Kinetic and mechanistic studies on the aquation of mixed ligand complexes of chromium(III): Acid catalysed aquation of cis-bis(oxalato)phenanthrolinechromate(III) and cis-bis(oxalato)bipyridinechromate(III)

S Adinarayana, C S T Sai & N R Anipindi*
School of Chemistry, Andhra University,
Visakhapatnam 530 003

Received 7 September 1990; revised 5 August 1991;
accepted 4 September 1991

The kinetics of the hydrolysis of Cr(ox)$_2$(phen)$^-$ and Cr(ox)$_2$(bpy)$^-$ have been studied. The rate expression is rate = $k_{app}$ [H$^+$] [complex]. At 40°C and at an ionic strength of 2.0 mol dm$^{-3}$, the respective second order rate constants, $k_{app}$ are 1.7 x 10$^{-5}$ and 6.6 x 10$^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$. The activation parameters are evaluated and the enthalpies of activation are compared with those of the racemisation for the same complexes.

Studies on the aquation of mixed ligand complexes of chromium(III) where both the ligands are multi-dentate having amine and carboxylate groups have attracted the attention of several workers. The interest in such systems has arisen because of the question whether Cr – N or Cr – O bond rupture occurs in such reactions. In many cases, Cr – N rupture competes with Cr – O bond substitution, in both acidic and basic solutions$^{1,2}$. In some instances, e.g., with Cr(trien)(ox)$^+$ and Cr(en)$_2$(ox)$^-$, Cr – N bond rupture appears to be the only substitution process in dilute acidic solutions under both thermal and photolytic conditions$^{3-5}$. However, with complexes of the type Cr(ox)(phen)$_2^+$ and Cr(ox)(bpy)$_2^+$, it was observed that aquation proceeds through Cr – O bond rupture with the loss of the more flexible oxalate ligand$^6$. It was reported that the racemisation of these complexes and the title complexes also involve Cr – O bond breaking$^6,7$.

In view of the above observations for the aquation of Cr(ox)(phen)$_2^+$ and Cr(ox)(bpy)$_2^+$, one would expect the corresponding process for the title complexes. The present study was undertaken to test this assumption.

Experimental

Potassium cis-bis(oxalato)diaquochromate(III) was prepared by the method of Palmer$^8$. The purity of the complex was checked by micro analysis and spectrophotometry.

K[Cr(ox)$_2$(phen)] and K[Cr(ox)$_2$(bpy)] were prepared by the method outlined by Banerjea & Roy$^9$. The ligand (1.10-phenanthroline/2,2'-bipyridine) was added to an aqueous solution of Cr(ox)$_2$(H$_2$O)$_2$ in the ratio of 2:1 (w/w). This mixture was kept at 65°C for 24 hr until the reaction was complete, as indicated by a change in colour from purple to wine red. The excess ligand was removed by filtration. The filtrate containing the complex was taken in an evaporating dish and allowed to solidify by aerial evaporation at room temperature. The solid residue was treated several times with dry ethanol and the complex was completely freed from the unreacted/adsorbed ligand and finally dried in vacuum for 2 hr. The purity of the complex was checked by micro analysis and the UV-visible absorption spectra. All other chemicals used were of reagent grade.

Kinetics

The kinetic runs were carried out using a spectrophotometer (Shimadzu UV-260) in which the temperature can be regulated to within ±0.1°C. Requisite quantities of the complex solution was transferred into a 25 ml volumetric flask, together with calculated volume of NaClO$_4$ (to keep ionic strength at 2 mol dm$^{-3}$) and desired concentration of HClO$_4$. The reaction was followed by measuring the absorbance at 540 nm. The rate constants were evaluated by a standard least squares programme.

