Substitution of Aquo Ligands from Hydroxopenta-aqua-Chromium(III) Ion by Ethylenediaminetetraacetic Acid—A Kinetic Approach

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The kinetics of substitution of aquo ligands of hydroxopenta-aqua-chromium(III) ion by EDTA in water-ethanol medium has been studied spectrophotometrically. The reaction rate is found to be pH dependent in the pH range of 4.4 to 5.2. The reaction rate is higher compared to the rates of water exchange process of the substrate complex. Activation parameters have been calculated. A low ΔH‡ and a negative ΔS‡ are suggestive of a mechanism involving the formation of ion-pair followed by associative interchange ([I]) process for the title reaction.

Anation reactions of hexaaquochromium(III) ion have been studied by many workers. Significantly, no single mechanistic conclusion has been drawn for such reactions. Hydroxopenta-aqua-chromium(III) ion has not received similar attention. Interesting results are expected with this ion because of the presence of hydroxo group having both σ as well as π-bonding ability.

Ethylenediaminetetraacetic acid (EDTA) is a widely used chelating agent. Kinetics of reaction of EDTA with aquochromium(III) ion were first studied by Hamm who observed that the rate of anation was independent of [EDTA]. Yamamoto and Ohashi made similar observation in the reaction between Cr(III) ion and EDTA catalysed by H₂O₂. On the other hand Olson reported that the reaction of Cr(H₂O)₅²⁺ with EDTA involved reversible formation of an ion-pair followed by rate-determining anation. But Kimura et al. while studying the reaction of EDTA with hexaaqua-chromium(III) ions in mixed solvents (pH range 3.5 to 4.6) suggested that the reaction is independent of EDTA and proceeded only through the dissociation of water molecules. The above facts prompted us to carry out the title reaction under a variety of conditions with a view to gaining information on the mechanism of the reaction.

Materials and Methods
[Cr(H₂O)₆][ClO₄]₂ was prepared by the method of Moore and Basolo using AR quality reagents. Hydroxopenta-aqua-chromium(III) (complex-I) was prepared in situ from the hexaaquo complex by adjusting the pH to 5.0. The absorption spectrum of Complex-I exhibited λmax at 430 (log ε 1.447) and 590 nm (log ε 1.255) quite different from those of hexaaqua-chromium(III) ion.

The product of the reaction between Cr(H₂O)₅(OH)²⁺ and EDTA was prepared by mixing the two reactants in different molar ratios, viz. 1:1, 1:2, 1:3 and 1:30 thermostated at 45°C for 72 hr. Absorption spectra of all the mixtures were similar exhibiting λmax at 390 and 540 nm. The composition of the product in solution was determined by Jobs method of continuous variation. The metal-ligand ratio was found to be 1:1.

Complex-I and EDTA solution at pH 5.0 were mixed in 1:1 molar ratio, refluxed on water-bath for 10 hr, concentrated and the residue treated with acetone to get a solid mass. On drying violet coloured shining crystals were obtained. Elemental analyses of the isolated solid revealed the composition Na[Cr(EDTA)(H₂O)] (complex-II). The absorption spectrum in solution of the isolated product was identical with that of the violet forms of the EDTA complex with chromium(III) ion studied by Hamm.

The author established the composition of the violet product as H[Cr(EDTA)(H₂O)] in the pH range of 3-6 by spectrophotometric titration. In our case the reaction product [Cr(EDTA)(OH)]²⁻ first formed got protonated to form the final product [Cr(EDTA)(H₂O)]²⁻ in the pH range studied.

Kinetic experiments were carried out spectrophotometrically using a Hilger UVISPEK spectrophotometer. pH was adjusted by NaOH/HClO₄ using a Systronics digital pH meter. Ionic strength of the reaction medium was adjusted by adding NaClO₄. The course of the reaction was followed by measuring absorbances at 540 nm where a substantial difference existed in the spectra of the complexes-I and II. The [ligand] was always maintained high so that the pseudo-first order rate law could be applied. The pseudo-first order rate constants (kobs) were determined graphically.

