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The Alkaline Hydrolysis of some Phosphato Pentaammine Cobalt(III) Complexes

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Abstract

Second-order rate constants (k_{OH} (M^{-1} s^{-1}), 25.0 °C, $I = 1.0$ M ($NaClO_4$)) for the alkaline hydrolysis of the following complex ions are reported: $[Co(NH_3)_5OP(OR)_3]^{3+}$, R = Me (78.3), Et (44.5); $[Co(NH_3)_5OP(O)(OR)_2]^{2+}$, R = Me ($6.7 \times 10^{-2}$), Et ($4.9 \times 10^{-2}$), ^{n}Pr ($3.5 \times 10^{-2}$), ^{n}Bu ($3.5 \times 10^{-2}$); $[Co(NH_3)_5OP(O)_2(OR)]^+$, R = Et ($5.0 \times 10^{-5}$), ^{n}Pr ($3.1 \times 10^{-5}$); $[Co(NH_3)_5OPO_3]$ (8×10^{-7}). In every case hydrolysis occurs at the Co(III) centre; no hydrolysis occurs at the P(V) centre.

Introduction

In a recent paper Norman [1] described the synthesis and alkaline hydrolysis of the diethylphosphato complex ion $[Co(NH_3)_5OP(O)(OEt)_2]^{2+}$. Hydrolysis was followed spectrophotometrically (35 °C, $I = 1.0$ M, $[OH^-] = 2.5–7.5 \times 10^{-3}$ M) and by ^{31}P NMR (ambient temperature, pH = 11.3). The spectrophotometric rate data gave a good second order rate constant (k_{OH}) of 9.6 M^{-1} s^{-1}, reaction (1) (R = Et),

$$[Co(NH_3)_5OP(O)(OR)_2]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + PO_2(OR)_2^- \tag{1}$$

whereas the qualitative ^{31}P data relate to a rate of $\sim 4 \times 10^{-6}$ s^{-1} at pH 11.3, or to a k_{OH} value of $\sim 2 \times 10^{-3}$ M^{-1} s^{-1}. No comment was made on the fact that the two sets of data apparently disagree. Both k_{OH} values, particularly that derived from the supposedly more precise spectrophotometric measurements, also differ substantially from those we have recently obtained for the alkaline hydrolysis of the similar dimethyl (R = Me) and di-n-butyl (R = ^{n}Bu) complexes ($k_{OH} = 6.7 \times 10^{-2}$ M^{-1} s^{-1} for R = Me; $k_{OH} = 3.5 \times 10^{-2}$ M^{-1} s^{-1} for R = Bu at 25.0 °C, $I = 1.0$ M) [2]. Therefore, as part of an undergraduate physical chemistry exercise we set two pairs of students the task of checking Norman's and our own k_{OH} values. This report describes their results and includes some new data [3] on reaction (2)

$$[Co(NH_3)_5OP(OR)_3]^{3+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + PO(OR)_3 \tag{2}$$

the first reported rate data on reaction (3)

$$[Co(NH_3)_5OP(O)_2(OR)]^+ + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + PO_3(OR)^{2-} \tag{3}$$

and a ^{31}P NMR study at 25 °C on reaction (4)

$$[Co(NH_3)_5OPO_3] + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + PO_4^{3-} \tag{4}$$

for which our k_{OH} value is in agreement with earlier data obtained at higher temperatures [4]. The combined set of rate constants (k_{OH}) for these pentaammine cobalt(III) phosphato complexes make an interesting series, and extend the available range of such values for the alkaline hydrolysis of acido groups bound to cobalt(III).

Experimental

^{1}H, ^{13}C and ^{31}P spectra were recorded on a Varian VXR 300 spectrometer operating at 299.903 (^{1}H), 75.419 (^{13}C) and 121.405 (^{31}P) MHz and equipped with a 5 mm thermostatted (25.0 °C) probe. Samples were made up in acidified D_2O (CF_3SO_3H) or 80% H_2O:20% D_2O (external H_3PO_4 standard). ^{31}P kinetic data used H_2O as the solvent and an external H_3PO_4 standard in D_2O.

