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The Aquation Reaction of Methanol- and Ethanol-Pentaamminecobalt(III) and Rhodium(III) Cations

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The aquation reaction of $M(NH_3)_5OHR^{3+}$ cations ($M = Co, Rh$ and $R = CH_3, C_2H_5$) has been investigated by kinetic techniques. The kinetic parameters for the substitution of the coordinated alcohol molecule by water, when compared with those for the water-exchange reaction ($R = H$), confirm the previous suggestion that an associative interchange mechanism is operating in the substitution reactions of pentaamminerhodium(III) compounds.

Introduction

A comparison of the kinetic data for the water-exchange reaction of aquopentaamminerhodium(III) cation [1] with those previously obtained with the cobalt(III) analogue [2] suggests a shift of the substitution mechanism from a dissociative interchange (I_d), for the cobalt complex, to an associative interchange (I_a) for the heavier homologue. This conclusion, based mainly on entropy and enthalpy of activation data, has received further support from measurements of activation volume [2, 3].

Pentaamminecobalt(III) and rhodium(III) complexes containing ROH alcohols as labile ligands belong to a series of structurally related compounds which includes the corresponding aquo complexes (R = H). It appeared useful to study the aquation reaction of these systems (as an extension of the water-exchange studies) in order to confirm further the mechanism proposed for the water-exchange and study the influence of the R group on the reactivity.

This paper presents the results of a kinetic investigation of the reaction:

$$M(NH_3)_5OHR^{3+} + H_2O \longrightarrow M(NH_3)_5OH_2^{3+} + ROH \quad (1)$$

with M = Co, Rh and R = CH_3, C_2H_5.

Experimental

Chemicals

$NaClO_4 \cdot H_2O$ was a BDH reagent and was used as received. 70% $HClO_4$ was a C. Erba product and was spectroscopically pure. Triethylphosphate (TEP, BDH reagent chemical) was dried by azeotropic distillation with benzene. The fraction distilling at 215 °C under normal pressure was collected and stored in desiccator.

All other reagents were pure grade chemicals and were used as received.

Complexes

Literature methods have been used for the synthesis of aquopentaamminecobalt(III) and rhodium(III) [4], trichloroacetatopentaamminerhodium(III) perchlorate [5], triethylphosphatopentaammine cobalt(III) perchlorate [7] and methoxypentaamminecobalt(III) perchlorate [7].

Methoxypentaammine rhodium(III) perchlorate

The preparation of this compound is based on previous observations on the reactivity of the trichloroacetatopentamminerhodium(III) cation [6]. 500 mg of $[Rh(NH_3)_5OCOCCl_3](ClO_4)_2$ were dissolved in 20 ml of a 1 mol dm^{-3} MeONa solution in dry MeOH, at 65 °C, with vigorous stirring. After 15 min the yellow solution was filtered off on a frit. Yellow crystals were obtained by addition of 3 ml of a concentrated aqueous $LiClO_4$ solution and cooling. The crystals were washed thoroughly with MeOH and Et_2O and air-dried (yield: 200 mg). The product, impure from free methanol as revealed by the NMR spectrum, was purified by dissolving the complex in the minimum amount of cold water and precipitating by addition of a concentrated solution of $LiClO_4$. The NMR data for the purified product are listed in Table I. *Anal.*, found % (calcd for $CH_{18}Cl_2N_5O_9Rh$): C 3.00 (2.87); H 4.42 (4.34); N 16.28 (16.75).

TABLE I. NMR Spectra of Alkoxypentaamminecobalt(III) and Rhodium(III) Complexes in Neutral and Acid Aqueous Solutions.

Complex	δ^a(ppm from TMS)	
	M = Co	M = Rh
$[M(NH_3)_5OCH_3](ClO_4)_2$	2.61, s	3.06, d (J = 0.6 ± 0.1 Hz)
$[M(NH_3)_5ODCH_3](ClO_4)_3$	3.03, s	3.39, d (J = 0.6 ± 0.1 Hz)
$[M(NH_3)_5OC_2H_5](ClO_4)_2$	1.16, t (CH_3) 2.90, q (CH_2) (J = 7.3 ± 0.2 Hz)	^{b}, t (CH_3) 3.28, q (CH_2) (J = 6.8 ± 0.2 Hz)
$[M(NH_3)_5ODC_2H_5](ClO_4)_3$	1.18, t (CH_3) 3.37, q (CH_2) (J = 7.8 ± 0.2 Hz)	^{b}, t (CH_3) 3.66, q (CH_2) (J = 7.2 ± 0.2 Hz)

[a] s = singlet, d = doublet, t = triplet, q = quartet. Internal standard t-BuOH. [b] Overlapping the internal standard signal.

