Inorganica Chimica Acta, 64 (1982) L199–L201

Synthesis and Base Hydrolysis Kinetics of [Co([15]aneN$_5$)DMF]$^{3+}$. The Accelerated Hydrolysis of an O-Coordinated Amide and Base Hydrolysis of the Resulting Formato Complex

ROBERT W. HAY and RAMESH BEMBI

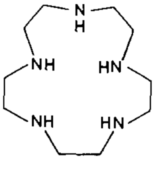
Department of Chemistry, University of Stirling, Stirling FK9 4LA, U.K.

Received October 26, 1981

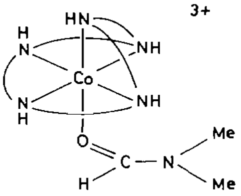
Very large rate accelerations (10^4–10^7 times) have been noted in the base hydrolysis of amino-acid amides incorporated as a chelate ligand in a transition metal complex [1]. This activation arises due to coordination of the carbonyl oxygen to the metal centre. Kinetically inert transition metal complexes of carbonyl-O bonded esters are not well characterised [2], but complexes of simple amides, particularly dialkylamides are relatively simple to prepare. Buckingham, Harrowfield and Sargeson [3] have described the preparation and base hydrolysis kinetics of [Co(NH$_3$)$_5$DMF]$^{3+}$ (DMF = N,N-dimethylformamide). Two reaction paths were detected, the major pathway corresponded to hydroxide ion attack at the carbonyl centre leading to [Co(NH$_3$)$_5$OOCH]$^{2+}$ and (CH$_3$)$_2$NH. The minor pathway led to [Co(NH$_3$)$_5$OH]$^{2+}$ and DMF, and is probably the dissociative conjugate base process. Compared with hydrolysis of the uncoordinated ligand, amide hydrolysis is accelerated $\geqslant 10^4$ fold. The present paper discusses analogous studies using 1,4,7,10,13-pentazacyclopentadecane ([15]aneN$_5$ = (I)) as the pentadentate ligand on cobalt(III), and describes the synthesis and base hydrolysis kinetics of the complex (II) The inert ligand is expected to play a role in these reactions, as stronger sigma donors would be expected to reduce the Lewis acidity of the metal centre and so lead to reduced reactivity in the reactant ligand.

Experimental

The ligand 1,4,7,10,13-penta-azacyclopentadecane ([15]aneN$_5$ = L) as its pentahydrochloride, and the complex [CoLCl](ClO$_4$)$_2$ were prepared as previously described [4]. The complex [CoL(DMF)](ClO$_4$)$_3$ was prepared as follows. [CoLCl](ClO$_4$)$_2$ (0.26 g, 0.5 mmol) was dissolved in dry DMF (10 cm^3, dried over molecular sieves) and treated with AgClO$_4$ (0.12 g, 0.55 mmol). The mixture was heated on a steam bath (*ca.* 10 min), cooled and the precipitated AgCl filtered off. The clear red filtrate on treatment with ether gave a red oil, which solidified on trituration with ethanol. The crude complex was dissolved in the minimum volume of water, solid sodium perchlorate (*ca.* 0.5 g) added and the solution cooled in ice. The red complex (0.1 g) was filtered off, washed with ethanol, then ether and dried *in vacuo*. The IR spectrum has a strong band at 1660 cm^{-1} assigned to νC=O. The electronic spectrum (water solvent) is λ_{max} 460 (ϵ = 228) λ_{max} 340(sh) (ϵ = 334) and λ_{max} 220 nm (ϵ = 18,250). *Anal.* Calc. for C$_{13}$H$_{32}$N$_6$O$_{13}$Cl$_3$Co: C, 24.18; H, 4.99; N, 13.01. Found: C, 24.57; H, 5.29; N, 13.32%.



