Effects of Ion-pairing on Solvolytic Aquation of Chloropentaammi-necobalt(III) Ion in Presence of Oxalate Anion

N. C. NAIK

Department of Chemistry, G. M. College, Sambalpur

and

R. K. NANDA*

Department of Chemistry, Utkal University, Bhubaneswar 751004

The rate of solvolytic aquation of chloropentaamminecobalt(III) ion has been measured in aqueous medium in the presence of oxalate anion at 40°, 45° and 50°C. The rate-accelerating effect of oxalate has been ascribed to the more reactive chloropentaamminecobalt(III) oxalate ion-pair. The rate and association constants of the ion-pair have been calculated. The rate constants for the formation of the oxalato-pentaammine complex by the entry of the ion-pairing oxalate ion have been evaluated from the product analysis experiment. The activation parameters of each of the reaction pathways and the thermodynamic parameters for the ion-association process have also been computed.

IN our previous communications[1-3], we reported that the marked acceleration of the rate of aquation of chloropentaamminecobalt(III) ion in the presence of bivalent anions, sulphate[1], maleate and phthalate[2] and malonate and succinate[3] was due to the formation of more reactive chloropenta-amminecobalt(III)-anion ion-pair. The release of chloride from the ion-pair has been shown to occur by two pathways : (i) aquation of the ion-pair (major path); and (ii) direct entry of the associating anion into the inner sphere of the complex (minor path). The present communication deals with the study of the rate-accelerating influence of oxalate ion on the acid hydrolysis reaction of chloropenta-amminecobalt(III) ion with a view to examining the effect of size and basicity of the ion-pairing anion on its rate-accelerating ability.

Materials and Methods

Chloropentaaminecobalt(III) perchlorate, [Co (NH$_3$)$_5$Cl] (ClO$_4$)$_2$ was prepared and purified as reported in literature[4]. (Found : Co, 15.45; Cl, 9.35. [Co(NH$_3$)$_5$ Cl] (ClO$_4$)$_2$ requires Co, 15.57; Cl, 9.4%).

Aquopentaaminecobalt(III) perchlorate, [Co (NH$_3$)$_5$ H$_2$O] (ClO$_4$)$_3$ was also prepared and purified as described in the literature[5]. The measured molar absorptivity of ϵ_{492} = 47.8 agreed fairly well with the values (ϵ_{492} = 47.7)[6] and (ϵ_{491} = 47.3)[5] reported previously.

Oxalatopentaamminecobalt III) perchlorate, [Co (NH$_3$)$_5$ HC$_2$O$_4$] (ClO$_4$)$_2$ was prepared and purified using standard methods[7,8] (Found : Co, 13.60. [Co(NH$_3$)$_5$HC$_2$O$_4$](ClO$_4$)$_2$ requires Co, 13.65%). The measured molar absorptivity of ϵ_{507} = 73.8 was in fair agreement with the value (ϵ_{507} = 74.0), reported in literature[9].

The sodium salts of oxalic acid were prepared by mixing together requisite amounts of sodium hydro-xide and oxalic acid of known concentrations. Sodium perchlorate of reagent grade was used for adjusting ionic strength. Doubly distilled water was used for preparing all solutions. Perchloric acid and other chemicals used were of reagent quality.

Kinetic experiments — The details of the method for following the rate of aquation and the formation of the oxalato complex were the same as reported earlier[1,2].

Evaluation of equilibrium constant — The stability constants of the aquo-oxalate ion-pairs were deter-mined spectrophotometrically at 270 nm and 30°C (I = 0.3 M). The reactants were mixed and the absorbance of the mixture measured immediately so as to avoid complications due to anation.

Results

The pseudo-unimolecular rate constants for the release of chloride ion from the complex have been calculated from the plots of log ($V\infty$ — V_t) versus time t, where V_t is the volume of silver nitrate con-sumed after time t, $V\infty$ being the volume computed from the weight of the complex taken for complete reaction. The results obtained are collected in Table 1.