The reaction solutions were also subjected to ion-exchange studies to isolate the intermediate Cr(xx)(ox)(oxH)(H$_2$O)$_2$ where xx = phen/bipy. For this purpose Cr(ox)$_2$(phen)$^-$ and Cr(ox)$_2$(bpy)$^-$ labelled with $^{51}$Cr were prepared using cis-Cr(ox)$_2$(H$_2$O)$_2$ labelled with $^{51}$Cr. This complex was prepared by adding few drops of sodium chromate labelled with $^{51}$Cr to the K$_2$Cr$_2$O$_7$-oxalic acid mixture and following the same procedure adopted in the preparation of the inactive complex. Reaction solutions which are 1.0 x 10$^{-3}$ mol dm$^{-3}$ in the substrate and 1.0 mol dm$^{-3}$ in HClO$_4$ were prepared and after allowing the solutions to stand for about one hour, the reaction was frozen adding ice-cubes (made from doubly distilled water) and passed successively through Dowex 50W-X8 cation exchange (H$^+$ form) and Dowex 2X8 anion exchange (NO$_3^-$ form) resin columns. The solutions obtained after passing through these two columns showed gamma activity indicating the presence of neutral chromium(III) intermediate species.
Product analysis: Ion-exchange chromatography

The product solutions were diluted with doubly distilled water such that the acidity was less than 0.1 mol dm\(^{-3}\). A portion of this solution (25 ml) was passed through a column of Dowex 50W-X8 (100-200 mesh) cation exchange resin column which is in H\(^+\) form. The column was washed with water. A narrow light red coloured band remained at the top of the column and this band could be separated from the resin column with 1.0 mol dm\(^{-3}\) HClO\(_4\) indicating that the product of aquation was unipositive.

The oxalate content of the eluants was estimated by permanganometry and it corresponded to 0.96 mole for each mole of the substrate.

Thin-layer chromatography

TLC technique was employed as part of the product analysis. Two to three drops of each of the authentic samples of phenanthroline, bipyridine and the light red coloured products were spotted on a silica gel-G coated glass plate (0.25 mm thick) with the help of a micro syringe, 10% CHCl\(_3\) in methanol was used as solvent and iron(II) solution as spray. The blood red coloured spots were found only in the case of phenanthroline/bipyridine but not with the products. This indicated that neither phenanthroline nor bipyridine was released from the chromium(III) centre during the course of aquation.

Results and Discussion

The effect of [acid] on the rate of aquation is shown in Fig. 1. The results show that the reaction is first order in [H\(^+\)] both for phenanthroline and bipyridine complexes. Since the linear plots in all cases passed through the origin there was no detectable acid-independent dissociation reaction. Second order constants \(k_{aqn}\) determined from the slopes of these linear plots at five temperatures, together with enthalpies and entropies of activation calculated from Eyring plots are given in Table 1. The activation parameters for the racemisation reactions for the same complexes under analogous conditions collected from ref. 8 are given in parenthesis.

It was suggested that the acid catalysed racemisation of the title complexes involved rapid protonation of carbonyl oxygen followed by ring opening of oxalate chelate to give a trigonal-bipyramidal complex\(^7\). Closure of this ring can then proceed with equal probability of generating either enantiomer. Broomhead \textit{et al.}\(^7\) from their spectral studies also observed some total dissociation of oxalate ligand.

It can be seen from the data in Table 1 that although the rate laws are different for aquation and racemisation the activation enthalpies are similar within the experimental error. This is analogous to that suggested for Cr(ox)(phen)\(_2^+\), Cr(ox)(bpy)\(_3^+\) and Cr(ox)\(_5\). This indicates that the major contribution to \(\Delta H^*\) arises from Cr – O bond rupture.

The mechanism in scheme 1 can explain all the above observations and the experimental results obtained.

The intermediate I could either reform into the other optical isomer through oxalate ring opening or react with a water molecule to give II, which further reacts with H\(_2\)O\(^+\) to give the products.
Scheme 1 leads to the rate law (1)

\[
k_{\text{obs}} = \frac{k_1 K [H^+]}{1 + K [H^+]} \quad \ldots \quad (1)
\]

Since \( K \) is usually very small, \( K [H^+] < < 1 \) and Eq. 1 reduces to the form

\[
k_{\text{obs}} = k_1 K [H^+] \quad \ldots \quad (2)
\]

\[
k_{\text{obs}} = k_{\text{aq}} [H^+] \quad \ldots \quad (3)
\]

where \( k_{\text{aq}} = k_1 K \).

Finally, it was found that, just as for the racemisation of the title complexes, in contrast to monooxalato complexes, there is specific cation effects for Cu\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\) in the concentrations ca:

\[6 \times 10^{-2} \text{ mol dm}^{-3}\]

It was suggested that the metal ion catalysed racemisation involves the above intermediate\(^7\).

These observations also support our mechanism.

References