Preparations

The two complexes $[Co(NH_3)_5OP(OR)_3](ClO_4)_3 \cdot H_2O$ (R = Me, Et) were synthesised from freshly prepared $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in a similar manner to that reported recently [5]. *Anal.* Calc. for R = Me: C, 6.00; H, 4.36; N, 11.66. Found: C, 6.02; H, 4.56; N, 11.38. Calc. for R = Et: C, 11.21; H, 5.02; N, 10.90. Found: C, 11.44; H, 5.10; N, 10.63%. ^{1}H NMR (δ): R = Me, 3.81(d); R = Et, 1.46(t), 4.08-

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(quin). ^{13}C NMR (δ, dioxane): R = Me, 56.2. The triethylphosphato complex (R = Et) was found to slowly revert to the aqua complex in the solid state; however the R = Me complex appeared to be quite stable.

$[Co(NH_3)_5OP(O)(OMe)_2](ClO_4)_2$ and $[Co(NH_3)_5OP(O)(OBu)_2](ClO_4)_2 \cdot H_2O$ were prepared as described previously [2]. ^1H NMR (δ): R = Me, 3.60(d); R = Bu, 0.90(t), 1.35(sextet), 1.61(quin), 3.88(quart). ^{13}C NMR (δ, dioxane): R = Me, 55.0; R = Bu, 13.5, 18.9, 32.1.

$[Co(NH_3)_5OP(O)(OEt)_2](ClO_4)(NO_3)$ and $[Co(NH_3)_5OP(O)_2(OEt)](ClO_4) \cdot H_2O$ were prepared as follows. To 7.4 g of technical grade diethylphosphate (70% diethylphosphoric acid, 30% monoethylphosphoric acid) in 40 cm^3 of sulpholane was added 2 g of triethylamine followed by 2.4 g of $[Co(NH_3)_5OSMe_2](ClO_4)_3$ [3]. The mixture was heated at 80 °C for 100 min and then diluted with water and loaded onto a column of Sephadex SP-C25 cation-exchange resin. On elution with 0.1 M pyridinium acetate the purple band split into two and both fractions were eluted by increasing the pyridinium acetate concentration to 1 M. These were reduced to dryness by rotary evaporation. The faster moving fraction (~30%) was crystallised as $[Co(NH_3)_5OP(O)_2(OEt)]ClO_4 \cdot H_2O$ by adding solid $NaClO_4 \cdot H_2O$ to a concentrated aqueous solution; it was recrystallised from hot water by cooling in an ice bath. *Anal.* Calc. C, 6.23; H, 5.75; N, 18.17. Found: C, 6.28; H, 5.88, N, 18.31%. ^1H NMR (δ): 1.21(t), 3.80(quin). ^{31}P NMR (δ, H_3PO_4): 12.55. The slower moving fraction was crystallised as $[Co(NH_3)_5OP(O)(OEt)_2](ClO_4)(NO_3)$ by adding solid $LiClO_4$ and $LiNO_3 \cdot H_2O$ to a concentrated aqueous solution and scratching the sides of the beaker; it was similarly recrystallised from water. *Anal.* Calc. C, 10.5; H, 5.5; N, 18.3. Found: C, 10.3; H, 5.5; N, 18.3%. ^1H NMR (δ): 1.26(t), 3.94(quin). ^{31}P NMR (δ, H_3PO_4): 8.47.