The acid hydrolysis rate constants of the free complex ion have been measured at 40°, 45° and 50°C. The free complex ion reacts with the added oxalate ion and results in the formation of ion-pairs of the type, {Co(NH$_3$)$_5$Cl^{2+}, HOx$^-$} and {Co(NH$_3$)$_5$Cl^{2+}, Ox^{2-}} where Ox^{2-} and HOx^{2-} stand for the oxalate and bioxalate anions respectively. Obviously, the observed rate constant would be a composite term consisting of the aquation rate cons-tant of the free complex ion and the product of the aquation rate constant of the ion-pair and its equili-brium constant. In accord with our earlier works[1-3] and those reported by Wyatt and Davies[10] and

Table 1 — Acid Hydrolysis of [Co(NH$_3$)$_5$Cl] (ClO$_4$)$_2$ in Aqueous Solution in the Presence of Oxalate (Ox^{2-}) Anion {[Complex] = 5 × 10^{-3} M; and ionic strength = 0.3 M}

[HClO$_4$] × 10^3 M	[HOx$^-$] × 10^3 M (as NaHOx)	[Ox^{2-}] × 10^3 M (as Na$_2$Ox)	k_{obs}×10^5/sec^a			k_{ip} × 10^5/sec		
			40°	45°	50°C	40°	45°	50°C
10	—	—	1.02	1.87	3.36	—	—	—
—	0.2	5.0	1.15	2.08	3.55	2.00	3.74	5.25
—	0.4	10.0	1.25	2.26	3.70	2.02	3.77	5.22
—	0.8	20.0	1.40	2.51	3.95	2.03	3 72	5.24
—	1.2	30.0	1.50	2 71	—	2.01	3.74	—
						(33.4)	(28.9)	(24.5)

(a) The observed rate constants are accurate upto ± 1 percent. The 'K_{ip}' values are given in the parantheses at the end of the k_{ip} readings.

Monk et al.[11] the reactivities of the H-oxalate ion pair and the free complex were assumed to be the same. The results were analysed in the same manner as described in our previous communication[1]. Taking pK (HOx$^-$) = 4.27,(ref. 12), pH value of the reaction was calculated to be ⩽5.2. Under this condition the base hydrolysis of chloropentamminecobalt(III) ion[13] does not contribute significantly towards the overall rate and as such this path of chloride release was neglected. Equations (1-3) were utilised to calculate the rate constants and the association constants of the ion-pair by an iterative procedure using the IBM 1130 computer.

$$\text{Rate} = -\frac{dc}{dt} = k_{obs} \times c = k_1 \left[C_p^{2+} \right] + k_{ip} [C_p\text{Ox}] \quad ..(1)$$

$$\frac{1}{k_{obs} - k_1} = \frac{1}{k_{ip} - k_1} + \frac{1}{(k_{ip} - k_1)K_{ip}\left[\text{Ox}^{2-}\right]_f} \quad ...(2)$$

$$\left[\text{Ox}^{2-}\right]_f = \frac{\left[\text{Ox}^{2-}\right]_T}{1 + \frac{\left[\text{HOx}^{2-}\right]_t}{\left[\text{Ox}^{2-}\right]_t} + \frac{K_{ip}C}{1 + K_{ip}\left[\text{Ox}^{2-}\right]_f} + K_{As}[\text{Na}^+]_T} \quad ...(3)$$

where $\left[C_p^{2+} \right] = \left[C_p^{2+} \right]_f + \left[C_p\text{HOx}^+ \right]$

c = total initial concentration of the complex

k_1 = acid hydrolysis rate constant of the free complex ion.

$\left[C_p^{2+} \right]_f$ = concentration of the free complex ion.

$[C_p\text{Ox}]$ = concentration of the ion-pair of the free complex ion with the oxalate ion.

$[C_p\text{HOx}^+]$ = concentration of the ion-pair of the free complex ion with the bioxalate ion.

k_{ip} = acid hydrolysis rate constant of the ion-pair, C_pOx

K_{ip} = association constant of the oxalate ion-pair.

$[\text{Ox}^{2-}]_f$ = concentration of the free oxalate ion

$[\text{Ox}^{2-}]_T$ = $[\text{Ox}^{2-}]_t$ + $[\text{HOx}^-]_t$

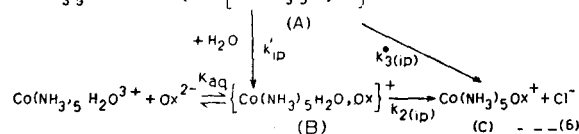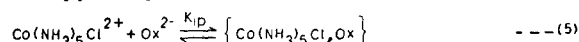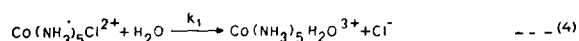$[\text{Ox}^{2-}]_T$ = total initial oxalate ligand concentration

$[\text{Ox}^{2-}]_t$ = total initial concentation of oxalate ion

$[\text{HOx}^-]_t$ = total initial concentration of the bioxalate ion

K_{AS} = ion-pair association constant involving ions (Na$^+$)$_f$ and (Ox^{2-})$_f$

The k_{ip} and K_{ip} values are recorded in Table 1.

