \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\) by nitrilotriacetic acid and iminodiacetic acid are in progress and will be communicated shortly.

Materials and Methods

\([\text{Cr}(\text{H}_2\text{O})_6]^3\)\textsubscript{+}\(\text{NO}_3\)\textsubscript{3} was prepared by the method of Hamm and Davis\(^1\). The reaction between \([\text{Cr}(\text{H}_2\text{O})_6]^3\)\textsubscript{+} and 1,10-phenanthroline in different molar ratios as \((1:1), (1:2), (1:3)\) and \((1:5)\) was carried out by refluxing on a water-bath for 2 hr and finally evaporated on a water-bath until crystallization commenced, filtered and washed with ethanol. Nitrogen and chromium estimations indicated that the product possessed the formula \([\text{Cr}(\text{Phen})_3]^3\)\textsubscript{+}\(\text{NO}_3\)\textsubscript{3}, i.e. a 1:3 complex was always formed. It was further supported by spectral studies of different solutions. The isolated product exhibited absorption maxima at 515 nm and \([\text{Cr}(\text{H}_2\text{O})_6]^3\)\textsubscript{+}\(\text{NO}_3\)\textsubscript{3} exhibited absorption maxima at 410 and 575 nm. The absorption spectra of mixtures of reactants in different molar ratios, viz. 1:1, 1:2, 1:3 and 1:5 duly thermostated at 45° for 30 hr showed absorption maxima closed to the product \([\text{Cr}(\text{o-phen})_3]^3\)\textsubscript{+}\(\text{NO}_3\)\textsubscript{3}. However, optical density values at the absorption maxima are different in different reaction mixtures owing to the fact that the product concentrations were different in each case.

Chemicals of AR quality were used in all the experiments. Solutions of 1,10-phenanthroline and complex, of desired concentration, were prepared by dissolving the calculated amounts in 30% (v/v) ethanol. The pH values of the reaction mixtures were adjusted with nitric acid. The rate constants were reproducible within \(\pm 3\%\).

Procedure for kinetic study — Equilibrated solutions of 1,10-phenanthroline and the complex (I) of desired concentrations, were mixed in reaction vessels and the course of the reaction followed by measuring optical density (Hilger UVISPEK spectrophotometer) at 510 nm, where a substantial difference existed in the spectra of the complexes \([\text{Cr}(\text{H}_2\text{O})_6]^3\)\textsubscript{+} and \([\text{Cr}(\text{phen})_3]^3\)\textsubscript{+}.

Results and Discussion

The pseudo-first order rate constants for the substitution reaction were obtained by plotting \(\log \frac{D_\infty - D_t}{D_\infty - D_0}\) against time where \(D_\infty\), \(D_t\) and \(D_0\) are the optical densities at infinite time, in the beginning and after time \(t\) respectively. The pseudo-first order plot were linear from start to the finish of the reaction.
**Effect of varying [complex (I)] on the rate constant**—In the first set of experiments the concentration of [Cr(H₂O)₆][NO₃]₂, complex (I) was varied at a fixed concentration (0-15M) of 1,10-phenanthroline and at constant ionic strength (0-10M) and pH 4-4. The values of pseudo-first order rate constant, kₜₜ were found to be 8-6×10⁻⁴ sec⁻¹, 9-7×10⁻⁴ sec⁻¹ and 10-5×10⁻⁴ sec⁻¹ at [complex (I)] of 0-015, 0-02 and 0-025M respectively at 45°C in 30% ethanol medium. The rate of reaction is first order with respect to complex (I), i.e. 

\[
\frac{d[\text{complex (II)}]}{dt} = k[\text{complex (I)}]
\]

**Effect of varying pH on the rate constant**—Concentration of complex (I) and 1,10-phenanthroline were kept at 0-02M and 0-15M respectively and the pH was varied by addition of requisite quantity of HNO₃. In 30% ethanol as the medium, the values of pseudo-first order rate constant, kₜₜ at 45°C and ionic strength 0-08M are 3-1×10⁻⁴, 8-5×10⁻⁴, 9-7×10⁻⁴, 19-2×10⁻⁴ and 28-5×10⁻⁴ sec⁻¹ at pH 3-65, 4-05, 4-4, 4-65 and 5-0 respectively. It is observed (Fig. 1) that there is sharp change in reaction rate in the pH range 4-4 to 5-0. Below pH 3-5, the reaction rate is slow and above pH 5-2, precipitation of chromium hydroxide occurs. Thus the reaction is inversely proportional to [H⁺] in the pH range 3-65 to 5-0. This dependence of reaction rate on [H⁺] can be explained on consideration of protonation of 1,10-phenanthroline as shown by Eq. (1):

\[
\phi K_a = \text{pH} + \log \frac{[\text{phen} H^+]}{[\text{phen}]} = 5-95
\]

where \(K_a\) = reciprocal of equilibrium constant (K) for the protonation reaction Phen⁺H⁺⇌Phen H⁺ and value of log \(K_a\) = 4-94 (ref. 9).