Ethoxypentaamminerhodium(III) perchlorate

This compoud was prepared following essentially the same procedure described for the methoxy derivative, using dry EtOH instead of MeOH.

The NMR spectrum of the compound isolated from the reaction mixture shows that uncoordinated ethanol is not present (see Table I). Purification was carried out as described for the methoxy analogue. *Anal.*, found % (calcd for $C_2H_{20}Cl_2N_5O_9Rh$); C 5.72 (5.56); H 4.63 (4.68); N 15.41 (16.21).

Ethoxypentaamminecobalt(III) perchlorate

This previously unreported complex was prepared following essentially the procedure described for the methoxy analogue. However, owing to its lower solubility in dry EtOH, triethylphosphatopentaamminecobalt(III) perchlorate was first dissolved in a 1:1 (v:v) mixture of dry EtOH and dry TEP. The crude material obtained by addition of excess EtONa to this solution was first washed with EtOH and Et_2O and then purified by dissolving the crystals in a small amount of ice-cold water and precipitating by addition of 5 mol dm^{-3} $NaClO_4$ (yield *ca.* 30%).

This complex showed the expected NMR spectrum reported in Table I. *Anal.*, found % (calcd for $C_2H_{20}Cl_2CoN_5O_9$): C 5.36 (6.19); H 4.92 (5.21); N 17.40 (18.05) [8].

Apparatus and Techniques

pK_a and equivalent weight measurements

The pK_a of the acid–base equilibrium [7] of the alkoxy complexes

$$M(NH_3)_5OR^{2+} + H^+ \rightleftharpoons M(NH_3)_5OHR^{3+} \qquad (2)$$

and their equivalent weight were measured by potentiometric titration with standard $HClO_4$. The ionic strength was kept constant by addition of $NaClO_4$ (I = 0.50 mol dm^{-3}) to both titrating and base solutions. The temperature was controlled at 25.0 ± 0.1 °C. A Radiometer PHM 22 r pH-meter was used for pH measurements, using a glass electrode/saturated calomel electrode couple.

Nitrogen was bubbled through the solution to ensure stirring and to avoid contamination by CO_2 in the alkaline pH range.

NMR spectra

^1H NMR spectra were run on a Bruker HX 90 spectrometer using D_2O as solvent and t-BuOH as internal standard. The alkoxy compounds (5–10 mg) were dissolved directly in the NMR tube with 0.50 ml of D_2O and a drop of standard was added. They were then converted into the protonated form by addition of 5.0×10^{-2} ml of 0.80 mol $dm^{-3}DClO_4$. The spectra were recorded before and after the addition of acid.

Electronic spectra of the alcohol complexes

UV and Vis spectra were taken on a Varian Techtron 635 recorder spectrophotometer, at room temperature, using 1-cm quartz cells. The methanol- and ethanol-pentaammine complexes of both metals were prepared *in situ* by dissolving a known amount of the corresponding alkoxy complex in a known volume of 3.0×10^{-1} mol dm^{-3} $HClO_4$, the latter solution being used also as the reference.

Kinetic measurements

Reaction 1 was followed kinetically by measuring the change of optical density of an alcohol-containing complex solution, at a suitable wavelength (Co: 255–256 nm; Rh: 210 nm) and constant temperature.

As a rule the following experimental procedure was adopted. The aqueous solution (2.7 ml) of known reagent concentration and ionic strength was poured

TABLE II. pK_a's and Equivalent Weights of Alkoxy- and Aquopentaamminemetal(III) Perchlorates[a].

Complex	Equivalent Weight		pK_a
	exper.	calc.	
$[Co(NH_3)_5OH_2](ClO_4)_3$	457.8	460.5	6.1
$[Co(NH_3)_5OMe](ClO_4)_2$	366.8	374.0	5.5[b]
$[Co(NH_3)_5OEt](ClO_4)_2$	402.4	388.0	5.6
$[Rh(NH_3)_5OH_2](ClO_4)_3$	492.4	504.4	6.4
$[Rh(NH_3)_5OMe](ClO_4)_2$	423.0	418.0	5.8
$[Rh(NH_3)_5OEt](ClO_4)_2$	424.0	432.1	6.0

[a] Estimated uncertainties are ±3% on the equivalent weight and ±0.1 on pK_a. [b] Previous value [7]: $pK_a = 5.58$ at 20 °C and $I = 0.1$ mol dm^{-3}.

into a 1 cm quartz cell, which was then allowed to equilibrate thermally in the temperature-controlled cell compartment of the spectrophotometer (Beckman DU or DU 2). After *ca.* 20 min, an amount (1–2 mg) of the alkoxy complex, weighed inside a melting-point capillary, was quickly dissolved in the solution. This time was taken as the zero-time of the kinetic run.

