The [Co([15]aneN₅)OH]²⁺ Promoted Hydrolysis of 4-Nitrophenyl Acetate

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In recent years there has been considerable interest in the reactivity of metal bound nucleophiles in both inter- and intramolecular reactions. Some aspects of the subject have been reviewed [1, 2]. Typical examples of such reactions have been the intramolecular hydrolysis of N-coordinated amino-acid esters and amides by Co–OH complexes [1], the hydration of CO_2 by metal hydroxides of the type $[(NH_3)_5-MOH]^{2+}$ where M = Co(III) [3], Rh(III) [4] and Ir(III) [4], the condensation of $[Co(en)_2(OH)-(OH_2)]^{2+}$ with acetylacetone [5] to give $[Co(en)_2-(acac)]^{2+}$, the reaction of $[(NH_3)_5CoOH]^{2+}$ with propionic anhydride to give $[(NH_3)_5CoOCOC_2H_5]^{2+}$ [6] and the hydrolysis of 4-nitrophenyl acetate by the complex $[(NH_3)_5CoOH]^{2+}$ [7]. All these reactions have demonstrated the ability of metal bound hydroxide to add rapidly to carbonyl substrates. These reactions are of considerable biological interest in view of the possible role of metal bound hydroxide in some enzymic reactions. Thus a 'zinc-hydroxide' mechanism has been considered for the enzyme carbonic anhydrase [1, 7].

The present paper discusses the hydrolysis of 4-nitrophenyl acetate by the macrocyclic complex $[Co([15]aneN_5)OH]^{2+}$ (where [15]aneN₅ = 1,4,7,-10,13-penta-azacyclopentadecane = I). In reactions of
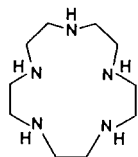
(1)

this type, the inert ligand system is expected to play a role. The macrocyclic ligand is a stronger sigma donor than the NH_3 ligand and this is expected to affect the Lewis acidity of the cobalt(III) centre and hence the pK_a and nucleophilicity of the hydroxo-ligand.

Experimental

The ligand 1,4,7,10,13-penta-azacyclopentadecane as its pentahydrochloride salt was prepared as previ-

ously described [8]. The aquo complex $[CoL(OH_2)]-(ClO_4)_3$ was also synthesised as previously described [8]. 4-Nitrophenyl acetate was prepared by acetylation of 4-nitrophenol with acetic anhydride and was recrystallised from ethanol by addition of water.

The kinetics of base hydrolysis of 4-nitrophenyl acetate were followed by monitoring the release of 4-nitrophenol at 420 nm. The pH was maintained using 0.01 *M* borax buffers adjusted to *I* = 0.1 *M* with $NaClO_4$. The reaction was initiated by the addition of 0.1 cm³ of a solution of 4-nitrophenyl acetate in acetonitrile (1 mg/cm³) to 2.9 cm³ of the equilibrated buffer, to give a final concentration of the ester of 1.84×10^{-4} *M*. Plots of log ($A_\infty - A_t$) *versus* time were linear for several half lives. The observed first order rate constants at constant pH (k_{obs}) were determined from the absorbance data using a desk top computer.

The metal complex promoted reactions were studied similarly using 0.01 *M* borax buffers adjusted to *I* = 0.1 *M* and an ester concentration of 1.84×10^{-4} *M*. In all cases the concentration of [CoL-(OH)]²⁺ was in at least a tenfold excess. All the reactions were first order in the concentration of 4-nitrophenyl acetate, and plots of log ($A_\infty - A_t$) *versus* time were linear for several half lives.

The pK_a value of $[CoL(OH_2)]^{3+}$ was determined by potentiometric titration of the perchlorate salt $(2 \times 10^{-4}$ mole = 0.1180 g) in 0.1 *M* sodium perchlorate at 25 °C, with potassium hydroxide (*Mw* = 592 by titration, Calc. = 590.64).

All pH measurements were made with a Radiometer PHM26 instrument which was standardised using borax and phthalate buffers. Kinetic measurements were made with a Gilford 2400S spectrophotometer. Hydroxide ion concentrations were determined from the pH using pK_w = 13.997 and a molar activity coefficient of 0.774 at *I* = 0.1 *M*.

Results and Discussion

The base hydrolysis of 4-nitrophenyl acetate was studied in the pH range 8.85–9.46 at 25 °C and *I* = 0.1 *M*. Values of k_{obs}, the observed first order rate constant at constant pH are listed in Table I as a function of the pH. Values of $k_{OH} = k_{obs}/[OH^-]$ are constant, giving k_{OH} = 16.6 $M^{-1} s^{-1}$ at 25 °C and *I* = 0.1 *M*. This value may be compared with k_{OH} = 9.5 $M^{-1} s^{-1}$ reported by Jencks and Gilchrist at 25 °C and *I* = 1.0 *M* [9]. Considering the marked difference in the ionic strength the constants are in general agreement.