A mixture of di- and mono- n-propylphosphate was prepared as follows [6]. To 560 g of n-propanol containing BF_3, at 0 °C was added with stirring 55 g of $POCl_3$. After 15 h 1 dm^3 of water was added and the mixture reduced to a viscous oil by rotary evaporation. This oil was distilled under vacuum giving three fractions: (1) boiling point (b.p.) 20 °C (2 mmHg); (2) b.p. 120 °C (4 mmHg); (3) residue. The second and third fractions gave the following analytical data: C, 45.94; H, 9.13 and C, 34.13; H, 7.26% respectively, which are to be compared with the expected values for the tri-, di- and mono- propyl phosphate esters of C, 48.20, 39.78, 26.10 and H, 9.44, 7.79, 5.11%. From these data the third fraction was considered to contain substantial amounts of di-n-propylphosphate and this was used in the following preparations of $[Co(NH_3)_5OP(O)_2(OPr)]ClO_4$ and $[Co(NH_3)_5OP(O)(OPr)_2](ClO_4)(NO_3)$. To 3.87 g of the phosphate ester dissolved in 15 cm^3 of dimethylsulfoxide was added 0.9 g of triethylamine and 3 g of $[Co(NH_3)_5OSMe_2](ClO_4)_3$. This mixture was heated at 80 °C for 2 h. The product was diluted with ethanol (100 cm^3) and water (300 cm^3), loaded onto a column of Sephadex SP-C25 cation-exchange resin and eluted with 0.1 M pyridinium acetate. Once the two purple products had separated the pyridinium acetate concentration was increased to 1 M and the bands collected. These fractions were reduced to dryness by rotary evaporation. $[Co(NH_3)_5OP(O)_2(OPr)]ClO_4 \cdot H_2O$ was easily crystallised by adding solid $NaClO_4 \cdot H_2O$ to a concentrated aqueous solution. It was recrystallised from warm water by cooling in an ice bath. *Anal.* Calc. C, 9.02; H, 6.05; N, 17.52. Found: C, 9.05; H, 5.69; N, 17.76%. ^1H NMR (δ): 0.89(t), 1.59(sextet), 3.70(quart). The more soluble di-n-propylphosphate complex proved more difficult to isolate but was finally obtained as $[Co(NH_3)_5OP(O)(OPr)_2](ClO_4)(NO_3)$ by adding $LiClO_4$ and $LiNO_3 \cdot H_2O$ to a concentrated solution in water. This was similarly recrystallised from the minimum volume of water. Large purple–red crystals separated following addition of MeOH and EtOH and standing at room temperature over two days. *Anal.* Calc. C, 14.81; H, 6.01; N, 17.27. Found: C, 14.81; H, 6.04; N, 17.28%. ^1H NMR (δ): 0.91(t), 1.63(sextet), 3.84(quart). ^{13}C NMR (δ, dioxane): 10.7, 24.4, 70.2.

$[Co(NH_3)_5OPO_3]$ was prepared as described previously [7] (^{31}P NMR 14.47 versus 5.75 ppm for $PO_4{}^{3-}$, aqueous NaOH (0.1 M).

Kinetics

Spectrophotometric rate data were obtained using a Durrum D-110 stopped flow spectrophotometer interfaced to a Northstar Horizon computer. Data were treated using an OLIS kinetic fitting routine. ^{31}P NMR rate data were collected on the Varian VXR 300 spectrometer by averaging 256, 512 or 1024 transients (pulse width 15 μs; acquisition time 0.750 s; delay 0.250 s) and spacing the collections at appropriate time intervals. Integrated areas (I_t) were treated using conventional $\ln(I_t)$ or $\ln(I_\infty - I_t)$ versus time (t) plots.

Results and Discussion

In the following account the $Co(NH_3)_5$ moiety is represented by A_5Co.

The preparation and alkaline hydrolysis of the $A_5Co{-}OP(OR)_3{}^{3+}$ complexes (R = Me, Et) follows an earlier report on $A_5Co{-}OP(OMe)_3{}^{3+}$ where rate constants for both the spontaneous and OH^--catalysed reactions were given ($k_o \sim 1.4 \times 10^{-4}$ s^{-1}; $k_{OH} = 79$ M^{-1} s^{-1}, $I = 1.0$ M, 25 °C) [3]. Our value for R = Me (Table 1) agrees with this k_{OH} value and extends the observed data to 0.1 M OH^-. Apparently the rate law $k_{obs} = k_{OH}[OH^-]$ holds over this ex-

TABLE 1. Rate data for the alkaline hydrolysis of phosphate ester complexes at 25 °C and $I = 1.0$ M ($NaClO_4$)