Results and Discussion
Effect of varying [complex-I] on rate constant
At [EDTA] = 0.05 mol dm$^{-3}$, ionic strength = 0.25 mol dm$^{-3}$ and $pH = 5.0$, three sets of experiments were carried out at 35° at different [complex-I]. The $k_{obs}$ values were $6.61 \times 10^{-4}$, $6.27 \times 10^{-4}$ and $6.4 \times 10^{-4}$ s$^{-1}$ at [complex-I] = 0.0025, 0.003 and 0.0035 mol dm$^{-3}$ respectively. Thus the rate showed first order dependence on [complex-I], i.e. $d[complex-II]/dt = k_{obs}$ [complex-I]

**Effect of varying $pH$ on rate constant**

At fixed [complex-I] = 0.0025 mol dm$^{-3}$, [H$_2$EDTA$^{2-}$] = 0.025 mol dm$^{-3}$ and ionic strength = 0.25 mol dm$^{-3}$, the values of $k_{obs}$ at 35° were found to increase with increase in $pH$ as shown in Fig. 1. The effect of $pH$ variation on rate can be explained by considering the $pK$ values of the ligand$^{12}$ and that of the aquo complex$^{13}$. From the dissociation equilibria of EDTA it can be assumed that in the $pH$ range of 4.4 to 5.2 the nature of the ligand remains almost unchanged and it exists mainly in the dinegative anionic form H$_2$EDTA$^{2-}$. So the increase in rate with the increase in $pH$ should be due to the change in nature of the substrate complex. Considering the acid dissociation equilibrium (1) ($pK_1 = 3.8$ at 25°C)

$$Cr(H_2O)_6^{3+} \rightleftharpoons Cr(H_2O)_5(OH)^{2+} + H^+ \quad \ldots (1)$$

it can be stated that at $pH$ 3.8 the percentage of hexaaquo species and the hydroxopentaaquo species is approximately same at the experimental temperature. But increase in $pH$ increases the percentage of the more reactive hydroxopentaaquo species. Enhanced reactivity of the hydroxopentaaquo species is due to well known labilising effect of the hydroxide ion adjacent to the water molecule by virtue of its lone pair of electron capable of exerting strong electromeric effect. Hydroxide ion is also a strong π-donor which facilitates the formation of very reactive hydroxo intermediate and hence increases the rate.

**Effect of varying [EDTA] on rate constants**

At fixed [complex-I] = 0.0025 mol dm$^{-3}$, ionic strength = 0.25 mol dm$^{-3}$ and $pH = 5.0$, the [ligand] was varied in the range of 0.0125 to 0.05 mol dm$^{-3}$ in 30% water-ethanol medium. The results of variation of [EDTA] on reaction rate at 25°, 31°, 35° and 40°C are summarised in Table 1. It is observed that the rate of reaction increases with the increase in [ligand] but at a high [ligand] the rate approaches a limiting value (Fig. 2), probably due to ion-pair formation. The limiting rate corresponds to completion of ion-pair formation. Scheme 1 can be proposed to explain the nature of variation of reaction rate with [ligand],

$$Cr(H_2O)_6(OH)^{2+} + H_2EDTA^{2-} \rightarrow Cr(H_2O)_5(OH)^{2+} \ldots H_2EDTA^{2-}$$

**Complex-I**

$$K_{ion} = Cr(H_2O)_5(OH)^{2+} \ldots H_2EDTA^{2-}$$

**ion-pair (IP)**

![Fig. 1 — Plot of log (D$_o$ - D$_o$/D$_o$ - D$_t$) versus time at 35°C, [complex-I] = 0.0025 mol dm$^{-3}$, [H$_2$EDTA$^{2-}$] = 0.025 mol dm$^{-3}$, $pH = (A)4.4,(B)4.6,(C)4.78,(D)5.0$ and (E) 5.2.](image1)

![Fig. 2 — Variation of $k_{obs}$ with [H$_2$EDTA$^{2-}$] at different temperatures, [complex-I] = 0.0025 mol dm$^{-3}$, $pH = 5.0$ (A) 25°C, (B) 31°C, (C) 35°C and (D) 40°C.](image2)
Table 1 — Variation of Rate Constant with \([H_2EDTA^{2-}]\) at Different Temperatures

\[
[\text{pH} = 5.0, \mu = 0.25 \text{ mol dm}^{-3} (\text{NaClO}_4)]
\]

\[
\begin{array}{cccccc}
[H_2EDTA^{2-}] & k_{\text{obs}} \times 10^4 (s^{-1}) \\
\text{mol dm}^{-3} & 25^\circ & 31^\circ & 35^\circ & 40^\circ & \\
0.0125 & 1.07 & 1.89 & 2.95 & 4.78 & \\
0.019 & 1.46 & 2.44 & 3.42 & 6.80 & \\
0.025 & 1.72 & 3.10 & 4.13 & 8.05 & \\
0.0375 & 2.18 & 3.48 & 5.12 & 9.75 & \\
0.050 & 2.50 & 4.18 & 6.61 & 11.60 & \\
\end{array}
\]