The reaction was followed until a constant absorbance value was reached. With some samples an additional, comparatively small and slow decrease of absorbance was observed, due very likely to some unknown impurity. This complication did not interfere seriously with the main reaction.

Results and Discussion

Structure and Hydrolytic Behaviour

Upon titration with $HClO_4$, all four alkoxy complexes showed a single titration step within the range $3 \leq pH \leq 10$. Moreover, it can be observed (see Table II) that the equivalent weights are close to the theoretical values and that the pK_a's are of the expected magnitude as compared with the pK_a's of the aquo complexes and that of the methanolpentaamminecobalt(III) cation already reported [7]; in particular for this latter complex our value agrees very well with the published one.

The NMR spectra of the methoxide complexes (see Table I) exhibit one signal. This signal, in the case of the rhodium complex, is a narrow doublet ($J = 0.6 \pm 0.1$ Hz) due to long-range coupling of the protons to ^{103}Rh ($I = 1/2$), as confirmed by running the spectrum also at 60 MHz.

The expected quartet plus triplet pattern of an ethyl group is observed for the ethoxide complexes.

Upon acidification, the proton signals of all the complexes show a considerable downfield shift. This is an indication that the electronic environment of

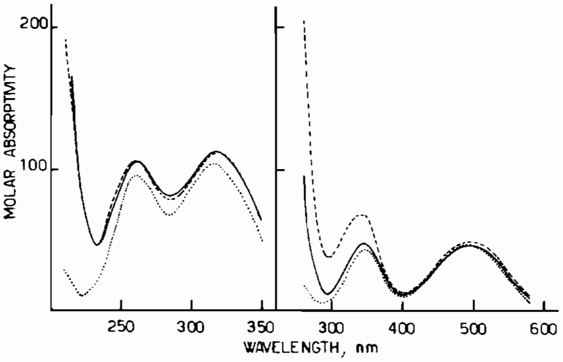

Figure. UV spectra of $M(NH_3)_5OHR^{3+}$ cations at room temperature. Left hand side: Rh(III) complexes; right hand side: Co(III) complexes. Full lines: R = Et; dashed lines: R = Me; dotted lines: R = H.

the alkyl groups is strongly modified upon addition of acid, as expected on the basis of reaction 2.

The electronic spectra of the alkoxy complexes dissolved in excess of acid are shown in the figure. It appears that for a given metal, the spectra are virtually independent of the alkoxy group and close to the spectrum of the aquo species. Only in the low-wavelength region is the absorbance of the alcohol derivatives significantly higher than that of the corresponding aquo complex.

On ageing the spectra change, as expected on the basis of reaction 1, and eventually become coincident with that of the aquo complex [9].

Kinetics

The optical data measured on acid solutions of the $M(NH_3)_5OHR^{3+}$ cations closely follow the first-order kinetic law up to 3 half-lives.

Tables III and IV list the rate constants obtained and the corresponding experimental conditions. The rate constant of reaction 1 appears to be slightly decreased by increasing both the ionic strength and the hydrogen ion concentration. The negative kinetic effect of the hydrogen ion is in contrast with a reported acid-catalysed release of MeOH from $Co(NH_3)_5OHMe^{3+}$ in the presence of H_2SO_4 [7]. The present results rule out any acid-catalysis and are consistent with previous observations on the lack of influence of acids on the water-exchange reactions of $Rh(NH_3)_5OH_2^{3+}$ and $Ir(NH_3)_5OH_2^{3+}$ [1, 10]. Hence, the observed enhancement of the rate of reaction 1 for the methanolpentaamminecobalt(III) ion in the presence of H_2SO_4 may be better explained as due to the formation of ion-pairs with SO_4^{2-}. Kinetic effects of this kind have been observed for the water-exchange reaction of both aquopentaamminerhodium(III) and iridium(III) cations [1, 10].

In all cases the Eyring plot was found to be strictly linear throughout the temperature range investigated. The activation parameters of reaction 1 (see Table V)

TABLE III. Rate of Aquation of $M(NH_3)_5OHR^{3+}$ Complexes[a].