Product distribution — The various path-ways for the chloride release and anation of the aquopentaamminecobalt(III) ion are delineated in Scheme 1.

$$\text{Co(NH}_3)_5\text{Cl}^{2+} + \text{H}_2\text{O} \xrightarrow{k_1} \text{Co(NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Cl}^- \quad ---(4)$$

$$\text{Co(NH}_3)_5\text{Cl}^{2+} + \text{Ox}^{2-} \underset{}{\overset{K_{ip}}{\rightleftharpoons}} \{\text{Co(NH}_3)_5\text{Cl,Ox}\} \quad ---(5)$$

(A)

$$+\text{H}_2\text{O} \downarrow k'_{ip} \qquad \searrow k^o_{3(ip)}$$

$$\text{Co(NH}_3)_5\text{H}_2\text{O}^{3+} + \text{Ox}^{2-} \underset{}{\overset{K_{aq}}{\rightleftharpoons}} \{\text{Co(NH}_3)_5\text{H}_2\text{O,Ox}\}^+ \xrightarrow{k_{2(ip)}} \text{Co(NH}_3)_5\text{Ox}^+ + \text{Cl}^-$$

(B) (C) ---(6)

$$k_{ip} = k'_{ip} + k^o_{3(ip)}$$

Scheme 1

On this basis, the time dependence of absorbance (D_t) of the reaction mixture is given by Eq. (8).

$$D_t = \epsilon_1 A_0 e^{-k_{obs}t} + \frac{\epsilon_2 A_0 k_{obs}}{k_2 - k_{obs}} (e^{-k_{obs}t} - e^{-k_2 t})$$

$$+ \epsilon_3 \left[\frac{A_0 k_{obs} e^{-k_2 t}}{k_2 - k_{obs}} + \frac{k_2 A_0 e^{-k_{obs}t}}{k_2 - k_{obs}} - \frac{k_{3(ip)} A_0 e^{-k_{obs}t}}{k_{obs}} + \frac{A_0 k_{3(ip)}}{k_{obs}} + A_0 \right] \quad ...(8)$$

where ϵ_1, ϵ_2 and ϵ_3 represent the molar absorptivities of the chloro, aquo and oxalatopentaamminecobalt(III) complexes at a path-length of 1 cm. A_0 refers to the concentration of $Co(NH_3)_5Cl^{2+}$ at zero time. $k_{3(ip)}$ was calculated using Eq. (8) with the help of a one parameter search programme (parameter being $k_{3(ip)}$ as already described[1]). $k_3{}^0{}_{(ip)}$ was calculated from Eq. (9)

$$k_{3(ip)} = \frac{k^0{}_{3(ip)}\ K_{ip}[Ox^{2-}]_f}{1+K_{ip}\ [Ox^{2-}]_f} \qquad ...(9)$$

The k_2, k_{ip}, $k_{3(ip)}$ and $k^0{}_{3(ip)}$ values are given Table 2. $\triangle G\ddagger_{40}$ (kcal/mol), $\triangle H\ddagger$ (kcal/mol) and $\triangle S\ddagger$ (e.u.) for the k_1, k_{ip} and $k^o{}_{3(ip)}$ paths have been estimated and are respectively as follows : 25.5, 23.4 $\pm$ 0.2, —6.7 $\pm$ 0.6; 25.05, 17.6 $\pm$ 0.2, —23.8 $\pm$ 0.6; 26.9, 31.9 $\pm$ 0.4, 16.0 $\pm$ 0.4. Values of $\triangle G_{40}{}^\circ$ (kcal/mole), $\triangle H\ddagger$ (kcal/mol) and $\triangle S\ddagger$ (e. u.) for the ion association process are found to be —2.2, —6.5 + 0.5 and —13.8 $\pm$ 1.6 respectively.