Effect of varying ionic strength on rate constant

At fixed \([\text{complex-I}] = 0.0025 \text{ mol dm}^{-3}, [\text{ligand}] = 0.025 \text{ mol dm}^{-3}, \text{pH} = 5.0\) and temperature = 35°C, the \(k_{\text{obs}}\) values were \(4.1 \times 10^{-4}, 3.9 \times 10^{-4}, 3.5 \times 10^{-4}\) and \(2.7 \times 10^{-4}\) s\(^{-1}\) for \(\mu = 0.25, 0.75, 1.0\) and \(1.5 \text{ mol dm}^{-3}\) respectively, i.e. increase in ionic strength (\(\mu\)) by adding \(\text{NaClO}_4\) decreases the rate of reaction. The results thus obtained can be supported by the theory of Bronsted, Bjerrum and Christiansen for the reaction between oppositely charged ions. But the rate of reaction increases with the increase of \(\mu\) by adding \(\text{NaN}_3\) (Fig. 3). The \(k_{\text{obs}}\) values were \(4.7 \times 10^{-4}\) and \(5.5 \times 10^{-4}\) s\(^{-1}\) for \(\mu = 0.25\) and \(0.5 \text{ mol dm}^{-3}\), respectively. This increase in rate in changing the anion from \(\text{ClO}_4^-\) to \(\text{NO}_3^-\) can be explained by the fact that nonsubstituting nitrate ion facilitates metal-water bond cleavage through specific attack on the coordinated water molecule. Consequently labilisation of water molecules catalyses the entry of the ligand and hence the increase in rate is observed in the presence of \(\text{NO}_3^-\). This typical ionic strength effect has also been observed by different authors\textsuperscript{14} - \textsuperscript{16}.

Effect of temperature on reaction rate

The reaction was studied at four different temperatures for different [ligand] to find out the effect of temperature on the rate constants for interchange process \((k_a)\). The \(k_a\) values at 25°, 31°, 35° and 40°C are \(4.00 \times 10^{-4}, 7.10 \times 10^{-4}, 11.11 \times 10^{-4}\) and \(18.86 \times 10^{-4}\) s\(^{-1}\), respectively. The values are considerably higher compared to the rates of isotopic water exchange process (\(< 10.0 \times 10^{-5}\) s\(^{-1}\) at 25°C) of the same substrate complex\textsuperscript{17}. Activation parameters were calculated from the linear Eyring plot of \(\log k_a\) and

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k_a} + \frac{1}{k_a K_E [H_2EDTA^{2-}]} \quad \text{(4)}
\]

or

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k_a} + \frac{1}{k_a K_E [H_2EDTA^{2-}]} \quad \text{(4)}
\]
versus $1/T$ and the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are found to be 74.8 kJ mol$^{-1}$ and $-44.3$ JK$^{-1}$ mol$^{-1}$ respectively.

**Mechanism**

The dependence of reaction rate on the nature of ligand clearly indicates outer sphere association between the two oppositely charged reacting species. The ion-pair equilibrium constant values are high as is expected for the interaction between a bipositive cation $[\text{Cr(H}_2\text{O)}_5(\text{OH})]^2^+ \text{ and a binegative anion } [\text{H}_2\text{EDTA}]^{-}\text{. The high anation rate constant (compared to the rates of isotopic water exchange$^{17}$ and other substitution reactions by Cl$^-$, Br$^-$, SCN$^-$, NCS$^-$ etc.)$^{18}$ suggest the associative character of the interchange process, i.e. bond formation by the incoming ligand plays a significant role in interchange step. The low values of $\Delta H^\ddagger (78.4 \text{ kJ mol}^{-1})$ also suggests ligand participation in the transition state. Further the activated complex formation through outer sphere association is stabilised by H-bonding between water molecule of the inner sphere complex and the negative end of the EDTA ion. This leads to the formation of a stable and compact activated state as is evidenced by the considerable negative $\Delta S^\ddagger$ value ($-44.33 \text{ JK}^{-1} \text{ mol}^{-1}$). The above facts indicate that the reaction occurs through an associative interchange ($I_s$) process.

**References**