M	R	t (°C)	k × 10^4 (s^{-1})
Co	CH_3	31.7	1.38
		31.9	1.41
		40.1	4.15
		40.1	4.19
		50.1	14.4
		50.1	14.6
Co	C_2H_5	32.7	1.99
		32.7	1.96
		40.1	5.18
		40.1	5.24
		49.9	18.2
		49.9	18.8
Rh	CH_3	40.1	2.22
		40.1	2.21
		49.9	6.90
		50.0	6.90
		60.0	19.2
		60.0	20.2
Rh	C_2H_5	40.1	1.79
		40.0	1.79
		40.1	1.75
		50.1	6.00
		50.1	5.96
		60.0	17.7
		60.0	17.3

[a] Ionic strength 0.50 mol dm^{-3}, hydrogen ion concentration 1.1×10^{-2} mol dm^{-3}.

follow a trend already observed for substitution reactions of pairs of structurally related Co(III) and Rh(III) complexes [11]. In fact, both the activation enthalpies and entropies of $Rh(NH_3)_5OHMe^{3+}$ and $Rh(NH_3)_5OHEt^{3+}$ are lower than those of the corresponding Co(III) compounds.

This situation is closely similar to that observed for the water-exchange reaction of $Co(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$ and indicates that in the transition state, the incoming water interacts with rhodium to an extent greater than with cobalt, thus leading to a more ordered (lower $\Delta S^{\ddagger}$) and energetically more stable (lower $\Delta H^{\ddagger}$ values) transition state.

It is interesting to note that the aquation of the $Co(NH_3)_5OHR^{3+}$ complexes, when compared to that of the $Rh(NH_3)_5OHR^{3+}$ systems, appears to be more sensitive to the nature of R. In fact, whilst for the cobalt series the change from R = H to R = alkyl group causes an increase of k by a factor of 10 (see Table V), for the rhodium series the k value increases by a factor smaller than 3. This lower sensitivity of the rhodium compounds towards the nature of the leaving group may be taken as further evidence of an associative mechanism [12].

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TABLE IV. Effect of Acidity and Ionic Strength on the Observed Aquation Rate Constant of $M(NH_3)_5OHR^{3+}$ Cations.

M	R	t (°C)	[H^+] (mol dm^{-3})	I (mol dm^{-3})	k × 10^3 (s^{-1})
Co	CH_3	50.0	0.011	0.50	1.45[a]
		49.9	0.50	0.50	1.28
		50.0	2.50	4.00	1.10
Co	C_2H_5	60.5	0.011	0.50	6.33[b]
		60.5	0.50	0.50	5.11
		60.6	2.50	4.00	3.89
Rh	CH_3	60.0	0.011	0.50	1.97[a]
		59.8	0.011	4.0	1.43
		59.9	0.50	0.50	1.89
		59.9	4.0	4.0	1.23
Rh	C_2H_5	60.0	0.011	0.50	1.75[a]
		59.9	0.50	0.50	1.75
		60.0	4.0	4.0	1.46
		59.9	0.011	4.0	1.40
		60.1	2.50	4.0	1.51
		59.9	0.50	4.0	1.42

[a] Average from values reported in Table III. [b] Value extrapolated from data at lower temperatures.

TABLE V. Activation Parameters for the Water-Exchange Reaction and Reaction 1.

Complex	$k \times 10^3$ [a] (s^{-1})	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (e.u.)	Ref.
$Co(NH_3)_5OH_2^{3+}$	0.19	26.6	6.7	2
$Co(NH_3)_5OHCH_3^{3+}$	1.44	24.3	3.5	This work
$Co(NH_3)_5OHC_2H_5^{3+}$	1.85	25.0	6.2	This work
$Rh(NH_3)_5OH_2^{3+}$	0.24	24.1	−0.3	1
$Rh(NH_3)_5OHCH_3^{3+}$	0.69	22.1	−4.7	This work
$Rh(NH_3)_5OHC_2H_5^{3+}$	0.60	23.8	+0.2	This work

[a] 50 °C and I = 0.50 mol dm^{-3}.

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8 It may be noted that the percent of carbon is appreciably lower than expected. Samples coming from the same preparation gave somewhat different sets of results for the elemental analysis, the reported set of values being the closest to the calculated one. Since the compound explodes on heating, this fact may likely lead to scattered analytical results. Nevertheless, the NMR spectrum, the equivalent weight and the kinetic behaviour (see further) indicate that the amount of impurities (if any) must be low.

9 A small difference was observed for the rhodium compounds below 250 nm, due to the absorbance of free methanol and ethanol.

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