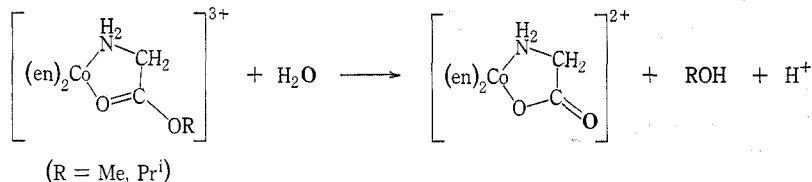


ALKYL-OXYGEN FISSION IN THE ACID HYDROLYSIS OF *t*-BUTYL GLYCINATE COORDINATED TO COBALT(III)

By D. A. BUCKINGHAM,* D. M. FOSTER,* and A. M. SARGESON*

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It has been established that the acid hydrolysis of *t*-butyl acetate proceeds largely by means of alkyl-oxygen fission.¹ A unimolecular dissociation is proposed,² in which transfer of negative charge from the alkyl group to the oxygen atom leads to the formation of the tertiary carbonium ion. Simple primary and secondary acetate esters, on the other hand, acid hydrolyse by acyl-oxygen fission initiated by the bimolecular attack of water at the carbonyl carbon atom.² The relative acid hydrolysis rates of simple alkyl acetates² suggest that, for simple carboxylate systems, alkyl-oxygen fission will proceed more rapidly than acyl-oxygen fission. In this connection, we have studied the mode of acid hydrolysis in glycine ester complexes of the form $[\text{Co}(\text{en})_2(\text{glyOR})](\text{ClO}_4)_3$ ^{3,4} in which the ester is chelated through the amino nitrogen and carbonyl oxygen atoms. The rates of hydrolysis⁴⁻⁶ in these chelated esters ($\text{R} = \text{Me} > \text{Et} > \text{Pr}^i$) are $c. 10^6$ times faster than the similar hydrolyses of the corresponding *N*-protonated glycine esters, and it is conceivable that this rate enhancement could reflect a change in mechanism.



However, a previous publication has shown that the acid hydrolysis of $[\text{Co}(\text{en})_2(\text{glyOMe})](\text{ClO}_4)_3$ proceeds by acyl-oxygen fission.⁴ The Hg^{2+} -induced hydrolysis of $[\text{carbonyl-}^{18}\text{O}]\text{-cis-}[\text{Co}(\text{en})_2\text{Br}(\text{glyOR})]\text{Br}_2$ ($\text{R} = \text{Me}, \text{Pr}^i$) is also known to proceed through the chelated ester intermediates,⁴ and also resulted in full retention of the oxygen label in the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ product.^{4,7} Thus, both primary and secondary

* Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600.

¹ Adam, K. R., Lauder, I., and Stimson, W. R., *Aust. J. Chem.*, 1962, **15**, 467 and references therein.

² Ingold, C. K., "Structure and Mechanism in Organic Chemistry." pp. 752 *et seq.* (Cornell University Press: Ithaca, N.Y., 1953.)

³ Buckingham, D. A., Marzilli, L. G., and Sargeson, A. M., *J. Am. chem. Soc.*, 1967, **89**, 4539.

⁴ Buckingham, D. A., Foster, D. M., and Sargeson, A. M., *J. Am. chem. Soc.*, 1968, **90**, 6032.

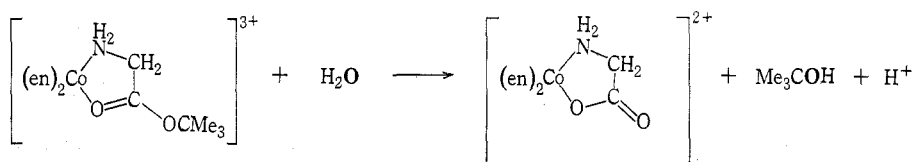
⁵ Buckingham, D. A., Foster, D. M., and Sargeson, A. M., unpublished data.

⁶ Alexander, M. D., and Busch, D. H., *J. Am. chem. Soc.*, 1966, **88**, 1130.