Substrate ($Co(NH_3)_5 = A_5Co$)	Method[a]	$[OH^-]$ (M)	k_{obs} (s^{-1})	k_{OH} ($M^{-1}\ s^{-1}$)
$A_5Co{-}OP(OMe)_3^{3+}$	S	0.10	7.83	78.3
$A_5Co{-}OP(OEt)_3^{3+}$	S	0.10	4.45	44.5
$A_5Co{-}OP(O)(OMe)_2^{2+}$	S	1.00	6.67×10^{-2}	6.67×10^{-2}
$A_5Co{-}OP(O)(OEt)_2^{2+}$	S	1.00	4.85×10^{-2}	4.85×10^{-2}
	^{31}P	0.04	1.62×10^{-3}	4.05×10^{-2}
	^{31}P	1.78×10^{-3}	7.60×10^{-5}	4.27×10^{-2}
$A_5Co{-}OP(O)(OPr)_2^{2+}$	S	1.00	3.5×10^{-2}	3.5×10^{-2}
	^{31}P	0.05	1.52×10^{-3}	3.0×10^{-2}
$A_5Co{-}OP(O)(OBu)_2^{2+}$	S	1.00	3.52×10^{-2}	3.52×10^{-2}
$A_5Co{-}OP(O)_2(OEt)^{+}$	^{31}P	1.00	5.0×10^{-5}	5.0×10^{-5}
$A_5Co{-}OP(O)_2(OPr)^{+}$	^{31}P	1.00	3.1×10^{-5}	3.1×10^{-5}
$A_5Co{-}OPO_3$	^{31}P	1.00	5.7×10^{-7}	5.7×10^{-7}

[a] S = spectrophotometric; ^{31}P = ^{31}P NMR measurements.

tended range, which implies that the acidity of coordinated NH_3 in these systems is not great ($K_a < 10^{-15}$). (For a recent account of the $S_N1(CB)$ mechanism see ref. 8). The R = Et complex is about twice as slow to hydrolyse as the R = Me complex.

The $A_5Co{-}OP(OR)_2^{2+}$ complexes (R = Me, Et, ^nPr, ^nBu) form a series of increasing alkyl chain length. They can be prepared from $[Co(NH_3)_5OSMe_2](ClO_4)_3$ or $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in sulfolane or dimethylsulfoxide as solvent using the neat ester, or its sodium salt. In the preparations reported here the absence of the pure dialkyl ester (R = Et, Pr) necessitated making a mixture of the di- and mono-ester complexes, and separating them by ion-exchange chromatography. Elemental, and ^1H and ^{31}P NMR analysis establish their purity. The $A_5Co{-}OP(OR)_2^{2+}$ ions were found to hydrolyse slowly (overnight) in neutral and acidic aqueous solutions, and the reported rate for the spontaneous reaction of $\sim 2 \times 10^{-5}\ s^{-1}$ (k_0) [1] appears to be reasonable. Their alkaline hydrolysis however is considerably slower than for the 3+ ions, with k_{OH} for $A_5Co{-}OP(O)(OEt)_2^{2+}$ ($4.5 \times 10^{-2}\ M^{-1}\ s^{-1}$) being some 10^3 smaller than for $A_5Co{-}OP(OEt)_3^{3+}$ ($44.5\ M^{-1}\ s^{-1}$). Also the series R = Me, Et, ^nPr, ^nBu show a decrease in k_{OH} with increasing chain length, with the limiting value appearing to be about $3.5 \times 10^{-2}\ M^{-1}\ s^{-1}$. Our value of $4.5 \times 10^{-2}\ M^{-1}\ s^{-1}$ for $A_5Co{-}OP(O)(OEt)_2^{2+}$ means that the earlier value of $9.6\ M^{-1}\ s^{-1}$ (at 35 °C) reported by Norman [1] is incorrect. For these 2+ ions some difficulty was experienced in obtaining spectrophotometric data (in 1.0 M OH^-) since the A_5CoOH^{2+} product itself undergoes further hydrolysis to give CoO(OH) (see below). Thus of the spectrophotometric data used in the kinetic analyses only that obtained over the first 60–70 s was useful ($\sim 3\ t_{1/2}$). However this problem was avoided with the ^{31}P NMR data since subsequent