The practical pK_a value of $[CoL(OH_2)]^{3+}$ was determined by potentiometric titration at 25 °C and *I* = 0.1 *M* ($NaClO_4$) to be 6.3. This constant is not

TABLE I. Base Hydrolysis of 4-Nitrophenyl Acetate at $I =$ 0.1 M (NaClO$_4$) and 25 °C.[a]

pH	10^6 [OH$^-$] (M)	10^4 k_{obs} (s^{-1})	10^{-1} k_{OH} $(M^{-1} s^{-1})$
8.85	9.23	1.52	1.65
8.98	12.46	2.14	1.72
9.17	19.29	3.23	1.67
9.46	37.62	5.95	1.58

[a]Reactions carried out using 0.01 M borax buffer.

markedly different from that reported for [Co-(NH$_3$)$_5$OH$_2$]$^{3+}$ where pK_a = 6.4 at I = 0.1 M [10]. The hydrolysis of 4-nitrophenyl acetate in the presence of [CoL(OH)]$^{2+}$ was studied using 0.01 M borax buffer pH 9.00 adjusted to I = 0.1 M with sodium perchlorate. In all reactions the ester concentration was 1.84 × 10^{-4} M, with the metal complex in at least a tenfold excess. Concentrations of the hydroxo-complex in the range 2 × 10^{-3} M to 7 × 10^{-3} M gave an excellent first order dependence on the ester concentration. Values of these observed first order rate constants (k_{obs}) are listed as a function of the concentration of [CoL(OH)]$^{2+}$ in Table II. A plot of k_{obs} *versus* the concentration of [CoL(OH)]$^{2+}$ is linear with a positive intercept, Fig. 1. The rate expression thus takes the form,

$$k_{obs} = k_o + k_N [CoL(OH)^{2+}]$$

The value of k_o determined from the intercept is 2.25 × 10^{-4} s^{-1} at pH 9.00 where [OH$^-$] = 1.30 × 10^{-5} M at 25 °C and I = 0.1 M. Since $k_{OH} = k_o/[OH^-]$, the estimated value of k_{OH} from this plot is 17.3 M^{-1} s^{-1}, in good agreement with the constant obtained in Table I. The slope of the plot gives k_N = 9.3 × 10^{-3} $M^{-1} s^{-1}$.

The reaction of oxygen anions with 4-nitrophenyl acetate is considered to occur by nucleophilic catalysis rather than general base catalysis [9]. Nucleophilic catalysis can be represented as shown in eqn. (1), and has been confirmed in the case of the reac-

TABLE II. The [CoL(OH)]$^{2+}$ Promoted Hydrolysis of 4-Nitrophenyl Acetate at 25 °C, I = 0.1 M and pH 9.00.[a]

10^3 [CoL(OH)]$^{2+}$ (M)	10^4 k_{obs} (s^{-1})
1.93	2.43
3.87	2.60
4.83	2.72
5.80	2.79
6.77	2.88

[a]Concentration of 4-nitrophenyl acetate = 1.84 × 10^{-4} M in every kinetic run. Reactions carried out in 0.01 M borax buffer.
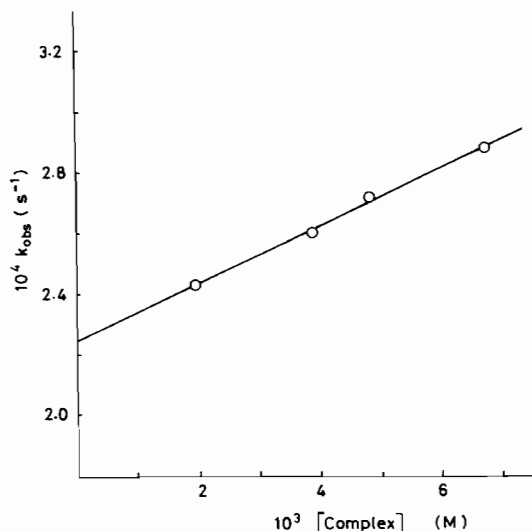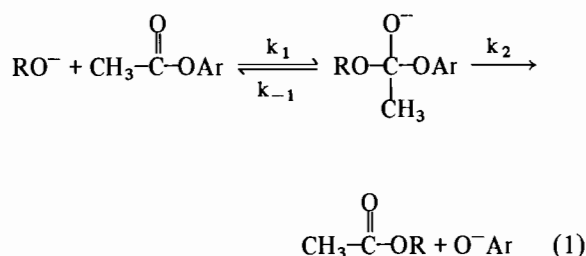