⁷ Buckingham, D. A., Foster, D. M., and Sargeson, A. M., *J. Am. chem. Soc.*, 1969, **91**, 4102.

alkyl esters of the type $[\text{Co}(\text{en})_2(\text{glyOR})]^{3+}$ acid hydrolyse by acyl-oxygen fission, and the large increase in rate compared to the *N*-protonated esters may be attributed to the increased susceptibility of the carbonyl carbon atom towards bimolecular attack by water.

The Hg^{2+} -induced acid hydrolysis of the bromo *t*-butyl ester complex was therefore of special interest, since it was conceivable that the greatly enhanced electrophilic character of the carbonyl carbon in the chelated *t*-butyl glycine ester might also induce hydrolysis by acyl-oxygen fission. We have now obtained results which show that the chelated *t*-butyl ester $[\text{Co}(\text{en})_2(\text{glyOCMe}_3)]^{3+}$ acid hydrolyses almost exclusively by alkyl-oxygen fission. The Hg^{2+} -induced acid hydrolysis of unlabelled *cis*- $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCMe}_3)]\text{Br}_2$ in labelled solvent gave a $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ product containing 4% of the solvent enrichment. The absence of label in the product and the large rate enhancement support hydrolysis through the chelated ester.



Attempts to prepare $[\text{Co}(\text{en})_2(\text{glyOCMe}_3)](\text{ClO}_4)_3$ by treatment of the bromo ester with AgClO_4 in acetone were unsuccessful; the isolated product was in each case $[\text{Co}(\text{en})_2\text{gly}](\text{ClO}_4)_2$, as shown by ion-exchange chromatography and p.m.r. spectroscopy. By contrast, $[\text{Co}(\text{en})_2(\text{glyOMe})](\text{ClO}_4)_3$ may be obtained in good yield by the identical procedure, despite its rapid rate of acid hydrolysis [$k(\text{H}_2\text{O})$ $2.7 \times 10^{-2} \text{ sec}^{-1}$].⁶ This indicates the susceptibility of the *t*-butyl ester complex to hydrolysis by traces of water in the solvent or during isolation, and suggests that the *t*-butyl ester is hydrolysing at a rate considerably faster than that for the corresponding methyl ester complex.

Coordination of the carbonyl oxygen atoms of glycine esters to cobalt(III) may be thought of as inducing incipient carbonium ion formation at the carbonyl carbon atom, and we propose that the increased electrophilic character of this carbon atom is responsible for the resulting acceleration of both bimolecular and unimolecular hydrolysis. The former may be considered as arising from the increased susceptibility of this carbon atom towards nucleophilic attack, and the latter as arising from the increased efficiency of the coordinated carboxyl moiety as a leaving group.

Experimental

cis- $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCMe}_3)]\text{Br}_2$ (1.5 g), prepared as previously described,⁷ was dissolved with $\text{Hg}(\text{NO}_3)_2$ (6 g) in labelled H_2O (20 ml, 2 atom % ^{18}O), taken to pH 1 with 70% HClO_4 , and left to stand for 2 hr. After filtration, excess NaI was added to the filtrate and the resulting precipitate of $[\text{Co}(\text{en})_2\text{gly}](\text{HgI}_4)$ collected, washed with water and methanol, and dried in an evacuated desiccator. The identity of the product was confirmed by comparison of its i.r. spectrum with that of an authentic sample, using a Perkin-Elmer 457 instrument. The ^{18}O content of the glycine was

then determined as previously described.⁴ Duplicate samples gave R values* of 0.005827 and 0.005758, corresponding to an enrichment of 0.089 and 0.086 atom % ^{18}O respectively, to be compared with the solvent enrichment of 1.80 atom %.[†]

Acknowledgments

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* $R = [46]/([44] + [45])$.

† Atom % ^{18}O represents the ^{18}O enrichment in atom % of the sample, less the atom % ^{18}O in CO_2 of normal isotopic composition (0.201).