From the above expression it is inferred that the lower the pH, higher is the protonation of donor N-atoms in phenanthroline and concentration of free donor N-atoms is decreased and consequently the rate is slowed down.

**Effect of varying [1,10-phenanthroline] on the rate constant**—The concentration of 1,10-phenanthroline was varied in the range 0-10-0-20M at a fixed concentration (0-02M) of the complex (I). In these experiments the ionic strength and pH were kept constant at 0-07M and 4-4 respectively. The results are presented in Table 1. The plots of kₜₜ versus [phen] at 35°C (Fig. 2A), 40°C (Fig. 2B), 45°C (Fig. 2C) and 50°C (Fig. 2D) are linear passing through the origin, implying that the rate law (2) is followed:

\[
\frac{d[\text{complex (II)}]}{dt} = k_2[\text{complex (I)}][1,10-\text{phenanthroline}]
\]

The values of second order rate constants \(k_2\) are 28-9×10⁻⁴, 42-9×10⁻⁴, 62-9×10⁻⁴ and 80-0×10⁻⁴M⁻¹ sec⁻¹ respectively at 35°C, 40°C, 45°C and 50°C. It is observed that the second order rate constant of phenanthroline substitution (28-9×10⁻⁴M⁻¹ sec⁻¹) is many times faster than water exchange rate (4-1×10⁻⁴ sec⁻¹) and by seven times faster than dipyridyl substitution following (4-1×10⁻⁴M⁻¹ sec⁻¹) at same temperature (35°C). This observation suggests significant bond formation by the reagent in the transition state. As o-phenanthroline is a stronger base than dipyridyl, difference in rate is explicable in terms of changes in basicity of the incoming ligand.

**Effect of varying ionic strength**—In these experiments concentrations of complex (I), 1,10-phenanthroline and pH were kept constant at 0-02M, 0-15M and 4-55M respectively and ionic strength was varied by the addition of NaNO₃. It was observed that the reaction rate is independent of ionic strength.

**Mechanism**—It is of interest to note that the studies so far reported by Hamm and coworkers as well as Banerjea and coworkers involve substitution of aquo ligands in hexaaquochromium(III) ion by various anionic ligands. Since the two reactants are oppositely charged the proposed mechanism,
as can be anticipated, involved ion-pair formation as a preliminary step to anation reaction. The transformation of this outer sphere complex into the product may then proceed by either a dissociative or associative path. The presently studied ligand o-phenanthroline stands in distinct contrast to the anionic ligands studied by the above two groups. No possibility of ion-pair formation exists in the present system. The present system follows a straight second order kinetics in o-phenanthroline and hexaaquochromium(III) ion at all temperatures and no change from second order to first order kinetics is observed as the concentration of o-phenanthroline is increased. Further it has been observed that the rate of o-phenanthroline substitution is many times faster than the water exchange rate and about seven times faster than dipyridyl substitution rate at the same temperature. The activation parameters have been calculated from the linear Arrhenius plot (log $k_2$ vs $1/T$) and found to be $\Delta H^\ddagger = 15.5 \pm 0.5$ kcal/mol; $\Delta S^\ddagger = -25.0 \pm 1$ e.u. The lower value of $\Delta H^\ddagger$ for the o-phenanthroline substitution as compared to water exchange and dipyridyl substitution processes indicates that there is a significant bond formation in the transition state by the incoming ligand and the mechanism is associative. The mechanism may be represented as shown in Scheme 1.

$$\begin{align*}
\text{Cr(H}_2\text{O)}_6^{3+} + \text{phenanthroline} & \rightarrow [\text{Cr(H}_2\text{O)}_6 \text{ Phen}]^{3+} \\
& \rightarrow [\text{Cr(H}_2\text{O)}_6 \text{ Phen}]^{3+} + 2\text{H}_2\text{O} \\
& \rightarrow [\text{Cr(Phen)}_2 \text{ Phen}]^{3+} + 2\text{H}_2\text{O} \\
& \rightarrow [\text{Cr(Phen)}_3^{3+} + \text{Phen}.
\end{align*}$$

Scheme 1

After the formation of tetraaquomonophenanthroline-chromium(III) complex, the electron density on chromium(III) is increased significantly due to inductive effect\textsuperscript{12}. As a result of inductive effect the remaining four coordinated water molecules are labilized and easily substituted by two o-phenanthroline molecules in two fast reactions as mentioned before. Thus the reaction follows the same mechanistic characteristics as found in the case of dipyridyl substitution with the difference that being a stronger base o-phenanthroline can establish a stronger bond in the transition state, which lowers the heat of activation.

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