Fig. 1. The [CoL(OH)]$^{2+}$ promoted hydrolysis of 4-nitro-phenyl acetate at 25 °C, I = 0.1 M and pH 9.00 as a function of the concentration of [CoL(OH)]$^{2+}$.

tion of [(NH$_3$)$_5$Co(OH)]$^{2+}$ with 4-nitrophenyl acetate by isolation and characterisation

$$RO^- + CH_3-\overset{\overset{O}{\|}}{C}-OAr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RO-\overset{\overset{O^-}{|}}{\underset{CH_3}{C}}-OAr \overset{k_2}{\longrightarrow}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OR + O^-Ar \quad (1)$$

of the acetato complex [(NH$_3$)$_5$CoOOCCH$_3$]$^{2+}$. If OR and OAr in eqn. (1) are identical, the tetrahedral intermediate will break down at equal rates to reactants and products in the symmetrical reaction. If OAr$^-$ has the more electron withdrawing substituent it will be less basic and a better leaving group. In this case $k_{-1} < k_2$ and almost every molecule of the tetrahedral intermediate formed, will go on to products and the first step k_1 will be rate determining. Such a situation arises in the present case as the pK_a of 4-nitrophenol is 7.14 [9] compared with 6.4 for [CoL(OH)$_2$]$^{3+}$.

The reactions of *strongly* basic oxygen anions with 4-nitrophenyl acetate exhibit very little sensitivity to the basicity of the nucleophile [9]. Brönsted-type plots of log k_N *versus* the pK_a of the conjugate acid nucleophile show levelling beyond pK_a *ca.* 10, Fig. 2 with an initial slope of β = 0.3 [9]. In absolute terms [CoL(OH)]$^{2+}$ is some 6 times more reactive towards 4-nitrophenyl acetate than [(NH$_3$)$_5$Co(OH)]$^{2+}$ where k_N = 1.52 × 10^{-3} M^{-1} s^{-1}, although the two complexes have similar pK_a values, Table III.
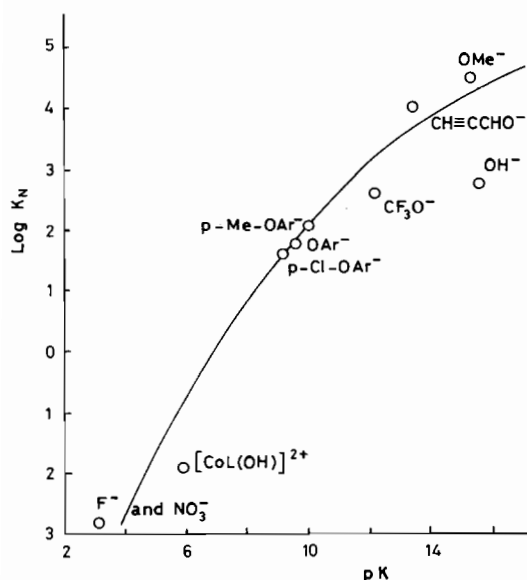
Fig. 2. Brönsted type plot for the reaction of various nucleophiles with 4-nitrophenyl acetate, using data from ref. 9.

TABLE III. Rate constants for the Hydrolysis of 4-Nitrophenyl Acetate by Various Bases.[a]

	k ($M^{-1} s^{-1}$, at 25 °C)	pK_a
OH^-	16.5	15.5
Imidazole	0.58	14
$(NH_3)_5CoIm^{2+}$	9	10.02
Carbonic anhydrase	460	7.5
$[CoL(OH)]^{2+}$	9.3×10^{-3}	6.3
$[(NH_3)_5Co(OH)]^{2+}$	1.52×10^{-3}	6.4

[a]The kinetic data is taken from ref. 7.

Such a result is not unexpected, since no single value of the Brönsted coefficient β describes the relationship between the basicity of oxygen and other anionic nucleophiles and their nucleophilicity towards esters over a large variation in the structure of the nucleophile. In addition nucleophiles which have an 'abnormally' high reactivity towards one ester may have a normal or low reactivity towards others. However, the general conclusion can be drawn that *oxygen nucleophiles on metal centres will have a nucleophilicity which broadly equates with their basicity.* Metal ions such as nickel(II), zinc(II) and manganese(II) with pK_a values for their complexes in the range 9–10 are thus expected to have nucleophilicities comparable with those phenoxide anions.

Acknowledgement

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