Evaluation of equilibrium constants — For the association reaction given in Eq. (10),

$$Co(NH_3)_5H_2O^{3+} + HOx^- \overset{K}{\rightleftharpoons} \{Co(NH_3)_5H_2O, HOx\}^{2+} \qquad ...(10)$$
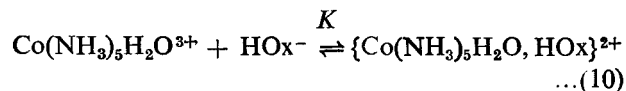
the equilibrium constant K is defined as

$$K = \frac{Z}{(m-z)\ (n-z)} \qquad ...(11)$$

where z is the concentration of the aquo-bioxalate ion-pair and m and n are the total concentrations of aquo complex and bioxalate ion respectively. It can be shown that

$$\frac{m}{d_T - \epsilon_2 m} = \frac{1}{(\epsilon_4 - \epsilon_2)} + \frac{1}{K(\epsilon_4 - \epsilon_2)(n-Z)} \qquad ...(12)$$

where d_T and ϵ_2 are the optical density of the reaction mixture and the extinction coefficient of the aquo complex respectively and ϵ_4, the extinction coefficient of aquo-bioxalate ion-pair. The values of K and ϵ_4 were calculated by an iterative procedure with the help of IBM 1130 computer from Eq. (12). The data are recorded in Table 3.

The formation constant K_{aq} of the formation of ion-pair in Eq. (13)

TABLE 3 — ABSORBANCES OF SOLUTION MIXTURES CONTAINING AQUOPENTAAMMINECOBALT(III) PERCHLORATE (2×10^{-3} M) AND VARYING AMOUNTS OF BIOXALATE AND OXALATE ANIONS AND EQUILIBRIUM CONSTANTS K AND K_{aq}

[Ionic strength = 0.3 M]

System	[HOx⁻] $10^3 M$ (as NaHOx)	[Ox²⁻]× $10^3 M$ (as Na₂Ox)	Absorbance[a] (270 nm)
Free ion	—	—	0.077
	20.0	—	0.080
	30.0	—	0.087
Bioxalate (K = 1.1)	40.0	—	0.120
	50.0	—	0.140
	60.0	—	0.150
	80.0	—	0.175
	0.08	2.0	0.120
	0.16	4.0	0.138
	0.24	6.0	0.153
	0.32	8.0	0.163
Oxalate ($K_{aq} = 10.0$)	0.40	10.0	0.170
	0.48	12.0	0.180
	0.64	16.0	0.208
	0.72	18.0	0.213
	0.80	20.0	0.228

(a) The recorded absorbance has been obtained after blank correction and correction for cell non-matching.

$$Co(NH_3)_5H_2O^{3+} + Ox^{2-} \overset{K_{aq}}{\rightleftharpoons} [Co(NH_3)_5H_2O,\ Ox]^+ \qquad ...(13)$$
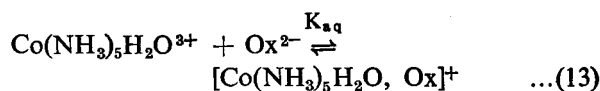
was computed using the values of K and ϵ_4.

The absorbance (d_X) of a solution containing aquopentaamminecobalt(III), bioxalate and oxalate ions is given by Eq. (14)

$$d_X = \epsilon_2\ [RH_2O^{3+}] + \epsilon_4\ K\ [RH_2O^{3+}]_f\ [HOx^-]_f$$
$$+ K_{aq}\ \epsilon_5[RH_2O^{3+}]_f\ [Ox^{2-}]_f = [RH_2O^{2+}]_f$$
$$\{\epsilon_2 + \epsilon_4\ K\ [HOx^-]_f + \epsilon_5\ K_{aq}\ [Ox^{2-}]\} \qquad ...(14)$$

where R stands for $Co(NH_3)_5{}^{3+}$ and ϵ_5 is the molar absorptivity of the aquo-oxalate ion-pair.