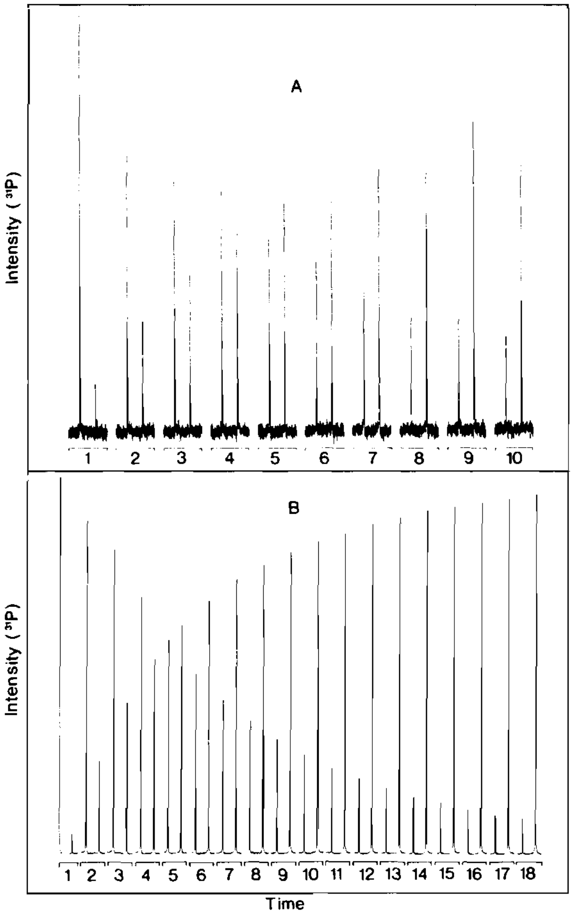

Fig. 1. ^{31}P data for the hydrolysis of (A) $[Co(NH_3)_5OP(O)(OEt)_2](NO_3)(ClO_4)$ in 0.2 M triethylamine buffer, pH = 11.02, 0.8 M $NaClO_4$, 25.0 °C, data at 40 min intervals (acquisition time, 0.750 s; delay, 0.250 s; transients, 512; pulse width, 15 μs); (B) $[Co(NH_3)_5OP(O)_2(OEt)](ClO_4)$ in 1.0 M NaOH, 25.0 °C, data at 50 min intervals (acquisition time, 0.750s; delay, 0.500s; transients 768; pulse width, 15 μs).

decomposition had no effect on the ^{31}P signals; good first order data were obtained over extended periods using both the reactant and product signals. An example of this is given in Fig. 1(A). The ^{31}P and ^{1}H NMR data also showed the complete absence of $PO_3(OR)^{2-}$, PO_4^{3-} and ROH products implying that no P–OR cleavage occurs in the coordinated or released ligand under the experimental conditions.

The $A_5Co-OP(O)_2(OR)^+$ complexes likewise are about 10^3 times slower to hydrolyse than the $A_5Co-OP(O)(OR)_2^{2+}$ ions (Table 1). Here precipitation of CoO(OH) occurs to such an extent as to prevent the collection of spectrophotometric rate data. The ^{31}P data however gave excellent first order traces. An example of this is shown in Fig. 1(B). A subsequent experiment using $[Co(NH_3)_5OH_2](ClO_4)_3$ in 1.0 M OH^- showed that CoO(OH) is rapidly formed from A_5CoOH^{2+} under such conditions. Thus it appears that $A_5Co-OP(O)_2(OR)^+$ does not directly give rise to CoO(OH); it is formed from the initially formed A_5CoOH^{2+} product. These data also show that CoO(OH) does not catalyse the hydrolysis reaction and that no paramagnetic Co(II) species are formed under the alkaline conditions since the ^{31}P and ^{13}C signals remained sharp and intense throughout the reaction.

Hydrolysis of $A_5Co-OPO_3$ is much slower again, with k_{OH} being $\sim 10^2$ times smaller than for the 1+ ions. This reaction has previously been studied at higher temperatures (60, 72.2, 82.4 °C) by Lincoln *et al.* using a ^{32}P-labelling method [4]. Our k_{OH} value of 5.7×10^{-7} s^{-1} in 1.0 M OH^- agrees well with their data extrapolated to 25 °C (4.6×10^{-7} s^{-1}). However, they suggested a concomitant hydrolysis pathway involving loss of NH_3; our data indicates this not to be the case since no additional ^{31}P signal corresponding to $[Co(NH_3)_4(OH)(OPO_3)]^-$ was seen. Indeed, it can be inferred from our ^{31}P results that all $[Co(NH_3)_5X]^{n+}$ complexes are very stable towards loss of coordinated ammonia and eventual formation of CoO(OH); only $[Co(NH_3)_5OH]^{2+}$ is unstable in this respect.

The combined data of Table 1 show that the alkaline hydrolysis of monodentate phosphate ligands bound to A_5Co^{3+} extends over a 10^8-fold range of reactivity.

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