(I) = L



(II)

The formato complex [CoL(OOCH)](ClO$_4$)$_2$ was prepared as follows. [CoLCl](ClO$_4$)$_2$ (0.26 g, 0.5 mmol) was suspended in formic acid (2 cm^3) and treated with AgClO$_4$ (0.12 g, 0.55 mmol). The mixture was stirred and warmed at 50 °C for *ca.* 10 min, then cooled and the precipitated AgCl filtered off. The bright red filtrate was treated with excess ethanol and some ether. The resulting red complex was filtered off, washed with ethanol, then ether and dried *in vacuo*. The IR spectrum has ν(CO$_2^-$)assy at 1385 cm^{-1}. The electronic spectrum (water solvent) has λ_{max} 485 (ϵ = 202), 345 (ϵ = 193) and 227 nm (ϵ = 16,400). *Anal.* Calc. for C$_{11}$H$_{26}$N$_5$O$_{10}$Cl$_2$Co: C, 25.50; H, 5.64; N, 13.51: Found: C, 25.10; H, 5.15; N, 13.75%.

The complex [CoL(OH$_2$)](ClO$_4$)$_3$ was prepared as previously described [4]. The perchlorate salt of the hydroxopentamine is relatively insoluble in water and can be readily isolated from perchlorate media.

Kinetics and Product Analysis

The kinetics of base hydrolysis of [CoL(DMF)]$^{3+}$ to give a mixture of the aquo and formato complexes was studied using 0.02–0.1 *M* sodium hydroxide solutions. The reaction was monitored by the increase

0020-1693/82/0000-0000/$02.75

in absorbance at 330 nm. The ionic strength was adjusted to I = 0.485 *M* with $NaClO_4$.

For product analysis the reaction was allowed to proceed for *ca.* 10 half lives in 0.1 *M* NaOH (*ca.* 25 min) at 25 °C. The reaction was then quenched with 2 *M* $HClO_4$ and cooled in ice. The product ratio was determined spectrophotometrically at 450 nm using an absorption coefficient of 305 M^{-1} cm^{-1} for the aquo complex and 155 M^{-1} cm^{-1} for the formato complex.

The kinetics of base hydrolysis of $[CoL(OOCH)]^{2+}$ to give the aquo species was monitored at 480 nm where an absorbance increase occurs. Sodium hydroxide solutions (0.08–0.4 *M*) adjusted to I = 0.485 *M* with $NaNO_3$ were employed. Sodium perchlorate could not be used to adjust the ionic strength due to the limited solubility of $[CoL(OH)](ClO_4)_2$ in water.

All the kinetic measurements were carried out with a Gilford 2400S spectrophotometer. Routine uvis spectra were determined using a Perkin Elmer 402 instrument. I.r. spectra were determined using KBr discs with a Perkin Elmer 457 spectrophotometer. Nmr spectra were measured with a Bruker WP-80 instrument using d_6-DMSO as solvent and TMS as internal reference.

Results and Discussion

The complex $[CoL(DMF)](ClO_4)_3$ could contain either N-bonded or O-bonded DMF. The infrared spectrum has νC=O at 1660 cm^{-1} similar to that of $[Co(NH_3)_5DMF]^{3+}$ at 1655 cm^{-1}. The visible spectrum of the present complex has the first ligand field band at 460 nm (ϵ = 228) with a shoulder at 340 nm (ϵ = 334) and a charge transfer band at 220 nm (ϵ = 18,250). The first ligand field band occurs at a similar energy to that of $[CoL(OH_2)]^{3+}$ (λ_{max} 450 nm (ϵ = 305)) so providing evidence for the CoN_5O chromophore in the DMF complex. This conclusion is confirmed by the ^1H NMR data. The occurrence of a doublet for the $N-CH_3$ resonances in the ^1H spectrum of uncoordinated DMF is due to restricted rotation about the N–CO bond due to partial double bonding involving the lone pair on nitrogen [5, 6]. This doublet also occurs in $[CoL(DMF)]^{3+}$ at 2.73 and 2.90 δ with a singlet at 7.96 δ which can be assigned to the formyl proton (d_6-DMSO solvent). The possibility that the nitrogen is coordinated and that the methyl doublet arises from coupling to the formyl proton can be excluded since the formyl resonance occurs as a sharp singlet. In addition, such coupling is not observed in the free ligand. The ^1H NMR data is very comparable to that of $[Co(NH_3)_5DMF]^{3+}$ where the $N(CH_3)_2$ doublet occurs at 2.88 and 3.03 δ and the formyl singlet at 7.43 δ, [3].

