Base Hydrolysis of the Ester Function in Complex Ions of the Type *cis*-$[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO_2Et)Cl]Cl_2$

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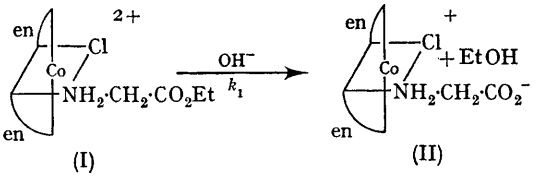
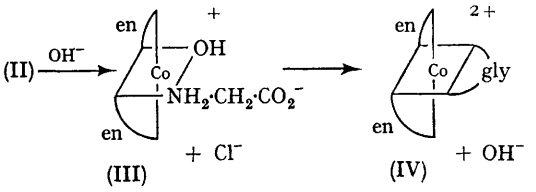
KINETIC studies of the transition-metal ion catalyzed hydrolysis of simple α-amino-acid esters of the glycine type are complicated by the uncertain nature of the labile metal complexes in solution.[1] Inert cobalt(III) complexes would be preferable for these studies. Alexander and Busch[2] have recently prepared a series of complexes of the type *cis*-$[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO_2R)Cl]Cl_2$ and have studied the mercury(II)-promoted hydrolysis of the "dangling" ester function in acid solution.[3] We now report the results of some kinetic measurements on the base hydrolysis of the ester function in (I).

The hydrolysis is conveniently followed in the pH range 8·8—9·5 at 25° using a pH-stat. The reaction is pseudo-first-order at constant pH. Hydrolysis of the chloride function also occurs quite readily in the pH range used, and more than the stoicheiometric amount of alkali required to hydrolyze the ester function is consumed. The mean value $k_1 = 3{\cdot}5 \pm 0{\cdot}5 \times 10^3$ mole^{-1} min.$^{-1}$ is obtained at 25° and a mean ionic strength of 0·1M for the hydrolysis of the ester function.

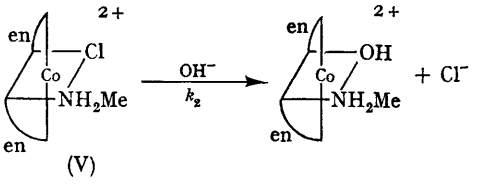


(I) (II)

Appreciable hydrolysis of the chloride function is also indicated by the orange colour which develops during the base hydrolysis of (I). Complexes (I) and (II) are red in colour, the hydroxypentammine (III) red-orange, and the chelated glycinato-complex (IV) orange. The hydrolysis of the ester function is concurrent with hydrolysis of the chloride to give the hydroxy-complex (III).† Hydroxide ion is then released due to intramolecular attack by the carboxyl anion to give the chelated glycine complex (IV).



An independent measurement of the rate of base hydrolysis of the chloride function can be made by studying the hydrolysis of the chloropentammine complex (V).



(V)

The average value obtained for k_2 is 1×10^3 mole^{-1} min.$^{-1}$ at 25° and $I = 0{\cdot}1$M, a similar value is obtained using the corresponding ethylamine complex.‡ These results also confirm that hydrolysis of the ester function is concurrent with hydrolysis of the chloride ligand to give the hydroxy-complex (III).

The chloro-glycine complex (II) can be prepared by hydrolysis of (I) with 4M-hydrochloric acid.[4] The thermodynamic ionisation constant of the carboxyl group is $pK_a = 2{\cdot}52$ at 25°. Base hydrolysis of the chloride function in (II) can readily be followed using a pH-stat. Hydroxide ion is initially consumed, then base consumption ceases, and hydroxide ion is then released due to

† The stereochemistry of the hydroxypentammine (III) produced on base hydrolysis has not been established. R. S. Nyholm and M. L. Tobe (*J. Chem. Soc.*, 1956, 1707) found for the reaction D-*cis*-$[Co(en)_2(NH_3)Cl]^{2+} + OH^- \rightarrow$ D-*cis*- + L-*cis*- + *trans*-$[Co(en)_2(NH_3)OH]^{2+}$ at 0° in aqueous solution that product analysis gives D-*cis* 59·5%, L-*cis* 24·5%, and *trans* 16%. 84% of the *cis*-product is therefore formed.

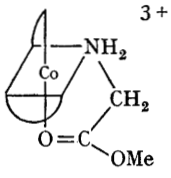
‡ Kinetic studies of the base hydrolysis of the complex ion $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)Cl]Cl_2$ also gave a value of *ca.* 1×10^3 mole^{-1} min. for the hydrolysis of the chloride ligand. A slower hydrolysis of the amide function also occurs. R. G. Pearson, R. E. Meeker, and F. Basolo (*J. Amer. Chem. Soc.*, 1956, 78, 709) quote a value of $3{\cdot}24 \times 10^3$ mole^{-1} min.$^{-1}$ at 25° for the hydrolysis, *cis*-$[Co(en)_2(NH_3)Cl]^{2+} + OH^- \rightarrow [Co(en)_2(NH_3)OH]^{2+} + Cl^-$ at an unspecified ionic strength.

the formation of the chelated glycinato-complex, (IV), glycinatobis(ethylenediamine)cobalt(III). This complex has a characteristic absorption spectrum, λ_{max} 487 mμ (ϵ 98) and 346 mμ (ϵ 107), and is readily identified as the end-product of the reaction. At 25° and I = 0·1M, the rate constant for the base hydrolysis of ethyl glycinate

$$H_2N{\cdot}CH_2{\cdot}CO_2Et + OH^- \xrightarrow{k} H_2N{\cdot}CH_2{\cdot}CO_2^- + EtOH$$

is k = 38 mole^{-1} min.$^{-1}$.[5] Incorporation of the ester in the cobalt(III) complex leads to a rate acceleration of *ca.* 100 times. Such an effect is readily understandable on an electrostatic basis since hydrolysis involves attack by an anionic nucleophile on a substrate carrying a double positive charge.[6]

Buckingham, Marzilli, and Sargeson[7] have recently isolated the chelated glycine ester complex $[Co(en)_2(glyOMe)](ClO_4)_3$. Treatment of this compound with amino-acid esters or peptide esters in anhydrous sulpholan, dimethyl sulphoxide, or acetone solutions results in the formation of the $[Co(en)_2(gly\text{-}amino\text{-}acid\ OR)]^{3+}$ and the $[Co(en)_2(gly\text{-}peptide\ OR)]^{3+}$ ions. Both reactions were complete within 1 min. at 20°. The complex ion acts as both an activating and *N*-protecting group. Buckingham *et al.* regard the chelated ester species as having the structure (VI) in which a metal–oxygen bond is formed with the carbonyl function



(VI)

of the ester. Base hydrolysis of the ester function in such a complex would be expected to occur extremely rapidly. We consider that our hydrolyses involve a purely "dangling" ester fuction.

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