Since

$$[RH_2O^{3+}]_f = \frac{[RH_2O^{3+}]_T}{1 + K[HOx^-]_f + K_{aq}\ [Ox^{2-}]_f} \qquad ...(15)$$

Eq. (14) rearranges to Eq. (16),

$$\frac{\dfrac{d_X}{[RH_2O^{3+}]_T}\ (1 + K[HOx^-]_f - \epsilon_2 + \epsilon_4\ K[HOx^-]_f}{[Ox^{2-}]_f}$$
$$= \epsilon_5\ K_{aq} - K_{aq}\ \frac{d_X}{[RH_2O^{3+}]_T} \qquad ...(16)$$

With $[HOx^-]_f = [HOx^-]_T$ (since $1 >> K[RH_2O^{3+}]_f$)

and $[Ox^{2-}]_f = \dfrac{[Ox^{2-}]_T}{1 + K_{aq}[RH_2O^{3+}]_f}$

K_{aq} was evaluated from Eq. (16) by a method of successive approximations starting with $[Ox^{2-}]_T = [Ox^{2-}]_f$. The relevant data are collected in Table 3.

TABLE 2 — RATE CONSTANTS FOR THE k_{ip}, k_2, $k_{3(ip)}$ AND $k_3{}^\circ{}_{(ip)}$ PATHWAYS OF REACTION AT DIFFERENT TEMPERATURES

[Ox²⁻] × $10^2\ M$ (as Na₂Ox)	Pathways	Temperature (°C)		
		40	45	50
—	$k_{ip} \times 10^5$/sec.	2.01±0.02	3.74±0.03	5.23±0.02
—	$k_2 \times 10^4$/sec.	1.13±0.11	2.15±0.10	4.00±0.00
5.0	$k_{3(ip)}10^6$/sec	0.31±0.00	0.57±0.01	1.84±0.01
10.0	do	0.46±0.00	0.88±0.01	2.72±0.02
20.0	do	0.69±0.00	1.42±0.01	4.29±0.01
	$k^\circ{}_{3(ip)} \times 10^6$/sec.	1.10±0.03	2.78±0.15	6.25±0.30

Discussion

The results clearly indicate that the rate of aquation of the complex is markedly accelerated in the presence of added oxalate ion. The enhancement in rate is ascribed to the formation of more reactive chloropentaamminecobalt(III), oxalate ion-pairs. The rate constant levels off at $[Ox^{2-}] \simeq 0.3$ mol. The rate constants of the ion-pairs, however, bear no correlation with the basicity and size of the dicarboxylate ions $[k_{ip} \times 10^6 \sec^{-1} (K_{HL}^- \times 10^5): 4.6 (26.6)$, 5.14 (0.845), 5.03 (1.03) at 25°C for $L^{2-} =$ oxalate, malonate and succinate respectively].

As such, a predominantly electrostatic process is visualised to account for the greater reactivity of the ion-pair via dissociative pathway. The transition state would, therefore, involve considerable degree of charge separation and hence loss of activation entropy. The low negative entropy of activation for the aquation of the ion-pair is, therefore, in accordance with an S^N1 pathway proceeding possibly through an incipient tetragonal pyramid intermediate[14].

At 40°C and $[Ox^{2-}] = 0.03$ mol it is seen that about 7.5% in the maximum of the total chloride release (k_1, k'_{ip} and $k_{3(ip)}$ pathways taken together) takes place through the $k_{3(ip)}$ path. The rate constant for the formation of the oxalatopentammminecobalt-(III) complex through $k_3°_{(ip)}$ path was calculated to be $1.10 \times 10^{-6} \sec^{-1}$ at 40°C ($I = 0.3M$) which is only 5.5% of the k_{ip} value at the same temperature. It is, therefore, justified to make a reasonable assumption that the chloride release takes place predominantly through the formation of the aquo-complex. At 350 nm, the molar absorptivities of chloro, aquo and oxalatopentaaminecobalt(III) comlexes are found to be 30, 43 and 160 M^{-1} cm^{-1} respectively. The minima in the absorbance versus time plots[15] lead us to believe that the formation of the oxalatopentaamminecobalt(III) complex takes place predominantly through the anation of the intermediate aquo-oxalate ion-pair, ($k_{2(ip)}$ at 40°C being 1.13×10^{-5} sec^{-1}; $k_2 = k_{2(ip)} \times K_{aq}$, $= 1.13 \times 10^{-4}$ sec$^{-1})^{12}$. This is further supported by the excellent agreement between experimental absorbance and the absorbance calculated on the basis of reaction Scheme 1.

The ion-pairing process for the association of the chloropentaamminecobalt(III) cation with oxalate ion may now be considered. The negative enthalpy change of -6.5 kcal/mol indicates an exothermic association.

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