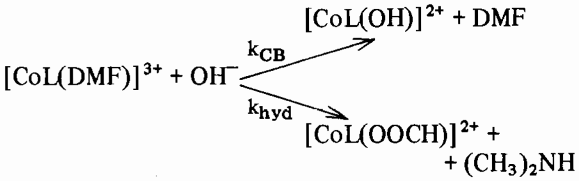
TABLE I. Base Hydrolysis of $[CoL(DMF)]^{3+}$ at I = 0.485 *M* ($NaClO_4$) and 25 °C.[a]

10^3 [OH^-] (*M*)	10^3 k_{obs} (s^{-1})	10^2 k_{obs}/[OH^-] (M^{-1} s^{-1})
19.3	1.03	5.3
38.6	2.10	5.4
58.0	2.94	5.1
77.3	3.85	5.0
96.6	4.94	5.1

[a] Reaction monitored spectrophotometrically at 330 nm.

Spectrophotometric monitoring of the base hydrolysis of $[CoL(DMF)]^{3+}$ in dilute sodium hydroxide solutions (0.02–0.1 *M*) indicated that there was an initial quite rapid reaction followed by a much slower reaction. The products produced in the initial reaction are likely to be both $[CoL(OH)]^{2+}$ (S_NICB pathway) and $[CoL(OOCH)]^{2+}$ (base hydrolysis of coordinated DMF). The slower reaction corresponding to base hydrolysis of $[CoL(OOCH)]^{3+}$ to give $[CoL(OH)]^{2+}$.

The initial rapid reaction, can essentially be studied in isolation, since the second hydrolysis step is quite slow. The reaction scheme will then be



with

$$k_{OH} = k_{CB} + k_{hyd} \tag{1}$$

and

$$\frac{k_{CB}}{k_{hyd}} = \frac{[CoL(OH)]^{2+}}{[CoL(OOCH)]^{2+}} \tag{2}$$

The products obtained in the first reaction were estimated spectrophotometrically at 450 nm, after quenching with perchloric acid (see Experimental). At this wavelength the absorption coefficients of $[CoL(OH_2)]^{2+}$ and $[CoL(OOCH)]^{2+}$ are 305 M^{-1} cm^{-1} and 155 M^{-1} cm^{-1}. The product ratio defined by eqn. (2) is 0.59 at 25 °C.

Table I lists values of k_{obs} obtained at various sodium hydroxide concentrations using spectrophotometric monitoring at 330 nm. The reaction shows a good first order dependence on [OH^-] with $k_{OH} = k_{obs}/[OH^-] = 5.2 \times 10^{-2}$ M^{-1} s^{-1} at 25 °C and I = 0.49 *M*. The use of eqns. (1) and (2) gives

TABLE II. Base Hydrolysis of $[CoL(OOCH)]^{2+}$ at I = 0.485 *M* ($NaNO_3$) and 25 °C.[a]

10^3 $[OH^-]$ (*M*)	10^4 k_{obs} (s^{-1})	10^3 $k_{obs}/[OH^-]$ (M^{-1} s^{-1})
77.3	1.75	2.3
96.6	2.07	2.1
193.3	4.22	2.2
290.0	6.21	2.1
386.6	8.15	2.1

[a] Reaction monitored spectrophotometrically at 480 nm.

TABLE III. Temperature Dependence of the Base Hydrolysis of $[CoL(OOCH)]^{2+}$ at I = 0.485 *M* (KNO_3).

Temp. (°C)	10^4 k_{obs} (s^{-1})	10^3 k_{OH}[a] (M^{-1} s^{-1})
25	4.22	2.19
28.5	5.07	2.63
32.5	7.88	4.08
37.0	12.16	6.30

[a] Values of k_{obs} determined using 0.193 *M* NaOH solutions, $k_{OH} = k_{obs}/[OH^-]$. $\Delta H^{\ddagger} = 71.0$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = -66$ JK^{-1} mol^{-1}.

$k_{hyd} = 3.27 \times 10^{-2}$ M^{-1} s^{-1} and $k_{CB} = 1.92 \times 10^{-2}$ M^{-1} s^{-1}. The value of k_{hyd} is somewhat lower than that for $[Co(NH_3)_5DMF]^{3+}$ ($k_{hyd} = 1.3$ M^{-1} s^{-1} at 25 °C) with $k_{CB} = 0.17$ M^{-1} s^{-1} [3]. For base hydrolysis of DMF, k_{OH} is *ca.* 1×10^{-4} M^{-1} s^{-1} at 25 °C [3], so that a rate acceleration of some 327 fold occurs with the macrocyclic system compared with 10,000 fold in the case of $Co(NH_3)_5^{3+}$. The magnitude of the metal promotion effect is clearly a function of the inert ligand. Ligands which are strong sigma donors will reduce the Lewis acidity of the central metal ion. Macrocycles of the present type contain only secondary nitrogen donors which are stronger bases than the primary amine donors in $Co(NH_3)_5^{3+}$. Similar effects have been noted in the $[CuL]^{n+}$ promoted hydrolysis of methyl glycinate [7].

The kinetics of base hydrolysis of the formato complex $[CoL(OOCH)]^{2+}$ to give the hydroxopentamine were also studied in detail. Values of k_{obs}, determined spectrophotometrically at 480 nm, as a function of the hydroxide ion concentration are listed in Table II. The reaction shows a good first order dependence on the hydroxide ion concentration with $k_{OH} = k_{obs}/[OH^-] = 2.1 \times 10^{-3}$ M^{-1} s^{-1} at 25 °C (I = 0.485 *M*). Base hydrolysis of the formato complex is some 25 fold slower than overall base hydrolysis of $[CoL(DMF)]^{3+}$ at 25 °C. Activation parameters for base hydrolysis of the formato complex were determined using values of k_{OH} obtained using 0.193 *M* NaOH solutions, Table III. The parameters are $\Delta H^{\ddagger} = 71.0$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -66$ JK^{-1} mol^{-1} consistent with a dissociative S_N1CB process [8].

Acknowledgement

We wish to thank the SRC for financial support and for the award of a Postdoctoral Fellowship to one of us (R.B.).

References

1 See for example, R. W. Hay and P. J. Morris, 'Metal Ions in Biological Systems', Vol. 5, Ed. H. Sigel, Marcel Dekker, N.Y., New York, 1976;
D. P. N. Satchell and R. S. Satchell, *Ann. Rep. Chem. Soc., A*, 25 (1978).
2 J. K. Hurst and H. Taube, *J. Am. Chem. Soc., 90,* 1174 (1968), for example have described the relatively difficult preparation of the methyl acetate complex of pentaamminecobalt(III).
3 D. A. Buckingham, J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc., 96,* 1726 (1974).
4 R. W. Hay, R. Bembi, P. R. Norman and T. Moodie, *J. Chem. Soc. Dalton,* in press.
5 W. D. Phillips, *J. Chem. Phys., 23,* 1363 (1955).
6 H. Gutowsky and C. H. Holm, *J. Chem. Phys., 25,* 1228 (1956).
7 J. K. Walker and R. Nakon, *Inorg. Chim. Acta, 55,* 135 (1981).
8 J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta, 11,* 47 (1974).